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Reduction of Nitroaromatic Compounds on Supported Gold Nanoparticles by Visible and Ultraviolet Light**

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Photocatalytic processes have attracted significant interest since the 1970s and are still very active research areas today.[1,2] The degradation of organic pollutants and the production of hydrogen and oxygen from water by using semiconductor photocatalysts such as TiO_2, ZnO, and CdS have been extensively studied. However, few studies on photocatalytic reactions under visible light with catalysts such as gold nanoparticles (AuNPs) have been reported in the area of organic chemistry. Although fine gold particles have been used for centuries in stained glass windows, researchers have only recently discovered two of the most significant properties of AuNPs.[3] Firstly, AuNPs can catalyze many reactions of organic compounds at elevated temperatures, including the oxidation of various substrates and the reduction of nitrobenzene.[4–6] Secondly, AuNPs can strongly absorb visible light because of the surface plasmon resonance (SPR) effect.[7–11] This effect is the collective oscillation of conduction electrons, which resonate with the electromagnetic field of the incident light to result in a significant enhancement of the local electromagnetic fields near the rough surfaces of the AuNPs. As a result of the SPR effect, light absorption for typical spherical AuNPs is generally observed between 520 and 550 nm,[5] which can generate excited electrons in the AuNPs and also cause rapid heating.[12] Together, these two properties offer an interesting hypothesis: the molecules on the AuNPs can be activated for reaction by their proximity to the heated AuNPs and their interaction with the oscillating electrons in the AuNPs. Thus, we may be able to drive reactions on the AuNPs by using visible light at ambient temperature. The AuNPs also exhibit significant ultraviolet UV absorption that causes an interband excitation of electrons from 5d to 6sp;[10,13,14] this excitation may also be used to drive chemical reactions. Given that visible light (wavelength 400–700 nm) and UV irradiation (wavelength $<$ 400 nm) constitute around 43 % and 4 % of the solar energy emitted by the sun, respectively,[15] a photocatalytic process with supported AuNP photocatalysts has the potential to use sunlight to efficiently drive chemical reactions. Light absorption by AuNPs is also a local effect that is limited to the gold particles, so that the light heats only the AuNPs, which generally account for a few percent of the overall catalyst mass.[4–6,16,17] Therefore, such a process, if successfully realized, can be conducted at ambient temperature; thus this photocatalytic process can produce compounds that would have been unstable intermediates in a thermal reaction at high temperature.

Aromatic azo compounds are widely used in the production of dyes, food additives, and pharmaceutical products.[5,18] Currently, the synthesis of these compounds is often conducted under high pressures and at high temperatures using transition-metal reducing agents.[5,18] The by-products formed from the reducing agent are harmful to the environment.[18] Recently, it was reported that aromatic azo compounds could be synthesized from the corresponding nitroaromatic compounds through a two-step, one-pot reaction with catalysts comprising AuNPs on TiO_2 or CeO_2 at 100 °C or higher.[6] Firstly, nitrobenzene was over-reduced to aniline on the gold catalysts by hydrogen (9 bar). The reaction was continued by flushing out the H_2 and introducing O_2 at 5 bar and 100 °C to oxidize aniline to azobenzene. Azobenzene was formed as an intermediate in the thermal hydrogenation of nitrobenzene to form aniline, but, in this case, the azobenzene was unstable under the reaction conditions and was rapidly reduced to aniline.[6,17] A subsequent oxidation step was thus required to produce the target azobenzene. As photocatalytic reactions are mostly conducted at ambient temperature and atmospheric pressure,[1,2] many intermediates are stable under such conditions and would not react further. If the direct reduction of nitroaromatic compounds to their corresponding azo aromatic compounds can be realized by a photocatalytic process, the synthesis of aromatic azo compounds would be a much more controlled, simplified, and greener process.

To test the possibility of driving the reduction of nitrobenzene with light, AuNPs were supported on zirconia powder by reducing $HAuCl_4$ with $NaBH_4$ in the presence of ZrO_2 powder (full details of the synthesis and characterization are given in the Experimental Section). Photocatalysts with three gold loadings (1.5, 3.0, and 5.0 wt % of the overall catalyst mass) on the ZrO_2 powder were prepared. TEM images of these samples showed that the gold existed on ZrO_2

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as nanoparticles of about 6 nm in size (Figure 1). These catalysts were used directly for photocatalytic reactions. The catalysts' performances in the reduction of nitroaromatic compounds under incandescent light illumination (mainly composed of visible light (see Figure S1 in the Supporting Information) are shown in Table 1.

