Journal of Environmental Sciences Vol. 13, No. 2, pp. 201—204, 2001
ISSN 1001-0742
CN11—2629/X

Article ID: 1001-0742(2001)02-0201-04 **CLC number:** X13 **Document code:** A

Enhanced photo – catalytic activity of gold ion and gold modified

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Abstract: The gold ion modified TiO_2 was prepared by means of sol-gel whereas gold deposited TiO_2 was prepared by means of photo-reduction. The physical properties were influenced significantly by the presence of gold ion or gold. The enhanced photo-activity of gold modified TiO_2 was quantified in terms of methylene blue degradation. The presence of gold ion in TiO_2 lattices or gold on TiO_2 surface enhanced their photo-activity. The optimum molar content of gold ion doping and gold deposition all was 0.5%. The first-order rates constants of gold modified TiO_2 was more than that of pure TiO_2, and decreased by increasing the content of gold ion and gold when their contents were more than 0.5%. Gold ion doped in TiO_2 lattices was more effective to enhance the photo-activity than gold on TiO_2 surface. Moreover, the relationship between physical properties, chemical properties and photo-activity has been discussed.

Key words: gold modification; titanium dioxide; photo catalysis; methylene blue

Introduction

TiO_2 photo-catalysis had been the focus of numerous investigations in recent years, particularly owing to its application for the complete mineralization of undesirable organic contaminants to CO_2, H_2O and inorganic constituent (Hoffmann, 1995). However, photo-oxidation was almost not industrially applied to treat wastewater due to its low reacting rate (Goswami, 1997). The low rate of electron transfer to oxygen and the higher recombination rate of electron/hole pairs limit the rate of photo-oxidation of organic compounds on the surface of a catalyst. Numerous investigation have reported that the addition of group VIII metals and polyvalent transition metal ions to TiO_2-based photo-catalytic systems are two effective ways to enhance the photo-catalytic reacting rate (Linsebigler, 1995). The noble metals gold (Wang, 1997; 1998) and platinum (Sclafani, 1998; Yang, 1997) were usually used to produce the highest Schotty barrier among the metals facilitating the electron capture. And metal ions act as electron or hole traps and promote the charge de-trapping, charge migration and interfacial charge transfer (Choi, 1994). However few of literature relate to the influence of gold ion doping in TiO_2. In present paper, we undertake a comparative study of gold ion doped or gold deposited in/on quantum-sized TiO_2 and discuss the relationship between physical properties, chemical properties and photo-activity.

1 Experiments

1.1 Catalysts preparation

(1) Gold ion doped TiO_2 samples were prepared by sol-gel method. A 17 ml tetra-*n*-butyl titanium ($Ti(O\text{-}Bu)_4$) dissolved in 80 ml absolute ethanol was added drop-wise under vigorous stirring to 100 ml mixture solution containing 80 ml 95% ethanol, 5 ml 0.1 mol/L tetrachloroauric acid and 15 ml CH_3COOH. The resulting transparent colloidal suspension was stirred for 2h and was aged for 2 days till the formation of a gel. The gel was dried at 373K under vacuum and then ground. The powder was amorphous and repeatedly washed by 95% ethanol in order to remove chloride ion and then centrifuged, dried and ground again. The powder was calcined at 973K for 2h, and then gold-doped TiO_2 was obtained in a nominal atomic doping level of 1.0%, and abbreviated as 1% Au^{3+}/TiO_2. Other gold-doped TiO_2 samples were prepared according to the above procedure. They were 0.5% Au^{3+}/TiO_2, 3% Au^{3+}/TiO_2 and 5% Au^{3+}/TiO_2 respectively. Pure quantum-sized TiO_2 was prepared in the absence of added tetrachloroauric acid.

(2) Au/TiO_2 samples were prepared by means of photo-reduction (Wang, 1997). The weighted amount of TiO_2 was suspended in a mixture of platinizing solution containing the required concentration of tetrachloroauric acid (supplied by South China University of Technology) and 0.1 mol/L methanol solution, as a hole scavenger. The

Foundation item: Guangdong Natural Science Foundation (No. 980012)

suspensions were irradiated with a 125W high-pressure mercury lamp. The irradiation lasted 60 minutes. The gold concentration in mixture solution was detected by PS-1000AT ICP. The molar concentration of gold on TiO_2 was determined on the basis of the decrease of the gold concentration. The Au/TiO_2 samples were separated by filtration, washed repeatedly with double distilled water and dried at 403K for 24h. The gold concentration of different samples is 0.5%, 2.6%, 4.1%, 5.0%, respectively.

