Chemical Engineering Journal 146 (2009) 42–48

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Preparation and studies of photocatalytic silver-loaded TiO_2 films by hybrid sol–gel method

Xing-Gang Hou[a,b], Mei-Dong Huang[a], Xiao-Ling Wu[b], An-Dong Liu[b,*]

[a] *Department of Physics, Tianjin Normal University, Tianjin 300387, China*
[b] *Key Laboratory of Beam Technology and Material Modification of Ministry of Education, Beijing Normal University, Beijing 100875, China*

ARTICLE INFO

Article history:
Received 6 December 2005
Received in revised form 5 May 2008
Accepted 13 May 2008

Keywords:
Ag/TiO_2 film
Photodegradation
Visible light
Catalytic efficiency

ABSTRACT

Ag/TiO_2 photocatalytic films were produced by hybrid sol–gel method. The photocatalytic degradation of methyl orange (MO) in aqueous solution under both UV and visible light irradiation on TiO_2 and Ag/TiO_2 thin films was investigated. The state and amount of Ag species within the film and the enhancement mechanism of photocatalytic activity of Ag/TiO_2 were discussed. The maximum catalytic efficiency was observed under both UV and visible light irradiation. The molar ratio of Ag/Ti corresponding to the best catalytic activity depends on the wavelength of the radiation employed.

1. Introduction

TiO_2 photocatalyst has been investigated for decades [1,2]. However, the basic research [3–9] and industrial development [10,11] of high-efficiency TiO_2 photocatalyst are still hot topics due to their prospective importance, and existing problems are still hard to solve. There are two main obstacles for the practical application of TiO_2 photocatalyst: low quantum efficiency and restriction to short wavelength excitation. A common way to enhance the quantum efficiency is to load noble metal on the surface of TiO_2 powder or thin film [12–23]. Especially, the deposition of silver has attracted much attention [17–23] because of its potential applications. Most of those studies focused on the improvement of photocatalytic activity of TiO_2 under UV irradiation. However, there are some results also reported showing the extension of Ag/TiO_2 wavelength response towards the visible region [24–27]. Up to now, most of the methods used for loading silver have been photoreduction. However, the photoreduction needs a quite long time of exposure (more than 1 h in general) and the metal particles are likely to fall off during their repeated utilization. Moreover, photoreduced Ag cannot be highly dispersed on the surface of TiO_2, so that the amount of active sites on the Ag/TiO_2 surface cannot markedly increase, and the electronic structure of TiO_2 photocatalyst cannot change greatly. To overcome these difficulties and disadvantages, we introduce the hybrid sol–gel method to prepare the Ag-modified TiO_2 films. Ag/TiO_2 catalysts with different Ag/Ti molar ratios have been prepared by a hybrid sol–gel method in the absence of light, which would avoid Ag^+ being photoreduced during the gel formation. A part of $AgNO_3$ was then thermal decomposed or reduced to metallic Ag, which can be deposited onto the surface of TiO_2; meanwhile, a small amount of Ag ions diffused into the lattice of TiO_2. This preparation method can dope and deposit Ag simultaneously. In this study, photocatalytic efficiency of the Ag/TiO_2 thin films was reported. SEM, XRD, RBS, XPS, UV–vis spectra and photo-oxidation of methyl orange (MO) were used to characterize and evaluate the photocatalytic activity of Ag/TiO_2 films, and the mechanism of silver-loaded TiO_2 for enhanced photocatalytic activity was discussed.

2. Experimental

2.1. Preparation of Ag/TiO_2 photocatalytic films

Ag/TiO_2 films were prepared by a hybrid sol–gel method. The sol was a mixture of tetrabutylorthotitanate ($Ti(OBu)_4$), ethanol, acetylacetone (AcAc), H_2O and HNO_3 in a molar ratio of 1:18:0.5:2:0.2 [5]. Different amounts of $AgNO_3$ were added into prepared sols to adjust the molar ratio of Ag/Ti in the sols from 0 to 0.48. The mixed sols were allowed to stand for gelation, and three layers of mixed gel were dip-coated on each glass substrate for all samples. Each

---

[*] Corresponding author at: Key Laboratory of Beam Technology and Material Modification of Ministry of Education, Beijing Normal University, Xinjiekouwai Street 19, Beijing 100875, China. Fax: +86 10 62231765.

E-mail addresses: hou226@163.com (X.-G. Hou), andongliu@bnu.edu.cn (A.-D. Liu).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.05.041

layer was annealed to 450 °C at a speed of 1.5 °C/min and then the film was calcined at 450 °C for 30 min.

2.2. Characterization of the photocatalytic films

An X-ray diffractometer (XRD, PANalytical, Holland) with Cu Kα radiation operated at 40 kV was used to study the crystal structure of Ag/TiO_2 films. X-ray photoelectron spectroscopy (XPS) spectra were measured using an Escalab MK II (VG Company, UK). All binding energies (BE) were calibrated by C 1s. The surface structure of Ag/TiO_2 films was investigated by a scanning electron microscope (SEM, Sirion, USA). In order to measure the amount of silver within Ag/TiO_2 thin films, a Rutherford backscattering spectrometry (RBS, General Ionex, Corp. USA) and an energy dispersive X-ray analyzer (EDX, EDAX, USA) attached to the SEM were used.

