1 "Gold Rush" in Modern Science: Fabrication Strategies and Typical

2 Advanced Applications of Gold Nanoparticles in Sensing

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48 Abstract

Gold nanoparticles (AuNPs), the huge potential functional nanoparticles in scientific 49 research, have attained tremendous interest for their unique physical-optical property 50 since they have been discovered. They have been very popularly used as labels in 51 diagnostics, sensors, etc. The use of AuNPs in sensor fabrication is widespread, and so 52 many papers have been reported over the past years. The development of AuNPs used 53 in sensor has been reviewed in some previous papers. Most of them tend to review a 54 55 certain kind of analyte using one kind of technique. However, few of these reviews include the detection of inorganic and organic contaminant, as we domolecules at 56 the same time. Besides, the development for AuNPs application is very fast in modern 57 science. Therefore, in this review we summarize some resent progresses made in the 58 field of AuNPs research. We summarize the type synthetic strategies of AuNPs, 59 tased sensors, and expound the role of classify the mechanism analysis of Au 60 61 AuNPs in these sensors. Typical advinced examples of the newly developed AuNPsbased colorimetric and electrochemical sensors and their applications in detection of 62 omolecules, metal ions, and organic environmental 63 various analytes, includi hormones are presented and discussed. 64

65 Keywords: God nanoparticles; Fabrication; Colorimetry; Electrochemistry; Sensor.

66 **1. Introduction**

Recently, nanomaterials are emerging as revolutionizing materials of research with 67 multiple disciplines of science like physics, chemistry, materials, medical science, and 68 biology [1-8]. Gold nanoparticles (AuNPs), one kind of promising functional 69 nanomaterial, have gained increasing scientific interests since the potable gold was 70 found and believed to have excellent medicinal properties by Paracelsus in 4th century 71 A.D [9, 10]. However, the real scientific research on gold sol did not start until the gold 72 73 hydrosols have been discovered by Michael Faraday in 1857 [11]. Later, people showed great interest in investigating the color, shape, size, synthetic strategies, optical property. 74 and applications of AuNPs [12-15]. It can be viewed as a "gold rust" in modern science. 75 AuNPs can be the remarkable scaffold for novel biological and chemical sensors 76 owing to the fascinating electrical, chemical, optical and catalytic properties like easy 77 synthesis, high surface-to-volume ratio, han extinction coefficients, strong distance 78 79 dependent optical features, and excelent biocompatibility, as well as the characteristic of suitable surface functionalization [16-20]. Number of papers concerning the 80 detection" on indexed journals are increasing year by 81 keywords "gold nanopar year and account for opproximately one-fifth of all "gold nanoparticles" in the past 82 twenty years (Fig.). Many excellent reviews have been published on the use of AuNPs 83 84 as sensor. For example, Kim et al. reported a review about the fluorescent and colorimetric sensors for detection of three heavy metal ions and mentioned some typical 85 sensors based on AuNPs [21]. Pingarron et al. reported a paper concerning AuNPs-86 87 based electrochemical biosensors, which discussed the application of AuNPs-based electrochemical enzyme biosensors, immunosensors, and DNA biosensors [22]. 88 Recently, some papers reviewed the application of AuNPs on metal ions, anions, small 89 molecules, proteins, and nucleic acids using various techniques [23-28]. However, most 90

of these reviews tend to describe a certain kind of material or use one kind of technique.
Few of them describe the inorganic and organic contaminants, as well as biomolecules
at the same time. In addition, the new review of AuNPs is very necessary for its rapid
development in recent years.



95

96 Fig. 1. Evolution of the number of productions concerning the keywords "gold 97 nanoparticles" and "gold nanoparticles" t detection" on indexed journals between 1997 98 and 2016. The insert pie graph which is the percentage of the available scientific reports 99 which concerned the Auroparased sensors using different techniques from 1997 to 100 2016. The data concession the research on "web of science".

As the development of nanotechnology, more and more papers focus their attention 101 on detecting different kinds of substances simultaneously, as well as using not only one 102 103 analytical technique [29, 30]. In addition, the development for the application of AuNPs is very fast and the reports of AuNPs-based sensors are increasing enormously [31]. 104 Therefore, this review presents a brief overview on the recent advances of AuNPs in 105 relation to the fabricating strategies and typical advanced applications on the 106 development of chemo- and bio- sensors for metal ions, anions, biomolecules, and 107 108 organic environmental hormones using colorimetric and electrochemical techniques.

Because of the explosion of papers published in this field, we could not mention all of 109 the published reports, but rather a description and summary of these methods are 110 discussed. On the other hand, the application of AuNPs-based sensor on colorimetric 111 detection is a relative independent part, which uses the optical properties of collective 112 oscillation of electrons on surfaces for AuNPs (known as the "surface plasmon 113 resonance", SPR or "localized surface plasmon resonance", LSPR) and their color 114 115 change [32-34]. The typical application using the properties of good catalysis, huge specific surface area, and wonderful electron transfer is located in electrochemical 116 sensor [35, 36]. Other applications of AuNPs-based sensors such as fluorescence sensor 117 and micro-electronic balance sensor are not mentioned here 118

Thus, the purpose of this review is to investigate the synthetic strategies for AuNPs 119 and to derive some general strategies with the basic understanding of sensing 120 application, to summarize the results of the basic properties in a vast variety of 121 applications on chemical, environmental, and medical science, and finally, also the 122 ultimate purpose, to open up the rewinsights via multi-approaches to many promising 123 applications from synthetic routes and theoretical perspectives. From this review, the 124 readers will understand the significant role of AuNPs in modern science and can see 125 and inherently fascinating field of investigation for advanced 126 this highly reward materials. We hope that readers can gain some inspiration from this review and push 127 128 further development of AuNPs application. We believe that the outlook of AuNPsbased materials is bright in the present situation of research. 129

130 2. Strategies to fabricate gold nanoparticles

Following the discovery of AuNPs, the research has been inundated with reports on relations among the parameters, including diameter, absorption maximum, and concentration of reactants and strategies for fabrication [37-39]. In this case, numerous

methods, such as reduction, photochemical reduction, seed-growth, etc., for the 134 fabrication of AuNPs have been reported [40, 41]. Conventional approaches, including 135 136 Turkevich-Frens (Fig. 2A) and Brust-Schiffrin (Fig. 2B) method, are still the most popular methods. Also, some new methods such as seed-mediated growth method (Fig. 137 2C) and green synthesis (Fig. 2D) have been developed. In addition, considerable 138 researchers have paid their attention to the fabrication of AuNPs with controllable size, 139 140 conditions, stability, and applications [42]. In this part, we will introduce some regular and new methods and review the development of that, as well as the advantages or 141



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Fig. 2. (A) Turkevich-Frens method for synthesis of AuNPs by reduction of gold salts in the presence of trisodium citrate; (B) Brust-Schiffrin strategy for two-phase fabrication of small-size AuNPs by reduction of gold salts in the presence of external thiol ligands; (C) Seed-mediated growth method for AuNPs synthesis by the process of nucleation, growth, and stability; (D) Green synthesis of non-toxic AuNPs through intra- and extra-cellular biosynthesis in the presence of proteins or cell-free extracts.

150 2.1. Turkevich-Frens method

The Turkevich-Frens method is also the called sodium citrate reduction method or 151 classical-citrate method. It was the first and comparatively systematic method to 152 fabricate AuNPs which was described by Turkevich in 1951 [43]. It was developed 153 based on many reported studies (Table S1). This method allows sodium citrate add into 154 155 the boiling chloroauric acid solution with thoroughly stirring, which leads to a series of 156 color change from light yellow to purple or black and finally to ruby red. The main principle is that the gold ions (Au³⁺) of chloroauric acid were reduced to gold atoms 157 (Au⁰) by the reducing and capping agents such as citrate [44]. There were evidences 158 demonstrated that the mechanism for stepwise formation of AuNes was based on three 159 stages: nucleation, growth, and possible agglomeration 45. However, this approach 160 was partly restricted by narrow range of synthesis size and many studies were 161 committed to solving this weakness. Excitingly, Frens fixed this problem by changing 162 the ratio of sodium citrate and gold chloride and achieved a wide range from 16 to 147 163 nm [46]. After that, the Turkevice frens method was formed, and widely applied to 164 biology, medicine, chemistry, and environment. Later, some researches introduced 165 several new methods or further development. It can be divided into three channels: 1) 166 ability by controlling the pH of the reducing agent or the whole vary the size an 167 mixed reagents; 2) simplify the steps of preparation via changing the reducing agent or 168 169 adding another stabilizing agent; 3) other new methods [47]. Shiba reported a size control method of monodisperse AuNPs through the citrate reduction process related to 170 a pH-shifting procedure. This report proposed an approach for different mean sizes of 171 AuNPs ranging from 6-15 nm by changing the interval time between the addition of 172 NaOH solutions and citric acid into the boiling chloroauric acid [48]. This procedure 173 induced a pH shifting and was presented without any growth modifiers. Interestingly, 174

Schulz et al. proposed a protocol of controlling the pH by adding a citrate buffer instead of sodium citrate solution as the stabilizer or reducing agent [49]. Recently, a paper introduced a facile approach with the size around 5 nm encapsulated with citrate and polythiophene sulfonate poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] sodium salt, which both helped to stabilize the AuNPs [50]. Furthermore, the stability of AuNPs at high chloroauric acid concentrations can also be enhanced by reversing the order of addition for the citrate solution and chloroauric acid [51].

In a word, these methods described above are all developed on the basis of the 182 Turkevich-Frens method and promote the further development. Afterwards, the 183 Turkevich-Frens method can prepare AuNPs with the wide diabeters ranging from 5 184 to 250 nm [52-54]. In general, this method is simple since the size can be controlled by 185 altering the molar ratio of HAuCl₄ and sodium citrate In addition, the citrate ions 186 stabilizer can be easily exchanged by other light with high affinity, especially thiols. 187 which allows for widespread application in sensors. However, there are still some 188 drawbacks needing to overcome: One size of relatively stable AuNPs is between 10-189 50 nm, which will aggregate and be nonspherical when go beyond this range; 2) the 190 NPs largely depends on the stabilizer and is susceptible to degree of stability for A 191 nced aggregation, such as pH, ion strength, and salt concentration, 192 environmentally which render them not ideal structures for further investigations on cells; 3) whether 193 194 the resulting AuNPs are poisonous or not is closely related to the stabilizer, which may be harmful to the environment. Although it has something unsatisfactory, the 195 Turkevich-Frens method is still one of the most common ways to fabricate AuNPs until 196 197 now.

198 **2.2. Brust-Schiffrin method**

AuNPs can be synthesized by Turkevich-Frens method in aqueous phase. It can be

also generated in organic phase or a two-phase liquid-liquid system, which was reported 200 by Brust and Schiffrin in 1994 and called the Brust-Schiffrin method [56]. This method 201 was inspired from the two phase system of Faraday and achieved a significant 202 breakthrough in the realm of AuNPs fabrication since the size ranging from 2 to 5 nm 203 of AuNPs can be obtained, which can remedy one of the defects of Turkevich-Frens 204 205 method [53]. In this procedure, a two-phase (water-toluene) system was designed to 206 reduce the AuCl₄⁻ by sodium borohydride (NaBH₄) to Au⁰ (AuNPs) in the presence of an alkanethiol. The tetraoctylammonium bromide (TOAB) was used as the phase-207 transfer reagent. AuCl4- was transferred from aqueous-phase to to the phase and 208 reduced by NaBH₄. When NaBH₄ added, the color of organic phase shifted from orange 209 to deep brown rapidly. The specific preparing process of this technique was described 210 by Brust and Schiffrin clearly. The prepared AuNPS are capped by densely packed 211 monolayers and quite stable. Moreover, the size AuNPs can be tuned by the reaction 212 conditions, like temperature, thiol/gold ratio, and reaction rate [57]. Maye and Zhong 213 found that the temperature determined noticeably change in size of AuNPs and the 214 chain length could influence the reactivity of AuNPs [58]. Teranishi et al. also used the 215 Brust-Schiffrin method to prepare AuNPs with TOAB as a phase transfer agent and an 216 ing agent [14]. To control the size, AuNPs were further aged in alkanethiol as a c 217 TOAB, which was melted at 150-250 °C. Besides, owing to the nucleation-growth-218 219 passivation kinetics model, larger mole ratio of S/Au can lead to smaller average core size. Furthermore, fast addition of NaBH₄ and immediate quenching of solutions give 220 smaller, more monodispersed AuNPs [59-61]. Compared with other methods, Brust and 221 222 Schiffrin method has some apparent advantages: 1) it introduces a simple way to fabricate the surface-functionalized AuNPs directly; 2) it can be repeatedly isolated and 223 dispersed with monolayer in organic solvents without irreversible aggregation; 3) the 224

prepared AuNPs are soluble in non-polar solvents and can be easily purified by gel-225 226 filtration chromatography, which means they can be handled like a simple chemical 227 compound without any apparent changes in properties; 4) the size of AuNPs can be adjusted by various conditions not only the thiol/gold ratio. 228

Due to the above advantages, Brust-Schiffrin method is often used for the synthesis 229 230 and application of thiol-ligand AuNPs [62, 63]. Recently, some thiolate-stabilized 231 AuNPs are fabricated via a modified Brust-Schiffrin method. Wieckowska and Dzwonek introduced an ultrasmall AuNPs preparing method functionalized with 232 hexanethiol and anthraquinone/hexanethiol monolayer by a modified Brust-Schiffrin 233 method [64]. Other thiolate ligands such as ω -functionalized skythiolate [65, 66], 234 arenethiolate [67, 68], bifunctional alkanethiolate [69], ind others have been used to fabricate functionalized AuNPs. 2.3. Seed-mediated growth method 235 236

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Size control of AuNPs has been investigated for ages. As for the two methods 238 referred above, they are limited viring elatively narrow size distribution or fast growth 239 to some extent. Seed-med and growth method, also called as step-by-step seed-240 mediated growth approach, is another common way to control the size of AuNPs. It can 241 89 when Wiesner et al. [70] added HAuCl₄ solution to the gold 242 be traced back seeds produced by HAuCl₄ reduction with phosphorus, which was similar with 243 244 Faraday's original colloidal synthesis [71]. In this approach, small size of AuNPs are prepared via reducing gold salts with strong reducing agent such as NaBH₄ or citrate 245 first and then used as seeds for the fabrication of larger size AuNPs by adding a solution 246 247 of gold salt in the presence of weak reducing agent such as ascorbic acid (AA). Finally, a structure directing agent is added to prevent further nucleation and promote the 248 growth of AuNPs [72, 73]. The physical properties of AuNPs were improved when 249

compared with other approaches. However, this synthetic procedure was still 250 unsatisfactory for the small population of impurities. Subsequently, Murphy improved 251 this approach using AA as reducing regent instead of citrate in the growth solution and 252 hexadecyltrimethylammonium bromide (CTAB) as stabilizer to fabricate uniform 253 AuNPs up to 40 nm [74]. Later, Han group used the same protocol to synthesize AuNPs 254 255 with the controlled size (10-90 nm) [75]. Recently, some researches tend to study the 256 reaction conditions, which can control the size of prepared AuNPs. Piella et al. introduced a precise control over the size between 3.5 and 10 nm by tuning the 257 temperature, pH, gold precursor to seed, and concentration of sodium citrate [76]. 258 Compared with other methods, the seed-mediated growth network inhibits any 259 secondary nucleation via providing a controlled number of seeds and growth condition. 260 Although the seed-mediated growth method provides broad size distribution, a work 261 reported by Jana et al. demonstrated that the resence of seeds often led to further 262 nucleation, rather than growth. To wooid additional nucleation, a slow addition of 263 reducing agent step was needed in this regard, Jana et al. further reported a step 264 by step seed-mediated growth method using the growth solution and AA, which 265 provided the diameter size of AuNPs ranging from 5 to 40 nm with narrow size 266 a popular technique for AuNPs synthesis, the seed-mediated 267 distribution [7 growth method amplifies the size step-by-step. The shape and size can be easier to 268 269 control. Therefore, this route is broadly used in the shape- and size-controlled AuNPs fabrication. However, there are some points limiting the application of such approach: 270 1) it is difficult to find a suitable growth condition which can inhibit the additional 271 272 nucleation during the growth stage; 2) the factors which influence the process of procedure are many, such as seed concentration, reducing agents, and rate of reducing 273 agent addition. 274

275 **2.4. Green synthesis**

Although the three methods mentioned above can efficiently produce AuNPs, a main 276 shortcoming of these approaches is that the toxic byproducts may induce environmental 277 consequences during large scale generation. Besides, the use of toxic solvents and 278 chemicals can be problematic for biological application [78]. Recently, in response to 279 280 these concerns, green synthesis methods using green materials such as prokaryotic 281 organisms (bacteria), eukaryotic organisms (fungi and extract of plants), and others (proteins and amino acid) [79, 80] and assisted techniques like photochemistry, 282 supersonic, or microwave [81-83] to synthesize AuNPs have been developed. 283

The way of AuNPs fabrication using prokaryotic organisms such as algae and 284 bacteria is mainly divided in two parts: the intra-cellular biosynthesis and extra-cellular 285 biosynthesis. Yasuhiro Konishi and co-workers ottal ed the crystalline AuNPs with 286 particle range of 10-20 nm via using the meson fic anaerobic bacterium, Shewanella 287 algae [84]. The crystalline AuNP presented in the periplasmic space and the 288 intracellular recovery of that was paractive as an eco-friendly alternative. The papers 289 . 85] and Singaravelu et al. [86] both introduced the reported by Husseiny et 290 extracellular synthesic of monodisperse AuNPs using the prokaryotic organisms of 291 hosa and marine alga, respectively. The sizes of AuNPs were in 292 Pseudomonas a the range of 15-30 nm and 8-12 nm, respectively. Another synthetic procedure is 293 294 proposed by using the Escherichia coli K12 cells without any addition of growth media, pH changes or stabilizing agents/electron donors [87]. The way of intra- or extra-295 cellular biosynthesis for AuNPs are both eco-friendly and practical. But a recent paper 296 297 showed that the production of AuNPs from biomass required longer time than the production of AuNPs from the cell-free extracts [88]. 298

299 So far, a large number of fungal species like Neurospora crassal, Aspergillus

foetidus, Aspergillus foetidus, Fusarium semitectum, and Aspergillus oryzae have been 300 reported to fabricate AuNPs through intra- or extra-cellular manners successfully [80]. 301 In 2001, Mukherjee et al. introduced a green chemistry approach that used the fungus, 302 *Verticillium sp.* (AAT-TS-4), to reduce AuCl₄ ions and form AuNPs with the diameter 303 around 20 nm [89]. For all we know, it is the first time that a eukaryotic organism was 304 305 used to synthesize AuNPs. From now on, many researchers stated to studying the green 306 method for fabricating AuNPs using eukaryotic organisms [90] such as plant leaves [91]. Many studies developed by using the extract of plant leaves, such as *Cinnamomum* 307 camphora [92], Tamarind [93], and Black tea [92] to fabricate different sizes of AuNPs. 308 These methods are often environment-friendly and have wide application in biosensors, 309 photonics, and others. Admirably, some of them are no devoted to the synthesis of 310 AuNPs, but to the toxicity and practical application prepared AuNPs using fungi 311 reduction. For example, Swarup Roy group so fied the extracellular biosynthesis of 312 AuNPs using Aspergillus foetidus. The cell cytotoxicity was less toxic compared with 313 that of the normal gold salt solution A549 cell [94]. Nune et al. obtained the tea-314 generated AuNPs (T-AuNIs) by using the phytochemicals in tea. T-AuNPs showed 315 a breast (MCF-7) and prostate (PC-3) cancer cells, which significant affinity towar 316 arching on molecular imaging and therapy with such AuNPs [95]. 317 paved the way f In general, the synthesis of AuNPs with fungi exhibits more environmental tolerance 318 319 since fungi are more tolerant to higher metal concentration and can secrete amount of extracellular redox proteins to reduce metal ions. 320

Except for those two approaches mentioned above, some other new green methods using some assistants e.g. dextrose [96], proteins [97], or amino acids [98] have been shown up, as well as some assistive techniques. Photochemistry is a green synthesis method, which can enhance the quality of AuNPs due to the reproducibility, simplicity,

and mild synthesis conditions [99, 100]. The source of light is usually sunlight or 325 326 ultraviolet light [101, 102]. The light irradiation makes the system produce radicals function as the reducing agent that are capable of reducing Au³⁺ to Au⁰ and form AuNPs 327 [103, 104]. The whole process occurs in only seconds to minutes, the reaction time is 328 greatly reduced. Actually, this is an energy transfer process, in which the energy of light 329 transfers to the electronic energy. Similar with this energy conversion method, 330 331 ultrasound- and microwave-assisted methods are well introduced [105, 106]. The electromagnetic radiation is converted into heat energy with the microwave-assisted 332 methods [107]. The process is rapid and do not show any cytotoxicity loward practical 333 application, creating a new field for synthesis of eco-friendly ANPs [108, 109]. 334 Although the energy conversion method do not need clemical reductant, it needs to 335 introduce energy and suffers from the limitations of shape and application in some 336 extent. Moreover, synthesizing in organism and lacking of good mechanical/regular 337 stirring for green methods usually make them irregularity. In spite of this, to date the 338 development of green synthesis and for AuNPs is still needed and plays an 339 important role in biosenso 340

341 3. Colorimetric application of AuNPs in sensing

Colorimetric application of AuNPs in sensing is one of the most promising analytical 342 343 methods which provides a rapid, simple, and inexpensive way for determination of analytes [110]. The main mechanism of this method lies in the interparticle distances 344 and interparticle surface plasmon coupling, which are very sensitive to the local 345 346 medium. When the interparticle distances are less than approximately the average particle diameter of AuNPs, the color will change from red to blue, which can be easily 347 observed by the naked eyes [111, 112]. Furthermore, the readout can be recorded using 348 a UV-vis spectrophotometer. The channel applied to sensors can be divided into two 349

strategies, the red shift and blue shift in the absorption, leading to aggregation and disaggregation of AuNPs, which present as the color changes from red to blue and blue to red, respectively. Furthermore, when pH or ionic strength of the AuNPs surface changed, the process of aggregation and redispersion can lead to a circle. Owing to the advantages of easy to observe and record, the colorimetric sensor based on AuNPs has been widely applied for detection of biomolecules, inorganic ions, and organic environmental hormones.

357 **3.1. Detection of biomolecules**

358 *3.1.1. Amino acids*

Colorimetric detection of typical amino acids based on AuNA is vital application 359 of AuNPs in sensing. The group of Mirkin introduced surface approach for highly 360 sensitive and selective detection of cysteine based on oligonucleotide-functionalized 361 AuNPs that included placed thymidine-thy old (T-T) mismatches which complexed 362 with Hg²⁺ [113]. The mechanism relied on the formation of thymine-Hg²⁺-thymine (T-363 Hg²⁺-T) structure and strong coordination of Hg²⁺ with cysteine, leading to a purple-to-364 red color change. As a result cysteine could be detected as low as 100 nM. Salt-induced 365 aggregation of AuNIs has been reported all the time. In order to overcome this 366 al. established a simple and sensitive colorimetric way to detect shortcoming, V 367 cysteine based on carboxymethyl cellulose-functionalized AuNPs (CMC-AuNPs) 368 369 [114]. CMC can prevent the salt-induced aggregation of AuNPs and is specific for cysteine, leading to aggregation in the presence of cysteine with the good linear range 370 of 10.0–100.0 µM. The application on real samples is crucial important for detecting 371 methodology, such as serum, urine, or cerebral system [115]. Recently, Zhang et al. 372 firstly reported a novel, specific, and sensitive sensor for cysteine using pectinase 373 protected AuNPs, where AuNPs tightly combined with pectinase via the strong 374

covalent Au-S bond and electrostatic binding [34]. This sensor provided wide linear range from 4.85 nM to 302 μ M (R²=0.996) and 3.25 to 10.3 mM and low LOD of 4.6 nM.

Monitoring of other amino acids such as arginine, histidine, methionine, and 378 tryptophan has also been reported [116, 117]. Importantly, parallel detection of them is 379 difficult to obtain in detecting field, especially in colorimetric detection. However, 380 381 Rawat and Kailasa have achieved this progress for parallel recognition of them by using 4-amino nicotinic acid-functionalized AuNPs [118]. The selectivity achieved mainly 382 depends on the longer wavelengths at different wavelength of the surface plasmon 383 resonance band which provided at 647, 676, 695, and 701 nm for tryptophan, arginine, 384 histidine, and methionine, respectively. Furthermore, some new strategies not only use 385 AuNPs but other materials such as graphene oxide (GQ) and dots have been developed 386 for colorimetric detection of amino acids, tamate, aspartate, and cysteine [119-387 123]. The results suggested this kind of sensor had better stability and linearity in dose-388 dependent responses for amino addistinan other particles. 389

390 *3.1.2. Peptides and protein*

are very important for life, e.g. adjusting physiological Peptides and proteins 391 functions of ead tem, composing cells and tissues, and taking charge of life [54]. 392 Colorimetric detection of main peptides and proteins like glutathione (GSH) and 393 394 enzymes based on AuNPs has been well developed [124]. The aggregation of AuNPs based on distance-dependent optical properties and interaction of a 2:1 GSH-Cu²⁺ 395 complex has been utilized for detection of GSH [125]. It is interesting that the peptides-396 397 metal complex is always used to detect metal ions but this method uses this complex to hold a specific selective detection of GSH and reaches the LOD of 10 nM. On the 398 contrary, the anti-aggregation of functionalized AuNPs for GSH detection has also been 399

reported. For example, Uehara et al. described a GSH colorimetric assay based on GSH-400 triggered disassembly of AuNPs and exhibited a bluish purple color [126]. The degree 401 of AuNPs anti-aggregation was proportional to the GSH concentration, and thus 402 making sensitive detection of GSH (LOD of 29 nM). Similarly, the sodium 403 piperazinebisdithiocarbamate [127] and 2-mercapto-1-methylimidazole (MMI) [128] -404 capped AuNPs based on anti-aggregation principle for determination of GSH have been 405 reported, respectively. However, the principles are different. For the first one, the anti-406 aggregation is dependent on the stronger affinity between AuNPs and GSH. As for the 407 other one reported in recent, the anti-aggregation relies upon the mixture between MMI 408 and GSH, which leading to MMI lose the ability of attaching n the AuNPs surface 409 rather than GSH had stronger binding ability with AuNP. 410

The visual detection of proteins based on AuNRs ver the past few years such as 411 thrombin (Thr), lysozyme (Lysz), etc., hav been well reviewed by some reviews [129, 412 130]. Hence, for this section, we just review some typical studies introduced by some 413 groups and new studies reported rockity. The groups of Chih-Ching Huang and Huang-414 Tsung Chang are well known for studying on protein and DNA, especially the detection 415 methodologies. In 2005, they have developed a highly of proteins using valiou 416 the platelet-derived growth factors and receptors using aptamer selective sensor p 417 modified AuNPs by monitoring the color changes and extinction of the UV-vis 418 419 absorption peak [131]. In the aptamer-based strategy, unmodified AuNPs probes using a branched DNA amplification strategy have been employed by Chang et al. to detect 420 vascular endothelial growth factor (VEGF) [132]. Additionally, by integrating the 421 422 signal amplification capacity, this sensor allowed highly selective and sensitive VEGF detection with the LOD of 5 ng mL⁻¹ (185 pM), which was much lower than that of 423 other aptamer sensors. The modified-AuNPs for detection of fibrinolytic-related 424

proteins was also reported by the group of Chih-Ching Huang [133]. As shown in Fig. 425 3, the fibrinogen was self-assembled on the surface of AuNPs (Fib-AuNPs) for 426 427 simultaneous detection of plasmin and plasminogen. In the first place, the salt-induced aggregation of Fib-AuNPs in the presence of plasmin leading to sensitive detection of 428 plasmin. Next, the Thr- and Fib-AuNPs (Thr/Fib-Au NPs) were used to analyze the 429 plasmin activity and plasminogen concentrations in serum by observing Thr-induced 430 431 aggregation of Fib-Au NPs. On this basis, the concentration of plasmin as low as 0.4 nM has been determined. Recently, a facile AuNPs based colorimetric sensor array for 432 various proteins detection was introduced using DNA as a nonspecific receptor [134]. 433 12 proteins in serum have been well discriminated with the paked eye, which provide 434 novel insight into proteins recognition. DNA and carbon dots can also be employed to 435 modify AuNPs for nucleic acid and protein detection nd it were successfully applied 436

to human serum samples [135].



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Fig. 3. Schematic illustration of plasmin (a) and plasminogen (b) sensors that design on
the basis of fibrinolysis-mediated aggregation and thrombosis-mediated agglutination

of Fib-AuNPs, respectively. Adopted from Ref. [133], Copyright (2013), with
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443 *3.1.3. Nucleic acids*

In this part, we mainly introduce the studies demonstrated by the group of Mirkin 444 and some papers reported recently. DNA-based rationally assembling AuNPs were 445 446 firstly demonstrated by Mirkin in 1996 [136]. In fact, the hybridization of one 447 oligonucleotide probe and target-induced aggregation of AuNPs contributes to the interparticle distance dependent effect and surface plasmon resonance of AuNPs [137]. 448 Thiolated DNA strand-functionalized AuNPs make researchers study be properties of 449 AuNPs probes according to this method [138]. The discovery has stimulated fabrication 450 of oligonucleotide structured assemblies on AuNPs and extensive use of colorimetric 451 detection of nucleic acids. The mechanism lies in one or two base 452 oligonucleotide or DNA sequences with thick ands or -SH attach to the surface of 453 AuNPs and then the mismatches or complementary structure formed in the presence of 454 target chains, thus leading to aggregation of AuNPs and following the color change 455 from red-to-blue [139]. On the basis, they further investigated the factors controlling 456 the melting properties of DNA-linked AuNPs assemblies and found that the melting 457 Ig DNA or oligonucleotides were the key controlling factors [140]. temperature and h 458 Therefore, some thermodynamic investigations on binding properties for DNA-459 460 functionalized AuNPs probes have been developed [141, 142]. Furthermore, they also demonstrated new strategies for colorimetric detection of DNA concerning potential 461 DNA-binding molecules which could form duplex or triplex DNA (Fig. 4A and B) [143, 462 463 144]. Using these principle, Li et al. presented an ultrasensitive colorimetric method for microRNAs using the isothermal exponential amplification reaction-assisted AuNPs 464 [145]. In the presence of DNA polymerase, the target RNA gradually detached by the 465

sensing system and the bare AuNPs aggregated in high salt concentration without DNA
protection. This method distinguished a single nucleotide among homologous
microRNAs and provided a good linear range from 50 fM to 10 nM with the LOD of
46 fM.



470

471 Fig. 4. Colorimetric detection of ENA concerning potential DNA-binding molecules
472 based on the formation of duplex (A) or triplex DNA (B). (A) Adopted from Ref. [143],
473 Copyright (2006), with remnission of Wiley-VCH. (B) Adopted from Ref. [144],
474 Copyright (2006), with permission of American Chemical Society.

In recent years, some new methods for nucleic acids detection based on AuNPs have 475 been shown up. For example, Liu et al. reported a non-aggregated AuNPs based on 476 colorimetric sensor that was dependent on oligonucleotide-functionalized AuNPs and 477 magnetic beads, which played important role in removing the capped-AuNPs to obtain 478 higher sensitivity [146]. Compared with other AuNPs sensors, the distinction was 479 looking at the dispersed AuNPs in the supernatant rather than the sedimentation of 480 aggregated AuNPs. In addition, this strategy provided potential to establish a simple 481 and simultaneous multi-color sensor based on the non-aggregated AuNPs. It is reported 482

that because of the SPR phenomenon, namely the distance-dependent property of 483 AuNPs, single stranded (ss) DNA can interact with AuNPs and well stabilize in high 484 salt concentrations [147, 148]. In this case, a direct colorimetric sensor for unamplified 485 pathogen DNA has been developed based on dextrin-capped AuNPs, in which AuNPs 486 are aggregated in the absence of target ssDNA and this strategy achieves very low LOD 487 of 2.94 fM [149]. Strategies for nucleic acids detection based on AuNPs and other 488 materials, such as grapheme [19] and GO [150], have also been developed. Yun et al. 489 recently have introduced a novel strategy based on salt-induced aggregation of AuNPs 490 for enzyme-free ultrasensitive DNA detection [151]. This platform revied on the three 491 hairpin auxiliary probes are assembled on the surface of AuNPs in the absence of target 492 DNA. AuNPs are well dispersed in high salt concentration. When target DNA existed, 493 the hairpin auxiliary probes are activated and form additional branched junctions, which 494 cannot prevent the salt-induced aggregation. This idea is simple and selective and is 495 promising for colorimetric detection of other target molecules based on AuNPs. 496

497 3.2 Detection of inorganic ions

498 *3.2.1. Mercury ions*

tal ions, Hg^{2+} can bond with many groups like -NH₂, -SH, Different from other m 499 allows it form strong affinity with amino and amino acids. The and -COOH, which 500 basis of Hg²⁺-thymine complex (T-Hg²⁺-T) makes it is easily detected by 501 502 oligonucleotide-functionalized AuNPs sensors. In particular, the affinity between nitrogen atom and Hg²⁺ is always used to fabricate Hg²⁺ sensors based on the blue shift 503 of AuNPs process [152, 153]. A simple approach for selective visual sensing of Hg²⁺ 504 has been reported based on Hg²⁺ breaking the Au-S bonds between AuNPs thiol ligand 505 modified AuNPs and inducing aggregation of AuNPs [154]. Furthermore, a highly 506 sensitive and selective detection sensor for Hg²⁺ in drinking water through the sulfur-507

508 Hg²⁺-sulfur interaction has been reported [155]. This strategy provided the widest 509 detection range of 3×10^{-8} -1 $\times 10^{-2}$ M with a LOD of 30 nM.