All the dopant concentration mentioned in this work was the nominal atomic concentration. All chemicals in this work were of analytical grade, and double distilled water was used for solution preparation.

1.2 The characterization of photo-catalysts

X-ray powder diffraction (XRD) measurements was performed with a Rigaku D/MAX-IIIA diffractometer using CuK α radiation (λ = 0.15418 nm) to determine the phase transformation and mean crystal sizes.

The particle sizes were determined by a JEOL-100 CXII transmission electron microscope (TEM).

The surface areas of samples were measured by means of the BET method by N_2 adsorption at 77K, with ALTA AMI-100 instruments.

X-ray photoelectron spectroscopy (XPS) were recorded with a PHI Quantum ESCA Microprobe System, using the MgK α line of a 250W Mg *X*-ray tube as the radiation source with the energy of 1253.6 eV, 16 mA × 12.5 kV. The working pressure was less than 2×10^{-7} N/m^2. As an internal reference for the absolute binding energies, the Cls peak of hydrocarbon contamination set at 284.6 eV was used. The fitting XPS curves were analyzed by use of Multipak 6.0A.

1.3 Photo-catalytic activity experiments

Methylene blue (Guangzhou Chemicals Plant) was of analytical grade. Irradiation was performed with a 125W high-pressure mercury lamp (Foshan Lamp. Guangdong). Photo-reactor had been described in details by Li *et al*. (Li, 1999a; 1999b). The volume of solution is 200ml. Aqueous suspensions of titanium dioxide containing dyes were irradiated under constant magnetic stirring. The optimum dosage of titanium dioxide is 1 g/L (Wang, 1998b). In 5 min. time intervals samples of the suspension were taken. The samples were immediately centrifuged at 70 r/s for 30 min. and the supernatant was analyzed.

1.4 Analytical methods

The decolorization rate of methylene blue was used to express the photo-activity of catalysts. The concentration of methylene blue was analyzed by UNICAM UV-visible spectroscopy at 664 nm. The concentration of chloride ion, ammonium ion, nitrate ion, and sulfate ion formed was determined by Ion Chromatography with conductivity detection (Shimadzu HIC-6A). Shim-Pack IC-Al anion columns was used. The mobile phase was 2.5 mmol phthalic acid/2.4 mmol tris (hydroxymethyl) aminomethane. Flow rate was 1.5 ml/min at 313K oven temperature. The use of Shim-Pack IC-Cl cationic column was required for the determination of ammonium ion. The mobile phase was 5.0 mmol nitrate acid. Flow rate was 1.0 ml/min at 313K oven temperature.

2 Results and discussions

2.1 The physical properties of catalysts

The physical properties of photo-catalysts are listed in Table 1. The mean crystal sizes and particle sizes of all samples were less than 35 nm according to TEM and XRD results. Quantum-sized photo-catalysts were in the matrix of anatase and rutile. Gold deposition on titanium dioxide surface enlarged the particles of catalyst. And the particle of Au^{3+}/TiO_2 was less than that of pure TiO_2. The specific surface area of gold modified titanium dioxide samples all decreased.

Table 1 Physical characterization of pure TiO_2 and gold modified TiO_2 samples

Samples	Properties					
	$T_{calcination}$, K	Phase	Crystal size, nm	Mean particle size, nm	Specific surface area, m^2/g	Gold loading, $\mu mol/m^2$
Pure TiO_2	973	A/R	20.56	25.4	101.9	0
0.5% Au/TiO_2	973	A/R	21.79	31.8	29.0	2.16
0.5% Au^{3+}/TiO_2	973	A/R	13.31	17.3	49.4	1.27

2.2 The photo-catalytic activity

2.2.1 Gold deposited on Q-sized TiO_2

The pseudo-first-order kinetics of methylene blue (with initial concentration of 6.94 mg/L) photo-degradation is described in Fig.1. The observed rate constants of pure TiO_2, 0.5%, 1.1%, 2.6%, 4.1%, 5.0% Au/TiO_2 was

0.0014/s ($r^2=0.96$), 0.0035/s ($r^2=0.99$), 0.003/s ($r^2=0.98$), 0.0024/s ($r^2=0.99$), 0.0016/s ($r^2=0.93$), 0.0004/s ($r^2=0.97$) respectively. The optimum dosage of gold was 0.5%. The higher dosage of gold was detrimental to the photo-activity.

