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RESEARCH ARTICLE

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# Studies on photocatalytic activity of $Ag/TiO_2$ films

**Abstract** $Ag/TiO_2$ photocatalytic films were produced by hybrid sol–gel method. The photocatalytic degradation of methyl orange (MO) in aqueous solution under 365 nm 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. With a loading molar ratio of Ag/Ti = 0.135 in $TiO_2$ film, the maximum catalytic efficiency was observed.

**Keywords** $Ag/TiO_2$ film, photocatalysis, hybrid sol-gel method, catalytic efficiency

## 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 a noble metal on the surface of $TiO_2$ powder or thin film by photochemical deposition method [12–23]. Especially, the deposition of silver has attracted much attention [17–23]. Up to now, most of the methods used for loading silver has been photoreduction. However, loading silver by hybrid sol-gel method (mixing silver nitrate to prepared gel) is also an efficient way to produce $Ag/TiO_2$ films. In this study, $Ag/TiO_2$ films with different molar ratios of Ag/Ti were prepared via hybrid sol-gel method and photocatalytic efficiency of the $Ag/TiO_2$ thin films was reported. SEM, XRD, RBS, XPS 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 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-$K_\alpha$ 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.

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### 2.3 Measurement of photocatalytic activity

A 1000 W mercury lamp (BELSRI, China) 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 $5 \times 10^{-5}$ 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. The extent of photo-degradation of MO was determined by the optical density at 465 nm measured by a UV-Visible spectrometer (UV-160, Shimadzu, Japan).

## 3 Results and discussion

### 3.1 Characterization of $Ag/TiO_2$ films

Figure 1 shows XRD patterns of $Ag/TiO_2$ films. The strongest peak at $2\theta = 25.3°$ clearly demonstrates the (101) anatase phase of $TiO_2$ crystal. No observable rutile phase is observed in all samples. The data from Fig. 1(a) to (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 (331) 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 patterns from Fig.1 (a) to (f) are observed, which indicates that the presence of different amounts of Ag species has no substantial influence on the size of $TiO_2$ particles. $TiO_2$ crystallite size can be estimated as 30 nm by the Scherrer equation.

The surface structure of $Ag/TiO_2$ films with different molar ratios of Ag/Ti was studied by SEM. The SEM pictures (Fig. 2b and c) show a uniform distribution of $TiO_2$ nano-particles. The size of these particles can be estimated to be around 10–40 nm. The SEM pictures also reveal that the surface structure of the $Ag/TiO_2$ films is rough and porous, which is favorable to the enhancement of the photocatalytic activity. Figure 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. Figure 2(a) 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.

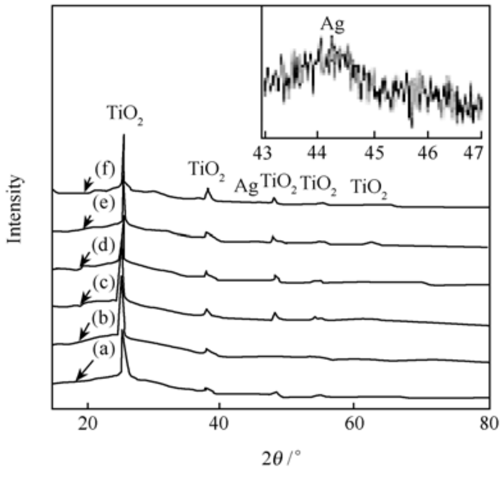

**Fig. 1** XRD spectra of $Ag/TiO_2$ films: Ag/Ti in prepared gel (a) 0, (b) 0.032, (c) 0.064, (d) 0.128, (e) 0.192, (f) 0.48