2.3. Measurement of photocatalytic activity

A 1000-W mercury lamp (BELSRI, Beijing) was used as UV radiation source. The lamp was hosted by an irradiation house with cooling water and circulation fan. A 365-nm band pass filter was used to select the 365 nm peak of the lamp in the experiment. 100 mL aqueous solution of MO with a concentration of 5×10^{-5} mol/L was placed in a shallow round glass vessel with a diameter of 10 cm. The solution was irradiated above the TiO_2 films under continuous stirring. A metal cover with an open slit was placed on top of the vessel to limit the illumination area. An UV irradiance meter (UV-A, BNU, China) with a 365 nm sensor was used to measure the UV power. For all experiments, an average intensity of around 4.63 mW/cm^2 was used at a distance 20 cm away from the lamp. To measure the degradation of MO under the visible light illumination, a 150-W high-pressure sodium lamp with emission peak above 420 nm (BELSRI, Beijing) was used and 72,000 lx at the sample position was obtained (measured by an illumination photometer ST-85, BNU). 60 mL aqueous solution of MO with concentration of 3.5×10^{-5} mol/L was placed in a shallow round glass vessel with a diameter of 7.5 cm. A UV-cut filter was used to cut off the light under 420 nm of the lamp in the experiment. The extent of photo-degradation of MO was determined by the optical density (OD) at 465 nm measured by a UV–vis spectrometer (UV-160, Shimadzu, Japan).

3. Results and discussion

3.1. Characterization of Ag/TiO_2 films

3.1.1. XRD patterns

Fig. 1 shows XRD patterns of Ag/TiO_2 films. The strongest peak at $2\theta = 25.3°$ clearly demonstrates the (1 0 1) anatase phase of TiO_2 crystal. No observable rutile phase is observed in all samples. The data from Fig. 1a–e suggest that silver particles are not crystallized on the TiO_2 surface. However, with increasing molar ratio of Ag/Ti (0.48) in prepared gel, a weak peak ($2\theta = 44.3$, Fig. 1f) of silver (3 3 1) is found, which implies the presence of crystal state of Ag^0 when the concentration of silver nitrate is high in prepared gel, indicating that Ag species are dispersed uniformly within the surface at low concentration and could be reduced and aggregated at high concentration. Except for the Ag^0 weak peak, no obvious differences of XRD substantial influence on the size of TiO_2 particles. TiO_2 crystallite size can be estimated as 30 nm by the Scherrer equation.

3.1.2. FESEM observation

The surface structure of Ag/TiO_2 films with different molar ratios of Ag/Ti was studied by SEM. The SEM pictures with the equal magnification reveal that the surface structure (the porosity, thickness) of the Ag/TiO_2 films is identical with original TiO_2 film, which is favorable to the enhancement of the photocatalytic activity. Fig. 2c is the magnified image of Fig. 2a, which shows a uniform distribution of TiO_2 nano-particles compared with Fig. 2b. The size of these particles can be estimated to be around 10–40 nm. Fig. 2 proves that the films made by hybrid sol–gel method are satisfactory. The similar particle size (Fig. 2b and c) of Ag/TiO_2 films with different molar ratios of Ag/Ti implies that the presence of Ag has no substantial influence on the size of the TiO_2 particles. Only a few Ag clusters are observed on the surface of Ag/TiO_2 film made from the prepared gels with molar ratio of Ag/Ti = 0.48 (Fig. 2a), so surface density (number per surface unit) and average diameter of Ag cluster in Ag/TiO_2 films increase with the amount of Ag species in the prepared gel. Fig. 2a also shows that the size of Ag cluster is smaller than that of Ag cluster produced by photoreduction method [21]. It is known that the Ag species dispersed in prepared gel will aggregate during the annealing process. However, the aggregating speed in prepared gel is slower than in aqueous solution. Therefore, when the molar ratio of Ag/Ti is small, most of Ag species in the films made by sol–gel method is unable to form an Ag cluster. Even though a few Ag species have the opportunity to form a cluster, its size is smaller than the photoreduction method, and most of the Ag clusters are too small to be distinguished by SEM pictures. On the other hand, the distribution of Ag clusters formed in the hybrid sol–gel method must be more uniform than that in the photoreduction method for the same reason. Therefore an Ag cluster was only observed on the surface of Ag/TiO_2 film with molar ratio of Ag/Ti = 0.48 in prepared gel.

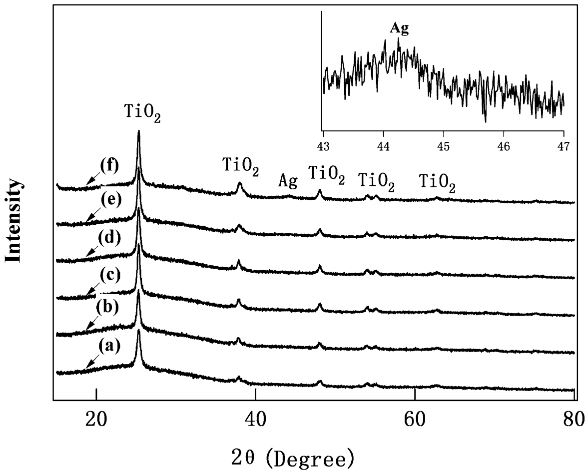

Fig. 1. XRD spectra of Ag/TiO_2 films. Ag/Ti in prepared gel: (a) 0; (b) 0.032; (c) 0.064; (d) 0.128; (e) 0.192; (f) 0.48.

