

Supported noble metal nanoparticles as photo/sono-catalysts for synthesis of chemicals and degradation of pollutants

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This review summarizes the utilization of supported noble metal nanoparticles (such as Au/TiO₂, Au/ZrO₂, Ag/AgCl) as efficient photo/sono-catalysts for the selective synthesis of chemicals and degradation of environmental pollutants. Supported noble metal nanoparticles could efficiently catalyze the conversion of solar energy into chemical energy. Under UV/visible light irradiation, important chemical transformations such as the oxidation of alcohols to carbonyl compounds, the oxidation of thiol to disulfide, the oxidation of benzene to phenol, and the reduction of nitroaromatic compounds to form aromatic azo compounds, are effectively achieved by supported noble metal nanoparticles. Under ultrasound irradiation, supported noble metal nanoparticles could efficiently catalyze the production of hydrogen from water. Moreover, various pollutants, including aldehydes, alcohols, acids, phenolic compounds, and dyes, can be effectively decomposed over supported noble metal nanoparticles under UV/visible light irradiation. Under ultrasound irradiation, pollutant molecules can also be completely degraded with supported noble metal nanoparticles as catalysts.

noble metal nanoparticles, photocatalyst, sonocatalyst

1 Introduction

Supported noble metal nanoparticles as heterogeneous catalysts have attracted a lot of research attention recently due to the increasing global energy and environmental concerns [1–6]. From the energy aspect, the noble metal nanoparticles can efficiently catalyze the conversion of various natural energy such as solar energy into chemical energy, which meets the demand for sustainable energy besides the traditional fossil fuel energies [7–10]. Such energy conversion can be used to drive many selective chemical transformations, which provides a ‘green’ path-

way for the synthesis of chemicals. From the environment aspect, many hazardous pollutants can be completely degraded through the redox processes catalyzed by the noble metal nanoparticle [11, 12]. There are many merits associated with noble metal nanoparticles such as reuse, environmental-friendliness and high catalytic efficiency [13, 14]. To achieve the target of reducing carbon emission and restricting environmental pollution, the successful application of noble metal nanoparticles can be essential.

Several kinds of noble metal nanoparticles such as Au and Ag have been intensively investigated for their catalytic properties [15, 16]. Generally, the noble metal nanoparticles need to be supported when being utilized as heterogeneous catalysts although in a recent study non-supported noble metal nanoparticles have also been reported [17]. Metal

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oxides such as TiO_2 , SiO_2 and ZrO_2 are generally chosen as the support for the noble metal nanoparticles because they are stable and in some cases can provide additional redox abilities [18]. Other supports such as Ag halides (AgCl , AgBr , etc.) have also been employed [19, 20]. The reactions with supported noble metal nanoparticles as catalysts can be driven by thermal, light, ultrasonic energy and so on [7, 8, 21, 22]. We have focused on the application of supported noble metal nanoparticles as photocatalysts and sonocatalysts for the synthesis of chemicals and degradation of pollutants recently and reported some promising results which may have long-term significances in energy and environmental aspects. In this review, we will highlight some selected research advances in this field and try to illustrate the reaction mechanisms and benefits of utilizing supported noble metal nanoparticles as photo/sono-catalysts.

2 Supported noble metal nanoparticles as photo/sono-catalysts for the synthesis of chemicals

Noble metal nanoparticles are able to efficiently catalyze the conversion of solar energy into chemical energy as their optical absorption covers almost the full solar spectrum [23, 24]. Here we will take Au nanoparticle as the example since it has been most intensively studied and try to show the mechanism for the visible and UV response of the noble metal nanoparticles. Figure 1 shows a typical optical absorption spectrum of Au nanoparticles [25]. As observed, the spectrum exhibits bands which are assigned to a broad interband transition appearing in the UV region and a narrow intraband transition (a surface plasmon band) appearing in the visible region.

The mechanism for the photo-excitation of Au nanoparti-

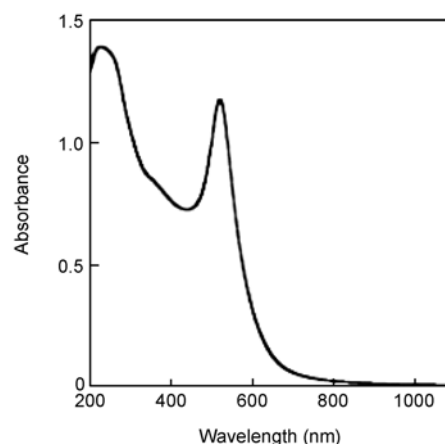
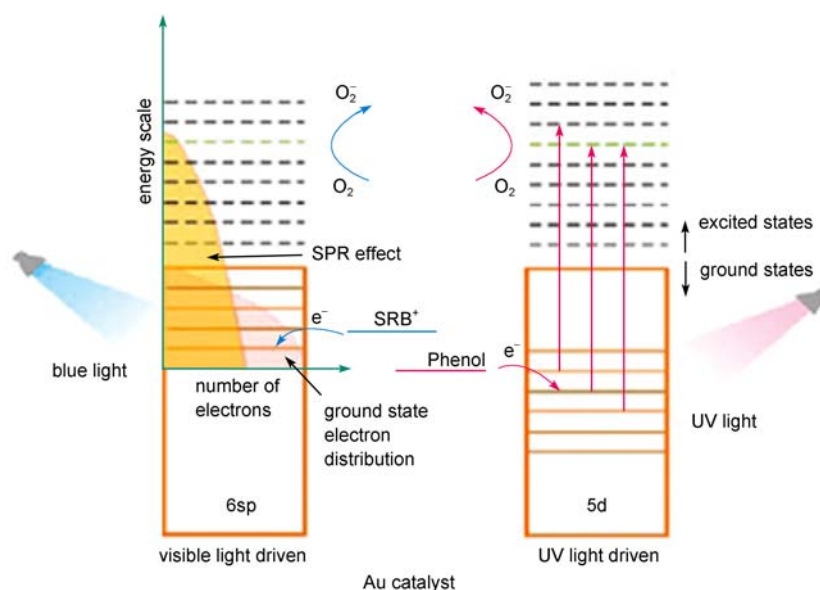