The photocatalytic reduction of nitrobenzene resulted in a high conversion and a high selectivity for azobenzene when light of wavelengths above 400 nm and an intensity of 0.30 $\mathrm{W\,cm^{-2}}$ (measured at the reaction system) were used. After 5 hours, 100 % of the nitrobenzene was reduced and the product was found to contain more than 99 % azobenzene. The photocatalyst with a gold content of 3 wt % was found to have the highest activity. Photocatalysts with a lower or higher gold content (1.5 wt % or 5 wt %) clearly showed a poorer performance (see Table in the Supporting Information). TEM observations showed that a gold loading higher than 3 wt % led to aggregation of the NPs (data not shown). This aggregation reduces the area of the AuNP surface on which the catalytic reaction takes place. The temperature of the reaction system was 40 °C because of the irradiation, and a control experiment showed that a negligible reduction of nitrobenzene occurred in the dark at 40 °C. No reaction was observed in a blank experiment conducted in with ZrO_2 powder instead of AuNPs under otherwise identical conditions. Furthermore, when the light intensity was reduced from 0.30 $\mathrm{W\,cm^{-2}}$ to 0.15 $\mathrm{W\,cm^{-2}}$, 0.03 $\mathrm{W\,cm^{-2}}$, and 0.017 $\mathrm{W\,cm^{-2}}$ but all the other experimental conditions remained unchanged, the conversion activity of nitrobenzene decreased from 100 % to 76.5 %, 50 %, and 30 %, respectively. It was thus evident that the reaction was driven by visible light. Furthermore, the new photocatalyst also showed high conversion activities in the highly selective reduction of other nitroaromatic compounds to produce the corresponding azo compounds (Table 1).

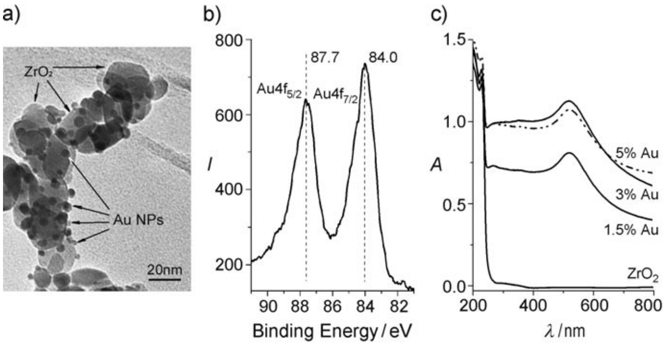
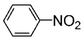
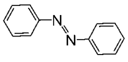
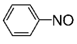
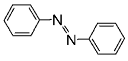
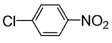
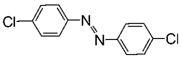
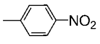
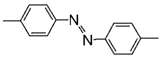
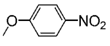
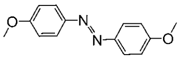


Figure 1. Characterization of the catalysts. a) TEM image of 3 wt % Au/ZrO_2 (3 wt % of gold nanoparticles on ZrO_2); b) X-ray photoelectron spectra (XPS) of 3 wt % Au/ZrO_2; and c) UV/Vis diffuse reflectance spectra of the ZrO_2 support and 3 wt % Au/ZrO_2 photocatalysts.

Table 1: Reduction of nitroaromatic compounds in the presence of supported metal nanoparticles.[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.

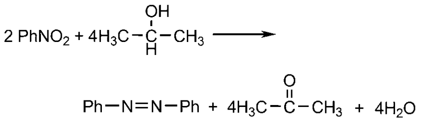
The photonic efficiency of the reduction reaction could be estimated from the radiation absorbed by the photocatalyst (details of the measurement and calculation of the photonic efficiency of the current study are given in Figure S1 in the Supporting Information).[19] The reduction of nitrobenzene using 3 wt % AuNPs supported on ZrO_2 proceeded with an efficiency of 6.9 %, which exceeded that of the well-known photocatalytic reaction that uses a TiO_2 catalyst under UV irradiation (efficiency < 1.5 %). The AuNP photocatalysts are able to catalyze the reduction of 0.1 $\mathrm{mol\,L^{-1}}$ nitrobenzene (the molar ratio of reacted nitrobenzene to gold in the photocatalyst is 197).