Although the formation of Au-Hg alloy is unbeneficial to design Hg²⁺ sensor in 510 electrochemical sensor using gold-based electrode (GE), recent researches provide new 511 insight for designing Hg^{2+} colorimetric sensing probe [156]. Interestingly, a recent 512 paper based on three color changes from red through sandy beige (Au-Hg alloy) to 513 celandine green (larger Au-Hg alloy) has been proposed with a LOD of 8.76×10^{-9} M, 514 which is much lower than 30 nM [157]. Another novel headspace colorimetric sensor 515 for specific Hg²⁺ detection has been introduced based on the strong metallophilic Hg-516 Au interaction, and resulting in a LOD of 5 nM. In this strategy, AuNPs experience 517 etching and amalgamation process by Hg^0 and a red-to blue color change [158]. In 518 addition, because of excellent peroxidase-mimic in activity, the Au-Hg amalgam 519 strategy exhibits highly sensitive, rapid and two st for Hg^{2+} and H_2O_2 detection at the 520 same time [159]. Particularly, a gold anozyme-based paper chip was further prepared 521 on the basis of Au-Hg amalgan enhanced enzyme-like catalytic activity, which 522 provided a simple, sensitive rapid, and cost efficient sensor for trace of Hg^{2+} [160]. 523

DNA or oligonuc eoride-conjugated AuNPs have been used to colorimetric 524 recognition of Hotton the basis of T-Hg²⁺-T coordination chemistry (Fig. 5). Sensors 525 based on DNA or oligonucleotide were also well developed by the group of Mirkin. In 526 527 2007, they reported a colorimetric way by DNA-functionalized AuNPs [161]. This visual inspection sensor was highly sensitive and selective and simpler than the 528 conventional methods, but the requirement of precise heating and careful monitoring of 529 denaturation temperature limited the application. In order to overcome this drawback, 530 Xue et al. developed this method, which the operating temperature could be adjusted in 531 room temperature and simplify the step on detection of Hg^{2+} [162]. Owing to the 532

properties of DNA or oligonucleotide conjugated AuNPs, Mirkin et al. designed a new 533 class of G-rich oligonucleotides or guanosine monophosphate derivatives modified 534 AuNPs to simple and efficient detection of metal ions [163]. On this basis, some 535 recognition methods based on G-quadruplex-induced aggregation of AuNPs were 536 developed. Li et al. have proposed the design on selective detection of Hg²⁺ using the 537 T-T base pair in a DNA duplex, which Hg²⁺ can specifically bind to and form the 538 folding G-quadruplex DNAs and T-Hg²⁺-T complex [164]. Thus, the facial method to 539 sense Hg²⁺ with colorimetry is proposed and the concentration was as low as 50 nM 540



542

541

Fig. 5. Colorimetric detection of Hg²⁺ based on AuNPs aggregation by T-Hg²⁺-T
coordination chemistry on the basis of three formations, which lie in one (A), two (B),
and three (C) DNA or oligonucleotide strand, respectively. (A) Adopted from Ref.
[165], Copyright (2008), with permission of Wiley-VCH. (B) Adopted from Ref. [161],
Copyright (2007), with permission of Wiley-VCH. (C) Adopted from Ref. [166],
Copyright (2008), with permission of American Chemical Society.

Amino acid-functionalized AuNPs to visual detection of Hg²⁺ have been proposed. 549 A colorimetric sensing strategy for melamine (MA) and Hg²⁺ using cysteamine-550 modified AuNPs (Cys-AuNPs) has been introduced by Ma et al [167]. This strategy 551 achieved a LOD of 30 nM for Hg²⁺ detection with sensing mechanism of electrostatic 552 attraction for N-Hg²⁺-N structure in alkaline pH. Interestingly, this sensor could also 553 detect MA by adjusting the pH to acidity since the surface of Cys-AuNPs was 554 positively charged because of the protonated amine groups. The amine groups might 555 electrostatically bind with MA and then induced aggregation of AuNPs. The proposed 556 sensing strategy opened new opportunities for parallel detection of metal ions and 557 organic environmental hormones. The idea of using N-Hg2+-N structure to achieve 558 efficient detection of Hg²⁺ is worth learning but many of them may only imitate this 559 process to obtain a new method or use a new amno cid to modify AuNPs for Hg²⁺ 560 detection. Different from these strategies, Sere al. proposed novel thinking by using 561 the same property. Citrate-stabilized AuNPs were well dispersed in aqueous solutions 562 even Hg²⁺ coated on the surface [10]. Making use of the N-Hg²⁺-N structure obtained 563 -coated AuNPs aggregated and distinct color change from the lysine and Hg²⁺, the Pg 564 from red to blue occurred This proposal provided the LOD as low as 2.9 nM and was 565 very fast and se 566

The groups of carboxylic and amino (-COOH and -NH₂) are easy to complex with metal ions, especially Hg^{2+} [169-171]. A carboxylated peptide-functionalized AuNPs (peptide-AuNPs) for detection of Hg^{2+} was introduced by Si et al. in 2007 [172]. The main driving force of this sensor was laid on the dipole-dipole interaction between carboxylated peptide and Hg^{2+} . In fact, the mechanistic pathway should owe to the interaction between Hg^{2+} and -NH₂ or -COOH. In addition, the dynamic light scattering (DLS) measurement was used for verifying successful assembly of the peptide-AuNPs. A paper developed by Xu et al. described a novel approach for simple and rapid detection of Hg^{2+} in high salt solutions based on Hg^{2+} -induced aggregation of mononucleotides-functionalized AuNPs (dTTPs-AuNPs) [173]. As we all known, the citrate-stabilized AuNPs are easy to aggregate in high salt solutions. However, the dTTPs-stabilized AuNPs were well dispersed in high salt solutions, and quickly reaggregated when Hg^{2+} presented.

580 Proteins are made up of one or more polypeptides, which are formed from many kinds of amino acids, and play various important roles in all aspects of biology. Hence, 581 there is no doubt that protein-functionalized AuNPs can be used to detect metal ions. 582 Guo et al. have developed a simple and rapid visual approach for Hg^{+} , Cu^{2+} , and Pb^{2+} 583 determination using papain, which is a protein who some cysteine residues, 584 functionalized AuNPs [174]. To improve the sensitivity and selectivity, our group 585 modified this sensor by adding the cheirting agent, 2,6-pyridinedicarboxylic acid 586 (PDCA), which could form strong complex with Hg²⁺. The LOD was decreased from 587 200 to 9 nM and provided wide line mrange of 0.01 to 14 μ M [175]. To obtain the green 588 colorimetric sensor based in huNPs, Tripathi et al. have demonstrated a rapid and 589 simple sensor of biogenic AuNPs by mixing the fungal biomass from T. harzianum 590 a solution [176]. The sensor based on proteins-functionalized with chloroauric 591 AuNPs for colorimetric detection of metal ions provides a good idea, but the selectivity 592 593 should be improved in some extent.

In addition to the principles mentioned above, the colorimetric sensing for Hg²⁺ based on blue shift of absorbance peak is popular since it is very sensitive and highly selective. The details of these sensors are showed in **Table S2.** Among these strategies, the most interesting one is the paper reported by Tripathi et al [176]. In this work, the thiocyanuric acid (TCA) attached to the surface of AuNPs and induced aggregation of AuNPs with the color change of red to blue because the thiol group of TCA could easily bind with the AuNPs through Au-S bond. But the thiols were more apt to interact with Hg^{2+} , so when Hg^{2+} added, AuNPs were dispersed again and TCA separated from AuNPs forming complex with Hg^{2+} , which induced the color change from blue to red. Without the stabilization of citrate, AuNPs were easily aggregated in high concentration of Hg^{2+} , which showed reaggregation.

605 *3.2.2. Lead ions*

Table S3 exhibits the visual sensors for Pb²⁺ dealing with different capping agents 606 based on AuNPs aggregation. The AuNPs aggregation approaches based on ions 607 dependent chelation, including thiols and acids, were used to coortinetric recognition 608 of Pb²⁺. Also, the peptides, DNAzymes, and DNA can be the capping agents to 609 functionalize AuNPs for Pb^{2+} detection. The group of hupp pioneered the development 610 of visual sensors for Pb²⁺ based on aggregate and uNPs using 11-mercaptoundecanoic 611 acid (MUA) as the capping agent [177]. Later, Fan et al. improved this approach by 612 performing the chelation mechanism on a polydimethylsiloxane microfluidic chip and 613 the lower concentration with $10 \ \mu M$ of Pb²⁺ was determined [178]. Similarly, maleic 614 acid-functionalized AuNPs tends to aggregate when Pb²⁺ exists. The free -COOH of 615 ecifically with Pb²⁺ because of the strong affinity between them maleic acid reads 616 [179]. A strong demonstration reported by Ratnarathorn et al. has introduced the 617 618 mechanism clearly [180]. In a related study, Giannakopoulos et al. [181], Yoosaf et al. [182], and Huang et al. [183] have all demonstrated the determination of Pb^{2+} using the 619 gallic acid (GA) stabilized AuNPs. These studies have all revealed that Pb²⁺ prefers to 620 binding to the phenolic group that induced aggregation of GA-AuNPs in the presence 621 of Pb²⁺. 622

A series of colorimetric assays for detection of Pb^{2+} by using thiols-functionalized

AuNPs have been reported by the group of Huang. Firstly, a lable-free and 624 nonaggregation-based AuNPs probe has been introduced in 2009 [184]. The 625 mechanism based on the fact that AuNPs reacted with thiosulfate to form Au $(S_2O_3)_2^{3-1}$ 626 complexes, which lead to the decreasing of SPR absorption. When Pb2+ and 2-627 mercaptoethanol (2-ME) added, the Au⁺-2-ME complexes formed immediately and 628 induced the SPR absorption decreasing dramatically. Later, they reported an improved 629 label-free AuNPs-based probe, operating on the mechanism that Pb²⁺ controlled the 630 ligands shell of AuNPs using $S_2O_3^{2-}$ and 4-mercaptobutanol (4-MB). As a result, the 631 SPR absorption of AuNPs started red-shift and became broadened. This probe showed 632 high selectivity [185]. The group further developed a simple colorimetric approach for 633 selective parallel determination of Hg^{2+} , Ag^+ , and Pb^{2+} using the alkanethiols and label-634 free AuNPs [186]. For the detection of Pb²⁺, they used the probe of 2-ME/AuNPs as 635 mentioned above with a little modification, where Na_2S is the ligand instead of $S_2O_3^{2-}$. 636 This method provided simultaneously selective detection of many different metal ions, 637 but the sensitivity for detection $Abel{eq:beta} Pb^{2+}$ was not as good as the aforementioned 638 approaches. In addition, Linet II. reported a disaggregation-based method by using the 639 crown ether (15-crovn-j) and thioctic acid-bifunctionalized AuNPs [187]. In this 640 procedure, the ways aggregation formed because of the hydrogen bonds between 641 carboxylic acid residues. However, the aggregation was disrupted because of the 642 643 presence of Pb²⁺, and leading to a red-shift, which exhibited with a color change from blue to red. On the contrary, Mehta et al. reported a dithiocarbamate (DTC) derivative 644 of 4'-aminobenzo-18-crown-6 modified AuNPs colorimetric sensor based on the 645 scheme of affinity between crown ether and Pb²⁺, but it induced a red to blue color 646 change [188]. 647

 $Just like Hg^{2+}$, peptides-functionalized AuNPs have been used for visual

determination of Pb²⁺. The group of Chai demonstrated the GSH-functionalized AuNPs 649 (GSH-AuNPs) for cost-effective and sensitive colorimetric detection of Pb²⁺ in aqueous 650 solution [189]. Later, Bega et al. further developed this method to improve the 651 sensitivity by using DLS probe at pH 8 [190]. Then, Zhu et al. reported a new 652 colorimetric assay based on GSH and pentapeptide (CALNN) stabilized AuNPs in both 653 aqueous solution and living cell [191]. In the real sample application, it detected Pb^{2+} 654 655 in living cell downed to 2.9 fM with the wide linear relationship from 2.9 to 37.7 fM per cell. Recent year, an interesting ultrasensitive sensor using whispering gallery mode 656 based on GSH-AuNPs complex came true on an optical microcavity [92]. The signal 657 was found to be very proportional to the concentration of Pb²⁺ with the range of 2.4-658 48.26 nM. 659

Another kind of vital sensor for selective \mathbb{N}^2 etection was based on the 660 DNAzymes-functionalized AuNPs. For the the group of Liu and Lu have made 661 outstanding contributions. Initially, wey described a design of disaggregated sensors 662 based on DNAzyme-directed assuring of AuNPs ("8-17" DNAzyme system), which 663 provided high sensitivity and electivity [193]. In this design, sequence of substrate 664 with AuNPs and enzyme carried out catalytic reactions. strand (17DS) hybridize 665 gregation of AuNPs. When Pb²⁺ presented, "8-17" DNAzyme which led to the 666 cleaved the substrate strand, thereby preventing the aggregation of AuNPs and retaining 667 red color. This Pb²⁺ sensor was highly specific and provided a tunable dynamic range. 668 However, the temperature dependent and requiring heating and cooling limited the 669 simple application. Fortunately, they reported an improved version that allowed very 670 671 fast and room temperature determination by using larger size of AuNPs (42 nm) with a tail-to-tail formation instead of the earlier head-to-tail formation [194]. Furthermore, 672 they further developed a new design based on the controlled disassembly aggregated-673

AuNPs via a Pb²⁺-dependent RNA-cleaving DNAzyme [195]. Later, they reported a 674 sensor to tune the dynamic range based on unlabeled DNAzyme and AuNPs by 675 changing the pH. They added NaCl to adjust ionic strength and EDTA to quench the 676 chelating reaction [15]. As a variant of method introduced by Liu and Lu, Zhao et al. 677 developed a simpler DNAzyme-based technique [196]. Through the Au-S chemistry, 678 the sequence of S1-2 was modified on the surface of AuNPs (Au/S1-2) and then cleaved 679 680 by the DNase I leading to well dispersed S1-AuNPs. On the other hand, the aforementioned 8-17 DNAzyme system added a significant negative charge, hence 681 increasing the electrostatic stability in relatively high ionic strength. In the presence of 682 Pb^{2+} , the 8-17 DNAzyme was cleaved. The electrostatic and steric stabilization are 683 significantly reduced, which resulting in rapid AuNPs aggregation. Compared with 684 previous reports mentioned above, this strategy is use simple. In recent, the group of 685 Guo [197], Yang [198] and Sang [199] have reported the colorimetric detection of Pb²⁺ 686 based on DNAzyme-AuNPs amplification strategy and obtained a LOD of 2, 5, and 687 0.02 nM, respectively. 688

689 3.2.3. Cadmium and arsenic io

) and arsenic (As^{3+}) ions in rice and drinking water can Presence of cadmium 690 alth hazards, especially Cd²⁺, which easily accumulates in rice and 691 lead to significant be then makes its way via the food chain [200-203]. Colorimetric detection of Cd²⁺ ions 692 693 mainly includes functionalized Ag nanoparticles and AuNPs [204, 205]. The channels based on AuNPs can be divided three parts, the chemicals functionalized AuNPs, amino 694 acid or peptides stabilized AuNPs, and thiols capped AuNPs. Kalluri et al. introduced 695 696 a sensitive colorimetric sensor based on three kinds of chelating ligands functionalized-AuNPs through an As-O linkage or stable complex to sensitive detection of As^{3+} [206]. 697 This method provided a LOD as low as 13 nM. In 2013, Wang et al. demonstrated a 698

selective colorimetric detection method based on the 4-amino-3-hydrazino-5-mercapto-699 1, 2, 4-triazol (AHMT) functionalized AuNPs via chelation interaction between Cd²⁺ 700 and chelating ligands of hydrazine and triazol groups [207]. This paper obtained a LOD 701 of 30 nM with good linear range from 0 to 0.48 µM. As a confirmatory analysis, DLS 702 was used to determine changes in particle radius. Furthermore, the aptamers-capped 703 AuNPs for colorimetric detection of As³⁺ and Cd²⁺ were developed. The group of Zhou 704 demonstrated an arsenic-binding aptamer sensor for As³⁺ via an As³⁺-aptamer complex, 705 which led to the aggregation of AuNPs and caused an obvious color change from red 706 to blue [208]. It provided high selectivity and a low LOD of 70 nM (Fig. 6B). 707 Afterwards, they developed this method and used an aptamer to hum Cd-4 aptamer for 708 (Fig 6C) [209]. recognition of Cd²⁺ based on the aggregation of AuNPs 709



710

description Fig. 6. Schematic of (A) biosensor based 711 on poly(diallyldimethylammonium chloride) (PDDA) and specific aptamer mediated 712 AuNPs which are dispersed in the absence of metal ions; (B) biosensor for detection of 713 As³⁺ based on PDDA and Ars-3 aptamer mediated AuNPs that is aggregated in the 714 present of As³⁺; Adopted from Ref. [208], Copyright (2012), with permission of the 715 Royal Society of Chemistry. (C) colorimetric detection of Cd²⁺ on the basis of cationic 716

polymer mediated aggregation of AuNPs using Cd-4 aptamer as a recognition element.

Adopted from Ref. [209], Copyright (2014), with permission of the Royal Society ofChemistry.

Peptides-functionalized AuNPs for determination of Cd²⁺ have been developed. A 720 colorimetric assay using peptide-modified AuNPs (P-AuNPs) for parallel 721 determination of Cd^{2+} , Co^{2+} , and Ni^{2+} has been developed by Zhang et al [210]. The 722 peptide ligand was self-assembled on the surface of AuNPs via S-Au bond. The P-723 AuNPs aggregated with the presence of Cd²⁺, Co²⁺, and Ni²⁺, accompanying 724 remarkable color change. Guo et al. introduced an interesting simple and label-free 725 colorimetric approach to selective detection of Cd²⁺ utilizing unmodified AuNPs [211]. 726 In this paper, GSH presented and could prevented upper aggregating in high 727 concentration of NaCl, which led to efficient detection in high-salt medium. In addition, 728 the formation of spherical-shaped complex to read and the formation of spherical-shaped complex to rea 729 aggregation of AuNPs, which exhibited excellent selectivity to other metal ions. The 730 details of other recent colorimetros based on AuNPs for detection of Cd²⁺ are 731

shown in **Table S4**.

733 *3.2.4. Anions*

F⁻, cyanide (CN⁻ and SCN⁻), sulfide (SO₄²⁻, SO₃²⁻, and S²⁻), Some anions, K 734 nitrite (NO_2) , and nitrate (NO_3) , etc., play important role in human activities [212]. 735 736 They are widely present in environment and actively involved in food and biological systems [213]. However, excessive accumulation of these anions in living system with 737 high quantities can result in a series of deleterious disorders [214]. Thus, the detection 738 739 of anions has gained much attention. But the publications about detection of anions with AuNPs-based approaches are not so many compared with the detection of metal 740 ions because of the high pH sensitivity, low charge to ratio, and solvent dependent 741

binding affinity and selectivity [130]. Besides, some reviews have mentioned the 742 detection of typical anions based on AuNPs-supported method [215-217]. Hence, this 743 review just discusses some typical reports published in the last seven years. In this 744 manner, the Yang group have made a tremendous contribution to highly sensitive and 745 selective detection of anions. Besides, it is worth mentioning that the detection of anions 746 based on AuNPs-supported electrochemical method usually relies on the catalytic or 747 748 oxidation reaction of anions [218-220], while few of them have this ability. AuNPs on the electrochemical sensor for anions often serve as the medium connecting the ligands 749 or assistant improving the performance, which is similar with the detection of metal 750 ions [221-223]. On the other hand, metal ions such as Pb^{2+} . Hg^{2} , and Cu^{2+} are capable 751 of forming metal-ligands complexes with many groups of ligands, making them easier 752 detection [158, 224]. Hence, the detection of anions is only discussed in the colorimetric 753 method. 754

The basic design principle of anions detection is mainly divided into two channels. 755 One depends on exploiting a serve of possible interactions, like hydrogen bonding 756 atraction, and metal coordination bonds. Another is the interaction, electrostatic 757 signaling subunit which is responsible for the signal transduction. It is reported that 758 ty to etch metals to form a metal-cyanide complex, especially Au 759 cyanide has the and Ag [225-227]. With this respect, many ligands, which served as the protecting and 760 761 stabilizing agents, are removed from the surface of AuNPs by cyanide, thereby inducing the aggregation of AuNPs [228, 229]. And cyanide can be detected selectively [230]. 762 On the contrary, because the strong interaction between SCN⁻ and AuNPs, the 763 aggregated AuNPs inducing by Au-N interaction are redispersed again. The color of 764 AuNPs changes from blue to red [231]. In addition, in the "cyanide process", Au was 765 leached out by CN^{-} to form an $[Au(CN)_2]^{-}$ soluble complex which resulted in on-site 766

cyanide monitoring as low as 0.06 mg L⁻¹ [232]. By combining the ligands removal and 767 Au leached mechanism, Cheng et al. creatively proposed an AuNPs-based dual 768 769 fluorescence-colorimetric sensor for highly sensitive and selective detection of cyanide with low and high concentration [233]. This strategy gives a new insight in pollutant 770 detection. The visual detection of NO₂⁻ and NO₃⁻ based on AuNPs often relies on the 771 Griess reaction, which combines two kinds of amides by NO₂⁻ and NO₃⁻ to form a N=N 772 bond. The dispersed or aggregated AuNPs are aggregated or redispersed respectively, 773 thus results in highly sensitive detection of NO_2^- and NO_3^- [234, 235]. However, they 774 775 sometimes interfere with each other. Typical halogen ions including I⁻, F⁻, and ClO⁻ also have been de ected by AuNPs-776 based colorimetric method. It is reported that ClO- has strong oxidizing ability to some 777 ligands, especially thiols. Zhang et al. introduced a visual method for selective detection 778 of CIO by converting the alkanethiol to a subject derivative, which induced a red to 779 blue color change. However, the real sample detection were not so sensitive and 780 selective [236]. Thus, Lu et al. proposed a different idea by taking advantage of the 781 strong oxidizing ability of CN⁻ to dithiothreitol (DTT). In the present of ClO⁻, the 782 aggregated DTT-AuNPs were dispersed again because DTT was oxidized and could 783 n AuNPs surface, hence achieving highly sensitive and selective not be chemisor 784 detection of ClO⁻ [237]. Recently, on the basis of oxidizing Ag⁰ to Ag⁺ ions by ClO⁻ in 785 786 the Au/Ag alloy NPs, an effective colorimetric method for ClO⁻ detection was reported with the LOD of 300 nM in the linear range from 2400 to 24000 nM [238]. I- and F-787 can combine with metal ions and ligands to form metal-ions complex or ligand-ions 788 complex, making AuNPs aggregate as a result of lose the protector or changes of SPR 789 [239-241]. Interestingly, a novel sensing strategy for F⁻ detection was introduced based 790 on F-thiols, providing specific fluorous-fluorous interactions, which resulted in the 791

generation of precipitation, thus inducing a color change of red to colorless [242].
Besides, simultaneous detection of metal ions and anions has gained much more
attention. With this respect, Kumar et al. proposed a sunlight induced reduction of
AuNPs method, using polyacrylate functionalized AuNPs, to detect Al³⁺ and F⁻
simultaneously [100].

Sulfide is another kind of important anion, which exists in environment widely. 797 Hydrogen bonding interaction plays important role in sulfide detection since sulfide has 798 strong binding ability with some molecular receptors, like Cys and DTC, which induced 799 aggregation of protected AuNPs [105, 243]. Conversely, Yang group proposed a 800 different report [244]. Owing to the directional hydrogen bonding on-NH…O between 801 sulfite and probe, the electrostatic repulsion increases drama ically, hence contributing 802 to the enhancement in the stability of AuNPs. It is projed that AuNPs have an intrinsic 803 peroxidase-like activity that can catalyze axidation of 3,30,5,50-tetramethylbenzidine 804 (TMB) by H_2O_2 , thus generating Que colored products [245]. However, S^{2-} has 805 confirmed that it is capable of rewring Au^{3+} to form AuNPs, Au_2S , or their mixture 806 S² spields the peroxidase-like activity and triggers the [246-248]. Therefore, 807 aggregation of ligards-sapped AuNPs through hydrogen bond and electrostatic 808 aramatically decreases the catalytic activity of AuNPs [249]. interaction, which 809 Inevitably, the chromogenic reaction of TMB is inhibited by S²⁻, which contributes to 810 the sensitive and selective detection of S^{2-} [250]. 811

3.3. Detection of organic environmental hormones

Recent years, the organic environmental hormones including some persistent organic pollutants, food additives, and medicines have been widely used in agriculture, industry, food, and medical field [251-255]. Some of them are released into the environment, resulting in serious environmental problems [256, 257]. On the other hand, these molecules accumulate through biologic chain and eventually bring about serious side
effects of health for all living species [258, 259]. In the above section, we discussed
AuNPs-based colorimetric assays for biomolecules and inorganic ions. Similar
detection systems also proposed for organic environmental hormones such as MA,
pesticides, drugs, and others (Table S5).

822 *3.3.1. Melamine*

823 As reported by many papers, MA contains a three nitrogen hybrid ring and three exocyclic amino groups which makes it easily bind onto the surface of AuNPs and be 824 recognized via hydrogen bonding. Ai et al. reported the use of hydrogen bonding 825 recognition for MA based on 1-(2-mercaptoethyl)-1,3,5-triazinale-24,6-trione (MTT) 826 stabilized AuNPs, with the LOD of 0.2 nM and linear range from 4 to 200 nM and 280 827 to 440 nM [260]. Given the mechanism, it is the first time to demonstrate the triple 828 hydrogen-bonding recognition between M MA based on AuNPs can be used to 829 detect MA. Later, as shown in **Fig.** [¶] some papers reported that many materials such 830 ssDNA [263] could form hydrogen-bonding as DBA [261], PD [262], 831 and AS interaction with MA due to it had the ability to provide nine hydrogen-bonding sites 832 [264]. Besides the argregation of AuNPs based on hydrogen-bonding recognition, 833 n of MA based on non-aggregation of AuNPs has reported by Cao 834 colorimetric detec et al. [261] and Wu et al. [262] with the LOD of 0.8 and 0.64 nM respectively. 835 836 Interestingly, the principle of this two assays was similar that AuNPs were reduced by the stabilizers and aggregated at the same time. However, in the presence of MA, 837 AuNPs were well dispersed in solution attribute to hydrogen-bonding interaction 838 839 between the stabilizing agents and MA (Fig. 7B).


Fig. 7. Hydrogen bonding interaction induced aggregation (A) and anti-aggregation (B)
of AuNPs between MTT, HS-ssDNA, DBA and PD and MA, respectively. The colorlabeled chemical construction is the potential hydrogen bonding sites, which can form
the hydrogen bonding interaction

840

Except for the hydrogen-bending recognition, other colorimetric strategies based on 845 aggregation of AuNP been reported. Chen et al. [265] and Ni et al. [266] 846 at gives based on MA inducing aggregation of bare AuNPs and demonstrated 847 provided high sensitivity. The difference was that the paper reported by Ni et al. utilized 848 the proxidase-like activity of AuNPs, which produced a blue color change. In addition, 849 Guan et al. designed a simple label-free approach for sensitive detection of MA based 850 on chitosan-stabilized AuNPs. The presence of MA induced a red-shift in surface 851 plasmon bond and a red-to-dark blue color change [267]. Recently, methanobaction 852 (Mb) reduced Au^{3+} to Au^{0} and mediated the fabrication of AuNPs for colorimetric 853 detection of MA has been reported [268]. In the presence of MA, the oxazolone ring of 854 Mb interacts with MA, the formation of AuNPs is interrupted and aggregation of 855

AuNPs shows up simultaneously. This strategy provides the synthesis of AuNPs andanalysis of MA in one-step.

858 *3.3.2. Pesticides*

Visual detection of pesticides based on AuNPs has been well developed in recent 859 years since the pesticide contamination has become a serious problem all over the world 860 [269]. Organophosphorus pesticides (OPs), a kind of important pesticide, are widely 861 862 used in agriculture. Acetylcholinesterase (AChE) is a very important cholinesterase enzyme. It sustains the level of neurotransmitter acetylcholine for living organisms via 863 catalyzing the hydrolysis reaction from acetylcholine to thiocholine. However, the 864 catalytic activity of AChE can be thoroughly inhibited by trace amount of OPs. This 865 property makes AChE inhibition biosensor become the excellent way for colorimetric 866 detection of OPs based on non-aggregation of AuNP (as shown in Table S5) [270, 867 271]. The mechanism of this approach can be cassified into two steps. The first step is 868 that the catalytic hydrolysis of Achi promotes the growth of AuNPs seeds and then 869 leads to a red-to-blue color change the second step is that OPs inhibit the enzymatic 870 catalytic hydrolysis product and thus preventing AuNPs aggregation with well 871 I is very sensitive for recognition of OPs. However, the dispersion. This appload 872 ample applications for some are still needed to improve. For 873 sensitivity and example, the paper reported by Sun et al. demonstrated a simple label-free visual sensor 874 875 for OPs detection based on the catalytic reaction of AchE and aggregation of lipoic acid-capped AuNPs, but the sensitivity was not so satisfied [272]. In order to overcome 876 these weaknesses, the group of Wu developed a highly sensitive colorimetric method 877 878 for parathion detection based on the enzymatic hydrolysis reaction of AchE and dissolution of AuNPs in Au³⁺-CTAB solution [273]. As a result, parathion was 879 sensitively and selectively detected in tap water, sea water, and apple washing solution 880

with the LOD of 2.4 nM under optimal condition.

882 Bai et al. reported a quick colorimetric detection approach for recognition of six OPs 883 based on aptamer-stabilized AuNPs in high-salt concentration solutions [274]. Aptamer prevented the aggregation of AuNPs in high-salt concentration solutions. Upon the 884 addition of targets, aptamer bond to the targets and detached from AuNPs, leading to 885 886 eventual aggregation of AuNPs. The results showed that only isocarbophos had the 887 highest sensitivity. Although the specific of this method is still needed to improve, it provides potential application of aptamer-functionalized AuNPs to detect OPs. 888 Similarly, Balaet al. used an aptamer and a positively charged, water-soluble 889 polyelectrolyte, PDDA to stabilize AuNPs and detect Malathion velectively [275]. 890 PDDA and aptamer could form the PDDA-apt duple, and prevented the AuNPs 891 aggregation. When Malathion presented, the aptanen bond to Malathion and further 892 formed apt-mal complex, the aggregation fac Ps was induced with a color change 893 from red to blue. In addition, this approach provided high sensitivity and selectivity 894 with the linear range of 0.5–1000 pM and LOD of 0.06 pM. 895

896 3.3.3. Drugs and other organic environmental hormones

of drugs based on AuNPs has been developed because of the Colorimetric detect on 897 y and easy functionalization [276, 277]. As shown in Table S5, good biocompa 898 the principle of this sensor almost lies in the hydrogen-bonding interaction mentioned 899 900 above. Particularly, Zhang et al. [278] proposed a novel one step preparation of AuNPs using pyrocatechol violet (PCV) as the reducer agent to parallel detect four kinds of 901 antibiotics, including kanamycin, neomycin, streptomycin, and bleomycin. This sensor 902 903 was simple and practical, but the selectivity should be further improved. On the basis of hydrogen-bonding interaction, our team demonstrated the colorimetric detection of 904 kanamycin using AHMT- [279] and chitosan [280]-functionalized AuNPs, respectively. 905

The hydrogen-bonding interaction between kanamycin and functionalized agents 906 allows the AuNPs aggregate rapidly with the color change from red to blue. In addition, 907 these sensors can be used for various real samples detection such as environmental 908 water, milk, and urine with good sensitivity and satisfied selectivity. However, more 909 specific sensors should be further developed for visual detection of antibiotics. The 910 911 colorimetric aptasensor has been designed for selective and fast detection of target 912 either [281]. Ramezani et al. developed a triple-helix molecular switch and AuNPs assembled biosensor for colorimetric detection of tetracycline [282]. In the present of 913 tetracycline, the salt-induced aggregated AuNPs dispersed again due captamer bond 914 to its target and induced obvious blue-to-red color change. 915

916 4. Electrochemical applications of AuNPs in sursing

Electrochemical sensor has gained much attention 917 ecause of its distinct properties such as rapidness, convenience, sensitivity dhandling, in-situ monitoring, low cost, 918 919 and miniaturization [283, 284]. Until tow, indirect electrochemical methods for various samples detection have been will developed [285, 286]. Specifically, the 920 ually performed by a three-electron system including a electrochemical sensor 921 (VE) counter electrode (CE), and reference electrode (RE). A working electrode 922 platinum wire and Ag/AgCl (saturated KCl) usually act as the CE and RE, respectively. 923 924 Different electrodes, such as GE, GCE, etc., are used as the WE broadly [287]. Because of the high price and easy abrasion, GE is used less. To improve the specificity, WE is 925 often covered with different materials. The presence of substances causes the change 926 of current, potential, capacitance, or electrochemical impedance, which indicates the 927 change of different concentration of substances and provides specific detection 928 approach [22]. Based on the detection signals, the common electroanalytical techniques 929 employed for sensor system mainly include electrochemiluminescence (ECL), 930

electrochemical impedance spectroscopy (EIS) and voltammetry which can be briefly 931 divided into these parts: differential pulse voltammetry (DPV), cyclic voltammetry 932 (CV), square wave voltammetry (SWV), and anodic stripping voltammetry (ASV). 933 Generally, electrochemical sensor provides rapid response and well portability and 934 offers high sensitivity and selectivity, which makes the chemical recognition of species 935 being determined [288, 289]. Moreover, the surface area of WE is the most important 936 937 factor that affects the sensitivity because more functional groups or chemical moieties can be exposed to the target in the case of enhanced surface area [290]. Owing to the 938 properties of good biocompatibility, huge surface area, effective amplification of 939 electric signal, and easy to modify, electrochemical sensor employing AuNPs has many 940 advantages [291]. Firstly, an electrode employing AuNPs provides much larger surface 941 area, which results in higher current signals. Secondly the biologic chain can contact 942 with the AuNPs more "intimately", which and ditate electron transport. Thirdly, the 943 sensitivity, selectivity, and robustness can be further enhanced. 944

945 4.1. Detection of biomolecues

946 4.1.1. Amino acids and provin

AuNPs have been set for electrochemical detection of amino acids and proteins 947 with very low Loo, even picomole. The techniques include aptasensor, immunosensor, 948 molecularly imprinted polymers (MIPs), and ECL, etc. For example, Miao et al. 949 developed a simple ultrasensitive electrochemical sensor for picomle determination of 950 GSH using two GE and two complementary thiolated oligonucleotides [288]. One GE 951 was immobilized with one oligonucleotide at first and then replaced by GSH. 952 953 Subsequently another GE immersed in the solution and captured the released oligonucleotide. The goal reached by immobilizing the complementary oligonucleotide 954 functionalized AuNPs, which located large numbers of [Ru(NH₃)₆]³⁺, and measured the 955

chronocoulometry (CC) response. The stronger response meant more $[Ru(NH_3)_6]^{3+}$ 956 were adsorbed onto the surface, which indicated a higher concentration of GSH existed. 957 On the contrary, Chen et al. developed a cationic polyelectrolyte-functionalized 958 graphene/AuNPs composites modified electrode for angiogenin sensing [292]. Upon 959 the aptamer combined with AuNPs and $[Fe(CN)_6]^{3-/4-}$ redox couple presented, the 960 angiogenin pushed the structure conversion of loose random coil DNA sequence into 961 the secondary stem-loop structure. Then $[Fe(CN)_6]^{3-/4-}$ redox couple released in the 962 solution and led to an increase in the electron transfer resistance, which induced a 963 significant decrease in SWV current and the sensing process came true. Moreover, the 964 electrochemical immunoassay supported by AuNPs composited with carbon nanotubes 965 (CNTs) and GO has also been used for highly sensitive letection of alpha-fetoprotein 966 [293], antibodies [294], and biotin [295]. AuNPs an used to improve the reaction 967 activity and enhance the electrical conductivity 968

AuNPs are used to provide a large surface area for effective immobilization of 969 ligands, ascertain the bioactivity we stability for immobilization of target, as well as 970 trigger the catalysis reaction some case [296, 297]. This design provides excellent 971 selectivity. Similar strategy based on MIPs technique has been further proposed. For 972 ingh reported the concerted effect of MIP@graphite/multi-walled 973 instance, Prasadar carbon nanotubes (MWCNTs)/AuNPs/sol-gel composite for L-cysteine detection by 974 975 measuring the signal intensity of differential pulse anodic stripping voltammetric (DPASV) (Fig. 8) [298]. On one hand, the incorporation of MWCNTs and AuNPs was 976 significant in terms of the possible detrimental effect on ohmic contact due to the sol-977 978 gel × graphite interface. On the other hand, the electro active surface area was obviously enhanced owing to its abundant porous structure via incorporation of MWCNTs and 979 AuNPs, which resulted in a sensitivity augmentation. Other electrochemical biosensors 980

based on AuNPs using different techeniques such as ECL and bi-enzyme biosensor 981 were used for detection of glycosylated hemoglobin [299], inosine monophosphate 982 [300], etc. In ECL, luminol and $Ru(bpy)_3^{2+}$ are significant luminophores and always 983 used as the ECL indicators [301-304]. Owing to the excellent electrical conductivity of 984 AuNPs, ECL of indicators can be promoted [305]. There are many reports demonstrated 985 that AuNPs could promote the electron transfer between electrode and indicator and 986 987 increase the sensitivity of proposed ECL sensor [306, 307]. When composed with other materials like MWCNTs and polyamidoamine dendrimer, the energy transfer can be 988 further improved [308]. Particularly, the group of Huang et al. developed the pulsed-989 laser desorption/ionization mass spectrometry (LDI-MS) for detection of Thr [309] and 990 plasmin [310] by analyzing gold clusters desorbed from aptamer or Fib-modified 991 AuNPs on a nitrocellulose membrane or mixed cellulo e ester membrane. This kind of 992 technique provided ultrahigh sensitivity and ellent application on human serum. 993 Importantly, it showed high potential for aptamers, proteins, even other biological 994 signals recognition. QDs are we known for their ability to generate photocurrent. 995 However, a recent pape demonstrated that an AuNPs/CdAgTe QDs hybrid 996 photoelectrochemical (P immunosensing system was successfully synthesized to 997 ac troponin I based on energy transfer between QDs and AuNPs 998 sensitively dete [311]. The electrons produced by QDs were quickly transferred to the surface of AuNPs 999 and finally moved onto GCE to generate photocurrent. 1000



Fig. 8. Outline L-cysteine micro-contact 1002 of imprinting: (A) graphite/MWCNTs/AuNPs/sol-gel layered Si-C abraded composite paper support 1003 modified with cross-linker and initiator, and the coverlass is coated with template and 1004 has bught into contact with the modified functional monomer; (B) the cover-glass 1005 paper support and then placed in UX reactor; (C) the cover-glass is removed; (D) a 1006 single bead presentation of MIP adjuct; (E) template is extracted by washing; (F) 1007 introluced into MIP cavities; and (G) rebinding of template potassium ferricyanide is 1008 by replacing potassium ferricyanide from MIP-cavities. Adopted from Ref. [298], 1009 1010 Copyright (2013 with permission of Elsevier.

