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How to Construct DNA Hydrogels for Environmental Applications: Advanced Water Treatment and Environmental Analysis

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Abstract: With high binding affinity, porous structures, safety, green, and programmability, etc., DNA hydrogels have gained increasing recognition in environmental field, i.e., advanced treatment technology of water and analysis of specific pollutants. DNA hydrogels have been demonstrated versatile potential as adsorbents, immobilization carriers of bioactive molecules, catalysts, and sensors, etc. Moreover, altering components or choosing appropriate functional DNA optimizes environment-oriented hydrogels. However, the lack of comprehensive information hinders the

continued optimization. The principle to fabricate the most suitable hydrogels in terms of the requirements is the focus of the review. We first introduce different fabrication strategies and point out the ideal characteristic for environmental applications. Subsequently, a summary on the recent environmental applications and development of diverse DNA hydrogels regarding their synthesis mechanism. Finally, the review provides an insight into the remaining challenging and future perspectives in environmental applications.

1. Introduction

With porous microstructures and large surface areas, DNA hydrogels are hydrophilic polymer networks capable of holding or capturing targets.[1] Generally, attributing to their high security, DNA hydrogels are brought into sharp focus in the field of medicine and therapeutics.[2] Such excellent properties will also naturally be favored by the research in the field of environment, i.e., DNA hydrogels can be positioned as multifunctional platforms for deep purification of micro-polluted water and specific recognition of trace of pollutants as illustrated in **Figure 1**. Their enrichment ability bringing by comparative large surface area, porous structures, rich functional group, specific functional DNA and specific surface charge, are endowed hydrogels with high sensibility and adsorption ability[3], which is even superior to those of carbon nanomaterials, to some extent.[3a] Meanwhile, compared to some common materials for wastewater treatment, e.g., carbon-based materials,[4] clay mineral,[5] and metallic materials,[6] DNA hydrogels are more suitable for the treatment of micro-polluted water,[7] which refers to the waters containing a small quantity of various kind of pollutants and even concluding pollutants factors of mutagenesis, carcinogenesis, and teratogenesis, such as drinking waters, rain, snow, and ground water. Although having the characteristics of easy preparation, low cost, high treatment efficiency, and so on,

carbon-based materials, clay mineral, and metallic materials may dissatisfy the micro-polluted disposal because they are difficult to degrade resulting in the potential toxicity.[8] To DNA hydrogels, alternatively, as for their safety, biodegradability, permeability, self-support, high capacity, and programmability, the properties (**Figure 2**) make them continue to be great impetus as adsorbents,[3] immobilization carriers,[9] catalysators,[10] and so on for advanced wastewater treatment, especially, the treatment of micro-polluted water. For instance, hydrogels can be re-used as immobilized matrices with catalysts modification on the surface and interior for low-concentrated wastewater disposal, and with the specific components, they can effectively remove metal ions and persistent organic pollutants (POPs)[11] in drinking water for deep purification. Notably, they also can load and transport modified or encapsulated enzymes as well as other rational active substrates to the specified site for catalytic degradation of target pollutants in ground water. Moreover, taking advantage of their sensitive, specific components or their 3D network conformation which mainly non-covalent intermolecular interaction act as string to sew separated part together, DNA hydrogels can go through volume-change or state-transition owing to their response to environmental factors, such as pH,[12] temperature,[12b] ionic strength,[13] solvent composition,[14] specific molecules,[15] and light,[16] etc. Accordingly, stimulus-responsive hydrogels have sparked great interest as bioanalytical tools.[17] It is not hard to envisage their potential environmental application with rational and sophisticated design and modification.

The idea of DNA hydrogels was first introduced by in 1910,[18] followed by Nagahara who developed DNA hydrogels by hybridizing the oligonucleotides with vinyl polymers in 1996,[19] notwithstanding, the comprehensive reports of them were not appeared until 2006[1a] and most developments have occurred during the just past decades. The development of various special DNA

sequence, especially functional DNA, and hybrid DNA have enormously spurred an increasing number of DNA hydrogels and their extensive applications. Recent years, with the in-depth research of DNA, such as functional DNA, involving i-motif,[20] G-quadruplex,[21] aptamer,[22] DNAzyme,[23] and T-rich/C-rich sequence,[24] etc., various DNA endow hydrogels with broadened diversity, selecting affinity, and high sensitivity, affording potential for environmental treatment and detection applications. To specific, i-motif is sensitive to environmental pH, and T-rich or C-rich sequence tends to undergo substantial conformational changes to form T-Hg^{2+}-T or C-Ag^{+}-C by metal coordination in the appearance of Hg^{2+} or Ag^{+}, respectively. As for aptamer and DNAzyme, they can bind specific molecule targets with remarkable accuracy. Furthermore, adjusting the properties of DNA hydrogels by the rational combination of various DNA fabrication and advanced materials such as organic polymer materials[12c, 14] and carbon allotropes,[25] via blending, doping, and chemical modification, etc., DNA hydrogels probably become more stable, versatile, and also more suitable for environment applications.

As mentioned above, many types of DNA hydrogels involving pure DNA hydrogels[1a, 26] and hybrid hydrogels[2-3, 12b] have been explored. They were fabricated according to different mechanism and presented distinct characteristics, as illustrated in **Table 1**. For environmental applications, it is easy to hold a promising future of pure DNA hydrogels with high safety and specific components that can be used for deep purification of drinking water. Whilst involving more complex environmental water and specific environmental locations, the environmental tolerance, the physicochemical and stable property, and other versatile function of DNA hydrogels have to be considered, unavoidably. Through the previous literatures, it can be found that the hybrid DNA hydrogels constructed with carbon-based materials and organic polymer etc. were gradually

emerged and exhibited potential for the challenges. Even so, how to develop, optimize, and innovate more flexible and practical DNA hydrogels by learning, digging, and inspiring from the literatures, there is still a long way to go. Certainly, it is encouraging that, in term of gelation mechanism, many conceptions involving DNA hydrogels-adsorbents, catalyzer, encapsulated carriers, and sensors, etc. have been made certain progress, to date. It is believed that rational and flexible use of the corresponding mechanism to construct a cheaper, greener, safer, and more efficient DNA hydrogel will have a bright future in the environmental applications.

Accordingly herein, an attempt of induction of formation mechanism of DNA hydrogels and their application outlook is provided. The principle to choose the most suitable hydrogels in terms of the requirements is the focus of the review. Given the mechanism properties and disposal effect can be optimized using different synthetic method or processes, which could broaden their applications as effective platform for environmental disposal and detection, to great extent, therefore, we collected and discussed novel and practical strategies with regard to the formation mechanism in hoping to design a desired hydrogel. In the review, we classify them from the aspect of gelation mechanism considering the real environment requirements. Subsequently, in term of their gelation mechanism, potential applications and their development of various DNA hydrogels are discussed. The last part of the review provides an insight into the remaining limitations and prospects of DNA hydrogels.

2. Strategies for Constructing DNA Hydrogels

Generally, the properties and applications of DNA hydrogels are with relation to their components, structures, and sequences, etc. Herein, in this chapter, we will briefly introduce their components (pure DNA or combing with organic polymer and carbon allotropes) and structures

(mainly including i-motif and G-aggregates, etc.) in hoping to figure out the optimal arrangements. And the applications of special DNA sequences, especially aptamer, DNAzyme, and C/T-rich sequences, etc., which possess additional recognition capability, are presented detailedly in the third chapter.

2.1. Pure DNA Hydrogels

DNA is an ideal scaffolding and natural polymer, and constructs senior structures by the combination of canonical/non-canonical base pairs.[27] It has been reported that the formation of DNA hydrogels is via physical or chemical reaction, e.g., enzyme ligation[1a, 26, 28] or even self-assembly[9a, 10a, 29] by special DNA motif structures.

In 2006, Luo et al. first reported the construction of pure hydrogels made from branched DNA via T4 DNA ligase.[1a] X-, Y-, T- branched DNA molecular is the most initial and common pure hydrogel scaffolding as illustrated in **Figure 3a**. These hydrogels were biodegradable and easily moulded into desired size and shapes, especially the X-scaffolding. Moreover, the hydrogels could entrap solute in situ (no post-gelation loading was needed) and the encapsulation efficiency was close to 100%, thus maybe rudimentary expanding the use of hydrogel into new applications for immobilization technology. Subsequently, to make further efforts to extend the technology, the same group incorporated sufficient X-DNA with actual plasmid genes through T4 DNA ligase to obtain cell-free protein-producing gel.[28d] The protein-producing efficiency of gel was about 300 times higher than solution phase systems and 1.52 times higher than the simple mixture of X-DNA and Rluc gene, suggesting that the hydrogel format is necessary to reach the highest expression level. Besides, the proposed system is a universal protein-producing system, i.e., other systems in a similar fashion can also produce various proteins using the cross-linking between different plasmids

and DNA scaffolding. We are looking forward to such systems might apply in pollutant disposal by rational designing a hydrogel consisting of degradative plasmids and DNA scaffoldings.

Another type of enzyme-catalyzed assembly of DNA hydrogel is designed based on the procedure of rolling circle amplification (RCA) and subsequent multiprimed chain reaction (MCA) (Figure 3b).[26, 28b, 28e] After running RCA and MCA, a coil of DNA would be prolonged and entangled by phi29 polymerase whereby a physically crosslinked hydrogel would be obtained. According to the strategy, a new cell-free protein-producing microgel platform was expanded, which was proved by the expression and display of the model protein wild-type green fluorescent protein or wtGFP. Following RCA and MCA, extremely high local gene concentrations of up to 32 000 gene repeats in hydrogels with a diameter of 1-2 μm was produced. Noteworthily, chemical cross-linking of psoralen into the hydrogels, endowed them with the capacity of withstanding extreme conditions which will absolutely boost real application.[26] The hydrogel system provides a new platform for producing protein, solving the matter of stability in real environment, to some extent.

However, the above-mentioned two kinds of enzymatic ligation are rather time-consuming with at least overnight ligation,[1a, 26, 28b, 28e] some reports have pointed out DNA could self-assemble into hydrogels through the formation of intermolecular i-motif structures or just complementary sticky ends within several minutes.[9a, 10a, 29] The fast trapping and ligation processes sometimes are vital for environmental disposal and monitoring. In 2009, Liu et al. developed a pH-triggered, fast-responding DNA hydrogel. 0.75 mM Y-DNA could crosslink into hydrogel within one minute, owing to the assembly of intermolecular i-motif structures by the three sticking out interlocking domains of the Y-DNAs.[29a] To visualize the gelling transition, gold nanoparticles (AuNPs) were

utilized as "tracer agents". The AuNPs were trapped in the formed DNA hydrogel, but were dispersed into the upper layer solution within one minute with adding base solution. Subsequently, a permeable hydrogel with thermal and enzymatic responsiveness by mixing the Y-DNA and linker whose sticky ends are complementary to each other was also successfully developed.[29d] With the concentration of 0.5 mM of Y-DNA and 0.75 mM of linker, the solution lost its fluidity within a minute. The stability of these DNA hydrogels depended on the length and composition of the sticky ends. Moreover, by introducing specific recognition sequences, these hydrogels were endowed with enzyme-responsiveness. In 2013, considering an enzyme-responsiveness strategy, a hydrogel was creatively designed as a cover to envelop and release single cells in microwells as illustrated in Figure 3c.[9a] The adopted Y-DNA and linker contained restriction site, and the hydrogel was formed within 3 min via complimentary base pairing. Compared with normal cover glass and polydimethylsiloxane membrane, the pure DNA hydrogel shows great potentials as its permeability and safety to cells. In biomolecule encapsulation/immobilization and biocompatibility sense, such technology might solve some problems in sewage treatment to great extent, e.g., sludgebulking, regeneration, and so on.