3.1.3. XPS analysis

XPS measurement was carried out to elucidate both the titanium structure and the chemical state of silver particles. The existence of Ti^{4+} as the major titanium species is not doubted because the binding energy of the Ti 2p electron is 458.1 eV, but the Ti 2p binding energy (Fig. 3a) of the sample with an Ag/Ti ratio of 0.48 is slightly shifted from 458.1 eV to 458.25 eV as compared to that of raw TiO_2. This is because the Fermi level of Ag is lower than that of TiO_2, so that the conduction band electron of TiO_2 may transfer to the Ag species deposited on the surface of TiO_2, resulting in a decrease in the outer electron cloud density of Ti ions [20]. The XPS spectra of $Ag3d_{5/2}$ of samples with molar ratio of Ag/Ti = 0.192 (Fig. 3b) and Ag/Ti = 0.48 (Fig. 3c) were fitted with a nonlinear least-squares fit program using Gauss-Lorentzian peak shapes. The XPS spectra of $Ag3d_{5/2}$ indicate that there are three components after

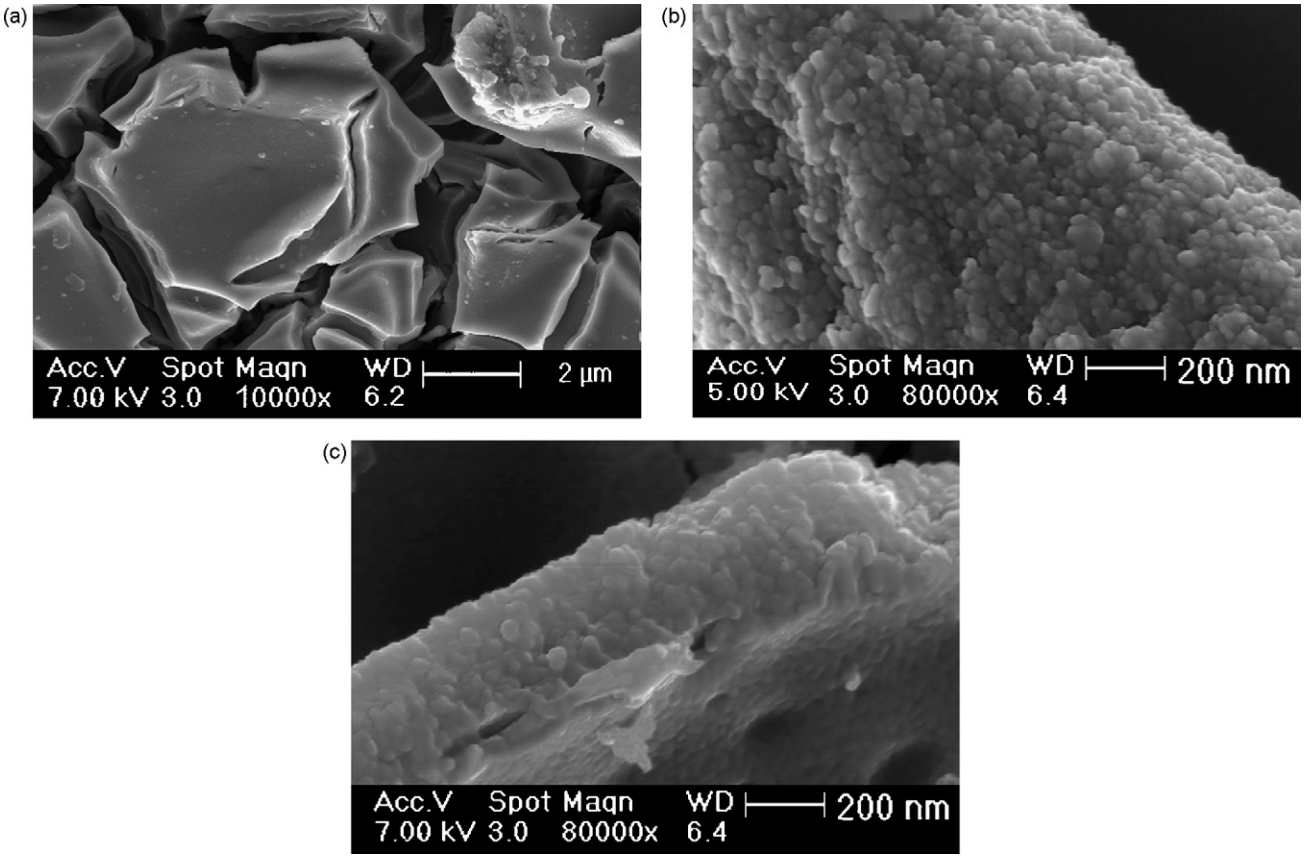

Fig. 2. (a) SEM image of Ag/TiO_2 film with molar ratio of Ag/Ti = 0.48 in prepared gel. (b) The TiO_2 thin film without $AgNO_3$ in prepared gel. (c) The Ag/TiO_2 film with molar ratio of Ag/Ti = 0.48 in prepared gel.

deconvolution, attributed to AgO (367.0 eV), Ag_2O (367.7 eV), and Ag^0 (368.2 eV) [20], respectively. Fig. 3b shows that at low concentration, Ag species exist as the three components with similar amounts. While at high concentration, a part of AgO is turned into Ag_2O and Ag^0, but the amount of Ag^0 species on the surface increases more. The result is corresponding to the weak peak of Ag^0 with molar ratio of Ag/Ti = 0.48 sample in XRD pattern (Fig. 1f).

3.1.4. UV–vis spectra

The optical absorbance spectra of the Ag/TiO_2 films were measured in the region of 300–800 nm and are shown in Fig. 4. It exhibits clearly the red shift of the absorption edge with increasing Ag doping concentration. It indicates the decrease of energy of excited photon owing to the presence of Ag and the absorption of visible light. The changing can be attributed to the local structures of TiO_2 were altered by Ag doping, which made acceptor level in the forbidden band of TiO_2.