1011 *4.1.2. Nucleic acids*

1001

There is no doubt that most of the electrochemical sensors for nucleic acids detection are on the basis of nucleic acid hybridization since it prefers to form complementary, non-complementary base-pairing, and mismatched oligonucleotides. The signal response is enormously increased in the presence of AuNPs [312]. The attachment of AuNPs to sensor can dramatically decreased the electron transfer resistance [313].

the electrons to further increase the signal for nucleic acids detection [315]. A label-1018 free ECL sensor using a CdTe quantum dots (QDs) co-immobilized with AuNPs on a 1019 1020 chitosan-modified electrode has been designed for DNA detection [316]. The target DNA hybridizes with a molecular beacon to form the hemin/G-quadruplex architecture 1021 for signal inhibition. The results reviewed that the ECL signal could be decreased 1022 linearly following the logarithmic value of DNA concentration in the range of 5 fM to 1023 1024 0.1 nM, with a LOD of 0.9 fM. As shown in Fig. 9A, an original sensitively electrochemical-based DNA biosensor on the basis of direct relation between redox 1025 complex concentration and hybridization has been reported by using methylene blue 1026 (MB) as electroactive indicator [317]. The peak current of DRV acreased with the 1027 increasing concentration of target DNA, which attributed to the complementary base-1028 pairing interaction leading to MB turn to leucomethyle 1029 e blue. In addition, it was found that when the redox complex bond more strongs with the unhybridized biorecognition 1030 molecule, higher selectivity was achievable. Recently, a highly efficient PEC sensor 1031 was reported for microRNA-21 detection based on the energy transfer between CdS:Mn 1032 doped structure and AuNPs [3] 8]. AuNPs were employed to adjust the exciton states 1033 through energy transfer. This method was realized for in CdS:Mn doped st 1034 n in a linear range of 1.0 fM-10.0 pM with LOD of 0.5 fM. 1035 microRNA-21 Increasing electrical signal, namely signal amplification, is a typical way for target 1036 1037 recognition. AuNPs used here can amplify the signal and be the attachment between

- targets and ligands [319]. The dual-amplification strategy for analyte recognition highly
 improves the sensitivity and has well application on real samples [320]. Besides, a
 highly sensitive and selective aptasensor for adenosine on the basis of target-induced
 strand release from the electrode and AuNPs amplification labels was developed [321].
- 1042 The results showed excellent selectivity toward adenosine recognition in serum samples.

The optical approach for nucleic acid detection supported by unmodified AuNPs using 1043 differential affinity of single- or double-stranded nucleic acids is always limited by 1044 relatively low sensitivity. To improve the sensitivity, the group of Li demonstrated an 1045 amplified electrochemical strategy based on the selective preconcentration of AuNPs 1046 [322]. As exhibited in Fig. 9B, the protected AuNPs formed by capturing the probe 1047 ssDNA on the surface, which produced significant negligible amperometric signal in 1048 the presence of $Fe(CN)_6^{3-}$. However, experiencing a hybridization reaction, the 1049 ssDNA/microRNA heteroduplex could not bind with AuNPs anymore. And lately, the 1050 free-AuNPs were preconcetrated on the surface of electrode, indusing significant 1051 improvement of amperometric signal. In another one-pot assay concept, the target 1052 microRNA served as a shear, which opened the biotin MBs, and captured AuNPs, 1053 Furthermore, the LOD was further resulting efficient detection of microRNA-21. 1054 improved from 100 fM to 4 fM by depositive A 1055 onto AuNPs [323].



1056

1057 Fig. 9. Schematic representation of electrochemical biosensor (A) for DNA recognition

1058 based on polylactide-stabilized AuNPs modified electrode; Adopted from Ref. [317],

1059 Copyright (2016), with permission of Elsevier. (B) Cartoon drawing for 1060 electrochemical detection of target nucleic acid sequence. Adopted from Ref. [322], 1061 Copyright (2016), with permission of Elsevier.

1062 *4.1.3. Enzymes*

Thr plays central role in large number of cardiovascular diseases and regulates many 1063 processes like inflammation and tissue repair at the blood vessel wall [324]. It is 1064 1065 necessary for assessing its concentration at trace level and many efforts have been tried. Zhang et al. [325] and Bai et al. [326] both introduced the detection method of Thr 1066 based on the hybridization chain reaction depending on DPV response. The difference 1067 is that Zhang et al. used two kinds of DNA as aptasensor and Po²⁺ was necessary here 1068 to indicate the concentration of targets. AuNPs served as the connection between 1069 aptamerII and barcode binding DNA to capture more rgets. However, Bai et al. used 1070 HRP and DNA as the aptasensor and obtained he DPV signal through exonuclease-1071 catalyzed target recycling. AuNPs were deposited on the surface of GCE to attach the 1072 capture probe. These aptasensors sensitive and selective but the achievement of 1073 target detection is dependent on other materials, which limits the further development. 1074 ECL, a super-sensitive electrochemical approach for tracing detection of target, has 1075 eful as simple strategy in Thr recognition. As displayed in Fig. 1076 been proved very 10A, a ECL DNA sensing platform on the basis of energy transfer between CdS:Mn 1077 1078 nanocrystals (NCs) and AuNPs has been introduced [327], where CdS:Mn NCs served as ECL luminophores and AuNPs functionalized as both the ECL quencher and 1079 enhancer. The quenching of fluorescence by AuNPs is because of the Förster resonance 1080 1081 energy transfer (FRET) when luminophores and AuNPs are at close proximity. When the target DNA hybridizes with hairpin-DNA probe, an ECL enhancement achieved 1082 due to the interactions of the excited CdS:Mn NCs with ECL-induced SPR in AuNPs 1083

at large separation. Inspired by this sensor, Deng et al. developed a Thr-binding aptamer-related ECL "off-on-off" platform as well based on the energy transfer between AuNPs and CdS:Eu NCs film (**Fig. 10**B) [328]. AuNPs played a critical role in triggering on or turning off the energy transfer. Results showed that this "off-on-off" ECL sensor exhibited a maximum 7.4-fold changes of ECL intensity and offered obvious sensitivity improving for Thr detection in a widespread detection range from 50 aM to 1 pM with the low LOD of 1 aM.



1091

Fig. 10. (A) DNA ECL sensing platform based on energy transfer between CdS:Mn
NCs and AuNPs; Adopted from Ref. [327], Copyright (2009), with permission of the
Royal Society of Chemistry. (B) TBA-related ECL "off–on–off" sensing platform
based on energy transfer between CdS:Eu NCs film and AuNPs. Adopted from Ref.
[328], Copyright (2014), with permission of Elsevier.

Other aptamer-based ECL protocols have been reported for highly sensitive detection
of Thr [329, 330]. Other material such as graphene was used to composite with AuNPs

for further amplifying the signal [331]. In addition, the label-free bifunctional ECL 1099 aptasensor to simultaneously detect many kinds of targets trough switching structures 1100 of aptamers was introduced [332]. But the study was not intended to eliminate the 1101 interference. Especially, Chen et al. further simplified the design by using TCA/AuNPs 1102 modified with ssDNA and improved the sensitivity ranging from 5 pM to 1 nM and 1103 LOD as lower as 0.1 pM [333]. AuNPs were used as the carriers to load more ssDNA 1104 1105 and further enhance the sensitivity owing to their huge surface area. Recently, an interesting work for Lysz detection has been proposed by Shamsipur et al [334], who 1106 also used AuNPs to capture large amount of aptamer. The most interesting thing is that 1107 they used two kinds of electrochemical assay with two different redox probes to indicate 1108 the electrochemical signal and induced responses of signal-on" and "signal-off" 1109 respectively. Generally, it is very difficult to express opposite signal in the same system 1110 but this strategy indicates a new trend for upper ation of sensor. Not only for Thr and 1111 Lysz, other enzyme sensors have been developed either [335, 336], as well as other 1112 electrochemical techniques such [337]. They also provide excellent selectivity 1113 and high sensitivity and are worthy of consideration for wider application. 1114

1115 4.2. Detection of heavy metal ions

1116 4.2.1. Mercury **N**

Similar with the principle reviewed about the colorimetric sensor for Hg^{2+} above, the main mechanism of electrochemical sensor can be divided into four parts: 1) the interaction between Au and Hg^{2+} ; 2) the formation of T- Hg^{2+} -T coordination chemistry; 3) the formation of cooperative metal-ligand complex; and 4) the strong affinity of S-Hg²⁺ bond. **Table S6** reviews the developments in the design of electrochemical sensor for Hg^{2+} with different strategies in recent years. The details of these strategies will be elaborated as follows.

CNTs-supported AuNPs composites have been synthesized by Xu et al. and first 1124 applied for the detection of trace Hg²⁺ via ASV based on the strong interaction between 1125 Au and Hg^{2+} [338]. It provides remarkable decrease of reaction time and improves the 1126 performance comparing with solid GE. However, the performance on real samples and 1127 interferences are not clear. CNTs serve as the bridge links and transmit the electron 1128 between GCE and AuNPs. Except for CNTs, other materials such as GO and carbon 1129 1130 fiber can also be the bridge between electrode and AuNPs [339, 340]. Recent research using 3D graphene/gold film has been proven for highly efficient detection of Hg²⁺ 1131 [341]. This newly-designed strategy opens the door towards fabricating 3D graphene-1132 based AuNPs hybrid films simply, and such structures possesses excellent properties 1133 of high structure stability, substrate binding strength, significantly large specific area, 1134 and good electrical conductivity due to the synergistic effect of AuNPs and graphene. 1135 Most importantly, it offers an ultralow LOR of aM, which is the lowest one among 1136 we have ever mentioned in this review. On the other hand, the bare GCE deposited with 1137 AuNPs for detection of Hg²⁺ have developed by using a Square Wave Anodic 1138 Stripping Voltammetry (SWANV) procedure [342]. 1139

Most of the curren researches related to electrochemical methods for detection of 1140 are based on T-Hg²⁺-T coordination chemistry. For the strong Hg²⁺ using Au 1141 affinity between gold and some groups, GE is always used relatively early based on T-1142 Hg²⁺-T coordination chemistry [343, 344]. It is simple and convenient, but GE is 1143 expensive, easy to abrade and structurally change because of amalgam formation, the 1144 methods using GCE have been developed. The groups of Zhang [345] and Tang [346] 1145 with their co-workers have been developed an electrochemical sensor using GCE for 1146 Hg²⁺ detection based on target-induced formation of AuNPs, coupling with the cycling 1147 signal amplification strategy using DPV. The main mechanism of the two strategies is 1148

shown in Fig. 11. They are both sensitive and selective and provide a low LOD of 0.02 1149 and 0.06 nM with the linear range of 0.5 to 120 nM and 0.02 to 1000 nM, respectively. 1150 Recently, a thymine (T)/CA/AuNPs/rGO modified electrode has been fabricated and 1151 obtained high sensitivity in the range of 0.05 to 5 nM and LOD of 0.008 nM [347]. In 1152 this case, AuNPs always serve as the connection to link rGO and T. Moreover, they can 1153 be the capture probe to attach more T. It is reported that DPV is one of the most sensitive 1154 1155 approaches for heavy metal ions detection because of the low LOD [348]. Interestingly, an enzyme-triggered formation of enzyme-tyramine concatamers on AuNPs-1156 functionalized dendrimer using EIS with enhanced sensitivity was reported [349]. A 1157 wide dynamic working range from 0.001 to 100 nM and LOD of 0.0004 nM were 1158 obtained, and the method exhibited high selectivity and specificity towards Hg²⁺ against 1159 other metal ions. ECL is also one of the important approaches for electrochemical 1160 detection of Hg^{2+} [350]. For example, a **Ksigra** on" ECL biosensor based on DNA 1161 hybridization was designed on the AtNPs nanopatterned electrode surface [351]. In the 1162 presence of Hg²⁺, the loop sequence of hairpin-DNA opened and the ECL "signal-on" 1163 was triggered at the same time. Cai et al. designed a multiple signal amplification 1164 protocol based on graphene conjugated with CdSe QDs and horseradish peroxidase 1165 AuNPs [352]. The presence of AuNPs greatly accelerated the 1166 (HRP) labeled electron transfer and enhanced the electrochemical reaction efficiency owing to their 1167 1168 excellent electrical conductivity and large effective surface areas. The ECL intensity was linearly dependent on wide Hg²⁺ concentration from 1 to 4985 nM with the LOD 1169 of 0.3 nM. Lately, a label-free ECL assay was developed through oligonucleotide 1170 mediated assembly of AuNPs, in which AuNPs well preserved electronical 1171 conductivity and significantly enhanced the ECL signal [353]. This method provided 1172 specific Hg²⁺ detection over the range of 8 pM-2 nM with a LOD of 2 pM. 1173



1174

Fig. 11. Schematic diagram of electrochemical sensor for Hg²⁺ detection based on (A)
catalytic formation of AuNPs; Adopted from Ref. [346], Copyright (2014), with
permission of Elsevier. (B) target-induced AuNPs aggregation formed on DNA-based
polyion complex membrane by coupling with voting signal amplification strategy.
Adopted from Ref. [345], Copyright (2014), with permission of Elsevier.

Cooperative metal T-rich DNA sequences ligand interaction is very attractive for 1180 metal ions detection. The groups, including -COOH and -NH₂, are typically and can 1181 ith Hg²⁺. In fact, as shown in Fig. 12, the T-Hg²⁺-T form metal-ligand complex 1182 mismatches as described above use the cooperative binding between Hg²⁺ and N atoms 1183 [354, 355]. On these basis, Safavi and Farjami [356] reported a new strategy based on 1184 thiolated amino acids-functionalized AuNPs through cooperative Hg²⁺-ligand 1185 1186 interactions. The carbon ionic liquid electrode served as the WE to avoid amalgam. The proposed electrode showed high sensitivity and selectivity and good applicability in tap 1187 1188 and waste water. Moreover, attempts have been done by using new method such as imprinting films to enhance the performance. For example, Fu et al. [357] demonstrated 1189 a surface imprinted electrode utilizing the strong coordination between Hg^{2+} and S, 1190 which produced excellent selectivity in natural water samples. AuNPs served as a 1191

reinforcing substrate material to synthesis core-shell structural ion imprinting material,



1193 due to the high surface area, excellent catalytic and sensing properties.

Fig. 12. Schematic illustration of electrochemical detection of Hg²⁺ based on T-Hg²⁺.
T mismatches using the cooperative binding between Hg²⁺ and N atoms. (A) Adopted
from Ref. [354], Copyright (2012), with permission of Elsevier. (B) Adopted from Ref.
[355], Copyright (2017), with permission of Elsevier.

1199 *4.2.2. Lead ions*

1194

Electrochemical sensor for specific recognition of Pb2+ consisting of AuNPs-1200 supported electrode has been successfully applied for the enhanced sensitivity and 1201 selectivity. On the basis of G-quadruplex formation between Pb^{2+} and aptamer, 1202 DNAzyme cleavage-based sensors are the most popular techniques (Fig. 13). As an 1203 example, a DNAzyme-immobilized GE through thiol-gold interaction has been 1204 designed [358]. On the basis of binding Pb²⁺ to DNAzyme, the hydrolytic cleavage of 1205 substrate is catalyzed by DNAzyme, which leads to the removal of substrate strand and 1206 bound $\text{Ru}(\text{NH}_3)_6^{3+}$ from the GE surface (**Fig. 13**A). Different with this procedure, Yang 1207 et al. have demonstrated a DNAzyme functionalized AuNPs amplification strategy to 1208 enhance the sensitivity [359]. As shown in Fig. 13B, the DNA2 of ds-DNA coated on 1209 AuNPs is cleaved by Pb²⁺, remaining DNA1 which could be matched with the 1210 complementary strand (DNA3) and resulting in the CC signals when $Ru(NH_3)_6^{3+}$ 1211

existed. Similar to this strategy, our team provided an amplified detection strategy employing AuNPs and nanoporous Au for Pb^{2+} detection in various samples [287]. As the result of Pb^{2+} -specific DNAzyme, the aptasensor showed high selectivity and sensitivity with wide linear range of 0.05–100 nM, following a LOD as low as 0.012 nM.



Fig. 13. Principle of electrochemical sensor for Pa²⁺ on the basis of (A) DNAzyme
catalyzed Pb²⁺-induced hydrolytic cleavase anthe substrate; Adopted from Ref. [358],
Copyright (2008), with permission of American Chemical Society. (B) Pb²⁺-induced
cleavage of DNA strand. Adopted from Ref. [359], Copyright (2010), with permission
of the Royal Society of (thermstry.

1217

In terms of G-quadruplex-based sensor, Hai et al. [360] reported a GE coated Fe₃O₄-1223 AuNPs-Aptamer ECL sensor, which formed a G-quadruplex owing to the opening of 1224 "stem-loop" structured hairpin aptamer by Pb²⁺. This "turn-on" ECL sensor could be 1225 separated easily and enhanced the selectivity and sensitivity, resulting in a linear 1226 relationship in the range from 0.2 to 10 nM and LOD of 0.00108 nM. Based on the 1227 distance-dependent quenching of ECL from CdSe QDs by nanocomposites of graphene 1228 and AuNPs, Lu et al. developed a highly sensitive ECL method and provided the linear 1229 1230 range of 0.1-10 nM and LOD of 0.1 nM for Pb²⁺ detection [361]. RET, providing indeed energy transfer between the donors and acceptors at a certain distance, is a novel and 1231

powerful strategy for highly sensitive recognition on DNA binding events. Based on 1232 this strategy, a "signal-on" PEC detection system supported by the energy transfer 1233 between CdS QDs and AuNPs was used to verify the presence of Pb²⁺ [362]. Compared 1234 with other methods reported previously, this sensing device provided acceptable linear 1235 range and LOD. On the development of RET technique, a novel ECL-RET system from 1236 $O_2/S_2O_8^{2-}$ to the amino-terminated perylene derivative (PTC-NH₂) was demonstrated, 1237 in which AuNPs and fullerene nanocomposites coated on GCE and then the thiol-1238 modified assistant probes attached on [363]. $O_2/S_2O_8^{2-}$ served as an ECL donor and 1239 PTC-NH₂ acted as the acceptor. The developed aptasensor offers an alternative 1240 analytical method with outstanding properties of high sensitivity, selectivity, and 1241

accuracy (Table S7). 1242

4.2.3. Copper ions 1243

 $_{rr}$ er lons Avenues have emerged making use of elementation due to the state of elementation du hemical approach supporting with 1244 AuNPs for Cu^{2+} detection due to the similar properties with Pb^{2+} . Cu^{2+} ions prefer to 1245 bind with ligands containing N down atoms like cysteine, Cys, and aptamer, etc. Based 1246 on this theory, aminounder this base layer modified GE supporting with cysteine-1247 functionalized AuNPr was fabricated via CV analysis [364]. Another example is the 1248 protocol that two artial complementary scaffold DNA strands are linked to AuNPs, 1249 which attach on the surface of GE through -SH of 4-aminothiophenol [365]. Upon Cu²⁺ 1250 1251 binding, self-cleaving occurs at two different locations of the recognition strand into three fragments, driving $[Fe(CN)_6]^{3-/4-}$ to approach the surface of electrode and produce 1252 redox signal. AuNPs are used to increase the surface area of the electrode and anchor 1253 more aptamers, which helps obtaining the LOD of 0.1 pM for Cu²⁺ via SWV. On the 1254 basis of the same mechanism that the distance between signal tag and electrode surface 1255 determines the electrochemical signal producing or not, an ultrasensitive DNA 1256

biosensor through electroactive MA-Cu²⁺ complex attached on the end of hairpin-like 1257 probe using AuNPs as the signal amplification platform has been introduced [366]. 1258 When complementary chain presented, the distance of signal tag and electrode surface 1259 was so far that the response of CV signal was broken off, which leading the intensity 1260 of signal was proportional to the concentration of Cu²⁺. Besides N atom-based 1261 coordination, some electrochemical sensors with the catalytic reaction are prepared. As 1262 shown in Fig. 14, Jumade group use the interaction between Cu^{2+} and Cys to selectively 1263 detect Cu²⁺ via copper-catalyzed oxidation of thiol compounds (R-SH) to disulfide 1264 compounds (R-S-S-R) [367]. For all of the proposals mentioned above using AuNPs, 1265 few of them have paid their attention to the size effects of AuNPA Increasingly, taking 1266 the advantage of 13 and 45 nm AuNPs, Foroushani e a) [368] prepared a novel 1267 ultrasensitive Cu2+ sensor based on L-cysteine-functionalized core-satellite AuNPs 1268 networks to obtain tunnelling the recognition 1269



1270

Fig. 14. Schematic drawing of (A) Cu^{2+} -catalyzed oxidation of Cys to disulfide cystamine by O₂, (B) preparation of dithiobis[succinimidyl-propionate] encapsulated AuNPs and (C) electrochemical detection process of Cu^{2+} . Adopted from Ref. [367], Copyright (2014), with permission of Elsevier.

1275 4.2.4 Bimetallic ions

Simultaneously detecting two kinds of metal ions (bimetallic ions) supported by 1276 1277 AuNPs is the advantage of electrochemical techniques. Most of them use stripping voltammograms technique, as the quantitative range of metal ions is calculated by the 1278 changes of current peak value in accordance with concentration of metal ions. That is 1279 to say, as long as the changes of current peak value under a certain potential are regular, 1280 1281 many kinds of ions can be detected simultaneously. But it is worth noting that these ions should have similar properties. For example, Ting et al. [369] demonstrated a 1282 sensitive electrochemical detection method for Hg^{2+} and Cu^{2+} using Graphene quantum 1283 dots (GQDs)-functionalized AuNPs modified GCE with ASV. In his sensor, the -1284 COOH of Cys, which capped AuNPs, interacted with 1g2 in the form of R-COO-1285 (Hg²⁺)-OOC-R and Cu²⁺ competed for the limited unding sites on the surface of 1286 electrode. Importantly, Cu2+ has higher binding affinity. Thus, a peak of stripping 1287 potential at 0.42 V and 0 V was observed for Hg^{2+} and Cu^{2+} respectively and the peak 1288 intensity of Cu²⁺ was higher. An or typical kind of bimetallic detection is for Cu²⁺ 1289 and Pb^{2+} . As mentioned alow, Cu^{2+} and Pb^{2+} have some similar properties, which 1290 provide excellent strategy for determining them at the meantime. Wang et al. [370] 1291 the acid/L-cysteine/AuNPs-modified microelectrode for parallel developed a L 1292 detection of Cu²⁺ and Pb²⁺ using SWV with the peak potential locating at 0.27 V and -1293 1294 0.09 V, respectively. The complex of -COOH and AuNPs leads to satisfied sensitivity and selectivity. Other supporting materials equipped AuNPs including carbon-based 1295 materials like GO, single-walled carbon nanotubes (SWCNTs), and carbon foams have 1296 1297 been used for bimetallic detection as well. The sensitivity and selectivity are acceptable. More information of these researches is exhibited in Table S8. Recently, development 1298 for simultaneous recognition of metal ions and other inorganic salt has been proposed. 1299

Bui et al. [371] reported the first dual functional electrochemical sensor based on selenium particles (SePs) and AuNPs-functionalized disposable carbon paper electrodes for Hg^{2+} and NO_3^- detection in water. The main mechanism for Hg^{2+} detection was the high binding affinity between SePs and Hg^{2+} , and AuNPs here served as a nucleation sites for Hg^{2+} .

1305 **4.3. Detection of organic environmental hormones**

1306 *4.3.1. Pesticides*

The electrochemical detection of pesticides based on AuNPs as the signal tags-1307 supported electrodes is one of the most popular techniques since x provides high 1308 sensitivity, super selectivity, low LOD, and fast responses [3]? **73**]. Colorimetric 1309 method mentioned above mostly uses AChE due to OPs can inhibit the catalytic activity 1310 of AChE. On this basis, AChE inhibition-based electrochemical biosensor has also been 1311 developed. Using AuNPs offers faster signal transluction and larger surface area, which 1312 improves the performance of senser [374 . Du group have made a tremendous 1313 contribution to detection of pesticides based on electrochemical method. In 2011, they 1314 designed a versatile processing approach for biosensing of organophosphorus 1315 compounds with in-site ACnE-AuNPs immobilization [375]. When OPs presented, the 1316 hal became weakened, resulting in the intensity decreasing electrochemica 1317 proportional to the concentration of OPs. Further, they carried out a nanohybrid strategy 1318 1319 using AuNPs, polypyrrole, and rGO as the hybrids (Au-PPy-rGO) based on the same property to enhance the sensitivity. The Au-PPy-rGO nanocomposite exhibited 1320 excellent conductivity and high electrocatalytic activity for AChE, and thus obtaining 1321 a wide detection range of 1.0 to 5.0 µM [376]. An AChE/AuNPs/rGO-based sensor for 1322 detecting paraoxon by using 'all in one' hybrid synthesis strategy in the presence of 1323 PDDA was developed [377]. Compared with many steps synthesis, this method is 1324

simpler and faster for assessing low-dose exposure to paraoxon. Wei et al. [378]
reported a highly sensitive DPV biosensor for determination of chlorpyrifos and methyl
parathion using an AChE enzyme immobilized boron-doped diamond electrode
modified with AuNPs and carbon spheres (AuNPs-CS). As many OPs have the ability
to inhibit the catalysis of AChE, the selectivity of this method should be improved in
the future.

1331 The electrochemical immunosensors have attracted significant interest for pesticides detection because of their high sensitivity, inherent miniaturization, and low cost [379]. 1332 In this field, carbon and noble nanomaterials especially AuNPs are been used 1333 extensively [380]. In addition, inhibition biosensors based on AChA are not selective 1334 to OPs because AChE itself is the target of carbamate perticide. Thus, Du and the 1335 coworkers also turned to seek effective method to solve this problem. An amperometric 1336 biosensor for methyl parathion detection was developed by using a dual-signal 1337 amplification, which included a large amount of enzyme attached on the electrode 1338 surface because of the CdTe covalent attachment and enzymatic catalysis 1339 improvement in the present of AuNPs and MWCNTs [381]. Unlike the AChE-based 1340 potentially reused and selectively detect methyl parathion sensor, this sensor can be 1341 mL⁻¹ in garlic samples. Compared with the enzyme inhibition with LOD of 1 1342 biosensor, the sensitivity should be enhanced further. Hence, for sensitive and specific 1343 1344 detection of methyl parathion, they demonstrated a nanocomposite biosensor based on formation of AuNPs on silica particles and mixing with MWCNTs. It obtained linear 1345 concentration of methyl parathion in the range of 0.001-5.0 µg mL⁻¹ with the LOD of 1346 0.3 ng mL⁻¹, which was lower than the amperometric biosensor [382]. Additionally, 1347 they presented the first report on $Fe_3O_4(a)TiO_2$ magnetic nanoparticles-based 1348 immunosensor combining with multi-enzyme, including HRP and anti-BChE antibody 1349

(Ab), labeled AuNPs amplification strategy for selective and sensitive detection of OPs 1350 [383]. The magnetic nanoparticles not only provided easy separation of samples, but 1351 also overcame the difficult availability of commercial OP-specific antibody. The 1352 immunosensor for sensitive and selective detection of herbicide, another typical 1353 pesticide, has also been well developed. A rapid disposable immunomenbrane-based 1354 electrochemical sensor for sensitive and selective detection of picloram in the 1355 1356 agricultural field samples was developed by our team [258]. This sensor possessed good reproducibility for fabrication in batch and provided a congenial microenvironment for 1357 picloram. AuNPs shuttled the electron transfer between the electrode surface and 1358 immobilized enzyme to improve the sensitivity. The immunosencor based on antigen-1359 antibody reaction has been developed for estimation of atlazine and diuron, etc. AuNPs 1360 serve as the electronic transmitters or antibody attachment and promote high sensitivity 1361 and excellent selectivity [384-386]. These petiteds all successfully detect herbicide in 1362 plant samples that provides tremendous future for other pesticides analysis in practice. 1363 witch for aldicarb detection has been introduced Recently, an effective ECL aptasetor 1364 on the basis of energy tracsfor which occurs between AuNPs and the ECL signal 1365 ignal is enhanced because of effective energy transfer indicator (Ru(bpy 1366 [387]. 1367

Electrochemical designers based on AuNPs and other materials such as DNA [388], Nafion film [389, 390], graphene nanosheets [391, 392], and Ca²⁺ cross linked pectin [35] modified electrode have been developed for highly sensitive recognition of pesticides. However, the selectivity of these sensors is still needed to be improved. Another electrochemical strategy like MIPs-based sensor has been reported to overcome this shortcoming due to its excellent selectivity [393, 394]. The MIP techniques usually include preassembled template molecule, functional monomer, and

final copolymerization with the cross-linking monomers [395]. The recognition sites 1375 for analysis of target are generated by removing template molecules from the polymer 1376 matrix. In other words, the recognition sites directly decide the sensitivity. Hence, how 1377 to provide more recognition sites is crucial. The simplest way is to introduce a larger 1378 surface area electrode, via the immobilization of AuNPs on the surface. In this respect, 1379 Sun et al. [396] introduced a visible light PEC sensing platform for selective 1380 1381 pentachlorophenol detection by combining the MIP technique and microfluidic paperbased analytical device (µ-PAD). As shown in Fig. 15, a water-compatible surface-1382 MIPs based sensor prepared on AuNPs was synthesized via click chemistry and 1383 addition-fragmentation chain transfer precipitation polymerization reversible 1384 (RAFTPP) for highly selective and sensitive detection of fem trothion [397]. When this 1385 system immobilized on the ionic liquid-functionalized graphene coated GCE, the 1386 resulting electrode provided the linear range μM, with the sensitivity and LOD 1387 of 6.1 μ A μ M⁻¹ mm² and 8 nM, respectively 1388



1389

Fig. 15. Preparation of surface-imprinted polymer coated AuNPs grafted with watercompatible external layer via reversible addition–fragmentation chain transfer precipitation polymerization. Adopted from Ref. [397], Copyright (2014), with permission of Elsevier.

1394 *4.3.2. Drugs*

The detection of drugs that used in animals and humans based on AuNPs supported 1395 1396 electrochemical sensor can be divided into three parts: ligands combined with AuNPs, carbon-based material decorated AuNPs, and aptamer sensors. It is well known that 1397 thiol ligands can capture AuNPs via Au-S bond and this is widely used for sensors [398]. 1398 Gevaerd et al. [399] prepared a modified biphasic method for diltiazem detection based 1399 dodecanethiol-captured different size of AuNPs and investigated the 1400 on electrochemical activity through changing the molar ratio of Au : thiol. AuNPs 1401 decorated poly-MA modified GCE has been used for CV detection of domperidone in 1402 pharmaceuticals and biological fluids as urine and serum [400]. The response of this 1403 sensor shows stable, selective, and sensitive with the linear range of 0.05-100 μM and 1404 a LOD of 6 nM. Recently, AuNPs-supported porous covalent organic polymers (COPs) 1405 applied to sensors have received attention due the high surface area, porosity, high 1406 stability, and nitrogen content of COPs, which are very favorable for the decoration of 1407 nanoparticles distribution withou geregation [401]. Typical examples are the studies 1408 reported by Vilian et al. Initially, they reported a paper for vanillin detection based on 1409 palladium nanopartices supporting porous aromatic frameworks (Pd/PAF-6) and 1410 fucibility, high selectivity, as well as good stability [402]. In light received good r 1411 of the role of PAF-6, they further demonstrated an AuNPs decorated PAF-6 modified 1412 1413 electrode for determination of quercetin (QC) via electrocatalytic oxidation of QC at reduced potential and obtained remarkable analytical performance [403]. The Au-PAF-1414 6 modified electrode showed a good DPV response in the QC concentration of 1-600 1415 pM with the LOD of 0.2 pM. 1416

1417 Carbon-based materials such as GO, graphene sheets, and WCNTs equipped with1418 AuNPs have gained much attention in electrochemical sensor because of their

properties of direct electron transfer and large availability of active sites [404]. 1419 Pruneanu et al. [405] has developed a novel carbamazepine sensor with the help of 1420 graphene-AuNPs/MgO composite-deposited electrode, which shows excellent 1421 oxidation toward carbamazepine. However, the selectivity should be further 1422 investigated. In terms of the selectivity, a new generation electrochemical sensor using 1423 electrochemical oxidation of graphene nanosheets/AuNPs/Nafion nanocomposite has 1424 1425 been developed for selective determination of silodosin for the first time [406]. Compared with the voltammetric response of 400-fold concentration of other molecules, 1426 the nanocomposite-modified electrode has satisfied selectivity. As a graphite-like 1427 structure, graphite-like carbon nitride (g-C₃N₄) is good, cardidate for potential 1428 application on sensors. AuNPs functionalized g-C3N4 nanosheets was introduced to 1429 amplify the ECL signal for penicillamine enantioned detection [407]. This strategy 1430 exhibited high selectivity, stability and reproduct lity and opened a new door based on 1431 ECL to discriminate drugs. MIP technique is also applied to detect patulin using carbon 1432 dots, chitosan, combined with A PAs (Fig. 16) [408]. This strategy provides a wide 1433 detection range of 1-1000 pM vith a low LOD of 7.57 pM. 1434





1436 Fig. 16. Schematic illustrations of the fabrication procedure of chitosan and carbon dots

1437 combined with AuNPs to modify MIP sensor for patulin recognition. Adopted from Ref.
1438 [408], Copyright 2017, with permission of Elsevier.

