



## Review

# Synthetic strategies and application of gold-based nanocatalysts for nitroaromatics reduction



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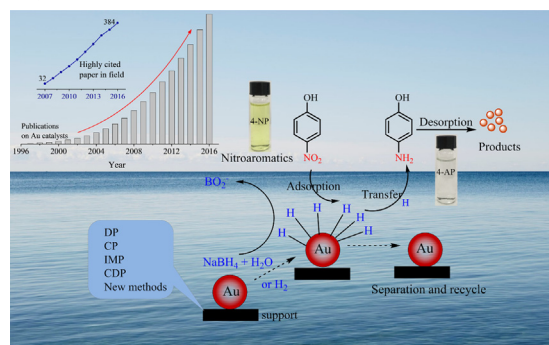
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## HIGHLIGHTS

- Synthetic strategies of Au nanocatalysts are discussed comprehensively.
- Mechanism and routes for nitroaromatics reduction by Au nanocatalysts are reviewed.
- Factors affected catalytic performance based on different Au nanocatalysts is discussed.
- An insight of prospects and challenges for the development of Au nanocatalysts is taken.

## GRAPHICAL ABSTRACT

The procedure for different synthetic methods of Au catalysts and the reduction process for nitroaromatics based on Au catalysts (The insert images show the evolution for the publications about the key words of “Gold catalyst” on indexed journal sand the highly cited papers republished in this field from web of science in the past 20 years.).



## ARTICLE INFO

## Article history:

Received 23 August 2018

Received in revised form 15 October 2018

Accepted 15 October 2018

Available online 18 October 2018

Editor: Daniel CW Tsang

## Keywords:

Au nanocatalysts

Synthesis

Reduction

Nitroaromatics

Metal nanoparticles

## ABSTRACT

With the increasing requirement of efficient organic transformations on the basic concept of Green Sustainable Chemistry, the development of highly efficient catalytic reaction system is greatly desired. In this case, gold (Au)-based nanocatalysts are promising candidates for catalytic reaction, especially for the reduction of nitroaromatics. They have attracted wide attention and well developed in the application of nitroaromatics reduction because of the unique properties compared with that of other conventional metal-based catalysts. With this respect, this review proposes recent trends in the application of Au nanocatalysts for efficient reduction process of nitroaromatics. Some typical approaches are compared and discussed to guide the synthesis of highly efficient Au nanocatalysts. The mechanism on the use of H<sub>2</sub> and NaBH<sub>4</sub> solution as the source of hydrogen is compared, and that proposed under light irradiation is discussed. The high and unique catalytic activity of some carriers, such as oxides and carbons-based materials, based on different sizes, structures, and shapes of supported Au nanocatalysts for nitroaromatics reduction are described. The catalytic performance of Au combining with other metal nanoparticles by alloy or doping, like multi-metal nanoparticles system, is further discussed. Finally, a short discussion is introduced to compare the catalysis with other metallic nanocatalysts.

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## 1. Introduction

Metal nanoparticle (NP) catalysts play a dominating role in production of chemicals, polymers, and fuels (Lim, 2016; Mitsudome et al., 2015; Lai et al., 2018). They are the keys to the environmental protection, like clean-up of effluent gases and degradation of pollutant substance (Wang et al., 2014; Zhao et al., 2016a). Gold (Au), one kind of noble metals, is historically considered as a catalytic inert element until Hutchings and Haruta observed that Au catalysts were highly efficient in chlorination of acetylene and carbon monoxide oxidation at 1980s (Haruta et al., 1989; Hutchings, 1985). When subdivided to nanoscale, Au-based catalysts provide incredible reactivity for catalysis, which is hard to be replaced by other metals, especially for the reduction process like oxygen and carbon dioxide reduction, water reduction for hydrogen production, and reduction of nitroaromatics because of its unique properties of localized surface plasmon resonance (LSPR), large surface-to-volume ratio, and electron transfer (Chung et al., 2018; Hutchings and Haruta, 2005; B. Li et al., 2018; Qin et al., 2018; Wang et al., 2018a). Au nanocatalysts also have been demonstrated to be attractive in industry and environmental protection due to their green and efficient redox properties (Scurrill, 2017). They are widely used and the topic of Au nanostructured catalysts has been augmented exponentially in the last 20 years.

Gold nanoparticles (AuNPs) with small size show excellent catalytic performance for many chemical reactions, especially for the reduction of nitroaromatics in water (Hirakawa et al., 2016; Moghaddam et al., 2017). Some nitroaromatics, such as nitrophenol compounds, organic dyes, etc., are important intermediates in industrial and agricultural processes (Chen et al., 2015; Cheng et al., 2016b; Cheng et al., 2017; Gong et al., 2009; Hamidouche et al., 2015). However, environment has been suffered from pollution at significant levels because of the high toxicity of these compounds (Cheng et al., 2016a; Huang et al.,

2017a; Tang et al., 2014; Xue et al., 2018). The use of nitroaromatics is difficult to forbid, hence, these chemicals are inevitably discharged into the environment (Cheng et al., 2016c; Huang et al., 2016; Rafatullah et al., 2010; Yang et al., 2010). Therefore, remove and degrade these compounds to less toxic chemicals are very important. In this case, AuNPs exhibit good catalytic activity for reduction of nitroaromatics to its corresponding amines, because they have the advantages of large surface-to-volume ratio and unique electronic properties (Downing et al., 1997; Kuroda et al., 2009). They stabilize the 6s<sup>2</sup> electron pairs by combining the size and relativistic effect, thus determining the catalytic property for nitroaromatics reduction because of the high energy and reactivity of 5d electrons (Narayanan and Sakthivel, 2011; Pyykko, 1988). Compared with other metal catalysts, AuNPs have two distinct advantages: 1) the catalytic activity is highly and directly related to the particle size that must be nanoscale but not microscale. Besides, the catalytic activity is increased with the decrease of particle size. Thus, the catalytic activity of Au can be well controlled by adjusting the size; 2) the high catalytic performance can be obtained under mild conditions even on low temperature. This is benefit for the reduction under ambient temperature and energy saving.

Unfortunately, free AuNPs cannot be recycled and are easy to aggregate due to the high surface energy, which significantly decreases the catalytic efficiency and obviously slows the reaction kinetics (Pocklanova et al., 2016; Qin et al., 2017). The surface active sites and interfacial free energy are reduced due to the aggregation, hence weakening the catalytic activity (Varma, 2016). In order to solve this problem, great efforts are being devoted to immobilize AuNPs on carriers, such as oxides (Lee et al., 2008; Song and Hensen, 2013), carbon-based materials (Tan et al., 2015; Yang et al., 2013), etc., for obtaining effectively stable and highly dispersed Au nanocatalysts, offering more surface active sites, and enhancing the interfacial free energy. Moreover, some strategies tend to investigate the size and structure of AuNPs by using

different reducing agent and stabilizer, alloying other metal NPs, and decorating some ligands to form smaller and bimetallic or multi-metallic catalysts (Conte et al., 2009; Fountoulaki et al., 2014; Huang et al., 2017b; Sau et al., 2001). Due to the size effect, synergistic effect, interfacial effect and shape effect between the supports and Au, easily separated, well cycled, and highly efficient Au nanocatalysts can be obtained. Thus, Au nanocatalysts provide promising potential in catalytic reaction.

Some wonderful reviews have been published about nitroaromatics reduction on the basis of Au and other metal NPs (Mitsudome and Kaneda, 2013; Pan et al., 2013). For example, Kadam et al. reviewed the different methods for nitroaromatics reduction based on the source of hydrogen (Kadam and Tilve, 2015). Aditya et al. reported a comprehensive paper, which mainly focused on the reaction process, mechanism, and catalytic performance of different kinds of catalysts (Aditya et al., 2015). However, none of them have reviewed the nitroaromatics reduction by Au nanocatalysts only. Zaho et al. synthetically reviewed the nitrophenol reduction by Au- and other transition metal nanoparticles and discussed the difference between them in detail (Zhao et al., 2015). But the synthetic methods for Au nanocatalysts were not mentioned. Furthermore, the investigation of Au nanocatalysts for nitroaromatics reduction has been developed in the past four years, especially for the reduction under light irradiation. Hence, in this review, some typical synthetic approaches for Au nanocatalysts including the traditional and novel methods have been reviewed and discussed to guide the fabrication of highly efficient Au nanocatalysts. The unique catalytic activity of them in reduction of nitroaromatics has been discussed. The kinetic model and route of this reaction are represented to reveal the potential mechanism under different conditions, including the reaction medium and light effect. This review further emphasizes some typical and recent examples of Au nanocatalysts that have achieved high activity and compares the catalytic performance of them. A short discussion is introduced to compare the catalysis with other metallic nanocatalysts. Through this review, the readers will understand the role of Au nanocatalysts in catalytic reaction profoundly. We hope that readers can be inspired by this review and gain more highly efficient Au nanocatalysts, pushing further development of Au catalysts application.

## 2. Synthetic strategies for Au nanocatalysts

The preparation of colloidal AuNPs has been well described in many researches (Dykman and Khlebtsov, 2012; Qin et al., 2017; Zhang et al., 2014a). AuNPs fabricated through Brust-Schiffrin method are primarily used for catalysis because it provides smaller size of AuNPs. The procedure has been well described in our previous works (Fang et al., 2017; Guo et al., 2016; Lai et al., 2015; Lai et al., 2017; Zeng et al., 2017). In this section, we mainly retrospect some typical synthetic strategies for supported Au nanocatalysts, which are widely applied in the reduction of nitroaromatics. They can be usually divided into five parts: the deposition-precipitation (DP), co-deposition (CP), impregnation (IMP), colloid deposition (CDP), and newly developed methods.

### 2.1. Deposition-precipitation

DP is one of the earliest strategies for preparation of supported Au nanocatalysts, which was recognized by Haruta and co-workers, who reduced AuNPs on titanium dioxide (TiO<sub>2</sub>) firstly (Tsubota et al., 1991). The operation procedure consists in allowing Au salt become Au(OH)<sub>3</sub> by adding alkali, the precipitant, into the Au salt solution to adjust the pH with the range of 6 to 10. After aging for a while, the aforementioned Au solution is adsorbed by the support and the mixture is incubated with properly selected concentration, temperature, stir, and time. Subsequently, the suspension is treated by a series procedure of filtration, washing and drying. The last and most important procedure is the reduction of AuNPs from Au<sup>3+</sup>. Some studies kept it under a

flow of H<sub>2</sub>, and others made it be calcined in a flow of O<sub>2</sub> or air (Song et al., 2015; Ulrich et al., 2017; Wang et al., 2015a). The calcined Au nanocatalyst provides better performance but some deactivation has been observed due to the increasing particle size when sintering.

The key procedure of this method is the strict control of pH. It can be adjusted by precipitant, which usually uses Na<sub>2</sub>CO<sub>3</sub>, urea, NaOH, etc. (Torres et al., 2016). DP requires deposition occurs in alkaline condition, so it is applicable in supports which have a point zero charge at a high pH (≥6), e.g. TiO<sub>2</sub>, ceria (CeO<sub>2</sub>), zirconia (ZrO<sub>2</sub>), ferric oxide (Fe<sub>2</sub>O<sub>3</sub>), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), and magnesium dihydroxide (Prati and Martra, 1999; Xu et al., 2012b). Other supports, e.g. carbon, silica dioxide (SiO<sub>2</sub>), and tungsten trioxide, cannot obtain well dispersed and small size of AuNPs by using this method (Chen et al., 2006). Before reduction step, AuNPs are partially deposited on the supports. Hence, the loading of Au may be incomplete, but much higher than CP method (mentioned as follows) (Khoudiakov et al., 2005). Besides, the most attractive merit of DP is that AuNPs can deposit on supports with any kind of shapes, including powder, honeycomb, bead, or thin film (Torres et al., 2016). AuNPs are mostly deposited on the surface of supports, which contributes to the catalytic performance of Au nanocatalysts.

### 2.2. Co-deposition

Similar with DP, CP uses an aqueous solution of Au salt. The Au salt is mixed with a corresponding metal salt precursor and stirred under a certain temperature. The precipitant is added to obtain hydroxide or carbonate coprecipitate. After that, the slurry is filtered, washed, and dried. Finally, the precursor is calcined for AuNPs reduction as DP method (Waters et al., 1994). The difference of CP and DP is the mixture of reaction. In this regard, CP also can be called the one-step synthetic method. The Au particles are regularly dispersed and in nanoscale but the particle size may be increased during calcine as the DP method and the size is difficult to control sometimes. This procedure requires the precursor compound of support to become hydroxide or carbonate, which can be deposited with Au(OH)<sub>3</sub> at the step of deposition (Solsona et al., 2009).

### 2.3. Impregnation

IMP is the simplification of DP and CP. It is unnecessary to adjust the pH, namely, there is no need to add alkali salts as the precipitant (Solsona et al., 2006). When the Au source salts injected into the dried support, after technical filtration, washing and drying in appropriate temperature, the resulting catalysts are further calcined in a flow of O<sub>2</sub> or H<sub>2</sub> (Grisel et al., 2001). IMP is much simpler and usually used to prepare Au nanocatalysts which need certain mechanical strength rather than high content of active component. As a result, it has been widely used in industry. However, the low content of active component is not conducive to catalytic reaction. It is reported that this is commonly related to the size and size distribution. But there are evidences demonstrate that the low activity of MIP is due to the lack of some kind of interaction between AuNPs and support (Lin and Vannice, 1991; Lin et al., 1993). Additionally, the pH of Au salts solution is always very low, so this method is not so suitable for some supports which can be dissolved in a strong acidic solution, e.g. Al<sub>2</sub>O<sub>3</sub> and magnesium oxide (MgO).

### 2.4. Colloid deposition

CDP method, also called the immobilization method, is theoretical different with these traditional methods mentioned above. Generally, AuNPs are reduced first by appropriate methods, e.g. Turkevich-Frens and Brust-Schiffrin method, to obtain colloids rather than load on the support through sintering and reduction. Thus, the size can be well controlled by this method. Subsequently, the prepared AuNPs are injected into the support or the support is dipped into the AuNPs solution for

incubation a few days until AuNPs are completely adsorbed by support. Resulting catalyst is finally prepared by filtering, washing, and drying. The key procedure lies in the adsorption of AuNPs by support. In this case, the support should have large surface area with strong adsorption ability and can be washed so clean that it would not induce aggregation of AuNPs. With this respect, the adsorption of AuNPs into gel has been well developed. A typical example is the silica gel. [Tai et al. \(2001\)](#) prepared an Au cluster/SiO<sub>2</sub> nanocomposite catalyst by spontaneous wet-gel formation. Results demonstrated that the colloids were penetrated into the gel and were adsorbed only on the surface of the gel due to the reaction between gel and polar solution. The anchoring of AuNPs was because the surrounding thiol molecules of AuNPs had a permanent dipole moment, which induced the dipole interaction. In addition, the particle sizes and size distribution were not changed. On the basis of this mechanism, thermally stable and highly loaded AuNPs/TiO<sub>2</sub>-coated SiO<sub>2</sub> aerogels are prepared with the controlled size and loading amount of Au ([Tai et al., 2004](#); [Tai and Tajiri, 2008](#)).