3.2. Silver loadings within Ag/TiO_2 films

At first, the amount of silver on the surface of Ag/TiO_2 films was detected by EDX analysis. However, silver was only found on the films made from the gels with molar ratios of Ag/Ti = 0.192 and Ag/Ti = 0.48 samples, and the corresponding values of the films are 0.0625 and 0.18. Then the amount of silver was measured by RBS again. Fig. 5 shows RBS spectra of Ag/TiO_2 films made from gels with different molar ratios of Ag/Ti. According to Fig. 5, the molar ratio of Ag/Ti within Ag/TiO_2 films can be calculated. The relationship of molar ratio of Ag/Ti in both Ag/TiO_2 films and prepared gels is shown in Fig. 6, which confirms the presence of silver within all Ag/TiO_2 samples. Corresponding to the molar ratios of Ag/Ti in prepared gels 0.032, 0.064, 0.128, 0.192 and 0.48, the molar ratios of Ag/Ti within Ag/TiO_2 films are 0.021, 0.135, 0.1823, 0.225, and 0.44, respectively. A reasonable good linear relationship of Ag/Ti ratios between gel and Ag/TiO_2 films can be found in Fig. 6. However, when silver was measured by EDX analysis, silver was only found on Ag/TiO_2 films made from gels with Ag/Ti molar ratios of 0.192 and 0.48, and the corresponding Ag/Ti molar ratios 0.0625 and 0.18 measured by EDX are considerably smaller than 0.225 and 0.44 by RBS. The possible reason for the smaller molar ratio of Ag/Ti value by EDX analysis is attributed to following: Ag species within Ag/TiO_2 films produced by hybrid sol–gel method is enclosed in body by gel and some of it may aggregate during the calcining procedure. When Ag concentration is low, most of Ag species locate at a depth exceeding the escape length of the Kα-radiation within the films. Meanwhile the amount of aggregated Ag on the surface of Ag/TiO_2 films is too small to be detected by the EDX instrument, therefore no silver was observed by EDX analysis. When Ag concentration is high, though more amount of Ag can aggregate on the surface of Ag/TiO_2 films, Ag located within Ag/TiO_2 films still cannot be detected by EDX analysis, leading to the smaller value detected by EDX analysis than RBS. From the above discussion, it can be conclude that the molar ratio of Ag/Ti within Ag/TiO_2 films only can be determined by RBS exactly.

3.3. The photocatalytic efficiency of Ag/TiO_2 films

The MO solutions contained original TiO_2 and Ag-modified TiO_2 films were allowed to equilibrate in the dark for 1 h before the UV lights were switched on, and the concentration of MO was mea-

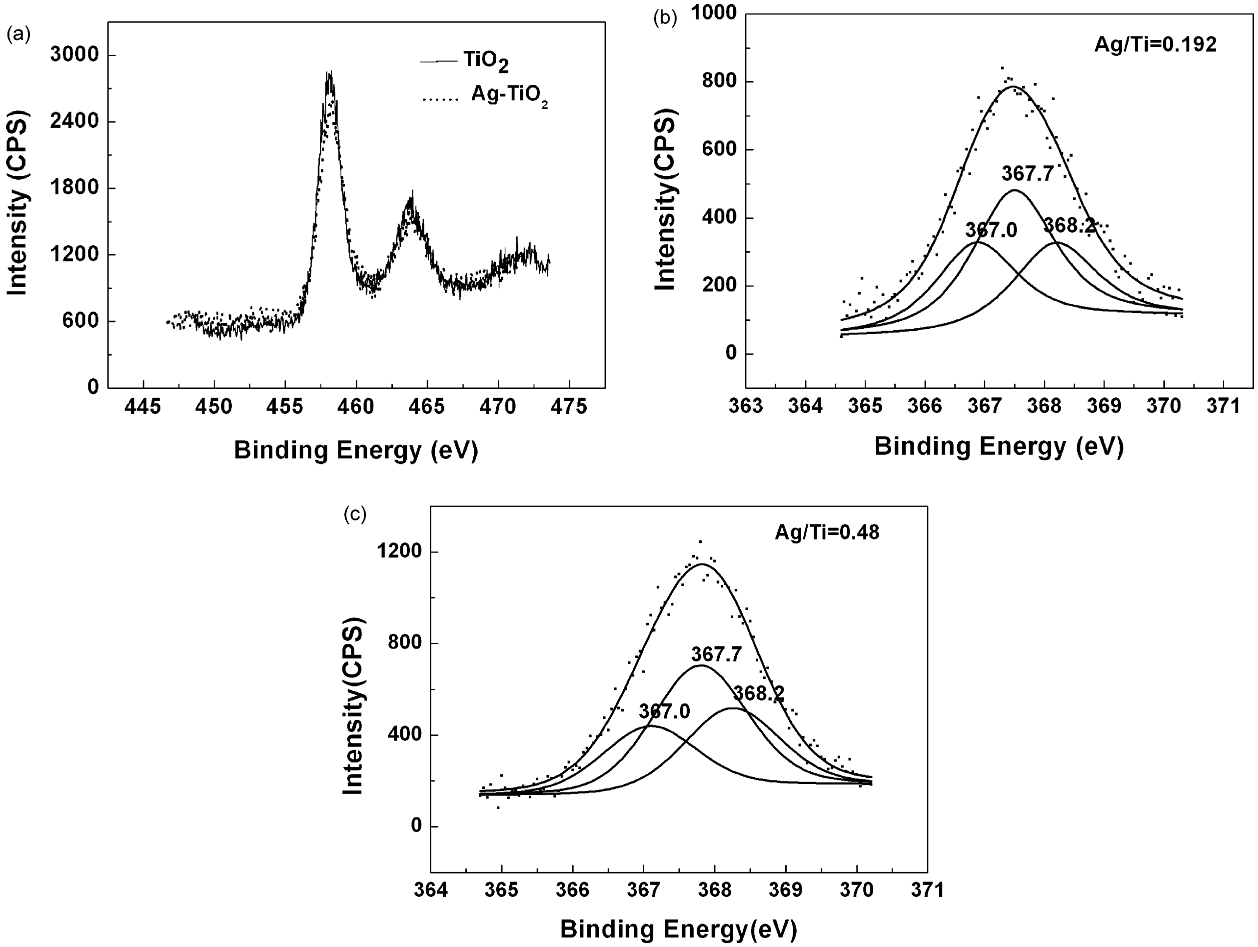

Fig. 3. (a) XPS spectra of Ti 2p of TiO_2 and Ag/TiO_2 (molar ratio of Ag/Ti = 0.48). (b) XPS spectra of $Ag3d_{5/2}$ of Ag/TiO_2 (molar ratio of Ag/Ti = 0.192). (c) XPS spectra of $Ag3d_{5/2}$ of Ag/TiO_2 (molar ratio of Ag/Ti = 0.48).

