

Reduction of Light-Decomposition and Enhancement of Photocatalysis of Photocatalyst by Au-Coat

Yoshihiro Nemoto* and Takayuki Hirai

Research Center of Solar Energy Chemistry, Osaka University, Toyonaka, Osaka 560-8531

Received March 27, 2003; E-mail: basic77@dk.pdx.ne.jp

A photocatalyst can be used for various applications. Such materials are semiconductors which are stable to photoirradiation, for example, TiO_2 . Most of these materials require UV light. There are many kinds of semiconductors which are unstable to photoirradiation, but which have a visible light response. In this study, it is shown that a thin Au film or Au nano particles on the surface of the photocatalyst reduced the photodecomposition of the photocatalyst. Although the surfaces of the samples were completely covered by Au, photocatalytic activity was observed in all the Au-coated samples. The Au-coating on the surface enhances the photocatalysis of a coated photocatalyst.

The photocatalyst^{1–4} has recently received considerable attention because it has certain useful properties. These include the decomposition of organic material, superhydrophilic phenomena^{5,6} and remote oxidation.^{7,8} Remote oxidation is oxidizing the materials that are remote from the photocatalyst by hydroxyl radicals that are generated by decomposing H_2O using the photocatalyst.

In this study, we found a new photodecomposition phenomenon which occurred not only for unstable semiconductors, but also for stable semiconductors, such as anatase TiO_2 and SnO_2 . The effect of Au-coating to reduce the photodecomposition was investigated. Photocatalysis of the Au-coated photocatalytic materials, such as Au/WO_3 , Au/TiO_2 , and Au/SnO_2 photocatalysts, was examined by the efficiency of remote oxidation. Au-coated photocatalytic materials such as Au/WO_3 , Au/TiO_2 , and Au/SnO_2 are proposed.

Experimental

WO_3 , TiO_2 , and SnO_2 were prepared on SiO_2 substrates by the sol–gel method and spin-coat method. These were sintered at 450 degrees centigrade for 30 min in air. The Au was uniformly coated using a sputtering device. The Au coatings were 1, 2.5, 5, 10, 20, and 40 nm thick. The texture of the Au was examined using a high-resolution scanning electron microscope. The photocatalytic property was examined based on its remote oxidation efficiency. Remote oxidation by the hydroxyl radicals that were generated by decomposing the H_2O using a photocatalyst is one of the photocatalytic functions (Fig. 1(a)).^{7,8} The photocatalyst was stacked on a SiO_2 plate and H_2O was inserted between the photocatalyst and the SiO_2 plate (Fig. 1(b)). The plate was photoirradiated for the remote oxidation. The light was irradiated on the back surface of the photocatalyst avoiding the light reflection by Au. The substrate, SiO_2 , can transmit the light of wave lengths greater than 240 nm. The light sources were an incandescent lamp (100 W, wavelength: UV–IR) for Au/WO_3 and a sterilizing lamp (20 W, wavelength: 250 nm) for Au/TiO_2 and Au/SnO_2 . However, in the experiment of the photoirradiation time dependence of the contact angle between the H_2O and the SiO_2 plate, which was remotely oxidized

by bare WO_3 and Au/WO_3 (Au: 40 nm), the light source was black-light (20 W, wavelength: 330–370 nm). Because of the remote oxidation by photocatalyst, the remotely oxidized SiO_2 plate was covered with adsorbed hydroxyl radicals, so it became like the top figure of Fig. 1(c). The photocatalyst decomposes the H_2O into a proton and a hydroxyl radical. The generated hydroxyl radicals generated from the H_2O by the photocatalyst adsorb on the surface of the SiO_2 plate because the hydroxyl radical has the strongest oxidizing power of all the radicals. The SiO_2 plate then becomes superhydrophilic because the hydroxy group is a hydrophilic group, which is due to the hydrogen bond. The photocatalyst, which has a higher photocatalytic efficiency, can generate greater amount of hydroxyl radicals and make the SiO_2 plate more hydrophilic. The contact angle between the water and the SiO_2 plate decreases with the increase in the number of hydroxy groups on the surface of the SiO_2 plate. The hydroxy groups on the SiO_2 plate were examined with detection by a H_2O_2 chemical detection test paper (Fig. 1(c)). The SiO_2 plate whose surface was covered by a little water was washed in a supersonic bath and the hydroxy groups were dissociated into the water from the surface of the SiO_2 plate. After ten minutes, the hydroxyl radicals reacted with each other and became H_2O_2 . The H_2O_2 was detected by pieces of H_2O_2 chemical detection test paper. Therefore, the photocatalysts exactly decomposed the water and the hydroxyl radicals were generated from the water, and the generated hydroxyl radicals adsorbed on the surface of the SiO_2 plate. The durability of the Au-coated photocatalyst and the bare photocatalyst was evaluated by photoirradiation for 24 h or 96 h with the construction like Fig. 1(b). The light was irradiated on the back surface of the photocatalyst, avoiding any light reflection by Au. Therefore, light of the same intensity was irradiated to the Au-coated photocatalyst and the bare photocatalyst. The samples were not so thick that the photoirradiation effect appeared on the surface of the samples. Therefore, the durability test was considered to reflect the electric function to the surface of photocatalyst of Au.