The X-ray photoelectron spectroscopy (XPS) spectra of the supported gold photocatalysts with different gold contents all showed the same pattern. The binding energies of Au $4f_{7/2}$ and Au $4f_{5/2}$ electrons are 84.0 eV and 87.7 eV, respectively (Figure 1 b). These values are identical to those for metallic gold, and suggest that the photocatalysts exists in the metallic state. Therefore, the absorption peak at approximately 520 nm in the UV/Vis spectrum of the gold supported on ZrO_2 (Figure 1 c) can be attributed to a SPR absorption by the AuNPs, as ZrO_2 exhibited little absorption of light with wavelengths longer than 330 nm. The band gap of ZrO_2 is about 5 eV.[20] These results further confirm the conclusion that the AuNPs supported on ZrO_2 were the photocatalysts and the reduction of nitroaromatic compounds was driven by visible light (further details on the choice of oxide support are given in the Supporting Information).

The significant UV absorption of AuNPs (Figure 1 c) can also drive the photocatalytic reduction of nitrobenzene. The conversion of nitrobenzene under UV irradiation with an intensity of 0.017 $\mathrm{W\,cm^{-2}}$ was found to be 36 %, which is higher than that under visible light of the same intensity (30 %). This result demonstrates that the wavelength of the irradiation can influence the reaction rate of the photocatalytic reduction.

As oxygen gas was released as an unforeseen by-product, a deflated gas expansion bag was connected to the sealed round-bottom flask in order to collect the gas released throughout the photocatalytic reduction. The gas in the bag was analyzed by using GC. The quantity of the released oxygen was estimated from its volume, which was equivalent to about (82 ± 5) % of the amount derived from the quantity of the reacted nitrobenzene. The release of oxygen was not observed in reduction reactions under thermal reaction conditions.[6] The photocatalytic reduction evidently proceeded by a mechanism different to that of conventional reduction or catalytic reduction in a thermal reaction process.

We also found that the choice of solvent substantially affected the reduction activity of the AuNPs. Solvents such as ethanol, isopropyl alcohol, benzyl alcohol, and hexyl alcohol were used, but the best performance was achieved when isopropyl alcohol was used. For example, when the reduction reaction was carried out in isopropyl alcohol, only 30 % conversion and 60 % selectivity were achieved with the 3 wt % Au/ZrO_2 photocatalyst after 5 hours, when all the other experimental conditions remained unchanged. It has been reported that isopropyl alcohol can be oxidized to acetone in a catalytic reaction with heating, thereby effecting the simultaneous reduction of the compound that is dissolved in the isopropyl alcohol.[21] If isopropyl alcohol did act as a reducing agent, the reaction would be:



$$2\,PhNO_2 + 4\,H_3C-\underset{H}{\overset{OH}{C}}-CH_3 \longrightarrow Ph-N{=}N-Ph + 4\,H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + 4\,H_2O \qquad (1)$$

Careful analysis of the product by GC confirmed the formation of acetone during the reaction. However, the amount of acetone was only one eighth of the quantity calculated from Equation (1). It was also noted 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 (Figure 2). Hence, isopropyl alcohol acted only as an initiator and did not participate in any of the subsequent reactions. Clearly, the photocatalytic reaction, especially after the first hour, did not proceed according to Equation (1). This reaction should involve two processes; in the first process (the reaction in the first hour), isopropyl alcohol was oxidized. In the second process (the reaction after the first hour), the production of aromatic azo compounds proceeded with species formed in the first process, but did not rely on the oxidation of isopropyl alcohol.

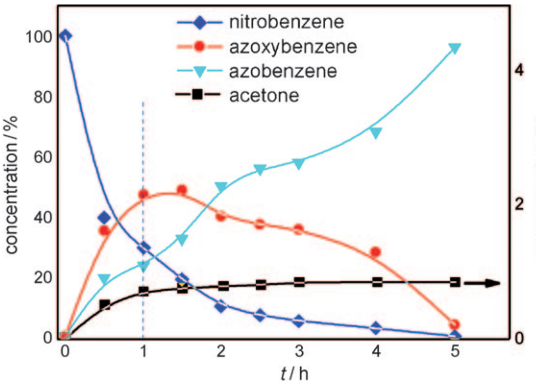
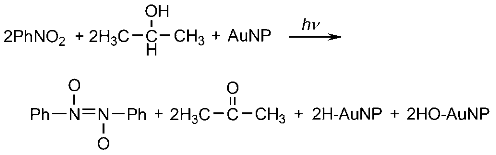
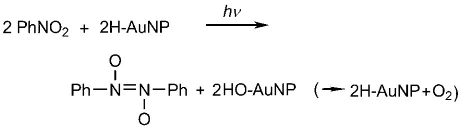


Figure 2. Time-conversion plot for nitrobenzene reduction and acetone formation with 3 wt % Au/ZrO_2 and irradiation intensity of 0.3 $W\,cm^{-2}$. The reduction reaction was conducted in an argon atmosphere at 40 °C using 30 mL isopropyl alcohol with 0.3 mmol KOH, 3 mmol substrate, and 100 mg catalyst. The axis on the right-hand side refers to the acetone content, which is below 1 %.

