RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Enhanced visible-active photochromism of polyoxometalates/TiO_2 composite film by combining Bi_2O_3 nanoparticles

Xiansheng Wang[1], Yan Sun[1], Changcheng Liu[2], Wei Feng[1]*, Donglei Zou[1]

[1] Key Lab of Groundwater Resources and Environment, Ministry of Education, Jilin University, Changchun 130021, P. R. China

[2] Department of Aviation Oil and Materials, Air and Force Service College, Jiangsu Xuzhou, 221000, P.R.china

Abstract

Novel photochromic hybrid film was successfully synthesized by introducing Bi_2O_3 into phosphomolybdic acid (PMoA)/TiO_2 system as visible light sensitizer. The influence of Bi_2O_3 addition on microstructure and photochromic properties was studied via transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FT-IR), ultraviolet-visible spectra (UV-vis) and X-ray photoelectron spectroscopy (XPS). Results revealed that Keggin geometry of PMoA and basic structure of Bi_2O_3 were preserved in the obtained film, and the interaction between PMoA and TiO_2 was strengthened after combining Bi_2O_3. Upon visible light irradiation, the composite films changed from colorless to blue and showed reversible photochromism in the presence of oxygen. Moreover, pho-

tochromic performance of Bi_2O_3/PMoA/TiO_2 film was better than that of PMoA/TiO_2 film. The amount of PMoA participating in photo-reductive reaction increased after adding Bi_2O_3 into PMoA/TiO_2 composite, which resulted in photochromic efficiencies enhancing.

Keywords: Polyoxometalates; Bi_2O_3 nanoparticles; Visible light photochromism; Composite film

1. Introduction

Photochromic materials, whose optical absorption properties change in response to light, have been the focus of intensive investigations for several decades because of their potential applications in a variety of fields, such as information display, optical switching, optical memories and sensors, and high-density optical storage.[1-4] Polyoxometalates (POMs), which usually refers to a series of multi-core inorganic metal-oxide clusters, can accept one or more electrons to yield mixed-valency colored species due to their fundamental structures and versatile electronic properties.[5,6] Consequently, it has become one of the most attractive photochromic materials. By entrapping POMs into inorganic or organic networks, various photosensitive systems were built up and photochromic properties of materials were related to the reduction potentials of POMs.[7] Up to now most studies on photochromism of POMs are based on UV light irradiation, however, the development of photochromic materials with superior visible light response is highly anticipated for the purpose of efficient utilization of solar energy and common semiconductor laser sources.[8,9]

Some efforts have been made to promote the photoresponse of materials in visible light region. Ramirez confirmed that the photochromic response of MoO_3 improved with the addition of CdS as a visible light sensitizer.[10] By depositing Au nanoparticles on the surface of MoO_3 film, the Mo/Au film became more sensitive to visible light than MoO_3 film.[11] Such a combination of the third functional phrase allowed the achievement of a new system by using visible light excitation. After that, Yao et al. reported the preparation of hybrid film fabricated from phosphomolybdic acid (PMoA) and PVP with photochromism under blue light (400-500 nm) and the absorbance can be enhanced dramatically through subsequent thermal treatment.[12] Embedding PMoA into appropriate inorganic system via chemical bond might fabricate novel PMoA/inorganic system which was fairly sensitive to visible light.

Lately, bismuth oxide (Bi_2O_3), an inorganic semiconductor, has showed promise in the conversion of solar energy because of its visible-light response and good photo-chemical stability.[13,14] Especially, Bi_2O_3 can provide electrons to induce the reduction of heteropolyacids (heteropolyblues generated) in the photochemical reaction. In this study, we introduce Bi_2O_3 as visible light sensitizer into PMoA/TiO_2 system and the photochromic properties of as-prepared films were investigated. Experimental results demonstrated that the photochromic performance of PMoA/TiO_2 film has improved with addition of Bi_2O_3 nanoparticles in visible light region.

2. Experimental section

2.1 Materials

Phosphomolybdic acid (PMoA) was purchased from Sinopharm Chemical Reagent (China) and recrystallized before use. N-butyl titanate and Bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$] were obtained from Tianjin Guangfu Fine Chemicals Research Institute (China) and used as received. All other chemical reagents were of analytical grade and used as received.