Results and Discussion

The Au on the surface of the samples was uniformly coated when over 10 nm thick Au was coated; however in this case un-

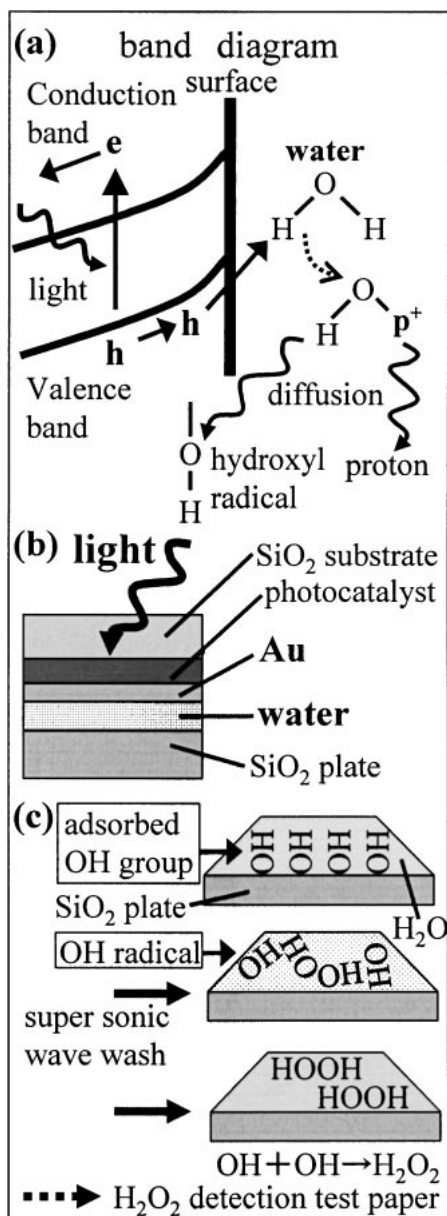


Fig. 1. Band diagram of photocatalyst and principle of photocatalysis and remote oxidation is shown in (a). The experimental construction of the remote oxidation to the SiO₂ plate by a photocatalyst is shown in (b). The method to detect the hydroxy groups on the SiO₂ plate, which was remotely oxidized by the photocatalyst, is shown in (c).

der 3 nm thickness of Au was coated. Some cluster-like particles were found on the surface of the Au-coated samples when under 3 nm thickness of Au was coated.

Based on the results of the examination of the durability of the photocatalyst which was evaluated by photoirradiation for 96 hours, the Au thin film on the samples reduced the photodecomposition of the semiconductor. Many large mountain-like defects and crater-like defects were formed on the samples without the Au-coating (Fig. 2). There were two kinds of defects: the mountain-like defect and the crater-like defect. Both of them were large (over 10 micrometers). The defects were formed by the self decomposition. The chemical stability of