1439 Aptamer-based biosensors for picomolar detection of drugs have been proposed [36, 409]. In addition to the promising sensors for one drug, a novel "dual potential" ECL 1440 aptasensor using CdS QD and luminol-AuNPs as labels for simultaneous determination 1441 of chloramphenicol and malachite green has been reported by Feng et al [410]. Different 1442 1443 with other dual potential sensors, this designed sensor is consisted of two screen-printed carbon WE for simultaneous detection in one single assay. AuNPs are deposited on 1444 electrode to immobilize luminol, which hybridizes with the complementary DNA 1445 sequences. This procedure provides high sensitivity with the linear anges of 0.2-150 1446 nM and 0.1-100 nM for chloramphenicol and malachite green respectively. Meanwhile, 1447 it has successfully applied to real fish samples, which holds great potential in the food 1448 analysis. Besides the "dual potential" EC -amplification ECL for detection of 1449 chloramphenicol was developed [411]. Because of the SPR of AuNPs, the ECL 1450 intensity was effectively enhance intensity, incorporating the merits of ECL and 1451 serson was creatively introduced for sensitive detection of MIP, a new MIP-ECL 1452 fumonisin B₁, where Autres greatly amplified the ECL signal of MIP on the basis of 1453 hemical effect [412]. New methods not only cooperate different 1454 LSPR and electro techniques, but also combine bimetallic NPs have been developed. For instance, a 1455 1456 recent paper reported by Hu et al. has introduced an ECL brombuterol immunoassay using Ag@Au core shell NPs as the substrate [413]. AuNPs are used to facilitate 1457 electron transfer, as well as capture more biomolecules. This is a novel tendency for 1458 1459 target analysis.

1460 *4.3.3. Other organic environmental hormones*

1461 A considerable effort of studies are devoted to explore effective methods which can

be used to detect trace organic environmental hormones like polycyclic aromatic 1462 hydrocarbons (PAHs), phenolic, and nitroaromatic compounds due to their inherent 1463 property of poisonousness, persistence, bioaccumulation, and non-biodegradable [414-1464 419]. Electrochemical strategy supported by AuNPs provides a novel effective 1465 approach, where AuNPs have high effective surface area and excellent catalysis 1466 properties, enhancing electrode conductivity and facilitating the electron transfer [420, 1467 1468 421]. Kang et al. [415] carried out a PEC immunosensor for ultrasensitive detection of PAH amplified by bifunctional AuNPs modified with PAH antigen and HRP. The 1469 electron transfer prompted by HRP-catalyzed reaction caused an excellent 1470 photocatalytic performance, which achieved linear range of 0.355 pM to 3.15 nM on 1471 the logarithm of Benzo(a)anthracene (BaP) concentration and LOD of 0.315 pM. 1472 Another interesting electrochemical immunoten for bisphenol-A (BPA) 1473 determination via competition and displacence assays has been developed [422]. 1474 Other immunosensors are rarely focused on the comparison of different assay formats, 1475 ion in investigation in the results limiting the application of 1476 demonstrated that the displacement assay took longer time to detect target but LOD was 1477 much lower than the competition assay. The electrochemical oxidation and 1478 uque of AuNPs-based electrochemistry for pollutant treatment have 1479 photocatalytic tech been used recently owing to their effective surface area of resulting electrode and high-1480 1481 efficiency [416]. The most interesting is Hu et al. performed a photorefreshable and photoenhanced electrochemical sensing platform for BPA recognition on the basis of 1482 AuNPs decorated carbon doped TiO_2 nanotube assays [423]. Under UV irradiation, the 1483 1484 performance of resulting electrode was significantly improved because it provided fresh reaction surface continuously. The photogenerated electron-hole pairs, which derived 1485 from the consumption of holes by BPA, improved the separation efficiency and further 1486

1487 increased photocurrent. It is a promising sensor for long-time BPA monitoring.

MIPs and ECL-based electrochemical sensor has been reported. The details of these 1488 1489 sensors are reviewed in **Table S9**. However, it is worth noting that the papers reported by Yuan et al. [424] and Lu et al. [425], which both use the L-Cys assembled AuNPs-1490 modified electrode for detection of various kinds of phenolic compounds at the same 1491 time. This is a new trend for electrochemical sensor, but it also can be regarded that the 1492 1493 selectivity should be further improved in the future. The material employed as an electrochemical sensor consists of AuNPs supporting by polymer, which has been used 1494 for organic contaminant detection successfully. In 2011, Liu and co-workers [426] 1495 demonstrated that on polyacrylonitrile electrospun nanofiber. AuNPs could be 1496 synthesized simply and effectively and exhibited excellent catalytic effect on the ECL 1497 of $Ru(bpy)_3^{2+}$. Recently, Li et al. [427] have provided a similar strategy supporting by 1498 poly(caffeic acid)/AuNPs composite modif GCE to detect acetaminophen 1499 effectively by using electrocatalytic activity of modified electrode toward the oxidation 1500 of acetaminophen. The response of a alytic current versus target concentration exhibits 1501 two linear segments in the anges of 0.2-20 µM and 50-1000 µM. It has been 1502 successfully applied indivalidated by analyzing acetaminophen in urine, blood and 1503 uples. Making use of polydopamine, MWCNTs and AuNPs 1504 pharmaceutical composites modified electrode, a selective sensor for hydroquinone and catechol 1505 1506 monitoring has been developed by Wang and his group [428], in which MWCNTs provide large specific area and AuNPs offer superexcellent electroconductibility. It is 1507 found that under optimal conditions, the CV and DPV can be used to perform the 1508 1509 response of hydroquinone and catechol separately. Compared with other approaches, this strategy shows good stability and reproducibility. 1510

1511 **5. Summary and outlook**

Detection of chemical and biological molecules plays important role in medical, 1512 industrial, and environmental researches. Unique properties of nanoparticle materials 1513 make them have tremendous potential in creating new sensors and improving the 1514 sensitivity and selectivity of sensors. This review has provided a brief overview of the 1515 history of AuNPs from discovery to application in sensing fields, the fabrication of 1516 AuNPs and sensors supported by AuNPs for colorimetric and electrochemical detection 1517 1518 in the past few years. There are many wonderful researches on the synthesis of AuNPs, as well as the control of size, shape, and application in various fields. They have made 1519 a significant contribution to the application of AuNPs. Turkevich-Frens and Brust-1520 Schiffrin methods are still the most popular approaches secure the synthetic AuNPs 1521 are uniform, stable, and regular, as well as easy to operate. The seed-mediated growth 1522 ore shell coated nanoparticles. And green method provides a good idea for fabricating 1523 1524 strategies make excellent contribution to biological and medical researches. However, it is still necessary to develop sy thesis approaches for regular, uniform, stable, and 1525 y factors including pH, ligand, solvent, temperature, non-toxic AuNPs becau 1526 ionic strength, and reaction time may have a side effect on AuNPs. It is difficult to 1527 obtain large size of AuNPs, which can well disperse in aqueous solution. Non-toxic 1528 1529 strategies are more and more popular and more suitable approaches synthesizing AuNPs for clinical research are well needed. 1530

Research on AuNPs is obviously evolving rapidly. It takes a long time for AuNPs to be applied in chemical and biological sensing and analysis since it was discovered. The advantages of well stability, biocompatibility to aqueous medium, easy to surface functionalization, huge surface area, and fast electron transport have allowed them preferred candidates in colorimetric and electrochemical sensing compared to the

conventionally used techniques. It provides an effective platform for cost-effective and 1536 feasible analysis by overcoming the traditional techniques that contain lengthy 1537 protocols and complicated instrumentation. Particularly, many of the sensing systems 1538 offer LOD at low level even aM level for analytes testing. Recently, many of the 1539 developed sensors were successfully applied to determine the analytes in real-life 1540 samples not only in environmental waters, but also in biological samples. Owing to the 1541 1542 unique optical properties (i.e. resonance light scattering and SPR absorption) of AuNPs, colorimetric sensor based on analytes-induced AuNPs aggregation and anti-aggregation 1543 has well developed for sensitive detection. It starts turning to detect organics and small 1544 molecules, not only inorganic ions. Interestingly, Au-Hg alloy, considered as unpopular 1545 reaction before, has been used in specific detection of Hg² due to the excellent catalytic 1546 activity. More and more new colorimetric strategies with excellent selectivity will be 1547 developed in the future. Colorimetric method, intuitive, sensitive, and simple, but 1548 requires high experimental conditions due to the easy aggregation of AuNPs. The 1549 strategies based on aggregation of the selectivity is still 1550 needed to improve. The antiaggregation approach has good selectivity, but the process 1551 is difficult to realize In addition, the simultaneous detection of different kinds of 1552 id, but the colorimetric sensor based on AuNPs are limited in this 1553 analytes is a new field. Hence, more sensitive, selective and simper colorimetric sensor is still necessary. 1554 1555 Electroanalytical method well overcomes some drawbacks of colorimetric sensor. It provides satisfied sensing platform for simultaneous monitoring of different kinds of 1556 analytes, but is also expected to have further development with higher sensitivity. In 1557 1558 generally, AuNPs are widely used in electrochemical sensor as the assisting portion. Their larger specific surface areas, small dimensions, and effective increase in electron 1559 transfer rate between the base electrode and analytes can bring more recognition sites, 1560

leading to more rapid and sensitive current response. Functionalized AuNPs may act as 1561 both signal transducer and molecular receptor in one single sensing platform, thereby 1562 1563 simplifying the sensor design and enhancing the sensitivity. In addition, some electrochemical sensors prefer to search the electro-catalytic performance of AuNPs 1564 and make it in the sensing system, especially the redox property. Such effort results in 1565 robust development of AuNPs-based sensor. The electrochemical sensor are 1566 1567 ultrasensitive and highly selective, it can be used for various analytes simultaneously. However, it is more complex and tedious for procedure when compared with the 1568 colorimetric sensor. 1569

Currently, the single detection of one contaminant has been w leveloped, but the 1570 combined pollution detection is just at the start line. The portable devices have a great 1571 interest in the determination of both biological and environmental analytes. 1572 Recognition of more biological fluids not as sweat, saliva, tears, etc., 1573 is being considered for developing partable sensors. On the other hand, it will make a 1574 big difference if the biomolecule of as DNA can be monitored accurately with the 1575 wearable sensors, which car b applied to criminal investigation. In the near future, it 1576 is very expected that Aurys-supported materials with lower detection limits, better 1577 ivity with high robustness will be developed as sensing materials. 1578 sensitivity, and In terms of commercialization, the development of effective sensor with reusability and 1579 1580 system integration and mass production is very necessary. Strategies simultaneously detecting vary kinds of analytes such as heavy metal ions, anions, organic contaminants, 1581 small molecules, and nucleic acids etc., supported by AuNPs and other nanomaterials 1582 1583 based nanocomposites are worth trying. Incorporation of different analysis methods including colorimetric, electrochemical or fluorescent approach is also a new trend and 1584 needed to be further investigated. Except for sensing, the investigation of catalysis and 1585

1586 other properties of AuNPs can be combined. Furthermore, the long-term possible impacts of AuNPs supported materials on environment and human health should be pay 1587 1588 attention.

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1598 **References**

- [1] K.B. Narayanan, N. Sakthivel, Synthesis and characterization of nano-gold composite using
 Cylindrocladium floridanum and its heterogeneous catalysis in the degradation of 4-nitrophenol, J.
 Hazard. Mater. 189 (2011) 519-525.
- 1602 [2] Y. Zhou, L. Tang, G. Zeng, J. Chen, J. Wang, C. Fan, G. Yang, Y. Zhang, X. Xie, Amplified
 1603 and selective detection of manganese peroxidase genes based on enzyme-scaffolded-gold
 1604 nanoclusters and mesoporous carbon nitride, Biosens. Bioelectron. 65 (2015) 382-389.
- 1605 [3] L. Tang, X. Xie, Y. Zhou, G. Zeng, J. Tang, Y. Wu, B. Long, B. Peng, J. Zhu, A reusable
- electrochemical biosensor for highly sensitive detection of mercury ions with an anionic intercalatorsupported on ordered mesoporous carbon/self-doped polyaniline nanofibers platform, Biochem.
- 1608 Eng. J. 117, Part A (2017) 7-14.
- 1609 [4] G. Zeng, M. Chen, Z. Zeng, Risks of neonicotinoid pesticides, Science 340 (2013) 1403.
- 1610 [5] J.-L. Gong, B. Wang, G.-M. Zeng, C.-P. Yang, C.-G. Niu, Q.-Y. Niu, W.-J. Zhou, Y. Liang,
- 1611 Removal of cationic dyes from aqueous solution using magnetic multi-way carbon nanotube
- 1612 nanocomposite as adsorbent, J. Hazard. Mater. 164 (2009) 1517-1522.
- 1613 [6] Y. Cheng, H. He, C. Yang, G. Zeng, X. Li, H. Chen, G. Yu, Challenges and solutions for1614 biofiltration of hydrophobic volatile organic compounds, Biotechnol. Adv. 34 (2016) 1091-1102.
- 1615 [7] D.-L. Huang, R.-Z. Wang, Y.-G. Liu, G.-M. Zeng, C. Lai, P. Vu B.-A. Lu, J.-J. Xu, C. Wang,
- 1616 C. Huang, Application of molecularly imprinted polymers in vastewater treatment: a review,
 1617 Environ. Sci. Pollut. Res. 22 (2015) 963-977.
- 1618 [8] C. Zhang, C. Lai, G. Zeng, D. Huang, C. Yang, Y. Wang, Y. Zhou, M. Cheng, Efficacy of
 1619 carbonaceous nanocomposites for sorbing antibiotic sulfamethazine from aqueous
 1620 solution, Water Res. 95 (2016) 103-112.
- 1621 [9] G.J. Higby, Gold in medicine, Gold b (1.15 (1982) 130-140.
- 1622 [10] S.K. Ghosh, T. Pal, Interparticle Cupling Effect on the Surface Plasmon Resonance of Gold
 1623 Nanoparticles: From Theory to Applications, Chem. Rev. 107 (2007) 4797-4862.
- 1624 [11] M. Faraday, The Bakerian lecure: experimental relations of gold (and other metals) to light,
 1625 Philosophical Transaction of the Royal Society of London 147 (1857) 145-181.
- 1626 [12] C. Lai, G.-M. Zerg, L. Huang, M.-H. Zhao, Z. Wei, C. Huang, P. Xu, N.-J. Li, C. Zhang,
- M. Chen, Synthesis et ged-cellobiose nanocomposites for colorimetric measurement of cellobiase
 activity, Spectrochin. Acta Part A. 132 (2014) 369-374.
- 1629 [13] C. Lai, G.-M. Zeng, D.-L. Huang, M.-H. Zhao, M. Chen, Z. Wei, C. Huang, P. Xu, N.-J. Li, X.
- 1630 Li, Colorimetric screening of β-glucosidase inhibition based on gold nanocomposites, Anal.
 1631 Methods. 6 (2014) 312-315.
- 1632 [14] T. Teranishi, S. Hasegawa, T. Shimizu, M. Miyake, Heat-Induced Size Evolution of Gold
 1633 Nanoparticles in the Solid State, Adv. Mater. 13 (2001) 1699-1701.
- 1634 [15] Z. Wang, J.H. Lee, Y. Lu, Label-Free Colorimetric Detection of Lead Ions with a Nanomolar
 1635 Detection Limit and Tunable Dynamic Range by using Gold Nanoparticles and DNAzyme, Adv.
 1636 Mater. 20 (2008) 3263-3267.
- 1637 [16] Y. Zhou, L. Tang, G. Zeng, C. Zhang, X. Xie, Y. Liu, J. Wang, J. Tang, Y. Zhang, Y. Deng,
- 1638 Label free detection of lead using impedimetric sensor based on ordered mesoporous carbon–gold1639 nanoparticles and DNAzyme catalytic beacons, Talanta 146 (2016) 641-647.
- 1640 [17] Y. Zhou, L. Tang, G. Zeng, C. Zhang, Y. Zhang, X. Xie, Current progress in biosensors for 1641 heavy metal ions based on DNAzymes/DNA molecules functionalized nanostructures: A review,

- 1642 Sens. Actuators, B. 223 (2016) 280-294.
- 1643 [18] L. Tang, G. Zeng, G. Shen, Y. Zhang, Y. Li, C. Fan, C. Liu, C. Niu, Highly sensitive sensor1644 for detection of NADH based on catalytic growth of Au nanoparticles on glassy carbon electrode,
- 1645 Anal. Bioanal.Chem. 393 (2009) 1677-1684.
- 1646 [19] C. Chen, N. Li, J. Lan, X. Ji, Z. He, A label-free colorimetric platform for DNA via target-
- 1647 catalyzed hairpin assembly and the peroxidase-like catalytic of graphene/Au-NPs hybrids, Anal.1648 Chim. Acta 902 (2016) 154-159.
- [20] C. Zhang, G. Zeng, D. Huang, C. Lai, C. Huang, N. Li, P. Xu, M. Cheng, Y. Zhou, W. Tang,
 Combined removal of di (2-ethylhexyl) phthalate (DEHP) and Pb (ii) by using a cutinase loaded
 nanoporous gold-polyethyleneimine adsorbent, RSC Adv. 4 (2014) 55511-55518.
- [21] H.N. Kim, W.X. Ren, J.S. Kim, J. Yoon, Fluorescent and colorimetric sensors for detection of
 lead, cadmium, and mercury ions, Chem. Soc. Rev. 41 (2012) 3210-3244.
- 1654 [22] J.M. Pingarron, P. Yanez-Sedeno, A. Gonzalez-Cortes, Gold nanoparticle-based
 1655 electrochemical biosensors, Electrochim. Acta 53 (2008) 5848-5866.
- [23] G. Korotcenkov, V. Brinzari, B.K. Cho, Conductometric gas sensors based on metal oxides
 modified with gold nanoparticles: a review, Microchim. Acta 183 (2016) 11331054.
- [24] C. Pezzato, S. Maiti, J.L. Chen, A. Cazzolaro, C. Gobbo, L.J. Prins, Monolayer protected gold
 nanoparticles with metal-ion binding sites: functional systems for chemisensing applications, Chem.
 Commun. 51 (2015) 9922-9931.
- [25] A. Chen, M. Yan, S. Yang, Split aptamers and their applications in sandwich aptasensors, TrAC,
 Trends Anal. Chem. 80 (2016) 581-593.
- [26] J. Deng, P. Yu, Y. Wang, L. Yang, L. Mao, Visna varion and quantification of neurochemicals
 with gold nanoparticles: opportunities and challenger, Adv. Mater. 26 (2014) 6933-6943.
- 1665 [27] E. Priyadarshini, N. Pradhan, Gold nanoparticles as efficient sensors in colorimetric detection
 1666 of toxic metal ions: A review, Sens. Actuator, B. 238 (2017) 888-902.
- [28] D.-L. Huang, G.-M. Zeng, C.-L. Yerg, S. Hu, X.-Y. Jiang, L. Tang, F.-F. Su, Y. Zhang, W.
 Zeng, H.-L. Liu, Degradation of Nad-contaminated lignocellulosic waste by Phanerochaete
 chrysosporium and the reduction of lead toxicity, Environ. Sci. Technol. 42 (2008) 4946-4951.
- 1670 [29] X. Li, Y. Zhang, Y. Ghang, B. Xue, X. Kong, W. Chen, Catalysis-reduction strategy for sensing
 1671 inorganic and organic mercury based on gold nanoparticles, Biosens. Bioelectron. 92 (2017) 3281672 334.
- 1673 [30] C. Zhang, Y. Zhou, L. Tang, G. Zeng, J. Zhang, B. Peng, X. Xie, C. Lai, B. Long, J. Zhu,
 1674 Determination of Cd2+ and Pb2+ based on mesoporous carbon nitride/self-doped polyaniline
 1675 nanofibers and square wave anodic stripping voltammetry, Nanomaterials 6 (2016) 7.
- 1676 [31] D. Huang, C. Niu, X. Wang, X. Lv, G. Zeng, "Turn-On" fluorescent sensor for Hg2+ based on
 1677 single-stranded DNA functionalized Mn: CdS/ZnS quantum dots and gold nanoparticles by time1678 gated mode, Anal. Chem. 85 (2013) 1164-1170.
- 1679 [32] G. Aragay, J. Pons, A. Merkoçi, Recent Trends in Macro-, Micro-, and Nanomaterial-Based
 1680 Tools and Strategies for Heavy-Metal Detection, Chem. Rev. 111 (2011) 3433-3458.
- 1681 [33] T. Lou, Z. Chen, Y. Wang, L. Chen, Blue-to-Red Colorimetric Sensing Strategy for Hg²⁺ and
- Ag⁺ via Redox-Regulated Surface Chemistry of Gold Nanoparticles, ACS Applied Materials &
 Interfaces 3 (2011) 1568-1573.
- 1684 [34] Y. Zhang, J. Jiang, M. Li, P. Gao, Y. Zhou, G. Zhang, S. Shuang, C. Dong, Colorimetric sensor
- 1685 for cysteine in human urine based on novel gold nanoparticles, Talanta 161 (2016) 520-527.
- 1686 [35] V. Mani, R. Devasenathipathy, S.-M. Chen, V.S. Vasantha, M. Ajmal Ali, S.-T. Huang, F.M.A.
- Al-Hemaid, A simple electrochemical platform based on pectin stabilized gold nanoparticles for
 picomolar detection of biologically toxic amitrole, Analyst 140 (2015) 5764-5771.
- 1689 [36] C. Wang, C. Liu, J. Luo, Y. Tian, N. Zhou, Direct electrochemical detection of kanamycin
 1690 based on peroxidase-like activity of gold nanoparticles, Anal. Chim. Acta 936 (2016) 75-82.
- 1691 [37] Y. Sun, Y. Xia, Shape-Controlled Synthesis of Gold and Silver Nanoparticles, Science 2981692 (2002) 2176.
- 1693 [38] S. Link, M.A. El-Sayed, Size and Temperature Dependence of the Plasmon Absorption of1694 Colloidal Gold Nanoparticles, J. Phys. Chem., B. 103 (1999) 4212-4217.
- 1695 [39] C. Zhang, L. Liu, G.-M. Zeng, D.-L. Huang, C. Lai, C. Huang, Z. Wei, N.-J. Li, P. Xu, M.
- 1696 Cheng, Utilization of nano-gold tracing technique: Study the adsorption and transmission of laccase
 1697 in mediator-involved enzymatic degradation of lignin during solid-state fermentation, Biochem.
 1698 Eng. J. 91 (2014) 149-156.
- 1699 [40] P. Zhao, N. Li, D. Astruc, State of the art in gold nanoparticle synthesis, Coord. Chem. Rev.
 1700 257 (2013) 638-665.
- [41] M. Shah, V. Badwaik, Y. Kherde, H.K. Waghwani, T. Modi, Z.P. Aguar, H. Rodgers, W.
 Hamilton, T. Marutharaj, C. Webb, Gold nanoparticles: various methods of synthesis and
 antibacterial applications, Front. Biosci 19 (2014) 10.2741.
- [42] I. Ojea-Jiménez, J.M. Campanera, Molecular Modeling of the Reduction Mechanism in the
 Citrate-Mediated Synthesis of Gold Nanoparticles, J. Phys. Chem., C 116 (2012) 23682-23691.
- [43] J. Turkevich, P.C. Stevenson, J. Hillier, A study of the nucleation and growth processes in the
 synthesis of colloidal gold, Discussions of the Facadar Society 11 (1951) 55-75.
- [44] M. Wuithschick, A. Birnbaum, S. Witte, A. Birnbaum, S. Witte, M. Vainio, N. Pinna, K. Rademann, F.
 Emmerling, R. Kraehnert, J. Polte, Turkevich in New Robes: Key Questions Answered for the Most
 Common Gold Nanoparticle Synthesis. ACS Nano 9 (2015) 7052-7071.
- 1711 [45] J. Turkevich, P.C. Stevenson, J. Viller, The formation of colloidal gold, J. Phys. Chem. 57 1712 (1953) 670-673.
- [46] G. Frens, Controlled nucleation for the regulation of the particle size in monodisperse goldsuspensions, Nature 241 (19):220-22.
- 1715 [47] J.W. Slot, H.J. Genze, A new method of preparing gold probes for multiple-labeling
 1716 cytochemistry, Europeell Biol. 38 (1985) 87-93.
- [48] F. Shiba, Size control of monodisperse Au nanoparticles synthesized via a citrate reduction
 process associated with a pH-shifting procedure, Crystengcomm 15 (2013) 8412-8415.
- 1719 [49] F. Schulz, T. Homolka, N.G. Bastus, V. Puntes, H. Weller, T. Vossmeyer, Little adjustments
- significantly improve the Turkevich synthesis of gold nanoparticles, Langmuir 30 (2014) 10779-
- **1721** 10784.
- 1722 [50] R.C. Sanfelice, A. Pavinatto, V.C. Goncalves, D.S. Correa, L.H.C. Mattoso, D.T. Balogh,
 1723 Synthesis of a Nanocomposite Containing a Water-Soluble Polythiophene Derivative and Gold
 1724 Nanoparticles, J. Polym. Sci., Part B: Polym. Phys. 54 (2016) 1245-1254.
- 1725 [51] S.K. Sivaraman, S. Kumar, V. Santhanam, Monodisperse sub-10 nm gold nanoparticles by
- reversing the order of addition in Turkevich method The role of chloroauric acid, J. Colloid
 Interface Sci. 361 (2011) 543-547.
- 1728 [52] B.V. Enustun, J. Turkevich, Coagulation of Colloidal Gold, JACS 85 (1963) 3317-3328.
- 1729 [53] X. Yang, M. Yang, B. Pang, M. Vara, Y. Xia, Gold Nanomaterials at Work in Biomedicine,

- 1730 Chem. Rev. 115 (2015) 10410-10488.
- 1731 [54] D.A. Giljohann, D.S. Seferos, W.L. Daniel, M.D. Massich, P.C. Patel, C.A. Mirkin, Gold
 1732 Nanoparticles for Biology and Medicine, Angew. Chem. Int. Ed. 49 (2010) 3280-3294.
- [55] D. Ghosh, D. Sarkar, A. Girigoswami, N. Chattopadhyay, A fully standardized method of
 synthesis of gold nanoparticles of desired dimension in the range 15 nm-60 nm, J. Nanosci.
 Nanotechnol. 11 (2011) 1141-1146.
- 1736 [56] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, Synthesis of thiol-derivatised
- gold nanoparticles in a two-phase liquid–liquid system, J. Chem. Soc., Chem. Commun. (1994) 801-802.
- 1739 [57] M.J. Hostetler, J.E. Wingate, C.-J. Zhong, J.E. Harris, R.W. Vachet, M.R. Clark, J.D. Londono,
- 1740 S.J. Green, J.J. Stokes, G.D. Wignall, Alkanethiolate gold cluster molecules with core diameters
- 1741 from 1.5 to 5.2 nm: core and monolayer properties as a function of core size, Langmuir 14 (1998)1742 17-30.
- [58] M.M. Maye, C.-J. Zhong, Manipulating core-shell reactivities for processing nanoparticle sizes
 and shapes, J. Mater. Chem. 10 (2000) 1895-1901.
- 1745 [59] S. Chen, R.W. Murray, Arenethiolate Monolayer-Protected Gold Clusters, Langmuir 15 (1999)1746 682-689.
- [60] M.J. Hostetler, S.J. Green, J.J. Stokes, R.W. Murray, Monolayers in Three Dimensions:
 Synthesis and Electrochemistry of ω-Functionalized Alkaretricitate-Stabilized Gold Cluster
 Compounds, JACS 118 (1996) 4212-4213.
- 1750 [61] R.S. Ingram, M.J. Hostetler, R.W. Murray, Pory herero-ω-functionalized Alkanethiolate1751 Stabilized Gold Cluster Compounds, JACS 119 (1997) 975-9178.
- 1752 [62] B.T. Reid, S.M. Reed, Improved method for evaluating the environmental impact of1753 nanoparticle synthesis, Green Chem. 18 (2016) 4263-4269.
- [63] O. Zaluzhna, Y. Li, C. Zangmeister, T.C. Allison, Y.J. Tong, Mechanistic insights on onephase vs. two-phase Brust-Schiffrin menod synthesis of Au nanoparticles with dioctyl-diselenides,
 Chem. Commun. 48 (2012) 362,264.
- 1757 [64] A. Wieckowska, M. Dzycowk, Ultrasmall Au nanoparticles coated with hexanethiol and
 1758 anthraquinone/hexanethiol for inzyme-catalyzed oxygen reduction, Sens. Actuators, B. 224 (2016)
 1759 514-520.
- 1760 [65] S.E. Kudahergenov, G.S. Tatykhanova, B.S. Selenova, Polymer Protected and Gel
 1761 Immobilized Gold and Silver Nanoparticles in Catalysis, J. Inorg. Organomet. Polym Mater. (2016)
 1762 1-14.
- 1763 [66] R. Sardar, J.S. Shumaker-Parry, 9-BBN Induced Synthesis of Nearly Monodisperse ω 1764 Functionalized Alkylthiol Stabilized Gold Nanoparticles, Chem. Mater. 21 (2009) 1167-1169.
- 1765 [67] E.R. Zubarev, J. Xu, A. Sayyad, J.D. Gibson, Amphiphilicity-Driven Organization of1766 Nanoparticles into Discrete Assemblies, JACS 128 (2006) 15098-15099.
- [68] R.K. Gupta, M.P. Srinivasan, R. Dharmarajan, Synthesis of short chain thiol capped gold
 nanoparticles, their stabilization and immobilization on silicon surface, Colloids Surf. A. 390 (2011)
 149-156.
- 1770 [69] A.F.G. Leontowich, C.F. Calver, M. Dasog, R.W.J. Scott, Surface Properties of Water-Soluble
- 1771 Glycine-Cysteamine-Protected Gold Clusters, Langmuir 26 (2010) 1285-1290.
- 1772 [70] J. Wiesner, A. Wokaun, Anisometric gold colloids. Preparation, characterization, and optical
- 1773 properties, Chem. Phys. Lett. 157 (1989) 569-575.

- 1774 [71] P. Priecel, H. Adekunle Salami, R.H. Padilla, Z. Zhong, J.A. Lopez-Sanchez, Anisotropic gold
 1775 nanoparticles: Preparation and applications in catalysis, Chin. J. Catal. 37 (2016) 1619-1650.
- 1776 [72] J. Rodríguez-Fernández, J. Pérez-Juste, F.J. García de Abajo, L.M. Liz-Marzán, Seeded
 1777 Growth of Submicron Au Colloids with Quadrupole Plasmon Resonance Modes, Langmuir 22
 1778 (2006) 7007-7010.
- [73] K.R. Brown, D.G. Walter, M.J. Natan, Seeding of Colloidal Au Nanoparticle Solutions. 2.
 Improved Control of Particle Size and Shape, Chem. Mater. 12 (2000) 306-313.
- [74] N.R. Jana, L. Gearheart, C.J. Murphy, Seeding Growth for Size Control of 5–40 nm Diameter
 Gold Nanoparticles, Langmuir 17 (2001) 6782-6786.
- [75] K. Kwon, K.Y. Lee, Y.W. Lee, M. Kim, J. Heo, S.J. Ahn, S.W. Han, Controlled Synthesis of
 Icosahedral Gold Nanoparticles and Their Surface-Enhanced Raman Scattering Property, J. Phys.
 Chem., C 111 (2007) 1161-1165.
- 1786 [76] J. Piella, N.G. Bastús, V. Puntes, Size-Controlled Synthesis of Sub-10-nanometer Citrate-
- 1787 Stabilized Gold Nanoparticles and Related Optical Properties, Chem. Mater. 28 (2016) 1066-1075.
- [77] N.R. Jana, L. Gearheart, C.J. Murphy, Evidence for Seed-Mediated Nucleation in the Chemical
 Reduction of Gold Salts to Gold Nanoparticles, Chem. Mater. 13 (2001) 2313-1322.
- [78] Y. Qu, X. Pei, W. Shen, X. Zhang, J. Wang, Z. Zhang, S. Li, S. You, F. Ma, J. Zhou,
 Biosynthesis of gold nanoparticles by Aspergillum sp. WL-Are for degradation of aromatic
 pollutants, Physica. E 88 (2017) 133-141.
- [79] S.K. Das, A.R. Das, A.K. Guha, Microbial synthesis of nulconaped gold nanostructures, Small
 6 (2010) 1012-1021.
- [80] C. Shi, N. Zhu, Y. Cao, P. Wu, Biosynthesis of gold nanoparticles assisted by the intracellular
 protein extract of Pycnoporus sanguineus and the catalysis in degradation of 4-nitroaniline,
 Nanoscale Res. Lett. 10 (2015) 1-8.
- 1798 [81] Y. Huang, D.-H. Kim, Light-controlled synthesis of gold nanoparticles using a rigid,
 1799 photoresponsive surfactant, Nanoscale (1012) 6312-6317.
- 1800 [82] K. Brajesh, S. Kumari, S. Frike, G. Sara, C. Luis, Ecofriendly ultrasound-assisted rapid
 1801 synthesis of gold nanoparticle using Calothrix algae, Adv. Nat. Sci.: Nanosci. Nanotechnol. 7 (2016)
 1802 025013.
- 1802 (82) M.E. El-Naggar, M.M.G. Fouda, A.A. Hebeish, Eco-friendly microwave-assisted
 1804 green and rapid stratesis of well-stabilized gold and core-shell silver-gold nanoparticles,
 1805 Carbohydr. Polym. 136 (2016) 1128-1136.
- 1806 [84] Y. Konishi, T. Tsukiyama, K. Ohno, N. Saitoh, T. Nomura, S. Nagamine, Intracellular recovery
 1807 of gold by microbial reduction of AuCl₄⁻ ions using the anaerobic bacterium Shewanella algae,
 1808 Hydrometallurgy 81 (2006) 24-29.
- 1809 [85] M.I. Husseiny, M.A. El-Aziz, Y. Badr, M.A. Mahmoud, Biosynthesis of gold nanoparticles
 1810 using Pseudomonas aeruginosa, Spectrochim. Acta Part A. 67 (2007) 1003-1006.
- 1811 [86] G. Singaravelu, J.S. Arockiamary, V.G. Kumar, K. Govindaraju, A novel extracellular
 1812 synthesis of monodisperse gold nanoparticles using marine alga, Sargassum wightii Greville,
 1813 Colloids Surf. B. 57 (2007) 97-101.
- 1814 [87] S.K. Srivastava, R. Yamada, C. Ogino, A. Kondo, Biogenic synthesis and characterization of
- 1815 gold nanoparticles by Escherichia coli K12 and its heterogeneous catalysis in degradation of 4-
- 1816 nitrophenol, Nanoscale Res. Lett. 8 (2013) 70.
- 1817 [88] S. Dozie-Nwachukwu, J. Obayemi, Y. Danyo, G. Etuk-Udo, N. Anuku, O. Odusanya, K.