Figure 1 Optical absorption spectrum of Au nanoparticles stabilized in sodium dodecyl sulfate (SDS) aqueous solution. The average size of the Au nanoparticles is 10.4 ± 4.0 nm [25].

cles has already been proposed (Scheme 1) [26]. The intraband peaked at around 520 nm originates from the intraband excitation of 6sp electrons while the interband in the UV region results from the interband excitation of electrons from 5d to 6sp. The visible light excitation of Au nanoparticles is due to the well-known surface plasmon resonance (SPR) effect. The SPR effect is the collective oscillation of conduction electrons in the nanoparticles, which resonate with the electromagnetic field of the incident light. The precise nature of the UV light excitation of Au nanoparticles is still not clear and requires further studies. Upon either visible or UV light excitation, the electrons can be transferred to electron acceptors such as O_2 , generating oxidative species like superoxide ($\text{O}_2^{\cdot-}$); consequently, positive charges will be left in Au's 6sp or 5d energy levels. To neutralize these positive charges, Au nanoparticles will capture electrons



Scheme 1 The band structures of Au nanoparticles and the proposed mechanism for photocatalysis using Au nanoparticles [26].

from the organic molecules adsorbed on them. This also constitutes the major oxidizing power of Au nanoparticles when being used as photocatalysts. Moreover, the position of the positive charges determines the ability of Au nanoparticles to capture electrons. The positive charges in Au's 6sp band resulting from visible light absorption can only capture electrons from the molecules that are easier to be oxidized such as formaldehyde and methanol, while positive charges in the lower 5d band of Au resulting from UV light absorption are able to oxidize the molecules that are more difficult to be oxidized such as phenol. By this way, Au nanoparticles can efficiently catalyze chemical reactions under UV/visible light irradiation, indicating a successful conversion of solar energy to chemical energy. This principle can be similarly applied to other noble metal nanoparticles such as Ag. To be used as catalyst, the noble metal nanoparticles need to be supported on metal oxides (or others) to provide structural stability. Various synthetic strategies have been developed for the preparation of supported noble metal nanoparticles, such as deposition precipitation [27], impregnation [28], photo-reduction [22, 29, 30], chemical reduction [31] and so on. A lot of recent studies have focused on the exploitation of supported noble metal nanoparticles as efficient photocatalysts and developed many different chemical synthetic reactions catalyzed by those catalysts. Hereafter we will briefly introduce some researches and show the excellent ability of supported noble metal nanoparticles in the efficient conversion of solar energy to chemical energy.

2.1 Selective photocatalytic oxidation of alcohols to carbonyl compounds by supported noble metal nanoparticles

The selective catalytic oxidation of alcohols to corresponding carbonyl compounds is a key reaction for the synthesis of fine chemicals since ketone/aldehyde derivatives are widely used in the flavor, confectionary, and beverage industries [32–34]. Traditional synthetic procedures for this transformation include the use of large amounts of transition-metal complexes which could potentially lead to serious environmental pollution [35]. The photocatalytic oxidation process by supported noble metal nanoparticles provides an alternative for this transformation. This approach possesses many merits since it is driven by light irradiation and uses molecular O₂ as the oxidant, which can be taken as a 'green' chemical process.

The selectivity of the oxidation of the alcohols to corresponding aldehydes photocatalyzed by supported noble metal nanoparticles can be quite high [26, 36, 37]. For example, the selectivity of the oxidation of benzyl alcohol to benzaldehyde could achieve almost 100% when the process was performed under UV light irradiation with Au nanoparticles supported on zeolite Y (Au/Zeolite Y) as catalyst [26]. This reaction was carried out in the solvent of toluene and uses O₂ as the oxidation agent. NaOH was also added in

order to increase photocatalytic conversion and selectivity. After 48 h irradiation, the conversion of benzyl alcohol can achieve 23%. Ag nanoparticles supported on zeolite Y (Ag/Zeolite Y) can also catalyze the selective oxidation of benzyl alcohol to benzaldehyde under UV light irradiation [36]. This reaction was performed under air atmosphere and in the solvent of toluene, too. In 48 h, the conversion of benzyl alcohol can achieve 11% with the selectivity towards benzaldehyde being 62%. The selectivity for benzaldehyde can be further increased to 100% when adjusting pH with NaOH solution and using pure O₂ instead of air, though the overall conversion fell to 4% after 48 h of UV light irradiation. Recently, Pt nanoparticles supported on TiO₂ (Pt/TiO₂) were also found to be able to catalyze the selective oxidation of aromatic alcohols to aldehydes in water at ambient temperature under visible light irradiation [37]. It is found that the conversion of the reaction gets higher when the size of the Pt nanoparticles gets smaller, which could be due to large surface area of small nanoparticles. Meanwhile, it is also found that larger Pt nanoparticles give higher selectivity toward aldehyde.

The selective oxidation of 2-propanol to acetone can be also accomplished with Au nanoparticles supported on TiO₂ (Au/TiO₂) as the catalyst and under visible light irradiation [38]. An action spectrum analysis (Figure 2) on this transformation has been performed and the mechanism of the photo-induced reaction by Au/TiO₂ suspensions was proposed [38]. The action spectrum of bare TiO₂ (Aldrich-rutile) and the absorption spectrum of Au/TiO₂ that is measured in a diffuse reflection mode are also shown in Figure 2. The right y-axis of Figure 2 is the apparent quantum yield of the reaction, which was calculated as the ratio of the rate of e⁻ consumption assuming the two electron process of oxidation of 2-propanol to acetone. As observed, the tested Au/TiO₂ sample gave action spectrum that resembled the diffuse reflectance spectrum of it. The action and absorption spectra of Au/TiO₂ coincided in their peak positions, ca. 575–585 nm. The good resemblance of the two spectra clearly indicated the visible light excitation of Au-SPR was the driving force for the oxidation of 2-propanol.