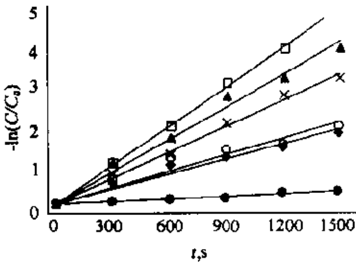

Fig. 1 The pseudo-first-order kinetic of methylene blue photo-degradation in presence of pure TiO_2 (◆), 0.5% Au/TiO_2 (□), 1.1% (▲), 2.6% (×), 4.1% (○), 5.0%, (●) with initial concentration of 6.94 mg/L, pH 7.0

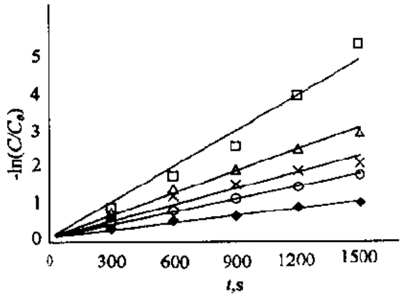

Fig. 2 The concentration of methylene blue versus irradiation time for photo-activity experiments carried out in presence of TiO_2 (◆), 5% Au^{3+}/TiO_2 (○), 3% Au^{3+}/TiO_2 (×), 1% Au^{3+}/TiO_2 (△), 0.5% Au^{3+}/TiO_2 (□) with initial concentration of 16.45 mg/L, pH 7.0, 25 minutes

2.2.2 Gold ion doped Q-sized TiO_2

The degradation process is described in Fig. 2 exhibited pseudo-first-order kinetics with respect to methylene blue concentration. And the observed rate constants of pure TiO_2 and 0.5%, 1.0%, 3.0%, 5.0% gold ion doped TiO_2 was 0.0006/s ($r^2=0.98$), 0.0033/s ($r^2=0.97$), 0.002/s ($r^2=0.99$), 0.0015/s ($r^2=0.99$), 0.0011/s ($r^2=0.99$) respectively. The observed photo-activity was low in the presence of pure TiO_2 and increased greatly by increasing the content of gold ion up to 0.5%, then decreased by increasing the content of gold ion. That implies there was an optimum molar content of gold ion, which was 0.5%. The results showed that gold ion should enhance the photo-catalytic activity of quantum-sized TiO_2.

2.2.3 The comparison of gold ion or gold modified Q-sized TiO_2

The photo-catalytic activity of gold ion or gold modified Q-sized TiO_2 samples was studied comparatively in Fig. 3 with initial concentration of 16.45 mg/L. The observed rate constants of pure TiO_2, 0.5% Au/TiO_2, 0.5% Au^{3+}/TiO_2 was 0.0005/s ($r^2=0.99$), 0.001/s ($r^2=0.97$), 0.0029/s ($r^2=0.98$) respectively. The 0.5% Au^{3+}/TiO_2 sample was the most active among all catalysts tested.

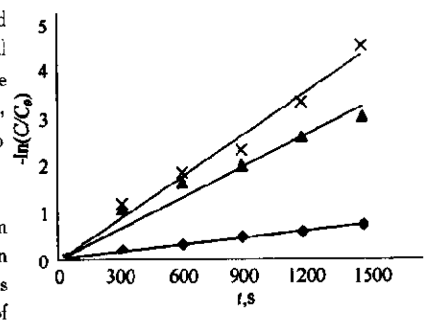

Fig. 3 The pseudo-first-order kinetic of methylene blue photo-degradation in presence of pure TiO_2 (◆), 0.5% Au/TiO_2 (▲), 0.5% Au^{3+}/TiO_2 (×), with initial concentration of 16.45 mg/L, pH 7.0

2.3 The mineralization of methylene blue

In Table 2, inorganic species including chloride ion, ammonium ion, nitrate ion and sulfate ion formed during photo-catalytic oxidation of methylene blue. It showed that a part of organic compounds molecular had been completely mineralized. Moreover, the quantity of formation of inorganic species using 0.5% Au^{3+}/TiO_2 was much more than that using 0.5% Au/TiO_2 and TiO_2.

