第 31 卷 第 5 期　　无 机 材 料 学 报　　Vol. 31 No. 5
2016 年 5 月　　Journal of Inorganic Materials　　May, 2016

Article ID: 1000-324X(2016)05-0555-06　　**DOI:** 10.15541/jim20150535

Preparation of Silver Nanoparticle Loaded Mesoporous TiO_2 and Its Photocatalytic Property

WANG Hui-Lei[1,2], LIU Xiao-Heng [1]

(1. Key Laboratory for Soft Chemistry and Functional Materials, Nanjing University of Science and Technology, Ministry of Education, Nanjing 210094, China; 2. School of the Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, China)

Abstract: A series of Ag-modified mesoporous titania (TiO_2) particles with various silver contents were prepared by photoreduction. The prepared Ag-TiO_2 samples were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), energy dispersive X-ray spectrometry (EDX) and UV-visible diffuse reflectance spectroscopic (DRS) techniques. The visible light photocatalytic property was demonstrated for photodegradation of methylene blue (MB) solution. The results showed that Ag nanoparticles were firmly immobilized on the TiO_2 surface, which improved electron-hole separation by forming the Schottky barrier at the Ag-TiO_2 interface. The diffusion of reflectance UV-Vis spectra were also served as an indication that the Ag-TiO_2 samples displayed higher red shifts in comparison with un-modified TiO_2 sample. Under visible light, the optimal photoactivity was obtained for the sample m-TiO_2-Ag-2.0wt%. The TiO_2-Ag catalyst is likely to be used again for a number of times without any additional treatment.

Key words: silver nanoparticles; mesoporous titania; photodegraduation; photoreduction

TiO_2 is one of the most popular photocatalysts, for it is high in photosensitivity, resistant to chemical change, harmless, easy to obtain, friendly towards the environment and finally cheap[1-4]. Upon ultraviolet light irradiation, TiO_2 has been substantially examined for photocatalytic degradation of organic pollutants out of wastewater[5-9]. Nonetheless, the application of pure TiO_2 is limited by its UV activation requirement.

In order to overcome this shortcoming, a host of studies have been undertaken to intensify the separation between electron and hole and to widen the range of absorption of TiO_2 into the visible light region. The studies are instrumental in improving the visible light activity of TiO_2 by transition metal ion doping[10-13], dye sensitization[14] and nonmetal doping[15-17]. Among them, noble TiO_2 photocatalysts modified by metals prove to be one of the most crucial ways to enhance the photocatalytic performance[18-21]. In comparison with the expensive Pt, Pd, Rh, and Au noble metals, TiO_2 photocatalyst modified by Ag turns out to be a more profitable material in actual usage[22-24]. Because of the Schottky barrier on the Ag-TiO_2 interface, Ag acts as a snare of the photogenerated electrons. As a result, combination of photoinduced electrons and holes again is effectually restrained. Further, the surface plasmonic resonance (SPR) impact of the nanoparticles of Ag can be red shift the absorption to an area with visible light.

Because of its weak affinity for organic pollutants and the small surface area of TiO_2 nanoparticles, organic pollutants were adsorbed on TiO_2 surface in a poor manner, which led to the degradation of photocatalysis at a slow rate. TiO_2 nanoparticles have been designed to various porous solids[25-28]. Employment of advanced mesoporous materials to treat water has proved to be quite a profitable way for water purification[29-30].

In this research, the synthesis of Ag-modified mesoporous TiO_2 was achieved with the help of photoreduction method. Methylene blue (MB), a dye that is not biodegradable, was made use of as probes to examine the degradation of photocatalysis under visible light irradiation. Investigations were made into the impact of loadings of Ag on performance of the catalyst and the function of nanoparticles of Ag in the degradations of photocatalysis.