2.2. Hybrid DNA Hydrogels

Very high concentrations (10 mM for guanine-based DNA hydrogels,[21] 0.5 mM for branched DNA hydrogels,[9a, 29a, 29d] while only 1-10 μM DNA for acrylamide/acrydite-DNA hydrogels[30]) are adopted to construct pure DNA hydrogels which extremely restrict their practical environmental disposal (Table 1). Therefore, pure hydrogels are generally applied in water with extremely high purity requirement, i.e., drinking water. To broaden the application of hydrogels and solve the problem of high cost of pure DNA hydrogels, many ingredients are introduced and, subsequently,

make DNA hydrogels as multi-functional, multi-stimulant and strong environmental adaptability hydrogels.

2.2.1. DNA Hydrogels Grafted with Organic Polymers

Incorporation of DNA (generally acrydite-modified DNA or peptide-modified DNA (**Figure 4**)) and organic polymers is another novel way to construct DNA hydrogels, which is a comparatively economic strategy and provide strong mechanical strength. The extensively adopted polymer monomers involve acrylamide[3b, 12a, 12c, 14, 17b, 30b, 31] and its analogues[1b, 12b, 32], thiolated carboxymethyl hyaluronic acid (CMHA-SH),[33] and 2-acrylamido-2-methyl-1-propansulfonic acid (AMPS)[17b, 31a], etc. (**Figure 5**). When the organic polymers graft with versatile acrydite-modified DNA subunits to conform DNA hydrogels, such as i-motif, G-quadruplex, duplex, hairpin, hoogsteen, and triplex structures in which hydrogen bond is dominant, the involved DNA hydrogels show three predominant properties: (1) The hydrogels still maintain the inherently specific recognition to DNA and sensitivity to external triggers; (2) The hydrogels possess more multitriggers and multifunctional structures by incorporating organic polymers and various motif structures , e.g., poly(N-isopropylacrylamide) helps construct the thermosensitive DNA hydrogel and the i-motif scaffolding makes a pH-sensitive hydrogel; (3) The hydrogel backbone of the organic polymers not only serves as a matrix to incorporate DNA and sustains hydrogel conformations, but also influences the electrostatic interaction between the involved molecules.

Liu et al. first comprehensively elaborated the influence of different synthetic organic polymers including positive, neutral, or negative polymers on hydrogels.[31a] They pointed out that addition of positively charged SYBR Green to the neutral or negatively charged gels resulted in an

intense yellow background fluorescence, while by introducing a little positively charged allylamine monomer, the background fluorescence was significantly reduced. This is because the state of DNA changes from unfolded to strong bind to the gel backbone and a strong repulsion between positively charged SYBR Green and the positively charged gel backbone, as illustrated in **Figure 6**. Therefore, most strategies adopted neutral monomer because it general offers more diversity of DNA structures.

Inspired by the emergence of a variety of functional hydrogels, Willner's group designed bioinspired switchable catalytic hydrogels, mimicking the function of horseradish peroxidase, which integrated the acrydite-modified guanine-rich DNA sequence and neutral acrylamide monomer in 2013 (Table 1).[31b] It is not hard to imagine that DNA is not wrapping to gel backbone, and in the presence K^+, G-rich sequence stretching out cross-linked into G-quadruplexes to yield the hydrogel. The hydrogel trapped hemin which catalyze the oxidation of $ABTS^{2-}$, by the reduction of H_2O_2 to H_2O. But addition of 18-crown-6 ether would dissociate the hydrogel, and thus catalytic functions subsequently disappeared. Although was not strong enough since the hydrogel with just five bases in sticky end for the linking between the components, the coordination of K^+ and 18-crown-6 ether as a switch "ON" and "OFF" in the system, represents a new approach for fabricating functional switchable hydrogels.

In addition to homogeneous hydrogel solution, another switchable catalytic hydrogel with thioMC6-D-modified DNA had been strived to assemble on the gold-coated surfaces.[14] The method involved two copolymer chains: H_A, H_B, consisting of acrydite-modified DNA and neutral acrylamide. H_A and H_B were linked by G-quadruplexes in the presence of K^+. The basic principle is similar to the previous one in 2013, while the length of DNA sequence was prolonged and stability

was subsequently enhanced. Another point of concern, the hydrogel permits an exercisable electrochemical detection when forming on the electrode surface.

Instead of switchable catalytic capacity, shape-memory DNA hydrogels were conducted by expanding the applications of acrylamide/acrydite units as well. The shape-memory system involves two cooperative functional motives. One of the basic motives is vulnerable to external triggers, leading to the sol-to-gel changes. And another motives function as a memory code to restore original shape, e.g., duplex structures. Willner's group grafted typical pH-reversible structures including i-motif,[12a, 31c, 31d] hoogsteen,[12c, 31c, 31f] and G structures[31c] into acrylamide by chemical modifying acrydite. The approximate pore sizes of the above polymer-assistant hydrogels are ranging from 1 μm to 5 μm related to the length of DNA sequences (11 bases to 60 bases). And the reasonability of adopting acrylamide/acrydite units were also proved in virtue of the high storage modulus (50 Pa to 80 Pa), and low loss modulus (2 Pa to 7.8 Pa). Namely, these hydrogels were relatively stable and easily molded into desired shapes and sizes by varying the length of DNA sequences.

In DNA hydrogels grafted with organic polymers, Willner's group made many attempts and provided a lot of valuable experience. In 2014, they found that neutral N-isopropylacrylamide/acrydite can work the same way as acrylamide/acrydite units.[12b] Grafting cytosine-rich DNA sequences into N-isopropylacrylamide endowed the hydrogels with pH-sensitive property by i-motif structures or Ag^+-sensitivity by C-Ag^+-C bridge. Remarkably, the potential of adopting N-isopropylacrylamide/acrydite units were also proved via comparatively high storage modulus (G' = 320 Pa) at pH = 5.2, and low loss modulus (G'' = 5 Pa). On top of this, according to our literature comparison, the high (G+C) % (ca. 57.14%) and the quadruplet structure also

contribute to the stiff hydrogel.[12a, 12c, 17b, 30b, 31a, 31c, 31d]

Additionally, others novel assemblies were explored by other groups. J. Kopeček and his team reported a hydrogel via complexation of DNA and PNA in 2015. PNA is a DNA analog in which nucleobases are grafted on the neutral N-(2-hydroxypropyl)-methacrylamide backbone rather than the phosphodiester backbone.[32a] This is a new paradigm of hybrid hydrogels self-assembling system utilizing peptide-modification rather than acrydite-modification. Notedly, PNAs are resistant to hydrolytic (enzymatic) cleavage and have high specificity to complementary DNA, thus they are more stable in real environment when bound with their complementary DNA. In 2016, Rakszewska et al. developed a hydrogel bead with a totally different strategy.[33] In the system, thiolated carboxymethyl hyaluronic acid, as matrix, linked LNA-containing primer. Oil and surfactant separated the mixture into hydrogel bread. Interestingly, the method extends the potential to capture specific targets and quantitative analysis.

Therefore, the organic polymers act as matrix to sustain the structures and enhance the stability of hydrogels, while grafted DNA tethers link together to make stiff hydrogels and endow hydrogel with new property. High stability and sensibility make designable hybrid hydrogels potential for pharmaceutical, biomedical and environmental applications, except for most researchers fail to mention the safety of synthetic polymer hydrogels.

2.2.2. DNA Hydrogels Based on New Carbon Allotropes

Carbon nanotubes (CNT) and graphene as star members of carbon family have received widespread attention since they were first invented in 1991 and 2004, respectively.[34] Recently, crosslinking DNA with these carbon-based substances into hydrogels have been sparking in the field of nanotechnology and materials. For one thing, although those carbon materials and their

derivatives were still focused on in intelligent materials,[25c] electronic devices,[35] photocatalysis,[36] biocatalysis,[37] sensors,[38] fuel cell,[39] adsorbents,[40] etc. attributed to their biocompatibility, mechanical, thermal, and unique electrochemical properties, their applications were limited by the poor dispersibility or solubility in most common solvents. Alternatively, mixing carbon-based materials with DNA, can offset the shortage of self-aggregation, simultaneously endow DNA with new admirable properties and more versatility, more importantly, for instance, the higher surface area and electroconductivity. Thus, the combination of the two kinds of materials recently are of great interest. For another, as lack of the ability of self-support, the application of the simple mixture solution of DNA and carbon-based materials is always confined to sensors, electronics- and optics-based biochips.[41] So far, the strategy using carbon-based nanoparticles as a crosslinker to construct DNA/carbon hybrid hydrogels has broken the limitations and realized self-support[25b], which endows the DNA hydrogels with vastly higher mechanical strength, environmental stability, dye-loading capacity and even self-healing properties.[42]

As conformation covalent linkages is a relatively time-consuming and costly process, dsDNA or ssDNA general immobilize onto the surface and inside the opened cavity of graphene-based materials in a non-specific manner including π-π staking, electrostatic interaction and hydrogen bonding interaction, etc.[25c, 43] Three general strategies are implemented to develop carbon-based supermolecule DNA hydrogels. One is that DNA locally wraps carbon-based materials while the residual DNA fragment links an adjacent DNA sticky domain via i-motif structure or others to form the hydrogels, especially stimuli-sensitive hydrogels.[43b] Different from the linkage of DNA-to-DNA, the second strategy to construct hydrogel is to link specific DNA fragments with graphene-derivatives by strong noncovalent interactions.[3a, 25] Although the fundamental reactions

are similar to CNTs, the interaction between graphene sheets and DNA still exist some differences. CNT can be linked together by ssDNA or dsDNA, while graphene sheets have been reported to have lower binding affinity for dsDNA or ssDNA with secondary or tertiary structure owing to strongly electrostatic repulsive interaction with negatively charged phosphate backbone.[44] Furthermore, the third strategy uses organic polymers as matrix and mixes the complex of carbon material and DNA,[45] which have the noteworthy potential to contain substantial complex components. Interestingly, the types of nucleotide vary the interaction strength between graphene-based nanosheets and ssDNA. Grimme et al. pointed out that the relative interaction energies of the nucleobases decrease in the order guanine (G) > adenine (A) > thymine (T) > cytosine (C) in aqueous solutions[46]. Although the order of A and T is under debate,[46-47] guanine undoubtedly has high affinity to carbon materials. Guanine, nevertheless, can self-associate into higher-order aggregates, such as G-ribbons, G-quadruplexes,[48] accordingly, the DNA linker sequences generally contain substantial A and T. In the meantime, Frochtzwajg found polyA tends to form spherical particles and polyT has tendency to form network strands.[49] While oligT has aroused concern due to the feasibility of strong binding to graphene.[25a, 25b] Thus, it is expectable that the oligT bridge will become a new route for solving the problem of binding DNA with senior structure into graphene sheets.