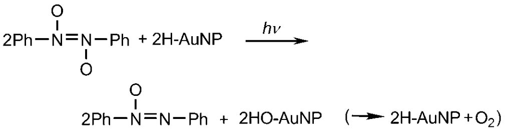
The presence of KOH enhances the abstraction of a hydrogen atom from isopropyl alcohol, which is a hydrogen-donor solvent.[22] Indeed, hydrogen atoms bound to the AuNP surface (H–AuNP) have been detected from supported AuNPs in the presence of isopropyl alcohol.[23] The Au–H bond is relatively stable, hence, H–AuNP species can form on the surface of AuNPs in the reaction system of the present study. These H–AuNP species are capable of combining with the oxygen atoms of N–O bonds to yield HO–AuNP species. The electrons that are excited when the AUNPs absorb light can provide the activation energy that is required for the cleavage of the N–O bond. The HO–AuNP species, which have been previously reported,[24] can release oxygen gas and transform into H–AuNP species that can be recycled in the subsequent reaction process (see Figure 3). We therefore tentatively propose the following elementary reactions that may be involved in this photocatalytic process:



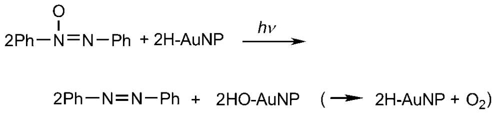
$$2PhNO_2 + 2H_3C-\underset{H}{\overset{OH}{C}}-CH_3 + AuNP \xrightarrow{h\nu} Ph-\overset{O}{N}{=}\underset{O}{N}-Ph + 2H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + 2H\text{-}AuNP + 2HO\text{-}AuNP \qquad (2)$$



$$2\,PhNO_2 + 2H\text{-}AuNP \xrightarrow{h\nu} Ph-\overset{O}{N}{=}\underset{O}{N}-Ph + 2HO\text{-}AuNP \quad (\rightarrow 2H\text{-}AuNP + O_2) \qquad (3)$$

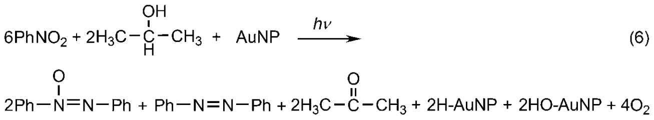


$$2Ph-\overset{O}{N}{=}\underset{O}{N}-Ph + 2H\text{-}AuNP \xrightarrow{h\nu} 2Ph-\overset{O}{N}{=}N-Ph + 2HO\text{-}AuNP \quad (\rightarrow 2H\text{-}AuNP + O_2) \qquad (4)$$



$$2Ph-\overset{O}{N}{=}N-Ph + 2H\text{-}AuNP \xrightarrow{h\nu} 2Ph-N{=}N-Ph + 2HO\text{-}AuNP \quad (\rightarrow 2H\text{-}AuNP + O_2) \qquad (5)$$

As shown in Figure 2, the azoxybenzene/azobenzene ratio was approximately 2:1 after the first hour of reaction. Thus, the overall reaction of the first process can be derived by summing the above elementary reactions [(2 × Eq. (2)) + (4 × Eq. (3)) + (3 × Eq. (4)) + Eq. (5)] to give:



$$6PhNO_2 + 2H_3C-\underset{H}{\overset{OH}{C}}-CH_3 + AuNP \xrightarrow{h\nu} 2Ph-\overset{O}{N}{=}N-Ph + Ph-N{=}N-Ph + 2H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + 2H\text{-}AuNP + 2HO\text{-}AuNP + 4O_2 \qquad (6)$$