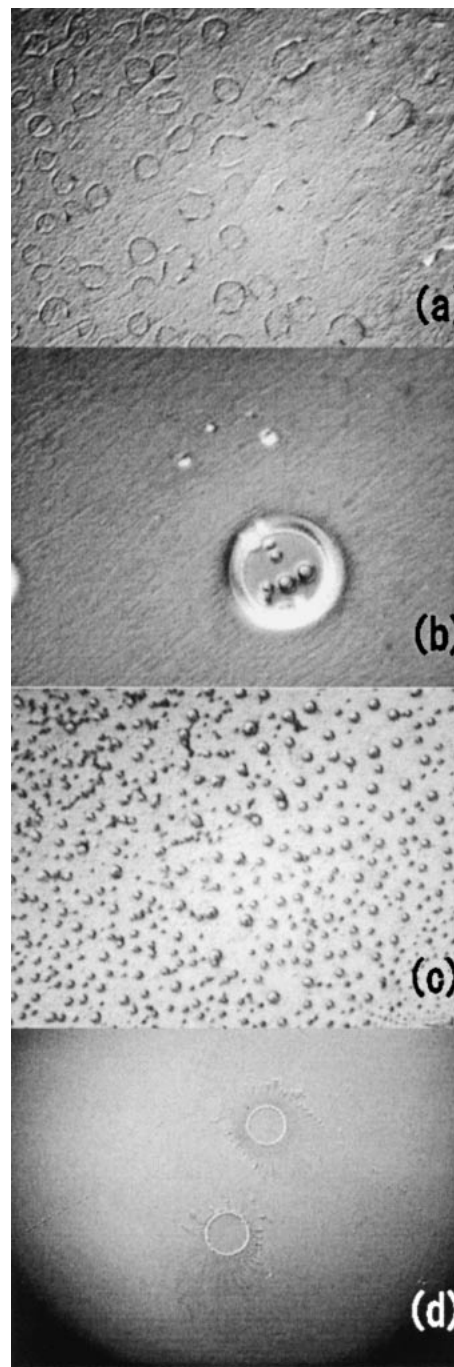


Fig. 2. Photograph using optical microscopy. It shows the surface of the bare SnO₂ ((a), (b)) ($\times 200$), TiO₂ ((c)) ($\times 1000$), and WO₃ ((d)) ($\times 200$) which were light irradiated by a sterilizing lamp and an incandescent lamp for 24 hours, respectively. Large Mont Blanc-like defects and large crater-like defects were found on the surface of the bare semiconductors.

TiO₂ and SnO₂ are higher than that of WO₃. However, these defects were not only on the surface of the WO₃, but also on the surface of the TiO₂ and SnO₂. However, the Au-coated samples had few defects and they were very small. Even the sample whose Au was only 1 nm thick had few defects (Fig. 3 (a) (b)). However, Au-coated WO₃, whose Au was 1

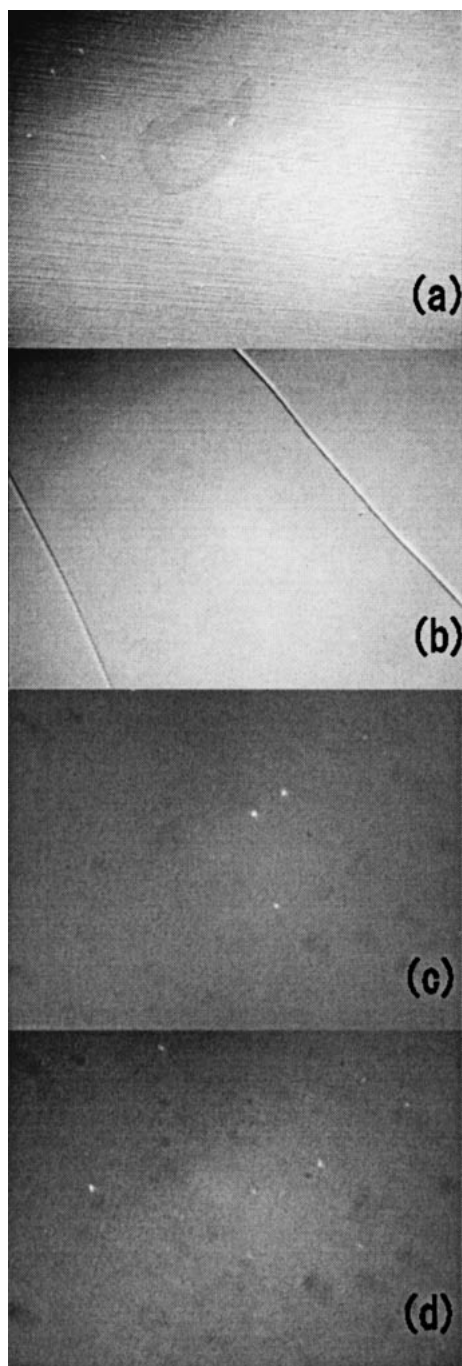


Fig. 3. Photograph using optical microscopy ($\times 1000$). It shows the surface of Au/SnO₂ (Au: 1 nm) ((a)), Au/TiO₂ (Au: 1 nm) ((b)), Au/WO₃ (Au: 1 nm) ((c)), and Au/WO₃ (Au: 10 nm) ((d)) which were light irradiated by a sterilizing lamp and an incandescent lamp for 96 hours. Large Mont Blanc-like defects and large crater-like defects were not found on the surface. However, small mountain-like defects were found on the surface of Au/WO₃ (Au: 1 nm).