The first strategy was used to build various functional hydrogels, which have attracted attention from many fields, especially in stimuli-responsive systems. In 2011, Liu and Deng designed a DNA-SWCNT hybrid hydrogel via simply heating and cooling procedures, which is pH responsive and strength tunable.[43b] Notably, the mechanical property of the hybrid hydrogel was comparatively high via varying the optimal concentration of hydrogel components. Besides, the use

of the i-motif structure as a crosslinker resulted in the pH-sensitivity and stability of these hydrogels, but only at acidic pH, thus preventing their application under actually environmental conditions.

In contrast to the first strategy which is more suitable for building stimuli-responsive hydrogels, the hydrogels from the second strategy are more applicable and more in-depth studied. Shi et al. described a convenient route for the hydrogel by assembly of GO sheets and the in situ formed ssDNA chains via a simple hydrothermal treatment.[3a] GO is a kind of amphiphilic macromolecule with a hydrophobic basal plane and hydrophilic edges, important to the gelation of the DNA hydrogels. The in situ formed ssDNA obtained by heating dsDNA bridged adjacent GO sheets via strong π-π stacking and hydrogen bond. Remarkably, the hydrogel possesses vastly improved environment stability and mechanical property (G' 4.6kPa, G'' 0.8kPa) (Table 1), for example, it is capable of maintaining its shape after a week immersion in strong acidic (pH 2), basic (pH 13), or salty (1 M NaCl) aqueous solution and even after cut by razors, it can self-heal using a mild heat treatment. Furthermore, the formed hydrogel shows high-effective dye-loading capacity because of the strong electrostatic interaction and large surface area, but it has not been shown to be specific application.

Interestingly, Yu-Kyoung Oh et al. produced the second type of hydrogels which can distinctly recognize and capture organic compounds.[25a, 25b] They incorporated specific aptamer sequences with GO or rGO by oligT bridge, and then constructed hybrid hydrogels through single-step rolling circle amplification. Notably, the authors, not directly linking aptamer to GO/rGO, creatively introduced oligT bridge domain to weaken the electrostatic repulsive interaction between senior DNA structures and GO/rGO sheets. The application of oligT brings more feasibility for assembly DNA/GO hydrogels.

Similarly, Kim and Kang adopted the second strategy to develop the DNA/PPy/CNT hybrid fibers coated with porous structured DNA hydrogel.[25c] Stability of the approximately 20,000 base pairs dsDNA, much stronger than other methods, may prove CNTs can enhance long-chain DNA stability even in turbulence environment thus representing a new approach to stabilize DNA hydrogels.

Beside the consideration of taking DNA as "molecular glue" as the first two strategies mentioned, in 2014, a hydrogel using DNA as dopant was constructed as the third strategy.[45] It provides insight into a strategy to construct a novel and low-cost hydrogel with complicated contents, despite its time-consuming, complicated and difficult multi-step procedures. The mixture including polyethylenimine (PEI), GO nanosheets complexed and DNA_{VEGF} are incorporated into low-modulus methacrylated gelatin hydrogel. Graphene oxide nanosheets was utilized to ionically bond to cationic polymers such as PEI. And the contents of hydrogels can be adjustable with respect to our requirements. Attractively, the complex was gelated upon exposing to UV at 6.9 $mW \cdot cm^{-2}$ (wavelength 360~480 nm).

Anyway, the preeminent advantages of graphene-based hydrogels, such as environmental stability, large surface area, high porosity, high mechanical, non-toxic, electroconductivity and electrochemical properties make it a promising candidate in application in pollutant adsorbents, sensors and catalytic agents for environmental treatment and detection.

2.3. Hydrogels Based on Special DNA Motifs

2.3.1. Hydrogels Based on i-motif Units

The i-motif structure is a four-strand DNA tetrad consisting of two cytosine repeat base-paired antiparallel-stranded duplexes. The concept was first introduced by Gehring and his

group in 1993.[50] They contributed the formation of i-motif structure to hemiprotonated C·CH$^+$ pairs, in which proton donor (protonated cytosines, d(C3)) connects to the intrinsic proton acceptor (unprotonated cytosines, d(C3)) represented in **Figure 7a**.[27c] Moreover, the stability of i-motif structure highly relies on the environment proton concentration, and the lifetime of i-motif tetramer is longer than all DNA duplex due to the base-pair intercalation geometry.[27c] On top of this, hydrogels based on i-motif structure show more outstanding stability than those based on duplex structure.

Three possibly conformations of i-motif units, i.e., tetramer i-motif structure, dimer i-motif structure, intramolecular i-motif structure were illustrated in Figure 7 according to Dong et al.[51] The three conformations widely used in DNA nanotechnology, such as controllable assembly,[52] hydrogel and others. [53] In this review, we focus on the hydrogel based on the first two i-motif structures as their easy formation.

Liu et al. designed a pH-triggered, fast-responding DNA hydrogel with three 37-mer ssDNAs based on dimer i-motif structure.[29a] As illustrated in **Figure 8a**, the cytosine-rich black domains, form the i-motif structure as a crosslinker for the remaining domains to form the ds-Y shape. As i-motif structure only exist in slight acid environment, this type of hydrogel consisting entirely of DNA is highly sensitive to pH. When pH is lower than 5, the solution turned to a transparent strong hydrogel with the formation of inter-Y-unit by i-motif effect. A reverse process would turn the rigid gel into liquid by adjusting pH in the alkaline direction. The solid-liquid phase transformation process was proved by a visible AuNPs indicated discoloration with pH change.

Afterwards, Guo and his coworkers designed a bifunctional stimuli-triggered poly-N-isopropylacrylamide/DNA hydrogel.[12b] They adapted dimer i-motif structure strategy as

mentioned above (Figure 8b). Different from the work of Liu, the hydrogel was polymerized with the cytosine-rich nucleic acid-functionalized acrylamide and N-isopropylacrylamide monomer. The hydrogel can not only form in the slight acid environment, but also reveal solution-to-hydrogel transitions in the presence of Ag^{+} by Ag^{+}-stimulated crosslink (C-Ag^{+}-C).

More recently, Willner's group reported similar pH-stimulated shape-memory DNA hydrogels based on both dimer i-motif structures and intramolecular i-motif structures.[12a] The two functioned gels consist of cytosine-rich sequence corresponding to the i-motif structure and self-complementary double-helix, as respectively illustrated in Figure 8c and Figure 8d. In the cooperative cross-link, i-motif change acts as a sensitive factor response to external condition, and the self-complementary duplex is "memory-code" to regenerate original structure. The differences between the two pH-sensitive hydrogels are the position of linker and DNA sequence.

2.3.2. DNA Hydrogels Based on Guanine and Analogs

Except for conventional Watson-Crick double-helix DNA, hoogsteen,[12c, 31c, 31f, 32a] i-motif, guanine and its analogues (**Figure 9**), important building blocks for hydrogels, can self-assemble into complex and versatile highly ordered aggregates with their multiple self-complementary hydrogen bonding edges and aromatic surfaces for π-π stacking.[21, 54] Generally, there are two typical types of arrangements attributing to different hydrogen bonding patterns. In the presence of alkali metal cations or other specific metal cations, such as Na^{+}, K^{+}, Li^{+}, Cs^{2+}, Ba^{2+}, Mg^{2+}, Sr^{2+}, Pb^{2+}, Ca^{2+}, guanine and its analogues will spontaneously self-associate into G-quartet, along with other related structures such as G-dimer, G-ribbon (**Figure 10**) and four-stranded G-quadruplex (**Figure 11**) consisting of a core of two or more π–π stacked G-quartets and stabilized by centrally located metal cations through electrostatic interactions.[3c, 31b, 55] The stability of the arrangement

results from a combination of hydrogen binding, electrostatic interactions and aromatic base stacking, etc., especially the hydrogen bonding between N(1)H/N(2)H and O6/N7. Notedly, hydrogen binding pattern can be altered if we replace the initial metal ions with other metal ions such as Ag^{+}. For instance, the binding of Ag^{+} and guanine will produce Ag-GMP dimers which is similar to the cardinal T-Hg^{2+}-T coordination, rather than G-quartet. Because Ag^{+} competitively binds the O6 and N7 sites in purine ring to produce metal ion-linked H-bonded architectures prohibiting the basic requirement for the quartet arrangement.[56] This means to form the guanine hydrogels, it is relied on H-bonding and π–π stacking of G-ribbons, G-quadruplex and M-GMP.

In 1910, Ivar Bang first reported that high concentration of boiling 5′-guanosine monophosphate (5′-GMP) could form a gel upon cooling in the presence of sodium acetate.[18] However, the requirement of high concentration components obstructs gel stability and narrows its applicational region. Subsequently, unremitting efforts have been made to seek for more effective hydrogelators and strategies to enhance the hydrogelation process.

Guanosine hydrazide is a strong hydrogelator. In 2005, Lehn et al. used dynamic covalent chemistry to develop highly viscous dynamic hydrogels consisting of guanosine hydrazide (Figure 9) and various aldehydes.[57] The resulting library constitution displayed that guanosine hydrazide yielded a preferential hydrogel based on the formation of G-quartets with comparatively high stability.

However, high concentration of hydrogelators, poor lifetime stability (propensity to crystallize after a couple of hour, leading to collapse of the gel) and specific pH as well as excessive requirement of salt concentrations are still the problems of limiting the guanine hydrogels application, which many researchers exert themselves to work out.

Altering the syn-anti conformation helps to enhance hydrogels lifetime stability. David et al. found that guanine and its corresponding derivatives are preferential anti-conformation, but syn-conformation guanines are prone to self-assembly to form G-quartets. They also pointed that guanine derivatives with bulky 8-substituents existed in syn-conformation.[58] Rowan and coworkers synthesized a new guanosine-based hydrogelator, 8-methoxy-2′,3′,5′-tri-O-acetylguanosine, via the placement of the methoxy unit on the 8-position of guanosine to make a conformational shift.[59] Thus, the gel can easily form at lower hydrogelator concentrations and simultaneously prolonged its lifetime. Noteworthily, the property of hydrogel could be tailored by mixing the new gelator with non-gelator 2′,3′,5′-tri-O-acetylguanosine, which combined the binary component hydrogels and opened the door to the possibility of systematically tailoring the properties of various kinds of hydrogels.