- Malatesta, C. Chi, W. Soboyejo, Biosynthesis of Gold Nanoparticles with Serratia marcescens
 Bacteria, Advanced Materials Research, Trans. Tech. Publ. 1132 (2016) 19-35.
- 1820 [89] P. Mukherjee, A. Ahmad, D. Mandal, S. Senapati, S.R. Sainkar, M.I. Khan, R. Ramani, R.
- Parischa, P.V. Ajayakumar, M. Alam, M. Sastry, R. Kumar, Bioreduction of AuCl₄⁻ Ions by the
 Fungus, Verticillium sp. and Surface Trapping of the Gold Nanoparticles Formed, Angew. Chem.
- 1823 Int. Ed. 40 (2001) 3585-3588.
- 1824 [90] A. Vágó, G. Szakacs, G. Sáfrán, R. Horvath, B. Pécz, I. Lagzi, One-step green synthesis of
- 1825 gold nanoparticles by mesophilic filamentous fungi, Chem. Phys. Lett. 645 (2016) 1-4.
- [91] S.S. Shankar, A. Ahmad, R. Pasricha, M. Sastry, Bioreduction of chloroaurate ions by geranium
 leaves and its endophytic fungus yields gold nanoparticles of different shapes, J. Mater. Chem. 13
 (2003) 1822-1826.
- [92] H. Jiale, L. Qingbiao, S. Daohua, L. Yinghua, S. Yuanbo, Y. Xin, W. Huixuan, W. Yuanpeng,
 S. Wenyao, H. Ning, H. Jinqing, C. Cuixue, Biosynthesis of silver and gold nanoparticles by novel
 sundried Cinnamomum camphora leaf, Nanotechnology 18 (2007) 105104.
- [93] B. Ankamwar, M. Chaudhary, M. Sastry, Gold nanotriangles biologically synthesized using
 tamarind leaf extract and potential application in vapor sensing, Synthesis and Reactivity in
 Inorganic Metal-Organic and Nano-Metal Chemistry 35 (2005) 19-26
- 1835 [94] S. Roy, T.K. Das, G.P. Maiti, U. Basu, Microbial biosynthesis of nontoxic gold nanoparticles,
 1836 Mater. Sci. Eng. B. 203 (2016) 41-51.
- 1837 [95] S.K. Nune, N. Chanda, R. Shukla, K. Katti, R.R. Kulkarni, S. Thilakavathy, S. Mekapothula,
 1838 R. Kannan, K.V. Katti, Green nanotechnology from ter. My ochemicals in tea as building blocks
 1839 for production of biocompatible gold nanoparticles of Advier. Chem. 19 (2009) 2912-2920.
- 1840 [96] V.D. Badwaik, J.J. Bartonojo, J.W. Evans, A. Sahi, C.B. Willis, R. Dakshinamurthy, Single1841 step biofriendly synthesis of surface modifiable, near-spherical gold nanoparticles for applications
- in biological detection and catalysis, Langnue 27 (2011) 5549-5554.
- [97] M. Gholami-Shabani, M. Shams-Chahfarokhi, Z. Gholami-Shabani, A. Akbarzadeh, G. Riazi,
 S. Ajdari, A. Amani, M. Razzaghi Abbaneh, Enzymatic synthesis of gold nanoparticles using sulfite
 reductase purified from Eschercha coli: A green eco-friendly approach, Process Biochem. 50
 (2015) 1076-1085.
- 1847 [98] T. Maruyama, Y Funnoto, T. Maekawa, Synthesis of gold nanoparticles using various amino
 1848 acids, J. Colloid Interface Sci. 447 (2015) 254-257.
- [99] L. Huang, M. Zhai, J. Peng, L. Xu, J. Li, G. Wei, Synthesis, size control and fluorescence
 studies of gold nanoparticles in carboxymethylated chitosan aqueous solutions, J. Colloid Interface
 Sci. 316 (2007) 398-404.
- [100] A. Kumar, M. Bhatt, G. Vyas, S. Bhatt, P. Paul, Sunlight Induced Preparation of
 Functionalized Gold Nanoparticles as Recyclable Colorimetric Dual Sensor for Aluminum and
 Fluoride in Water, ACS Appl. Mater. Interfaces. 9 (2017) 17359-17368.
- [101] M. Ganeshkumar, T.P. Sastry, M. Sathish Kumar, M.G. Dinesh, S. Kannappan, L. Suguna,
 Sun light mediated synthesis of gold nanoparticles as carrier for 6-mercaptopurine: Preparation,
 characterization and toxicity studies in zebrafish embryo model, Mater. Res. Bull. 47 (2012) 21132119.
- 1859 [102] M.D.P. Rodrígueztorres, L.A.D. Torres, UVA mediated synthesis of gold nanoparticles in
- pharmaceutical-grade heparin sodium solutions, SPIE NanoScience + Engineering, 8809 (2013)
 782-789.

- [103] S. Gudlur, C. Sandén, P. Matoušková, C. Fasciani, D. Aili, Liposomes as nanoreactors for the
 photochemical synthesis of gold nanoparticles, J. Colloid Interface Sci. 456 (2015) 206-209.
- 1864 [104] K.L. Mcgilvray, M.R. Decan, D. Wang, J.C. Scaiano, Facile photochemical synthesis of
 1865 unprotected aqueous gold nanoparticles, JACS 128 (2006) 15980-15981.
- 1866 [105] A. Pandya, K.V. Joshi, N.R. Modi, S.K. Menon, Rapid colorimetric detection of sulfide using
 1867 calix[4]arene modified gold nanoparticles as a probe, Sens. Actuators, B. 168 (2012) 54-61.
- 1868 [106] M.A. Bhosale, D.R. Chenna, B.M. Bhanage, Ultrasound Assisted Synthesis of Gold
- 1869 Nanoparticles as an Efficient Catalyst for Reduction of Various Nitro Compounds, ChemistrySelect
 1870 2 (2017) 1225-1231.
- [107] N. Vo Ke Thanh, N. Dang Giang, H. Trong Phat, L. Quang Vinh, A low cost technique for
 synthesis of gold nanoparticles using microwave heating and its application in signal amplification
 for detecting Escherichia Coli O157:H7 bacteria, Adv. Nat. Sci.: Nanosci. Nanotechnol. 7 (2016)
 035016.
- 1875 [108] E. Detsri, K. Kamhom, C. Detsri, Microwave-Assisted Synthesis of Unmodified Gold
 1876 Nanoparticles for Colorimetric Detection of Dopamine, Key Eng. Mater. 730 (2017).
- 1877 [109] C. Fan, W. Li, S. Zhao, J. Chen, X. Li, Efficient one pot synthesis of chitosan-induced gold
 1878 nanoparticles by microwave irradiation, Mater. Lett. 62 (2008) 3518-2520.
- 1879 [110] A. Üzer, U. Yalçın, Z. Can, E. Erçağ, R. Apak, Indirect Determination of Pentaerythritol
 1880 Tetranitrate (PETN) with a gold nanoparticles-based colorimetric consor, Talanta 175 (2017) 2431881 249.
- 1882 [111] U. Kreibig, L. Genzel, Optical absorption of small metallic particles, Surf. Sci. 156 (1985)
 1883 678-700.
- 1884 [112] B. Dusemund, A. Hoffmann, T. Salznand, D. Kreibig, G. Schmid, Cluster matter: the
 1885 transition of optical elastic scattering to regular reflection, Z. Phys. D: At. Mol. Clusters 20 (1991)
 1886 305-308.
- 1887 [113] J.-S. Lee, P.A. Ulmann, M.S. Han, C.A. Mirkin, A DNA–Gold Nanoparticle-Based
 1888 Colorimetric Competition Assay for the Detection of Cysteine, Nano Lett. 8 (2008) 529-533.
- 1889 [114] X. Wei, L. Qi, J. Tan, F. Wang, A colorimetric sensor for determination of cysteine
 1890 by carboxymethyl cellulore-in-tionalized gold nanoparticles, Anal. Chim. Acta 671 (2010) 80-84.
- [115] Q. Qian, J. Deng, D. Wang, L. Yang, P. Yu, L. Mao, Aspartic Acid-Promoted Highly Selective
 and Sensitive Colorbeau Sensing of Cysteine in Rat Brain, Anal. Chem. 84 (2012) 9579-9584.
- 1893 [116] W. Pu, H. Zhao, C. Huang, L. Wu, D. Xu, Visual detection of arginine based on the unique 1894 guanidino group-induced aggregation of gold nanoparticles, Anal. Chim. Acta 764 (2013) 78-83.
- 1895 [117] G. Sener, L. Uzun, A. Denizli, Colorimetric Sensor Array Based on Gold Nanoparticles and
- 1896 Amino Acids for Identification of Toxic Metal Ions in Water, ACS Appl. Mater. Interfaces. 6 (2014)
- **1897** 18395-18400.
- 1898 [118] K.A. Rawat, S.K. Kailasa, 4-Amino nicotinic acid mediated synthesis of gold nanoparticles
 1899 for visual detection of arginine, histidine, methionine and tryptophan, Sens. Actuators, B. 222 (2016)
 1900 780-789.
- [119] Q. Zhang, D. Zhang, Y. Lu, G. Xu, Y. Yao, S. Li, Q. Liu, Label-free amino acid detection
 based on nanocomposites of graphene oxide hybridized with gold nanoparticles, Biosens.
 Bioelectron. 77 (2016) 963-970.
- 1904 [120] L. Kuang, L. Zhang, A.-Z. Xu, Z.-M. Li, R.-P. Liang, J.-D. Qiu, Bio-dots assembly-induced 1905 aggregation of gold nanoparticles for highly sensitive and selective colorimetric detection of

- 1906 methionine, Sens. Actuators, B. 244 (2017) 1031-1036.
- 1907 [121] T. Liu, N. Li, J.X. Dong, Y. Zhang, Y.Z. Fan, S.M. Lin, H.Q. Luo, N.B. Li, A colorimetric
 1908 and fluorometric dual-signal sensor for arginine detection by inhibiting the growth of gold
 1909 nanoparticles/carbon quantum dots composite, Biosens. Bioelectron. 87 (2017) 772-778.
- 1910 [122] K. Farhadi, M. Forough, A. Pourhossein, R. Molaei, Highly sensitive and selective
 1911 colorimetric probe for determination of l-cysteine in aqueous media based on Ag/Pd bimetallic
 1912 nanoparticles, Sens. Actuators, B. 202 (2014) 993-1001.
- [123] D. Zhong, K. Yang, Y. Wang, X. Yang, Dual-channel sensing strategy based on gold
 nanoparticles cooperating with carbon dots and hairpin structure for assaying RNA and DNA,
 Talanta 175 (2017) 217-223.
- 1916 [124] C. Lai, L. Qin, L. Chen, G.-M. Zeng, D.-L. Huang, C. Zhang, P. Xu, M. Cheng, Sensitive and
 1917 selective detection of glutathione based on anti-catalytical growth of gold nanoparticles colorimetric
 1918 sensor, Int. J. Environ. Anal. Chem. 97 (2017) 71-84.
- 1919 [125] Z. Chen, Z. Wang, J. Chen, S. Wang, X. Huang, Sensitive and selective detection of
 1920 glutathione based on resonance light scattering using sensitive gold nanoparticles as colorimetric
 1921 probes, Analyst 137 (2012) 3132-3137.
- 1922 [126] N. Uehara, K. Ookubo, T. Shimizu, Colorimetric Assay of Gretathione Based on the
 1923 Spontaneous Disassembly of Aggregated Gold Nanocomposites Conjugated with Water-Soluble
 1924 Polymer, Langmuir 26 (2010) 6818-6825.
- 1925 [127] Y. Li, P. Wu, H. Xu, H. Zhang, X. Zhong, Anti-aggregation of gold nanoparticle-based
 1926 colorimetric sensor for glutathione with excellent selection, and sensitivity, Analyst 136 (2011)
 1927 196-200.
- 1928 [128] J.-F. Li, P.-C. Huang, F.-Y. Wu, Highly structure and sensitive detection of glutathione based
 on anti-aggregation of gold nanoparticles via pH regulation, Sens. Actuators, B. 240 (2017) 5531930 559.
- 1931 [129] D. Vilela, M.C. González, A. Ercapa, Sensing colorimetric approaches based on gold and
 1932 silver nanoparticles aggregation: Chebrical creativity behind the assay. A review, Anal. Chim. Acta
 1933 751 (2012) 24-43.
- 1934 [130] K. Saha, S.S. Agrsti, Kim, X. Li, V.M. Rotello, Gold nanoparticles in chemical and 1935 biological sensing, Clem. Rev. 112 (2012) 2739-2779.
- [131] C.-C. Huang, T.-F. Huang, Z. Cao, W. Tan, H.-T. Chang, Aptamer-Modified Gold
 Nanoparticles for colorimetric Determination of Platelet-Derived Growth Factors and Their
 Receptors, Anal. Chem. 77 (2005) 5735-5741.
- 1939 [132] C.-C. Chang, C.-Y. Chen, T.-L. Chuang, T.-H. Wu, S.-C. Wei, H. Liao, C.-W. Lin, Aptamer-
- based colorimetric detection of proteins using a branched DNA cascade amplification strategy andunmodified gold nanoparticles, Biosens. Bioelectron. 78 (2016) 200-205.
- [133] J.-W. Jian, W.-C. Chiu, H.-T. Chang, P.-H. Hsu, C.-C. Huang, Fibrinolysis and thrombosis of
 fibrinogen-modified gold nanoparticles for detection of fibrinolytic-related proteins, Anal. Chim.
 Acta 774 (2013) 67-72.
- [134] X. Wei, Y. Wang, Y. Zhao, Z. Chen, Colorimetric sensor array for protein discrimination
 based on different DNA chain length-dependent gold nanoparticles aggregation, Biosens.
 Bioelectron. 97 (2017) 332-337.
- 1948 [135] N. Li, S.G. Liu, Y.D. Zhu, T. Liu, S.M. Lin, Y. Shi, H.Q. Luo, N.B. Li, Tuning gold 1949 nanoparticles growth via DNA and carbon dots for nucleic acid and protein detection, Sens.

- 1950 Actuators, B. 251 (2017) 455-461.
- [136] C.A. Mirkin, R.L. Letsinger, R.C. Mucic, J.J. Storhoff, A DNA-based method for rationallyassembling nanoparticles into macroscopic materials, Nature 382 (1996) 607-609.
- 1953 [137] R. Elghanian, J.J. Storhoff, R.C. Mucic, R.L. Letsinger, C.A. Mirkin, Selective colorimetric
 1954 detection of polynucleotides based on the distance-dependent optical properties of gold
 1955 nanoparticles, Science 277 (1997) 1078-1081.
- 1956 [138] Y. Huo, L. Qi, X.-J. Lv, T. Lai, J. Zhang, Z.-Q. Zhang, A sensitive aptasensor for colorimetric
- detection of adenosine triphosphate based on the protective effect of ATP-aptamer complexes onunmodified gold nanoparticles, Biosens. Bioelectron. 78 (2016) 315-320.
- [139] R.A. Reynolds, C.A. Mirkin, R.L. Letsinger, Homogeneous, Nanoparticle-Based Quantitative
 Colorimetric Detection of Oligonucleotides, JACS 122 (2000) 3795-3796.
- [140] R. Jin, G. Wu, Z. Li, C.A. Mirkin, G.C. Schatz, What Controls the Melting Properties ofDNA-Linked Gold Nanoparticle Assemblies?, JACS 125 (2003) 1643-1654.
- 1963 [141] A.K.R. Lytton-Jean, C.A. Mirkin, A Thermodynamic Investigation into the Binding
 1964 Properties of DNA Functionalized Gold Nanoparticle Probes and Molecular Properties,
 1965 JACS 127 (2005) 12754-12755.
- 1966 [142] J.-S. Lee, S.I. Stoeva, C.A. Mirkin, DNA-Induced Size-Selective Sparation of Mixtures of1967 Gold Nanoparticles, JACS 128 (2006) 8899-8903.
- 1968 [143] M.S. Han, A.K.R. Lytton-Jean, B.-K. Oh, J. Heo, C.A. Mickin, Colorimetric Screening of
- 1969 DNA-Binding Molecules with Gold Nanoparticle Probes, Angew. Chem. 118 (2006) 1839-1842.
- 1970 [144] M.S. Han, A.K. Lytton-Jean, C.A. Mirkin, A gold multiparticle based approach for screening
 1971 triplex DNA binders, JACS 128 (2006) 4954-4955.
- 1972 [145] R.-D. Li, B.-C. Yin, B.-C. Ye, Ultrasensitive polorimetric detection of microRNAs based on
 1973 isothermal exponential amplification reaction-assisted gold nanoparticle amplification, Biosens.
 1974 Bioelectron. 86 (2016) 1011-1016.
- 1975 [146] Y. Liu, Z. Wu, G. Zhou, Z. H. I. Zhou, A. Shen, J. Hu, Simple, rapid, homogeneous
 1976 oligonucleotides colorimetric detection based on non-aggregated gold nanoparticles, Chem.
 1977 Commun. 48 (2012) 3164-3165
- 1978 [147] L.A. Gearheart, H.J. Phein, C.J. Murphy, Oligonucleotide adsorption to gold nanoparticles:
 a surface-enhanced Raman spectroscopy study of intrinsically bent DNA, J. Phys. Chem., B 105
 (2001) 12609-126 3
- 1981 [148] H. Li, L. Rothberg, Colorimetric detection of DNA sequences based on electrostatic
 1982 interactions with unmodified gold nanoparticles, Proceedings of the National Academy of Sciences
 1983 of the United States of America 101 (2004) 14036-14039.
- 1984 [149] A.M. Baetsen-Young, M. Vasher, L.L. Matta, P. Colgan, E.C. Alocilja, B. Day, Direct
 1985 colorimetric detection of unamplified pathogen DNA by dextrin-capped gold nanoparticles, Biosens.
 1986 Bioelectron. 101 (2018) 29-36.
- 1987 [150] J. Thavanathan, N.M. Huang, K.L. Thong, Colorimetric detection of DNA hybridization
 1988 based on a dual platform of gold nanoparticles and graphene oxide, Biosens. Bioelectron. 55 (2014)
 1989 91-98.
- 1990 [151] W. Yun, J. Jiang, D. Cai, P. Zhao, J. Liao, G. Sang, Ultrasensitive visual detection of DNA
- 1991 with tunable dynamic range by using unmodified gold nanoparticles and target catalyzed hairpin
- assembly amplification, Biosens. Bioelectron. 77 (2016) 421-427.
- 1993 [152] J. Yang, Y. Zhang, L. Zhang, H. Wang, J. Nie, Z. Qin, J. Li, W. Xiao, Analyte-triggered

- autocatalytic amplification combined with gold nanoparticle probes for colorimetric detection ofheavy-metal ions, Chem. Commun. 53 (2017) 7477-7480.
- 1996 [153] Y. Chen, S. Han, S. Yang, Q. Pu, Rhodanine stabilized gold nanoparticles for sensitive and1997 selective detection of mercury (II), Dyes Pigm. 142 (2017) 126-131.
- 1998 [154] Y.R. Kim, R.K. Mahajan, J.S. Kim, H. Kim, Highly sensitive gold nanoparticle-based
 1999 colorimetric sensing of mercury(II) through simple ligand exchange reaction in aqueous media,
 2000 ACS Appl. Mater. Interfaces 2 (2010) 292-295.
- [155] D. Liu, W. Qu, W. Chen, W. Zhang, Z. Wang, X. Jiang, Highly Sensitive, Colorimetric
 Detection of Mercury(II) in Aqueous Media by Quaternary Ammonium Group-Capped Gold
 Nanoparticles at Room Temperature, Anal. Chem. 82 (2010) 9606-9610.
- [156] L. Li, L. Zhang, T. Lou, Z. Chen, Iodide-responsive Cu@Au nanoparticle-based colorimetric
 assay for sensitive mercury (II) detection, Sens. Actuators, B. 252 (2017) 663-670.
- 2006 [157] Y. Liu, Y. Liu, L. Xu, J. Li, X. Liu, J. Liu, G. Li, Highly selective, colorimetric detection of
- Hg2+ based on three color changes of AuNPs solution from red through sandy beige to celandine
 green, Sens. Actuators, B. 249 (2017) 331-338.
- 2009 [158] T. Tolessa, Z.-Q. Tan, Y.-G. Yin, J.-F. Liu, Single-drop gold nanoparticles for headspace
- 2010 microextraction and colorimetric assay of mercury (II) in environmental waters, Talanta 176 (2018)
 2011 77-84.
- [159] N. Sui, F. Liu, K. Wang, F. Xie, L. Wang, J. Tang, M. Lin, W. Yu, Nano Au-Hg amalgam
 for Hg2+ and H2O2 detection, Sens. Actuators, B. 252 (201) 100-1015.
- [160] K.N. Han, J.-S. Choi, J. Kwon, Gold nanozyme, oared paper chip for colorimetric detection
 of mercury ions, Sci. Rep. 7 (2017).
- [161] J.S. Lee, M.S. Han, C.A. Mirkin, Coloringerry detection of mercuric ion (Hg²⁺) in aqueous
 media using DNA-functionalized gold nanoparticles, Angew. Chem. Int. Ed. Engl. 46 (2007) 40934096.
- [162] X.J. Xue, F. Wang, X.G. Liu, On-step, room temperature, colorimetric detection of mercury
 (Hg²⁺) using DNA/nanoparticle conjugates, JACS 130 (2008) 3244-3245.
- 2021 [163] Z. Li, C.A. Mirkin, Convet-Induced Nanoparticle Assembly, JACS 127 (2005) 115682022 11569.
- [164] T. Li, S. Dong, C. Wang, Label-Free Colorimetric Detection of Aqueous Mercury Ion (Hg²⁺)
 Using Hg²⁺-Modulard G-Quadruplex-Based DNAzymes, Anal. Chem. 81 (2009) 2144-2149.
- 2025 [165] D. Li, A. Wieckowska, I. Willner, Optical analysis of Hg²⁺ ions by oligonucleotide-gold-
- 2026 nanoparticle hybrids and DNA-based machines, Angew. Chem. Int. Ed. Engl. 47 (2008) 3927-3931.
- [166] X. Xue, F. Wang, X. Liu, One-Step, Room Temperature, Colorimetric Detection of Mercury
 (Hg²⁺) Using DNA/Nanoparticle Conjugates, JACS 130 (2008) 3244-3245.
- 2029 [167] Y. Ma, L. Jiang, Y. Mei, R. Song, D. Tian, H. Huang, Colorimetric sensing strategy for
- 2030 mercury(ii) and melamine utilizing cysteamine-modified gold nanoparticles, Analyst 138 (2013)
 2031 5338-5343.
- 2032 [168] G. Sener, L. Uzun, A. Denizli, Lysine-promoted colorimetric response of gold nanoparticles:
 2033 a simple assay for ultrasensitive mercury (II) detection, Anal. Chem. 86 (2013) 514-520.
- [169] C.C. Huang, H.T. Chang, Parameters for selective colorimetric sensing of mercury(II) in
 aqueous solutions using mercaptopropionic acid-modified gold nanoparticles, Chem. Commun.
 (2007) 1215-1217.
- 2037 [170] G.K. Darbha, A.K. Singh, U.S. Rai, E. Yu, H. Yu, P. Chandra Ray, Selective detection of

- 2038 mercury (II) ion using nonlinear optical properties of gold nanoparticles, JACS 130 (2008) 80382039 8043.
- [171] Y. Gao, X. Li, Y. Li, T. Li, Y. Zhao, A. Wu, A simple visual and highly selective colorimetric
 detection of Hg²⁺ based on gold nanoparticles modified by 8-hydroxyquinolines and oxalates, Chem.
 Commun. 50 (2014) 6447-6450.
- 2043 [172] S. Si, A. Kotal, T.K. Mandal, One-dimensional assembly of peptide-functionalized gold 2044 nanoparticles: an approach toward mercury ion sensing, J. Phys. Chem., C 111 (2007) 1248-1255.
- [173] Y. Xu, L. Deng, H. Wang, X. Ouyang, J. Zheng, J. Li, R. Yang, Metal-induced aggregation
 of mononucleotides-stabilized gold nanoparticles: an efficient approach for simple and rapid
 colorimetric detection of Hg(ii), Chem. Commun. 47 (2011) 6039-6041.
- 2048 [174] Y. Guo, Z. Wang, W. Qu, H. Shao, X. Jiang, Colorimetric detection of mercury, lead and
 2049 copper ions simultaneously using protein-functionalized gold nanoparticles, Biosens. Bioelectron.
 2050 26 (2011) 4064-4069.
- 2051 [175] C. Lai, Q. Lei, Z. Guangming, L. Yunguo, H. Danlian, Z. Chen, X. Piao, C. Min, Q. Xiangbin,
- W. Manman, Sensitive and selective detection of mercury ions based on papain and 2,6pyridinedicarboxylic acid functionalized gold nanoparticles, RSC Adv. 6 (2013) 3259-3266.
- pyridinedicarboxylic acid functionalized gold nanoparticles, RSC Adv.o (2013) 5259-5266.
- 2054 [176] R.M. Tripathi, R.K. Gupta, P. Singh, A.S. Bhadwal, A. Shrivastav, N.Kumar, B.R. Shrivastav,
- 2055 Ultra-sensitive detection of mercury(II) ions in water sample using gold nanoparticles synthesized
 2056 by Trichoderma harzianum and their mechanistic approach, Sense Actuators, B. 204 (2014) 6372057 646.
- [177] Y. Kim, R.C. Johnson, J.T. Hupp, Gold Nanoparticle Based Sensing of "Spectroscopically
 Silent" Heavy Metal Ions, Nano Lett. 1 (2001) 165-165
- [178] C. Fan, S. He, G. Liu, L. Wang, S. Song, *Portable and Power-Free Microfluidic Device for* Rapid and Sensitive Lead (Pb²⁺) Detection Sensors 12 (2012) 9467-9475.
- [179] E. Priyadarshini, N. Pradhan, Metal induced aggregation of valine capped gold nanoparticles:
 An efficient and rapid approach for contributive detection of Pb²⁺ ions, Sci. Rep. 7 (2017).
- [180] N. Ratnarathorn, O. Chailepakot, W. Dungchai, Highly sensitive colorimetric detection of
 lead using maleic acid functionalized gold nanoparticles, Talanta 132 (2015) 613-618.
- [181] E. Giannakopoulos K. Shristoforidis, A. Tsipis, M. Jerzykiewicz, Y. Deligiannakis, Influence
 of Pb (II) on the radical properties of humic substances and model compounds, J. Phys. Chem., A
 109 (2005) 2223-323
- [182] K. Yoosaf, B. Ipe, C.H. Suresh, K.G. Thomas, In situ synthesis of metal nanoparticles and
 selective naked-eye detection of lead ions from aqueous media, J. Phys. Chem., C 111 (2007)
 12839-12847.
- [183] K.-W. Huang, C.-J. Yu, W.-L. Tseng, Sensitivity enhancement in the colorimetric detection
 of lead (II) ion using gallic acid–capped gold nanoparticles: Improving size distribution and
 minimizing interparticle repulsion, Biosens. Bioelectron. 25 (2010) 984-989.
- 2075 [184] Y.-Y. Chen, H.-T. Chang, Y.-C. Shiang, Y.-L. Hung, C.-K. Chiang, C.-C. Huang,
 2076 Colorimetric Assay for Lead Ions Based on the Leaching of Gold Nanoparticles, Anal. Chem. 81
 2077 (2009) 9433-9439.
- 2078 [185] Y.-L. Hung, T.-M. Hsiung, Y.-Y. Chen, C.-C. Huang, A label-free colorimetric detection of
- lead ions by controlling the ligand shells of gold nanoparticles, Talanta 82 (2010) 516-522.
- 2080 [186] Y.L. Hung, T.M. Hsiung, Y.Y. Chen, Y.F. Huang, C.C. Huang, Colorimetric Detection of
- 2081 Heavy Metal Ions Using Label-Free Gold Nanoparticles and Alkanethiols, J. Phys. Chem. C 114

2082 (2010) 16329-16334.

2083 [187] S.-Y. Lin, S.-H. Wu, C.-h. Chen, A Simple Strategy for Prompt Visual Sensing by Gold
2084 Nanoparticles: General Applications of Interparticle Hydrogen Bonds, Angew. Chem. Int. Ed. 45
2085 (2006) 4948-4951.

[188] V.N. Mehta, J.N. Solanki, S.K. Kailasa, Selective visual detection of Pb(II) ion via gold
nanoparticles coated with a dithiocarbamate-modified 4'-aminobenzo-18-crown-6, Microchim.
Acta 181 (2014) 1905-1915.

- [189] F. Chai, C. Wang, T. Wang, L. Li, Z. Su, Colorimetric detection of Pb²⁺ using glutathione
 functionalized gold nanoparticles, ACS Appl. Mater. Interfaces 2 (2010) 1466-1470.
- 2091 [190] L. Beqa, A.K. Singh, S.A. Khan, D. Senapati, S.R. Arumugam, P.C. Ray, Gold Nanoparticle-
- 2092 Based Simple Colorimetric and Ultrasensitive Dynamic Light Scattering Assay for the Selective
- 2093 Detection of Pb(II) from Paints, Plastics, and Water Samples, ACS Appl. Mater. Interfaces. 3 (2011)2094 668-673.
- 2095 [191] D. Zhu, X. Li, X. Liu, J. Wang, Z. Wang, Designing bifunctionalized gold nanoparticle for
 2096 colorimetric detection of Pb²⁺ under physiological condition, Biosens. Bioelectron, 31 (2012) 5052097 509.
- 2098 [192] S. Panich, K.A. Wilson, P. Nuttall, C.K. Wood, T. Albrecht, J.B. Edel, Label-Free Pb(II)
 2099 Whispering Gallery Mode Sensing Using Self-Assembles Olutathione-Modified Gold
 2100 Nanoparticles on an Optical Microcavity, Anal. Chem. 86 (2014) (229-6306.
- [193] J. Liu, Y. Lu, A Colorimetric Lead Biosensor Using NAzyme-Directed Assembly of Gold
 Nanoparticles, JACS 125 (2003) 6642-6643.
- [194] J. Liu, Y. Lu, Accelerated color change of globanoparticles assembled by DNAzymes for
 simple and fast colorimetric Pb2+ detection, JASS No (2004) 12298-12305.
- [195] J. Liu, Y. Lu, Stimuli-responsive disassembly of nanoparticle aggregates for light-up
 colorimetric sensing, JACS 127 (2005) 1267 12683.
- [196] W. Zhao, J.C. Lam, W. Chiuman, MA. Brook, Y. Li, Enzymatic cleavage of nucleic acids on
 gold nanoparticles: a generic platform for facile colorimetric biosensors, Small 4 (2008) 810-816.
 [107] B. Chen, Z. Wang, D. H. D. Ma, L. Huang, C. Yu, Z. Cus, Y. Forg, Superscription and J. Statistical Science and Scien
- [197] B. Chen, Z. Wang, D. H. C. Ma, L. Huang, C. Xv, Z. Guo, X. Jiang, Scanometric nanomolar
 lead (II) detection using DNA functionalized gold nanoparticles and silver stain enhancement, Sens.
 Actuators, B. 200 (20(4) 310-316.
- 2112 [198] Y. Huang, Y. K. Y. Chen, X. Wu, L. Fang, Z. Zhu, C.J. Yang, Target-responsive DNAzyme
- cross-linked hydrogel for visual quantitative detection of lead, Anal. Chem. 86 (2014) 11434-11439.
- [199] W. Yun, D. Cai, J. Jiang, P. Zhao, Y. Huang, G. Sang, Enzyme-free and label-free ultrasensitive colorimetric detection of Pb²⁺ using molecular beacon and DNAzyme based amplification
 strategy, Biosens. Bioelectron. 80 (2016) 187-193.
- [200] T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yang, M. Zhou, H. Zhou, Z. Tan, X. Wang, Biosorption
 of cadmium (II), zinc (II) and lead (II) by Penicillium simplicissimum: Isotherms, kinetics and
 thermodynamics, J. Hazard. Mater. 160 (2008) 655-661.
- [201] Y. Feng, J.-L. Gong, G.-M. Zeng, Q.-Y. Niu, H.-Y. Zhang, C.-G. Niu, J.-H. Deng, M. Yan,
 Adsorption of Cd (II) and Zn (II) from aqueous solutions using magnetic hydroxyapatite
 nanoparticles as adsorbents, Chem. Eng. J. 162 (2010) 487-494.
- [202] C. Yang, H. Chen, G. Zeng, G. Yu, S. Luo, Biomass accumulation and control strategies in
 gas biofiltration, Biotechnol. Adv. 28 (2010) 531-540.
- 2125 [203] D. Huang, W. Xue, G. Zeng, J. Wan, G. Chen, C. Huang, C. Zhang, M. Cheng, P. Xu,