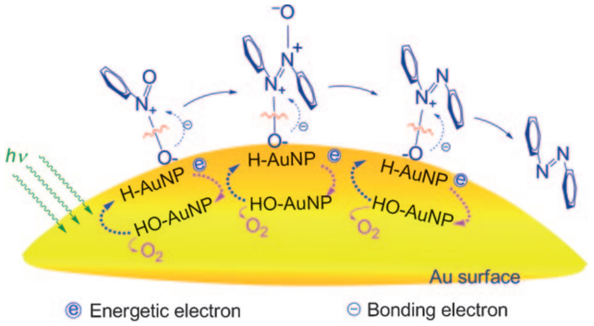
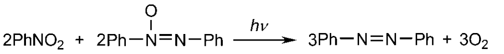


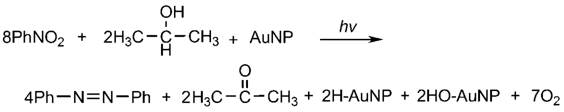
Figure 3. Mechanism for the photocatalytic reduction of nitroaromatic compounds. H–AuNP reacts with the N–O bonds to produce HO–AuNP species, which subsequently decompose to produce oxygen molecules and H–AuNP species.

In the second process, the oxidation of isopropyl alcohol was negligible and a large amount of azoxybenzene formed in the first process (Figure 2) was reduced. Hence, we exclude the reaction in Equation (2) and sum up the elementary reactions [(2 × Eq. (3)) + Eq. (4) + (2 × Eq. (5))] to give:



$$2\mathrm{PhNO_2} + 2\mathrm{Ph{-}\overset{O}{\overset{|}{N}}{=}N{-}Ph} \xrightarrow{h\nu} 3\mathrm{Ph{-}N{=}N{-}Ph} + 3\mathrm{O_2} \quad (7)$$

The above equation suggests that an intramolecular oxidation/reduction reaction of nitrobenzene and azoxybenzene took place in the second stage of the reaction; the oxygen atoms were oxidized from an oxidation state of −2 to oxygen molecules (oxidation state of 0), and the nitrogen atoms were reduced from an oxidation state of +3 to a state of −1. By summing together the reactions in Equations (6) and (7), the reaction for the overall photocatalytic process is:



$$8\mathrm{PhNO_2} + 2\mathrm{H_3C{-}\underset{H}{\overset{OH}{C}}{-}CH_3} + \mathrm{AuNP} \xrightarrow{h\nu} 4\mathrm{Ph{-}N{=}N{-}Ph} + 2\mathrm{H_3C{-}\overset{O}{\overset{\|}{C}}{-}CH_3} + 2\mathrm{H\text{-}AuNP} + 2\mathrm{HO\text{-}AuNP} + 7\mathrm{O_2} \quad (8)$$

The azobenzene/acetone ratio (2:1) and the amount of oxygen released (87.5 % of amount of the reacted nitrobenzene) in this equation are consistent with the experimental results ((82 ± 5) %). Azoxybenzene, which is produced by the removal of a single oxygen atom from the dimeric structure of nitrosobenzene, was also detected in our experiments (the azoxybenzene content during the reaction is shown in Figure 2). Azobenzene was produced by loss of the oxygen atom of the N–O bond in azoxybenzene [Eq. (5)]. The product of reactions [Eqs. (2) and (3)] and the dimeric structure of nitrosobenzene have also been previously reported.[25]

According to Equation (2), the oxidation of isopropyl alcohol results in the H–AuNP species. After the initial reaction stage, the oxidation of isopropanol should cease when the surface of AuNPs in the reaction system becomes saturated with H–AuNP and HO–AuNP species, and the acetone content of remains unchanged. It follows that the amount of acetone, which is the product of the first reaction process, should be directly proportional to the quantity of AuNPs in the reaction system. Indeed, when the photocatalyst quantity, which is proportional to the surface area of AuNPs, was increased from 100 mg to 200 mg, the content of acetone in the reaction system doubled after one hour of reaction.

According to Figure 3, the H–AuNP species play a pivotal role in this photocatalytic reaction. It is, therefore, expected that the removal of the species would prohibit the reaction. 2,2′,6,6′-tetramethylpiperidine *N*-oxyl (TEMPO) is a hydrogen abstractor and can abstract hydrogen atoms from the surface of gold to form hydroxylamine.[26] When 200 mg of TEMPO was added to the reaction system with 100 mg of 3 wt % Au/ZrO_2 photocatalyst, almost no reduction of nitrobenzene occurred. We did not detect any products or intermediates of the reactions between TEMPO and reactant. This result confirms the existence and role of H–AuNP species in the systems in the present study. To further verify the important role of the H–AuNP and HO–AuNP species, after 5 hours of reaction, 3 mmol of fresh nitrobenzene was injected into a sealed reaction system in which 3 mmol nitrobenzene had already been converted into azobenzene. Two hours later, more azobenzene and azoxybenzene formed, with a negligible increase in the amount of acetone. Evidently, the conversion of the injected nitrobenzene was mainly due to the H–AuNP and HO–AuNP species.