Binary component hydrogels, consisting of hydrophobic and hydrophilic guanine analogs or derivatives, can also improve the lifetime stability of guanosine-derived hydrogels. In 2008, McGown et al. developed the guanine-derived hydrogel in terms of hydrophobic guanosine and hydrophilic 5′-GMP in KCl solution.[60] For one thing 5′-GMP contributes to solubilize insoluble guanosine, for another the insolubility of gelator guanosine promotes the gelation of 5′-GMP at lower concentrations. Thus, the resulting binary system has the potential to possess high stability with adjusting the proportion of 5′-GMP and guanine. Similarly, aimed at solving the insoluble problem of guanine, Rowan and Jamieson adopted soluble 2′,3′,5′-tri-O-acetylguanosine to form a novel hydrogel a year later.[61] The authors suggested that the long lifetime and thermomechanical behavior derived from appropriate ratio of hydrophilic and hydrophobic contents. Consequently, controlling the ratio of soluble and insoluble solvents is the key of applying binary component.

Next, it is found that the gelation concentration can sharply decreased as well with aid of borate ester. In 2014, Davis and Peter constructed a hydrogel utilizing borate ester and only 0.5 equiv. $MB(OH)_4$. Due to the chelation of two guanosine with a single borate anion, insoluble guanine and the accompanying crystal problems were resolved.[62] In the following year, the exploration of the effect of central metal cations was conducted by the same group. The strongest hydrogel was produced by adding K^+, while the weakest one was from Li^+.[3c] Thus, they tried to improve the stability of Li^+ guanine borate ester system. With thioflavin T as a molecular chaperone, a faster hydrogelation and stronger lifetime stability were obtained via electrostatic interactions. The interesting result presents a potential value in disposing environmental pollution as the fibrillar network of hydrogel makes it easy to bind cationic dyes.[63] Nevertheless, the non-specific electrostatic interactions between dyes and hydrogel might limit the application of hydrogels to positively charged pollutants.

Apart from the forementioned typical G-quadruplex hydrogel, a supramolecular one deriving from Ag-GMP dimers was also developed for dealing with dye effluents.[56a] The construction of Ag-GMP nanofilament hydrogels is based on the chelating between Ag^+ ions and GMP. Notably, without using repeated heating/cooling or acidic pH, or by adding excess alkai metals e.g., sodium and potassium, the application range of the self-associated hydrogel can be extended, accordingly. For example, without addition of substantial sodium solution, the hydrogel can be extended to mobilize of active proteins such as cytochrome c and thus bring peroxidase activity.

These studies based on guanine-based hydrogels demonstrated that they have various of potential applications including sensors, sorbents, and immobilization carriers. We can systematically vary the gelators and non-gelators to expend the elasticity and long-term stability of

the hydrogels, and subsequently improve the application scope of DNA hydrogels.

3. Applications in Wastewater Disposal and Environmental Analysis

Although DNA hydrogels are widely applied in biomedicine and therapy,[64] their characteristics including selective binding, porousness, permeability catalysis, stability, safety and self-support are very suitable for wastewater treatment and monitoring, especially the micro-polluted environmental water.[7, 65] A combination of different effective molecular interactions exists in the DNA hydrogels and environmental pollutants, e.g., physically adsorption, electrostatic interaction, metal coordination, hydrophobic interactions and hydrogen bond, etc. which prove their reasonability, to some extent. Many efforts have been made to explore the feasible DNA hydrogels for the applications in environmental field. Some exciting novel DNA hydrogels have appeared in the past few years. Certainly, there are quite a lot of factors to affect properties and applications of DNA hydrogels. The principle to choose the most suitable hydrogels in terms of the requirements is focused on. Two main questions involving the reaction efficiency and their environmental suitability need to be solved. As for the efficiency, on top of the pollutants types, morphologic property of the hydrogels plays a vital role. In term of morphologic property, these hydrogels are generally divided into three well-adopted types including monoliths, thin films and micro/nanoparticles.[17b] Due to diverse morphology, these hydrogels show different pollutant adsorption capacity, releasing property and reaction kinetics. For example, gel monoliths are easy to observe and incorporate into device, while thin film gels are ideal for the fabrication of smart responsive surfaces, and bread or micro/nanoparticles with comparatively short diffusion distances are used as selective adsorbents. Likewise, various hydrogel systems exhibit the difference of the suitability in different environments. Micro/nanoparticles hydrogels display excel stability in

turbulence water, while the monoliths may show a longer lifetime in slow flow. Thus, we prefer to different format according to the requirement of application involving the molecular interactions between pollutants, DNA hydrogels, and the environmental background. Aimed to provide us a general way for DNA hydrogels design and screening, the following section will discuss the development of various kinds of DNA hydrogels from the aspect of wastewater disposal and environmental monitoring (Figure 1).

3.1. Wastewater Disposal

The universal strategies applied to treat wastewater include physical treatment,[66] biological treatment,[67] and chemical treatment,[68] involving sedimentation,[69] flocculation,[70] activated sludge process,[71] biomembrane process,[72] and photocatalysis,[73] etc. These strategies show extensive applications in high-polluted water. Nonetheless, when it turns to micro-polluted water, especially drinking water, the aforementioned methods do not show ideal removal efficiency. In some case, the water contaminated by low-concentration POPs[74] and metal ions is one previously ignored area now of increasing concern. Due to the long process of bioaccumulation of the nondegradable compounds, the threat of the micro-polluted water is more concealed, and the same high as that of the high-polluted water, or even higher. DNA hydrogel, as an advanced material and method, are of great interest to purify the micro-polluted water. DNA hydrogels can not only be an effective adsorbent for pollutants in water on the basis of physically adsorption, electrostatic interaction, metal coordination, hydrogen bond, and hydrophobic interactions, etc., but also be a promising matrix for immobilization technology and accordingly catalytic applications. As immobilization matrices, they are very suitable for protection, transference and controlled release of bioactive molecules.

The first attempt to apply DNA hydrogel into environmental treatment was made by Maeda et al. in 1998.[75] The DNA hydrogel was incorporated by polyacrylamide and applied as an absorbent for DNA-binding mutagenic molecular such as ethidium dyes. The ethidium dyes were selectively adsorbed through the intercalation binding of ethidium to DNA, and the dye concentration decreased ca. 90% after 24 h. However, this protocol is laborious and time-consuming. Recently, different strategies are designed to optimize the treatment.[3a, 3c, 3d, 25a, 63] Among them, the most attractive one is the GO/DNA hydrogel[3a], which is shaped by just heating and cooling. More impressively, the adsorption capacity reached 960 mg·g^{-1}, which is comparable to those of many carbon nanomaterials, such as mesoporous carbon (520-650 mg·g-1),[76] graphene-based hydrogel (186mg·g-1),[77] reduced graphene-based hydrogel (242mg·g-1),[77] ordered mesoporous carbon (83-540mg·g-1).[78]

Although the hydrogels possess high capacity and specific binding capability brought by DNA, the cost problem is unavoidable. Alternatively, a recyclable hydrogel is a candidate for cost-cut.[30b, 30d, 31h, 79] In 2005, Liu et al. synthesized a salmon milt DNA hydrogel with selective adsorption and high removal amount of dioxin, and regenerated the hydrogel by rinsing with hexane.[31h] The removal amount was circa 95% for the first time, and after four times adsorption-regeneration process, no significant decrease in the dioxin removal capacity was observed. Obviously, a recyclable DNA hydrogel could be applied in pretreatment of high concentration effluents. Such reusability is important to be desired for the automation and economization of applications.

Another strategy to cut cost is to incorporate other cheap components into DNA hydrogels instead of completely relying on the DNA. For example, polyacrylamide, a widely used water-soluble high molecular polymer was incorporated into a thymine-rich DNA hydrogel in

2010.[30d] It is well-known that thymine-rich DNA can bind mercury by T-Hg^{2+}-T metal coordination which is much stabile than T-A Watson-Crick pair. At the same time, acrylamide can bind Hg^{2+} via the amide nitrogen. Therefore, to further cut the cost, the group reduced the DNA concentration to 10 μM, and improved the acrylamide concentration to more than 10 000 times higher than the DNA concentration. The resulting DNA hydrogel showed high capacity than pure DNA hydrogel. Nevertheless, in this system, few as it is, DNA is indispensable because it endowed hydrogel with high detecting sensibility and selectivity, and the Hg^{2+} detection limit was 10 nM. Therefore, the resulting system could perform Hg^{2+} detection and removal tasks simultaneously. In addition, after a simple acid treatment, the hydrogels were regenerated and thus regained the capability of detection and adsorption. High capacity, low detection limit and regeneration make hydrogel a potential candidate for detecting and removing Hg^{2+} for environmental protection.

In addition, DNA hydrogel have been expanded to catalytic pollutants in wastewater.[10b, 31b, 80] In 2014, Zinchenko et al. found that DNA hydrogel comprising spherical Au nanoparticles could catalyze nitrophenol[80] and Au nanoparticle size may be the decisive factor for achieving highly active catalysts.[81] When $HAuCl_4$ solution inside the hydrogel was reduced, the Au nanoparticles with a diameter of 2-3 nm could well disperse in the hydrogel, resulting in a certain shrinkage. The metalized DNA hydrogel possess high catalytic activity for nitrophenol (according to the first-order kinetics: $\ln(c/c_0) = \ln(A/A_0) = -kt$, k was found to be 1.5×10^{-3} s^{-1}). Two year later,[10b] the same group broadened the catalytic agent from Au nanoparticles to cheaper Ag, Pt, Pd, Cu nanoparticles. Likewise, the hydrogel specific shrinking was found after absorbing different metal precursors. The shrinking could be a symbol of the adsorption of metal ions. The catalytic activity of the metallized hydrogels showed as follows: Pd＞Ag＞Au＞Cu＞Ni＞Pt. Moreover, Pt- and Pd-metallized

hydrogels showed resistance to DNase digestion, because the binding between transitions metals and DNA would induce structural DNA changes, which prevented DNase binding to DNA and its functioning. Excitingly, the metallized hydrogels are promising in catalytic applications. Another catalytic DNA hydrogel is a well-known hemin/G-quadruplex horseradish peroxidase (HRP)-mimicking DNA hydrogel for catalyzing peroxides.[31b] In the presence of K^+, the side copolymer chain would cross link with each other, forming G-quadruplexes structures. Addition of hemin resulted the generation of a hydrogel with the catalyzed oxidation function, biomimicing the function of horseradish peroxidase.

On top of these, some attempts are made to expand the scope of applications to immobilization.[9-10, 28c, 54a, 82] Because the hydrogel format solves the problem of self-support and encapsulation, compared with DNA mixture solution, meanwhile it possesses comparatively higher permeable than solid state. Immobilization technique facilitates the cyclic utilization of enzymes or cells, and automated process. Moreover, immobilization by DNA hydrogels will not cause any damage to active enzymes and cells. In 2013, a DNA hydrogel was designed as a cover to envelop single cells in PDMS microwells.[9a] The cells remained in microwells even after several washing processes, and maintained activity to digest external nutrition as the permeability of hydrogel. The strategy would provide a new direction for the DNA-based materials application, e.g., to solve the sludgebulking problem. It is conceivable that DNA hydrogel immobilized bacterium or other single cell living beings for modifying activated sludge process. Recently, a great progress had been made. A new DNA hydrogel took advantage of the affinity between protein and specific DNA to immobilize enzyme in the DNA-protein porous hydrogel.[82] The dsDNA building blocks tailored with biotin residues were triggered to format the hybrid hydrogels by the addition of streptavidin.