2.2 Preparation

2 mL N-butyl titanate was dissolved in the 10 mL absolute ethanol and stirred the mixture for 30 min. Then 2 mL acetic acid and 0.7 mL triethanolamine were added to the N-butyl titanate solution. With constant stirring for 1 h, 10 mL absolute ethanol and 0.2 mL deionized water was gradually added to the mixed solution, for 1 h stirring shallow yellow transparent sol was obtained. Then, 0.5 mL acetylacetone was added to the transparent sol for 30 min stirring. Finally, the transparent TiO_2 sol was obtained after 24 h aging.[15]

Bismuth oxide (Bi_2O_3) nanoparticles were fabricated hydrothermally by utilizing $Bi(NO_3)_3.5H_2O$ (0.025 mol/L) as starting material, which was then added with 10% NH_3H_2O under vigorous stirring and pH value was modified to 8.5. Then the mixture was charged into polyterafluoroethene-lined parr autoclave with a filling capacity of 80% and hydrothermal synthesis of Bi_2O_3 was conducted at 180°C for 12h.

PMoA were dissolved in ethanol with a concentration of 10 mg/mL. Then 1 mL PMoA solution was slowly dripped into the 10 mL TiO_2 sol and mixed together.

A transparent solution was obtained by slowly adding 500 μL Bi_2O_3 (2 mg/mL) etha-

nol solution into the mixture and vigorously stirring at room temperature for 2 h. Finally, PMoA/TiO_2 and Bi_2O_3/PMoA/TiO_2 composite films were prepared by dripping the transparent solution on various substrates by using a 100 μL syringe. All films were dried in a chamber with stable air humidity controlled within 60% in order to obtain optically perfect film. The thickness of hybrid film was approximately 2.2 μm, which was measured by a FCT-103 Film Thickness Measurement System (LCD Lab, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science).

2.3 Instrumental analysis

TEM images of samples were observed on a JEOL JEM-200CX transmission electron microscope by dripping complex solution onto copper grids. FT-IR spectra were determined by the samples deposited on the KBr pellets at room temperature with a Nicolet Impact 410 FT-IR spectrometer in the wavenumber range of 2000-400 cm^{-1}. Absorption of all samples was measured on an UV-vis spectrophotometer (Shimadzu UV-1601PC) with 1 nm optical resolution in the range of 300-900 nm. XPS measurements were taken in an ESCALAB 250 photoelectron spectrometer to acquire the information on chemical binding energy of hybrid film. Photochromic experiments were carried out by using a 500 W Xe lamp as the light source and the light was passed through a glass filter (λ>422 nm, ZUL0422 ASAHI Co). All the measurements were carried out at room temperature.

3. Results and discussion

3.1 TEM measurements

The microstructure of the composite films was observed by TEM images. TiO_2 sol-gel film was uniform without particles aggregation. The PMoA particles exhibited regular spherical shape with average diameter of 60 nm in PMoA/TiO_2 film. As shown in Fig.1b, Bi_2O_3 nanoparticles were sphere with the size of 30 nm. Compared Fig.1d with Fig.1c, the participation of Bi_2O_3 had no effect on morphology of PMoA in composite system except slight aggregations and Bi_2O_3 well dispersed in the composite. Inset selected area electron diffraction (SAED) pattern took on samples exhibited that PMoA still maintained the single crystal structure after Bi_2O_3 adding, which further illustrated that there was no impact on distribution of PMoA in PMoA/TiO_2 film by Bi_2O_3 nanoparticles.

3.2 FT-IR spectra

To confirm the molecular structure and chemical bonds of films gotten from the experiment, comparisons of FT-IR spectra for PMoA, Bi_2O_3, TiO_2 sol-gel film, PMoA/TiO_2 and Bi_2O_3/PMoA/TiO_2 composite films were performed. The characteristic bands of TiO_2 appeared and verified the presence of TiO_2 without any decomposition in the composite film. The records of spectra for PMoA of Keggin structure presented four characteristic vibration bands for P-Oa, Mo-Od, Mo-Ob-Mo and Mo-Oc-Mo at 1064, 960, 867, 780 cm^{-1} respectively.[16] In the composite films of PMoA/TiO_2 and Bi_2O_3/PMoA/TiO_2, those characteristic bands were similar to pure PMoA with slight shifts, which demonstrated that the basic structure of Keggin ge-

ometry was still preserved.