1 Experimental

1.1 Synthesis of Ag-modified mesoporous TiO_2

All chemicals were analytical-grade reagents and were

Received date: 2015-11-02; **Modified date:** 2015-11-27
Foundation item: National Natural Science Foundation of China (51272107); Natural Science Foundation of Jiangsu Province, China (BK2011024)

Biography: WANG Hui-Lei (1982–), female, candidate of PhD. E-mail: wanghuilei1982@163.com
Corresponding author: LIU Xiao-Heng, professor. E-mail: xhliu@mail.njust.edu.cn

used without further purification. In a typical synthesis procedure, 5.7 g $TiCl_4$ was slowly added into 10 mL HCl under vigorous and constant stirring. Subsequently with 300 mL n-butyl alcohol and 5 g PEG (M = 20000) added to the mixture under refluxing conditions at 80 ℃ for 20 h, which was used to prepare mesoporous TiO_2..

Modification of mesoporous TiO_2 with Ag nanoparticles was conducted using a photoreduction method[31]. 1.0 g of m-TiO_2 was suspended in 300 mL of water, followed by sonication for 10 min to completely disperse the solid. Then, $AgNO_3$ solution was added to the suspension. After stirring for 20 min in the dark, the mixture was irradiated with a 500 W high-pressure mercury lamp for 4.0 h. The resulting pale-gray solids were collected, washed with water and dried at ambient temperature. No Ag ion was detected in the filtrate indicating that all Ag had been completely loaded onto the m-TiO_2. Different volumes of $AgNO_3$ solution with a concentration of 0.1 g/L were used to vary the loading of Ag. The samples thus obtained are denoted as TiO_2-Ag-*x*wt%, where *x*wt% indicates the weight percentage of Ag on the composite particles.

1.2 Characterization

The as-synthesized samples were characterized by X-ray diffraction (XRD) with a Bruker D8 diffractometer with monochromatic Cu Kα radiation (λ = 0.1542 nm). Transmisson electron microscopy (TEM) observations were performed using a transmission electron microscope (JEOL-2100) at 200 kV and a Gatan 794 charge-couple device (CCD) camera. The samples were ultrasonically dispersed in 5 mL deionized water for 5 min. Next, the solution was dropped to a copper grid. UV-visible spectra were recorded on a Shimadzu UV-2500 spectrophotometer in a 1 cm optical path quartz cuvette over a 200–800 nm range at room temperature.

1.3 Photocatalytic measurement

The photocatalytic activities of the samples were evaluated by the photodegradation of MB in an aqueous solution at room temperature under visible light irradiation (VB). During the process, the catalyst (0.01 g) was suspended in a fresh dye aqueous solution (C_0(MB) = 1×10^{-5} mol/L, 50 mL). The suspension was ultrasonically dispersed for 10 min, then stirred in the dark for 30 min to allow an adsorption-desorption equilibrium of MB dye. After 30 min, the solution was illuminated whilst stirring. At a certain interval, a certain amount of sample (8 mL for the VB-induced reaction) was drawn from the system, centrifuged and then the absorption spectrum at 660 nm of the dye was monitored. The visible light irradiation source (λ > 400 nm) was obtained by putting an appropriate cut-off filter in the front of a 500 W Xe-lamp to completely remove wavelengths shorter than 400 nm. The photoreactor was placed a magnetic stirrer to ensure homogeneous mixing during irradiation.

2 Results and discussion

XRD patterns of the mesoporous TiO_2 and as synthesized Ag-TiO_2 with various amounts of Ag are displayed Fig. 1, which can give the information of crystalline structure. It can be seen that all samples conform to the pure anatase (JCPDS 21-1272). In addition to sample TiO_2-Ag-24.0wt%, not any reflection peak because of metallic Ag is in evidence in Fig. 1, possibly by reason of a low concentration.

The morphologies of undoped TiO_2, TiO_2-Ag-0.25wt%, TiO_2-Ag-2.0wt% and TiO_2-Ag-24.0wt% were observed with TEM. As shown in Fig. 2, the samples (Fig. 2(a), 2(c), 2(d)) are made up of spherical nanoparticles with a diameter of 100 nm, which implies that Ag doping does not have much impact on the morphology and distribution of TiO_2 nanoparticles. TEM micrograph (Fig. 2(a)) of Ag/TiO_2 particles indicates a predominance of Ag deposits on the surface of TiO_2 with a diameter approximately 10 nm, the size of those Ag particles is similar. Figure 2(b) shows that it formed large Ag particles with a small number of TiO_2 particles on the surface of Ag, because of a high concentration. The EDX (Fig. 3) confirms the large deposit in Fig. 2(a) to be silver.