Other supports, e.g. metal-oxide particles ([Nutt et al., 2006](#); [Zheng and Stucky, 2006](#)), activated carbon (AC) ([Biella et al., 2002](#)), mesoporous carbon (MC) ([Ma et al., 2013](#)), oxidized mesoporous carbon (OMC), carbon nanotubes (CNTs), and graphite (GR) ([Qi et al., 2015](#)) have been well developed for supported Au nanocatalysts synthesis using both weak and strong interactions. In particular, the adsorption way of MC or OMC-supported Au nanocatalysts is that AuNPs with small size are incorporated into the larger size of mesopore channels thus preventing the aggregation of AuNPs. In addition, the stabilizer plays an important role in the size and catalytic performance ([Shi et al., 2008](#); [Zhong et al., 2013](#)). Robert group has developed a series of experiments about the *n*-hexanethiolate-stabilized AuNPs catalysts supported by metal oxide. Results showed the size of AuNPs increased during subsequent thermolysis ([Almukhlifi and Burns, 2015a](#)). The length of *n*-hexanethiolate and Au content had influences on the catalytic performance of Au nanocatalysts ([Almukhlifi and Burns, 2015b, 2016a](#)). Furthermore, the presence of small amount of sulfate enhanced the catalytic activity owing to an Au-enhanced Mars-van Krevelen mechanism ([Almukhlifi and Burns, 2016b](#)).

### 2.5. Newly developed methods

The aforementioned methods for Au nanocatalysts preparation are traditional and mainly applied in some simple supports and the size and size distribution may be difficult to control. In this case, for the controlling of size and size distribution and some relatively complicated supports and structure like polyhedral anatase, Au@oxide/yolk@shell nanospheres, some novel methods including polyols reduction ([Yang et al., 2013](#)), photo- and electro-deposited method ([Nguyen et al., 2016](#); [Wei et al., 2017b](#)), etc., have been well developed. The photo-deposited method is usually proposed by putting the mixture of supports and Au salt under the UV/vis irradiation and using methanol as the sacrificial agent ([Maicu et al., 2011](#)). Other photo-deposited method like pulsed laser ablation was also developed ([Wei et al., 2017a](#); [Xu et al., 2014](#)). This method is suitable for the preparation of photocatalyst, in which the supports have good photocatalytic activity and AuNPs are easy to deactivate in air when using other methods. Pulse electrodeposition method is another newly developed method, in which the size and dispersion of AuNPs can be easily achieved via changing the electrochemical parameters. The prepared Au nanocatalyst by this method exhibits excellent plasmon-induced photoelectrocatalytic activity ([Wu et al., 2015a](#)). Au nanocatalysts synthesized by photo- and electro-deposition only need one-step and do not need the use of surfactant or additive. The catalytic activity of them is improved by making use of the plasmonic effect of AuNPs, which is conducive to the application of Au nanocatalysts in photoelectrocatalysis. But the introduction of light energy or electricity is necessary.

Au@oxide/yolk@shell nanospheres provide good catalytic performance because of their low density, high specific surface area, stability,

and selectivity. They can propose promising application on selective catalysis by controlling the pore size of the shell accurately. However, this kind of Au nanocatalyst is usually prepared by using etching or template method, which are suitable for single oxide shell. Interestingly, the group of Zhang ([J. Li et al., 2018](#)) recently has proposed a new strategy for preparation of Au@multi-oxide/yolk@shell nanospheres system by integrating redox self-assembly and redox etching process. This simple strategy provides new avenue for facile and clean synthesis of complex noble metal@multi-oxide/yolk@shell nanospheres. Although these newly developed methods illustrated here are mainly for photocatalysis or other catalytic processes, they are still instructive for the preparation of highly efficient Au nanocatalyst and guidance of nitroaromatics reduction reaction.

## 3. Mechanism of catalytic reaction

### 3.1. Kinetic model

The traditional Langmuir–Hinshelwood (LH) model is usually used in the kinetic analysis of nitroaromatics reduction by Au nanocatalysts. Namely, all of the reactants are absorbed on the surface of AuNPs to react. Kinetic data can be obtained by monitoring the concentrations of nitroaromatics via UV–vis spectroscopy. The subsequent data calculation yields the apparent reaction rate,  $k_{app}$ , one of the most important parameters to assess the catalytic property of Au nanocatalysts. The analysis of kinetic data has been well described by [Wunder et al. \(2010\)](#), who used the reduction of 4-nitrophenol (4-NP) as a model reaction to test the catalytic activity of Au/platinum (Pt) NPs ([Fig. 1](#)). They proposed a series of studies by immobilizing AuNPs on the spherical polyelectrolyte brushes and demonstrated that  $k_{app}$  was not only concerned with the total surface of all AuNPs ( $S$ ), but also the rate-determining step, as well as the adsorption constants of 4-NP and borohydride ( $K_{4-NP}$  and  $K_{BH_4}$ ). Moreover, as  $k_{app}$  is strictly proportional to  $S$  ([Panigrahi et al., 2007](#); [Saha et al., 2009](#)), the relations are well depicted as the following equations ([Wunder et al., 2011](#)):

$$\frac{dC_{4-NP}}{dt} = -k_{app} \cdot C_{4-NP} = -k_1 \cdot S \cdot C_{4-NP} \quad (1)$$

$$k_{app} = \frac{k \cdot S \cdot K_{4-NP}^n \cdot C_{4-NP}^{n-1} \cdot K_{BH_4} \cdot C_{BH_4}}{(1 + (K_{4-NP} \cdot C_{4-NP})^n + K_{BH_4} \cdot C_{BH_4})^2} \quad (2)$$

where  $S$  is the total surface of all AuNPs,  $n$  is the Langmuir–Freundlich exponent and when using the classical Langmuir isotherm, the value of  $n$  is 1 ([Gu et al., 2014](#)). Another important parameter, which implies the catalytic activity, is the normalized rate constant ( $k_{nor}$ ). It is associated with the amount of Au nanocatalyst and  $k_{app}$ , i.e.,

$$k_{nor} = k_{app}/m. \quad (3)$$

With this respect, almost all of the researches demonstrate that Au dependent catalysis of nitroaromatics reduction is well accorded with the pseudo-first-order kinetics; that is, the logarithm of absorption intensity of 4-NP ( $A_t$ ) has a good linear correlation with reaction time ( $t$ ), then  $k_{app}$  can be determined from the plot of  $\ln(A_t)$  vs  $t$  ([Que et al., 2015](#); [Ramirez et al., 2017](#)).

$$\ln(A_t/A_0) = -kt \quad (4)$$

Interestingly, there are several evidences proved that the reduction of nitroaromatics by Au nanocatalysts may fit the zero-order kinetic model; i.e. the  $A_t$  rather than  $\ln(A_t)$  varies linearly with  $t$  ([Gupta et al., 2014](#); [Saha et al., 2009](#)). They believe that this is due to the different rate-determining steps. [Gupta et al. \(2014\)](#) presented the six sequential electron transfer had critical role on this rate-limiting step. However, they did not provide any experimental data to support the

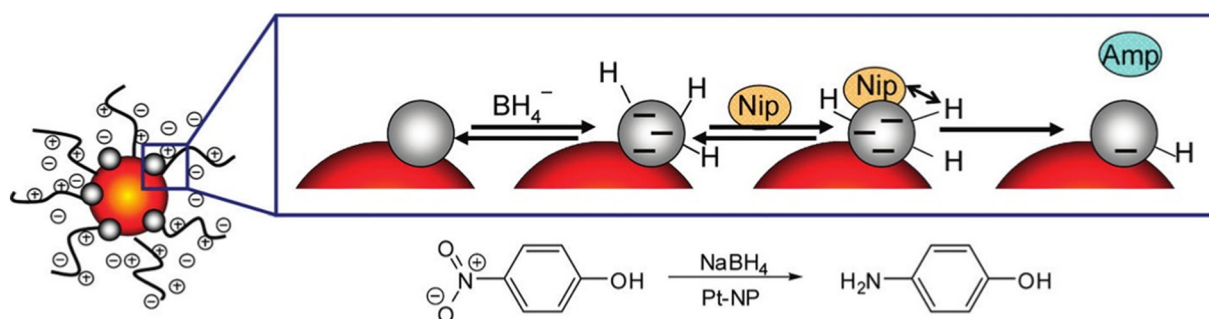


Fig. 1. Langmuir–Hinshelwood model for reduction of 4-NP by Au/Pt NPs catalysis. Adapted with permission from ref. (Wunder et al., 2010) Copyright 2010 the American Chemical Society.

speculation. While some studies considered that with the excess of both Au nanocatalysts and sodium borohydride ( $\text{NaBH}_4$ ), the reaction rate was the pseudo-first-order (Lee et al., 2008; Pozun et al., 2013). In any case, there may be some other factors result in the different kinetic reaction, such as temperature, supports, concentration of reactants, etc. This should be further investigated. One relatively clear thing is that the group of Ballauff has demonstrated that the second step, i.e. the reduction of the 4-hydroxylaminophenol is the rate-determining step (Gu et al., 2014). The reduction of the 4-hydroxylaminophenol is involved in the route of reduction reaction, so it will be discussed in Section 3.2.

### 3.2. Route of reaction and possible mechanism

The reductants type and effect on this reaction has been well introduced by Kadam and Tilve (2015). Hence, in this part we just discuss the reaction triggered by  $\text{H}_2$  and borohydride. In order to understand the mechanism better, researchers begin paying their attention to the investigation of route of reaction since Haber proposed that there were two probable routes for reduction of nitroaromatics by Au nanocatalysts, which used  $\text{H}_2$  as the reductant to attack the nitro group to form corresponding amino group (Fountoulaki et al., 2014; Layek et al., 2012). One is the generally accepted direct route and another is the condensation route. In the direct route, the nitroso compounds are reduced firstly, and then the corresponding hydroxylamine is fast consecutively produced. Finally, the corresponding aniline derivatives are generated in the rate determining step (Fig. 2). The whole process is very fast and relatively simple. While in the condensation route, the azoxy compounds are synthesized after combining one molecule of nitroso compound and hydroxylamine respectively. The corresponding aniline derivatives can be obtained after a series of steps to azo and hydrazo (Fig. 2). Obviously, the condensation route is much more

tedious. As the reaction of nitroaromatics reduction by Au nanocatalysts is always fast, some researchers are skeptical about this conclusion. Thus, confirmatory experiment has been proposed based on supported Au nanocatalysts. Corma et al. (2007) elaborated on the reduction of nitroaromatics by Au/ $\text{TiO}_2$  catalyst and perfectly proved this reduction process followed the direct route. However, in these processes, the reduction of nitroaromatics was proposed by  $\text{H}_2$  as the reductant, the process using  $\text{NaBH}_4$  is different.

Based on the LH model, Layek et al. (2012) proposed a probable surface reduction mechanism making use of Nano Active™ Magnesium Oxide Plus (NAP)-Mg-Au(0) catalyst for reduction of nitroaromatics by  $\text{NaBH}_4$  (Fig. 3). To verify the reaction pathway, possible intermediates were separately subjected to the reduction process. Results showed that the direct route including nitrobenzene  $\rightarrow$  nitrosobenzene  $\rightarrow$  phenylhydroxylamine  $\rightarrow$  aniline was the most possible route. In addition, the authors introduced that the possible reduction mechanism laid the foundation for the six electron transfer process. AuNPs reacted with borohydride ions to form an Au-H complex firstly. Then, the targets adsorbed on the surface of AuNPs and a hydrogen transfer occurred. Finally, the nitro group was reduced to amino group. In 2014, Gupta et al. (2014) proposed a six-electron transfer process between  $\text{NaBH}_4$  and nitrophenol compounds, but how did the electron transfer was not reported. Recently, a paper based on the magnetic Ni-Au/graphene nanocomposites introduced that the transition metal composited had the ability to catalyze hydrolysis of  $\text{NaBH}_4$  (Li et al., 2017). The  $\text{NaBH}_4$  reacted with  $\text{H}_2\text{O}$  to form activated hydrogen ( $\text{H}_2$ ) and then the metal-hydrogen species formed on the surface of catalyst. Finally, these active metal-hydrogen species attacked 4-NP to reduce it. In conclusion, no matter reducing by  $\text{H}_2$  or  $\text{NaBH}_4$ , the critical step is the attack of  $-\text{NO}_2$  by hydrogen. AuNPs play important role to transfer and promote the attack. Recently, Wang et al. (2017a) concluded the same

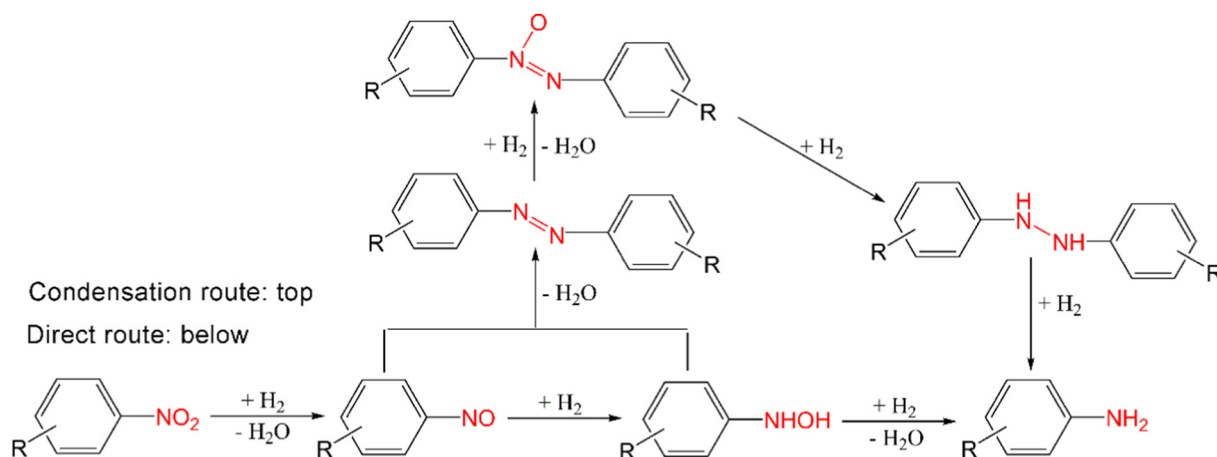


Fig. 2. Mechanism illustration for direct and condensation route of nitroaromatics reduction by Au nanocatalysts and  $\text{H}_2$ .