Generally, the Mo-Od vibration was considered as a pure stretching one, whose peak position was greatly impacted by the anion-anion interaction.[17] The Mo-Od asymmetrical stretching frequency of PMoA/TiO_2 hybrid film had a red shift by 4 cm^{-1}. This was attributed to the influence of TiO_2, which led to the increase of the anion-anion distance and the weakness of anion-anion electrostatic interaction. Because *v*(Mo-Ob-Mo) and *v*(Mo-Oc-Mo) vibrations were not pure stretching and cannot be free from bending character, there was a competition of opposing effects. The electrostatic anion-anion interaction led to an increase of the frequencies of vibrations.[16] So the Mo-Ob-Mo and Mo-Oc-Mo bands can be considered as foundation to evaluate the interaction between the two inorganic components. Meantime, the bands of *v*(Mo-Ob-Mo) and *v*(Mo-Oc-Mo) had blue shifts by 2 and 8 cm^{-1} respectively, which was due to the formation of Mo-O-Ti band between PMoA and TiO_2.[18,19]

In addition, the *v*(P-Oa) band had no change because there was no impact on P-Oa vibration after Bi_2O_3 adding. Comparing with PMoA/TiO_2 film, the Mo-Od had red shifts and Mo-Ob-Mo and Mo-Oc-Mo had blue shifts, illustrating that Bi_2O_3 strengthened the bonded interaction between PMoA and TiO_2. Irradiated with visible light, the *v*(Mo-Ob-Mo) and *v*(Mo-Oc-Mo) vibration bands associated with PMoA in the composite film shifted, which should be attributed to the formation of heteropoly-blues. Additionally, the presence of the characteristic vibration (at 400-600 cm^{-1} assigned to Bi-O band) for Bi_2O_3 were found in the composite film either with or with-

out irradiation.[20] Results revealed the Bi_2O_3 nanoparticles were preserved during the composite process.

3.3 Photochromic behavior

The coloration process was collected by UV-vis absorption spectra of $PMoA/TiO_2$ and $Bi_2O_3/PMoA/TiO_2$ composites with irradiation of visible light (Fig.3a and b). There was no obvious absorption before irradiation. When subjected to visible light, the colorless films turned deep blue and one broad absorption band at 730 nm was detected, attributing to intervalence charge transfer (IVCT, $Mo^{6+} \rightarrow Mo^{5+}$).[21,22] With prolonging irradiation time, the absolute absorbance of $PMoA/TiO_2$ and $Bi_2O_3/PMoA/TiO_2$ films increased and reached saturation gradually with irradiation for 14 and 16 min respectively. For $Bi_2O_3/PMoA/TiO_2$ film, the intensity of absorbance at 730 nm was 0.152 after irradiating for 16 min, which was 1.42 times stronger than that of $PMoA/TiO_2$ film under the same condition. Results indicated that Bi_2O_3 were in favor of the formation of heteropolyblues and improved the light absorption efficiency of composite film.

The kinetics of the coloration process was also investigated by monitoring the absorbance changes at 730 nm as a function of irradiation time (see Fig.4). The photochromic process of the two retained films followed first-order kinetics with rate constants k_1=0.17 min^{-1} and k_2=0.21 min^{-1} for $PMoA/TiO_2$ and $Bi_2O_3/PMoA/TiO_2$ film respectively.

For the $PMoA/TiO_2$ and $Bi_2O_3/PMoA/TiO_2$ composite films, the similar bleaching

process was shown up. Fig.5 only showed the bleaching process of Bi_2O_3/PMoA/TiO_2 composite film. After visible light was turned off, the colored film began to bleach gradually in air. But if it was placed to avoid exposure to oxygen, such as protected by nitrogen or placed in vacuum, the color of composite film kept stable for a long time, which suggested that oxygen played an important role in the oxidation of Mo^{5+} to Mo^{6+} during the bleaching process. In particular, the increase of temperature will rapidly accelerate the bleaching process of colored film. The bleaching process finished in 30 min when heating the colored film at 100℃. And the photochromic reversibility of composites was quite good, as shown in Fig.6. The maximum of absorbance was almost consistent with the increasing of irradiation times.