nm thick, has small defects which were not so large or so many, and crater-like defects. Au-coated WO₃ whose Au was 2.5 nm thick has less defects than Au-coated WO₃ whose Au was 1 nm thick (Fig. 2 (c) (d)). The reason why the number of defects on the surface of Au-coated WO₃ was larger than that on the Au-

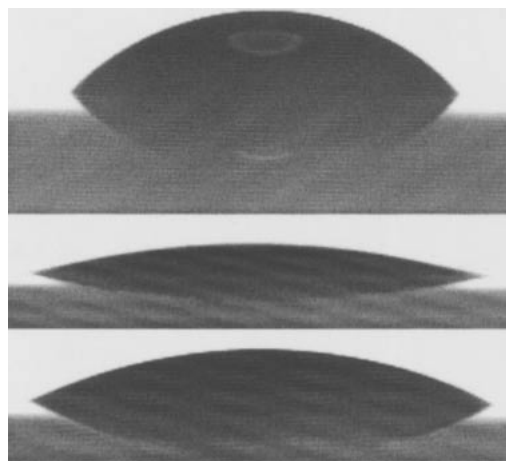


Fig. 4. Water on the surface of the superhydrophilic state SiO₂ plates which were an untreated SiO₂ plate (upper) and remotely oxidized by Au/WO₃ (Au: 40 nm) (middle) and Au/SnO₂ (Au: 1 nm) (lower). The contact angle was measured using the optical contact angle meter and calculated by the theta/2 method. The contact angle between the water and the SiO₂ plate, which was untreated, was 46.6 degrees and that of the remotely oxidized by Au/WO₃ was 15.8 degrees, while for the Au/SnO₂, it was 26.3 degrees.

coated TiO₂ and the Au-coated SnO₂ is considered to be because the chemical stability of WO₃ is lower than that of TiO₂ and SnO₂. The number of these defects did not increase with long irradiation. However, the number of these defects slightly increased only on the surface of the 1 nm thick Au-coated WO₃ after a long irradiation (over 192 hours). The change in the number of these defects on the surface of a 2.5 nm thick Au-coated WO₃ was small even after a long irradiation. The sample was covered by Au clusters when it was coated by sputtering and the thickness of Au was less than 3 nm. The effective cover of a photocatalyst for the reduction of self-decomposition was achieved not only by an Au film, but also by isolated Au clusters. However, the gaps between Au clusters must be narrow.

One of the photocatalytic functions, remote oxidation by the hydroxyl radicals which were generated from the H₂O by the photocatalyst,^{7,8} was successful for all the Au-coated samples. Even the thicker Au-coated sample had high photocatalytic efficiency. Photographs of the superhydrophilic SiO₂ plates, which were remotely oxidized by Au/WO₃ (Au: 40 nm) and Au/SnO₂ (Au: 1 nm), are shown in Fig. 4. The contact angle between the water and the SiO₂ plate which was remotely oxidized by Au/WO₃ was 15.8 degrees, and that for Au/SnO₂ was 26.3 degrees. The Au on the Au/WO₃ (Au: 40 nm) was a thin Au film and the Au on the Au/SnO₂ (Au: 1 nm) was in the form of Au clusters. The superhydrophilic state SiO₂ has a contact angle of 5 to 15 degrees and the normal SiO₂ has a contact angle of about 45 degrees.

The existence of the hydroxy groups on the SiO₂ plate was confirmed. The color of the H₂O₂ chemical detection test paper changed for the water on the remotely oxidized SiO₂ plate, but not for that on the untreated SiO₂ plate. Therefore, hydroxyl radicals exactly generated from H₂O and hydroxy groups were formed on the surface of the remotely oxidized SiO₂ plate.