The hydrogel, possessed a flower-like porous structure (6.7±2.1 μm), served as a reservoir system for enzyme encapsulation. More importantly, the hydrogel-encapsulated enzyme exhibited improved stability in the presence of various denaturants such as elevated temperature, freeze-thaw cycles and organic solvents. Similar protective function was also found in DNA hydrogels fabricated by click chemistry which could encapsulate enzyme without loss of protein function.[83] It is not hard to envisage that high effective treatment of pollutants could be achieved by encapsulating functional cell, enzymes or other reagents, etc. into DNA hydrogels. Moreover, with the form of hydrogel, it is not hard to recycling and automation application in the flow as illustrated in **Figure 12**.

3.2. Environmental Monitoring

According to the US EPA and UNEP, the maximal containment level of toxic metals or other containments in drinking water are general in the low micromolar concentrations and even reach nanomolar concentrations. From sensitivity point of review, atomic absorption and emission spectroscopy,[84] fluorometer,[85] mass spectrometer,[86] etc. can meet such detection standards, however, these sophisticated instrumentations are always cumbersome and operating-complicated. Alternatively, a more simple and flexible strategy such as sensing is attractive. DNA has a relatively long history of crafting sensor which is capable of moulding into desired shapes and sizes and providing selective quantitative or semi-quantitative analytical information about target molecules,[38a, 38b, 87] and the recent discovery of DNA hydrogels has opened doors for new research in DNA sensor. Four main advantages make DNA hydrogel becoming a promising rapidly visual detection platform. (i) Phase transition or volume change of DNA hydrogels can be controlled under specifically environmental condition, such as pH, temperature, ionic concentration, etc., especially,

it possible to expand the spectrum of stimuli to chemical and biological molecule with the exploit of aptamer. (ii) DNA hydrogel is transparent and thus possesses low optical background. (iii) Hydrogels are easy to manipulate and convenient for device incorporation. (iv) With the enrichment of the analytes by hydrogel, the biosensors would easily result in high sensitivity of low nanomolar concentrations to sub-nanomolar concentrations.[30a, 88]

This recognition[89] between pollutants and hydrogels induced volumetric change or gel-to-sol transition creates a new kind of sensing system as alternative to classical biosensors based on electrochemical,[90] immunosensor,[91] or fluorescent sensing.[92] In 2008, an adenosine-target aptamer was utilized as crosslinker to construct the visual detection hydrogel.[89c] In the absence of adenosine, the hydrogel maintained original state. Instead, in the presence of only 2 mM adenosine, the hydrogel collapsed within 15 minutes, because adenosine would combine with the crosslinker aptamer and break the crosslinking. Importantly, it can be developed as a general strategy for fast-visual and simple detection of various targets. As long as the aptamer is rationally engineered, the aptamer-based hydrogel is feasible to recognize various pollutants.

Nevertheless, one to one mod between target and aptamer might limit the efficiency of hydrogel considering its volume and load. The DNAzymes exactly bring more available strategies to improve detection performance. DNAzyme possesses high catalytic capability, namely, a DNAzyme can cleave a large amount of DNA linker. However, most of DNAzymes require synergizing with cofactors, some specific metal cations. The indispensable of specific metal ions provides a novel idea for detecting methods.[93] To prove the feasibility, Yang et al. introduced a copper dependent DNAzyme to crosslink hydrogel.[17c] Only in the presence of copper ions, the DNAzyme was activated and thus the formed hydrogel was breakdown. Besides the mentioned

copper dependent DNAzyme hydrogel, many other metal-dispensable DNAzyme such as Pb^{2+},[75, 94] Hg^{2+},[95] Cr^{6+},[96] Cu^{2+},[97] Ca^{2+},[98] Zn^{2+},[99] independent DNAzymes etc. were also explored. Notably, Tang creatively constructed a DNA hydrogel as an electrochemical impedance biosensor to detect Hg^{2+} whose amplification strategy was based on Mg^{2+}-DNAzyme.[100] DNAzyme functionalized hydrogels are filled with anticipation in metals detection. To clearly distinguish the state between solution and hydrogel and further improve the hydrogel sensibility, AuNPs as an indicator were introduced.[17c] In the absence of Cu^{2+}, an apparent boundary emerged between the hydrogel and supernatant. Upon adding Cu^{2+}, the boundary disappeared and a homogeneous solution showed up.

In addition to AuNPs, various of colorimetric reagents, such as dyes[17b, 30a, 30c, 30e, 31a] and photon[101] can be utilized as indicator to improve its sensibility. Recently, fluorescent dyes attract much attention as they just require a hand-held UV lamp and a dark environment to acquire high sensitivity of nanomolar concentrations omitting the need for analytical instrument.[17b, 30a, 30c, 30e, 31a] The Liu's group in Canada stringently explored the effect of fluorescent dyes. In 2011, they developed a Hg^{2+} response monolithic hydrogel based on DNA staining dye (SYBR Green).[31a] A thymine-rich DNA was covalently bonded the hydrogel skeleton of the synthetic organic polymer. The adopted neutral polyacrylamide gel had a yellow background fluorescence from the dye, and would emit green fluorescence in the presence of Hg^{2+}. The Hg^{2+} detection limit of 10 nM , was much lower than the aforementioned order of magnitudes of mM or μM obtained from the gel-to-sol transition. In the following year, they further extend the monolithic system called AGRO100, which even could visually detect 20 nM Pb^{2+} with naked eyes.[30a] The system was based on a guanine-rich DNA and DNA dyes included thiazole orange and SYBR Green. The

AGRO100 was found to selectively bind Pb^{2+} with high affinity in the form of G-quartets, even compared with K^+. Remarkably, the good generality of the system was also demonstrated to detect a great number of analytes in one pot by gel shaped encoded detection. Recently, they developed the first AgNC-based fluorescence hydrogel to detect Hg^{2+} with a detecting limit of 50 nM by the naked eyes.[30c] Needless to add the extra dyes, the AgNCs sensors could emission different color by varying the DNA sequence. The presence of Hg^{2+} induced AgNCs fluorescence quenching, producing the resulting orange-to-green visual fluorescence transition.

Although the sensitivity of monolithic hydrogel is acceptable, the stable optical fluorescence signal was obtained over 1 h, or even overnight. Moreover, constructing monolithic hydrogels require comparative higher DNA concentration, it would sacrifice the cost. Obviously, the long equilibration time and high cost restrict the wide application of the monolithic hydrogel. To speed up the reaction, hydrogel microparticles with short diffuse distance and fast kinetic of signal generation are explored. In 2012, a hydrogel microparticles based on DNA staining dye (SYBR Green) was creatively developed.[30e] Similarly, the hydrogel microparticles incorporated by T-rich acrydite-modified DNA (0.2 μm) and polyacrylamide. Different from the monolithic one (~2 mm), most size of the breads were between 10 μm and 50 μm. Notably, a stable signal was obtained within 2 min with a detection limit of 10 nM, same as the monolithic one[31a]. Namely, it speeded up detection at least 30 times without sacrificing sensitivity at the same time. Moreover, the hydrogel microparticles could be processed on a solid substrate, because they were not damaged by drying, and would rehydrate by adding buffer. It follows that the hydrogel has the potential to fast and sensitively detect containments, even in the extreme dry condition.

4. Conclusions and Perspectives

Increasingly serious environmental contamination and increasingly rigorous standards have urged us to develop strategies for environmental disposal and analysis. DNA hydrogels have been expected to be new and promising platforms in environmental field, attributing to their high binding affinity, tunable porous structures, permeability, biodegradability, and relative mechanical stability. Such properties allow the design and fabrication of DNA hydrogels that can act as adsorbents for hazardous pollutants. They also enable DNA hydrogels to serve as protective matrices for active substrates immobilization which have the potentials for automatic wastewater processing. In this case, when encapsulated enzyme or other catalytically active reagents, the hydrogels will be endowed with extra catalytic and disposal property. DNA hydrogels can also conduct catalytical activities and specific recognition through introducing AuNP-modified bases[102] and functional nucleic acids, such as i-motif structure, G-quartet structure, aptamer, and DNAzyme, etc. Besides, the recognition between a specific target and a designed hydrogel component, and the subsequently induced volumetric change phase transition or a visual colorimetric output also enables functionalization of the hydrogel acted as a new quantitative and semi-quantitative analytic platform. Notably, it is even optimistic to develop a lab-on-chip system for in-situ detection. Additionally, when incorporated with other materials, e.g., GO/rGO and artificial polymers, the hydrogels possess superior stability and electric properties. Briefly, the properties of DNA hydrogels can be precisely programmed by altering the monomer composition and structures. Thus far, DNA hydrogels have been implemented as adsorbents, catalytic agents, encapsulated carriers, and sensors[17b, 17c] to directly or indirectly dispose or analyze low-concentration pollutants, especially heavy metal and POPs. With the maturation of the fabricated mechanism, it is conceivable that increasingly

environment-oriented DNA hydrogels are to arise as a multifunction platform to meet the diverse requirements involving environmental advanced disposal and analysis. The applicable potentials of DNA hydrogels in environment are depicted in **Figure 13**.

However, several challenges involving preparation and commercial application must be addressed.

(i) **Environmental Function**. Although DNA hydrogels have shown their great potential in versatile environmental issues, their principle superiority and development orientation should be focus on advanced treatment of micro-polluted water. On account of their biocompatibility and sensibility, DNA hydrogels are applicable in drinking water. Likewise, by their capability including encapsulation and transportation, sustained release, sensibility, and precise programmability, DNA hydrogels can be tailored to load and site-specific release reagents for disposal of pollutants at special positioning points, e.g., ground water, and are going to develop advanced and customizable strategies for special water treatment similar targeted treatment in some special cases. Notably, DNA hydrogels have been proved the capability of binding GO or other carbon materials. Thus, as a potential and alternative method, the DNA hydrogels would be considered to remove carbon-based nanomaterials (CNTs, graphene) which are popularizing in worldwide and may become a latent and thorny environmental threat due to their difficulty in degradation and separation.[103] Indeed, how to balance and find the appropriate strategies combing the environmental requirements and function is a very practical and intellectual challenge. Besides, with low optical background and high loading capability, DNA hydrogels deserve development as analytic platforms.