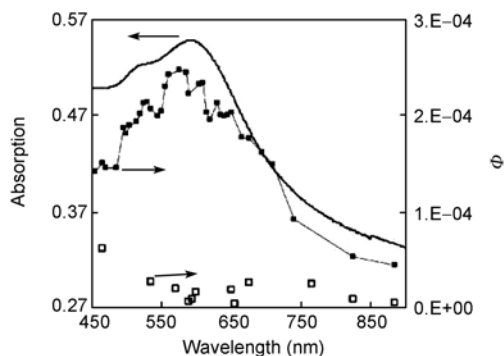
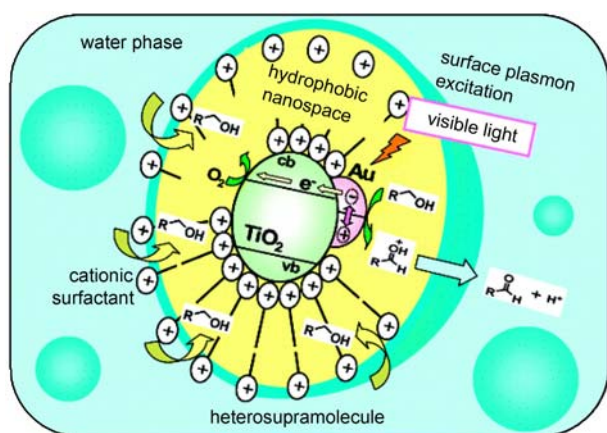


Figure 2 Action spectrum of 2-propanol oxidation on Au/TiO₂: (■) Au-modified, (□) bare and diffuse reflectance spectrum of Au/TiO₂ [38].

Recently, a heterosupramolecular photocatalyst comprised of Au/TiO₂ and a cationic surfactant has been developed to enhance the chemoselective oxidation of alcohols to carbonyl compounds in water under visible-light irradiation [39]. A picture-description of the heterosupramolecular photocatalyst is shown in Scheme 2. The cationic surfactant used in this study was trimethylstearylammmonium chloride (C₁₈TAC). The basic mechanism of the heterosupramolecular photocatalyst can be described as follows: At the critical admicelle concentration (CAMC), C₁₈TAC forms admicelle on Au/TiO₂ surface. Then alcohol in the water phase is incorporated into the hydrophobic nanospace of the admicelle to be concentrated near the Au nanoparticle surface. Upon visible light excitation, the Au nanoparticle-SPR of Au/TiO₂ induces the electron transfer from Au to TiO₂ [40]. The alcohol is oxidized on the surface of Au nanoparticle with lowered Fermi energy, while O₂ is reduced by the electrons accumulated in TiO₂. The resulting hydrophilic intermediate such as R-C=O⁺H is spontaneously transported into the water phase to yield a carbonyl compound, while the substrate alcohol is further supplied from the water phase. Compared with bare Au/TiO₂, this heterosupramolecular photocatalyst can remarkably accelerate the chemoselective oxidation of alcohols to carbonyl compounds. At the starting concentration of 5 × 10⁻⁴ M of 4-Cl-C₆H₄CH₂OH or 4-HO-C₆H₄CH₂OH with bare Au/TiO₂ as the photocatalyst, the total concentration of the generated corresponding aldehyde after 6 h visible light irradiation is only 0.33 × 10⁻⁵ and 0.21 × 10⁻⁵ M, respectively. Upon formation of the as-discussed heterosupramolecular photocatalyst after addition of 0.1 mM C₁₈TAC to the reaction system, the concentration of the yielded aldehydes after 6 h visible light irradiation increased to 1.89 × 10⁻⁵ and 6.22 × 10⁻⁵ M, which is about 5.7 and 29.6 times larger than the original concentration. These results obviously indicate the superiority of this new heterosupramolecular photocatalyst and could help expanding the efficient and selective organic synthesis with solar energy.

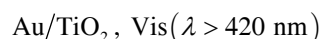


Scheme 2 The self-assembled heterosupramolecular visible-light photocatalyst which is comprised of Au/TiO₂ and cationic surfactant [39].

2.2 Selective photocatalytic oxidation of thiol to disulfide by supported noble metal nanoparticles

The redox ability of supported noble metal nanoparticles can be also used to promote the photocatalytic oxidation of thiol to disulfide [41]. This conversion is one of the most important reactions in biological processes, such as transformations of cysteine-cystine and dihydro lipoic acid-lipoic acid, as well as the controls of the secondary and tertiary structures in proteins. Stoichiometric amounts of oxidants are generally required to accomplish this conversion. The photocatalytic conversion of thiol to disulfides by supported noble metal nanoparticles obviously provides an alternative 'green' pathway.

In the approach to implement this conversion, Au/TiO₂ was utilized as the catalyst and 2-mercaptopyridine (PySH) was chosen as the substrate. The reaction was performed in aqueous solution and aerobic condition under visible light irradiation. Within the reaction, PySH was stoichiometrically transformed to 2,2'-dipyridyl disulfide (PySSPy). The value of [PySH + 2 × PySSPy] remained almost constant as the reaction proceeded. No over-oxidation products such as sulfoxide were yielded. The kinetic of this reaction was apparently zero-order toward the concentration of PySH, which would result from the constant supply of the sufficient amount of PySH due to the extremely high affinity of Au nanoparticles to sulfur containing compounds. At the reaction time of 25 h, the turnover number (the molecule number of PySH consumed/the number of Au surface atoms) was calculated to be 17.7, which confirmed the photocatalytic nature of the reaction. Under anaerobic conditions and under aerobic conditions using TiO₂ without Au nanoparticles loading, no reaction proceeded, which indicated that the reaction was driven by the visible light excitation of Au-SPR and O₂ played an acceptor of electrons injected to TiO₂ from Au nanoparticles. In summary, the total reaction can be written as equation 1:



2.3 Selective photocatalytic oxidation of benzene to phenol by supported noble metal nanoparticles

The development of highly efficient photocatalysts for the selective conversion of benzene to phenol is of high significance since phenol is one of the most important chemicals in industry. The control of the reaction selectivity as well as the utilization of visible light constitutes the biggest challenges in the research. Recently, an Au-nanoparticle-pillared layered titanate (Au-titanate) catalyst was proved to be able to catalyze the highly selective oxidation of benzene to phenol in water under visible light irradiation [42]. The synthetic procedure was performed in a controlled fashion

so that the as-obtained Au-titanate catalyst possessed unique structure. A layered titanate, $K_{0.66}Ti_{1.73}Li_{0.27}O_{3.93}$ was chosen as the support for the Au nanoparticles. Firstly, the particle surface of the pristine titanate was modified with a silane coupling reagent octadecyltrimethoxysilane. Then, the interlayer of the titanate was modified with another silane coupling reagent (3-mercaptopropyl)trimethoxysilane which possessed a thiol group. This thiol-modified layered titanate was mixed with $HAuCl_4$ followed by reduction with $NaBH_4$. The selective thiol group modification of the titanate ensured that the Au nanoparticles were only intercalated into the interlayer nanospace of the titanate instead of being dispersed onto the surface of it. The SEM and TEM images of the Au-titanate catalyst confirmed that almost all the Au nanoparticles were located in the interlayer space of the titanate (Figure 3). Based on the gallery height of Au-titanate and the particle size of Au (the inset of Figure 3), the morphology of the intercalated Au is determined to be a disk with a thickness of less than 1 nm and diameter of ca. 3.5 nm.

The unique structure of the Au-titanate catalyst ensures that it can combine the visible-light-induced Au-SPR effect with the molecular recognition ability of layered titanate to achieve the selective conversion of benzene to phenol under visible light irradiation. To fully utilize the benzene/phenol recognition ability of the catalyst, the photocatalytic reaction was conducted in the presence of the product 'phenol'. In a typical reaction, the concentration of the substrate benzene was 600 ppm, while the amount of the pre-added phenol was 18000 ppm. Under visible light irradiation and in the presence of Au-titanate, the benzene was oxidized to phenol in 62% yield and 96% selectivity, which were all superior or comparable to the results reported in other direct oxidations using catalysts or photocatalysts [43, 44]. When the Au-titanate catalyst was replaced by a layered titanate where Au nanoparticles were deposited only at the particle surface or a ruthenium complex-sensitized titania particulate,

the yield and the selectivity of the conversion all fell significantly in both cases. These results clearly indicate that the unique structure of the Au-titanate catalyst is essential to the selective oxidation of benzene to phenol. The strategy for the design of Au-titanate may be similarly applied to the fabrication of other supported noble metal nanoparticle photocatalysts, which could potentially improve the efficiency and selectivity of existing photocatalytic processes.

2.4 Selective photocatalytic reduction of nitroaromatic compounds by supported noble metal nanoparticles

The selective reduction of nitroaromatic compounds to form aromatic azo compounds is of great importance since aromatic azo compounds are high-value chemicals widely used as dyes, pigments, food additives, and drugs [45]. Traditional approaches for the synthesis are often conducted under high pressures and at high temperatures using environmentally unfriendly transition-metal reducing agents [46]. The photocatalytic process of supported noble metal nanoparticles provides an improved approach for the reduction of nitroaromatic compounds to form aromatic azo compounds since the reactions are performed at ambient temperature and pressure with light energy as the driving force. A successful example of the transformation is the selective reduction of nitrobenzene to azobenzene under visible light irradiation with Au nanoparticles supported on ZrO_2 (Au/ZrO_2) as the catalyst [47]. Table 1 shows the performances of the Au/ZrO_2 catalyst in the reduction of nitroaromatic compounds under visible light irradiation.

The high selectivity towards aromatic azo products and relatively high photonic efficiency of the transformation as shown in Table 1 demonstrates the outstanding performance of Au/ZrO_2 when being used as photocatalyst in the reduction of nitroaromatic compounds. To elucidate the mechanism of this transformation, the reduction of nitrobenzene

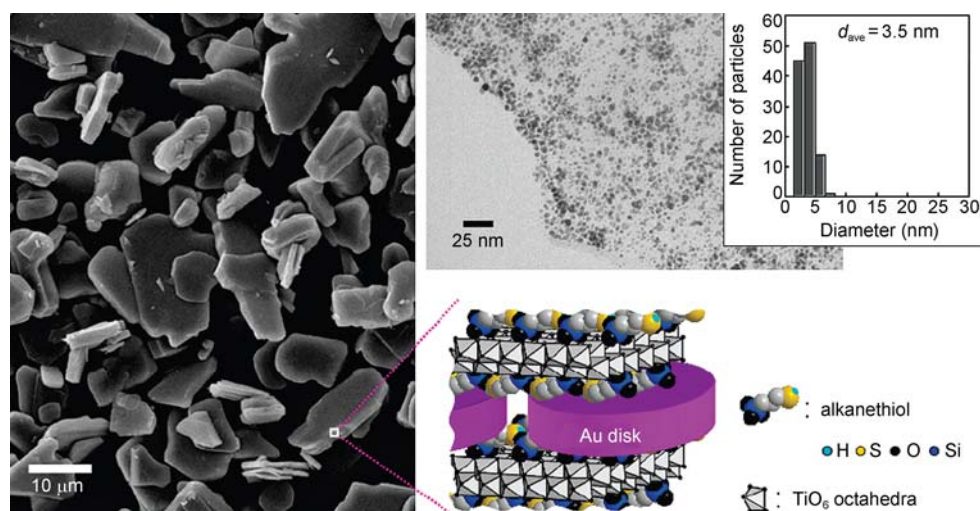
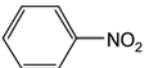
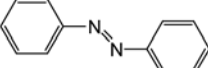
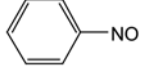
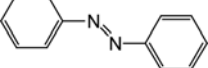
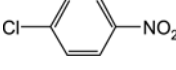
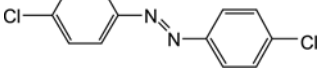
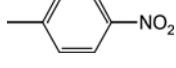
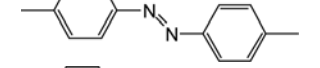
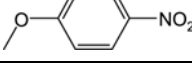
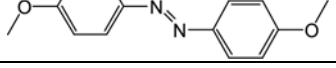


Figure 3 SEM and TEM images of Au-titanate. Insets show the size distribution of Au nanoparticles and schematic structure of Au-titanate [42].