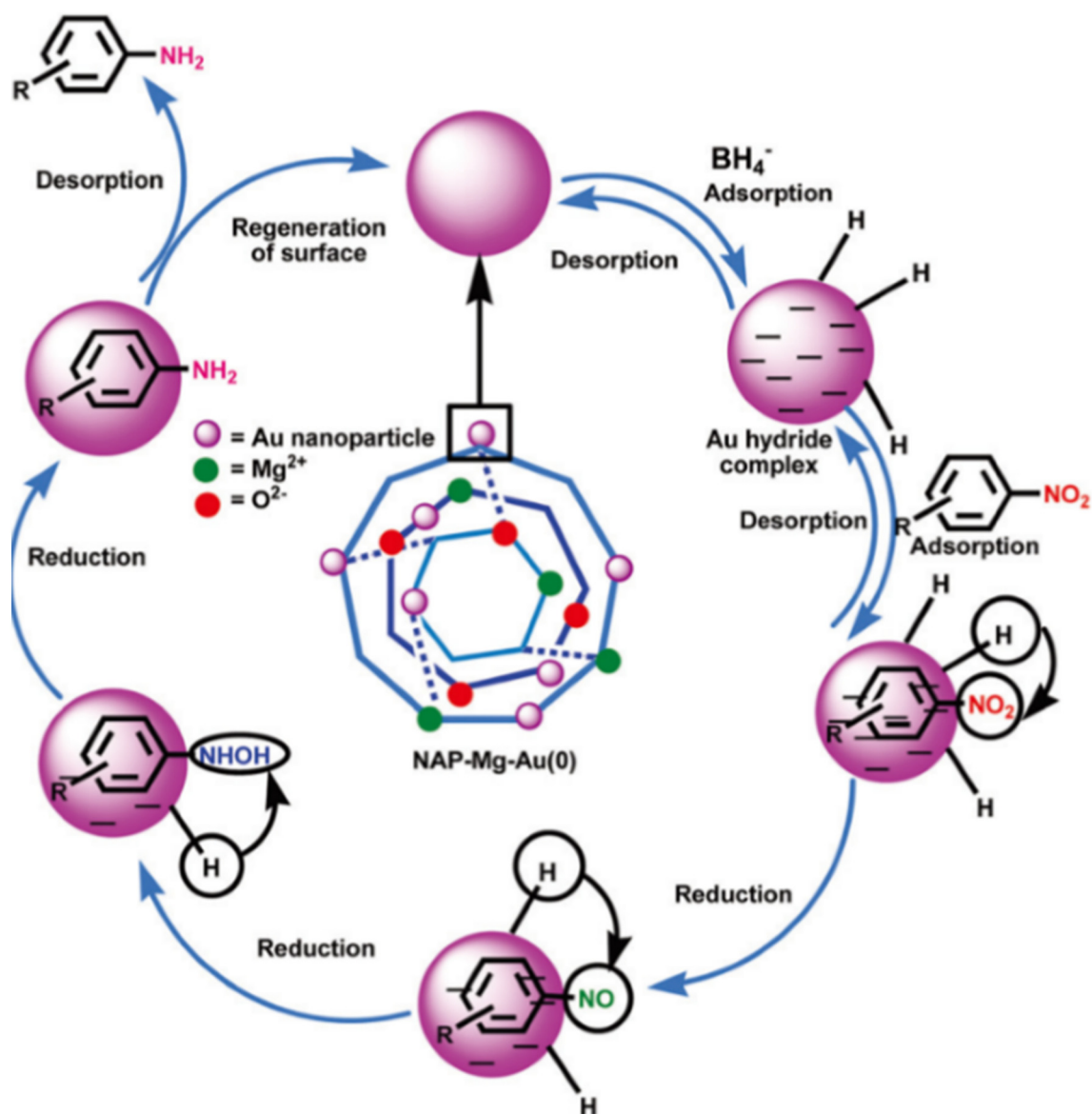


Fig. 3. Reaction mechanism for reduction of nitroarene by (NAP)-Mg-Au(0) catalyst. Adapted with permission from ref. (Layek et al., 2012) Copyright 2012 the Royal Society of Chemistry.

route as Layek et al. for reduction of nitroarenes by SiO<sub>2</sub>-supported Au nanocatalyst. However, different results were proposed by Fountoulaki et al. (2014), in which the nitrosoarene intermediates were skipped following the routes of nitroarene → aryl hydroxylamine → aniline. In addition, Noschese et al. (2016) found that both the direct and condensation routes were possible on the basis of a nanoporous polymer matrix supported Au nanocatalyst, but the condensation route was preferred when the Au active sites were more accessible.

Interestingly, when exposed to light, the catalytic mechanism changes. As described by Koklioti et al. (2017), the presence of photoillumination yields an electron-hole pair, and therefore increases the density of active sites on the surface of Au clusters, resulting in enhanced catalytic performance for 4-NP reduction. There are three possible ways that can cooperate to the reduction of 4-NP: i) common hydride transfer from Au—H bond both in the absence and presence of light; ii) specific hydride transfer by photoinduced Au—H bond; iii) active hydrogen generated via photoreduction of water (Fig. 4). In addition, the photogenerated electrons may also play an important role in the enhancement of catalytic performance. As introduced by a recent paper (Fu et al., 2017), under the exposure of visible light, electrons in the valence band of support were excited to the conduction band (CB),

resulting in rapid electron transfer from CB of support to AuNPs. This makes AuNPs store abundant electron. With the continuously increasing of electron density, the Fermi level of them becomes more negative potential, thereby further improving the catalytic activity.

As we all know, the reduction of nitroaromatics by Au based-nanocatalysts are almost proposed in aqueous medium at ambient temperatures because most of them use NaBH<sub>4</sub> as the resource of H<sub>2</sub>. However, the reaction proposed by other metal nanocatalysts such as nickel (Ni) based-nanocatalysts has been proceeded in other medium. For example, Xia et al. (2016) introduced a carbon black supported nano-Ni catalyst for reduction of 4-NP and compared the catalytic performance of it under different medium. The results showed that the catalyst exhibited higher activity in methanol than that in aqueous solution because the methanol-NaBH<sub>4</sub> reaction system generated much more amount of H<sub>2</sub> than the water-NaBH<sub>4</sub> system. Inspired by this, we also investigated the effect of reaction medium by using methanol and ethanol as the medium and found that the generation of H<sub>2</sub> was very less in these medium. We speculate this is because NaBH<sub>4</sub> is less soluble in methanol and ethanol. In addition, the nitrophenol reduction in most cases is proceeded by nitrophenolate ion which is mainly prompted in aqueous medium. This also maybe the reason that most researchers

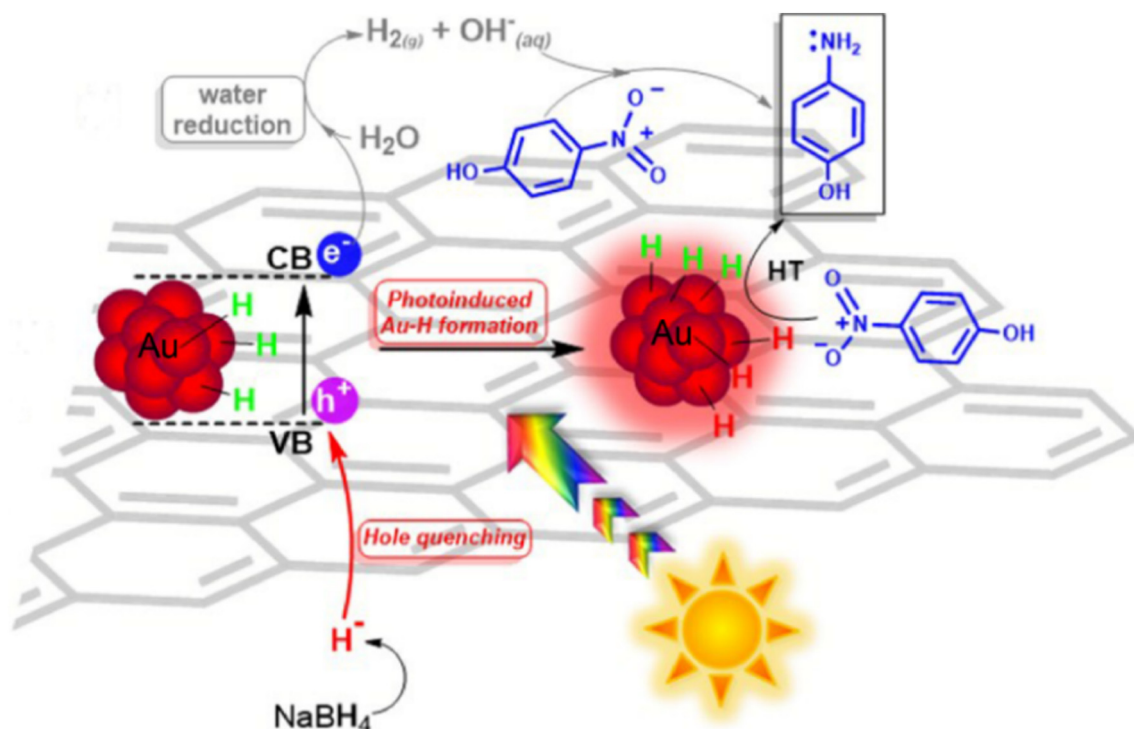


Fig. 4. Mechanism illustration for reduction of 4-NP under the illumination of light. Adapted with permission from ref. (Koklioti et al., 2017) Copyright 2012 the Royal Society of Chemistry.

have chosen the reaction in aqueous medium. Thus, the illustrated studies for reduction by Au nanocatalysts in this review are almost proposed using  $\text{NaBH}_4$  as the reductant.

#### 4. Reduction of nitroaromatics with free AuNPs: size-dependent effect

Free AuNPs for reduction of nitroaromatics have been investigated for many years. The study of catalysis by free AuNPs mainly focuses on the influence of size and synthetic method. Generally, the catalytic activity is enhanced for smaller size of AuNPs. But the catalytic activity is also related to the surface area and mass of particles. For example, Sau et al. (2001) investigated the effect of particle size with the range of 10–46 nm under the same surface area and found that the catalytic rate of eosin reduction did not increase proportionately with the increase of size. It decreased first in the size range of 10–15 nm and then increased with the size over 15 nm. Thus, we discussed the catalytic activity of free AuNPs by the synthetic methods and stated the size effect systematically.

##### 4.1. Extract of biomass stabilized free AuNPs

Bioreduction of metal ions in organism, such as plants, fungi, and bacteria is regarded as an eco-friendly, low cost, and highly efficient way and is important for biomedical application. Plants reduced AuNPs are mostly used in sensors, while Sharma et al. (2007) firstly reported plant-mediated AuNPs for directly reducing 4-NP. Unlike other biological methods, the synthesis of AuNPs by the stem extract of *Breynia rhamnoides* is very fast and the size of that can be tuned (Gangula et al., 2011). Recent researches for bioreduction of AuNPs used in catalysis primarily lie in the extract or some parts of them, including dextrose (Badwaik et al., 2011), mycelia (Narayanan and Sakthivel, 2011), protein (Guria et al., 2016; Shi et al., 2015), and membrane-bound peptides (Srivastava et al., 2013) etc. Most of the results proved that the catalytic rates increased with the size decrease (Badwaik et al., 2011; Zhu et al., 2016). It is noteworthy that the size

and shape controlled synthesis of AuNPs is always achieved a seed mediated grown approach by using some chemical agents. But a research reported by Das et al. (2012) has introduced a simple one-pot green method for biosynthesis of AuNPs and obtains super high catalytic rate for 4-NP reduction with the range of  $8.6 \times 10^4$ – $2.6 \times 10^6 \text{ min}^{-1}$  by controlling the size and shape. The catalytic rate it achieved is much higher than the other methods (Table 1). Particularly, the increasing catalytic rate can be induced by the decrease of the particle size which could be obtained by adjusting the  $\text{HAuCl}_4$ –extract ratio. Except the size and biomass, the concentration of AuNPs plays an important role in catalytic performance. As illustrated by Qu et al. (Shen et al., 2017b), the reaction rate constant was linearly related to the concentration of AuNPs, which resulted in an increase rate from  $0.59 \text{ min}^{-1}$  to  $1.51 \text{ min}^{-1}$  with the increasing AuNPs concentration of  $1.46 \times 10^{-6}$  to  $17.47 \times 10^{-6} \text{ mmol}$ .

##### 4.2. Gel and other ligands stabilized free AuNPs

Hydrogels, with tunable structure, are excellent carrier for easy aggregated nanoparticles, especially AuNPs (Kong et al., 2016). The obtained AuNPs–hydrogel nanocomposites have unique property of both metal NPs and hydrogels, which are appealing in terms of green catalysis (Wang et al., 2017c). For example, Zinchenko et al. (2014) prepared well dispersed and spherical AuNPs with small size of 2–3 nm by injecting the Au precursor into a DNA hydrogel, which allowed for the reduction of  $\text{HAuCl}_4$ . The DNA hybrid hydrogel containing AuNPs provided highly catalytic activity in the reduction of 4-NP to 4-aminophenol (4-AP) with  $k_{\text{app}}$  of  $0.09 \text{ min}^{-1}$ . Some biocompatible molecules such as chitosan can be prepared as hydrogel. However, AuNPs are difficult to reduce by this system. Hence, an in-situ photoreduction method for producing AuNPs in chitosan– $\text{Au}^{\text{III}}$  hydrogel system was reported (Wu et al., 2015b). In particular, this strategy had good catalytic performance for reduction of 4-NP to 4-AP with following a pseudo-first-order kinetics.

Cetyltrimethylammonium bromide (CTAB), a well-known surfactant, can be used as a stabilizer for AuNPs synthesis (Li et al., 2014).

**Table 1**  
Comparison of some typical strategies for reduction of 4-NP using free AuNPs.

Type of composition	Composition	Particle size (nm)	$k_{app}$ ( $\text{min}^{-1}$ )	Concentration of catalyst (mM)	$k_{nor}$ ( $\text{min}^{-1} \text{mM}^{-1}$ )	Ref.
Bacteria stabilized AuNPs	<i>Breynia rhamnoides</i>	25	0.552	–	–	(Gangula et al., 2011)
	<i>Escherichia coli</i> bacterium	10	0.210	–	–	(Badwaik et al., 2011)
	<i>Escherichia coli</i> K12	50	0.014	0.0042	3.33	(Srivastava et al., 2013)
	<i>Shewanella haliotis</i>	<10	0.654	0.005	130.8	(Zhu et al., 2016)
Fungi	<i>Cylindrocadium floridanum</i>	25	0.027	0.0051	5.29	(Narayanan and Sakthivel, 2011)
	<i>Rhizopus oryzae</i> protein extract	5–65	$2.60 \times 10^6$ – $4.99 \times 10^9$	0.0101	$2.57 \times 10^8$ – $4.94 \times 10^7$	(Das et al., 2012)
	<i>Pycnoporus sanguineus</i>	6.07	0.066	0.019 mg	3.47 $\text{mg}^{-1}$	(Shi et al., 2015)
	<i>Fusarium</i> sp. MMT1 strain.	30.6	0.102	–	–	(Guria et al., 2016)
	<i>Trichosporon montevidense</i>	12	1.5	0.0015	1000	(Shen et al., 2016)
	<i>Aspergillus</i> sp. WL	4.4	9.8–25.2	0.58	16.9–43.45	(Shen et al., 2017b)
		28.4	10.6	3	3.53	(Qu et al., 2017)
						(Zinchenko et al., 2014)
Gel	DNA hydrogel	2–3	1.5	100 mg	0.015 $\text{mg}^{-1}$	(Wu et al., 2015b)
	Hydrogels	–	2.6	0.005	520	(Fenger et al., 2012)
Others	CTAB	13	6	0.25	24	(Guadie Assefa et al., 2017)
	Olibanum gum	3±4	5.8	–	–	(Bhosale et al., 2017)
	Dimethyl sulfoxide	15–40	5.4	–	–	

CTAB stabilized AuNPs were successfully fabricated for reduction of 4-NP and demonstrated an intermediate size (13 nm) of AuNPs exhibited highest reaction rate, which was 60 times higher than the biggest one (56 nm) (Fenger et al., 2012). Generally, smaller AuNPs propose higher catalytic performance, while the intermediate size of AuNPs is more active than the seeds AuNPs (Nigra et al., 2013). This might be due to the convergence of increasing surface area of AuNPs versus the size of molecule and charge transfer during the reduction process. Besides, seeds AuNPs were too small to efficiently absorb 4-NP. The adsorption process of nitroaromatics was accompanied by a significant charge-transfer from the surface of AuNPs to the N-atom of nitroaromatics. Thus, the charge-transfer played very important role in reduction of nitroaromatics by Au nanocatalysts. The mechanism of this process needs to be further investigated in the future. In conclusion, reducing AuNPs by biomass is fast and green. The size of them can be controllably varied (Gangula et al., 2011).