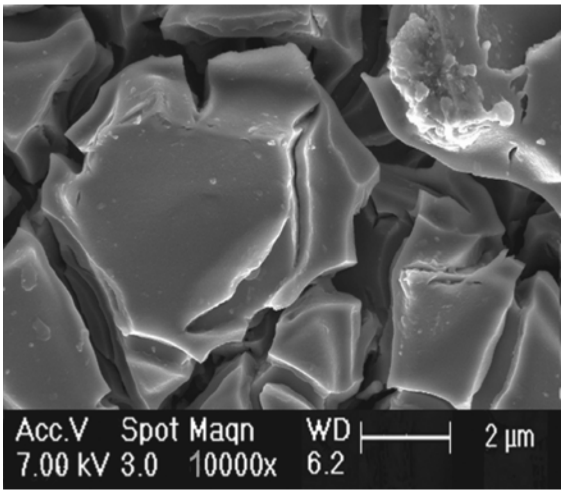

**Fig. 2a** SEM image of $Ag/TiO_2$ film with molar ratio of Ag/Ti = 0.48 in prepared gel

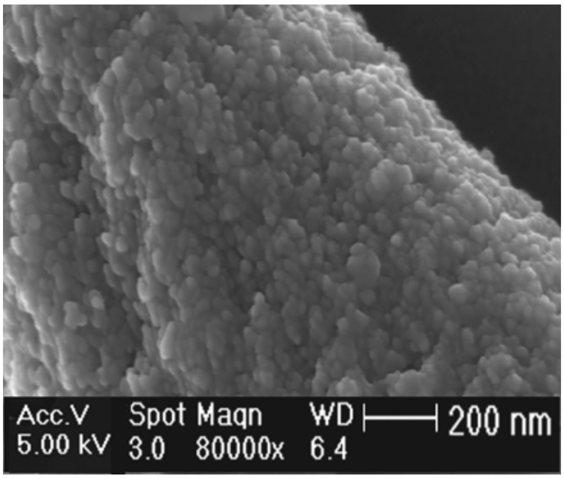

**Fig. 2b** The $TiO_2$ thin film without $AgNO_3$ in prepared gel

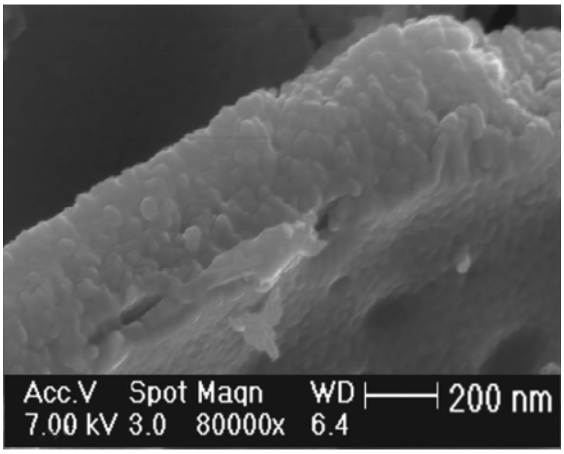

**Fig. 2c** The $Ag/TiO_2$ film with molar ratio of Ag/Ti = 0.48 in prepared gel.

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 a 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 deconvolution, attributed to AgO (367.0 eV), $Ag_2O$ (367.7 eV), and $Ag^0$ (368.2 eV) [20], respectively. Figure 3(b) 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).

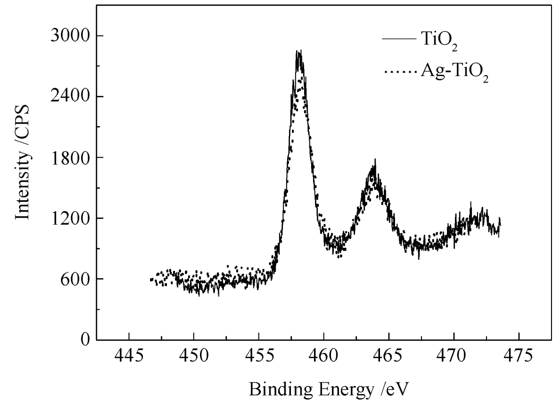

**Fig. 3a** XPS spectra of Ti2p of $TiO_2$ and $Ag/TiO_2$ (molar ratio of Ag/Ti = 0.48)

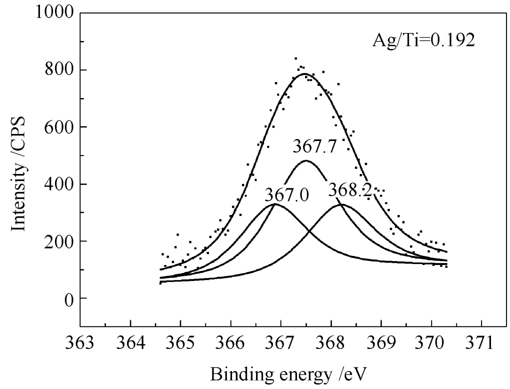

**Fig. 3b** XPS spectra of $Ag3d_{5/2}$ of $Ag/TiO_2$ (molar ratio of Ag/Ti = 0.192)

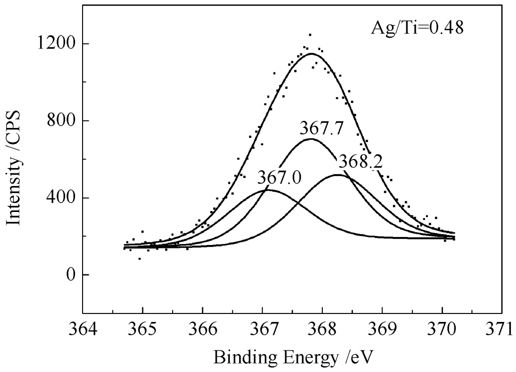

**Fig. 3c** XPS spectra of $Ag3d_{5/2}$ of $Ag/TiO_2$ (molar ratio of Ag/Ti = 0.48)

## 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. Figure 4 shows RBS spectra of Ag/$TiO_2$ films made from gels with different molar ratios of Ag/Ti. According to Fig. 4, 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. 5, 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. 5. 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 $K_\alpha$-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 can't 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.