3.4 Photochromic mechanism

Optical band gap studies have proven to be an effective tool for investigating the optical response of composites. The band gap energy values can be determined through the optical absorption spectra at the fundamental absorption edge of materials. Fig.7 showed the UV absorbance edge of the two as-prepared films before irradiation, which reflected the influence of Bi_2O_3 on the optical properties. The absorption edge of Bi_2O_3/PMoA/TiO_2 had a red shift from 402 nm to 433 nm compared with PMoA/TiO_2 and the shift of optical response to visible region could be well understood from the decrease in the band gap value from 3.08 eV to 2.86 eV. This demonstrated that the addition of Bi_2O_3 narrowed the band gap and improved the optic absorbance performance of PMoA/TiO_2 hybrid film.

XPS spectra were used to investigate the influence of Bi_2O_3 nanoparticles on the variation of electronic structure of the films during photochromic process so as to find the mechanism (as shown in Fig.8a and b). By employing Gaussian deconvolution, Mo_{3d} binding energies were separated into two degenerated energy levels ($Mo_{3d5/2}$ and $Mo_{3d3/2}$) and the values were listed in Table 1.[23] The Mo_{3d} doublet of Mo^{5+} were all detected in PMoA/TiO_2 and Bi_2O_3/PMoA/TiO_2 hybrid films, which indicated that the reductive reaction took place after films exposed to visible light. Compared with the binding energies of PMoA/TiO_2, the values of $Mo_{3d5/2}$ and $Mo_{3d3/2}$ were both lower for Mo^{6+} and Mo^{5+} by introducing Bi_2O_3. Evidently, different binding energies in Bi_2O_3/PMoA/TiO_2 system presented different reductive valence state during the photo-reduction process, which illustrated the chemical microenvironment of Mo was changed. Moreover, the Mo^{5+}/Mo ratio of PMoA/TiO_2 was 0.38, much lower than that of Bi_2O_3/PMoA/TiO_2 (0.49). It can be concluded that photo-reduction degree was enhanced with participation of Bi_2O_3, which led to better photochromic response under the same irradiated condition.

As for the PMoA/TiO_2 system, the mechanism was further interpreted according to the energy levels of the two starting materials (as shown in Fig.9a). The lowest energy excitation was from TiO_2 valance band (VB) to PMoA condition band (CB), 2.09eV through calculation, which was just located at visible light absorption range.[24] However, the electron transfer between TiO_2 VB and PMoA CB was achieved with the formation of Mo-O-Ti bond with charge transfer characteristic at the composite inter-

face, which was forbidden normally. Irradiated with visible light, electrons excited from TiO_2 valance band migrated to condition band of PMoA through Mo-O-Ti bond. And the electron transfer was promoted by Mo-O-Ti bond, consequently Mo^{6+} was reduced to Mo^{5+}. Thus, it can be concluded that the photo-reduction process of $PMoA/TiO_2$ composite film occurred according to electron transfer mechanism.

The driving force for electron transfer between PMoA and Bi_2O_3 was the relative energy difference between the conduction band of the two starting materials (as shown in Fig.9b).[25] Bi_2O_3, a visible light sensitizer, acted as a donor providing more electrons under visible light irradiation since it is good photoresponsive materials. The bottom of conduction band for PMoA was lower than that of Bi_2O_3, favoring electrons arising from Bi_2O_3 injected into the conduction band of PMoA. Heteropolyblues was produced by the reaction of PMoA and the conduction-band electrons. Thus PMoA obtained electrons provided by both TiO_2 and Bi_2O_3 and more Mo^{6+} was reduced to Mo^{5+}. This may be concluded as the main cause for the enhancement of photochromic properties with the addition of Bi_2O_3, which was in good agreement with the XPS measurements.

4. Conclusion

Novel photochromic hybrid film sensitive to visible light was developed by combining Bi_2O_3 with $PMoA/TiO_2$ composite. The participation of Bi_2O_3 strengthened the interaction between PMoA and TiO_2. When exposed to visible light, the hybrid film turned blue in color and the photochromic process was fitted to be first-order kinetics.

Moreover, Bi_2O_3/PMoA/TiO_2 composite film showed better photochromic response than PMoA/TiO_2 film. PMoA obtained electrons provided by Bi_2O_3 and TiO_2 simultaneously during the photo-reduction process, resulting in the improvement of photochromic properties. This study presented the method to construct a hybrid film with visible light photochromism by the deposition of a light sensitizer and paved a novel strategy to explore composite films practically used in solar energy application.