Table 1 Reduction of nitroaromatic compounds photocatalyzed by Au/ZrO₂^{a)}

Reactant	Main product	Conv. (%)	Sel. (%)	Photonic efficiency (%)
		100 ^{b)}	> 99	6.9
		100 ^{c)}	95	7.3
		100 ^{d)}	56	3.6
		58 ^{d)}	> 99	2.1
		100 ^{d)}	82	3.6

a) Reduction reaction was conducted in an argon atmosphere at 40 °C using 30 mL of isopropyl alcohol mixed with 0.3 mmol KOH, 3 mmol nitrobenzene, and 100 mg catalyst; b) reaction time 5 h; c) reaction time 3 h; d) reaction time 6 h [47].

was chosen as the model reaction for intensive studies. Careful analysis of the reaction system showed that O₂ was released as a by-product and the amount of it was equivalent to about (82 ± 5)% of the amount derived from the quantity of the reacted nitrobenzene. Azoxybenzene and acetone were also detected as by-products through GC analysis. The temporal concentration changes of the substrate and products as the reaction proceeds are shown in Figure 4(a). The kinetic curves showed that most of the acetone in the reaction system was formed in the first hour of the reaction. Thereafter, the amount of acetone remained almost constant even though the reaction proceeded further to produce more azobenzene. Thus, the reaction could be divided into two stages. In the first stage (the reaction in the first hour), isopropyl alcohol was oxidized. In the second stage (the reaction after the first hour), the production of aromatic azo compounds proceeded with species formed in the first stage, but did not rely on the oxidation of isopropyl alcohol. It was proposed that hydrogen atoms would be abstracted from isopropyl alcohol in the first stage and bound to the surface of Au nanoparticle (H–AuNP). These H–AuNP species would

combine with the oxygen atoms of N–O bonds to yield HO–AuNP species. The electrons that were excited when the Au nanoparticles absorbed visible light could provide the activation energy that was required for the cleavage of the N–O bond. The HO–AuNP species could release O₂ and transformed into H–AuNP species that could be recycled in the subsequent reaction process (Figure 4(b)). In the second reaction stage, the surface of Au nanoparticles in the reaction system became saturated with H–AuNP and HO–AuNP species. Thus, the oxidation of isopropyl alcohol ceased and the acetone content remained unchanged. To summarize, the electrophilic N–O bond cleavage was realized by the H–AuNP species, and occurred preferentially in the presence of excited electrons provided by the illuminated Au nanoparticles.

2.5 Sonochemical hydrogen production catalyzed by supported noble metal nanoparticles

Supported noble metal nanoparticles can be also utilized as

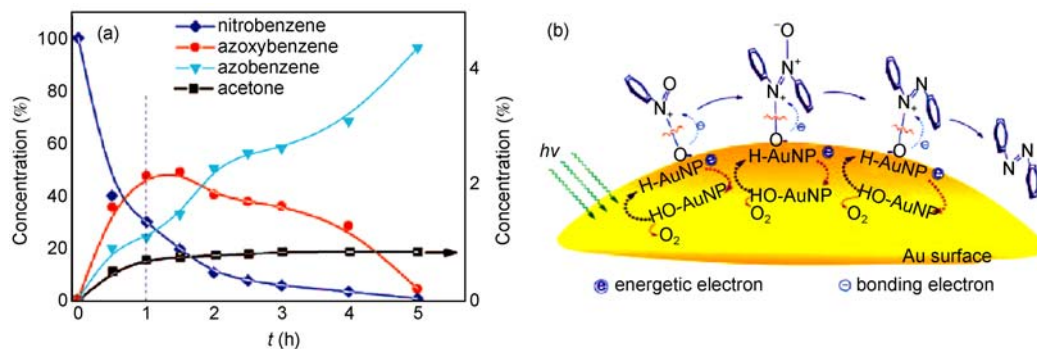


Figure 4 (a) Time-conversion plot for nitrobenzene reduction and acetone formation with Au/ZrO₂. The axis on the right-hand side refers to the acetone content, which is below 1%; (b) proposed mechanism for the photocatalytic reduction of nitroaromatic compounds [47].

efficient sonocatalysts to promote the production of H₂ [30]. Recently, we reported that Au/TiO₂ can be used as the catalyst to produce H₂ from water or aqueous solutions under ultrasound irradiation [30]. The rate of H₂ evolution from water could reach 21.6 μmol/h in the presence of Au/TiO₂ during sonolysis. The Au/TiO₂ catalyst was also quite stable under ultrasound irradiation, as evidenced by the high and reproducible H₂ evolution rate in three repeated runs. Within 15 h, the total turnover number (molecules of H₂ per atom of surface-loaded Au) reached 506. When methanol was added to the aqueous solution, the production of H₂ was greatly enhanced, which reached as high as 282.3 μmol/h.

The mechanism for H₂ evolution can be depicted as follows: (i) The propagation of ultrasonic waves through water causes numerous tiny cavitation bubbles which subsequently collapse and cause high local temperature (> 4000 K) and pressure (> 1000 atm) [48]; (ii) under these extreme conditions, water molecules undergo homolytic cleavage and form ·OH and ·H radicals (equation 2); (iii) subsequent recombination of ·H radicals gives rise to H₂ (equation 3).



The Au/TiO₂ catalyst can dramatically accelerate the cleavage of H₂O under ultrasound irradiation. A spin-trap, 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO), was used to capture ·OH and ·H radicals and the concentration of the as-formed DMPO-OH and DMPO-H was determined by electron spin resonance (ESR) spectroscopy. In the presence of Au/TiO₂, the average rates of formation of DMPO-OH and DMPO-H within the first 10 min were calculated to be 0.32 and 0.12 μM/min, respectively, whereas in the presence of bare TiO₂, the corresponding rates were only 0.11 and 0.033 μM/min. Since ·H was generated much faster when Au/TiO₂ was used as sonocatalyst compared with bare TiO₂, a higher rate of H₂ formation in the presence of Au/TiO₂ than in the presence of bare TiO₂ could be expected. This was indeed true as the rate of H₂ evolution from water was only 1.3 μmol/h in the presence of bare TiO₂ during sonolysis, which was much lower than the rate of 21.6 μmol/h in the presence of Au/TiO₂. In the case that no catalyst was used, the rate of H₂ evolution dropped to nearly zero. These results clearly indicate the pivotal role of Au/TiO₂ in the sonocatalytic H₂ production.

