

Functionalization of a plasmonic Au/TiO₂ photocatalyst with an Ag co-catalyst for quantitative reduction of nitrobenzene to aniline in 2-propanol suspensions under irradiation of visible light†

Cite this: *Chem. Commun.*, 2013, **49**, 2551

Received 20th December 2012,
Accepted 7th February 2013

DOI: 10.1039/c3cc39096a

www.rsc.org/chemcomm

Atsuhiko Tanaka, Yuri Nishino, Satoshi Sakaguchi, Takayuki Yoshikawa, Kazuya Imamura, Keiji Hashimoto and Hiroshi Kominami*

A functionalized plasmonic Au/TiO₂ photocatalyst with an Ag co-catalyst was successfully prepared by the combination of two types of photodeposition methods, and it quantitatively converted nitrobenzene and 2-propanol to aniline and acetone under irradiation of visible light.

Reduction of nitro aromatics to amino aromatics without side reactions such as re-oxidation reaction remains a challenging task. Amino aromatics are widely used as intermediates for many fragrances, drugs, and dyes in chemical industries. Catalytic reduction of nitro aromatics with hydrogen (H₂) has been proposed as the most plausible method.¹ These thermocatalytic systems promote nitro hydrogenation but require reducing gases such as H₂ and carbon monoxide.

Organic synthesis by using semiconductor photocatalysts such as titanium(IV) oxide (TiO₂) has attracted much attention.² However, less attention has been paid to reduction of organic compounds by photogenerated electrons,³ and these photocatalytic reductions by TiO₂ are performed under irradiation of UV light. Therefore, the development of visible-light-responding photocatalysts is an important topic for chemical syntheses using solar energy in the future. However, to the best of our knowledge, there are no reports on selective reduction of organic compounds using visible-light-responding photocatalysts.

Nanoparticles of gold (Au) show strong photoabsorption of visible light at around *ca.* 550 nm due to surface plasmon resonance (SPR). Supported Au nanoparticles have been applied to a visible-light-responding photocatalyst.^{4,5} In our previous study,^{5h} we found that TiO₂ having both small metal nanoparticles and large Au particles without alloying and nanoparticle coagulation could be successfully prepared by the combination of traditional photodeposition of metal in the presence of a hole scavenger (PH)

and subsequent Au colloid photodeposition in the presence of a hole scavenger (CPH)^{5g} onto TiO₂-metal. The functionalized Au/TiO₂ sample with a platinum (Pt) co-catalyst, *i.e.*, Au/TiO₂-Pt, exhibited a much larger rate of H₂ formation than that of the Pt-free Au/TiO₂ sample.^{5h} Therefore, functionalization of Au/TiO₂ samples with a co-catalyst is an effective method for enhancing performance, especially when electron scavenging is important.

In this study, we used an Au/TiO₂ sample for photocatalytic reduction of nitrobenzene in a 2-propanol suspension without using reducing gases under irradiation of visible light. Here we report, for the first time, that photocatalytic reduction of nitrobenzene to aniline under irradiation of visible light was achieved and that the photocatalytic performances (reaction rate and stoichiometry) were drastically improved by functionalization of Au/TiO₂ with Ag nanoparticles as a co-catalyst.

Nanocrystalline TiO₂ powder was prepared using the HyCOM method at 573 K,⁶ and the product was calcined at 1273 K for 1 h in a box furnace. Transformation of the anatase phase to the rutile phase occurred upon calcinations, and the crystallinity was improved. The HyCOM TiO₂ sample is denoted hereafter simply as TiO₂. Other experimental procedures are described in the ESI.†

Fig. 1(a) shows a TEM photograph of TiO₂ with a 0.5 wt% Ag co-catalyst (TiO₂-Ag) sample simply prepared by the traditional PH method and the distribution of Ag particles in the sample. Small Ag particles were observed and the average diameter was determined to be 3.3 nm, indicating that the Ag nanoparticles were successfully deposited on the surface of TiO₂ by using the PH method. Fig. 1(b) shows a TEM photograph and distribution of colloidal Au nanoparticles, revealing that Au nanoparticles have an average particle size of 13 nm within a relatively sharp distribution with a standard deviation of 1.4 nm. Fig. 1(c) shows a TEM image of TiO₂ with 2.0 wt% Au nanoparticles (Au/TiO₂) prepared by the CPH method using the Au colloidal solution, indicating that Au nanoparticles were deposited on the TiO₂ surface by the CPH method. The average diameter of Au particles in the sample was determined to be 13 nm, which is in good agreement with the average diameter of original colloidal Au nanoparticles before Au loading (Fig. 1(b)). By using the CPH method,

Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Kowakae, Higashiosaka, Osaka 577-8502, Japan.
E-mail: hiro@apch.kindai.ac.jp

† Electronic supplementary information (ESI) available: Experimental procedure, Fig. S1 and Table S1. See DOI: 10.1039/c3cc39096a

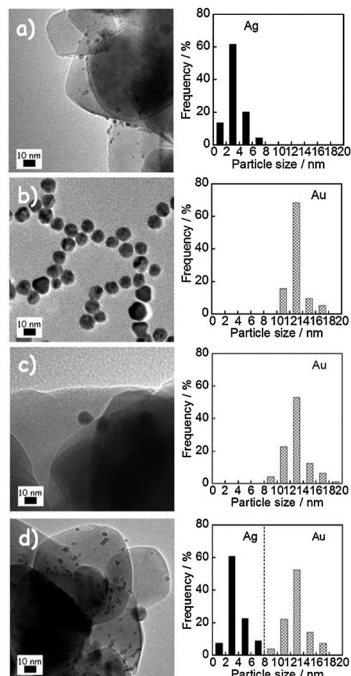


Fig. 1 TEM photographs (left) and size distributions (right) of (a) $\text{TiO}_2\text{-Ag}$ (0.5 wt%), (b) colloidal Au nanoparticles, (c) Au (2.0 wt%)/ TiO_2 and (d) Au (2.0 wt%)/ $\text{TiO}_2\text{-Ag}$ (0.5 wt%).

Au nanoparticles (2.0 wt%) were introduced on the $\text{TiO}_2\text{-Ag}$ sample, and Fig. 1(d) shows a TEM photograph of the Au/ $\text{TiO}_2\text{-Ag}$ sample, indicating that both smaller particles and larger particles were present with average diameters determined to be 3.7 nm and 13 nm, respectively. From the TEM images of $\text{TiO}_2\text{-Ag}$ and Au/ TiO_2 samples, the smaller and larger particles of the Au/ $\text{TiO}_2\text{-Ag}$ sample were assigned to Ag and Au, respectively. These results indicate that the CPH method induced no change in Ag nanoparticles during loading of Au particles and that Au nanoparticles were successfully loaded on $\text{TiO}_2\text{-Ag}$ without changes in the original particle size as in the case of loading Au onto bare TiO_2 . In our previous study using the CPH method, we found that the presence of a hole scavenger was indispensable for quantitative loading of Au particles, *i.e.*, a reductive condition should be created on the TiO_2 surface.^{5g} Therefore, in the case of loading of Au particles on $\text{TiO}_2\text{-Ag}$ by the CPH method, Au particles were probably deposited in contact with Ag nanoparticles because Ag particles loaded on TiO_2 often act as reduction sites in various reaction systems. The numbers of Ag and Au particles in $\text{TiO}_2\text{-Ag}$ and Au/ TiO_2 samples were calculated to be 2.5×10^{16} and 9.0×10^{14} per gram of TiO_2 , respectively, from the average sizes, contents and densities of Ag and Au assuming that both Ag and Au particles were spherical. Since the number of Ag particles was much larger than that of Au particles, the decrease in the number of exposed Ag particles due to contact with Au particles by the CPH method is negligible in the Au/ $\text{TiO}_2\text{-Ag}$ sample. Fig. S1 (ESI[†]) shows absorption spectra of the TiO_2 , $\text{TiO}_2\text{-Ag}$, Au/ TiO_2 and Au/ $\text{TiO}_2\text{-Ag}$ samples, in which strong photoabsorption was observed at around 550 nm for the Au-loaded samples.