EDX could be used to investigate the presence or absence of silver. EDX mapping of all the prepared TiO_2 samples are almost same. Therefore, Fig. 3 only presents the EDX mapping of the sample TiO_2-Ag-2.0wt%. From basic mapping mode observation, the Ag particles on the TiO_2 are highly and uniformly dispersed.

Diffuse reflectance absorption spectra of mesoporous TiO_2 and Ag modified mesoporous TiO_2 are demonstrated in Fig. 4. The m-TiO_2 samples display complete absorption close to the UV area with a keen edge of absorption

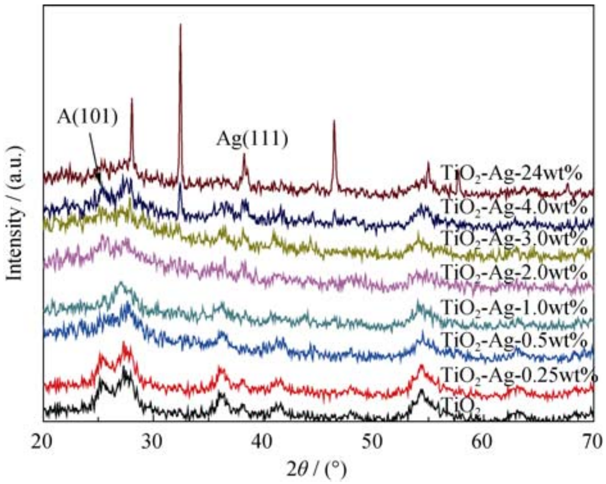

Fig. 1 XRD patterns of the m-TiO_2 and Ag-modified TiO_2 catalysts

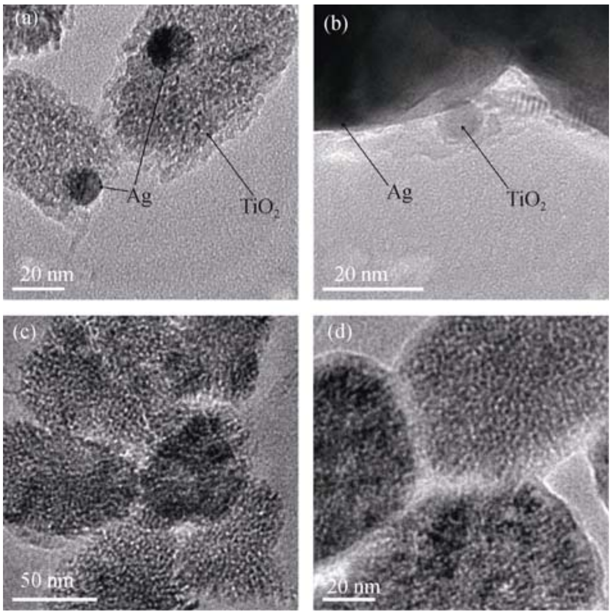

Fig. 2 TEM micrographs of the prepared samples
(a) TiO_2-Ag-2.0wt%; (b) TiO_2-Ag-24.0wt%; (c) TiO_2-Ag-0.25wt%; (d) m-TiO_2