## 5. Reduction of nitroaromatics with supported AuNPs: structure-dependent effect

Easy aggregation of free AuNPs results in much loss of catalytic activity, so researchers tend to anchor them on the carrier to retain the catalytic activity and recyclability of AuNPs. The supports, including polymer, oxide, carbon, as well as the combination of them, have been well developed to anchor AuNPs with good dispersion, large loading amount, and narrow size distribution. In this part, we discuss some critical and new studies developed recently, concerning different carrier supported Au nanocatalysts (Table 2-5).

### 5.1. Polymer

The research on polymer supported AuNPs mainly follows three directions: i) different shapes which provide different active sites; ii) different kinds of polymers which offer different ligands or functional group; iii) different synthetic routes of supported Au nanocatalysts which achieve several sizes of AuNPs. Different shapes of polymer, e.g. dendrimer, brushes, beads, micelles, nanotubes, flowers, and stars are used for synthesis of supported Au nanocatalysts (Table 2). In the early years, most of these structures preferred to make AuNPs encapsulate into the polymer networks, rarely on outside, which restricted the contact between nitroaromatics and AuNPs in some degree (Wang et al., 2007). Interestingly, Haruta and co-workers (Kuroda et al., 2009) developed a deposition reduction method that directly deposited








AuNPs on the surface of poly(methyl methacrylate) (PMMA) beads with 6.9 nm average size of AuNPs. This reported Au nanocatalysts provided a highest rate constant of  $0.432$ – $0.474 \text{ min}^{-1}$  among ever reported Au/polymers catalysts. In addition, this report proposed the importance of moderate interaction between polymer supports and AuNPs, which indicates the structure-dependent effect. Hence, many research groups have concentrated their attention on deposition sites of AuNPs and structure of polymers. For example, Qiu et al. (2012) successfully prepared an efficient electrocatalyst, polypyrrole nanotube (PPyNTs)-supported AuNPs, for catalytic reduction of 4-NP. Hu et al. (2017) carried out a hyperstar polymer-Au<sub>25</sub>(SR)<sub>18</sub> nanocomposite for 4-NP reduction using hyperbranched copolymers as macroinitiators to polymerize the polymer. This obtained hyperstar-Au<sub>25</sub>(SR)<sub>18</sub> catalyst showed great stability and convenient recovery and could be reused without losing any catalytic efficiency.

Some polymers, such as poly(amidoamine), poly(propyleneimine), poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA), and poly(glycidyl methacrylate), etc., are well reported for reducing and stabilizing AuNPs. Most interests concern the catalytic performance of different polymers supported AuNPs, but speculation is starting concerning the reactions between AuNPs and the ligands of polymer. For instance, Zeng et al. (2013) developed a polydopamine (PDA)-encapsulated magnetic microspheres supported Au nanocatalyst for catalytic reduction of nitrobenzene on the basis of interaction between PDA and AuNPs. The strong combination of AuNPs and —NH<sub>2</sub> of PDA made AuNPs be well reduced and dispersed. It is reported that some ligands such as —SH, —NH<sub>2</sub>, —OH, etc., have an effect on the properties of AuNPs surface, thus affecting the available free active sites (Ansar and Kitchens, 2016; Menuel et al., 2016). In addition, the catalytic performance is significantly related to the loading amount of AuNPs. Chen group demonstrated a raspberry-like polymer composite sub-microsphere with tunable AuNPs coverage for 4-NP reduction (Liu et al., 2013). The results indicated this model reaction followed the pseudo-first-order reaction kinetics, but the study of kinetics was probably oversimplified. Therefore, they further developed this mechanism and investigated the effects of many factors (Fig. 5) (Li and Chen, 2013).

Deposition of AuNPs on polymer is important for synthesizing well dispersed Au nanocatalysts. There are two routes for depositing AuNPs on polymer, the direct one and indirect one. The two routes are all based on the formation of polymer supported core-shell structure or brushes. The direct one deposits AuNPs on polymer carrier using NaBH<sub>4</sub> or other weak reducing agent. The ligands or functional groups of polymer molecules play very important role in the formation of



**Table 2**  
Different shapes of typical polymer-supported Au nanocatalysts.

Shape	Schematic	Preparation procedure	Particle size (nm)	Ref.
Dendrimer		i. Graft dendrimer on the surface of silica; ii. Reduce AuNPs on dendrimer-modified silica by NaBH <sub>4</sub> ; iii. Self-assemble with polyelectrolytes and remove silica cores.	2.3 ± 0.8	(Wu et al., 2006)
Brush		i. Functionalize SiO <sub>2</sub> NPs with APTES to provide amino groups; ii. Graft PDMAEMA onto them with SIPGP; iii. Reduce AuNPs onto the PDMAEMA brushes.	3.0	(Chen et al., 2014a)
Bead		i. Prepare AuNPs of different size using Frens method; ii. Immobilize prepared AuNPs into the resin beads.	20	(Panigrahi et al., 2007)
Micelle		i. Synthesize block copolymer by ATRP; ii. Prepare core-corona micelles and micelle supported-AuNPs by NaBH <sub>4</sub> reduction.	2–4	(Wang et al., 2007)
Nanotube		i. Synthesize PPyNTs by a self-degraded template method and ILS/PPyNTs; ii. Reduce AuNPs on the ILS/PPyNTs and by NaBH <sub>4</sub> to form Au/ILS/PPyNTs hybrids and Au/PPyNTs hybrids.	5.7	(Qiu et al., 2012)
Flower		i. Prepare BP; ii. Synthesize hybrid BP–AuNPs by deposition reduction approach;	5.5 ± 1.7	(Matsushima et al., 2012)
Star		i. Synthesize MAOELP and microemulsion copolymerize inimer BIEM with it; ii. Prepare hyperstar polymer by polymerization; iii. Form HS-Au <sub>25</sub> (SR) <sub>18</sub> nanocomposites via ligand exchange.	–	(Hu et al., 2017)

APTES: 3-aminopropyltriethoxysilane; PDMAEMA: Poly(2-(dimethylamino) ethyl methacrylate); SIPGP: self-initiated photografting and photopolymerization; ATRP: atom transfer radical polymerization; PS-PBIEM: polystyrene-polymerizing 2-(2-bromoisobutyryloxy) ethylmethacrylate; PPyNTs: polypyrrole nanotubes; ILS: ionic liquids; BP: boronate microparticles; MAOELP: 2-methacryloyloxyethyl lipolate.

well-dispersed AuNPs by electrostatic conjunction of the negatively charged AuCl<sub>4</sub><sup>−</sup> or positively charged Au(en)<sub>2</sub><sup>3+</sup>. Thus the Au precursor salts should be chosen selectively. For example, Chen et al. (2014a) reported a smart hybrid system that AuNPs were absorbed by SiO<sub>2</sub>@PDMAEMA carrier and reduced by NaBH<sub>4</sub>. Recently, polystyrene/polyaniline/Au (PS/PANI/Au) composites were fabricated based on the electrostatic attraction between positively charged Au(en)<sub>2</sub><sup>3+</sup> and sulfonated PS particles (Sun et al., 2017). The sulfonated PS particles

can absorb more Au(en)<sub>2</sub><sup>3+</sup>, hence enhancing the amount of loaded AuNPs and exhibiting excellent catalytic performance with k<sub>app</sub> of 3.5196 min<sup>−1</sup>. Another way of depositing AuNPs on the carrier is AuNPs are prepared firstly by Frens or Brust methods, the definite sizes of AuNPs are absorbed by some ligands such as —SH and —NH<sub>2</sub> subsequently (Liu et al., 2013). This route provides tunable loading amount of AuNPs by changing the pH of solution and concentration of polymer and AuNPs. In addition, the catalytic performance can be

**Table 3**  
Details of different parameters and reaction conditions of oxides-based Au nanocatalysts for 4-NP reduction.

Catalyst type	Particle size (nm)	Amount of Au (μmol)	Amount of NaBH <sub>4</sub> (mmol)	Amount of 4-NP (μmol)	k <sub>app</sub> (10 <sup>−3</sup> s <sup>−1</sup> )	Reaction time (min)	Recycle	Ref.
Au@SiO <sub>2</sub>	104–43	1.6	1.2	3400	14–3.9	60	–	(Lee et al., 2008)
Au@hm <sup>a</sup> -ZrO <sub>2</sub>	6.3	25	12,000	6.8	5.17	12	4	(Huang et al., 2009)
AuNPs/SNTs	3–5	1	0.15	3.6	10.64	4.7	–	(Zhang et al., 2011b)
Au/SBA-15	2.5	0.133 g/L	0.4	30	17.42	4	5	(Miah et al., 2017)
AuAS	3.9	0.8 g/L	0.04	0.1	2.92	24	5	(Xing et al., 2017)
Au@meso-SiO <sub>2</sub>	2.5	0.05 mL 0.0125 wt %	0.025	0.0625	1.33	20	5	(Chen et al., 2014b)
Au/TiO <sub>2</sub>	–	1.5 g/L	0.036	0.6	2.83	20	–	(Li et al., 2015)
Dumbbell-like Au-Fe <sub>3</sub> O <sub>4</sub>	5	2 mg	0.016	0.4	10.5	5	6	(Lin and Doong, 2011)
flower-like Au-Fe <sub>3</sub> O <sub>4</sub>	10	–	–	–	6.33	6.67	–	–
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Au MNCs <sup>b</sup>	5	0.5 mg	0.2	0.25	14.2	4	9	(Zheng et al., 2013)

<sup>a</sup> hm, hollow mesoporous.

<sup>b</sup> MNCs, magnetic nanocomposites.

**Table 4**  
Comparison of different carbon-supported Au nanocatalysts for reduction of nitroaromatics.

Catalyst	Nitroaromatics	Structure	Particle size (nm)	$k_{app}$ (min <sup>-1</sup> )	$k_{nor}$ (s <sup>-1</sup> g <sup>-1</sup> )	Ref.
USP Au/C	4-NP	Encapsulated	33	0.600	1500	(Guo and Suslick, 2012)
Au/GR hydrogel	4-NP	Gel	14.6	0.190	31.7	(Li et al., 2012)
	MB		–	0.237	39.5	
CNFs@Au	4-NP	Core-shell nanofiber	–	0.325	54.2	(Zhang et al., 2013)
GO@NH <sub>2</sub> -Au NCS	4-NP	Nanosheets	14.0 ± 1.0	2.136	2967	(Ju et al., 2014)
Fe@Au-GO	4-NP	Core-shell	10–12	0.121	–	(Gupta et al., 2014)
	2-NP			0.120	–	
Au/AC	<i>m</i> -Dinitrobenzene	Nanowhisker	4	2.100	–	(Cárdenas-Lizana et al., 2015)
Au/MC-O	4-NP	Tube	10	0.465	0.1	(Guo et al., 2016)
Au/mSiO <sub>2</sub> @RGO	4-NP	Two-dimensional nanohybrid	3–5	0.900	37.5	(Maji and Jana, 2017)
	MB			0.726	30.25	
Au/g-C <sub>3</sub> N <sub>4</sub>	4-NP	–	2.6	0.479	7.99	(Fu et al., 2017)
Polydopamine-g-C <sub>3</sub> N <sub>4</sub> /Au	4-NP	–	25	3.084	10.28	(Qin et al., 2019)
Fe <sub>3</sub> O <sub>4</sub> @Carbon	4-NP	Core-shell	15.9	5.34	89	(Gong et al., 2018)

adjusted by using different size of AuNPs, which opens a new sight in reduction of nitroaromatics by Au nanocatalysts.

## 5.2. Oxides for lots of materials

### 5.2.1. SiO<sub>2</sub>

SiO<sub>2</sub>, a kind of very stable porous material, has been demonstrated as an ideal nonmetallic oxide support for encapsulation of metal NPs due to the confinement effect, offered by their unique properties of mesoporous channels structure, good thermal, and chemical stability (Xie et al., 2015; Zhao et al., 2016b). The way of encapsulated AuNPs in SiO<sub>2</sub> for nitroaromatics reduction can be divided into three channels: i) AuNPs are confined by SiO<sub>2</sub> to form yolk-shell or core-shell structure Au nanocatalyst, where SiO<sub>2</sub> is a microsphere; ii) AuNPs are deposited on the inside or outside the surface of SiO<sub>2</sub> nanotubes (SNTs); iii) AuNPs are embedded on the surface of SiO<sub>2</sub> microsphere (Fig. 6).

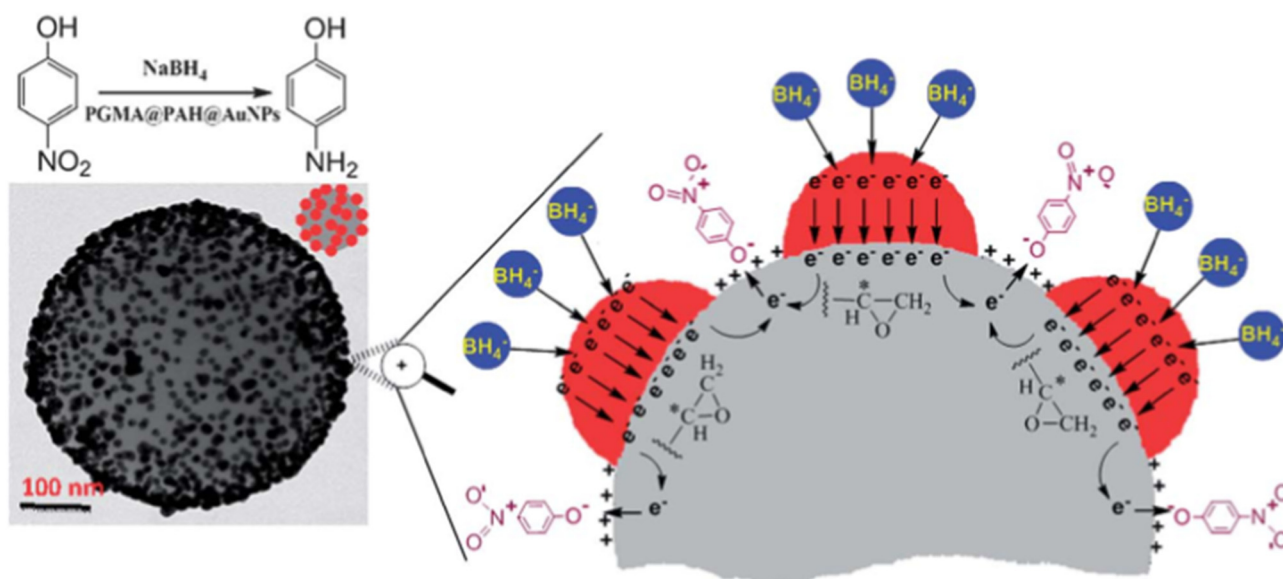
SiO<sub>2</sub> is always formed by a sol-gel process using tetraethyl orthosilicate (TEOS) as silica source. This procedure can be used in synthesizing Au@SiO<sub>2</sub> yolk-shell or core-shell structure. With this respect, Lee et al. (2008) introduced a nanoreactor framework for 4-NP reduction using Au@SiO<sub>2</sub> yolk-shell catalyst. The prefabricated-AuNPs were firstly coated by the shell thickness of SiO<sub>2</sub> through TEOS undergoing hydrolysis. Then the Au cores were selectively etched by different concentration of KCN, which provided different sizes of AuNPs. Thus the rate constants varied as the size of Au core changes. This designed framework was easily separated and dispersed and served as an efficient platform for nitroaromatics reduction. Different with this strategy, Huang et al. (2009) reported a similar strategy confining AuNPs in SiO<sub>2</sub>

shell, but the etched one was SiO<sub>2</sub> rather than Au core. In this case, each sphere only contained one AuNP. AuNP presented anywhere inside the hollow zirconia sphere, which allowed 4-NP access the active sites of AuNPs easily, thus further enhancing the catalytic performance. Similar with this design, a new core-shell Au@resorcinol-formaldehyde nanosphere based on multiple Au cores have been reported by Chen et al. (2014b) This catalyst exhibited uniform pore size (2.5 nm) of SiO<sub>2</sub> hollow nanospheres and good catalytic performance for 4-NP reduction with a reaction rate constant 0.08 min<sup>-1</sup>. The conversion percentage retained 94% after five cycles.