sured. The difference of the amount of MO adsorbed on original TiO_2 and Ag-modified TiO_2 surfaces was negligible. The results indicated that the presence of silver on the surface of TiO_2 films prepared by this method did not affect the adsorption properties of the organics on TiO_2 films before and after surface modification.

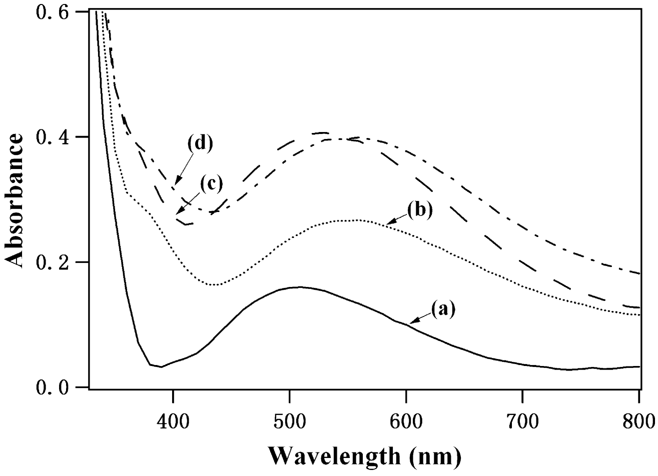

Fig. 4. Optical absorption spectra of Ag/TiO_2 films. Molar ratio of Ag/Ti in prepared gel: (a) 0; (b) 0.064; (c) 0.128; (d) 0.192.

The catalytic efficiency of Ag/TiO_2 films was evaluated by the degradation of MO in aqueous solution. Firstly, the direct degradation of MO under 365 nm irradiation was checked in the absence of TiO_2 films. The result showed that MO is not decomposed under 365 nm UV irradiation. Secondly, the photocatalytic degradation of MO on Ag/TiO_2 films with different molar ratios of Ag/Ti was measured. Fig. 7 shows the typical time profiles of this degradation. The

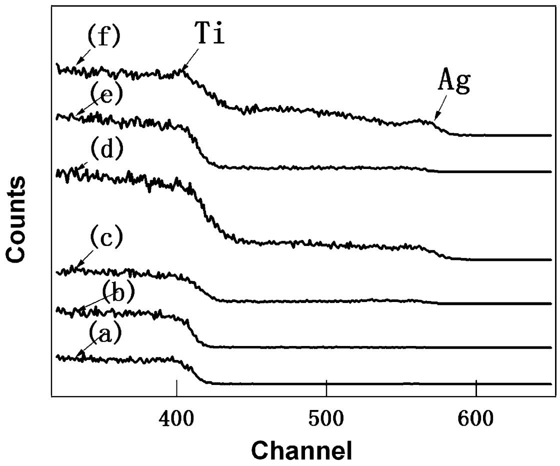

Fig. 5. RBS spectra of Ag/TiO_2 films. Molar ratio of Ag/Ti in prepared gel: (a) 0; (b) 0.032; (c) 0.064; (d) 0.128; (e) 0.192; (f) 0.48.

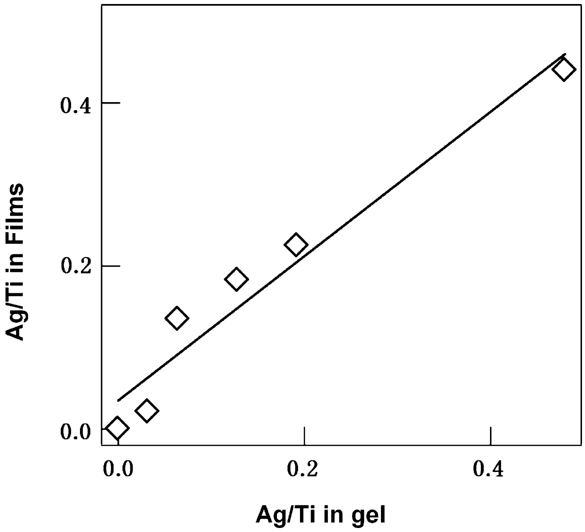

Fig. 6. Relationship of molar ratio of Ag/Ti between Ag/TiO_2 films and gel.

solid lines are exponential fits to the experimental data that gives the pseudo-first-order rate constants k (min^{-1}). It is obvious that rate constant k varies upon the amounts of silver in Ag/TiO_2 films. For films with lower molar ratio of Ag/Ti, the decomposition rate (k) increases with the increasing molar ratio Ag/Ti. A maximum of k ($0.0014\,min^{-1}$) is observed when molar ratio of Ag/Ti = 0.064 in prepared gel (0.135 in Ag/TiO_2 film). Comparing with original TiO_2 film, an increase of 73% of k at this maximum is obtained. Further increasing of molar ratio of Ag/Ti will result in a considerable decrease of k. However, the rate constant k of film with molar ratios of Ag/Ti = 0.192 in gels is similar to the film with molar ratios of Ag/Ti = 0.48 in gels. In other works [17,18,20,21,23], a similar trend was reported that the amounts of loaded silver had an optimal value that varies upon different reactants and reaction environments. With the increase in the time of irradiation, the activity of the catalyst decreases weakly.