As mentioned before, the addition of methanol can greatly enhance the production of H₂. This is because methanol is highly volatile and can readily enter the interior of the cavitation bubbles generated under ultrasound irradiation. The ·OH is scavenged by methanol so that the reverse reaction of equation (2) is prohibited. The ·H would form H₂ either through equation (3) or through abstracting a hydrogen atom from methanol. Moreover, the high temperature of the interior of the cavitation bubbles could cause

the thermal reforming of methanol to generate H₂. The above deductions were supported by the experimental observation that H₂, HD and D₂ were all generated when CD₃OD/H₂O solution was used. The isotopic distribution of generated hydrogen gas showed that, although the addition of methanol in the presence of Au/TiO₂ resulted in a 12-fold increase in the rate of H₂ evolution, nearly half of the hydrogen atoms were nevertheless derived from water molecules. Furthermore, these results indicate that the main function of Au/TiO₂ in the catalytic reactions should be that the thermal reactions in the interior of the cavitation bubbles are enhanced by it under ultrasound irradiation.

3 Supported noble metal nanoparticles as photo/sono-catalysts for the degradation of pollutants

As discussed in section 2.1, noble metal nanoparticles would be excited under UV/visible light irradiation. Besides driving chemical synthetic reactions, the redox ability of the excited noble metal nanoparticles can be also utilized in the degradation of environmental pollutants. Many researches on this issue have been performed recently and we will briefly introduce some selected examples hereafter.

3.1 Photocatalytic decomposition of small-molecule organic pollutants by supported noble metal nanoparticles

Many small-molecule organic pollutants can be effectively decomposed by supported noble metal nanoparticles [49–52]. For example, a common air contaminant, HCHO, has been successfully decomposed by Au/ZrO₂ under visible light irradiation [49]. In a typical process, the HCHO with the initial concentration of 100 ppm in air was treated with Au/ZrO₂ under blue light irradiation (with wavelength between 400 and 500 nm and the irradiation energy of 0.17 W/cm²). Under irradiation, the HCHO was oxidized to CO₂ and the content of it decreased by 64% in two hours. The turnover frequency was calculated to be about 1.2 × 10⁻³ molecules of HCHO per gold atom per second, which was comparable to those for the CO oxidation on gold catalysts by heating the reaction system to 80 °C or above. When red light (with wavelengths between 600 and 700 nm) was applied, the catalytic activity of Au/ZrO₂ catalyst was slightly lower compared with that of the blue light; 50% of HCHO was oxidized in two hours. Sunlight could also be used as the light source for HCHO oxidation although the intensity of it was much lower (0.02 W/cm²). Within two hours, 8% of HCHO was converted into CO₂.

The Au nanoparticles supported on other oxides have also been tested for HCHO decomposition (Figure 5(A)). The TEM images of the gold catalysts on different oxide supports are also shown here (Figure 5(B)). The results showed that the gold catalysts exhibited marked activity if an oxide of a transition metal or rare earth element was used

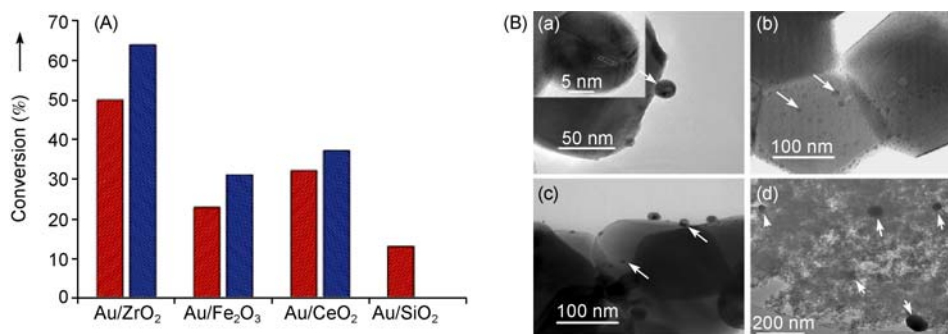


Figure 5 (A) The comparison of Au nanoparticles supported on different oxide supports on the activity of HCHO oxidation reaction. Red bars: HCHO conversion (%) under illumination of red light; blue bars: conversion under blue light; (B) TEM images of the supported Au catalysts. (a) Au/ZrO₂, (b) Au/CeO₂, (c) Au/Fe₂O₃, (d) Au/SiO₂. Arrows indicate Au nanoparticles [49].

as support, whereas a gold catalyst on SiO₂ exhibited moderate activity under red light only. It was proposed that the different oxygen adsorption ability of the supports determined the different catalytic activities of the catalysts since oxygen was the oxidation agent in the reactions. As we all know, SiO₂ is an inert support which has the function of stabilizing the small gold nanoparticles but does not adsorb oxygen, whereas the active supports such as ZrO₂ and CeO₂ can adsorb oxygen molecules. When the decomposition of HCHO was performed in pure nitrogen, about 5% of HCHO was degraded on the Au/ZrO₂ catalyst under blue light, but no HCHO oxidation was observed on the Au/SiO₂ catalyst. This was because the strongly-adsorbed oxygen in Au/ZrO₂ was able to take part in the oxidation in the deaerated condition while no such oxygen existed in Au/SiO₂. The result was also consistent with the fact that Au/ZrO₂ exhibited better catalytic activity than Au/SiO₂ in air (Figure 5(A)).