The photocatalytic activity of Au/ $\text{TiO}_2\text{-Ag}$ for the reduction of nitrobenzene (initially 75 μmol) was evaluated. Fig. 2(a) shows

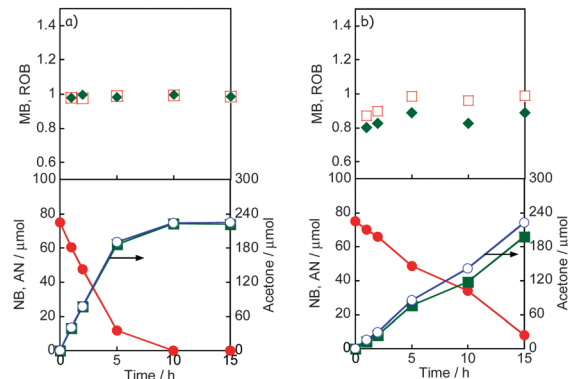
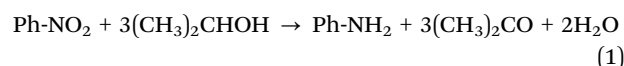


Fig. 2 Time courses of the amounts of nitrobenzene (closed circles), aniline (closed squares), acetone (open circles), MB (open squares) and ROB (closed diamonds) in 2-propanol suspensions of (a) Au/ $\text{TiO}_2\text{-Ag}$ and (b) Au/ TiO_2 under irradiation of visible light from a Xe lamp with a Y-48 cut filter.

the time course of photocatalytic reduction of nitrobenzene in a 2-propanol suspension of Au/ $\text{TiO}_2\text{-Ag}$ under irradiation of visible light from a Xe lamp with a Y-48 cut filter (Fig. S1, ESI[†]). The amount of nitrobenzene decreased linearly with photoirradiation, while aniline as the reduction product of nitrobenzene and acetone as the oxidation product of 2-propanol were formed. We noted that the plot of aniline always overlapped with the plot of acetone almost completely (Fig. 2(a)) (the scale in the right axis for acetone being three-times larger than that in the left axis), indicating that this photocatalytic reaction occurred with maintenance of high stoichiometry. Nitrobenzene was completely consumed after irradiation for 10 h, while 75 μmol of aniline was formed as the reduced product by photoirradiation for 10 h. The result indicates that aniline was formed with quite high selectivity (>99%) at >99% conversion of nitrobenzene; *i.e.*, quantitative conversion of nitrobenzene to aniline was achieved, in the present photocatalytic reaction system under irradiation of visible light. The amount of aniline (75 μmol) after photoirradiation for 10 h was larger than the amounts of Au (5.0 μmol) and Ag (2.3 μmol) loaded on TiO_2 , indicating that the reduction of nitrobenzene observed in the present study was a (photo)catalytic reaction. As the oxidized product, 224 μmol of acetone was formed by photoirradiation for 10 h, while no CO_2 was detected during the photoirradiation. The overall photocatalytic reaction is expressed as eqn (1).



Material balance (MB) and redox balance (ROB) were calculated from eqn (2) and (3), respectively,

$$\text{MB} = [n(\text{Ph-NO}_2) + n(\text{Ph-NH}_2)]/n_0(\text{Ph-NO}_2), \quad (2)$$

$$\text{ROB} = [3 \times n(\text{Ph-NH}_2)]/n(\text{acetone}), \quad (3)$$

where $n(\text{Ph-NO}_2)$, $n(\text{Ph-NH}_2)$ and $n(\text{acetone})$ are the amounts of nitrobenzene, aniline and acetone during the photocatalytic reaction, respectively, and $n_0(\text{Ph-NO}_2)$ is the amount of nitrobenzene before the photocatalytic reaction. As shown in Fig. 2(a), the values of ROB and MB were almost unity regardless of irradiation time. These results indicate that reduction of nitrobenzene to

aniline and oxidation of 2-propanol to acetone occurred with high stoichiometry as shown in eqn (1); in other words, 2-propanol was used only for reduction of nitrobenzene. We also confirmed that further irradiation to the reaction mixture did not alter the amount of aniline (Fig. 2(a)). From these results, we can point out two excellent aspects of this reaction system as well as stoichiometry. The first is that only 2-propanol was oxidized even in the presence of a reduced product, *i.e.*, aniline. In our previous study,^{5f} we examined intermolecular competitive oxidation of benzyl alcohol and aniline to benzaldehyde and nitrobenzene, respectively, in aqueous suspensions of Au/CeO₂ under irradiation by green light from an LED and we found that the oxidation on Au nanoparticles prioritized the hydroxyl group of alcohol over the amino group. The second excellent aspect is that no other reactions, *i.e.*, re-oxidation of aniline, fruitless decomposition of acetone and 2-propanol, and reduction of TiO₂, occurred even by excessive photoirradiation after complete consumption of nitrobenzene as shown in Fig. 2(a).