Ag/TiO_2 films were also tested by the visible light excitation and the results are shown in Fig. 8. Apart from the very weak degradation of MO by original TiO_2 films under visible excitation, Ag/TiO_2 films exhibit a dramatic increase of the efficiencies with the same condition. The photocatalytic ability does not decrease with increasing Ag content when molar ratio of Ag/Ti is below 0.128 in prepared gel in our visible light excitation experiment. When molar ratio of Ag/Ti = 0.128 in prepared gel, the Ag/TiO_2 film has the best photocatalytic ability. This value is higher than that of UV excitation experiment. Comparing with original TiO_2 film, an increase of more than 3.8 times greater of photocatalytic ability at this maximum is obtained. Further increasing of molar ratio of Ag/Ti will result in a considerable decrease of photocatalytic ability, but which is still higher than that of original TiO_2. According to our study, it is clear that the catalyst activity depend on the wavelength of the radiation employed. Furthermore, value of OD cannot do the exponential fits like UV irradiation experiment. In the first 30 min, all the Ag/TiO_2 films almost have the same activity except for the film with molar ratio of Ag/Ti = 0.032 in prepared gel. With the increase in the time of irradiation, the activity of the catalyst decreases gradually.

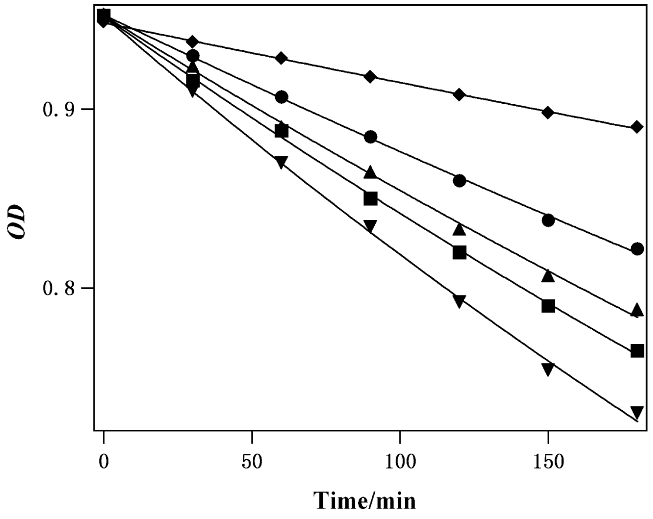

Fig. 7. A typical time profile of MO photodegradation under 365 nm irradiation with Ag/TiO_2 photocatalyst. Molar ratio of Ag/Ti in prepared gel: (●) 0; (▲) 0.032; (▼) 0.064; (■) 0.128; (♦) 0.192.

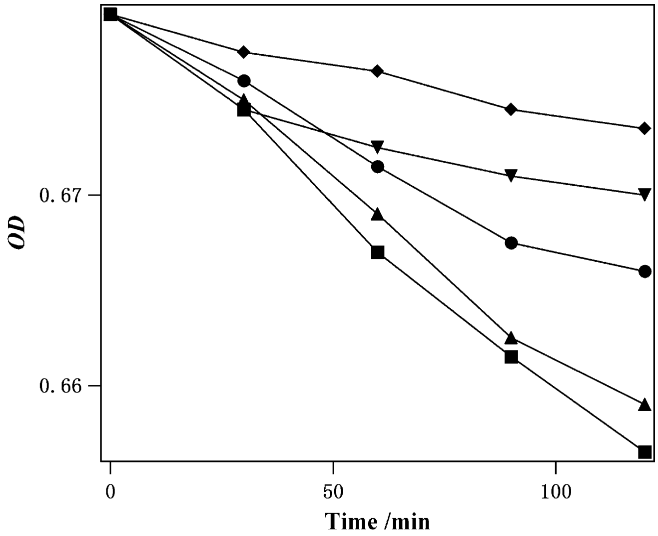

Fig. 8. MO photodegradation under visible light irradiation with Ag/TiO_2 photocatalyst. Molar ratio of Ag/Ti in prepared gel: (♦) 0; (●) 0.032; (▲) 0.064; (■) 0.128; (▼) 0.192.