The role of the H–AuNP and HO–AuNP surface species provides an explanation for the lower activity of the sample with larger AuNPs (obtained by heating the 3 wt % AuNPs on ZrO_2). When the surface area was reduced, the number of surface species also reduced, thus resulting in poorer performance. It is also known that AuNPs smaller than 2 nm exhibit a very weak SPR effect.[27] The mean size of the AuNPs (3 wt %) on ZrO_2 was approximately 6 nm; the AuNPs thus have a large surface to accommodate the surface species and good SPR light absorption. Hence the photocatalyst exhibited relatively high activity.

The key step of the reduction is to break the N–O bonds. 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 AuNPs. The absorption of visible light by AuNPs through the SPR effect caused changes in the electron distribution over the energy levels. The 6sp electrons of gold gained energy through SPR absorption and migrated to higher energy levels[9,11,13,14] (left panel, Scheme in the Supporting Information). UV irradiation can also generate energetic electrons by an interband excitation of electrons from 5d to 6sp (right panel, Scheme in the Supporting Information).

The oscillating electrons interact strongly with the electrophilic nitro groups of the nitrobenzene molecules, and assist the cleavage of the N–O bonds by H–AuNP species on the AuNPs (Figure 3). Increasing the irradiation intensity produces more oscillating electrons. To verify the important role of the oscillating electrons further, the light irradiation was turned off after 1.5 hours of reaction time. The reaction did not proceed further as the H–AuNP species could not break the N–O bonds without the oscillating electrons (which are not produced in the dark), although there were sufficient H–AuNP species.

The most outstanding feature of the new photocatalysts is their moderate ability in catalyzing redox reactions. The well-known TiO_2 semiconductor photocatalyst has a high oxidation potential (2.7 V).[4] These catalysts generally exhibit poor selectivity, thus making them a poor choice for catalytic synthesis of fine chemicals. It is also difficult to adjust the oxidation potential of the semiconductor photocatalysts in order to tune their selectivity. In contrast, the moderate catalyzing properties of the supported AuNP photocatalysts, combined with the ability to conduct photocatalytic reductions at lower temperature and pressure than those for thermal reactions, have enabled us to select an unstable intermediate of a thermal reaction as the product, such as in the case of aromatic azo compounds. This discovery reveals a new class of useful catalytic processes for fine chemical production. These processes are greener than thermal processes, have the potential to utilize solar energy, and can be applied in temperature-sensitive synthesis.

Experimental Section

Catalyst preparation: ZrO_2 powder (2.5 g; particle size less than 100 nm) was dispersed an aqueous solution of $HAuCl_4$ of a given concentration (93 mL). Lysine (0.53 M, 20 mL) was then added to the mixture under vigorous stirring for 30 min. An aqueous solution of $NaBH_4$ (0.35 M, 10 mL) was added gradually in about 10 min to the suspension, followed by hydrochloric acid (0.3 M, 10 mL). The mixture was left to stand for 24 h and then the solid was separated, washed with water and ethanol, and dried at 60 °C. The resulting solid was used directly in photocatalytic experiments.

Activity test: The reduction of nitrobenzene was conducted in an argon atmosphere at 40 °C unless otherwise specified. Nitrobenzene (3 mmol) was dissolved in isopropyl alcohol (30 mL), and a solution of KOH in isopropyl alcohol (0.1 M, 3 mL) and the catalyst (100 mg) were added. The mixture was stirred magnetically during reaction and illuminated with incandescent light or UV light. The gaseous samples were analyzed using a Shimadzu GC-2014 GC with 5 A molecular sieve column and the liquid products were analyzed using an Agilent HP-6890 GC with a DB-Wax column.

Characterization: TEM images were recorded with a Philips CM200 transmission electron microscope employing an accelerating voltage of 200 kV. The specimens were fine powders deposited onto a copper microgrid coated with a holey carbon film. The composition of some samples was determined by using the energy-dispersive X-ray spectroscopy attachment of an FEI Quanta 200 scanning electron microscope. The diffuse reflectance UV/Vis spectra of the samples were recorded on a Cary 5000 UV–Vis–NIR Spectrophotometer.

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