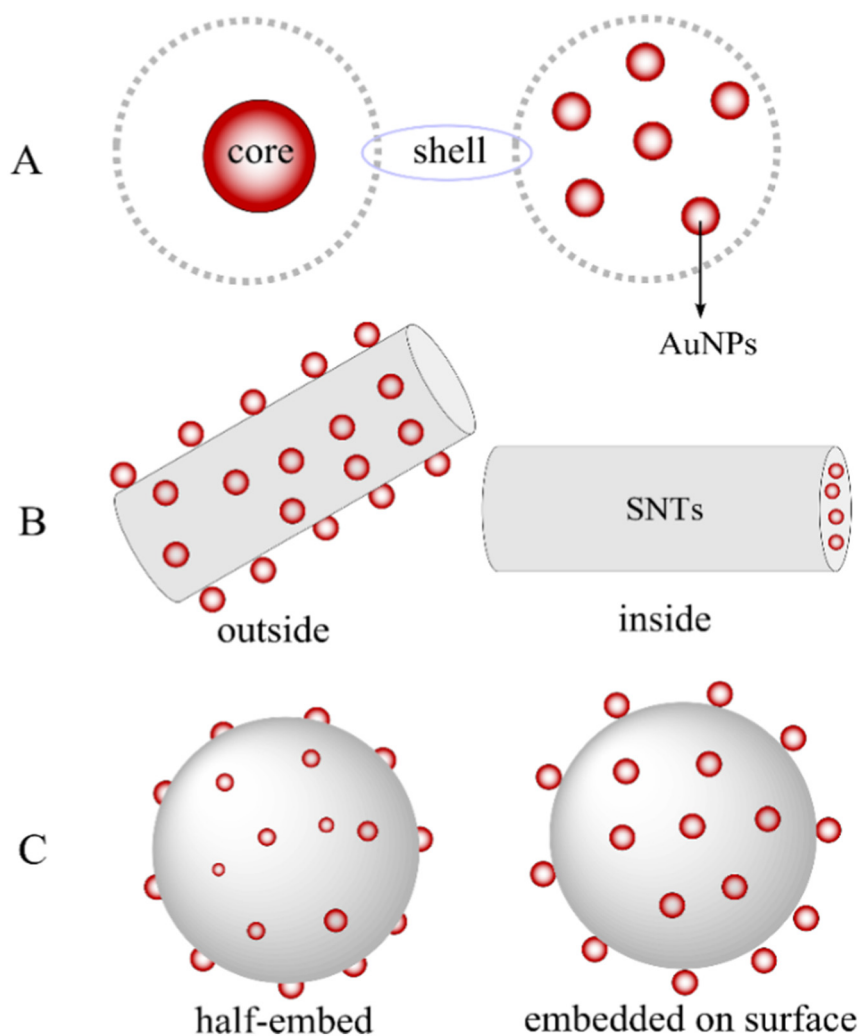
SNTs, providing a high surface area to volume ratio, are deemed as potentially good candidates for Au nanocatalyst supports. The deposited AuNPs onto the inside surface of SNTs are usually dispersed within the mesopore channels (Zhang et al., 2011b). Therefore, the pore diameter of SNTs should be big enough to accommodate encapsulated AuNPs and transit the reactant molecules. In addition, the loading amount of AuNPs has a great impact on the catalytic performance. A paper reported recently demonstrated that higher of the catalyst loading, the reaction time was faster (Miah et al., 2017). In this case, The  $k_{app}$  increased from 0.2187 to 2.587 min<sup>-1</sup> with the increase of Au loading from 0.033 to 0.167 g/L (Miah et al., 2017). Except for loading amount, other factors such as interaction between Au and supports, sites where AuNPs located, as well as reduction method are needed to further investigate (Xing et al., 2017). As shown in Fig. 7, two different synthetic methods of SiO<sub>2</sub>-confined Au nanocatalyst are proposed using calcine and grind, respectively. The calcined AuCS catalyst has much bigger size of AuNPs than the ground one (AuAS), thus results in lower catalytic performance for 4-NP and methylene blue (MB) reduction. Additionally,

**Table 5**  
Details of different parameters of Au-based multi-metal NPs for nitroaromatics reduction.

Catalyst	Molar ratio	Structure	Recycles	Nitroaromatics	$k_{app}$ (min <sup>-1</sup> )	$k_{nor}$ (s <sup>-1</sup> g <sup>-1</sup> )	Ref.
Ni@Au/SiO <sub>2</sub>	5:1	Core-shell dandelion	–	4-NP	0.498	307	(Le et al., 2014)
				2-Nitroaniline	0.282	174	
PtAu alloy/CeO <sub>2</sub>	1:1	Volcano	–	4-NP	6.522	2.174	(Zhang et al., 2014b)
Au-Ag/SiO <sub>2</sub>	6:1	Nanorods	–	Nitrobenzene	0.405	–	(Jayabal and Ramaraj, 2014)
PCP@Au-Ag	1:1	Core-shell	6	4-NP	0.1722	144	(Fu et al., 2018)
Au-Pd/GO	4.53:1	Flower	6	4-NP	–	–	(He et al., 2014)
PdAu/Fe <sub>3</sub> O <sub>4</sub>	1:1	Rod	8	4-NP	0.328	4.84	(Tuo et al., 2015)
Pt-Au/PDA@RGO	3:1	Dendrimer	6	4-NP	0.575	1700	(Ye et al., 2016)
Fe <sub>3</sub> O <sub>4</sub> @TiO <sub>2</sub> @Ag-Au	1:1	Core-shell	8	4-NP	0.115	3406.44	(Shen et al., 2017a)
Ni-Au/RGO	–	–	6	4-NP	0.662	36.77	(Li et al., 2017)
Au-Cu/RGO	3:1	–	–	4-NP	5.760	960	(Rout et al., 2017)
Pd/Au@g-C <sub>3</sub> N <sub>4</sub> -N	1:1	–	–	4-NP	0.791	52.72	(Fang et al., 2017)
Au@Pd@RuNPs	–	Porous	6	4-NP	1.452	–	(Sahoo et al., 2015)
				Congo red	1.494		
				Reactive red	0.804		
				Reactive black	5.694		



**Fig. 5.** Mechanism for reduction of 4-NP raspberry-like polymer supported Au nanocatalyst. Adapted with permission from ref. (Li and Chen, 2013) Copyright 2013 the Royal Society of Chemistry.



**Fig. 6.** Illustration of SiO<sub>2</sub> supported AuNPs for nitroaromatics reduction. (A) Core-shell structure of encapsulating one or many AuNP; (B) AuNPs are deposited on the inside or outside the surface of SiO<sub>2</sub> nanotubes; (C) AuNPs are half-embedded or combined on the surface of SiO<sub>2</sub> microsphere.

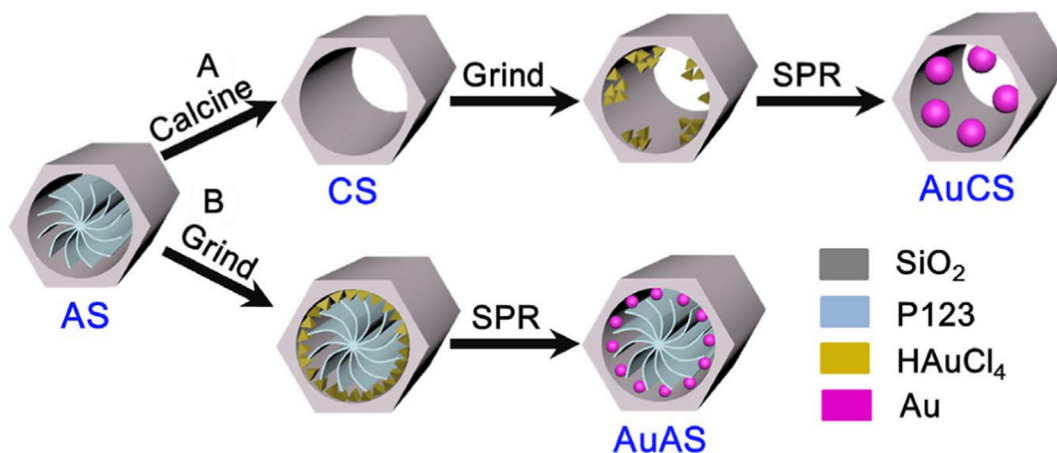


Fig. 7. Synthetic process of (A) calcine reduced AuCS and (B) grind formed AuAS catalysts. Adapted with permission from ref. (Xing et al., 2017) Copyright 2017 Elsevier.

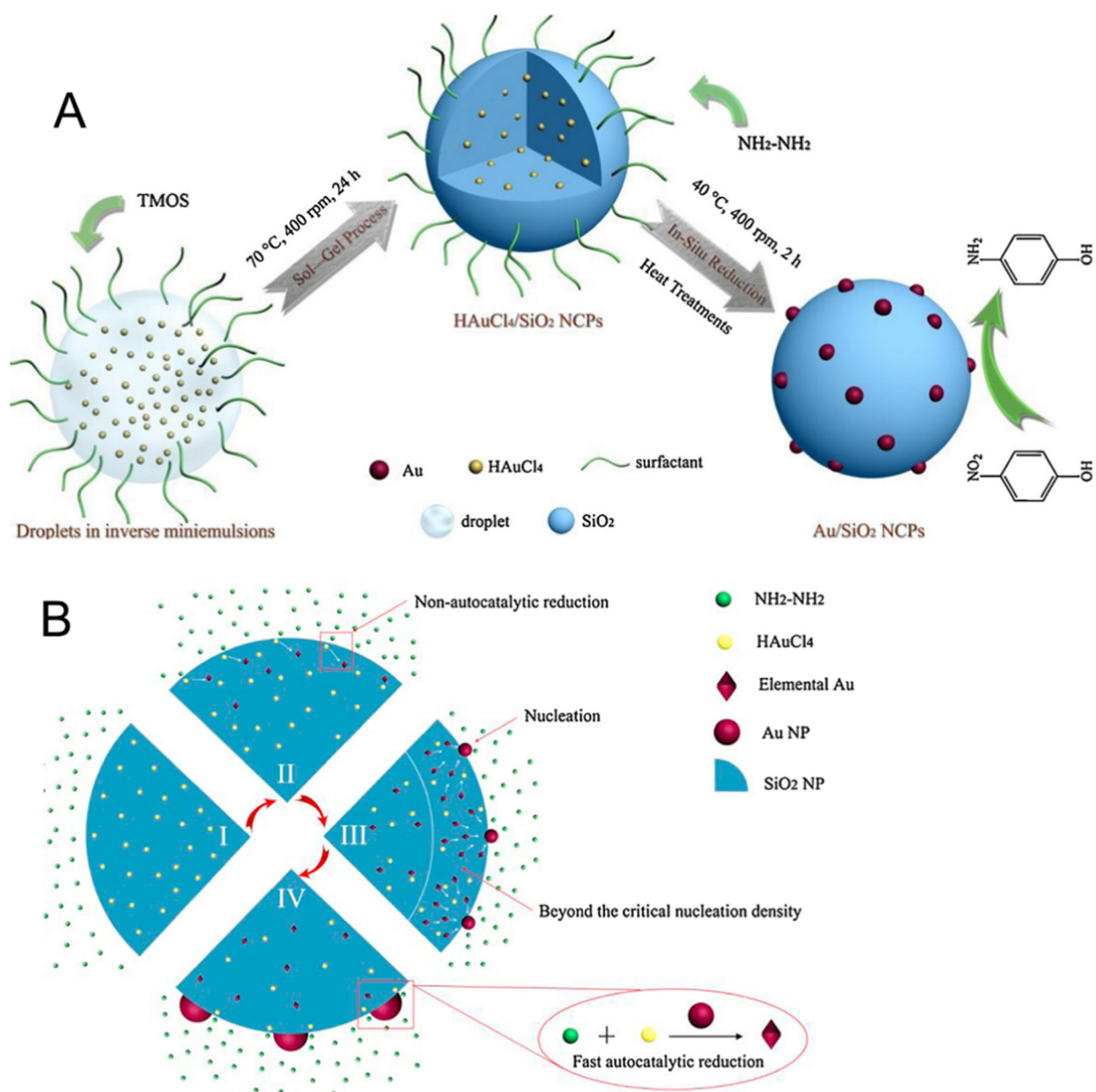


Fig. 8. Mechanism of (A) preparation process and (B) formation mechanism of raspberry-like Au/SiO<sub>2</sub> nanocomposite particles. Adapted with permission from ref. (Cao et al., 2016) Copyright 2016 Elsevier.

the strong interaction between Au and support and well dispersed Au in AuAs are responsible for highly active in catalytic reduction. By limiting AuNPs in the shell or tubes, the recyclability can be obviously enhanced.

Deposition AuNPs onto the outside of SNTs mainly uses the strong interaction between AuNPs and some ligands, such as —SH and —NH<sub>2</sub> (Jan et al., 2011). For example, Lin et al. (2012) prepared an amino groups-functionalized SNTs supported Au nanocatalyst for 4-NP reduction. Amino groups were served as active sites to host more AuNPs. Different with the deposition AuNPs onto inside or outside of the SiO<sub>2</sub> support, Cao et al. (2016) carried out raspberry-like Au/SiO<sub>2</sub> nanocomposite particles, in which AuNPs were half-embedded in the porous SiO<sub>2</sub>, toward reduction of 4-NP (Fig. 8). This structure not only offered a good morphological stability, but displayed a good catalytic activity and recycling performance, which remained 95% conversion of 4-NP after five cycles. Most importantly, hydrazinium hydrate with two amino groups was used to reduce HAuCl<sub>4</sub> and the organic ligands were removed through heating.