3.4. Photocatalysis mechanism

The mechanism of variation of photocatalytic activity for Ag/TiO_2 films can be explained as below. The size of TiO_2 particles in Ag/TiO_2 film is similar to that in TiO_2 film without Ag (Fig. 1, Fig. 2b and c); thus the variation of photocatalytic activity cannot be attributed to size effect as mentioned in the literature [19]. When two materials of different work functions get in contact, the Schottky barrier will be formed and electrons will transfer from the material with low work function to the material with high work function. Silver and TiO_2 have different work functions and the work function of silver is higher than TiO_2 (work function $\Phi_{TiO_2} = 4.2$ eV, $\Phi_{Ag} = 4.6$ eV) [23]. So when silver contacts with TiO_2, electrons will transfer from TiO_2 to silver. Those electrons transferred to silver and loaded on the surface of silver will be scavenged by the electron acceptor, commonly the oxygen molecules absorbed on the surface of silver. Meanwhile, some electrons transferred to silver are contained in the body of TiO_2. Though there was no electron scavenger, the transfer decreases the recombination between electron and hole. Whether in body or on the surface of silver, silver atoms act as electron traps that capture certain amount of photoelectrons produced by UV excitation and increase the separation between photoelectron and hole. Thus more holes will have the opportunity to escape from the geminate hole–electron recombination. It is well known that the geminate recombination is the main reason for low efficiency of TiO_2 photocatalysis. Therefore, the existence of silver atom in Ag/TiO_2 film can help more holes to transport to the surface and enhance the photocatalytic efficiency. However, too much silver loadings will result in a negative effect. By increasing the amount of silver deposited on the TiO_2, the chance of the photoelectron meeting the hole is also increased. Furthermore, not all the photoelectron on the silver can be scavenged in time, so the transferred photoelectron will accumulate on silver, and the electric field produced by the accumulated photoelectron will attract the hole [18,23]. The silver then becomes the recombination centre of electrons and holes induced by light. Though, in the hybrid sol–gel method, only a small amount of Ag cluster is found on the surface of the Ag/TiO_2 sample with a molar ratio of Ag/Ti = 0.44 in the film, the molar ratios of Ag/Ti within Ag/TiO_2 films are still excessive on the surface, which means that silver species highly dispersed in the surface of TiO_2. So, with the amounts of silver increasing, the main reason for the low efficiency of degradation of MO must be that: (i) more catalyst surface area is covered by silver, which acts as a barrier preventing light absorption by TiO_2, (ii) it prevents the organic substrate from contacting the TiO_2 surface and (iii) the excessive Ag becomes the recombination center for electron–hole pairs.

The results of photo degradation by visible light excitation show that the Ag/TiO_2 films made by the hybrid sol–gel method can absorb visible light. The mechanism of visible light photo sensitization can be explained in the following two ways—(i) that the MO absorbs visible light and injects electrons into the conduction band of TiO_2, and (ii) that Ag/TiO_2 itself absorbs visible light, probably facilitated sub-energy-levels between the band gaps of TiO_2 by the dispersion of Ag in the TiO_2 matrix. It is probable that the two mechanisms are happening in parallel. So the original TiO_2 exhibited slight photocatalytic ability because of (i) Since separating electron–hole pairs and absorbing visible light occurred simultaneously, the Ag/TiO_2 films showed higher enhanced photocatalytic ability when it was irradiated under UV light than visible light.

In this work, when Ag/Ti molar ratio is low, the silver cluster could not be observed by SEM and detected by EDX, which implies that most of the silver located in the body of TiO_2 film. Even with the increase of the molar ratio of Ag/Ti in the prepared gel, though some large silver cluster was formed on the surface, more silver still exist as small cluster. For the photoreduction case, the size of Ag cluster is thought to be a vital factor to influence the photocatalytic efficiency of Ag/TiO_2 films [17]. But in this work, the amount of silver is more important than the size of the cluster. The Ag/TiO_2 film with a molar ratio of Ag/Ti = 0.44 is the only one in which the Ag cluster can be observed clearly. However, this film has the worst photocatalytic efficiency. When the ratio of Ag/Ti is the optimal value, though no obvious Ag cluster is formed, Ag/TiO_2 film still has the best photocatalytic efficiency.

In different works, the state of silver was different. Silver existed as Ag^0 valance state in most of the works [17,18,23,24], and there was also a report that the silver was in Ag^+ valance state [21], but coexistence of Ag^{2+}, Ag^+ and Ag^0 (Fig. 1, Fig. 3b and c.) was observed in this work. During calcination, some Ag^+ ions would gradually migrate from the volume of the TiO_2 to the surface by enhancing their crystallinity, resulting in silver deposited on the surface on calcination. This results in the formation of Schottky barrier at the Ag/TiO_2 contact region, which improves the photocatalytic activity. Meanwhile, residual Ag^+ ions within TiO_2 acted as efficient electron traps also contribute to the enhanced photocatalytic activity of these samples. When silver species exist as Ag^+ and Ag^{2+} valance states, the electric field produced by Ag^+ and Ag^{2+} enhances the ability of separation between the photoelectron and hole [21]. So no matter what state the silver is, when the amount of silver on TiO_2 is appropriate, it can act as an electron trap to enhance the photocatalytic activity of TiO_2 film by decreasing recombination between electron and hole. In this work, when the concentration of Ag species is high, more Ag^0 appear, and hence the electric field effect will weaken, which may be another reason for the low efficiency of degradation of MO by Ag/TiO_2 photocatalyst at high Ag/Ti ratio.

4. Conclusions

Ag/TiO_2 thin films produced by hybrid sol–gel method demonstrate efficient photocatalysis activity. Three Ag species (AgO, AgO_2 and Ag^0) coexisting within the Ag/TiO_2 films are found to vary with the Ag/Ti ratio in Ag/TiO_2 films. Ag species were dispersed in the body of the Ag/TiO_2 film uniformly, and when the molar ratio of Ag/Ti is high, some of the Ag species can aggregate on the surface of the Ag/TiO_2 photocatalyst. Silver both in body and aggregated on the surface can act as electron traps to enhance photocatalytic activity of Ag/TiO_2 thin films. The absorbance spectra of Ag/TiO_2 films are shifted to the visible region. The photocatalytic efficiency of Ag/TiO_2 films depends strongly on the amount of Ag loaded in prepared gel. With a proper amount of silver loading, a maximum degradation of MO under both UV365 and visible light irradiation can be attained. The photocatalytic activity under both UV365 (73%) and visible light (3.8 times) can be enhanced dramatically.

Acknowledgement

This work was partly supported by Tianjin Municipal Natural Science Foundation under Grant No. 07JCYBJC14900.