(ii) **Environmental resistance**. The complicacy of real environments challenges the treatment and recognition of targets in real sample. Obviously, stable and specific hydrogels are needed. For

one thing, surrounding environmental pH, ionic strength, temperature, solvent composition, etc., and even a small quantity of hydrolase accidentally excreted by microbes may affect the mechanical stability of DNA hydrogels. For another, the coexist pollutants or analytes may have antagonistic or competitive influence on adsorption or binding process. Although the GO/rGO DNA hydrogels have proven the enhanced stability and aptamers/DNAzymes-targets responsive hydrogels have shown the optimistic binding affinity, it is necessary to design other new pattern DNA hydrogels with suitable mechanical strength, high environmental stability and binding affinity, especially in extreme real environment, such as turbulence or sunlight (ultraviolet rays) exposure. As an example, i-motif based hydrogels have been proven the ability to prolong DNA hydrogels lifetime, despite of the sharp stable pH range. Therefore, how to effectively improve environmental resistance of DNA hydrogels is substantive and critical in their environmental applications.

(iii) **Pollutant removal efficiency**. The removal efficiency of pollutants is directly related to the availability of DNA hydrogels, which is effected by gel size, gel percentage (gel crosslinking density) and pollutants type. For instance, monolithic hydrogels with long diffusion distance take a long equilibrium time for pollutants. The development of methods for preparation of nanohydrogels may speed up the diffusion rate. On top of this, different types of analytes will affect diffusion result. It can be quite clear that from the examples described above. For monolithic DNA hydrogel, less 1 min was required for OH^- to diffusion, while several minutes for adenosine, 10 min for cocaine, more than 1 h for metal ions and overnight for dyes. Adjusting the gel percentage and gel size will absolutely change the final result. However, there is no systemic research about the exact relationship between them.

(iv) **Screening for environmental requirements.** The changing environmental requirements

push the development of environmental technology becoming more efficient and targeted. To facilitate DNA hydrogels matching environmental requirements, it is rational and feasible to take scientific research strategies or assist by computer models, which can screen out appropriate DNA hydrogel to avoid relatively blind or costly labor attempts. The screening and comparison mainly involves the optimization and estimation a hydrogel for environmental application by considering the exact binding capacity of analytes or other convincing performance parameters. Therefore, it is positive to grasp how to scientifically, accurately and efficiently select the optimal DNA hydrogel with relation to pollutants by comparing their standard parameters.

(v) **Cost for environmental application**. The cost directly affects the acceptability and applicability of DNA hydrogels in environmental application. Given the large-scale application requirements, the high cost of DNA hydrogels cannot be ignored, although the cost problem has always been thorny for deep purification of micro-polluted water. One prevalent way to address the problem is to keep the processing efficiency by strengthening the function of DNA and reducing the use of DNA, or constructs the DNA hydrogels by incorporating DNA with other cheaper materials e.g., carbon nanomaterials, organic polymer for cost-cut and without any compromising of gel response and mechanical stability. Second, a renewable hydrogel is an available strategy for cost consideration. In some cases, the regeneration of the DNA hydrogels can be realized by a simple treatment such as acid rinse and organic solvent immersion etc. owing to the rational hydrogel design. Third, simplification the procedure of synthesis may make sense. So far, there is a little research focus on the self-assemble of one-pot mixtures which is noteworthy for automation. Apparently, more simple and efficient formation mechanism are required to be discovered. Undoubtedly, how to effectively reduce costs always is a realistic, sustainable theme for practical

application.

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Figures:

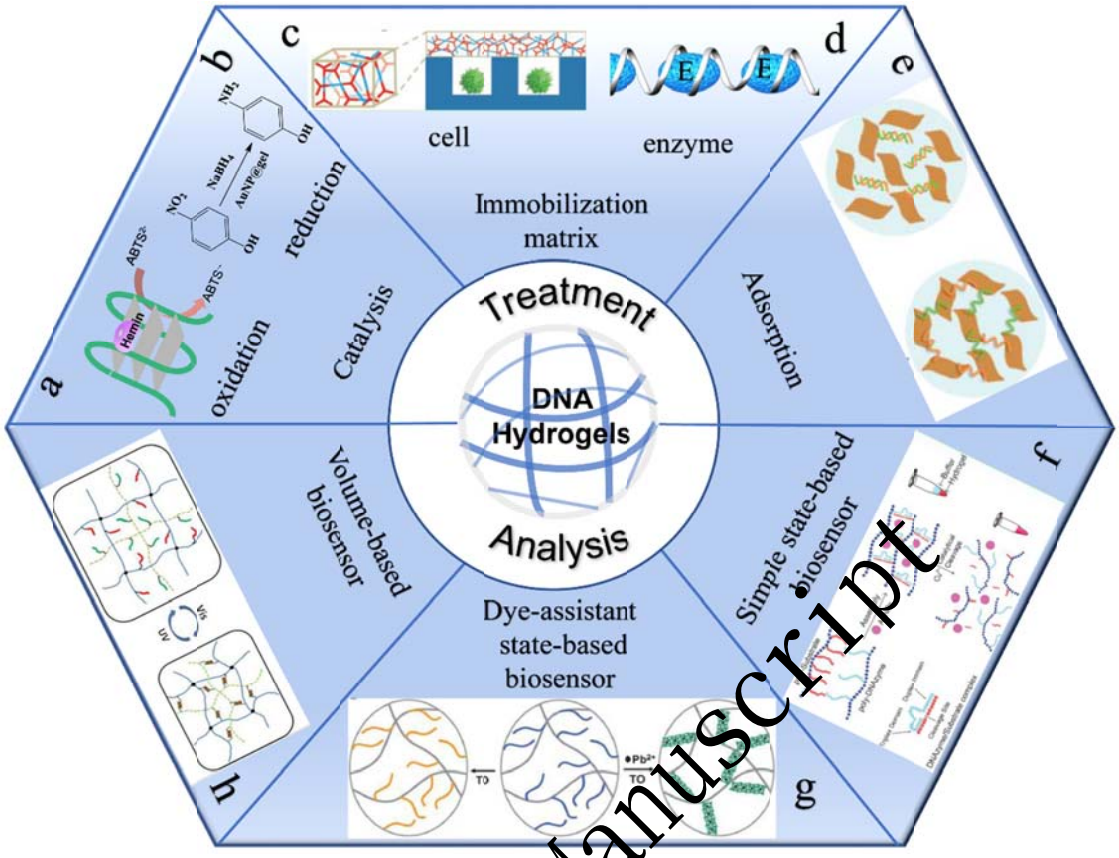

Figure 1. Applications of various DNA hydrogels in environmental treatment and analysis. Treatment: (a) Catalyze pollutants by oxidation processing. (b) Catalytic pollutants by reduction processing. Adapted with permission from Ref.[80]. Copyright 2014, American Chemical Society. (c) Encapsulate cells as immobilization matrix. Adapted with permission from Ref.[9a]. (d) Load enzymes as immobilization matrix. (e) Adsorb pollutants. Adapted with permission from Ref.[3a]. Copyright 2010, American Chemical Society. Analysis: Recognize pollutants by (f) simple sol-to-gel transition. Adapted with permission from Ref.[17c]. Copyright 2011, Royal Society of Chemistry. (g) sol-to-gel transition combined with dye-assistant signal amplification. Adapted with permission from Ref.[30a]. Copyright 2012, Royal Society of Chemistry. (h) visual volume change. Adapted with permission from Ref.[104]. Copyright 2012, American Chemical Society.

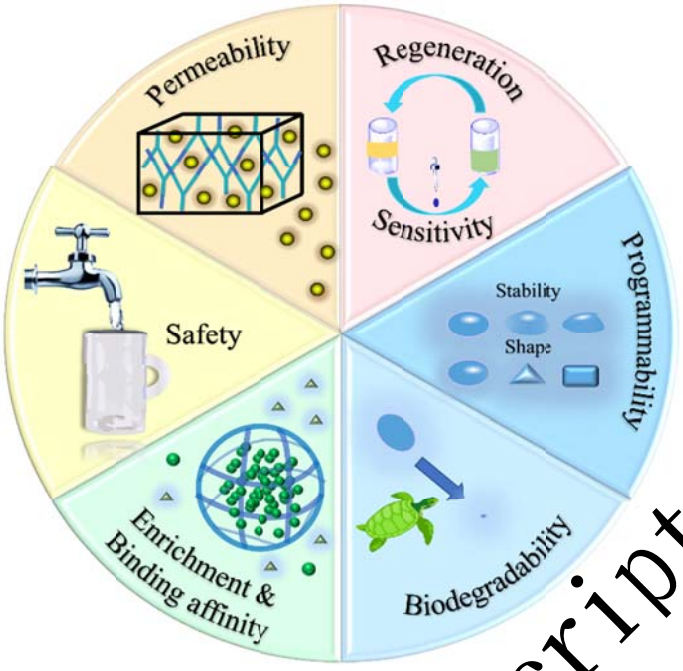

Figure 2. Favorable properties for environmental disposal and analysis, involving safety, enrichment, binding affinity, biodegradability, programmability, regeneration, sensitivity, and permeability.

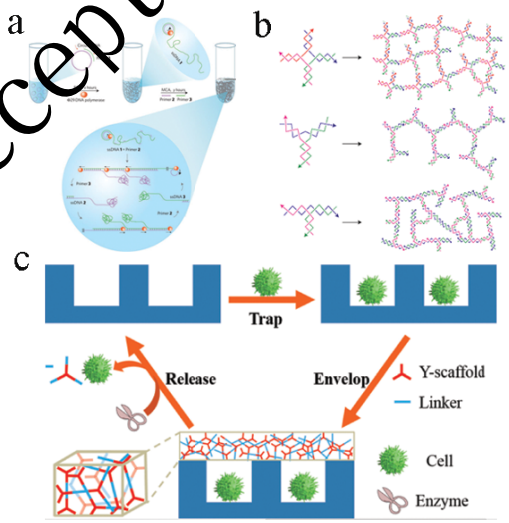

Figure 3. (a) phi29 polymerase-catalyzed RCA and MCA. Adapted with permission from Ref.[28b]. Copyright 2006, Nature Publishing Group. (b) T4 DNA enzyme-catalyzed ligation: X-, Y-, T-DNA

serve as crosslinkers to form networked gels. Adapted with permission from Ref.[1a]. Copyright 2012, Nature Publishing Group. (c) self-assemble through complementary sticky ends. Adapted with permission from Ref.[9a].

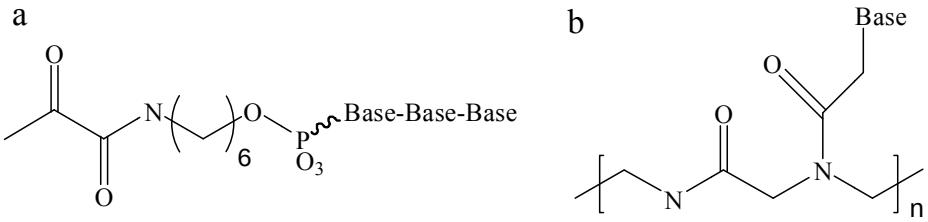

Figure 4. The molecular structures of (a) acrydite-modified DNA and (b) peptide-modified DNA.