To clarify the effects of the Ag co-catalyst on this reaction, the Ag-free Au/TiO₂ sample shown in Fig. 1(c) was also used under the same conditions, and the results are shown in Fig. 2(b). The Ag-free Au/TiO₂ sample exhibited rates of nitrobenzene consumption and aniline formation that were smaller (*ca.* 40%) than those of the Au/TiO₂-Ag sample. In addition, the ROB value of the Au/TiO₂ sample was lower (80–90%) than that of the Au/TiO₂-Ag sample (>98%), *i.e.*, the yield of acetone was larger than that of aniline, indicating that other side reactions consuming 2-propanol simultaneously occurred in the absence of the Ag co-catalyst. Therefore, it is clear that the Ag co-catalyst played an important role in the stoichiometric reaction shown in eqn (3). Tada *et al.* reported that Ag-loaded anatase-type TiO₂ was more active than bare TiO₂ in the photocatalytic reduction of nitrobenzene to aniline under irradiation of UV light and that nitrobenzene is adsorbed almost selectively on the Ag surfaces of Ag-loaded TiO₂,^{3g} although the type of TiO₂ was different from that in the present study (rutile). Their results indicate that Ag particles worked effectively as reduction sites for aniline formation. In the present study, photogenerated electrons tended to accumulate in the TiO₂ particles due to the relatively large rate of hole scavenging by 2-propanol and the small rate of nitrobenzene reduction, which caused a decrease in the value of ROB. Since the rate of nitrobenzene reduction was improved in the presence of the Ag co-catalyst, high stoichiometry was achieved as shown in eqn (3) in the case of Au/TiO₂-Ag. The apparent quantum efficiency was calculated to be 1.4% based on incident photons at 550 nm.

Results for nitrobenzene reduction under various conditions are summarized in Table S1 (ESI[†]). The Ag-free Au/TiO₂ sample exhibited activity lower than that of Au/TiO₂-Ag (entries 1 and 2). Four blank reactions of nitrobenzene at 298 K, (1) dark reaction in the presence of Au/TiO₂-Ag (entry 3), (2) photocatalytic reaction by Au-free TiO₂-Ag (entry 4), (3) photocatalytic reaction by TiO₂ (entry 5) and (4) photochemical reaction (entry 6), gave no or only a trace amount of aniline. From the results of the four blank tests, it can be concluded that Au, TiO₂ and visible light are indispensable for reduction of nitrobenzene to aniline. Rapid electron transfer from Au to the TiO₂ film under irradiation of visible light was observed using femtosecond transient absorption spectroscopy.^{4b}

The following is an expected working mechanism for reduction of nitrobenzene to aniline in 2-propanol suspensions of Au/TiO₂-Ag under irradiation of visible light. Four processes would occur: (1) the incident photons are absorbed by Au particles through their SPR excitation,^{4,5} (2) electrons are injected from the Au particles into the conduction band of TiO₂, (3) the resultant electron-deficient Au particles oxidize 2-propanol to acetone and return to their original metallic state, and (4) electrons in the conduction band of TiO₂ transfer to the reduction site, *i.e.*, the Ag nanoparticles as co-catalysts.

In summary, a plasmonic Au/TiO₂ photocatalyst was successfully functionalized with an Ag co-catalyst by combination of the PH method (Ag) and the CPH method (Au). In the photocatalytic reduction of nitrobenzene to aniline along with oxidation of 2-propanol to acetone under irradiation of visible light, Au/TiO₂-Ag was more active than Ag-free Au/TiO₂ and aniline was almost quantitatively formed with a stoichiometric amount of acetone.

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 23560935) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan.