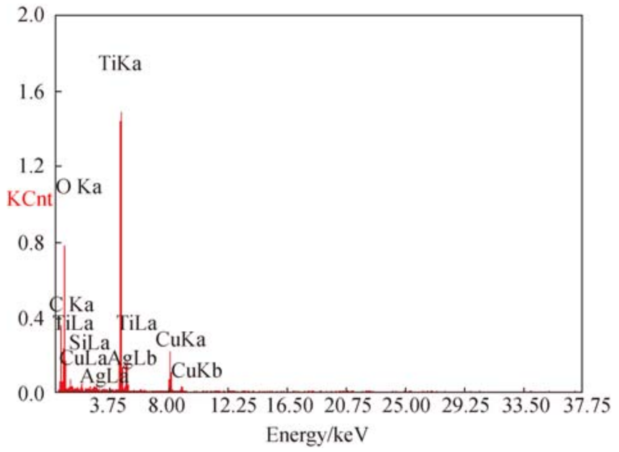

Fig. 3 EDX spectra of the sample TiO_2-Ag-2.0wt%

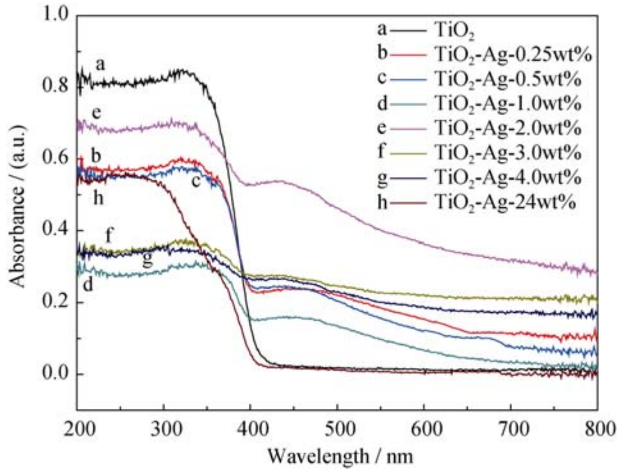

Fig. 4 Diffuse reflectance absorption spectra of mesoporous TiO_2 and Ag modified mesoporous TiO_2

which is situated at around 400 nm[32]. Nothing of the change in the edge of absorption is visible in course of loading varied amounts of Ag. A distinctive surface plasmon absorption of Ag nano-particles in the neighborhood of 400–550 nm came out by degrees and got larger with loading of Ag, which signified the placement of nanoparticles of Ag on the TiO_2 surface[33]. Nonetheless, the maximal wavelength of the surface absorption of plasmon differed from one sample to the next. With the increased loading of Ag from 1.0wt% to 3.0wt%, the wavelength of the top surface absorption of plasmon changed from 468 nm to 498 nm step by step, and the absorption peaks became wider at the same time. The TEM in Fig. 2(b) suggests that with gradual increase of Ag loading more and more Ag particles form clusters on the TiO_2 surface, which may lead to quantum efficiency affects of nanoparticles does not exist and surface plasmon resonance on the diffuse reflectance absorption spectra in the visible range disappear.

The ascription of powerful 200 nm to 380 nm broad band to the absorption of charge-transfer from the band of valence (2p orbital of the oxide anions) to the band of conduction (3d orbital of the Ti^{4+}cations) can be made inside the solid space. The inclusion of silver particles brings about great changes to the absorption spectra of TiO_2 in the visible region indicative of surface plasmon of absorption. The edge of absorption is achieved through the extension of the sharp portion of the UV adsorption towards the baseline in a linear manner. These band gaps of all Ag-TiO_2 catalysts change moderately to higher wavelength, which serves as an indication that there exists a possibility of transitions of energy at a slower rate. The spectra suggest that doping of Ag make a strong impact on the absorption of light in the noticeable area by TiO_2 to be augmented with an additional amount of silver. The edge of absorption shifts towards longer wavelengths in terms of the Ag-TiO_2 catalysts, which implies a drop in the band-gap energies of TiO_2 in case of a larger amount of silver.

In order to make an assessment of the activity of photocatalysis of the samples collected, a choice of MB was made as a major pollutant. The curves of degradation of MB over undoped TiO_2 and varied Ag-TiO_2 samples are displayed in Fig. 5. The photocatalytic activity of the photocatalysts is represented by the ratio of removed concentration to initial concentration of MB [$(C_0\text{-}C)/C_0$], in which C_0 and C represent the concentration of MB following the equilibrium between adsorption and desorption and that at a certain interval in time, respectively. In comparison with undoped TiO_2, all of the Ag-TiO_2 samples show more vigorous activity of photocatalysis, for Ag doping is likely to extend the visible light absorption of TiO_2 in an effective way. With regard to different Ag-TiO_2

samples, the activity of photocatalysis is initially on the increase with additional amount of Ag and afterwards on the decrease even with extra content of Ag. Since Ag and TiO_2 have different Fermi level, which could form the Schottky barrier at the contact surface. It means that there are more photo-generated electrons and holes generated by activating the samples under visible light irradiation, and these photo-generated electrons and holes participate in the photocatalytic reaction. The optimum level of Ag doping for achieving the most vigorous activity of photocatalysis is 2.0wt%.When the level of Ag doped exceeds 2.0wt%, the activity of photocatalysis is decreasing. This is due to the increase of Ag loading on the TiO_2 surface, which will reduce the electron-hole pairs and increase recombination of the electron-hole on the photo-induced surface under visible light irradiation.