- 2126 Immobilization of Cd in river sediments by sodium alginate modified nanoscale zero-valent iron:
- 2127 Impact on enzyme activities and microbial community diversity, Water Res. 106 (2016) 15-25.
- [204] Y. Gu, N. Li, M. Gao, Z. Wang, D. Xiao, Y. Li, H. Jia, H. He, Microwave-assisted synthesis
 of BSA-modified silver nanoparticles as a selective fluorescent probe for detection and cellular
 imaging of cadmium (II), Microchim. Acta 182 (2015) 1255-1261.
- [205] W. Jin, P. Huang, F. Wu, L.-H. Ma, Ultrasensitive colorimetric assay of cadmium ion based
 on silver nanoparticles functionalized with 5-sulfosalicylic acid for wide practical applications,
 Analyst 140 (2015) 3507-3513.
- 2134 [206] J.R. Kalluri, T. Arbneshi, S.A. Khan, A. Neely, P. Candice, B. Varisli, M. Washington, S.
- McAfee, B. Robinson, S. Banerjee, A.K. Singh, D. Senapati, P.C. Ray, Use of Gold Nanoparticles
 in a Simple Colorimetric and Ultrasensitive Dynamic Light Scattering Assay: Selective Detection
 of Arsenic in Groundwater, Angew. Chem. Int. Ed. 48 (2009) 9668-9671.
- [207] A.J. Wang, H. Guo, M. Zhang, D.L. Zhou, R.Z. Wang, J.J. Feng, Sensitive and selective
 colorimetric detection of cadmium(II) using gold nanoparticles modified with 4-amino-3hydrazino-5-mercapto-1,2,4-triazole, Microchim. Acta 180 (2013) 1051-1057.
- [208] Y.G. Wu, S.S. Zhan, F.Z. Wang, L. He, W.T. Zhi, P. Zhou, Cationic polymers and aptamers
 mediated aggregation of gold nanoparticles for the colorimetric detection of arsenic(III) in aqueous
 solution, Chem. Commun. 48 (2012) 4459-4461.
- [209] Y. Wu, S. Zhan, L. Wang, P. Zhou, Selection of a DNA practice for cadmium detection based
 on cationic polymer mediated aggregation of gold nanoparticles. Analyst 139 (2014) 1550-1561.
- [210] M. Zhang, Y.-Q. Liu, B.-C. Ye, Colorimetric as a viol parallel detection of Cd²⁺, Ni²⁺ and
 Co²⁺ using peptide-modified gold nanoparticles, Analyst 137 (2012) 601-607.
- [211] Y.M. Guo, Y. Zhang, H.W. Shao, Z. Wang, Y.Y. Jiang, Label-Free Colorimetric
 Detection of Cadmium Ions in Rice Samples Using Gold Nanoparticles, Anal. Chem. 86 (2014)
 8530-8534.
- [212] J. Du, Q. Shao, S. Yin, L. Jiang J Ma, X. Chen, Colorimetric Chemodosimeter Based on
 Diazonium-Gold-Nanoparticle Complexes for Sulfite Ion Detection in Solution, Small 8 (2012)
 3412–3416.
- [213] D.G. Smith, I.L. Torollicki, V.E. Zwicker, K.A. Jolliffe, E.J. New, Fluorescent sensing arrays
 for cations and anions, Analyst 142 (2017).
- [214] J. Shen, Y. Lour Gu, F. Xia, X. Zuo, Recent Development of Sandwich Assay Based on the
 Nanobiotechnologies for Proteins, Nucleic Acids, Small Molecules, and Ions, Chem. Rev. 114
 (2014) 7631.
- [215] D. Liu, Z. Wang, X. Jiang, Gold nanoparticles for the colorimetric and fluorescent detection
 of ions and small organic molecules, Nanoscale 3 (2011) 1421-1433.
- [216] C. Fang, R. Dharmarajan, M. Megharaj, R. Naidu, Gold nanoparticle-based optical sensors
 for selected anionic contaminants, TrAC, Trends Anal. Chem. 86 (2017) 143-154.
- [217] Y. Zhou, J.F. Zhang, J. Yoon, Fluorescence and Colorimetric Chemosensors for Fluoride-Ion
 Detection, Chem. Rev. 114 (2014) 5511-5571.
- [218] B. Wang, X. Ji, J. Ren, R. Ni, L. Wang, Enhanced electrocatalytic activity of graphene-gold
 nanoparticles hybrids for peroxynitrite electrochemical detection on hemin-based electrode,
 Bioelectrochemistry 118 (2017) 75-82.
- 2168 [219] D. Gligor, F. Cuibus, R. Peipmann, A. Bund, Novel amperometric sensors for nitrite detection
- using electrodes modified with PEDOT prepared in ionic liquids, J. Solid State Electrochem. 21

- 2170 (2017) 281-290.
- [220] W. Sroysee, K. Ponlakhet, S. Chairam, P. Jarujamrus, M. Amatatongchai, A sensitive and
 selective on-line amperometric sulfite biosensor using sulfite oxidase immobilized on a magnetitegold-folate nanocomposite modified carbon-paste electrode, Talanta 156-157 (2016) 154-162.
- 2174 [221] Y. Zhang, R. Yuan, Y. Chai, J. Wang, H. Zhong, Amperometric biosensor for nitrite and
- 2175 hydrogen peroxide based on hemoglobin immobilized on gold nanoparticles/polythionine/platinum
- 2176 nanoparticles modified glassy carbon electrode, J. Chem. Technol. Biotechnol. 87 (2012) 570-574.
- 2177 [222] A.A. Saeed, B. Singh, M.N. Abbas, Y.M. Issa, E. Dempsey, Electrocatalytic Nitrite
- 2178 Determination Using Iron Phthalocyanine Modified Gold Nanoparticles, Electroanalysis 27 (2015)
 2179 1086-1096.
- [223] M. Shamsipur, Z. Karimi, M. Amouzadeh Tabrizi, A novel electrochemical cyanide sensor
 using gold nanoparticles decorated carbon ceramic electrode, Microchem. J. 133 (2017) 485-489.
- [224] Y. Xu, W. Zhang, J. Shi, X. Zou, Y. Li, T. Haroon Elrasheid, X. Huang, Z. Li, X. Zhai, X.
 Hu, Electrodeposition of gold nanoparticles and reduced graphene oxide on an electrode for fast and
 sensitive determination of methylmercury in fish, Food Chem. 237 (2017) 423-430.
- [225] P. Pienpinijtham, X.X. Han, S. Ekgasit, Y. Ozaki, Highly Supprise and Selective
 Determination of Iodide and Thiocyanate Concentrations Using Surface-Enhanced Raman
 Scattering of Starch-Reduced Gold Nanoparticles, Anal. Chem. 82 (2011) 3655-3662.
- [226] A.J. McCarthy, R.G. Coleman, M.J. Nicol, The Mechanismon the Oxidative Dissolution of
 Colloidal Gold in Cyanide Media, J. Electrochem. Soc. 145 (1996) 408-414.
- [227] T. Pal, A. Ganguly, D.S. Maity, Determination of synaide based upon its reaction with
 colloidal silver in the presence of oxygen, Anal. Chem. 53 (1986) 1564-1566.
- [228] C.-Y. Liu, W.-L. Tseng, Colorimetric and or cyanide and cyanogenic glycoside using
 polysorbate 40-stabilized gold nanoparticles, Chem. Commun. 47 (2011) 2550-2552.
- [229] M.H. Kim, S. Kim, H.H. Jang, S.H. Seo, M.S. Han, A gold nanoparticle-based
 colorimetric sensing ensemble for the ofbrimetric detection of cyanide ions in aqueous solution,
 Tetrahedron Lett. 51 (2010) 4712-4716.
- [230] Z. Zhang, J. Zhang, C. D. Pan, Z. Chen, L. Chen, Label free colorimetric sensing of
 thiocyanate based on indicing aggregation of Tween 20-stabilized gold nanoparticles, Analyst 137
 (2012) 2682-2686.
- [231] D. Zhao, C. L. Lu, F. Yang, X. Yang, A dual-mode colorimetric and fluorometric "light
 on" sensor for thiodynate based on fluorescent carbon dots and unmodified gold nanoparticles,
 Analyst 140 (2015) 8157-8164.
- [232] C. Radhakumary, K. Sreenivasan, Rapid and highly selective dipchecking for cyanide ions in
 aqueous media, Analyst 137 (2012) 5387-5391.
- [233] C. Cheng, H.-Y. Chen, C.-S. Wu, J.S. Meena, T. Simon, F.-H. Ko, A highly sensitive and
 selective cyanide detection using a gold nanoparticle-based dual fluorescence–colorimetric sensor
 with a wide concentration range, Sens. Actuators, B. 227 (2016) 283-290.
- [234] Y. Ye, Y. Guo, Y. Yue, Y. Zhang, Facile colorimetric detection of nitrite based on antiaggregation of gold nanoparticles, Anal. Methods. 7 (2015) 4090-4096.
- [235] W.L. Daniel, M.S. Han, J.-S. Lee, C.A. Mirkin, Colorimetric Nitrite and Nitrate Detection
 with Gold Nanoparticle Probes and Kinetic End Points, JACS 131 (2009) 6362-6363.
- 2212 [236] J. Zhang, X. Wang, X. Yang, Colorimetric determination of hypochlorite with unmodified
- 2213 gold nanoparticles through the oxidation of a stabilizer thiol compound, Analyst 137 (2012) 2806-

- [237] L. Lu, J. Zhang, X. Yang, Simple and selective colorimetric detection of hypochlorite based
 on anti-aggregation of gold nanoparticles, Sens. Actuators, B. 184 (2013) 189-195.
- [238] K. Shanmugaraj, M. Ilanchelian, Visual and optical detection of hypochlorite in water samplesbased on etching of gold/silver alloy nanoparticles, New J. Chem. (2017).
- [239] I.L. Lee, Y.-M. Sung, C.-H. Wu, S.-P. Wu, Colorimetric sensing of iodide based on triazoleacetamide functionalized gold nanoparticles, Microchim. Acta 181 (2014) 573-579.
- [240] J.-A. Gu, Y.-J. Lin, Y.-M. Chia, H.-Y. Lin, S.-T. Huang, Colorimetric and bare-eye
 determination of fluoride using gold nanoparticle agglomeration probes, Microchim. Acta 180
 (2013) 801-806.
- [241] J. Boken, S. Thatai, P. Khurana, S. Prasad, D. Kumar, Highly selective visual monitoring of
 hazardous fluoride ion in aqueous media using thiobarbituric-capped gold nanoparticles, Talanta
 132 (2015) 278-284.
- [242] H. Niu, S. Wang, Z. Zhou, Y. Ma, X. Ma, Y. Cai, Sensitive Colorimetric Visualization of
 Perfluorinated Compounds Using Poly(ethylene glycol) and Perfluorinated Thele Modified Gold
- 2229 Nanoparticles, Anal. Chem. 86 (2014) 4170-4177.
- [243] M. Zhang, Y.-Q. Liu, B.-C. Ye, Colorimetric assay for sulfate using positively-charged gold
 nanoparticles and its application for real-time monitoring of redex process, Analyst 136 (2011)
 4558-4562.
- [244] J. Zhang, Y. Yuan, X. Wang, X. Yang, Sulfite recognition and sensing using Au nanoparticles
 as colorimetric probe: a judicious combination between anionic binding sites and plasmonic
 nanoparticles, Anal. Methods. 4 (2012) 1616-1618.
- [245] Y. Jv, B. Li, R. Cao, Positively-charged and hanoparticles as peroxidase mimic and their
 application in hydrogen peroxide and glucuse detection, Chem. Commun. 46 (2010) 8017-8019.
- [246] J.M. Liu, X.X. Wang, F.M. Li, L.P. Lin, W.L. Cai, X. Lin, L.H. Zhang, Z.M. Li, S.Q. Lin, A
 colorimetric probe for online analysis of sulfide based on the red shifts of longitudinal surface
 plasmon resonance absorption rapulting from the stripping of gold nanorods, Anal. Chim. Acta 708
 (2011) 130-133.
- [247] C. Chen, D. Zhao, J. Li, J. Yang, X. Yang, A simple and rapid colorimetric sensor for sulfide
 anion detection based on rediox reaction of ABTS with Au (III), Sens. Actuators, B 220 (2015) 12471253.
- [248] J. Zhang, X. Xu, X. Yang, Highly specific colorimetric recognition and sensing of sulfide
 with glutathione-modified gold nanoparticle probe based on an anion-for-molecule ligand exchange
 reaction, Analyst 137 (2012) 1556-1558.
- [249] D. Zhao, C. Chen, L. Lu, F. Yang, X. Yang, A label-free colorimetric sensor for sulfate based
 on the inhibition of peroxidase-like activity of cysteamine-modified gold nanoparticles, Sens.
 Actuators, B 215 (2015) 437-444.
- [250] H.H. Deng, S.H. Weng, S.L. Huang, L.N. Zhang, A.L. Liu, X.H. Lin, W. Chen, Colorimetric
 detection of sulfide based on target-induced shielding against the peroxidase-like activity of gold
 nanoparticles, Anal. Chim. Acta 852 (2014) 218.
- [251] Y. Zhang, W.-W. Li, G.-M. Zeng, L. Tang, C.-L. Feng, D.-L. Huang, Y.-P. Li, Novel neural network-based prediction model for quantifying hydroquinone in compost with biosensor measurements, Environ. Eng. Sci. 26 (2009) 1063-1070.
- 2257 [252] G.-M. Zeng, Y. Zhang, L. Tang, L.-J. Chen, Y. Pang, C.-L. Feng, G.-H. Huang, C.-G. Niu,

^{2214 2812.}

- Sensitive and renewable picloram immunosensor based on paramagnetic immobilisation, Int. J.Environ. Anal. Chem. 92 (2012) 729-741.
- [253] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C. Huang, G.X.
 Xie, Use of iron oxide nanomaterials in wastewater treatment: a review, Sci. Total Environ. 424
- 2262 (2012) 1-10.
- [254] D. Huang, C. Hu, G. Zeng, M. Cheng, P. Xu, X. Gong, R. Wang, W. Xue, Combination of
 Fenton processes and biotreatment for wastewater treatment and soil remediation, Sci. Total
 Environ. 574 (2017) 1599-1610.
- [255] D. Huang, L. Liu, G. Zeng, P. Xu, C. Huang, L. Deng, R. Wang, J. Wan, The effects of rice
 straw biochar on indigenous microbial community and enzymes activity in heavy metalcontaminated sediment, Chemosphere 174 (2017) 545-553.
- [256] Z. Yaoyu, T. Lin, Z. Guangming, Z. Yi, L. Zhen, L. Yuanyuan, C. Jun, Y. Guide, Z. Lu, Z.
 Sheng, Simultaneous determination of hydroquinone and catechol in compost bioremediation using
 a tyrosinase biosensor and artificial neural networks, Anal. Methods. 6 (2014) 2371-2378.
- 2272 [257] C. Lai, M.-M. Wang, G.-M. Zeng, Y.-G. Liu, D.-L. Huang, C. Zhang, R.-X. Wang, P. Xu, M.
- 2273 Cheng, C. Huang, Synthesis of surface molecular imprinted TiO 2/graphere photocatalyst and its
- highly efficient photocatalytic degradation of target pollutant under visible light irradiation, Appl.
 Surf. Sci. 390 (2016) 368-376.
- [258] L. Tang, G.-M. Zeng, G.-L. Shen, Y.-P. Li, Y. Zhang, D.J. Huang, Rapid Detection of
 Picloram in Agricultural Field Samples Using a Disposable Immunomembrane-Based
 Electrochemical Sensor, Environ. Sci. Technol. 42 (2018) 1207-1212.
- [259] Y. Zhou, L. Tang, G. Zeng, J. Chen, Y. Cai, Y. Jiang, G. Yang, Y. Liu, C. Zhang, W. Tang,
 Mesoporous carbon nitride based biosensor for heavy sensitive and selective analysis of phenol and
 catechol in compost bioremediation, Biostas. Bioelectron. 61 (2014) 519-525.
- [260] K. Ai, Y. Liu, L. Lu, Hydrogen-binding recognition-induced color change of gold
 nanoparticles for visual detection of netamine in raw milk and infant formula, JACS 131 (2009)
 9496-9497.
- [261] Q. Cao, H. Zhao, Y. H. X. Li, L. Zeng, N. Ding, J. Wang, J. Yang, G. Wang, Hydrogenbonding-induced colorimetric detection of melamine by nonaggregation-based Au-NPs as a probe,
 Biosens. Bioelectron. 25 (2010) 2680-2685.
- [262] Z. Wu, H. Zha, Y. Xue, Q. Cao, J. Yang, Y. He, X. Li, Z. Yuan, Colorimetric detection of melamine during the formation of gold nanoparticles, Biosens. Bioelectron. 26 (2011) 2574-2578.
- [263] H. Huang, L. Li, G. Zhou, Z. Liu, Q. Ma, Y. Feng, G. Zeng, P. Tinnefeld, Z. He, Visual detection of melamine in milk samples based on label-free and labeled gold nanoparticles, Talanta 85 (2011) 1013-1019.
- [264] D.C. Sherrington, K.A. Taskinen, Self-assembly in synthetic macromolecular systems via
 multiple hydrogen bonding interactions, Chem. Soc. Rev. 30 (2001) 83-93.
- [265] W. Chen, H.-H. Deng, L. Hong, Z.-Q. Wu, S. Wang, A.-L. Liu, X.-H. Lin, X.-H. Xia, Bare
 gold nanoparticles as facile and sensitive colorimetric probe for melamine detection, Analyst 137
 (2012) 5382-5386.
- 2298 [266] P. Ni, H. Dai, Y. Wang, Y. Sun, Y. Shi, J. Hu, Z. Li, Visual detection of melamine based on
- the peroxidase-like activity enhancement of bare gold nanoparticles, Biosens. Bioelectron. 60 (2014)286-291.
- 2301 [267] H. Guan, J. Yu, D. Chi, Label-free colorimetric sensing of melamine based on chitosan-

- stabilized gold nanoparticles probes, Food Control 32 (2013) 35-41.
- [268] J.-y. Xin, L.-x. Zhang, D.-d. Chen, K. Lin, H.-c. Fan, Y. Wang, C.-g. Xia, Colorimetric
 detection of melamine based on methanobactin-mediated synthesis of gold nanoparticles, Food
 Chem. 174 (2015) 473-479.
- [269] J. Du, H. Du, X. Li, J. Fan, X. Peng, In-situ colorimetric recognition of arylamine based on
 chemodosimeter-functionalized gold nanoparticle, Sens. Actuators, B. 248 (2017) 318-323.
- 2308 [270] V. Pavlov, Y. Xiao, I. Willner, Inhibition of the Acetycholine Esterase-Stimulated Growth of
- Au Nanoparticles: Nanotechnology-Based Sensing of Nerve Gases, Nano Lett. 5 (2005) 649-653.
- 2310 [271] D. Liu, W. Chen, J. Wei, X. Li, Z. Wang, X. Jiang, A Highly Sensitive, Dual-Readout Assay
- Based on Gold Nanoparticles for Organophosphorus and Carbamate Pesticides, Anal. Chem. 84(2012) 4185-4191.
- [272] J. Sun, L. Guo, Y. Bao, J. Xie, A simple, label-free AuNPs-based colorimetric ultrasensitive
 detection of nerve agents and highly toxic organophosphate pesticide, Biosens. Bioelectron. 28
 (2011) 152-157.
- [273] S. Wu, D. Li, J. Wang, Y. Zhao, S. Dong, X. Wang, Gold nanoparticles dissolution based
 colorimetric method for highly sensitive detection of organophosphate pesticides, Sens. Actuators,
 B. 238 (2017) 427-433.
- [274] W. Bai, C. Zhu, J. Liu, M. Yan, S. Yang, A. Chen, Goldmanoparticle–based colorimetric
 aptasensor for rapid detection of six organophosphorous pesticious, Environ. Toxicol. Chem. 34
 (2015) 2244-2249.
- [275] R. Bala, M. Kumar, K. Bansal, R.K. Sharma, N. Wangoo, Ultrasensitive aptamer biosensor
 for malathion detection based on cationic polymer and gold nanoparticles, Biosens. Bioelectron. 85
 (2016) 445-449.
- [276] A.S. Emrani, N.M. Danesh, P. Lavace, M. Ramezani, K. Abnous, S.M. Taghdisi, Colorimetric
 and fluorescence quenching aptasensors for detection of streptomycin in blood serum and milk
 based on double-stranded DNA and goar nanoparticles, Food Chem. 190 (2016) 115-121.
- [277] N. Mohseni, M. Bahram, T. Baheri, Chemical nose for discrimination of opioids based on unmodified gold nanoparticles, pars. Actuators, B. 250 (2017) 509-517.
- [278] X. Zhang, Y. Zhang, Y. Zhao, Y. He, X. Li, Z. Yuan, Highly sensitive and selective
 colorimetric sensing of antibiotics in milk, Anal. Chim. Acta 778 (2013) 63–69.
- [279] L. Qin, G. Xey, C. Lai, D. Huang, C. Zhang, P. Xu, T. Hu, X. Liu, M. Cheng, Y. Liu, A
 visual application orgoid nanoparticles: Simple, reliable and sensitive detection of kanamycin based
 on hydrogen-bonding recognition, Sens. Actuators, B. 243 (2017) 946-954.
- [280] C. Lai, X. Liu, L. Qin, C. Zhang, G. Zeng, D. Huang, M. Cheng, P. Xu, H. Yi, D. Huang,
 Chitosan-wrapped gold nanoparticles for hydrogen-bonding recognition and colorimetric
 determination of the antibiotic kanamycin, Microchim. Acta (2017) 1-9.
- [281] H.B. Seo, Y.S. Kwon, J.E. Lee, D. Cullen, H. Noh, M.B. Gu, A novel reflectance-based
 aptasensor using gold nanoparticles for the detection of oxytetracycline, Analyst 140 (2015) 66716675.
- [282] M. Ramezani, N. Mohammad Danesh, P. Lavaee, K. Abnous, S. Mohammad Taghdisi, A
 novel colorimetric triple-helix molecular switch aptasensor for ultrasensitive detection of
 tetracycline, Biosens. Bioelectron. 70 (2015) 181-187.
- 2344 [283] Y. Zhang, G.-M. Zeng, L. Tang, Y.-P. Li, Z.-M. Chen, G.-H. Huang, Quantitative detection
- of trace mercury in environmental media using a three-dimensional electrochemical sensor with an

anionic intercalator, RSC Adv. 4 (2014) 18485-18492.

- [284] L. Tang, J. Chen, G. Zeng, Y. Zhu, Y. Zhang, Y. Zhou, X. Xie, G. Yang, S. Zhang, Ordered
 mesoporous carbon and thiolated polyaniline modified electrode for simultaneous determination of
- cadmium (II) and lead (II) by anodic stripping voltammetry, Electroanalysis 26 (2014) 2283-2291.
- 2350 [285] Y. Zhou, L. Tang, X. Xie, G. Zeng, J. Wang, Y. Deng, G. Yang, C. Zhang, Y. Zhang, J. Chen,
- Sensitive impedimetric biosensor based on duplex-like DNA scaffolds and ordered mesoporous
 carbon nitride for silver (I) ion detection, Analyst 139 (2014) 6529-6535.
- [286] Y. Zhang, G.-M. Zeng, L. Tang, D.-L. Huang, X.-Y. Jiang, Y.-N. Chen, A hydroquinone
 biosensor using modified core–shell magnetic nanoparticles supported on carbon paste electrode,
 Biosens. Bioelectron. 22 (2007) 2121-2126.
- [287] C. Zhang, C. Lai, G. Zeng, D. Huang, L. Tang, C. Yang, Y. Zhou, L. Qin, M. Cheng,
 Nanoporous Au-based chronocoulometric aptasensor for amplified detection of Pb⁽²⁺⁾ using
 DNAzyme modified with Au nanoparticles, Biosens. Bioelectron. 81 (2016) 61-67.
- [288] P. Miao, L. Liu, Y. Nie, G. Li, An electrochemical sensing strategy for ultrasensitive detection
 of glutathione by using two gold electrodes and two complementary oligonuleotides, Biosens.
 Bioelectron. 24 (2009) 3347-3351.
- [289] J.A. Ribeiro, P.M.V. Fernandes, C.M. Pereira, F. Silva, Electrochemical sensors and
 biosensors for determination of catecholamine neurotransmitters. A leview, Talanta 160 (2016)
 653-679.
- [290] M. Sajid, M.K. Nazal, M. Mansha, A. Alsharaa, S.M. Jillani, C. Basheer, Chemically
 modified electrodes for electrochemical detection of copanime in the presence of uric acid and
 ascorbic acid: a review, TrAC, Trends Anal. Chem. 77 (2016) 15-29.
- [291] N. Yusoff, A. Pandikumar, R. Ramaraj, Lim, N.M. Huang, Gold nanoparticle based
 optical and electrochemical sensing of dopamine, Microchim. Acta 182 (2015) 2091-2114.
- [292] Z. Chen, C. Zhang, X. Li, H. Ma, C. Wan, K. Li, Y. Lin, Aptasensor for electrochemical
 sensing of angiogenin based on electrole modified by cationic polyelectrolyte-functionalized
 graphene/gold nanoparticles composites, Biosens. Bioelectron. 65 (2015) 232-237.
- [293] J. Tang, D. Tang, P. Se, J. Huang, B. Qiu, G. Chen, Enzyme-free electrochemical
 immunoassay with catalyne reduction of p-nitrophenol and recycling of p-aminophenol using gold
 nanoparticles-coated carbon nanotubes as nanocatalysts, Biosens. Bioelectron. 26 (2011) 3219-3226.
 [294] M.M. Khoo, & Kanim, N.T. Darwish, Y. Alias, S.M. Khor, Non-invasive control of protein-
- surface interactions for repeated electrochemical immunosensor use, Sens. Actuators, B. 224 (2016)
 683-691.
- [295] R. Elshafey, M. Siaj, A.C. Tavares, Au nanoparticle decorated graphene nanosheets for
 electrochemical immunosensing of p53 antibodies for cancer prognosis, Analyst 141 (2016) 27332740.
- [296] Y. He, L. Zheng, Gold Nanoparticle-Catalyzed Clock Reaction of Methylene Blue and
 Hydrazine for Visual Chronometric Detection of Glutathione and Cysteine, ACS Sustainable Chem.
 Eng. 5 (2017) 9355-9359.
- [297] H. Gao, X. Wang, M. Li, H. Qi, Q. Gao, C. Zhang, Proximity hybridization-regulated
 electrogenerated chemiluminescence bioassay of α-fetoprotein via target-induced quenching
 mechanism, Biosens. Bioelectron. 98 (2017) 62-67.
- [298] B.B. Prasad, R. Singh, A new micro-contact imprinted l-cysteine sensor based on sol-gel
 decorated graphite/multiwalled carbon nanotubes/gold nanoparticles composite modified sandpaper

- 2390 electrode, Sens. Actuators, B. 212 (2015) 155-164.
- [299] Q. Zhao, S. Tang, C. Fang, Y.-F. Tu, Titania nanotubes decorated with gold nanoparticles for
 electrochemiluminescent biosensing of glycosylated hemoglobin, Anal. Chim. Acta 936 (2016) 8390.
- [300] C. Sun, L. Gao, D. Wang, M. Zhang, Y. Liu, Z. Geng, W. Xu, F. Liu, H. Bian, Biocompatible
 polypyrrole-block copolymer-gold nanoparticles platform for determination of inosine
 monophosphate with bi-enzyme biosensor, Sens. Actuators, B. 230 (2016) 521-527.
- 2397 [301] X. Zhu, Q. Zhai, W. Gu, J. Li, E. Wang, High-sensitivity electrochemiluminescence probe
 2398 with molybdenum carbides as nanocarriers for α-fetoprotein sensing, Anal. Chem. 89 (2017) 121082399 12114.
- [302] P. Khashayar, G. Amoabediny, M. Hosseini, R. Verplancke, F. Razi, J. Vanfleteren, B.
 Larijani, An electrochemical biosensor based on AuNP-modified gold electrodes for selective
 determination of serum levels of osteocalcin, IEEE Sens. J. 17 (2017) 3367-3374.
- [303] Z. Guo, L. Wu, Y. Hu, S. Wang, X. Li, Potential-resolved "in-electrode" type
 electrochemiluminescence immunoassay based on functionalized gC 3 N 4 nanosheet and Ru-NH
 2 for simultaneous determination of dual targets, Biosens. Bioelectron. 95 (2017) 27-33.
- [304] H. Ke, H. Sha, Y. Wang, W. Guo, X. Zhang, Z. Wang, C. Huang, N. Jia,
 Electrochemiluminescence resonance energy transfer system between GNRs and Ru(bpy)₃²⁺:
 Application in magnetic aptasensor for β-amyloid, Biosens. Bioelectron. 100 (2018) 266-273.
- [305] J.-T. Cao, J.-J. Yang, L.-Z. Zhao, Y.-L. Wang, H. Wang, Y.-M. Liu, S.-H. Ma, Graphene
 oxide@gold nanorods-based multiple-assisted electrochemiluminescence signal amplification
- strategy for sensitive detection of prostate specific ant sen, Biosens. Bioelectron. 99 (2018) 92-98.
- [306] X. Zhang, W. Guo, Z. Wang, H. Ke, W. Ano, A. Zhang, C. Huang, N. Jia, A sandwich
 electrochemiluminescence immunosensor for highly sensitive detection of alpha fetal protein based
 on MoS2-PEI-Au nanocomposites and Au (2) SA core/shell nanoparticles, Sens. Actuators, B. 253
 (2017) 470-477.
- [307] W. Zhu, C. Wang, X. Li, M.S. Xhan, X. Sun, H. Ma, D. Fan, Q. Wei, Zinc-doping Enhanced
 cadmium sulfide Electrocherolynninescence behavior Based on Au-Cu alloy nanocrystals
 Quenching for Insulin Detection, Biosens. Bioelectron. (2017).
- [308] M.-S. Wu, R.-N. Chen, Y. Xiao, Z.-X. Lv, Novel "signal-on" electrochemiluminescence
 biosensor for the dependent of PSA based on resonance energy transfer, Talanta 161 (2016) 271-277.
- [309] Y.-C. Liu, H.-T. Chang, C.-K. Chiang, C.-C. Huang, Pulsed-Laser Desorption/Ionization of
 Clusters from Biofunctional Gold Nanoparticles: Implications for Protein Detections, ACS Appl.
 Mater. Interfaces. 4 (2012) 5241-5248.
- [310] W.-C. Chiu, C.-C. Huang, Combining Fibrinogen-Conjugated Gold Nanoparticles with a
 Cellulose Membrane for the Mass Spectrometry-Based Detection of Fibrinolytic-Related Proteins,
 Anal. Chem. 85 (2013) 6922-6929.
- [311] Y. Tan, Y. Wang, M. Li, X. Ye, T. Wu, C. Li, Enhanced photoelectrochemical immunosensing
 of cardiac troponin I based on energy transfer between N-acetyl-L-cysteine capped CdAgTe
 quantum dots and dodecahedral Au nanoparticles, Biosens. Bioelectron. 91 (2017) 741-746.
- [312] Y. Zhang, Y. Li, Y. Wei, H. Sun, H. Wang, A sensitive signal-off electrogenerated
 chemiluminescence biosensing method for the discrimination of DNA hydroxymethylation based
 on glycosylation modification and signal quenching from ferroceneboronic acid, Talanta 170 (2017)
- 2433 546-551.

- [313] Q. Gao, W. Zhang, Y. Guo, H. Qi, C. Zhang, Highly sensitive impedimetric sensing of DNA
 hybridization based on the target DNA-induced displacement of gold nanoparticles attached to
 ssDNA probe, Electrochem. Commun. 13 (2011) 335-337.
- [314] H. Xiong, X. Zheng, Electrochemiluminescence based determination of micro-RNA using
 target-guided assembly of gold nanoparticles on an electrode modified with Nafion, carbon
 nanotubes and polyvinylpyrrolidone, Microchim. Acta 184 (2017) 1781-1789.
- 2440 [315] Y. Wang, L. Zhang, L. Shen, S. Ge, J. Yu, M. Yan, Electrochemiluminescence DNA biosensor
- based on the use of gold nanoparticle modified graphite-like carbon nitride, Microchim. Acta (2017)
- 2442 1-10.
- [316] S. Deng, L. Cheng, J. Lei, Y. Cheng, Y. Huang, H. Ju, Label-free electrochemiluminescent
 detection of DNA by hybridization with a molecular beacon to form hemin/G-quadruplex
 architecture for signal inhibition, Nanoscale 5 (2013) 5435-5441.
- [317] N. Nordin, N.A. Yusof, J. Abdullah, S. Radu, R. Hushiarian, Sensitive detection of multiple
 pathogens using a single DNA probe, Biosens. Bioelectron. 86 (2016) 398-405.
- [318] B. Wang, Y.-X. Dong, Y.-L. Wang, J.-T. Cao, S.-H. Ma, Y.-M. Liu, Quenching effect of
 exciton energy transfer from CdS: Mn to Au nanoparticles: A highly efficient photoelectrochemical
 strategy for microRNA-21 detection, Sens. Actuators, B. 254 (2018) 159-165.
- [319] M. Xu, J. Zhuang, X. Chen, G. Chen, D. Tang, A diffunctional DNA-AuNP dendrimer
 coupling DNAzyme with intercalators for femtomolar detection of nacleic acids, Chem. Commun.
 49 (2013) 7304-7306.
- [320] N. Xia, L. Zhang, G. Wang, Q. Feng, L. Liu, Labar-free and sensitive strategy for microRNAs
 detection based on the formation of boronate ester bonds and the dual-amplification of gold
 nanoparticles, Biosens. Bioelectron. 47 (2013) 4400.
- [321] C. Yang, Q. Wang, Y. Xiang, R. Yuan, Y. Chai, Target-induced strand release and thioninedecorated gold nanoparticle amplification abels for sensitive electrochemical aptamer-based
 sensing of small molecules, Sens. Activitys, B. 197 (2014) 149-154.
- [322] Y. Li, R. Tian, X. Zheng, R. Muang, Amplified electrochemical detection of nucleic acid
 hybridization via selective producentration of unmodified gold nanoparticles, Anal. Chim. Acta
 934 (2016) 59-65.
- [323] Z. Fredj, S. Azzouci, A.P. Turner, M.B. Ali, W.C. Mak, Neutravidin biosensor for direct
 capture of dual-inventional biotin-molecular beacon-AuNP probe for sensitive voltammetric
 detection of microRNA, Sens. Actuators, B. 248 (2017) 77-84.
- [324] C. Ocaña, M. del Valle, Signal amplification for thrombin impedimetric aptasensor: Sandwich
 protocol and use of gold-streptavidin nanoparticles, Biosens. Bioelectron. 54 (2014) 408-414.
- [325] X. Zhang, B. Qi, Y. Li, S. Zhang, Amplified electrochemical aptasensor for thrombin basedon bio-barcode method, Biosens. Bioelectron. 25 (2009) 259-262.
- [326] L. Bai, Y. Chai, R. Yuan, Y. Yuan, S. Xie, L. Jiang, Amperometric aptasensor for thrombin
 detection using enzyme-mediated direct electrochemistry and DNA-based signal amplification
 strategy, Biosens. Bioelectron. 50 (2013) 325-330.
- [327] Y. Shan, J.-J. Xu, H.-Y. Chen, Distance-dependent quenching and enhancing of
 electrochemiluminescence from a CdS:Mn nanocrystal film by Au nanoparticles for highly sensitive
 detection of DNA, Chem. Commun. (2009) 905-907.
- 2476 [328] L. Deng, Y. Du, J.-J. Xu, H.-Y. Chen, An off-on-off electrochemiluminescence approach for
- 2477 ultrasensitive detection of thrombin, Biosens. Bioelectron. 59 (2014) 58-63.