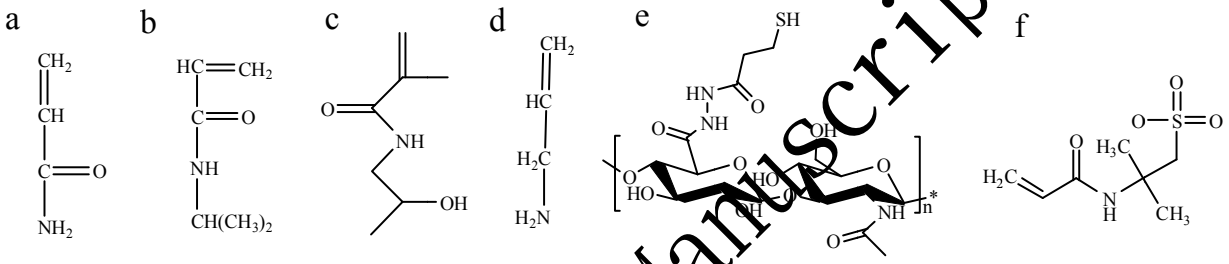

Figure 5. The molecular structures of (a) acrylamide, (b) N-isopropylacrylamide, (c) N-(2-hydroxypropyl) methacrylamide, (d) allylamine, (e)AMPS, (f) CMHA-SH.

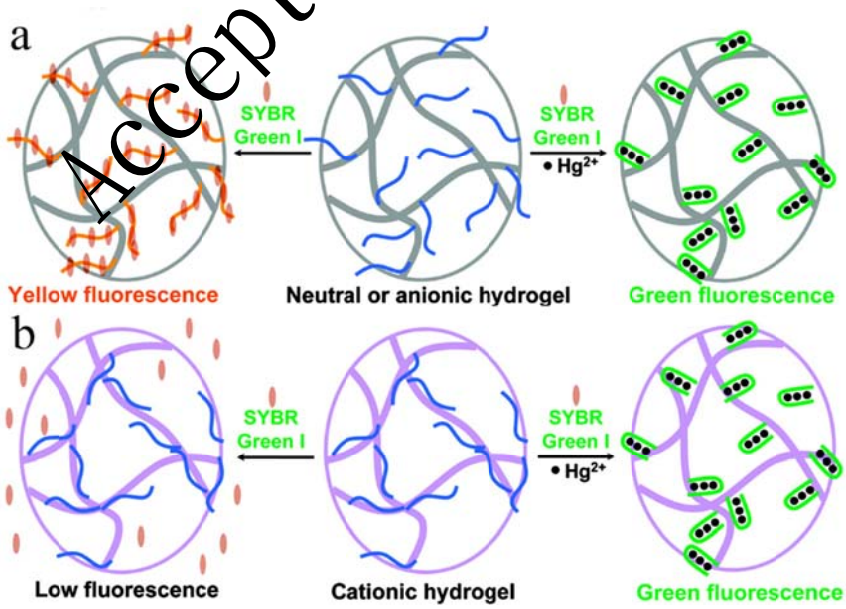

Figure 6. (a) Schematic presentation of covalent DNA immobilization within a neutral

(polyacrylamide) or negative (containing AMPS) hydrogel. Adapted with permission from Ref.[31a]. Copyright 2011, American Chemical Society. (b) or positive hydrogel (containing allylamine). Addition of Hg^{2+} and SYBR Green produces a visual fluorescence signal. For the cationic gel, the DNA interacts more with the gel backbone in the absence of Hg^{2+} and the diffusion of SG into the gel is also retarded, giving low background fluorescence. Adapted with permission from Ref.[31a]. Copyright 2011, American Chemical Society.

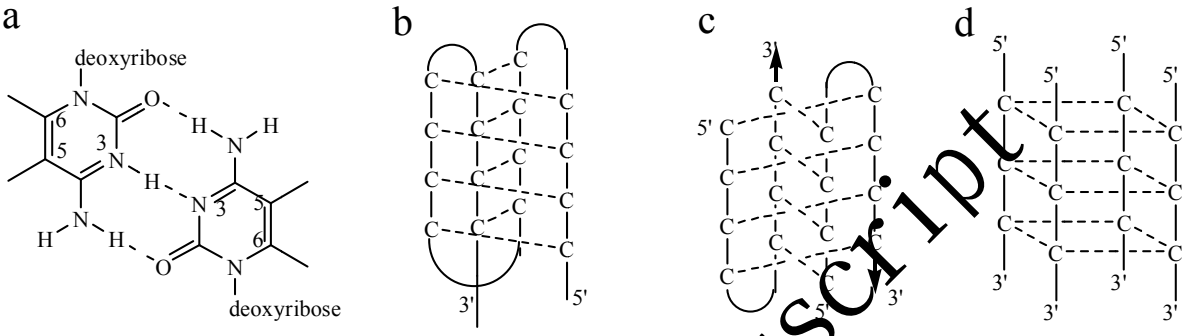

Figure 7. Schematic illustration of i-motif units: (a) hemiprotonated C-C^+ base pairs, (b) intramolecular i-motif structure, (c) dimer i-motif structure, (d) tetramer i-motif structure.

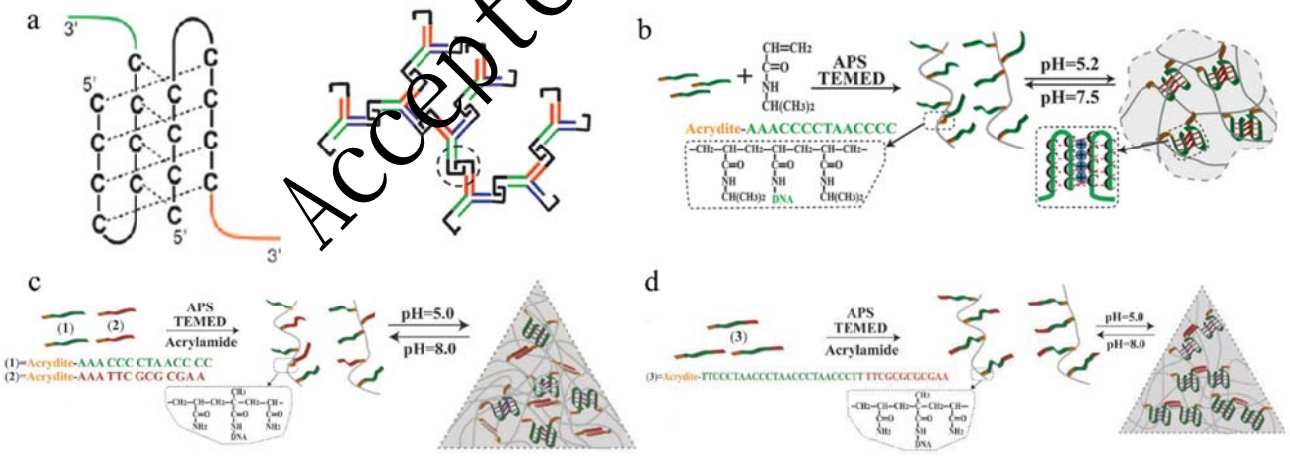

Figure 8. Examples of construction of DNA hydrogel based on i-motif: (a) pure DNA hydrogel constructed by ds-Y-DNA with dimer i-motif structure. Adapted with permission from Ref.[29a]. (b) poly-N-isopropylacrylamide/DNA hydrogel with dimer i-motif structure. Adapted with permission

from Ref.[12b]. (c) poly-acrylamide/DNA hydrogel with dimer i-motif structure. Adapted with permission from Ref.[12a]. (d) poly-acrylamide/DNA hydrogel with intramolecular i-motif structure. Adapted with permission from Ref.[12a].

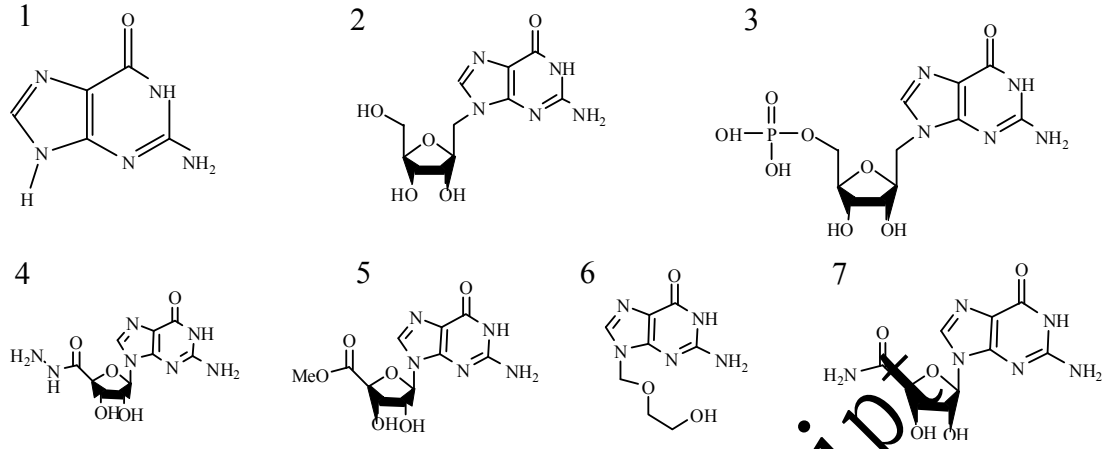

Figure 9. Guanine and its analogues including guanine 1, guanosine 2, guanosine monophosphate 3, guanosine hydrazide 4, and other derivatives 5, 6 and 7.

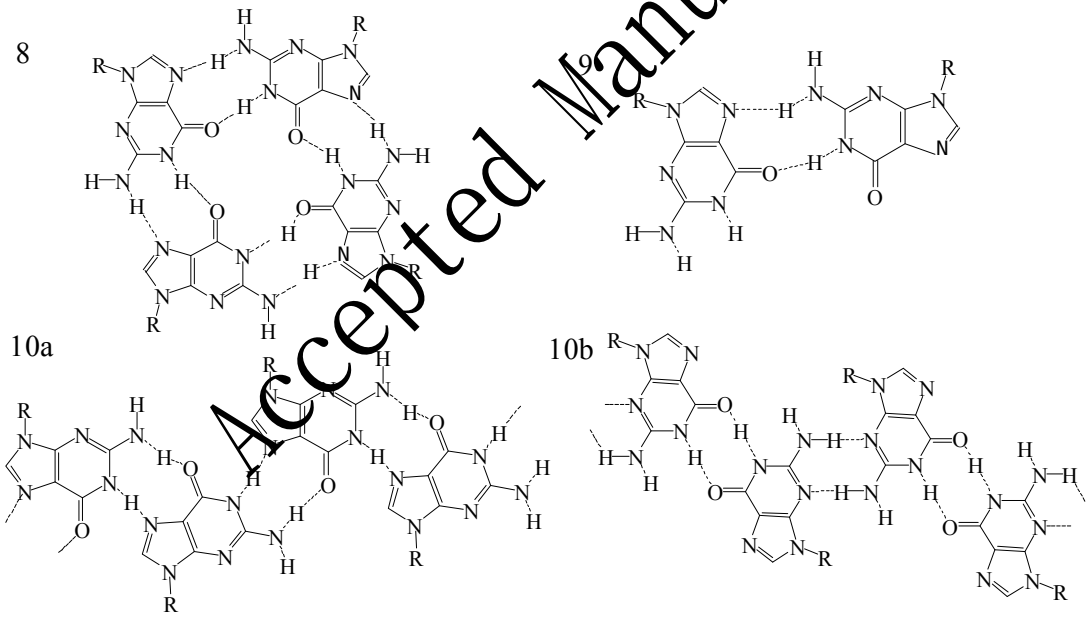

Figure 10. Guanine-containing molecules can form a variety of different self-assembled motifs, including G-quartet 8, G-dimer 9, G-ribbon 10a, G-ribbon 10b.