Following transparent irradiation for 2 h the rate of degradation of MB over 2.0wt%-Ag-TiO_2 is 75%, which is nearly 30 times higher than that over the undoped TiO_2.

The photodegradation process of MB under irradiation with visible light over mesoporous Ag-TiO_2 is illustrated in Fig. 6. Because of the big band gap of TiO_2, the electrons are not able to be raised to an excited state from the valence band to the conduction band under irradiation with visible light. Nonetheless, the electrons are able to be excited from MB to the conduction band of TiO_2, since MB was inspired electrons under irradiation with visible light. The electrons that are excited can be conveyed from the TiO_2 surface to the Ag particles because of the Schottky barrier forms at the interface between TiO_2 and Ag, with the adsorption of O_2 on the surface of Ag smoothing the way for the course of electron transfer. At the same time, reaction of the electrons with O_2 that is adsorbed on the surface of the catalyst brings about formation of superoxide anion radicals ($\bullet O_2^-$), which is likely to give rise to degradation of MB at a faster rate. As a result, a summary of the effect of the particles of Ag on the behavior of photocatalysis is likely to be made in this way: creation of a Schottky barrier which weakened recombination of the excited electrons-MB^+ and intensified the usage of exci tons was made by the Ag particles; besides, the particles of Ag strengthened the affinity of adsorption of the catalyst for oxygen that was dissolved, which resulted in the MB degradation at a faster rate.

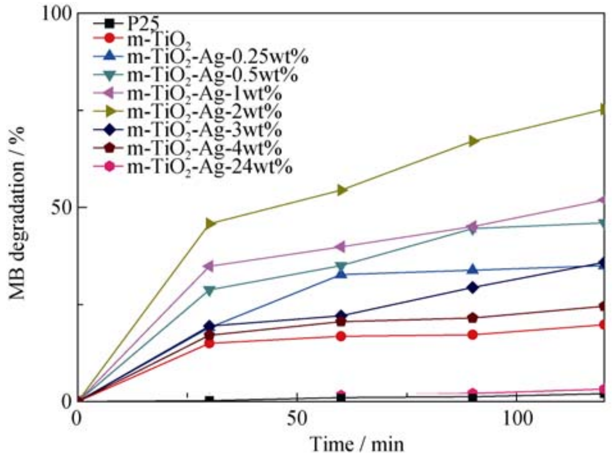

Fig. 5 Photocatalytic degradation curves of MB on samples and P25 under visible light

3 Conclusion

Mesoporous TiO_2 materials adjusted with nanoparticles of Ag showed considerable capacity for the degradation of MB under visible light. Under visible light, the optimal photoactivity was obtained for the sample m-TiO_2-Ag-2.0wt%. Investigations into the impact of Ag loadings upon the function of the catalyst and into the part of Ag nanoparticles in the degradations of photocatalysis were conducted.

References:

[1] FOX M A, DULAY M T. Heterogeneous photocatalysis. *Chem. Rev.*, 1993, **93:** 341–357.

[2] LEGRINI O, OLIVEROS E, BRAUN A M. Photochemical processes for watertreatment. *Chem. Rev.*, 1993, **93:** 671–698.

[3] LITTER M I. Heterogeneous photocatalysis transition metal ions in photo-catalytic systems. *Appl. Catal. B: Environ.*, 1999, **23:** 89–114.