Supported noble metal nanoparticles are also able to catalyze the decomposition of small-molecule organic pollutants in aqueous solution. For example, the decomposition of formic acid in water by supported Au nanoparticles has been tested under visible light irradiation [50]. It was found that Au/CeO₂ was the most efficient photocatalyst for formic acid decomposition. Within 28 hours, a total of 100 μmol of formic acid was completely oxidized to CO₂ under visible light irradiation in air and in the presence of 1.0 wt% Au/CeO₂. Other gold catalysts like Au/TiO₂, Au/SiO₂, and Au/ZrO₂ could also catalyze the decomposition of formic acid but the reactions all proceeded much slower compared to the case of Au/CeO₂. Methyl ter-butyl ether (MTBE) could also be effectively decomposed by supported noble metal nanoparticles under visible light irradiation [51]. Au/TiO₂ and Au/TiO₂-Al₂O₃ have been used as photocatalysts for MTBE decomposition. Within 2 hours, the total organic carbon (TOC) removal can reach as high as 80% using these gold catalysts. An Ag nanoparticle supported on AgBr (Ag/AgBr) catalyst was found to be able to efficiently catalyze the decomposition of isopropyl alcohol in water under visible light irradiation [20]. Within 5 min, as high as 40% of the isopropyl alcohol (7 mL in 70 mL water) was

oxidized to CO₂ after irradiating the solution over Ag/AgBr. In addition, a Pt nanoparticle supported on Bi₂O₃ (Pt/Bi₂O₃) catalyst was also determined to be able to catalyze the decomposition of formaldehyde, acetaldehyde and methanol in aqueous solution under visible light irradiation [52].

3.2 Photocatalytic decomposition of phenolic pollutants by supported noble metal nanoparticles

Phenolic compounds are highly toxic and difficult to degrade biologically, which pose great threat to the environment [53, 54]. The discovery that supported noble metal nanoparticles can efficiently catalyze the decomposition of phenolic pollutants under UV/visible light irradiation provides an alternative solution for this problem. Recently, an Ag-AgI supported on mesoporous Al₂O₃ (Ag-AgI/Al₂O₃) catalyst was found to be able to catalyze the decomposition of several ubiquitous water pollutant phenolic compounds, 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), and trichlorophenol (TCP), under visible/ simulated solar light irradiation [55]. In the synthetic approach, AgI/Al₂O₃ was first prepared and then Ag nanoparticles were deposited onto it to fabricate the final Ag-AgI/Al₂O₃ photocatalyst. Under visible light ($\lambda > 420$ nm) irradiation, 2-CP, 2,4-DCP and TCP with the initial concentration of 10 mg/L can be completely degraded by Ag-AgI/Al₂O₃ within 30, 15, and 20 min, respectively. After 120 min, the percent TOC removal for 2-CP, 2,4-DCP, and TCP can reach 93%, 81%, and 71%, respectively. The performance of the catalyst is much superior to that of N-doped TiO₂ in identical conditions. Electron spin resonance (ESR) and cyclic voltammetry (CV) analyses showed that O₂⁻ and excited h⁺ on Ag nanoparticles were the main active species in the degradation reactions, which were generated by charge separation and transfer from plasmon-excited Ag nanoparticles.

Phenol can be also effectively degraded by supported noble metal nanoparticles. We have tested the ability of supported Ag nanoparticles on the degradation of phenol under UV light irradiation [36]. In a typical process, 100 mL aqueous solution of phenol with the concentration of 1 mM

was treated by 100 mg supported Ag catalysts. Within 120 h, 41%, 37% and 38% of phenol were degraded by Ag/ZrO₂, Ag/Zeolite Y and Ag/SiO₂, respectively. Supported Au nanoparticles can also catalyze the degradation of phenol [26]. Under the same experimental conditions as described above, 45%, 21% and 28% of phenol can be degraded by Au/ZrO₂, Au/Zeolite Y and Au/SiO₂ after 120 h of UV light irradiation, respectively.

3.3 Photocatalytic decomposition of dyes by supported noble metal nanoparticles

Dyes constitute one of the largest groups of organic pollutants due to their great biotoxicity [54]. Traditional processes such as adsorption, chlorination and ozonation are proved to be insufficient and uneconomic for treatment of these pollutants [54]. The research on the photocatalytic decomposition of dyes by supported noble metal nanoparticles has just emerged recently but is already showing its great potential in this field. We have used supported Au nanoparticles as the catalyst to degrade dye sulforhodamine-B (SRB) under UV/blue light irradiation [26]. Table 2 shows the performances of three different Au catalysts and the comparison of the performances with those of N-doped TiO₂ and bare TiO₂ under identical conditions. These data clearly indicated the higher efficiency of supported Au nanoparticles than conventional titania materials for SRB degradation under both UV and visible light irradiation as determined by the turnover frequencies.

Besides these supported Au nanoparticles, supported Ag nanoparticles can also catalyze the degradation of dyes under UV/visible light irradiation. We have tested the ability of three different supported Ag nanoparticles on the degradation of SRB [36]. An aqueous suspension of SRB (50 mL, 2×10^{-5} M) was treated with 50 mg of the photocatalyst. Under blue light irradiation with intensity of 0.011 W/cm²,

the concentration of SRB decreased by 74%, 71% and 66% after 3 h with Ag/Zeolite Y, Ag/ZrO₂ and Ag/SiO₂ as the photocatalyst, respectively. When UV light was used as the light source, these values changed to 75%, 55%, and 64%, respectively. In the contrast experiments using N-doped TiO₂ as the photocatalyst, the concentration of SRB only decreased by 34% and 49% under blue light and UV light irradiation.

A highly efficient and stable photocatalyst, Ag nanoparticles supported on AgCl (Ag/AgCl), has been fabricated to catalyze the degradation of the dye methylic orange (MO) [19]. In a typical approach, 100 mL of MO solution (20 mg/L) was treated with 0.2 g of Ag/AgCl under visible light irradiation ($\lambda \geq 400$ nm). Within 15 min, the MO was completely decomposed, indicating the high efficiency of Ag/AgCl in the degradation of MO under visible light irradiation. The rate of the MO-dye decomposition over Ag/AgCl was estimated to be about 0.133 mg/min, which was eight times faster than that over N-doped TiO₂ (ca. 0.017 mg/min). The Ag/AgCl was also very stable during the treatment of MO. After being repeatedly used for ten times, the photo-decomposition rate of MO over Ag/AgCl was still almost the same as the initial one. It was proposed that the photon absorbed by Ag nanoparticle would be efficiently separated into an electron and a hole. The electron was transferred to the surface of the nanoparticle farthest away from the interface between Ag and AgCl, and the hole was transferred to the surface of the AgCl bearing the nanoparticle. Holes transferred to the AgCl surface would promote the oxidation of Cl⁻ ions to Cl⁰ atoms, which were able to oxidize MO and hence became reduced to Cl⁻ ions again. The electrons would be trapped by O₂ in the solution to form superoxide ions (O₂⁻) and other reactive oxygen species that could also promote the decomposition of MO. Based on this mechanism, another photocatalyst, Ag nanoparticles supported on AgBr (Ag/AgBr), was fabricated and could catalyze the