Notes and references

- (a) A. Corma, P. Concepcion and P. Serna, *Angew. Chem., Int. Ed.*, 2007, **46**, 7266; (b) K. Fuku, T. Sakano, T. Kamegawa, K. Mori and H. Yamashita, *J. Mater. Chem.*, 2012, **22**, 16243; (c) X. Huang, Y. Li, Y. Li, H. Zhou, X. Duan and Y. Huang, *Nano Lett.*, 2012, **12**, 4265.
- (a) M. Fagnoni, D. Dondi, D. Ravelli and A. Albini, *Chem. Rev.*, 2007, **107**, 2725; (b) G. Palmisano, E. Garcia-Lopez, G. Merzi, V. Loddo, S. Yurdakal, V. Augugliaro and L. Palmisano, *Chem. Commun.*, 2010, **46**, 7074.
- (a) F. Mahdavi, T. C. Bruton and Y. Li, *J. Org. Chem.*, 1993, **58**, 744; (b) J. L. Ferry and W. H. Glaze, *Langmuir*, 1998, **14**, 3551; (c) A. Maldotti, L. Andreotti, A. Molinari, S. Tollari, A. Penoni and S. Cenini, *J. Photochem. Photobiol., A*, 2000, **133**, 129; (d) H. Kominami, S.-i. Iwasaki, T. Maeda, K. Imamura, K. Hashimoto, Y. Kera and B. Ohtani, *Chem. Lett.*, 2009, **410**; (e) K. Imamura, S.-i. Iwasaki, T. Maeda, K. Hashimoto, B. Ohtani and H. Kominami, *Phys. Chem. Chem. Phys.*, 2011, **13**, 5114; (f) K. Imamura, K. Hashimoto and H. Kominami, *Chem. Commun.*, 2012, **48**, 4356; (g) H. Tada, T. Ishida, A. Takao and S. Ito, *Langmuir*, 2004, **20**, 7898; (h) Y. Shiraishi, Y. Togawa, D. Tsukamoto, S. Tanaka and T. Hirai, *ACS Catal.*, 2012, **2**, 2475; (i) K. Imamura, T. Yoshikawa, K. Hashimoto and H. Kominami, *Appl. Catal., B*, 2013, **134**–135, 193.
- (a) Y. Tian and T. Tatsuma, *J. Am. Chem. Soc.*, 2005, **127**, 7632; (b) A. Furube, L. Du, K. Hara, R. Katoh and M. Tachiya, *J. Am. Chem. Soc.*, 2007, **129**, 14852; (c) S. Naya, M. Teranishi, T. Isebe and H. Tada, *Chem. Commun.*, 2010, **46**, 815; (d) E. Kowalska, R. Abe and B. Ohtani, *Chem. Commun.*, 2009, 241; (e) E. Kowalska, O. O. P. Mahaney, R. Abe and B. Ohtani, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2344; (f) C. G. Silva, R. Juarez, T. Marino, R. Molinari and H. Garcia, *J. Am. Chem. Soc.*, 2011, **133**, 595; (g) H. Yuzawa, T. Yoshida and H. Yoshida, *Appl. Catal., B*, 2012, **115**, 294; (h) X. Ke, S. Sarina, J. Zhao, X. Zhang, J. Chang and H. Zhu, *Chem. Commun.*, 2012, **48**, 3509.
- (a) H. Kominami, A. Tanaka and K. Hashimoto, *Chem. Commun.*, 2010, **46**, 1287; (b) H. Kominami, A. Tanaka and K. Hashimoto, *Appl. Catal., A*, 2011, **397**, 121; (c) A. Tanaka, K. Hashimoto and H. Kominami, *ChemCatChem*, 2011, **3**, 1619; (d) A. Tanaka, K. Hashimoto and H. Kominami, *Chem. Commun.*, 2011, **47**, 10446; (e) A. Tanaka, S. Sakaguchi, K. Hashimoto and H. Kominami, *Catal. Sci. Technol.*, 2012, **2**, 907; (f) A. Tanaka, K. Hashimoto and H. Kominami, *J. Am. Chem. Soc.*, 2012, **134**, 14526; (g) A. Tanaka, A. Ogino, M. Iwaki, K. Hashimoto, A. Ohnuma, F. Amano, B. Ohtani and H. Kominami, *Langmuir*, 2012, **28**, 13105; (h) A. Tanaka, S. Sakaguchi, K. Hashimoto and H. Kominami, *ACS Catal.*, 2013, **3**, 79.
- (a) H. Kominami, M. Kohno, Y. Takada, M. Inoue, T. Inui and Y. Kera, *Ind. Eng. Chem. Res.*, 1999, **38**, 3925; (b) H. Kominami, S.-y. Murakami, J.-i. Kato, Y. Kera and B. Ohtani, *J. Phys. Chem. B*, 2002, **106**, 10501.