### 5.2.2. TiO<sub>2</sub>

Embedding AuNPs on metal oxide supports is an efficient way to immobilize AuNPs, which shows high activity and efficiency for nitroaromatics reduction. Metal oxides-supported Au nanocatalysts have gained increasing scientific interest because of the high activity to a variety of chemical reactions as heterogeneous catalysts (Sinatra et al., 2015; Zhou et al., 2018b). The nature of oxide supports plays an important role in the catalytic properties of supported Au nanocatalyst. It may limit the stabilization, activity, and catalytic efficiency because of the metal-support interface (Boronat and Corma, 2010). Thus, the interaction between AuNPs and supports should be considered cautiously in order to maximize the synergetic effects.

Although Au nanocatalysts have an efficient catalytic activity for nitroaromatics reduction, most of them do not have the ability of chemoselective reduction. It has been reported that TiO<sub>2</sub> supported Au nanocatalysts have unique behavior for chemoselective reduction of nitroaromatics (Corma and Serna, 2006; Tamiolakis et al., 2013). This is because the cooperative effect between Au and TiO<sub>2</sub> makes many very specific adsorption sites present at the boundary between Au and TiO<sub>2</sub> (Lai et al., 2016). During adsorption, H<sub>2</sub> is dissociated on Au and nitroaromatics are adsorbed selectively on the catalysts via nitro groups only, thus allows highly selective reduction (Boronat et al., 2007). The particle size of AuNPs plays a dominant role in determining the catalytic activity for nitroaromatics reduction (Wain, 2013). However, different synthetic methods of supported Au nanocatalysts have a great influence on the size of AuNPs. In order to obtain highly active TiO<sub>2</sub>-AuNPs catalyst, Damato et al. (2013) introduced a two-step polyol approach to prepare size-controlled TiO<sub>2</sub>-AuNPs catalyst through step-by-step reduction. This strategy successfully reduced different size of AuNPs about 12, 20, and 25 nm and obviously increased in catalytic activity.

Studies have reported that the substrate defects of TiO<sub>2</sub> could stabilize AuNPs (Chen and Goodman, 2006; Yang et al., 2008). Furthermore, AuNPs prefer to nucleate at the surface defects, especially step edges and oxygen vacancies. Significantly, under appropriate conditions, defect sites on the surface of TiO<sub>2</sub> can be produced (Barrett et al., 2016). Hence, TiO<sub>2</sub> is well developed for stabilizing AuNPs and improving the catalytic activity. In this case, Wang et al. (2016) introduced an efficient strategy for fabricating highly selective Au nanocatalyst in reduction of nitroaromatics by positioning AuNPs on the edge/corner sites of TiO<sub>2</sub> (Fig. 9). Results showed that AuNPs loaded on the edge/corner sites considerably enhanced the catalytic activities. The catalytic activities were much higher than the conventional Au-TiO<sub>2</sub> catalysts. Although the selectivity and activity are enhanced by TiO<sub>2</sub> supported Au nanocatalyst, the yields of desired anilines are still low and needed to improve. In very recent, they further proposed that the conversion of nitroarenes could be as high as 99.5% when using Sn decorate the Au/TiO<sub>2</sub> catalyst (Wang et al., 2018b). This research illustrated that the Sn-O-Ti linkage promoted the formation of oxygen vacancies on TiO<sub>2</sub>, which resulted in

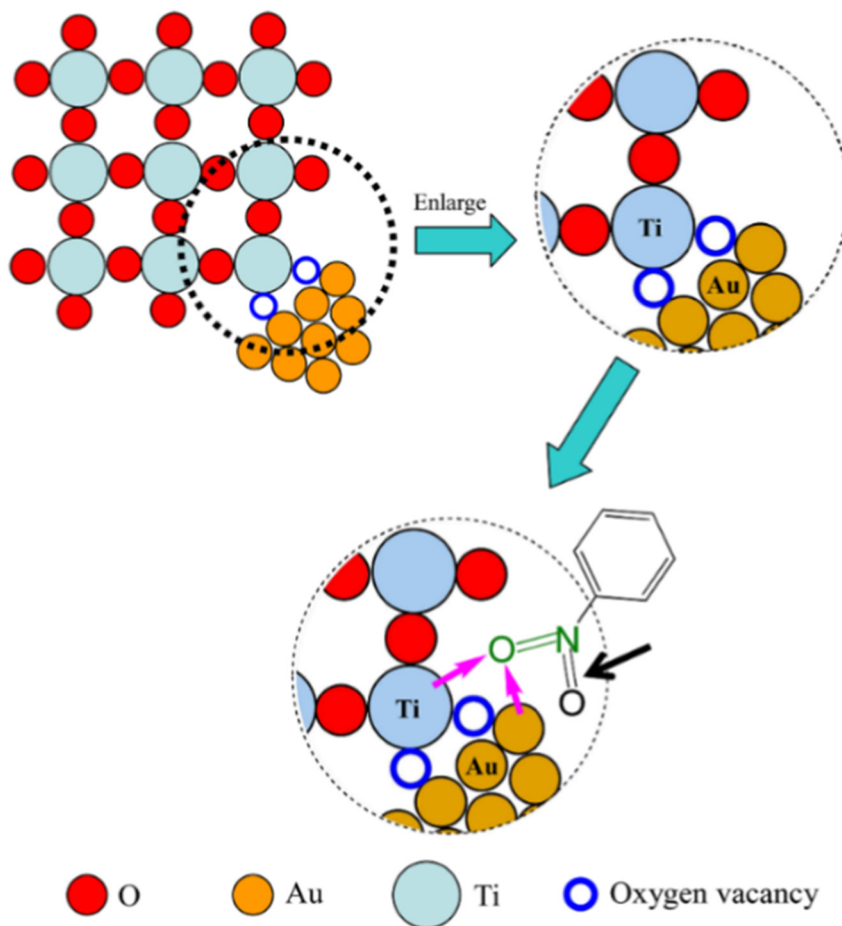
the high activity and selectivity for metal catalysts (Fig. 10). In addition, AuNPs were necessary for the formation of anilines because the AuNPs/support interface could only reduce nitrosobenzene from nitrobenzene. This strategy theoretically reveals the peculiarity of hydrogenation of nitrobenzene on the Sn-O-Ti interface and may open the door to highly selective hydrogenation of biomass.

### 5.2.3. Other metal oxides

Other metal oxides, such as MgO (Layek et al., 2012), Al<sub>2</sub>O<sub>3</sub> (Shimizu et al., 2009), and Fe<sub>3</sub>O<sub>4</sub> (Ge et al., 2008), have been well used as supports for stabilizing AuNPs to prevent aggregation. Most of them have a role in stabilizing free AuNPs and have a synergistic effect with AuNPs for providing more active sites (Chaplin et al., 2006; Han et al., 2017; Song et al., 2015). Nevertheless, the recyclability of AuNPs from many supports-containing systems is very difficult and also hinders the monitoring process of catalytic reaction by UV-vis spectrophotometer because of the presence of suspended NPs in reaction solution (Lee et al., 2010). As a consequence, pursuing for efficient separation technique to improve the efficiency is very important. Interestingly, as a magnetic metal oxide, Fe<sub>3</sub>O<sub>4</sub> has the properties of high-surface-area and accessibility, thereby possessing the advantages of being magnetically recoverable and low-cost (Chang and Chen, 2006; Long et al., 2011; Xu et al., 2012a; Yu et al., 2005). In this manner, Chang and Chen (2009) fabricated a novel magnetically recoverable Au nanocatalyst for 4-NP reduction by adsorption-reduction of Au<sup>3+</sup> ions on chitosan-coated Fe<sub>3</sub>O<sub>4</sub>. Results showed that the catalyst was well separated and did not need either solvent swelling before or catalyst filtration after the reaction.

Different heterostructures of AuNPs-Fe<sub>3</sub>O<sub>4</sub> exhibit different catalytic activity toward nitroaromatics reduction. For instance, the flower- and dumbbell-like AuNPs-Fe<sub>3</sub>O<sub>4</sub> heterostructures were prepared (Lin and Doong, 2017). They both exhibited bifunctional properties with excellent catalytic activity and high magnetization. However, the dumbbell-like heterostructure suggested much more obvious catalytic performance than the flower-like heterostructure with the pseudo-first-order rate constants of 0.63–0.72 min<sup>-1</sup>. Substantially, the catalytic activity can be further enhanced using AuNPs-Fe<sub>3</sub>O<sub>4</sub> heterostructures. Indeed, a paper reported by Chen et al. (Zheng et al., 2013) has well demonstrated this. Generally, Fe<sub>3</sub>O<sub>4</sub> is used as magnetic core, which is coated with SiO<sub>2</sub>. AuNPs are loaded on the Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> magnetic nanospheres through Sn<sup>2+</sup> linkage and reduction (Fig. 11). In the case of this design, the catalytic performance is improved with a rate constant of 0.85 min<sup>-1</sup>. Additionally, it provides convenient magnetic separation and good reusability with a stable conversion of 91% after six cycles.

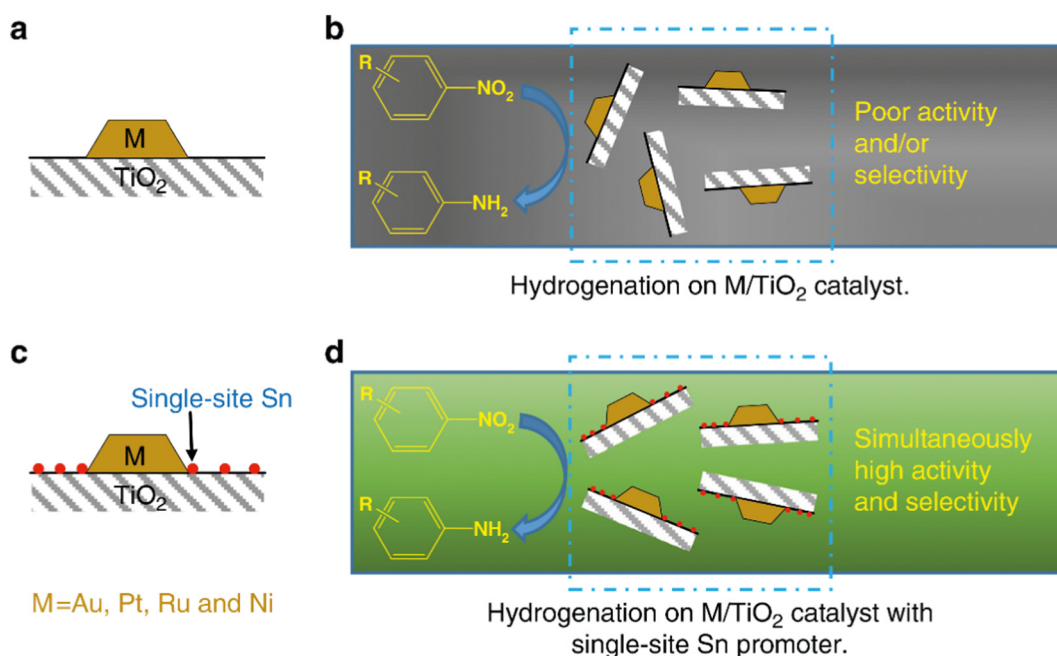
AuNPs have attracted wide attention and have been widely used in photocatalytic field, especially in the oxidation reaction, because of its SPR property, which provides strong absorption capacity of visible light (Si et al., 2016; Yang et al., 2015; Yang et al., 2014b). When combining with some semiconductors, the catalytic activity of the catalysts can be changed (Yang et al., 2016b; Zhang et al., 2018). Thus, some reports investigated the reduction of nitroaromatics by Au nanocatalysts under light illumination and compared the catalytic activity in the presence and absence of light. For example, Liu et al. prepared an Au-loaded Na<sub>2</sub>Ta<sub>2</sub>O<sub>6</sub> nanocomposite photocatalyst for 4-NP reduction and prepared the catalytic activity in the dark and under visible and solar light irradiation (Liu et al., 2017b) (Fig. 12). In the dark, AuNPs only acted as an electron donor and provided active sites for the reaction. While under visible light irradiation, the strong SPR of AuNPs excited electrons, more excess activated electrons were produced, which promoting the catalytic performance. Different with the reaction process under visible light irradiation, the Na<sub>2</sub>Ta<sub>2</sub>O<sub>6</sub> was easily excited and generated plenty of free electrons under UV-light irradiation. These electrons then transferred from the CB of Na<sub>2</sub>Ta<sub>2</sub>O<sub>6</sub> to the surface of AuNPs, which decreased the recombination rate of charge carriers, the catalysis was further enhanced. Thus, under the irradiation of solar light, the SPR promotion and charge transfer promotion were responsible for the high catalytic activity and the catalytic activity was



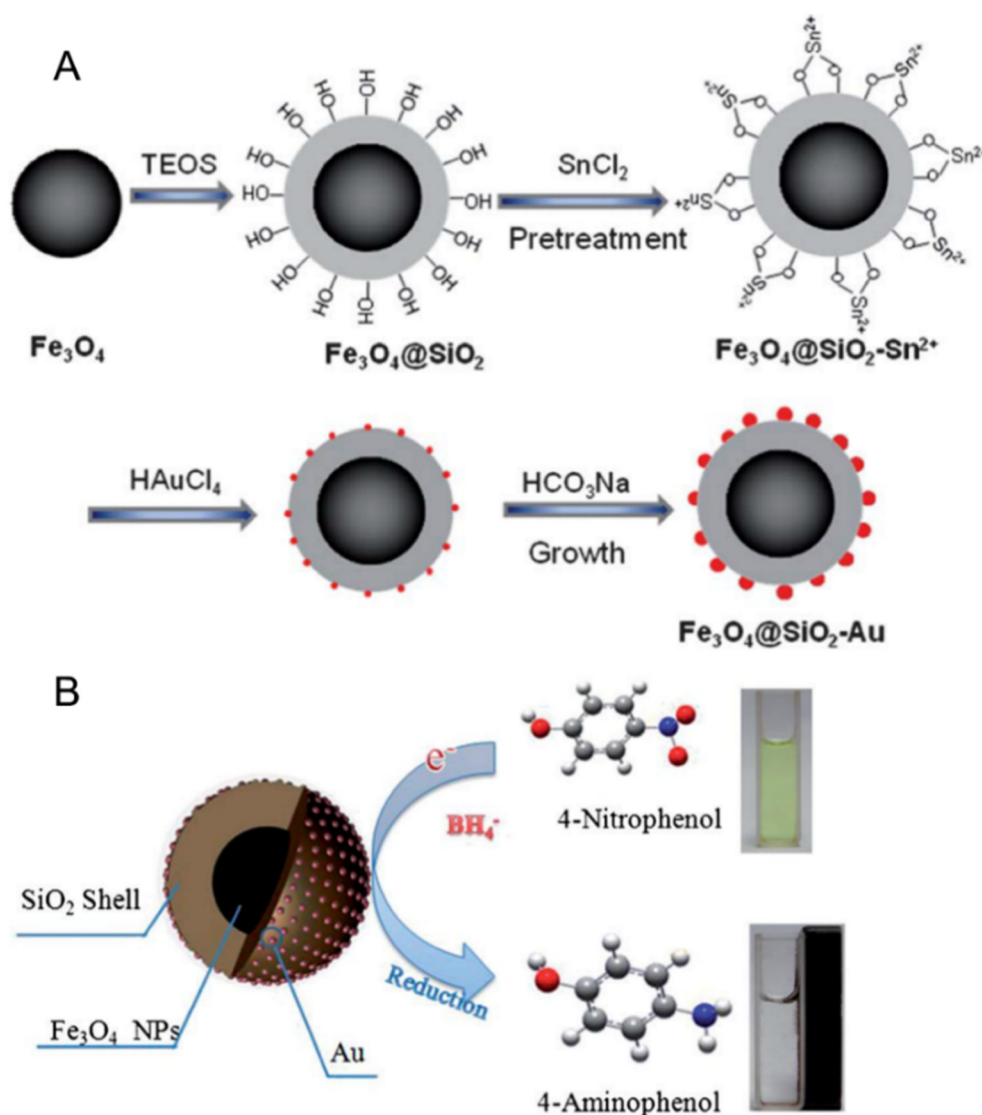
**Fig. 9.** Absorption of nitrobenzene on  $\text{TiO}_2$  supported Au nanocatalyst with oxygen vacancies. Adapted with permission from ref. (Wang et al., 2016) Copyright 2016 the American Chemical Society.