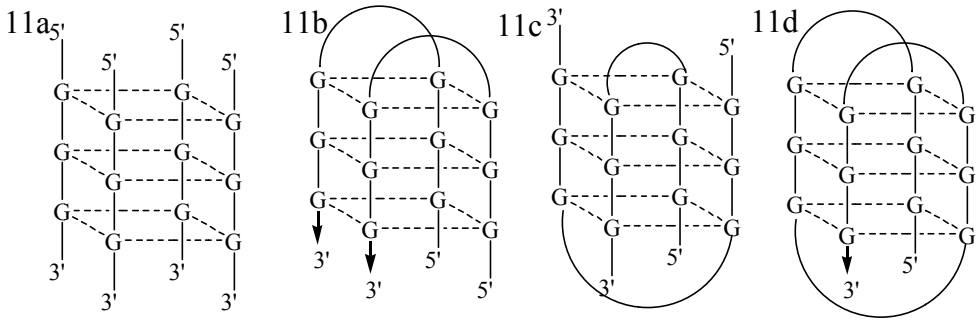

Figure 11. Different G-quadruplex DNA structures. (a) A parallel stranded tetraplex, (b) a bimolecular complex from hairpin dimerization with "edgewise" loops, (c) a bimolecular complex with "diagonal" loops, and (d) a unimolecular G-quadruplex.

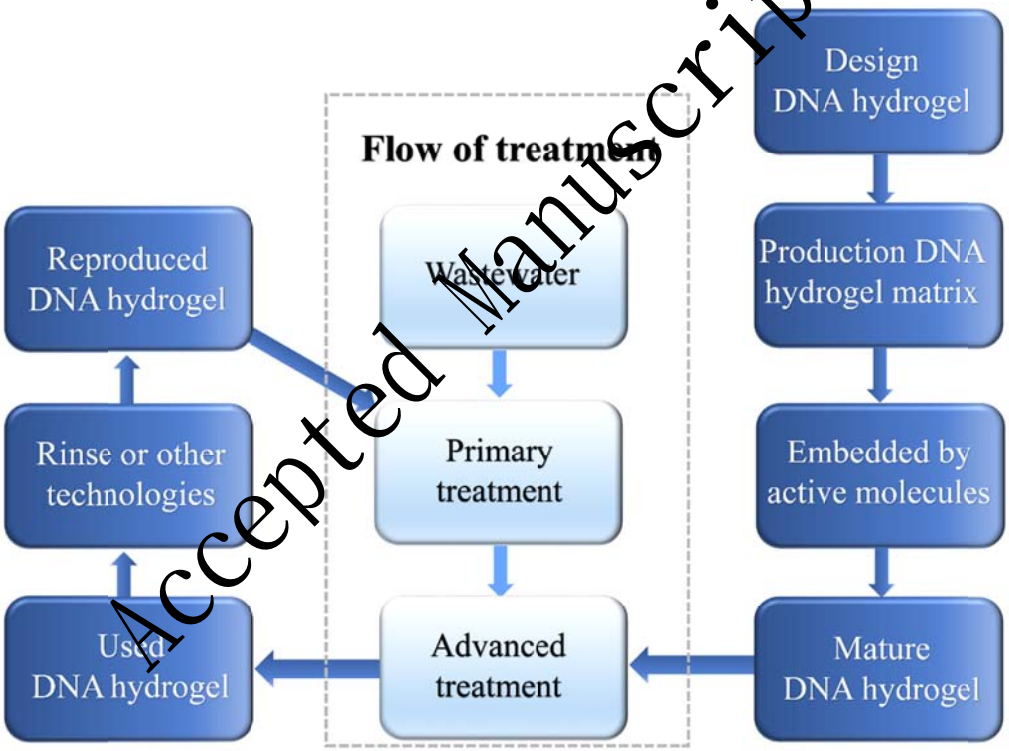

Figure 12. The flow of automation wastewater treatment

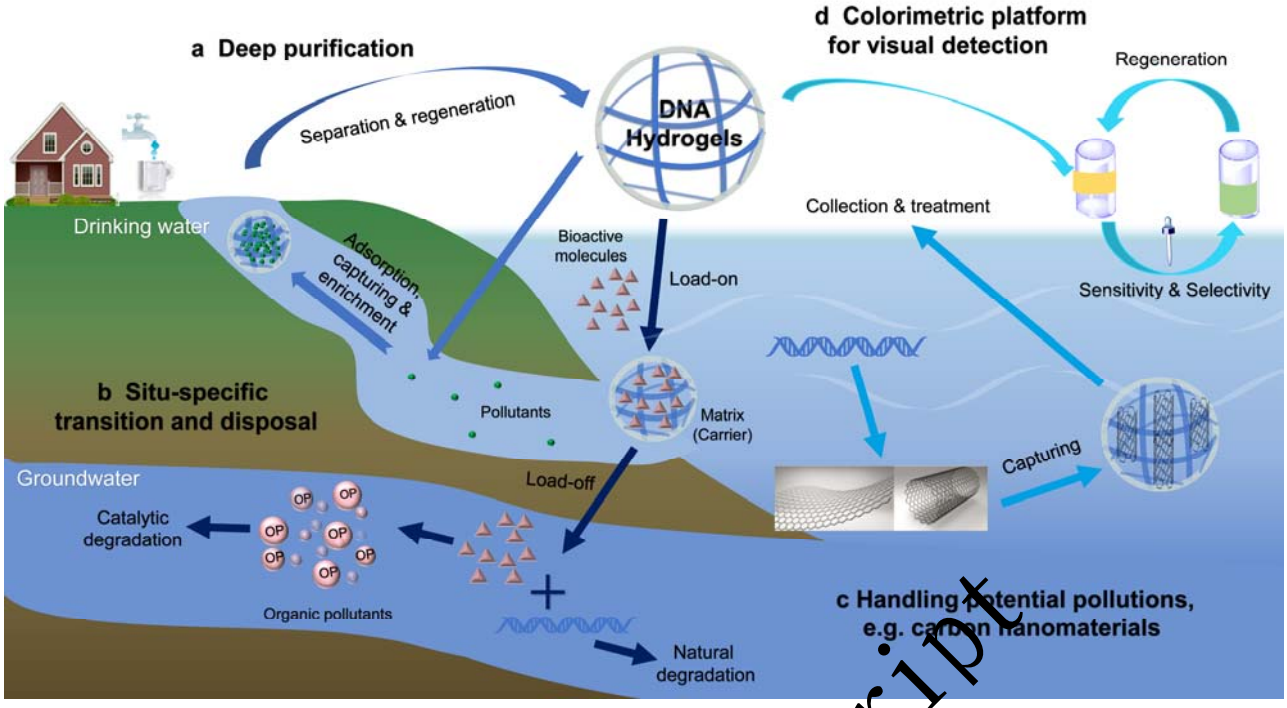

Figure 13. The typical and potential environmental application paths of DNA hydrogels: (a) deep purification of heavy metal and organics in micro-polluted water, such as drinking water, (b) situ-specific transition and disposal by protective carrying bioactive molecules to the specified site for disposal such as organic pollutants (typically, petroleum hydrocarbon) in groundwater, (c) disposal potential carbon nanomaterials pollutants, (d) colorimetric platform for visual detection.

Table:

Table 1. Properties and capability of typical DNA hydrogels

Type	Branched DNA hydrogels	Organic polymer-based DNA hydrogels			Carbon-based DNA hydrogels
Final DNA concentration	30 μM[1a] (minimum) 500 μM[9a, 29a, 29d] (general)	1-10 μM[30]			0.3 - 3 mg·mL^{-1}[3a, 43b]
Current analytical selectivities	pH,[29a] Enzyme,[9a, 29d] thermal,[29d] small molecular[1a]	metal ions,[17b, 30a, 30c, 30d, 31a] small moleculars,[30b, 31e] POPs,[3b] pH,[12a, 12c, 31c, 31d, 31f] Enzyme[82]			POPs,[3a] pH,[43b] molecular [25a, 25b]
fabrication mechanism	Y-scaffold + ds DNA	Polyacrylamide + Acrydite-Hg^{2+}aptamer	Poly(N-isopropyl acrylamide) + Acrydite-DNA (i-motif)	Polyacrylamide + Acrydite-DNA (G-quadruplexes)	Graphene oxide + ds DNA
Analytical targets	Enzyme	Hg^{2+}	Acid, Ag^{+}, temperature	2,2′-azinobis-(3-ethylbenzthiazoline-6-sulfonic acid	Dyes
Storage Modulus G’	1900 Pa	Unknown	320 Pa	5 Pa	4600 Pa
Loss Modulus G’’	100 Pa	Unknown	5 Pa	0.25 Pa	800 Pa
Application	Encapsulate cell	removal (efficiency: 97 %); detection (limit: 10 nM)	Sensing	Catalysis	Removal (960 mg·g^{-1})
Ref	[9a]	[30d]	[31d]	[31b]	[3a]

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Yingrong Wang obtained her B.S. degree in environmental science from China Pharmaceutical University in 2016. She is currently a postgraduate student in the college of Environmental Science and Engineering at Hunan University under the supervision of Prof. Guangming Zeng. Her research interests focus on the construction and application of nanomaterials for environmental treatment and biosensor for environmental analysis.

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Yi Zhang obtained his PhD in environmental science and engineering in 2015 from Hunan University. He is an associate professor of the college of Environmental Science and Engineering at Hunan University. His research interests include environmental biology and analytical technology for environmental pollution control involving mechanisms of novel nanomaterials for environmental treatment and biosensing strategies for environmental monitoring.

Entry for the Table of Contents

DNA hydrogels are very suitable for advanced water treatment and environmental analysis. Altering their components and structures, practical environment-oriented DNA hydrogels can be designed in terms of environmental requirements. The strategies and mechanisms are introduced to produce the most suitable green, safe, and effective hydrogels.

Keywords: DNA hydrogels; advanced water treatment; environmental analysis; heavy metals and organic pollutants recognition; construction mechanism;

Yingrong Wang, Yuan Zhu, Yi Hu, Guangming Zeng*, Yi Zhang*, Chang Zhang, Chongling Feng

Title: How to Construct DNA Hydrogel for Environmental Applications: Advanced Water Treatment and Environmental Analysis