- [329] F. Li, H. Cui, A label-free electrochemiluminescence aptasensor for thrombin based on novel
 assembly strategy of oligonucleotide and luminol functionalized gold nanoparticles, Biosens.
 Bioelectron. 39 (2013) 261-267.
- 2481 [330] X. Yu, H. Cui, Electrochemiluminescence bioassay for thrombin based on dynamic assembly
- of aptamer, thrombin and N-(aminobutyl)-N-(ethylisoluminol) functionalized gold nanoparticles,
 Electrochim. Acta 125 (2014) 156-162.
- [331] Y. Li, Y. Li, N. Xu, J. Pan, T. Chen, Y. Chen, W. Gao, Dual-signal amplification strategy for
 electrochemiluminescence sandwich biosensor for detection of thrombin, Sens. Actuators, B. 240
 (2017) 742-748.
- 2487 [332] H. Wang, W. Gong, Z. Tan, X. Yin, L. Wang, Label-free bifunctional
 2488 electrochemiluminescence aptasensor for detection of adenosine and lysozyme, Electrochim. Acta
 2489 76 (2012) 416-423.
- [333] Z. Chen, L. Li, Y. Tian, X. Mu, L. Guo, Signal amplification architecture for electrochemical
 aptasensor based on network-like thiocyanuric acid/gold nanoparticle/ssDNA, Biosens. Bioelectron.
 38 (2012) 37-42.
- [334] M. Shamsipur, L. Farzin, M.A. Tabrizi, Ultrasensitive aptamer-based on-off assay for
 lysozyme using a glassy carbon electrode modified with gold nanoparticles and electrochemically
 reduced graphene oxide, Microchim. Acta 183 (2016) 2733-2743
- [335] X. Liu, J. Zhang, S. Liu, Q. Zhang, X. Liu, D.K.Y. Worg, Cold Nanoparticle EncapsulatedTubular TIO2 Nanocluster As a Scaffold for Development of Terolated Enzyme Biosensors, Anal.
 Chem. 85 (2013) 4350-4356.
- 2499 [336] Q. Liu, Y.J. Peng, J.C. Xu, C. Matthewist, C.J. Mao, J.J. Zhu, Label-Free 2500 Electrochemiluminescence Aptasensor for Highly Sensitive Detection of Acetylcholinesterase 2501 Based on Au-Nanoparticle-Functionalized $g-C_3N_4$ Nanohybrid, ChemElectroChem (2017).
- [337] J. Zhu, X. Huo, X. Liu, H. Ju, Gold Naroparticles Deposited Polyaniline–TiO₂ Nanotube for
 Surface Plasmon Resonance Enhanced Photoelectrochemical Biosensing, ACS Appl. Mater.
 Interfaces. 8 (2016) 341-349.
- [338] H. Xu, L. Zeng, S. Xing, C. Shi, Y. Xian, L. Jin, Microwave-radiated synthesis of gold
 nanoparticles/carbon nanotube composites and its application to voltammetric detection of trace
 mercury(II), Electroclem. Commun. 10 (2008) 1839-1843.
- [339] N. Zhou, J. H. Chen, C. Liao, L. Chen, A functional graphene oxide-ionic liquid
 composites-gold nanoparticle sensing platform for ultrasensitive electrochemical detection of Hg²⁺,
 Analyst 138 (2013) 1091-1097.
- [340] D. Li, J. Li, X. Jia, E. Wang, Gold nanoparticles decorated carbon fiber mat as a novel sensing
 platform for sensitive detection of Hg(II), Electrochem. Commun. 42 (2014) 30-33.
- [341] L. Shi, Y. Wang, S. Ding, Z. Chu, Y. Yin, D. Jiang, J. Luo, W. Jin, A facile and green strategy
 for preparing newly-designed 3D graphene/gold film and its application in highly efficient
 electrochemical mercury assay, Biosens. Bioelectron. 89, Part 2 (2017) 871-879.
- 2516 [342] L. Laffont, T. Hezard, P. Gros, L.-E. Heimbürger, J.E. Sonke, P. Behra, D. Evrard, Mercury(II)
- trace detection by a gold nanoparticle-modified glassy carbon electrode using square-wave anodic
 stripping voltammetry including a chloride desorption step, Talanta 141 (2015) 26-32.
- 2519 [343] Z. Zhu, Y. Su, J. Li, D. Li, J. Zhang, S. Song, Y. Zhao, G. Li, C. Fan, Highly Sensitive
- Electrochemical Sensor for Mercury(II) Ions by Using a Mercury-Specific Oligonucleotide Probe
- and Gold Nanoparticle-Based Amplification, Anal. Chem. 81 (2009) 7660-7666.

[344] P. Miao, L. Liu, Y. Li, G. Li, A novel electrochemical method to detect mercury (II) ions,
Electrochem. Commun. 11 (2009) 1904-1907.

- [345] J. Chen, J. Tang, J. Zhou, L. Zhang, G. Chen, D. Tang, Target-induced formation of gold
 amalgamation on DNA-based sensing platform for electrochemical monitoring of mercury ion
 coupling with cycling signal amplification strategy, Anal. Chim. Acta 810 (2014) 10-16.
- 2527 [346] S. Tang, P. Tong, W. Lu, J. Chen, Z. Yan, L. Zhang, A novel label-free electrochemical sensor
- for Hg²⁺ based on the catalytic formation of metal nanoparticle, Biosens. Bioelectron. 59 (2014) 15.
- [347] N. Wang, M. Lin, H. Dai, H. Ma, Functionalized gold nanoparticles/reduced graphene oxide
 nanocomposites for ultrasensitive electrochemical sensing of mercury ions based on thymine–
 mercury–thymine structure, Biosens. Bioelectron. 79 (2016) 320-326.
- [348] Y. Liao, Q. Li, N. Wang, S. Shao, Development of a new electrochemical sensor for
 determination of Hg (II) based on Bis (indolyl) methane/Mesoporous carbon
 nanofiber/Nafion/glassy carbon electrode, Sens. Actuators, B. 215 (2015) 592-597.
- [349] Z. Qiu, D. Tang, J. Shu, G. Chen, D. Tang, Enzyme-triggered formation of enzyme-tyramine
 concatamers on nanogold-functionalized dendrimer for impedimetric detection of Hg(II) with
 sensitivity enhancement, Biosens. Bioelectron. 75 (2016) 108-115.
- 2539 [350] Y. Gao, T. Wang, F. Liu, Determination of Hg^{2+} in Sap Water Based on the 2540 Electrochemiluminescence of $Ru(phen)_3^{2+}$ and Thymine at Darc and Graphene Oxide-Modified 2541 Glassy Carbon Electrodes, Chin. J. Chem. 34 (2016) 1297-102
- [351] W. Gao, A. Zhang, Y. Chen, Z. Chen, Y. Chen, K. Lu, Z. Chen, A novel probe density
 controllable electrochemiluminescence biosenser for una-sensitive detection of Hg²⁺ based on
 DNA hybridization optimization with gold nanoparticles array patterned self-assembly platform,
 Biosens. Bioelectron. 49 (2013) 139-145.
- [352] F. Cai, Q. Zhu, K. Zhao, A. Deng, J Li Multiple Signal Amplified Electrochemiluminescent
 Immunoassay for Hg²⁺ Using Graphen Ooupled Quantum Dots and Gold Nanoparticles-Labeled
 Horseradish Peroxidase, Environ Scriffechnol. 49 (2015) 5013-5020.
- [353] D.-M. Wang, Q.-Q. Gai, K.P. Huang, X. Zheng, Label-free electrochemiluminescence assay
 for aqueous Hg²⁺ through oligonucleotide mediated assembly of gold nanoparticles, Biosens.
 Bioelectron. 98 (2017) 134-139.
- [354] Z. Zhao, X. Cool, Ultrasensitive electrochemiluminescence detection of mercury ions based
 on DNA oligonucleotides and cysteamine modified gold nanoparticles probes, Sens. Actuators, B.
 171–172 (2012) 860-865.
- [355] G. Zeng, C. Zhang, D. Huang, C. Lai, L. Tang, Y. Zhou, P. Xu, H. Wang, L. Qin, M. Cheng,
 Practical and regenerable electrochemical aptasensor based on nanoporous gold and thymine-Hg²⁺thymine base pairs for Hg²⁺ detection, Biosens. Bioelectron. 90 (2017) 542-548.
- [356] A. Safavi, E. Farjami, Construction of a carbon nanocomposite electrode based on amino
 acids functionalized gold nanoparticles for trace electrochemical detection of mercury, Anal. Chim.
 Acta 688 (2011) 43-48.
- 2561 [357] X.-C. Fu, J. Wu, L. Nie, C.-G. Xie, J.-H. Liu, X.-J. Huang, Electropolymerized surface ion
- imprinting films on a gold nanoparticles/single-wall carbon nanotube nanohybrids modified glassycarbon electrode for electrochemical detection of trace mercury(II) in water, Anal. Chim. Acta 720
- 2564 (2012) 29-37.
- 2565 [358] L. Shen, Z. Chen, Y. Li, S. He, S. Xie, X. Xu, Z. Liang, X. Meng, Q. Li, Z. Zhu,

- Electrochemical DNAzyme sensor for lead based on amplification of DNA- Au Bio-Bar codes,
 Anal. Chem. 80 (2008) 6323-6328.
- [359] X. Yang, J. Xu, X. Tang, H. Liu, D. Tian, A novel electrochemical DNAzyme sensor for the
 amplified detection of Pb²⁺ ions, Chem. Commun. 46 (2010) 3107-3109.
- [360] H. Hai, F. Yang, J. Li, Electrochemiluminescence sensor using quantum dots based on a Gquadruplex aptamer for the detection of Pb²⁺, RSC Adv. 3 (2013) 13144-13148.
- 2572 [361] L. Lu, L. Guo, J. Li, T. Kang, S. Cheng, Electrochemiluminescent detection of Pb²⁺ by
- 2573 graphene/gold nanoparticles and CdSe quantum dots, Appl. Surf. Sci. 388 (2016) 431-436.
- [362] Y. Zang, J. Lei, Q. Hao, H. Ju, "Signal-on" photoelectrochemical sensing strategy based on
 target-dependent aptamer conformational conversion for selective detection of lead (II) ion, ACS
- 2576 Appl. Mater. Interfaces. 6 (2014) 15991-15997.
- [363] Y.-M. Lei, W.-X. Huang, M. Zhao, Y.-Q. Chai, R. Yuan, Y. Zhuo, Electrochemiluminescence
 Resonance Energy Transfer System: Mechanism and Application in Ratiometric Aptasensor for
 Lead Ion, Anal. Chem. 87 (2015) 7787-7794.
- [364] J.J. Gooding, J. Shein, L.M.H. Lai, Using nanoparticle aggregation to give an ultrasensitive
 amperometric metal ion sensor, Electrochem. Commun. 11 (2009) 2015-2018.
- [365] Z. Chen, L. Li, X. Mu, H. Zhao, L. Guo, Electrochemical aptasensor for detection of copper
 based on a reagentless signal-on architecture and amplification by gold nanoparticles, Talanta 85
 (2011) 730-735.
- [366] Q. Wang, F. Gao, J. Ni, X. Liao, X. Zhang, Z. Lin, Fasil construction of a highly sensitive
 DNA biosensor by in-situ assembly of electro-active tars on ndirpin-structured probe fragment, Sci.
 Rep. 6 (2016).
- [367] L. Cui, J. Wu, J. Li, Y. Ge, H. Ju, Electrometrical detection of Cu²⁺ through Ag nanoparticle
 assembly regulated by copper-catalyzed oxidation of cysteamine, Biosens. Bioelectron. 55 (2014)
 272-277.
- [368] A. Foroushani, Y. Zhang, D. Li, Mathesh, H. Wang, F. Yan, C.J. Barrow, J. He, W. Yang,
 Tunnelling current recognition through core-satellite gold nanoparticles for ultrasensitive detection
 of copper ions, Chem. Commun. 51 (2015) 2921-2924.
- [369] S.L. Ting, S.J. Ee A. Ananthanarayanan, K.C. Leong, P. Chen, Graphene quantum dots
 functionalized gold nanoparticles for sensitive electrochemical detection of heavy metal ions,
 Electrochim. Acta 12 (2015) 7-11.
- [370] J. Wang, C. Bian, J. Tong, J. Sun, S. Xia, L-Aspartic acid/L-cysteine/gold nanoparticle
 modified microelectrode for simultaneous detection of copper and lead, Thin Solid Films 520 (2012)
 6658-6663.
- [371] M.-P.N. Bui, J. Brockgreitens, S. Ahmed, A. Abbas, Dual detection of nitrate and mercury in
 water using disposable electrochemical sensors, Biosens. Bioelectron. 85 (2016) 280-286.
- 2602 [372] S. Viswanathan, P. Manisankar, Nanomaterials for electrochemical sensing and
 2603 decontamination of pesticides, J. Nanosci. Nanotechnol. 15 (2015) 6914-6923.
- 2604 [373] R. Mossanha, C.A. Erdmann, C.S. Santos, K. Wohnrath, S.T. Fujiwara, C.A. Pessoa,
 2605 Construction of a biosensor based on SAM of thiolactic acid on gold nanoparticles stabilized by
- silsesquioxane polyelectrolyte for cathecol determination, Sens. Actuators, B. 252 (2017) 747-756.
- [374] N. Jha, S. Ramaprabhu, Development of Au nanoparticles dispersed carbon nanotube-basedbiosensor for the detection of paraoxon, Nanoscale 2 (2010) 806-810.
- 2609 [375] D. Lu, G. Shao, D. Du, J. Wang, L. Wang, W. Wang, Y. Lin, Enzyme entrapped nanoporous

- scaffolds formed through flow-induced gelation in a microfluidic filter device for sensitivebiosensing of organophosphorus compounds, Lab on a Chip 11 (2011) 381-384.
- [376] Y. Yang, A.M. Asiri, D. Du, Y. Lin, Acetylcholinesterase biosensor based on a gold
 nanoparticle-polypyrrole-reduced graphene oxide nanocomposite modified electrode for the
 amperometric detection of organophosphorus pesticides, Analyst 139 (2014) 3055-3060.
- [377] Y. Wang, S. Zhang, D. Du, Y. Shao, Z. Li, J. Wang, M.H. Engelhard, J. Li, Y. Lin, Self
 assembly of acetylcholinesterase on a gold nanoparticles–graphene nanosheet hybrid for
 organophosphate pesticide detection using polyelectrolyte as a linker, J. Mater. Chem. 21 (2011)
 5319-5325.
- [378] M. Wei, G. Zeng, Q. Lu, Determination of organophosphate pesticides using an
 acetylcholinesterase-based biosensor based on a boron-doped diamond electrode modified with gold
 nanoparticles and carbon spheres, Microchim. Acta 181 (2014) 121-127.
- [379] X. Liu, Y. Hu, X. Sheng, Y. Peng, J. Bai, Q. Lv, H. Jia, H. Jiang, Z. Gao, Rapid highthroughput detection of diethylstilbestrol by using the arrayed langasite crystal microbalance
 combined with gold nanoparticles through competitive immunoassay, Sens. Actu tors, B. 247 (2017)
 245-253.
- [380] A. Azadbakht, S. Beirnvand, Voltammetric aptamer-based switch probes for sensing
 diclofenac using a glassy carbon electrode modified with a composite prepared from gold
 nanoparticles, carbon nanotubes and amino-functionalized For the properties, Microchim. Acta
 184 (2017) 2825-2835.
- [381] D. Du, W. Chen, W. Zhang, D. Liu, H. Li, Y. Lin, Covalent coupling of organophosphorus
 hydrolase loaded quantum dots to carbon nanotub *(Approximation construction)* hydrolase for enhanced detection of
 methyl parathion, Biosens. Bioelectron. 25 (2014) 500-1375.
- [382] S. Chen, J. Huang, D. Du, J. Li, H. Cu, D. Llu, A. Zhang, Methyl parathion hydrolase based
 nanocomposite biosensors for highly sensitive and selective determination of methyl parathion,
 Biosens. Bioelectron. 26 (2011) 4320-221.
- [383] X. Ge, W. Zhang, Y. Lin D. Du, Magnetic Fe3O4@TiO2 nanoparticles-based test strip
 immunosensing device for order detection of phosphorylated butyrylcholinesterase, Biosens.
 Bioelectron. 50 (2013) 436-44.
- [384] E. Valera, J. Ramon Azcón, A. Barranco, B. Alfaro, F. Sánchez-Baeza, M.P. Marco, Á.
 Rodríguez, Determination of atrazine residues in red wine samples. A conductimetric solution, Food
 Chem. 122 (2010) 888-894.
- 2642 [385] P. Sharma, K. Sablok, V. Bhalla, C.R. Suri, A novel disposable electrochemical
 2643 immunosensor for phenyl urea herbicide diuron, Biosens. Bioelectron. 26 (2011) 4209-4212.
- [386] X. Liu, W.-J. Li, L. Li, Y. Yang, L.-G. Mao, Z. Peng, A label-free electrochemical
 immunosensor based on gold nanoparticles for direct detection of atrazine, Sens. Actuators, B. 191
 (2014) 408-414.
- 2647 [387] S. Li, C. Liu, B. Han, J. Luo, G. Yin, An electrochemiluminescence aptasensor switch for
 2648 aldicarb recognition via ruthenium complex-modified dendrimers on multiwalled carbon nanotubes,
 2649 Microchim. Acta 184 (2017) 1669-1675.
- 2650 [388] J.A. Ribeiro, C.A. Carreira, H.J. Lee, F. Silva, A. Martins, C.M. Pereira, Voltammetric
- determination of paraquat at DNA–gold nanoparticle composite electrodes, Electrochim. Acta 55(2010) 7892-7896.
- 2653 [389] T.-F. Kang, F. Wang, L.-P. Lu, Y. Zhang, T.-S. Liu, Methyl parathion sensors based on gold

- nanoparticles and Nafion film modified glassy carbon electrodes, Sens. Actuators, B. 145 (2010)
 104-109.
- [390] K. Zarei, A. Khodadadi, Very sensitive electrochemical determination of diuron on glassy
 carbon electrode modified with reduced graphene oxide–gold nanoparticle–Nafion composite film,
 Ecotox. and Environ. Safe. 144 (2017) 171-177.
- [391] J. Gong, X. Miao, T. Zhou, L. Zhang, An enzymeless organophosphate pesticide sensor using
 Au nanoparticle-decorated graphene hybrid nanosheet as solid-phase extraction, Talanta 85 (2011)
 1344-1349.
- [392] W. Huixiang, H. Danqun, Z. Yanan, M. Na, H. Jingzhou, L. Miao, S. Caihong, H. Changjun,
 A non-enzymatic electro-chemical sensor for organophosphorus nerve agents mimics and pesticides
 detection, Sens. Actuators, B. 252 (2017) 1118-1124.
- [393] J. Wackerlig, P.A. Lieberzeit, Molecularly imprinted polymer nanoparticles in chemical
 sensing–Synthesis, characterisation and application, Sens. Actuators, B. 207 (2015) 144-157.
- [394] J. Zhang, C. Wang, Y. Niu, S. Li, R. Luo, Electrochemical sensor based on molecularly
 imprinted composite membrane of poly(o-aminothiophenol) with gold nanoparticles for sensitive
 determination of herbicide simazine in environmental samples, Sens. Actuators B. 249 (2017) 747755.
- [395] C. Xie, H. Li, S. Li, J. Wu, Z. Zhang, Surface Molecular Self Assembly for Organophosphate
 Pesticide Imprinting in Electropolymerized Poly(p-aminothrophenol) Membranes on a Gold
 Nanoparticle Modified Glassy Carbon Electrode, Anal. Chen. 22 (2010) 241-249.
- [396] G. Sun, P. Wang, S. Ge, L. Ge, J. Yu, M. Yan, Photoelectrochemical sensor for
 pentachlorophenol on microfluidic paper-based analytical device based on the molecular imprinting
 technique, Biosens. Bioelectron. 56 (2014) 97-103
- [397] L. Zhao, F. Zhao, B. Zeng, Synthesis of water-compatible surface-imprinted polymer via click
 chemistry and RAFT precipitation polymerization for highly selective and sensitive electrochemical
 assay of fenitrothion, Biosens. Bioelector. 62 (2014) 19-24.
- [398] C. Ren, H. Li, X. Lu, J. Qian, M.Zhu, W. Chen, Q. Liu, N. Hao, H. Li, K. Wang, A disposable
 aptasensing device for label-free detection of fumonisin B1 by integrating PDMS film-based microcell and screen-printed caroon detectrode, Sens. Actuators, B. 251 (2017) 192-199.
- [399] A. Gevaerd, F.K. Caetano, P.R. Oliveira, A.J.G. Zarbin, M.F. Bergamini, L.H. MarcolinoJunior, Thiol-capper gord nanoparticles: Influence of capping amount on electrochemical behavior
 and potential application as voltammetric sensor for diltiazem, Sens. Actuators, B. 220 (2015) 673678.
- [400] Rosy, R.N. Goyal, Gold nanoparticles decorated poly-melamine modified glassy carbon
 sensor for the voltammetric estimation of domperidone in pharmaceuticals and biological fluids,
 Talanta 141 (2015) 53-59.
- [401] T. He, L. Liu, G. Wu, P. Chen, Covalent triazine framework-supported palladium
 nanoparticles for catalytic hydrogenation of N-heterocycles, J. Mater. Chem., A 3 (2015) 1623516241.
- [402] A.E. Vilian, P. Puthiaraj, C.H. Kwak, S.-K. Hwang, Y.S. Huh, W.-S. Ahn, Y.-K. Han,
 Fabrication of Palladium Nanoparticles on Porous Aromatic Frameworks as a Sensing Platform to
 Detect Vanillin, ACS Appl. Mater. Interfaces. 8 (2016) 12740-12747.
- [403] A.T.E. Vilian, P. Puthiaraj, C.H. Kwak, S.R. Choe, Y.S. Huh, W.-S. Ahn, Y.-K. Han,
 Electrochemical determination of quercetin based on porous aromatic frameworks supported Au

- 2698 nanoparticles, Electrochim. Acta 216 (2016) 181-187.
- [404] S. Kumar, W. Ahlawat, R. Kumar, N. Dilbaghi, Graphene, carbon nanotubes, zinc oxide and
 gold as elite nanomaterials for fabrication of biosensors for healthcare, Biosens. Bioelectron. 70
 (2015) 498-503.
- [405] S. Pruneanu, F. Pogacean, A.R. Biris, S. Ardelean, V. Canpean, G. Blanita, E. Dervishi, A.S.
 Biris, Novel Graphene-Gold Nanoparticle Modified Electrodes for the High Sensitivity
 Electrochemical Spectroscopy Detection and Analysis of Carbamazepine, J. Phys. Chem., C 115
 (2011) 23387-23394.
- [406] E. Er, H. Çelikkan, N. Erk, M.L. Aksu, A new generation electrochemical sensor based on
 Graphene nanosheets/Gold nanoparticles/Nafion nanocomposite for determination of Silodosin,
 Electrochim. Acta 157 (2015) 252-257.
- [407] X. Lin, S. Zhu, Q. Wang, Q. Xia, P. Ran, Y. Fu, Chiral recognition of penicillamine
 enantiomers using hemoglobin and gold nanoparticles functionalized graphite-like carbon nitride
 nanosheets via electrochemiluminescence, Colloids Surf. B. 148 (2016) 371-376.
- [408] W. Guo, F. Pi, H. Zhang, J. Sun, Y. Zhang, X. Sun, A novel moneularly imprinted
 electrochemical sensor modified with carbon dots, chitosan, gold naroparticles for the
 determination of patulin, Biosens. Bioelectron. 98 (2017) 299-304.
- [409] L. Jiang, J. Qian, X. Yang, Y. Yan, Q. Liu, K. Wang, K. Wang, Amplified impedimetric
 aptasensor based on gold nanoparticles covalently bound graphene beet for the picomolar detection
 of ochratoxin A, Anal. Chim. Acta 806 (2014) 128-135.
- [410] X. Feng, N. Gan, H. Zhang, Q. Yan, T. Li, Y. Group, Hu, H. Yu, Q. Jiang, A novel "dualpotential" electrochemiluminescence aptasensor analysing CdS quantum dots and luminol-gold
 nanoparticles as labels for simultaneous detection of malachite green and chloramphenicol, Biosens.
 Bioelectron. 74 (2015) 587-593.
- [411] Y.-B. Miao, H.-X. Ren, N. Gan, Y. Khou, Y. Cao, T. Li, Y. Chen, A triple-amplification SPR
 electrochemiluminescence assay for charamphenicol based on polymer enzyme-linked nanotracers
 and exonuclease-assisted target recycling, Biosens. Bioelectron. 86 (2016) 477-483.
- [412] W. Zhang, H. Xiong, M. Shen, X. Zhang, S. Wang, Surface-enhanced molecularly imprinted
 electrochemiluminescence sensor based on Ru@SiO2 for ultrasensitive detection of fumonisin B1,
 Biosens. Bioelectron. 96 (2017) 55-61.
- [413] L. Hu, T. Dour, K. Zhao, A. Deng, J. Li, Ultrasensitive electrochemiluminescent brombuterol
 immunoassay by applying a multiple signal amplification strategy based on a PAMAM-gold
 nanoparticle conjugate as the bioprobe and Ag@Au core shell nanoparticles as a substrate,
 Microchim. Acta 184 (2017) 3415-3423.
- [414] L. Tang, G. Zeng, J. Liu, X. Xu, Y. Zhang, G. Shen, Y. Li, C. Liu, Catechol determination in
 compost bioremediation using a laccase sensor and artificial neural networks, Anal. Bioanal.Chem.
 391 (2008) 679-685.
- [415] Q. Kang, Y. Chen, C. Li, Q. Cai, S. Yao, C.A. Grimes, A photoelectrochemical immunosensor
 for benzo[a]pyrene detection amplified by bifunctional gold nanoparticles, Chem. Commun. 47
 (2011) 12509-12511.
- [416] X. Niu, W. Yang, G. Wang, J. Ren, H. Guo, J. Gao, A novel electrochemical sensor of
 bisphenol A based on stacked graphene nanofibers/gold nanoparticles composite modified glassy
 carbon electrode, Electrochim. Acta 98 (2013) 167-175.
- 2741 [417] H. Wang, X. Yuan, Y. Wu, G. Zeng, W. Tu, C. Sheng, Y. Deng, F. Chen, J.W. Chew,

- 2742 Plasmonic Bi nanoparticles and BiOCl sheets as cocatalyst deposited on perovskite-type ZnSn(OH)₆
- 2743 microparticle with facet-oriented polyhedron for improved visible-light-driven photocatalysis, Appl.
 2744 Catal., B 209 (2017) 543-553.
- [418] X. Yuan, H. Wang, Y. Wu, X. Chen, G. Zeng, L. Leng, C. Zhang, A novel SnS₂–
 MgFe₂O₄/reduced graphene oxide flower-like photocatalyst: Solvothermal synthesis,
 characterization and improved visible-light photocatalytic activity, Catal. Commun. 61 (2015) 6266.
- [419] Z. Wu, X. Yuan, J. Zhang, H. Wang, L. Jiang, G. Zeng, Photocatalytic Decontamination of
 Wastewater Containing Organic Dyes by Metal–Organic Frameworks and their Derivatives,
 ChemCatChem 9 (2017) 41-64.
- [420] X. Chen, L. Ji, Y. Zhou, K. Wu, Synergetic enhancement of gold nanoparticles and 2mercaptobenzothiazole as highly-sensitive sensing strategy for tetrabromobisphenol A, Sci. Rep. 6
 (2016) 26044.
- [421] A.T.E. Vilian, K. Giribabu, S.R. Choe, R. Muruganantham, H. Lee, C. Roh, Y.S. Huh, Y.-K.
- 2756 Han, A spick-and-span approach to the immobilization of horseradish peroxidase on Au
- 2757 nanospheres incorporated with a methionine/graphene biomatrix for the determination of endocrine
 2758 disruptor bisphenol A, Sens. Actuators, B. 251 (2017) 804-812.
- [422] Y. Lu, M. Li, M. Ding, G. Liu, Y. Zhang, S. Wang, Detection of bisphenol-A using
 electrochemical immunosensor: Comparison between competition and displacement format assay,
- 2761 J. Electroanal. Chem. 779 (2016) 34-38.
- [423] L. Hu, C.-C. Fong, X. Zhang, L.L. Chan, P.K.S. Can, T.K. Chu, K.-Y. Wong, M. Yang, Au
 Nanoparticles Decorated TiO2 Nanotube Arrays and Recyclable Sensor for Photoenhanced
 Electrochemical Detection of Bisphenol A, Environ. sci. Technol. 50 (2016) 4430-4438.
- [424] D. Yuan, S. Chen, J. Zhang, H. Wang, R. Yuan, W. Zhang, An electrochemiluminescent
 sensor for phenolic compounds based on the inhibition of peroxydisulfate
 electrochemiluminescence, Sens. Actua of B. 185 (2013) 417-423.
- [425] Q. Lu, H. Hu, Y. Wu, S. Chen, D. Yuan, R. Yuan, An electrogenerated chemiluminescence
 sensor based on gold nanorasticles@C₆₀ hybrid for the determination of phenolic compounds,
 Biosens. Bioelectron. 60 (2014) 325-331.
- [426] Z. Liu, C. Zhou, B. Zheng, L. Qian, Y. Mo, F. Luo, Y. Shi, M.M. Choi, D. Xiao, In situ
 synthesis of gold proparticles on porous polyacrylonitrile nanofibers for sensing applications,
 Analyst 136 (2011) 4545-4551.
- [427] T. Li, J. Xu, L. Zhao, S. Shen, M. Yuan, W. Liu, Q. Tu, R. Yu, J. Wang, Au
 nanoparticles/poly(caffeic acid) composite modified glassy carbon electrode for voltammetric
 determination of acetaminophen, Talanta 159 (2016) 356-364.
- 2777 [428] Y. Wang, Y. Xiong, J. Qu, J. Qu, S. Li, Selective sensing of hydroquinone and catechol based
- on multiwalled carbon nanotubes/polydopamine/gold nanoparticles composites, Sens. Actuators, B.
- **2779 223** (2016) 501-508.

Supporting Information (SI)

"Gold rush" in modern science: Fabrication strategies and typical advanced applications of gold nanoparticles in sensing

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Name	Time	Materials	Process of reaction	Diameter and root-mean-square deviation
Faraday Sol	1857	White phosphorus + diethyl ether + chlorauric acid	brown, then grey, purple and red	5 nm, 30%
Bredig Sol	1898	Gold wires + Sodium hydroxide	Purple cloud drifted away	3-10 nm
Rinde Sol	1928	Hydrogen peroxide + gold chloride medium	Development of Faraday Sol	1.9 nm
Acetone Sol	1929	Chlorauric acid solution + acetone	faint coloration, deep red	20 nm, 13%
Donau Sol	1929	Carbon monoxide gas + chlorauric acid	darkened assuming finally a purple colour	20 nm diam and 400-800 nm long
Tannin Gold Sol	1933	Chlorauric acid + sodium carbonate + tannin solution	pink and a slight opalescence	12 nm, 28%
Oxalic Acid Sol	_	Chlorauric acid + oxalic acid	light blue	200 nm
Acetylene	_	Chlorauric acid + acetylene gas	Pink to dark ruby- red	28.5 nm, 22%
Sol		Chlorauric acid + sodium carbonate	Full color	17, 16%
Citric Acid Gold Sol	_	Chlorauric acid	Clear, dark blue- purple	10-50 nm
Sodium Citrate Sol	1940	Chlorautic acid + sodium citrate	faint greyish-pink or greyish-blue tone, gradually darkening, and deep wine red	20±5 nm, 12.5%
	R			

Table S1. Evolution of the development of Turkevich-Frens method.

Supporting	LOD (nM)	Linear range (µM)	Real samples	Ref.
Tween-20 and Ascorbic acid	5	0.5-10	Tap and drinking water	[1]
МА	50	0.05-0.25	Lake water and industrial wastewater	[2]
O-phenylenediamine	5 and 100 (naked eye)	0.01-2.0	Tap and lake water	[3]
4-mercaptophenylboronic acid	8	0.01–5	tap and lake water	[4]
2,2'-bipyridyl	38	0-0.8 and 0.2-2 (naked eye)	river and top water	[5]
Carboxymethylagarose	_	0.05-500	Lake water	[6]
TCA	0.5	0.0005-0.3	$c \lambda -$	[7]
2-mercaptobenzothiazole	6 and 100 (naked eye)	0.05-1.0	ake water and milk powder samples	[8]
Iodide	0.037	0.000 -0.07	tap water	[9]
Acce	Rted	W.O.		

Table S2. Summary of the colorimetric sensor for Hg^{2+} based on AuNPs antiaggregation

Supporting LOD (nM) Linear range (nM) and correlation coefficient Ref. 2-ME 0.5 2.5 -10 000, 0.97 [10] 4-MB 0.2 0.5-10, 0.96 [11] 45 2-ME and Na₂S 50-500, 0.96 [12] GA 10 10-800, 0.997 [13] MA 4 (naked eye) 0.0-79, 0.99 [14] Crown ether 50 100-75000, 0.9957 [15] GSH 100 100-50000, 0.9912 [16] 2 2-1000 [17] 5 0-100 DNAzyme [18] Accepted Manuscrit 0.02 0.05-5 [19]

Table S3. Summary of partial visual sensors for Pb²⁺ dealing with different capping agents based on AuNPs aggregation

Table S4. Comparison of recent colorimetric sensors based on AuNPs for detection of

 Cd^{2+}

Capping agent	LOD (nM)	Linear range (nM)	Correlation coefficient	Real samples	Ref.
6-mercaptonicotinic acid and	100	200-1700	0 9976	Lake water	[20]
L-Cysteine	100	200 1700	0.9970	Luke water	[20]
Peptide	50	500 2000	0.0488	Diver water	[21]
(CALNNDHHHHHH)	50	500-2000	0.9488	Kivel water	[21]
AHMT	30	60-480	0.9963	Lake and tap water	[22]
Di-(1H-pyrrol-2-	16.6	500 16000	0.006	I alza watar	[23]
yl)methanethione	10.0	500-10000	0.990	Lake water	[23]
chitosan dithiocarbamate	62	50 500uM	0.0001	Drinking, tap, canal	[24]
(CSDTC)	03	30-300µM	0.9991	and Nyer water	[24]
GSH	_	30–70 nM	_	V –	[25]
ETC ^{a)} modified Au-Fe3O4	2020	below	0.0020		[26]
nanoparticles	3020	80000	0.9930	-	[20]
Galactosamine (Galn)	3	1-100	0,9900	Lake water	[27]
DL-mercaptosuccinic acid	0.07	0.07.0.2.			[20]
(MSA)	0.07111111	0.07-0.2IIIM	009	-	[28]

(MSA) ETC^a, ethyl 1-(2-(3',4-dihydroxyphenyl)-2 okrethyl)-1H-1,2,3-triazole-4-carboxylate

Target	Supporting	LOD (nM)	Linear	Types of	Aggregation or	Ref
	Supporting		range (nM)	reaction	non-aggregation	i
	1-(2-mercaptoethyl)- 1,3,5-triazinane-2,4,6- trione (MTT)	0.2	4-200 and 280-440		aggregation	[29]
	3,5-dihydroxybenzoic acid (DBA)	0.8	1-10000	Hudrogen	non-aggregation	[30]
	Pyrocatechol-3,5- disodiumsulfonate (PD)	0.64	4.8-1600	bonding interaction	non-aggregation	[31]
	ss-T ₁₀ , HS-poly-T ₁₀	41.7 (label- free)	_	9, `,	aggregation	[32]
MA	HS-ssDNA	46.5 (label)	_	c	Aggregation	
	3-Mercapto-1- propanesulfonate	8	10 - 150 and 150 - 600	.0.	aggregation	[33]
	Bare AuNPs	1.6	40,486	Strong bond attraction	aggregation	[34]
	3,3',5,5'- tetramethlybenzidine (TMB)–H2O2; Bare AuNPs	× 0.2	1-800	Chormogenic reaction	aggregation	[35]
	Chitosan	Q 47.6	79-79000	Bond(chitosa n and MA)	aggregation	[36]
	Methanobactin	238	390-3970	Coordination	aggregation	[37]
	AchE, Acetylthiteraline iodide (ATI)	10	142-10062	Catalytic hydrolysis reaction	non-aggregation	[38]
	AchE, acetylthiocholine, and CuO NPs	3.6	3.6-363	Copper catalyzed click chemistry	non-aggregation	[39]
OPs	CTAB and AchE	2.4	51-223 and 480-3429	Enzymatic hydrolysis reaction	non-aggregation	[40]
	Aptamer and PDDA	6×10^{-5}	5×10^{-4} -1	Aptamer interaction	aggregation	[41]
	<i>p</i> -nitroaniline dithiocarbamate	350	1.0–1000 μM	Electrostatic and π - π interaction	aggregation	[42]

 Table S5 Summary of AuNPs-based colorimetric detection system for some organic

moles

Kanamycin	ssDNA aptamer	25	Not given	Aptamer interaction	aggregation	[43]
Kanamycin		1	10-500 and 1500-50000		aggregation	
Neomycin	Pyrocatechol violet	1	5-400 and 400-3000		aggregation	E 4 4 3
Streptomyci n	(PCV)	3	30-300		aggregation	[44]
Bleomycin		10	30-500 and 500-5000	Hydrogen- bonding	aggregation	
Neomycin	MA	0.03	0.1-5.0 and 5-100	interaction	aggregation	[45]
Clenbuterol	MA	0.028	0.28-280		aggregation	[46]
kanamycin	AHMT	4	5-100 and 100-20000	×	aggregation	[47]
kanamycin	Chitosan	8	10-40000	Q,	aggregation	[48]
Cartap	Bare AuNPs	146	183-2191	Electron-Nch nitrogen eaction	aggregation	[49]
Metsulfuro n-methyl	Dithiocarbamate-p- tertbutylcalix[4]arene	190	100030000 NO 1000	Host-guest (non- covalent) interactions	aggregation	[50]
Cyhalothrin	4-Amino-3- mercaptobenzoic acid (AMBA)	750	250-100000	Cooperative effect	aggregation	[51]
TNT	MA	2 7000	80000- 1200000	Electron donor– acceptor interaction	aggregation	[52]
Catechol	\sim	110	200-7000	Fanton	non-aggregation	
Hydroquino ne	ssDNA	1600	2700-19000	reaction	non-aggregation	[53]

F1 (1	Electrochemical	LOD	Sensitivity	Real sample	D (
Electrode	technique	(pM)	(nM)	analysis	Ref.
Carbon ionic					
liquid electrode	SWV	2300	_	Tap and waste water	[54]
(CILE)					
GCE	DPASV	80	0.4–96.0	River and tap water	[55]
_	ECL	50	_	_	[56]
GCE	ECL	100	1-100	River water	[57]
GCE	DPV	30	0.1-100	Tap, bottled, and seawater	[58]
GCE	DPV	60	0.5-120	Riverwiter	[59]
GCE	DPV	20	0.02-1000	Tap water	[60]
GCE	SWASV	80	—	Croundwater	[60]
				Aap, river water,	
GCE	SWV	0.001aM	1.001	and landfill	[61]
				leachate sample	
GCE	Cyclic ECL	300	O -4985	Lake, river, and tap water	[62]
ITO electrode	DPASV	<u>`</u>	0.5-50	tap, lake water, milk and soil	[63]
GCE	DPV	V ₇	0.05-5	Tap water	[64]
GCE	DPV	3.6	0.01-5000	river, tap water, and landfill leachate	[65]
GCE	DP	3.6	0.01-2.5	Tap drinking water	[66]
GCE	G PSV	30	0.1-130	Drinking river water	[67]
platinum auxiliary electrode	SWV	0.05	0.0001-100	Lake, tap water and serum	[68]
ITO electrode	ECL	2	0.008-2	Tap and lake water	[69]

Table S6. Comparison of different electrochemical sensors for Hg^{2+} detection in recent years.