2.4 XPS analyses

In Fig. 4a, the Au 4f peak of 0.5 Au^{3+}/TiO_2 consisted of three peaks at 84.24 eV, 85.68 eV, 87.93 eV, corresponding Au(0), Au (Ⅰ), Au (Ⅲ) respectively. The percent of them is 40.26%, 16.72%, 42.83% respectively. In Fig. 4b, for the sample of 0.5% Au/TiO_2, the Au 4f peak was fitted at 84.02 eV, 85.68 eV, 87.76 eV, corresponding Au (0), Au (Ⅰ), Au (Ⅲ) respectively, and the percent of them was 41.4%, 19.12%, 39.47% respectively. The results of XPS showed the valence state of Au made hardly difference for two samples.

Table 2 The formation of inorganic species from methylene blue with an initial concentration of 8.75 mg/L irradiated for 60 min

Unit: mg/L

Samples	NO_2^-	NO_3^-	NH_4^+	SO_4^{2-}
TiO_2	0.08	0.85	0.75	0.48
0.5% Au/TiO_2	0.12	1.55	1.23	0.96
0.5 Au^{3+}/TiO_2	0.15	2.46	2.31	1.26

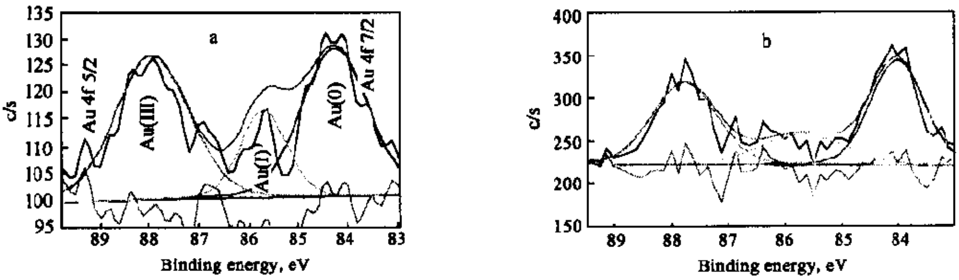

Fig.4 The XPS fitting curve of (a) 0.5% Au^{3+}/TiO_2 and (b) 0.5% Au/TiO_2

2.5 Discussions

The noble metals gold (Wang, 1997; 1998) were usually used to produce the highest Schotty barrier among the metals facilitating the electron capture. The presence of Au(0) on TiO_2 favors the migration of photo-produced electron to gold, thus improving the electron/hole separation. Subsequently, electrons migrate from gold to O_2 molecules (Linsebigler, 1995). Moreover, the density of free electrons of TiO_2 with gold deposit is less than that of TiO_2 without gold deposit, then that promotes the photo-adsorption of O_2 molecules on the surface of photo-catalysts. So, the rate of electron transfer to oxygen increases, and the recombination rate of electron/hole pairs decrease. Those promote photo-oxidation of organic compounds on the surface of gold modified TiO_2.

Gold ion enhanced the photo-activity of TiO_2 by acting as electron traps and by hindering the electron/hole pair recombination through Equation (1) and (2) (Choi, 1994). On the other hand, there was Au(Ⅰ) species in the TiO_2 lattice. Au(Ⅰ) or Au(Ⅲ) species could give rises to redox step as Equation (4) or (5) and promotes the charge migration, then favors the charge migration to O_2 and an enhancement the photo activity in comparison with pure TiO_2.

$$Au^{3+} + 2e_{cb} \rightarrow Au^{+} + 1.36V, \qquad (1)$$

$$Au^{+} + e_{cb} \rightarrow Au + 1.83V, \qquad (2)$$

$$O_{2(ads)} + e_{cb} \rightarrow O^{-}_{2(ads)} - 0.125V, \qquad (3)$$

$$Au^{3+} + 2O_{2(ads)} + 2e_{cb} \rightarrow Au^{+} + 2O^{-}_{2(ads)} + 1.11V, \qquad (4)$$

$$O_{2(ads)} + Au^{+} + 2e \rightarrow O^{-}_{2(ads)} + Au + 1.705V. \qquad (5)$$

Finally, the surface acidity and positive charge increased, and the point of zero charge decreased greatly owing to the presence of gold on TiO_2 surface (Pichat, 1989). The change of those properties significantly influenced the adsorption of substrate and its intermediates. In fact, the photo-catalytic process only occurs on the semiconductor surface, and not in bulk solution. The adsorption of substrates is indispensable for their photo-catalytic degradation. As is cationic dye, methylene blue was more effectively absorbed on Au^{3+}/TiO_2 surface and on Au/TiO_2 surface than on TiO_2. This is another of the reasons why the photo-activity of gold modified TiO_2 was higher than that of pure TiO_2.

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(Received for review February 29, 2000. Accepted June 19, 2000)