2.35 times higher than in the dark. This design also showed good stability and reusability. Similar with this investigation, other Au-based nanophotocatalysts like silica@apatite@Au composites (Chen et al.,

2018), apatite@Au composite nanosheet spheres (Wang et al., 2018c), and  $\text{TiO}_2/\text{Au}/\text{CNTs}$  catalyst (Xiang et al., 2014) have been developed for nitroaromatics reduction under light irradiation. Thus, the catalytic



**Fig. 10.** Enhanced activity and selectivity for nitrobenzene reduction by Sn decorated  $\text{M}/\text{TiO}_2$  catalyst. Adapted with permission from ref. (Wang et al., 2018b) Copyright 2018 Nature.



**Fig. 11.** Photographic representation for (A) preparation of  $\text{Fe}_3\text{O}_4\text{-SiO}_2$  magnetic nanospheres supported Au nanocatalyst and (B) in reduction of 4-NP using  $\text{NaBH}_4$ . Adapted with permission from ref. (Zheng et al., 2013) Copyright 2013 The Royal Society of Chemistry.

activity for nitroaromatics reduction can be improved by combining the AuNPs and some semiconductors. However, not all of the semiconductors have this function. The band potential of semiconductors should be matched with the Fermi energy of AuNPs, namely the CB of semiconductors should be higher in energy than the Fermi energy of AuNPs, making the direct transfer of electrons from semiconductors to AuNPs. More works would be proposed in the future.

### 5.3. Carbon materials

#### 5.3.1. Porous carbon

Carbon-based materials are well known as promising candidates for Au catalytic carriers owing to the characteristic properties of high specific surface area, wonderful mechanical stability, and unique electrical property (Huang et al., 2017b; Yi et al., 2018; Zhang et al., 2016). Carbon-based materials with tailored pore sizes can encapsulate AuNPs inside its pores and leave enough space for reactant passing. Thereby AuNPs are highly dispersed in porous carbon and the porous carbon-encapsulated Au nanocatalysts provide high efficient catalysis for nitroaromatics reduction with good recyclability (Guo and Suslick, 2012). MC has been done to disperse AuNPs on it to prevent aggregation and improve the catalytic activity (Wang et al., 2013). AuNPs occupy

both the adjacent pore walls and pore channels, but do not penetrate the walls (Wang et al., 2015b). In addition, MC can serve as both carrier and adsorbent for stabilizing AuNPs and adsorbing reactants, respectively. MC with some electron withdrawing groups, such as  $\text{—COOH}$  and  $\text{C=O}$  groups, promotes the catch of 4-NP, which exhibits high efficiency to remove 4-NP (Guo et al., 2016).

One of the advantages of carbon carriers is the electron-rich ability (Liang et al., 2017; Zhang et al., 2011a). When linked with AuNPs, the synergistic effect between carbon and Au makes excellent catalytic activity for nitroaromatics reduction. The large surface area of carbon nanomaterials possess high absorption of organic compounds via  $\pi\text{-}\pi$  stacking interactions, hence increasing the opportunity to access nitroaromatics and AuNPs (Geim, 2009; Wu et al., 2017). In this case, a electrospun carbon nanofibers (CNFs) supported Au core-shell catalyst is fabricated for 4-NP reduction (Zhang et al., 2013). Nitric acid, hydrochloric acid and  $\text{SnCl}_2$  treated CNFs with rich  $\text{—OH}$  can reduce and form small size of AuNPs. More 4-NP is absorbed on catalyst through  $\pi\text{-}\pi$  stacking interactions. The electron transfer between CNFs and AuNPs obviously facilitates the uptake of electrons by 4-NP molecules, further improving the catalytic efficiency. It could also be easily recycled for reuse. Distinct from CNFs loaded Au nanocatalyst, AC expresses surface oxygen-containing functionalities, which act as AuNPs anchoring

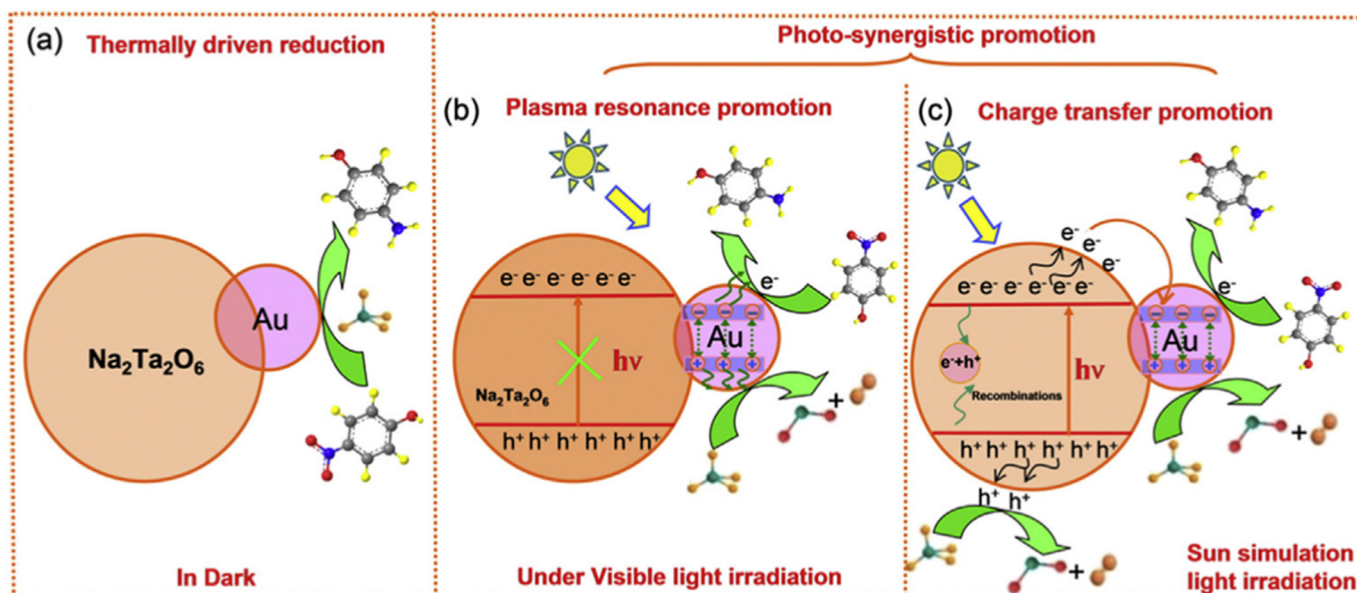


Fig. 12. 4-NP reduction process (a) in the dark, (b) under visible light and (c) solar light illumination. Adapted with permission from ref. (Liu et al., 2017b) Copyright 2017 Elsevier.

sites, promote the reduction of AuNPs, lower hydrophobicity of Au nanocatalyst and enhance catalyst accessibility during synthesis (Cárdenas-Lizana et al., 2015; Rodríguez-Reinoso, 1998). The ultimate goal is to obtain highly efficient Au-based nanocatalyst for nitroaromatics reduction. Nevertheless, the size of AuNPs is needed to decrease in some case.

### 5.3.2. Graphene

GR, consisting of single-layer and  $sp^2$ -hybridized carbon lattice with excellent electrical, thermal, and mechanical properties, has been extensively employed as a promising support for Au nanocatalysts (Deng et al., 2013; Liu et al., 2015; Novoselov et al., 2004; Yang et al., 2016a; Zhang et al., 2015). GR as a support for the Au nanocatalysts can improve the conductivity, provide more active sites, and exhibit synergistic effect between AuNPs and GR, which promote the absorption of targets via  $\pi$ - $\pi$  stacking interaction (Liu et al., 2015; Ying et al., 2017). The catalytic efficiency can be further improved. For example, a cylindrical piece of AuNPs/GR hydrogel has been synthesized using DP method and illustrates excellent catalytic performance for 4-NP reduction, which is about 14 times larger than the PMMA supported AuNPs mentioned above (Li et al., 2012). The details of these results are shown in Table 4. In recent, the development tendency of GR-supported Au nanocatalysts is diversification and high efficiency. Maji and Jana (2017) synthesized a two-dimensional GR and  $mSiO_2$  supported AuNPs (RGS@AuNPs hybrid) for simultaneous reduction of 4-NP and photo-degradation of MB dye. Graphitic carbon nitride ( $g-C_3N_4$ ), a sustainable and environmentally friendly metal-free semiconductor which possessing a GR-like two dimensional crystalline structure, is regarded as innovative photocatalytic material (Jiang et al., 2017; Qiu et al., 2018; Vidyasagar et al., 2018; Wang et al., 2017b; Zheng et al., 2016; Zhou et al., 2018a). There are a few researches mentioned it had highly contribution to nitroaromatics reduction, while a recent paper reported the Au/ $g-C_3N_4$  concerted contact system was highly efficient for reduction of 4-NP to 4-AP (Fu et al., 2017). Furthermore, under visible light irradiation, the catalytic efficient was largely enhanced owing to the charge-transfer effect induced by strong interaction between AuNPs and  $g-C_3N_4$ .

### 5.4. Multi-metal alloy or doping

Another important typical design for the application on nitroaromatic reduction by Au-based nanocatalysts is in conjunction

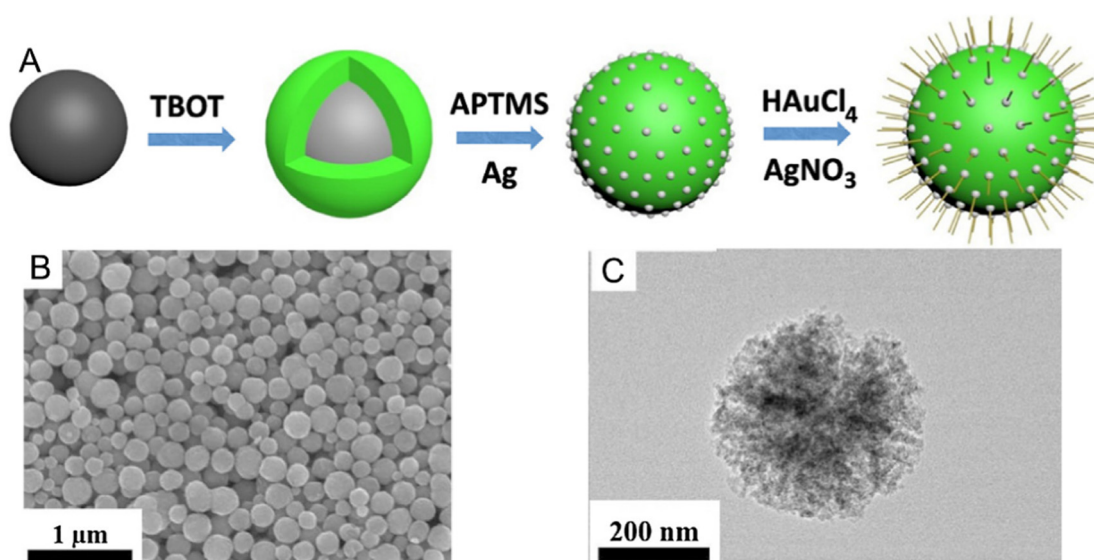
with other metal NPs e.g. Pt, silver (Ag), Ni, and palladium (Pd), which all have wonderful catalytic performance for chemical reactions (Gong, 2012; He et al., 2017). It is reported that AuNPs alloy or combine with other transition metals to form multi-metal NPs can potentially lead to higher catalytic activity as compared to monometallic NPs (Zhang et al., 2014b). Hammer-Nørskov model identifies that the synergistic effect induced by multi-metal NPs catalysis is mainly due to the d-band of metal surface, which is the controlling factor in chemisorption strength (Pozun et al., 2013). Introduction of another metal NPs results in geometric and electronic effects with structure changes (Tuo et al., 2015). With this respect, many wonderful reports have been published for nitroaromatics reduction by Au-based multi-metal NPs.

AuNPs served as core or shell combine with Ni (Le et al., 2014), Pd (Qian et al., 2014), and Ag (Jayabal and Ramaraj, 2014) to form dandelion- and volcano-like structures for highly efficient reduction of nitroaromatics. The bimetallic structure effects are responsible for providing more active sites and exhibiting maximum catalytic activity (Pretzer et al., 2016). Furthermore, the catalytic activity is improved not only by a multi-metallic system, but also by making porous structures (Sahoo et al., 2015). Interestingly, in order to improve the catalytic performance of mono-AuNPs, Godfrey et al. (2017) prepared an Au@Ag@Au (core@shell@shell) structure using the sequential citrate reduction technique. This structure provided a second Au–Ag interface. The extended X-ray absorption fine structure analysis suggested that this structure exhibited an increased proportion of bimetallic interactions and indicated higher catalytic activity than the Au@Ag structure.

The new trend of multi-metal NPs-based catalysts toward nitroaromatics reduction lies upon loading multi-metal NPs on other supports mentioned above, such as metal oxide and carbon materials. The metal oxide used as carrier mainly has  $TiO_2$  with corner or edges effect to improve the chemoselectivity and  $Fe_3O_4$  with excellent magnetism to separate easily (Boronat and Corma, 2010). Particularly, Shen et al. (2017a) synthesized multifunctional  $Fe_3O_4@TiO_2@Ag$ -Au microspheres by incorporating Au–Ag bimetallic nanostructures onto the  $Fe_3O_4@TiO_2$  microspheres, which significantly increased the ‘hot spot’ effect, thereby offering stronger electromagnetic field enhancements (Fig. 13).