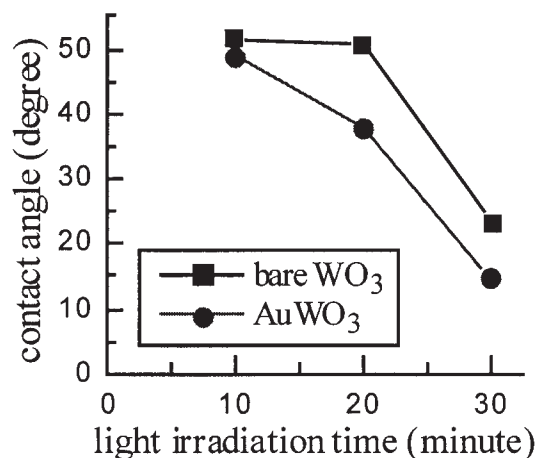


Fig. 5. The light irradiation time dependence of the contact angle between the H₂O and the SiO₂ plate which was remotely oxidized by bare WO₃ and Au/WO₃ (Au: 40 nm). The light source was black-light (20 W, wave length: 330–370 nm).

The photoirradiation time dependence of the contact angle between the H₂O and the SiO₂ plate, which was remotely oxidized by bare WO₃ and Au/WO₃ (Au: 40 nm), is shown in Fig. 5. The efficiency of remote oxidation photocatalysis of Au/WO₃ (Au: 40 nm) was higher than that of bare WO₃. A similar result was obtained from the same experiment using bare TiO₂ and Au/TiO₂ (Au: 40 nm). The efficiency of remote oxidation photocatalysis of the Au-coated sample was higher than that of the bare sample. These results suggest that the Au film on the surface of photocatalyst does not become an obstacle to the photocatalysis of a coated photocatalyst. Far from it, the Au film on the surface of photocatalyst enhances the photocatalysis of a coated photocatalyst.

The enhancement effect of photocatalysis by Au is comparable to that of the Pt particles on the surface of a photocatalyst. The energy of carriers in a metal is generally lower than that of carriers in a semiconductor. Therefore, a metal on the photocatalyst has an ability to absorb carriers. However, the metal particle effect is complicated and many discussions are continuing.^{9–13}

Summary

The thin Au film or the Au clusters on the surface of a photocatalyst can reduce the self-decomposition of a photocatalyst without reducing the photocatalysis. Far from it, the Au-coat on the surface of the photocatalyst enhances the photocatalysis of a coated photocatalyst. The required thickness of Au only for reducing decomposition of the unstable semiconductor was 2.5 nm; however, the stable semiconductor required only 1 nm. The sample was covered by Au clusters when the thickness of Au was less than 3 nm. The effective cover of a photocatalyst for the reduction of self-decomposition includes not only an Au film, but also Au clusters. However, the gaps of Au clusters must be narrow. Therefore, most of the semiconductors are expected to be able to be used as a photocatalyst by this technique.

References

- 1 A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).
- 2 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, *Science*, **293**, 269 (2001).
- 3 T. Umebayashi and H. Itoh, *Appl. Phys. Lett.*, **81**, 454 (2002).
- 4 P. H. Maruska and A. K. Ghosh, *Sol. Energy*, **20**, 443 (1978).
- 5 R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, and T. Watanabe, *Nature*, **338**, 431 (1997).
- 6 R. Wang, K. Hashimoto, A. Fujishima, M. Kojima, A. Kitamura, M. Shimohigoshi, and T. Watanabe, *Adv. Mater.*, **10**, 135 (1998).
- 7 T. Tatsuma, S. Tachibana, T. Miwa, D. A. Tryk, and A. Fujishima, *J. Phys. Chem. B*, **103**, 8033 (1999).
- 8 T. Tatsuma, S. Tachibana, and A. Fujishima, *J. Phys. Chem. B*, **105**, 6987 (2001).
- 9 T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, **1980**, 695.
- 10 K. Yamaguchi and S. Sato, *J. Chem. Soc., Faraday Trans. 1*, **81**, 1237 (1985).
- 11 K. Domen, S. Naito, T. Ohnishi, K. Tamaru, and M. Soma, *J. Phys. Chem.*, **86**, 3657 (1982).
- 12 H. Harada, *Chem. Express*, **6**, 961 (1991).
- 13 J. L. Muzyka and M. A. Fox, *J. Org. Chem.*, **55**, 209 (1990).