References

[1] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobiol. C 1 (1) (2000) 1–21.
[2] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, Prog. Solid State Chem. 32 (2004) 33–177.
[3] M. Fernández-García, A. Fuerte, M.D. Hernández-Alonso, J. Soria, A. Martínez-Arias, Platinization of sunlight active Ti–W mixed oxide photocatalysts, J. Catal. 245 (2007) 84–90.
[4] J.Y. Shi, J. Chen, Z.C. Feng, T. Chen, Y.X. Lian, X.L. Wang, C. Li, Photoluminescence characteristics of TiO_2 and their relationship to the photoassisted reaction of water/methanol mixture, J. Phys. Chem. C 111 (2007) 693–699.
[5] X.G. Hou, F.H. Hao, B. Fan, X.N. Gu, X.Y. Wu, A.D. Liu, The modification of photocatalytic ability of TiO_2 by V ion beam implanting, Nucl. Instrum. Meth. B 243 (2006) 99–102.
[6] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Visible-light photocatalysis in nitrogen-doped titanium oxides, Science 293 (2001) 269–271.
[7] G. Marc, M. Addamo, V. Augugliaro, S. Coluccia, E. Garćıa-López, V. Loddo, G. Martra, L. Palmisano, M. Schiavello, Photocatalytic oxidation of toluene on irradiated TiO_2: comparison of degradation performance in humidified air, in water and in water containing a zwitterionic surfactant, J. Photochem. Photobiol. A 160 (2003) 105–114.
[8] A.Q. Siham, R. Salman, Photocatalytic degradation of methyl orange as a model compound, J. Photochem. Photobiol. A 148 (2002) 161–168.
[9] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, Band gap narrowing of titanium dioxide by sulfur doping, Appl. Phys. Lett. 81 (3) (2002) 454–456.
[10] G.K. Mor, K. Shankar, M. Paulose, O.K. Varghese, C.A. Grimes, Enhanced photocleavage of water using titania nanotube arrays, Nano Lett. 5 (1) (2005) 191–195.
[11] S. Khan, M. Al-Shahry, W.B. Ingler, Efficient photochemical water splitting by a chemically modified *n*-TiO_2, Science 297 (2002) 2243–2245.
[12] Y. Ishibai, J. Sato, S. Akita, T. Nishikawa, S. Miyagishi, Photocatalytic oxidation of NO*x* by Pt-modified TiO_2 under visible light irradiation, J. Photochem. Photobiol. A 188 (2007) 106–111.
[13] S. Kumar, A.G. Fedorov, J.L. Gole, Photodegradation of ethylene using visible light responsive surfaces prepared from titania nanoparticle slurries, Appl. Catal. B 57 (2005) 93–107.
[14] C. He, Y. Xiong, X. Zhu, X. Li, A platinised TiO_2 film with both photocatalytic and non-photocatalytic activities towards the oxidation of formic acid, Appl. Catal. A 275 (2004) 55–60.
[15] P.V. Kamat, M. Flumiani, A. Dawson, Metal–metal and metal–semiconductor composite, Colloid Surf. A 202 (2002) 269–279.
[16] F.B. Li, X.Z. Li, The enhancement of photodegradation efficiency using Pt–TiO_2 catalyst, Chemosphere 48 (2002) 1103–1111.

[17] S.X. Liu, Z.P. Qu, X.W. Han, C.L. Sun, A mechanism for enhanced photocatalytic activity of silver-loaded titanium dioxide, Catal. Today 93 (2004) 877–884.
[18] V. Vamathevan, R. Amala, D. Beydoun, G. Lowb, S. McEvoy, Photocatalytic oxidation of organics in water using pure and silver-modified titanium dioxide particles, J. Photochem. Photobiol. A 148 (2002) 233–245.
[19] M.R. Sahyun, N. Serpone, Primary events in the photocatalytic deposition of silver on nanoparticulate TiO_2, Langmuir 13 (1997) 5082–5088.
[20] B.F. Xin, L.Q. Jing, Z.Y. Ren, B.Q. Wang, H.G. Fu, Effects of simultaneously doped and deposited Ag on the photocatalytic activity and surface states of TiO_2, J. Phys. Chem. B 109 (2005) 2805–2809.
[21] I.M. Arabatzis, T. Stergiopoulos, M.C. Bernard, D. Labou, S.G. Neophytides, P. Falaras, Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange, Appl. Catal. B 42 (2003) 187–201.
[22] J.M. Herrmann, H. Tahiri, Y. Ait-Ichou, G. Lassaletta, A.R. González-Elipe, A. Fernández, Characterization and photocatalytic activity in aqueous medium of TiO_2 and Ag–TiO_2 coatings on quartz, Appl. Catal. B 13 (1997) 219–228.
[23] T.T.Y. Tan, C.K. Yip, D. Beydoun, R. Amal, Effects of nano-Ag particles loading on TiO_2 photocatalytic reduction of selenate ions, Chem. Eng. J. 95 (2003) 179–186.
[24] H.M. Sung-Suh, J.R. Choi, H.J. Hah, S.M. Koo, Y.C. Bae, Comparison of Ag deposition effects on the photocatalytic activity of nanoparticulate TiO_2 under visible and UV light irradiation, J. Photochem. Photobiol. A 163 (2004) 37–44.
[25] A.V. Rupa, D. Manikandan, D. Divakar, T. Sivakumar, Effect of deposition of Ag on TiO_2 nanoparticles on the photodegradation of Reactive Yellow-17, J. Hazard. Mater. 147 (2007) 906–913.
[26] J.J. Liu, X.P. Li, S.L. Zuo, Y.C. Yu, Preparation and photocatalytic activity of silver and TiO_2 nanoparticles/montmorillonite composites, Appl. Clay Sci. 37 (2007) 275–280.
[27] M.K. Seery, R. George, P. Floris, S.C. Pillai, Silver doped titanium dioxide nanomaterials for enhanced visible light photocatalysis, J. Photochem. Photobiol. A 189 (2007) 258–263.