Benefiting from the high conductivity and tremendous surface area, GO is widely used as carrier for multi-metal NPs based catalyst. The connection between GO and substrate molecules relies on non-covalent bonding interactions such as hydrogen bonding, hydrophobic  $\pi$ - $\pi$





**Fig. 13.** Schematic for (A) fabrication, (B) SEM image, and (C) TEM image of  $\text{Fe}_3\text{O}_4@\text{TiO}_2@\text{Ag-Au}$  microspheres. Adapted with permission from ref. (Shen et al., 2017a) Copyright 2017 Elsevier.

stacking, and electrostatic interactions (Rout et al., 2017). GO can reduce metal precursors to form a stable suspension of metal NPs/GO without any reducing agent or surfactant (He et al., 2014). Depending on the design of Au-Pt NPs/GO structure, the catalytic activity for 4-NP reduction is significantly enhanced with  $k_{\text{app}}$  of  $0.228 \text{ min}^{-1}$ , which is about 12-fold and 5-fold higher than the value of homemade AuNPs ( $0.018 \text{ min}^{-1}$ ) and commercial Pt black ( $0.042 \text{ min}^{-1}$ ) (Lv et al., 2015). Moreover, the electron-enhanced effect of RGO support and strong synergistic effect between noble metal NPs play a significant role in long-life stability and excellent catalytic performance (Li et al., 2017). Recently, our team has reported a Pd/Au bimetallic NPs-loaded  $g\text{-C}_3\text{N}_4$  nanosheet for highly efficient catalytic reduction of 4-NP. The average diameter around 8 nm of Pd/Au NPs are homogeneously dispersed on the surface of support, which proposed special p-bonded planar structure and large surface area (Fang et al., 2017). The comparison of different parameters of Au-based multi-metal NPs for nitroaromatics reduction is shown in Table 5.

## 6. Reduction of nitroaromatics with non-spherical AuNPs: shape-dependent effect

### 6.1. Polyhedral Au nanocrystals

The catalytic efficiency of Au nanocatalysts not only depends on the particle structure and size, but also on the shape (Cao et al., 2001; Nehl and Hafner, 2008). Different shapes of AuNPs have diverse configuration, which provide various active sites, thus have a great impact on the catalytic activity. In early, most of studies concentrated on the synthetic method of different shapes of AuNPs (Rashid and Mandal, 2008). Conveniently, Premkumar et al. (2011) fabricated different shapes of polyhedral AuNPs in high yield and investigated the effect on catalytic performance for shape distribution. Differently, a seed-mediated growth approach was employed by Chiu et al. (2012) to synthesize cubic, octahedral, and rhombic dodecahedral AuNCs. With this respect, they compared the catalytic activity toward  $\text{NaBH}_4$  reduction of 4-NP and found that rhombic dodecahedral AuNCs showed the highest reduction rate.

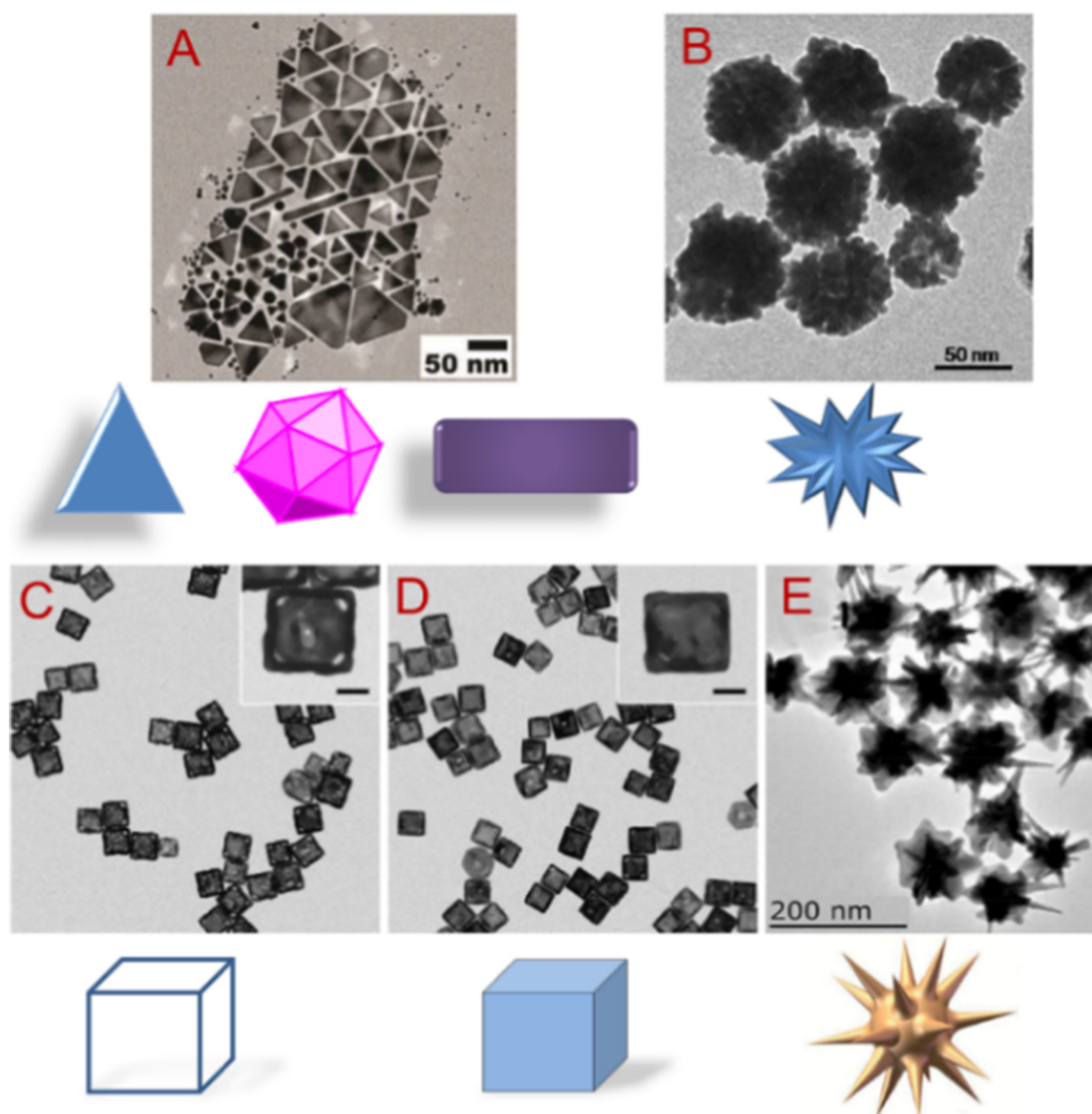
### 6.2. Irregular Au nanocrystals

Irregular AuNCs such as rods, flowers, cages, boxes, and stars have been introduced for reduction of nitroaromatics (Fig. 14). Nanorods

with high surface area of hollow structures show enhanced optical sensitivity and catalytic activity when compared to Au spheres, nanorods, and hollow spheres (Khalavka et al., 2009). Loading Au nanorods on the surface of carbon-coated magnetic nanoparticles ( $\text{Fe}_3\text{O}_4@\text{C}$  MNPs) further enhances the catalytic activity and exhibits wonderful recyclability and stability. Another factor affecting the catalytic activity is the thickness of the AuNCs wall. Compared the nanocages and nanoboxes, the kinetic data indicate that Au-based nanocages are catalytically more active due to the extremely thin but electrically continuous wall (Zeng et al., 2009). Also, the high content of Au and the accessibility of both outer and inner surfaces through the pores in wall are responsible for high efficient catalysis.

It is reported that branched Au nanostructures can enhance the performance in many reactions (Guerrero-Martínez et al., 2011). In this case, some researchers investigate the catalytic activity of multi-branched Au nanoantennas, nanostars, and nanoflowers (Soetan et al., 2016). The results showed that the efficient absorption of 4-NP on the surface of these shapes lied in the shorter protrusions. This is because there are (100) and (110) crystal planes on the shorter protrusions, where had high density of atomic steps and kinks, promoting higher catalytic activity for 4-NP reduction. Hence, it is very important to obtain Au nanocatalyst of crystal plane with high index facets.

In conclusion, the nature of supports has a significant impact on catalytic performance of Au nanocatalysts. As for most polymer-supported Au nanocatalysts, the shapes of the catalyst can be controlled. Many of them can reduce AuNPs in situ by specific ligands without adding any reducing agent. But the catalytic activity and stability of AuNPs should be further improved. The oxide supported Au nanocatalysts like  $\text{SiO}_2$  can effectively overcome this because of the confinement effect. With this design, the recycle and stability of Au nanocatalysts are greatly enhanced with no Au leaching. Other metal oxides as supports will form the synergistic effect with Au and the catalytic performance is improved because more active sites are provided. Interestingly, the catalysts are separated easily in the presence of some magnetic metal oxides (Gawande et al., 2014; Shokouhimehr et al., 2018). Nevertheless, the synthetic process is complex and the activity is easier to lose in air. The surface of carbon usually contains a large number of oxygen-containing groups, which benefits the deposition and stability of AuNPs. Some of them possess electron-rich ability and high absorption of organic compounds via  $\pi\text{-}\pi$  stacking interactions, hence increasing the opportunity to access nitroaromatics and AuNPs, improving the catalytic performance, and broadening the application of Au nanocatalysts,



**Fig. 14.** Figures and TEM images of Au nanocrystals with different shapes. (A) Polyhedral and nanorods; Adapted with permission from ref. (Premkumar et al., 2011) Copyright 2011 Springer. (B) flowers; Adapted with permission from ref. (Liu et al., 2017a) Copyright 2017 Elsevier. (C) cages; (D) boxes; Adapted with permission from ref. (Zeng et al., 2009) Copyright 2010 the American Chemical Society. (E) stars. Adapted with permission from ref. (Ma et al., 2017) Copyright 2017 Multidisciplinary Digital Publishing Institute.

especially photocatalysis. Other new supports, such as membrane (Zhong et al., 2018), montmorillonite (Rocha et al., 2018), and molecular sieve (Kusumawati et al., 2018), have been developed and showed highly catalytic performance. The investigation does not just tend to some new supports, but to some new technology like photocatalysis in recent.

## 7. Comparison with other metal catalysts

Except AuNPs, other metallic NPs including Pd (Shokouhimehr et al., 2013), Pt (Berillo and Cundy, 2018), Ag (Wu et al., 2013), Cu (Pi et al., 2018), and Ni (Xia et al., 2018) NPs have also been used for nitroaromatics reduction and the mechanism is similar to that of AuNPs. Just like AuNPs, these free metallic NPs are unstable and easy to aggregate. Accordingly, stabilized metal nanocatalysts are needed and desirable for nitroaromatics reduction (Kim et al., 2015; Shokouhimehr et al., 2014). Among these well stabilized metallic nanocatalysts, Pd-based nanocatalysts always show the highest catalytic activity for nitroaromatics reduction, even higher than Au nanocatalysts (Deraedt et al., 2014; Shokouhimehr et al., 2018). This is

because PdNPs have very strong adsorption for activated hydrogen, which is the rate-limiting step for nitroaromatics reduction (Durand et al., 2008). The catalytic activity is enhanced because of more activated hydrogen. While the rate-limiting step of Au nanocatalyst is the transfer ability of hydrogen to products. Even so, the high catalytic efficiency of Au nanocatalysts under low temperature is still significant. Simultaneously, the low toxicity of Au nanocatalysts is more suitable for practical application.

Ag-based nanocatalysts have widely used in nitroaromatics reduction because of its much lower cost, high activity and selectivity (Ji et al., 2016). However, in most cases, the catalytic activity is not as high as Au nanocatalysts. Besides, the bactericidal ability and toxicity of Ag nanocatalysts cannot be ignored, which will be harmful for beneficial microbes and humans. The other metallic nanocatalysts like Cu and Ni nanocatalysts are very cheap and have also been reported for the reduction of nitroaromatics in these years (Xia et al., 2016; Xiao et al., 2016). But the chemical tolerance and catalytic activity of them are obviously not as good as Au nanocatalysts. In addition, CuNPs also show high propensity for oxidation, which may affect the catalysis.

## 8. Conclusions, future outlook and challenges

Efficient reduction of nitroaromatics into corresponding amines compounds has paid much attention. Au nanocatalysts can offer an efficient way because of the high catalytic efficiency under low temperature and specific size, synergistic, interfacial, and shape effects. Due to the trends in size increase of AuNPs when sintering, several synthetic strategies of Au nanocatalyst are widely employed to suppress, including: i) immobilizing or depositing AuNPs on high-surface area substances; ii) encapsulating them in the channels or porous materials; iii) stabilizing them with surface bound ligands. Thus, new green and simple routes of Au nanocatalyst synthetic methods with large loading amount, highly dispersed AuNPs, and wonderful catalytic efficiency for nitroaromatics reduction are still needed. The future outlook and challenges are proposed as follows:

- i). Most of studies focus on the synthesis of highly efficient Au nanocatalysts for nitroaromatics reduction but ignore the reason for the high efficient. In addition, the combination of photocatalytic materials is a trend to improve the catalytic performance and energy saving, but the investigation on the mechanism of nitroaromatics reduction under light irradiation should be further developed.
- ii). Free AuNPs have high catalytic activity but are easy to aggregate. For this, supported Au nanocatalysts are development, but sometimes the recovery is still limited by unstably interfacial interaction between supports and Au. Thus, the design of core-shell or yolk-shell is a good choice.
- iii). For recycle, magnetic materials are usually used as a core to stabilize AuNPs and separate Au nanocatalyst easily, but the magnetic materials only act as a support. Some magnetic metal NPs with the ability to reduce nitroaromatics, such as Ni NPs, can be used to combine with AuNPs to enhance the catalytic performance by bimetallic synergetic effect.
- iv). An alternative promising way to enhance the catalytic performance is the synthesis of irregular AuNPs or multi-metallic NPs owing to the edge and corner effects or synergistic effect.
- v). Most of works provide efficiently active catalysts, but few of them have been suited to the large-scale industrial use. Thus, synthesis of large-scale industrial used catalysts is needed to further develop.
- vi). New materials supported Au nanocatalysts present huge potential in environmental applications. Particularly, a productive way of AuNPs may be combination with other biocompatible materials deposited on different supports either in micro- and nanometer scales. In this manner, metal-organic frameworks system provides a good choice.
- vii). Most consideration of researchers is on reducing nitroaromatics in aqueous phase by NaBH<sub>4</sub> solution, further investigation on other medium such as sediment and soil and organic solution is needed to consider.
- viii). Most of the papers focus on the reduction of nitroaromatics but few of them mention the reduction of aliphatic nitro compounds. Thus, more investigations on the mechanism and reduction of aliphatic nitro compounds by Au nanocatalysts should be developed in the future.
- ix). It is reported that the surface electron density of AuNPs would be somewhat responsible for the catalytic property of some materials like TiO<sub>2</sub> supported Au nanocatalysts (Yang et al., 2016a). The photo-induced electron transfer can further enhance the oxidability of Au nanocatalysts (Yang et al., 2014a). Thus, the electron behavior including electron transfer and density may have effect on the reduction also. In this case, the electron-dependent effect of Au nanocatalysts should be considered in the future work.

- x). For further improvement of the catalytic activity, the single-atom catalyst is deserved to investigate.

## Acknowledgement

This study was financially supported by the Program for the National Natural Science Foundation of China (51521006, 51408206, 51579098, 51278176, 51779090, 51709101, 51879101, 51809090, 51378190), Science and Technology Plan Project of Hunan Province (2017SK2243), the National Program for Support of Top-Notch Young Professionals of China (2014), the Program for Changjiang Scholars and Innovative Research Team in University (IRT-13R17), the Program for New Century Excellent Talents in University (NCET-13-0186), and Hunan Provincial Science and Technology Plan Project (2018SK20410, 2017SK2243, 2016RS3026), the Fundamental Research Funds for the Central Universities (531109200027, 531107050978, 531107051080).

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