Supporting	Electrochemical	Electrochemical	LOD		
methods	signal	technique	(nM)	Sensitivity (nM)	Ref.
	[Ru(NH ₃) ₆] ³⁺	DPV	1	5-100	[70]
Cleavage	$[Ru(NH_3)_6]^{3+}$	CC	0.028	0.1-35	[71]
	Hemin	ECL	0.1	_	[72]
	$[Fe(CN)_6]^{3-/4-}$	SWV	0.00029	0.001-1000	[73]
	$[Ru(NH_3)_6]^{3+}$	CC	0.012	0.05-100	[74]
	$[Fe(CN)_6]^{3-/4-}$	CV	0.2	0.5-50000	[75]
	_	ECL	0.00108	0.2-10	[76]
G-	—	PEC	0.05	0.1-50	[77]
quadruplex	Methylene blue	DPV	4.3 fM	0.1 fM-0.05 nM	[78]
	PTC-NH ₂	ECL-RET	0.00035	◆ 0.001-100	[79]
Others	Thionine	DPV	0.312	0.6-50	[80]
e un ens	_	SV	0.27	2.4-386	[81]
	Accer	ted M2	nus		

Table S7. Comparison of different electrochemical sensors for Pb^{2+} detection in recent years.

Electrochemical technique	Supporting	Metal ions	LOD (nM)	Sensitivity (nM)	Ref.	
		Hg ²⁺	0.02	0.02-1.5 and 1.5-100		
ASV	GQDs and Cys	Cu^{2+}	0.05	logarithmical	[82]	
CINCI	QUICNIT	Pb^{2+}	2.64	16-108	[02]	
5W5V	SWCN1s	Cu^{2+}	9.65	52-351	[83]	
CWWa	L-Aspartic	Pb^{2+}	4.8	24-9653	F0 4 1	
Swvs	acid/L-cysteine	Cu^{2+}	15.7	79-31473	[84]	
	Screen-printed	Pb^{2+}	10.6	96.5-965	F051	
SWASV	gold electrode	Cu^{2+}	25	315-4721	[03]	
SWASV	Screen-printed	Pb^{2+}	0.01	48-480	[06]	
SWASV	carbon arrays	Cu^{2+}	0.02	157-236	[00]	
DPASV	Carbon foams	Pb^{2+}	5.2	100-2000	[9 7]	
DIASV	Carbon Ioanis	Cu^{2+}	0.9	200-2000		
SWASV	Graphene and	Pb^{2+}	0.24	2.4-193	[88]	
SWASV	Cysteine	Cd^{2+}	0.87	4.4-356	լօօյ	

 Table S8. Details of electrochemical sensor for bimetallic detection supported by

 AuNPs.

ysteine Cd²⁺ 0.87

	Supporting	Electrochemical	LOD	Concentration	D C
Analyte	methods	techniques	(nM)	range (µM)	Ref.
p-nitrophenol	MIPs	DPV	5	0.03-350	[89]
Catechol			300	1.0-160.0	
Hydroquinone]	ECL	67	2.0–115	[90]
Resorcinol			1000	2.0–105	
Catechol			21	0.062-120	
Hydroquinone]	ECL	15	0.05-110	[91]
p-cresol			17	0.05-110	
Hydroquinone		ECL	80	0.55-37	[91]
Hydroquinone	Polymer	DPV	35	010	[92]
Catechol	-		47	X	
Acetaminophen		CV	14	0.2-20 50-1000	[93]
BPA	Electropotelyzeig	LSV	25	0.08-250	[94]
BPA	Electrocatarysis	CV		0.1-28.9	[95]
Streptomycin	Aptasensor	DPV	1.4	0.03-1.5	[96]
Cathecol	Aptasensor	DPY	852	6.0-46.0	[97]
Diethylcyanopho sphonate	3DGR	DPMIC	0.00345	0.00001-0.07	[98]
Carbofuran	SPCE	- PPV	220	1.0-250	[99]
٢	Accel				

Table S9. Details of different methods used in electrochemical detection of organic

 moles in recent reports.
References

[1] T. Lou, Z. Chen, Y. Wang, L. Chen, Blue-to-Red Colorimetric Sensing Strategy for Hg²⁺ and Ag⁺ via Redox-Regulated Surface Chemistry of Gold Nanoparticles, ACS Appl. Mater. Interfaces. 3 (2011) 1568-1573.

[2] J. Du, S. Yin, L. Jiang, B. Ma, X. Chen, A colorimetric logic gate based on free gold nanoparticles and the coordination strategy between melamine and mercury ions, Chem. Commun. 49 (2013) 4196-4198.

[3] Y.-L. Li, Y.-M. Leng, Y.-J. Zhang, T.-H. Li, Z.-Y. Shen, A.-G. Wu, A new simple and reliable Hg²⁺ detection system based on anti-aggregation of unmodified gold nanoparticles in the presence of O-phenylenediamine, Sens. Actuators, B. 200 (2014) 140-146.

[4] Y. Zhou, H. Dong, L. Liu, M. Li, K. Xiao, M. Xu, Selective and sensitive colorimetric sensor of mercury (II) based on gold nanoparticles and 4-mercaptophenylboronic and, Sens. Actuators, B. 196 (2014) 106-111.

[5] H. Chen, W. Hu, C.M. Li, Colorimetric detection of mercury(II) based on 2,2'-bipyridyl induced quasi-linear aggregation of gold nanoparticles, Sens. Actuators B. 215 (2015) 421-427.

[6] J.P. Chaudhary, A. Kumar, P. Paul, R. Meena, Carbox methylagarose-AuNPs generated through green route for selective detection of Hg^{2+} in auteous medium with a blue shift, Carbohydr. Polym. 117 (2015) 537-542.

[7] Z. Chen, C. Zhang, H. Ma, T. Zhou, Y. Luke, M. Chen, X. Chen, A non-aggregation spectrometric determination for mercury ons based on gold nanoparticles and thiocyanuric acid, Talanta 134 (2015) 603-606.

[8] W. Jin, P. Huang, G. Wei, Y. Gao, E Wu, Visualization and quantification of Hg²⁺ based on anti-aggregation of label-free cold hanoparticles in the presence of 2-mercaptobenzothiazole, Sens. Actuators, B. 233 (2010)232-229.

[9] L. Li, L. Zhang, T. Iou, Z. Chen, Iodide-responsive Cu@Au nanoparticle-based colorimetric assay for sensitive merculy (II) detection, Sens. Actuators, B. 252 (2017) 663-670.

[10] Y.-Y. Chen, H.-T. Chang, Y.-C. Shiang, Y.-L. Hung, C.-K. Chiang, C.-C. Huang, Colorimetric Assay for Lead Ions Based on the Leaching of Gold Nanoparticles, Anal. Chem. 81 (2009) 9433-9439.

[11] Y.-L. Hung, T.-M. Hsiung, Y.-Y. Chen, C.-C. Huang, A label-free colorimetric detection of lead ions by controlling the ligand shells of gold nanoparticles, Talanta 82 (2010) 516-522.

[12] Y.L. Hung, T.M. Hsiung, Y.Y. Chen, Y.F. Huang, C.C. Huang, Colorimetric Detection of Heavy Metal Ions Using Label-Free Gold Nanoparticles and Alkanethiols, J. Phys. Chem., C. 114 (2010) 16329-16334.

[13] K.-W. Huang, C.-J. Yu, W.-L. Tseng, Sensitivity enhancement in the colorimetric detection of lead (II) ion using gallic acid–capped gold nanoparticles: Improving size distribution and minimizing interparticle repulsion, Biosens. Bioelectron. 25 (2010) 984-989.

[14] N. Ratnarathorn, O. Chailapakul, W. Dungchai, Highly sensitive colorimetric detection of

lead using maleic acid functionalized gold nanoparticles, Talanta 132 (2015) 613-618.

[15] V.N. Mehta, J.N. Solanki, S.K. Kailasa, Selective visual detection of Pb (II) ion via gold nanoparticles coated with a dithiocarbamate-modified 4'-aminobenzo-18-crown-6, Microchim. Acta. 181 (2014) 1905-1915.

[16] F. Chai, C. Wang, T. Wang, L. Li, Z. Su, Colorimetric detection of Pb²⁺ using glutathione functionalized gold nanoparticles, ACS Appl. Mater. Interfaces. 2 (2010) 1466-1470.

[17] B. Chen, Z. Wang, D. Hu, Q. Ma, L. Huang, C. Xv, Z. Guo, X. Jiang, Scanometric nanomolar lead (II) detection using DNA-functionalized gold nanoparticles and silver stain enhancement, Sens. Actuators, B. 200 (2014) 310-316.

[18] Y. Huang, Y. Ma, Y. Chen, X. Wu, L. Fang, Z. Zhu, C.J. Yang, Target-responsive DNAzyme cross-linked hydrogel for visual quantitative detection of lead, Anal. Chem. 86 (2014) 11434-11439.

[19] W. Yun, D. Cai, J. Jiang, P. Zhao, Y. Huang, G. Sang, Enzyme-free and label-free ultrasensitive colorimetric detection of Pb²⁺ using molecular beacon and DNAzyme based amplification strategy, Biosens. Bioelectron. 80 (2016) 187-193.

[20] Y. Xue, H. Zhao, Z. Wu, X. Li, Y. He, Z. Yuan, Colorimetric, detection of Cd²⁺ using gold nanoparticles cofunctionalized with 6-mercaptonicotinic acid and 1-Cysteine, Analyst 136 (2011) 3725-3730.

[21] M. Zhang, Y.-Q. Liu, B.-C. Ye, Colorimetric as an for parallel detection of Cd^{2+} , Ni^{2+} and Co^{2+} using peptide-modified gold nanoparticles. Native 137 (2012) 601-607.

[22] A.J. Wang, H. Guo, M. Zhang, D.L. Zhou, R.Z. Wang, J.J. Feng, Sensitive and selective colorimetric detection of cadmium(II) using gold nanoparticles modified with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, 14ctpchim. Acta. 180 (2013) 1051-1057.

[23] Y.-M. Sung, S.-P. Wu, Colorimetric detection of Cd(II) ions based on di-(1H-pyrrol-2yl)methanethione functional 274 gold nanoparticles, Sens. Actuators, B. 201 (2014) 86-91.

[24] V.N. Mehta, H. Basu, B.K. Singhal, S.K. Kailasa, Simple and sensitive colorimetric sensing of Cd2+ ion using clitosan dithiocarbamate functionalized gold nanoparticles as a probe, Sens. Actuators, B. 220 (2015) 850-858.

[25] R. Manjumeena, D. Duraibabu, T. Rajamuthuramalingam, R. Venkatesan, P.T. Kalaichelvan, Highly responsive glutathione functionalized green AuNP probe for precise colorimetric detection of Cd²⁺ contamination in the environment, RSC Adv. 5 (2015) 69124-69133.

[26] Y. Zhang, Y. Zhao, Y. Yang, J. Shen, H. Yang, Z. Zhou, S. Yang, A bifunctional sensor based on Au-Fe3O4 nanoparticle for the detection of Cd²⁺, Sens. Actuators, B. 220 (2015) 622-626.

[27] S. Fu, X. Zhang, G. Ren, F. Chai, C. Wang, Facile Synthesis of Galactosamine-Stabilized Gold Nanoparticles with Sensitive Cd²⁺ Sensing, Eur. J. Inorg. Chem. 2015 (2015) 5656-5661.

[28] N. Chen, J. Chen, J.-H. Yang, L.-Y. Bai, Y.-P. Zhang, Colorimetric Detection of Cadmium Ions Using DL-Mercaptosuccinic Acid-Modified Gold Nanoparticles, J. Nanosci. Nanotechnol. 16 (2016) 840-843. [29] K. Ai, Y. Liu, L. Lu, Hydrogen-bonding recognition-induced color change of gold nanoparticles for visual detection of melamine in raw milk and infant formula, JACS 131 (2009) 9496-9497.

[30] Q. Cao, H. Zhao, Y. He, X. Li, L. Zeng, N. Ding, J. Wang, J. Yang, G. Wang, Hydrogenbonding-induced colorimetric detection of melamine by nonaggregation-based Au-NPs as a probe, Biosens. Bioelectron. 25 (2010) 2680-2685.

[31] Z. Wu, H. Zhao, Y. Xue, Q. Cao, J. Yang, Y. He, X. Li, Z. Yuan, Colorimetric detection of melamine during the formation of gold nanoparticles, Biosens. Bioelectron. 26 (2011) 2574-2578.

[32] H. Huang, L. Li, G. Zhou, Z. Liu, Q. Ma, Y. Feng, G. Zeng, P. Tinnefeld, Z. He, Visual detection of melamine in milk samples based on label-free and labeled gold nanoparticles, Talanta 85 (2011) 1013-1019.

[33] H. Su, H. Fan, S. Ai, N. Wu, H. Fan, P. Bian, J. Liu, Selective determination of melamine in milk samples using 3-mercapto-1-propanesulfonate-modified gold nanoparticles as colorimetric probe, Talanta 85 (2011) 1338-1343.

[34] W. Chen, H.-H. Deng, L. Hong, Z.-Q. Wu, S. Wang, A.-L. Liu, X.-M. Lin, X.-H. Xia, Bare gold nanoparticles as facile and sensitive colorimetric probe for melantine detection, Analyst 137 (2012) 5382-5386.

[35] P. Ni, H. Dai, Y. Wang, Y. Sun, Y. Shi, J. Hu, Z. Li, Vilual detection of melamine based on the peroxidase-like activity enhancement of bare gold nanoparticles, Biosens. Bioelectron. 60 (2014) 286-291.

[36] H. Guan, J. Yu, D. Chi, Label-free colorimetric sensing of melamine based on chitosanstabilized gold nanoparticles probes, Free Control 32 (2013) 35-41.

[37] J.-y. Xin, L.-x. Zhang, D.-d. Chen, K. Lin, H.-c. Fan, Y. Wang, C.-g. Xia, Colorimetric detection of melamine based in methanobactin-mediated synthesis of gold nanoparticles, Food Chem. 174 (2015) 473-479

[38] H. Li, J. Guo, Herber, L. Liu, M. Zhang, F. Guan, C. Sun, Q. Zhang, Visual detection of organophosphorus resucides represented by mathamidophos using Au nanoparticles as colorimetric probe, Talanta 87 (2011) 93-99.

[39] G. Fu, W. Chen, X. Yue, X. Jiang, Highly sensitive colorimetric detection of organophosphate pesticides using copper catalyzed click chemistry, Talanta 103 (2013) 110-115.

[40] S. Wu, D. Li, J. Wang, Y. Zhao, S. Dong, X. Wang, Gold nanoparticles dissolution based colorimetric method for highly sensitive detection of organophosphate pesticides, Sens. Actuators, B. 238 (2017) 427-433.

[41] R. Bala, M. Kumar, K. Bansal, R.K. Sharma, N. Wangoo, Ultrasensitive aptamer biosensor for malathion detection based on cationic polymer and gold nanoparticles, Biosens. Bioelectron. 85 (2016) 445-449.

[42] J.V. Rohit, H. Basu, R.K. Singhal, S.K. Kailasa, Development of p-nitroaniline dithiocarbamate capped gold nanoparticles-based microvolume UV–vis spectrometric method for facile and selective detection of quinalphos insecticide in environmental samples, Sens. Actuators,

B. 237 (2016) 826-835.

[43] S. Kyung-Mi, C. Minseon, J. Hunho, M. Kyoungin, J. Sung Ho, K. Taisun, H. Min Su, K. Ja Kang, B. Changill, Gold nanoparticle-based colorimetric detection of kanamycin using a DNA aptamer, Anal. Biochem. 415 (2011) 175-181.

[44] X. Zhang, Y. Zhang, H. Zhao, Y. He, X. Li, Z. Yuan, Highly sensitive and selective colorimetric sensing of antibiotics in milk, Anal. Chim. Acta 778 (2013) 63-69.

[45] C. Xiao, J. Liu, A. Yang, H. Zhao, Y. He, X. Li, Z. Yuan, Colorimetric determination of neomycin using melamine modified gold nanoparticles, Microchim. Acta. 182 (2015) 1501-1507.

[46] X. Zhang, H. Zhao, Y. Xue, Z. Wu, Y. Zhang, Y. He, X. Li, Z. Yuan, Colorimetric sensing of clenbuterol using gold nanoparticles in the presence of melamine, Biosens. Bioelectron. 34 (2012) 112-117.

[47] L. Qin, G. Zeng, C. Lai, D. Huang, C. Zhang, P. Xu, T. Hu, X. Liu, M. Cheng, Y. Liu, A visual application of gold nanoparticles: Simple, reliable and sensitive detection of kanamycin based on hydrogen-bonding recognition, Sens. Actuators, B. 243 (2017) 94-94.

[48] C. Lai, X. Liu, L. Qin, C. Zhang, G. Zeng, D. Huang, M. Chang, N Xu, H. Yi, D. Huang, Chitosan-wrapped gold nanoparticles for hydrogen-bonding recognition and colorimetric determination of the antibiotic kanamycin, Microchim. Acta, Con7) 1-9.

[49] W. Liu, D. Zhang, Y. Tang, Y. Wang, F. Yan, Z. Li, J. Wang, H.S. Zhou, Highly sensitive and selective colorimetric detection of cartap residuc in agricultural products, Talanta 101 (2012) 382-387.

[50] J.V. Rohit, R.K. Singhal, S.K. Kainsa, Dithiocarbamate-calix[4]arene functionalized gold nanoparticles as a selective and sensitive colorimetric probe for assay of metsulfuron-methyl herbicide via non-covalent interactions, Sens. Actuators, B. 237 (2016) 1044-1055.

[51] B. Imene, Z. Cui, X. Zhang, B. Gan, Y. Yin, Y. Tian, H. Deng, H. Li, 4-Amino-3mercaptobenzoic acid functionalized gold nanoparticles: Synthesis, selective recognition and colorimetric detection of chalothrin, Sens. Actuators, B. 199 (2014) 161-167.

[52] X.-D. Xia, H. Y. Juang, Using unmodified Au nanoparticles as colorimetric probes for TNT based on their competitive reactions with melamine, Chin. Chem. Lett. 25 (2014) 1271-1274.

[53] L.-p. Zhang, Y.-p. Xing, L.-h. Liu, X.-h. Zhou, H.-c. Shi, Fenton reaction-triggered colorimetric detection of phenols in water samples using unmodified gold nanoparticles, Sens. Actuators, B. 225 (2016) 593-599.

[54] A. Safavi, E. Farjami, Construction of a carbon nanocomposite electrode based on amino acids functionalized gold nanoparticles for trace electrochemical detection of mercury, Anal. Chim. Acta 688 (2011) 43-48.

[55] X.-C. Fu, J. Wu, L. Nie, C.-G. Xie, J.-H. Liu, X.-J. Huang, Electropolymerized surface ion imprinting films on a gold nanoparticles/single-wall carbon nanotube nanohybrids modified glassy carbon electrode for electrochemical detection of trace mercury(II) in water, Anal. Chim. Acta 720 (2012) 29-37.

[56] Z. Zhao, X. Zhou, Ultrasensitive electrochemiluminescence detection of mercury ions based

on DNA oligonucleotides and cysteamine modified gold nanoparticles probes, Sens. Actuators, B. 171–172 (2012) 860-865.

[57] W. Gao, A. Zhang, Y. Chen, Z. Chen, Y. Chen, F. Lu, Z. Chen, A novel probe density controllable electrochemiluminescence biosensor for ultra-sensitive detection of Hg2+ based on DNA hybridization optimization with gold nanoparticles array patterned self-assembly platform, Biosens. Bioelectron. 49 (2013) 139-145.

[58] N. Zhou, J. Li, H. Chen, C. Liao, L. Chen, A functional graphene oxide-ionic liquid composites-gold nanoparticle sensing platform for ultrasensitive electrochemical detection of Hg²⁺, Analyst 138 (2013) 1091-1097.

[59] S. Tang, P. Tong, W. Lu, J. Chen, Z. Yan, L. Zhang, A novel label-free electrochemical sensor for Hg^{2+} based on the catalytic formation of metal nanoparticle, Biosens. Bioelectron. 59 (2014) 1-5.

[60] J. Chen, J. Tang, J. Zhou, L. Zhang, G. Chen, D. Tang, Target-induced formation of gold amalgamation on DNA-based sensing platform for electrochemical monitoring of mercury ion coupling with cycling signal amplification strategy, Anal. Chim. Acta 810 (2014) 10-16.

[61] Y. Zhang, G.M. Zeng, L. Tang, J. Chen, Y. Zhu, X.X. H, Y. Me, Electrochemical sensor based on electrodeposited graphene-Au modified electrode prananoAu carrier amplified signal strategy for attomolar mercury detection, Anal. Chem. 87 (2005) 989-996.

[62] F. Cai, Q. Zhu, K. Zhao, A. Deng, J. Li, Multim Signal Amplified Electrochemiluminescent Immunoassay for Hg2+ Using Graphene-Couperd Quantum Dots and Gold Nanoparticles-Labeled Horseradish Peroxidase, Environ. Sci. Technol. 49 (2015) 5013-5020.

[63] Y. Lin, Y. Peng, J. Di, Electrochemical detection of Hg(II) ions based on nanoporous gold nanoparticles modified indium tin tride electrode, Sens. Actuators, B. 220 (2015) 1086-1090.

[64] N. Wang, M. Lin, H. Dai, H. Ma, Functionalized gold nanoparticles/reduced graphene oxide nanocomposites for ultraser tipe electrochemical sensing of mercury ions based on thymine-mercury-thymine structure biosens. Bioelectron. 79 (2016) 320-326.

[65] G. Zeng, C. Ange, D. Huang, C. Lai, L. Tang, Y. Zhou, P. Xu, H. Wang, L. Qin, M. Cheng, Practical and regenerable electrochemical aptasensor based on nanoporous gold and thymine-Hg 2+-thymine base pairs for Hg²⁺ detection, Biosens. Bioelectron. 90 (2017) 542-548.

[66] Z. Li, X. Miao, K. Xing, X. Peng, A. Zhu, L. Ling, Ultrasensitive electrochemical sensor for Hg2+ by using hybridization chain reaction coupled with Ag@Au core–shell nanoparticles, Biosens. Bioelectron. 80 (2016) 339-343.

[67] H. Wang, Y. Zhang, H. Ma, X. Ren, Y. Wang, Y. Zhang, Q. Wei, Electrochemical DNA probe for Hg2+ detection based on a triple-helix DNA and Multistage Signal Amplification Strategy, Biosens. Bioelectron. 86 (2016) 907-912.

[68] L. Shi, Y. Wang, S. Ding, Z. Chu, Y. Yin, D. Jiang, J. Luo, W. Jin, A facile and green strategy for preparing newly-designed 3D graphene/gold film and its application in highly efficient electrochemical mercury assay, Biosens. Bioelectron. 89, Part 2 (2017) 871-879.

[69] D.-M. Wang, Q.-Q. Gai, R.-F. Huang, X. Zheng, Label-free electrochemiluminescence assay S-16

for aqueous Hg^{2+} through oligonucleotide mediated assembly of gold nanoparticles, Biosens. Bioelectron. 98 (2017) 134-139.

[70] L. Shen, Z. Chen, Y. Li, S. He, S. Xie, X. Xu, Z. Liang, X. Meng, Q. Li, Z. Zhu, Electrochemical DNAzyme sensor for lead based on amplification of DNA- Au Bio-Bar codes, Anal. Chem. 80 (2008) 6323-6328.

[71] X. Yang, J. Xu, X. Tang, H. Liu, D. Tian, A novel electrochemical DNAzyme sensor for the amplified detection of Pb²⁺ ions, Chem. Commun. 46 (2010) 3107-3109.

[72] G. Pelossof, R. Tel-Vered, I. Willner, Amplified Surface Plasmon Resonance and Electrochemical Detection of Pb²⁺ Ions Using the Pb²⁺-Dependent DNAzyme and Hemin/G-Quadruplex as a Label, Anal. Chem. 84 (2012) 3703-3709.

[73] Y. Peng, L. Li, X. Yi, L. Guo, Label-free picomolar detection of Pb²⁺ using atypical icosahedra gold nanoparticles and rolling circle amplification, Biosens. Bioelectron. 59 (2014) 314-320.

[74] C. Zhang, C. Lai, G. Zeng, D. Huang, L. Tang, C. Yang, Y.◆Zhu, L. Qin, M. Cheng, Nanoporous Au-based chronocoulometric aptasensor for amplifier detection of Pb(2+) using DNAzyme modified with Au nanoparticles, Biosens. Bioelectron 81, (2016) 61-67.

[75] Y. Zhou, L. Tang, G. Zeng, C. Zhang, X. Xie, Y. Liu, Jorgng, J. Tang, Y. Zhang, Y. Deng, Label free detection of lead using impedimetric sensor based on ordered mesoporous carbon–gold nanoparticles and DNAzyme catalytic beacons, Talana 46 (2016) 641-647.

[76] H. Hai, F. Yang, J. Li, Electrochemilumines access sensor using quantum dots based on a Gquadruplex aptamer for the detection of Pb2+, RSC Adv. 3 (2013) 13144-13148.

[77] Y. Zang, J. Lei, Q. Hao, H. Ju, "Signal on" photoelectrochemical sensing strategy based on target-dependent aptamer conformational conversion for selective detection of lead (II) ion, ACS Appl. Mater. Interfaces. 6 (2010) 1991-15997.

[78] Y. Zhu, G.-m. Zeng, X. Zhung, L. Tang, J. Chen, M. Cheng, L.-h. Zhang, L. He, Y. Guo, X.x. He, Highly sensitive device device the sensor using a MWCNTs/GNPs-modified electrode for lead (II) detection based on Pb²⁺-induced G-rich DNA conformation, Analyst 139 (2014) 5014-5020.

[79] Y.-M. Lei, W.-X. Huang, M. Zhao, Y.-Q. Chai, R. Yuan, Y. Zhuo, Electrochemiluminescence Resonance Energy Transfer System: Mechanism and Application in Ratiometric Aptasensor for Lead Ion, Anal. Chem. 87 (2015) 7787-7794.

[80] S.M. Taghdisi, N.M. Danesh, P. Lavaee, M. Ramezani, K. Abnous, An electrochemical aptasensor based on gold nanoparticles, thionine and hairpin structure of complementary strand of aptamer for ultrasensitive detection of lead, Sens. Actuators, B. 234 (2016) 462-469.

[81] Y.-m. Cheng, H.-b. Fa, W. Yin, C.-j. Hou, D.-q. Huo, F.-m. Liu, Y. Zhang, C. Chen, A sensitive electrochemical sensor for lead based on gold nanoparticles/nitrogen-doped graphene composites functionalized with 1-cysteine-modified electrode, J. Solid State Electrochem. 20 (2016) 327-335.

[82] S.L. Ting, S.J. Ee, A. Ananthanarayanan, K.C. Leong, P. Chen, Graphene quantum dots S-17

functionalized gold nanoparticles for sensitive electrochemical detection of heavy metal ions, Electrochim. Acta 172 (2015) 7-11.

[83] M.-P. Ngoc Bui, C.A. Li, K.N. Han, X.-H. Pham, G.H. Seong, Simultaneous detection of ultratrace lead and copper with gold nanoparticles patterned on carbon nanotube thin film, Analyst 137 (2012) 1888-1894.

[84] J. Wang, C. Bian, J. Tong, J. Sun, S. Xia, L-Aspartic acid/L-cysteine/gold nanoparticle modified microelectrode for simultaneous detection of copper and lead, Thin Solid Films 520 (2012) 6658-6663.

[85] H. Wan, Q. Sun, H. Li, F. Sun, N. Hu, P. Wang, Screen-printed gold electrode with gold nanoparticles modification for simultaneous electrochemical determination of lead and copper, Sens. Actuators, B. 209 (2015) 336-342.

[86] P. Kanyong, S. Rawlinson, J. Davis, Gold nanoparticle modified screen-printed carbon arrays for the simultaneous electrochemical analysis of lead and copper in tap water, Microchim. Acta.
183 (2016) 2361-2368.

[87] W. Xiong, L. Zhou, S. Liu, Development of gold-doped carbon foams as a sensitive electrochemical sensor for simultaneous determination of Pb (II and Cu (II), Chem. Eng. J. 284 (2016) 650-656.

[88] L. Zhu, L. Xu, B. Huang, N. Jia, L. Tan, S. Yao, Singulaneous determination of Cd(II) and Pb(II) using square wave anodic stripping voltameters at a gold nanoparticle-graphene-cysteine composite modified bismuth film electrode, Electronam. Acta 115 (2014) 471-477.

[89] Q. Kang, Y. Chen, C. Li, Q. Sai, S. Yao, C.A. Grimes, A photoelectrochemical immunosensor for benzo[a]pyrene detect in implified by bifunctional gold nanoparticles, Chem. Commun. 47 (2011) 12509-12511

[90] D. Yuan, S. Chen, J. Zhang, H. Wang, R. Yuan, W. Zhang, An electrochemiluminescent sensor for phenolic impounds based on the inhibition of peroxydisulfate electrochemiluminescence end. Actuators, B. 185 (2013) 417-423.

[91] Q. Lu, H. Huwu, S. Chen, D. Yuan, R. Yuan, An electrogenerated chemiluminescence sensor based on gold nanoparticles@C60 hybrid for the determination of phenolic compounds, Biosens. Bioelectron. 60 (2014) 325-331.

[92] Y. Wang, Y. Xiong, J. Qu, J. Qu, S. Li, Selective sensing of hydroquinone and catechol based on multiwalled carbon nanotubes/polydopamine/gold nanoparticles composites, Sens. Actuators, B. 223 (2016) 501-508.

[93] T. Li, J. Xu, L. Zhao, S. Shen, M. Yuan, W. Liu, Q. Tu, R. Yu, J. Wang, Au nanoparticles/poly(caffeic acid) composite modified glassy carbon electrode for voltammetric determination of acetaminophen, Talanta 159 (2016) 356-364.

[94] X. Niu, W. Yang, G. Wang, J. Ren, H. Guo, J. Gao, A novel electrochemical sensor of bisphenol A based on stacked graphene nanofibers/gold nanoparticles composite modified glassy carbon electrode, Electrochim. Acta 98 (2013) 167-175.

[95] L. Hu, C.-C. Fong, X. Zhang, L.L. Chan, P.K.S. Lam, P.K. Chu, K.-Y. Wong, M. Yang, Au S-18

Nanoparticles Decorated TiO2 Nanotube Arrays as a Recyclable Sensor for Photoenhanced Electrochemical Detection of Bisphenol A, Environ. Sci. Technol. 50 (2016) 4430-4438.

[96] N. Mohammad Danesh, M. Ramezani, A. Sarreshtehdar Emrani, K. Abnous, S.M. Taghdisi, A novel electrochemical aptasensor based on arch-shape structure of aptamer-complimentary strand conjugate and exonuclease I for sensitive detection of streptomycin, Biosens. Bioelectron. 75 (2016) 123-128.

[97] R. Mossanha, C.A. Erdmann, C.S. Santos, K. Wohnrath, S.T. Fujiwara, C.A. Pessoa, Construction of a biosensor based on SAM of thiolactic acid on gold nanoparticles stabilized by silsesquioxane polyelectrolyte for cathecol determination, Sens. Actuators, B. 252 (2017) 747-756.

[98] W. Huixiang, H. Danqun, Z. Yanan, M. Na, H. Jingzhou, L. Miao, S. Caihong, H. Changjun, A non-enzymatic electro-chemical sensor for organophosphorus nerve agents mimics and pesticides detection, Sens. Actuators, B. 252 (2017) 1118-1124.

[99] A. Jirasirichote, E. Punrat, A. Suea-Ngam, O. Chailapakul, S. Chuanuwatanakul, Voltammetric detection of carbofuran determination using screan-printed carbon electrodes modified with gold nanoparticles and graphene oxide, Talanta 170 (2017) 331-337.