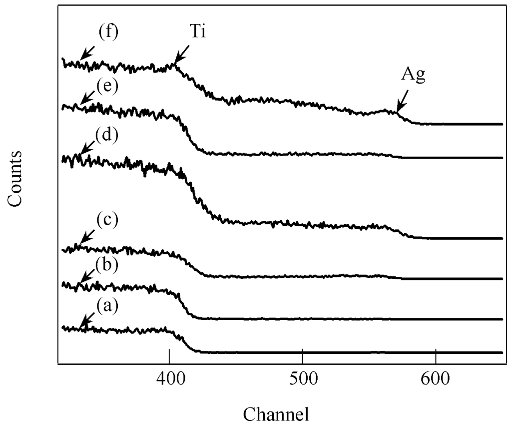

**Fig. 4** RBS spectra of Ag/$TiO_2$ films: molar ratio of Ag/Ti in prepared gel (a) 0, (b) 0.032, (c) 0.064, (d) 0.128, (e) 0.192, (f) 0.48

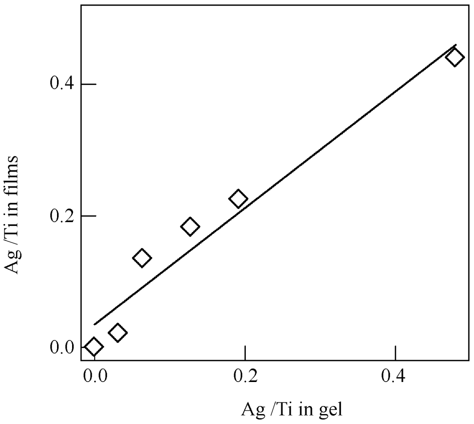

**Fig. 5** Relationship of molar ratio of Ag/Ti between Ag/$TiO_2$ films and gel

## 3.3 The photocatalytic efficiency of Ag/$TiO_2$ films

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 365nm 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. Figure 6 shows the typical time profiles of this degradation. The 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. Figure 7 shows the relationship between $k$ and molar ratio Ag/Ti in prepared gel (solid line is just for showing the data better). 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 raw $TiO_2$ 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 $k$. 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.

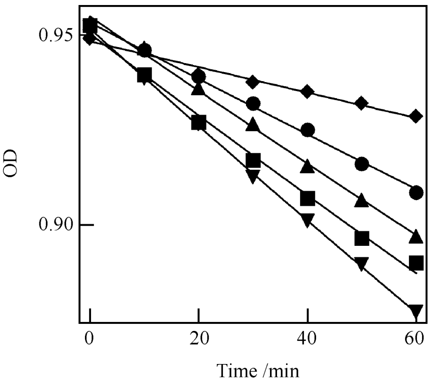

**Fig. 6** A typical time profile of MO photodegradation under 365 nm irradiation with Ag/$TiO_2$ photocatalyst. Molar ratio of Ag/Ti in prepared gel : (●): 0, (▲): 0.032, (▼): 0.064, (■): 0.128 and (◆):0.192

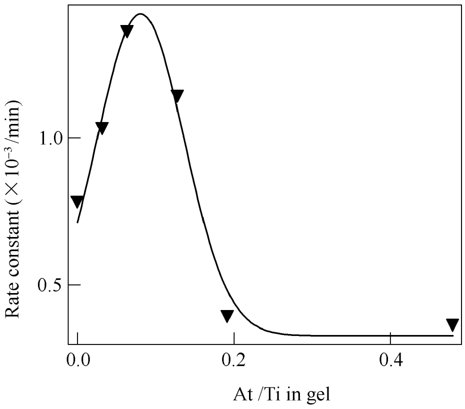

**Fig. 7** Variation of photodegradation rate constants (*k*) of MO with silver loadings in prepared gel

### 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 2c); thus the variation of photocatalytic activity cannot be attributed to size effect as mentioned in 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. With the amounts of silver increasing, for the photoreduction case, more catalyst surface area is covered by silver, which prevents $TiO_2$ from contacting with light and leads to the decrease of yield of photo-induced electron and hole [17]. However, 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. So the main reason for the low efficiency of degradation of MO must be that the excessive Ag becomes the recombination center.

In this work, when Ag/Ti molar ratio is low, the silver cluster couldn't 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, and 23], 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 3c.) was observed in this work. When silver species exist as $Ag^+$ and $Ag^{2+}$ valance states, in addition to the factor of different work functions between silver and $TiO_2$, the electric field produced by $Ag^+$ and $Ag^{2+}$ also 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 aggregated 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 photocalytic activity of Ag/$TiO_2$ thin films. 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 UV365 irradiation can be attained (molar ratio of Ag/Ti = 0.135 in the film). The photocatalytic activity under UV365 can be enhanced dramatically (73%).

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