Table 2 Catalytic activity of the gold photocatalysts to degrade SRB [26]

Photocatalyst	Au/Zeolite Y	Au/ZrO ₂	Au/SiO ₂	N-doped TiO ₂	TiO ₂ (P25)
Conversion under blue light (%) ^{a)}	37	46	27	34	14
Absorbed energy by Au nanoparticles or TiO ₂ under blue light (W/cm ²)	0.165	0.152	0.095	0.021	0.008
Turnover frequency under blue light (Au-atom ⁻¹ s ⁻¹ or Ti-atom ⁻¹ s ⁻¹) ^{b)}	5.1×10^{-6}	6.1×10^{-6}	3.6×10^{-6}	1.5×10^{-7}	8.8×10^{-9}
Normalized turnover frequency under blue light (cm ² J ⁻¹ Au-atom ⁻¹ or cm ² J ⁻¹ Ti-atom ⁻¹) ^{b)}	3.1×10^{-5}	4.0×10^{-5}	3.8×10^{-5}	7.1×10^{-6}	1.1×10^{-6}
Conversion under UV light (%) ^{a)}	51	64	44	49	75
Absorbed energy by Au nanoparticles or TiO ₂ under UV light (W/cm ²)	0.123	0.138	0.098	0.075	0.086
Turnover frequency under UV light (Au-atom ⁻¹ s ⁻¹ or Ti-atom ⁻¹ s ⁻¹) ^{b)}	5.4×10^{-6}	6.8×10^{-6}	4.7×10^{-6}	2.2×10^{-7}	3.3×10^{-7}
Normalized turnover frequency under UV light (cm ² J ⁻¹ Au-atom ⁻¹ or cm ² J ⁻¹ Ti-atom ⁻¹) ^{b)}	4.4×10^{-5}	4.9×10^{-5}	4.8×10^{-5}	2.9×10^{-6}	3.8×10^{-6}

a) 50 mg of photocatalyst powder was dispersed in aqueous suspension of SRB (50 mL, 2×10^{-5} M), the SRB conversions were obtained after 1 h of irradiation and determined from replicate runs agreeing to within $\pm 4\%$; b) turnover frequency data in Table 2 were calculated from the conversion after 1 h of irradiation [26].

decomposition of MO more efficiently than Ag/AgCl under visible light irradiation [20]. This catalyst could accomplish the complete decomposition of MO in 10 min under the same experimental conditions as indicated above and the rate of the MO decomposition over it was estimated to be about 0.2 mg min^{-1} . The main reason for the better performance of Ag/AgBr than Ag/AgCl is that the hole combines with Br^- to form Br^0 more easily as Br^0 has a lower electron affinity than Cl^0 .

3.4 Sonocatalytic degradation of environmental pollutants by supported noble metal nanoparticles

As discussed in section 2.2, supported noble metal nanoparticles can effectively catalyze the homolytic cleavage of water into $\cdot\text{OH}$ and $\cdot\text{H}$ radicals under ultrasound irradiation. These radicals are highly reactive and thus can be reasonably utilized in the degradation of environmental pollutants. In the sonocatalytic process, both $\cdot\text{OH}$ mediated oxidation and $\cdot\text{H}$ mediated reduction occur and contribute to the decomposition of the pollutant molecules. We have used Au/TiO₂ as sonocatalyst in the treatment of azo dyes and found that this process was very efficient [22]. Azo dyes are very useful in textile applications but also cause big problems in wastewater remediation and result in long-term pollution [54]. Common methods such as biodegradation are impractical for abatement of such dyes since the azo dyes are highly resistant to photolysis, O₂, common acids and bases, and microbial attack. The primary degradation products of azo dyes are generally aromatic amines which are toxic, carcinogenic, and teratogenic. Therefore, mineralization of the azo dyes is highly desirable to guarantee environmental safety.

In a typical approach, an azo dye, Orange II (Org II), was used as the model pollutant. 100 mL of Org II solution ($2.5 \times 10^{-4} \text{ M}$) was treated with 100 mg of Au/TiO₂ under ultrasound irradiation (the intensity was determined to be 0.045 W/cm^2). The percent TOC removal could reach 80% when the reaction was performed under Ar atmosphere for 8 h and 65% when the reaction was performed under air atmosphere for 14 h. All the Org II/ $\cdot\text{OH}$, Org II/ $\cdot\text{H}$ and Org II/ $\cdot\text{OH}+\cdot\text{H}$ adducts were detected as intermediates during the degradation of Org II, which confirmed the presence of $\cdot\text{OH}$ mediated oxidation and $\cdot\text{H}$ mediated reduction processes in the reaction. The main reason for the slower decomposition of Org II under air atmosphere was proposed to be that the $\cdot\text{H}$ mediated reduction was suppressed by the presence of O₂. The Au/TiO₂ catalyst was also very stable in the reactions, as confirmed by the maintenance of the catalyst's activity after being repeatedly used three times or used as long as twelve hours. In addition, other azo dyes such as ethyl orange (EO) and acid red G (ARG) could also be effectively decomposed over Au/TiO₂ under ultrasound irradiation. These results clearly indicate the promising

property of supported noble metal nanoparticles as sonocatalysts in the degradation of dye pollutants and further studies in this research field are definitely expected.

4 Conclusion

Although the catalytic property has only been recognized recently, supported noble metal nanoparticles are already showing great potential in many different aspects. Considering the photocatalytic and sonocatalytic applications of the supported noble metal nanoparticles as discussed in this review, the selective synthesis of chemicals and the degradation of pollutants can be taken as important achievements but we are definitely demanding more from these catalysts. The future developments rely on the fabrication of more delicate catalysts and the clarification of the mechanisms for the catalytic properties of the catalysts. The introduction of advanced analytical methods such as surface techniques can be quite helpful. It is expected that the principles for the design of the catalysts can be established so that the researchers can select proper supports and proper noble metal nanoparticles when fabricating a novel catalyst for some specific purpose.

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