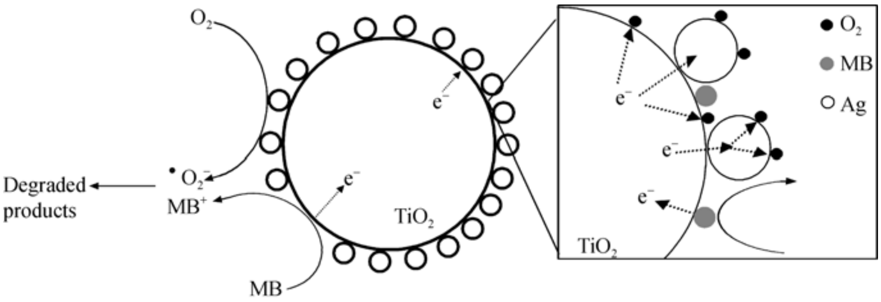

Fig. 6 Schematic illustration of the effect of Ag loadings on catalyst

[4] CARP O, HUISMAN C L, RELLER A. Photoinduced reactivity of titaniumdioxide. *Prog. Solid State Chem.*, 2004, **32:** 33–177.

[5] HOFFMANN M R, MARTIN S T, CHOI W, *et al*. Environmental applications of semiconductor photocatalysis. *Chem. Rev.*, 1995, **95(1):** 69–96.

[6] KONSTANTINOU I K, ALBANIS T A. TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review. *Appl. Catal. B*, 2004, **49(1):** 1–14.

[7] LIU S W, YU J G, CHENG B, *et al*. Fluorinated semiconductor photocatalysts: tunable synthesis and unique properties. *Adv. Colloid Interface Sci.*, 2012, **173:** 35–53.

[8] LIU S W, YU J G, JARONIEC M. Anatase TiO_2 with dominant high-energy {001} facets: synthesis, properties, and applications. *Chem. Mater.*, 2011, **23(18):** 4085–4093.

[9] LIU S W, YU J G, JARONIEC M. Tunable photocatalytic selectivity of hollow TiO_2 microspheres composed of anatase polyhedra with exposed {001} facets. *J. Am. Chem. Soc.*, 2010, **132(34):** 11914–11916.

[10] CHOI W Y, TERMIN A, HOFFMANN M R. The role of metal ion dopants in quantum-sized TiO_2: correlation between photoreactivity and charge carrier recombination dynamics. *J. Phys. Chem.*, 1994, **84:** 13669–13679.

[11] LITTER M I. Heterogeneous photocatalysis transition metal ions in photocatalytic systems. *Appl. Catal. B Environ.*, 1999, **23:** 89–114.

[12] DVORANOVA D, BREZOVA V, MAZUR M, *et al*. Investigations of metal-doped titanium dioxide photocatalysts. *Appl. Catal. B Environ.*, 2002, **37:** 91–105.

[13] CHOI H J, KANG M. Hydrogen production from methanol/water decomposition in a liquid photosystem using the anatase structure of Cu loaded TiO_2. *Int. J. Hydrogen Energy*, 2007, **32:** 3841–3848.

[14] DHANALAKSHMI K B, LATHA S, ANANDAN S, *et al*. Dye sensitized hydrogen evolution from water. *Int. J. Hydrogen Energy*, 2001, **26:** 669–674.

[15] IRIE H, WATANABE Y, HASHIMOTO K. Nitrogen-concentration dependence on photocatalytic, activity of $TiO_{2-x}N_x$ powders. *J. Phys. Chem. B*, 2003, **107(23):** 5483–5486.

[16] XU TH, SONG C L, LIU Y, *et al*. Band structure of TiO_2 doped with N, C and B. *J. of Zhejing Univ. Sci. B*, 2006, **7(4):** 299–303.

[17] LI D, HANEDA H, LABHSETWAR N K, *et al*. Visible light driven photocatalysis on fluorineedoped TIO_2 powders by creation of surface oxygen vacancies. *Chem. Physics Letters*, 2004, **401:** 579–584.

[18] ZHAO Z G, MIYAUCHI M. Nanoporous-walled tungsten oxide nanotubes as highly active visible-light-driven photocatalysts. *Angew Chem. Int. Ed.*, 2008, **47:** 7051–7055.

[19] LI X Z, LI F B. Study of $Au/Au^{(3+)}$-TiO_2 photocatalysts toward visible photooxidation for water and wastewater treatment. *Environ. Sci. Technol.*, 2001, **35(11):** 2381–2387.

[20] YU J G, XIONG J F, CHENG B, *et al*. Fabrication and characterization of Ag–TiO_2 multiphase nanocomposite thin films with enhanced photocatalytic activity. *Appl. Catal. B*, 2005, **60(3/4):** 211–221.

[21] YU J G, YUE L, LIU S W, *et al*. Hydrothermal preparation and photocatalytic activity of mesoporous Au–TiO_2 nanocomposite microspheres. *J. Colloid Interface Sci.*, 2009, **334(1):** 58–64.

[22] KAMAT P V. Photophysical, photochemical and photocatalytic aspects of metal nanoparticles. *J. Phys. Chem. B*, 2002, **106:** 7729–7744.

[23] ZANG L, MACYK W, LANGE C, *et al*. Visible-light detoxification and charge generation by transition metal chloride modified titania. *Chem.-Eur. J.*, 2000, **6:** 379–384.

[24] CHENG B, LE Y, YU J J. Preparation and enhanced photocatalytic activity of Ag@TiO_2 core–shell nanocomposite nanowires. *Hazard. Mater.*, 2010, **177:** 971–977.

[25] HIDAKA H, YAMADA S, SUENAGA S, *et al*. Photodegradation of surfactants. Complete photocatalytic degradation of anionic, cationic andnonionic surfactants in aqueous semiconductor dispersions. *J. Mol. Catal.*, 1990, **59:** 279–290.

[26] KANG C, JING L, GUO T, *et al*. Mesoporous SiO_2-modified nanocrystalline TiO_2 with highanatase thermal stability and large surface area as efficientphotocatalyst. *J. Phys. Chem. C*, 2008, **113:** 1006–1013.

[27] MOGYOROSI K, FARKAS A, DEKANY I, *et al.* TiO_2-based photocatalytic degradation of 2-chlorophenol adsorbedon hydrophobic clay. *Environ. Sci. Technol.*, 2002, **36:** 3618–3624.

[28] HOFFMANN M R, MARTIN S T, CHOI W Y, *et al*. Environmental applications of semiconductor photocatalysis. *Chem. Rev.*, 1995, **95:** 69–96.

[29] PAN J H, DOU H Q, XIONG Z G, *et al*. Porous photocatalysts for advanced water purifications. *J. Mater. Chem.*, 2010, **20:** 4512–4528.

[30] ZHAO D Y, JARONIEC M, HSIAO B S. High-flux thin-film nanofibrous composite ultrafiltration membranes containing cellulose barrier layer. *J. Mater. Chem.*, 2010, **20:** 4692–4704.

[31] TRAN H, SCOTT J, CHIANG K, *et al*. Clarifying the role of silver deposits on titania for the photocatalytic mineralisation of organic compounds. *J. Photochem. Photobiol. A*, 2006, **183:** 41–52.

[32] ZHANG F L, ZHENG Y H, CAO Y N, *et al*. Ordered mesoporous Ag-TiO_2-KIT-6 heterostructure: synthesis, characterization and

photocatalysis. *J. Mater. Chem.*, 2009, **19:** 2771–2777.

[33] LINSEBIGLER A L, LU G Q, YATES J T. Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results. *Chem. Rev.*, 1995, **95:** 735–758.

银粒子修饰下的介孔二氧化钛的制备及其光催化性能的研究

王慧蕾[1,2], 刘孝恒[1]

(1. 南京理工大学 化工学院, 软化学与功能材料教育部重点实验室, 南京 210094; 2. 江苏大学 环境与安全工程学院, 镇江 212013)

摘 要: 利用光还原的方法制备一系列不同银含量的改性介孔二氧化钛的颗粒。采用 X 射线粉末衍射(XRD)、透射电子显微镜(TEM)、紫外一可见漫反射谱(DRS)和 X 射线能谱仪(EDX)等技术手段对制备的样品进行了表征。结果表明, 银纳米粒子被牢牢固定在二氧化钛表面, 并在银和二氧化钛界面形成肖特基势垒用以提高电子–空穴的分离。而从紫外可见漫反射光谱中看出, 银二氧化钛样品与未改性的二氧化钛样品相比显示出更高的红移。以亚甲基蓝(MB)为光降解模型, 银改性二氧化钛表现出较高的活性。

关 键 词: 银纳米粒子; 介孔二氧化钛; 光催化; 光致还原

中图分类号: TQ174　　**文献标识码:** A