Acknowledgment

The authors acknowledge the financial support from the National Natural Science Foundation of China (No.61340048) and Industrial Technology Research and Development projects in Jilin province (No.2013C044).

References

1. R.C. Shallcross, P.O. Korner, E. Maibach, A. Kohnen and K. Meerholz, *Adv. Mater.*, 2013, **25**, 4807-4813.

2. Y.F. Chen, G .S. Yu, F. Li, C.F. Xie and G.P. Tian, *J. Mater. Chem. C*, 2013, **1**, 3842-3850.

3. M. Singer and A. Jaschke, *J. Am. Chem. Soc.*, 2010, **132**, 8372-8377.

4. J.J. Zhang, Q. Zou and H. Tian, *Adv. Mater.*, 2013, **25**, 378-399.

5. T. He and J.N. Yao, *J. Photoch. Photobio. C*, 2003, **4**, 125-143.

6. M.T. Pope, Heteroploy and Isopolyoxometalates, *Springer-Verlag, Berlin*, 1983.

7. G.J. Zhang, Z.H. Chen, T. He, H.H. Ke, Y. Ma, K. Shao, W.S. Yang and J.N. Yao, *J. Phys. Chem. B*, 2004, **108**, 6944-6948.

8. L.S. Zhang, W.Z. Wang, J.O. Yang, Z.G. Chen, W.Q. Zhang, L. Zhou and S.W. Liu, *Appl. Catal a-Gen.*, 2006, **308**, 105-110.

9. X.F. Jing, D.L. Zou, Q.L. Meng, W. Zhang, F.J. Zhang, W. Feng and X.K. Han, *Inorg. Chem. Commun.*, 2014, **46**, 149-154.

10. M.A. Quevedo-Lopez, R.F. Reidy, R.A. Orozco-Teran, O. Mendoza-Gonzalez and R. Ramirez-Bon, *J. Mater. Sci-Mater. El*, 2000, **11**, 151-155.

11. T. He, Y. Ma, Y. Cao, Y.H. Yin, W.S. Yang and J.N. Yao, *Appl. Surf. Sci.*, 2001, **180**, 336-340.

12. G.J. Zhang, W.S. Yang and J.N. Yao, *Adv. Funct. Mater.*, 2005, **15**, 1255-1259.

13. R. Chen, Z.R. Shen, H. Wang, H.J. Zhou, Y.P. Liu, D.T. Ding and T.H. Chen, *J. Alloy. Compd.*, 2011, **509**, 2588-2596.

14. C.H. Wang, C.L. Shao, L.J. Wang, L. Zhang, X.H. Li and Y.C. Liu, *J. Colloid. Interf. Sci.*, 2009, **333**, 242-248.

15. C. Lu, Y. Sun, J.L. Liu, X.S. Wang, S.L. Liu and W. Feng, *J. Appl. Polym. Sci.*, 2015, **132**, 41583-41589.

16. Q.Y. Wu, H.H. Lin and G.Y. Meng, *J. Solid State Chem.*, 1999, **148**, 419-424.

17. C. S. Ha, H. D. Park and C. W. Frank, *Chem. Mater.*, 2000, **12**, 839-844.

18. J. Wang, G.J. Zhang, W.S. Yang and J.N. Yao, *Acta Chim. Sinica*, 2005, **63,** 1951-1956. (in Chinese)

19. R.B. Watson and U.S. Ozkan, *J Phys Chem B*, 2002, **106**, 6930-6941.

20. F. Miyaji, T. Yoko and S. Sakka, *J. Non-Cryst. Solids*, 1990, **126**, 170-172.

21. T. Yamase, *Chem. Rev.*, 1998, **98**, 307-326.

22. K. Adachi, T. Mita, S. Tanaka, K. Honda, S. Yamazaki, M. Nakayama, T. Goto and H. Wataraic, *RSC Advances*, 2012, **2**, 2128-2136.

23. Z.L. Wang, R.L. Zhang, Y. Ma, L.D. Zheng, A. Peng, H.B. Fu and J.N. Yao, *J. Mater. Chem.*, 2010, **20**, 1107-1111.

24. S.H. Elder, F.M. Cot, Y. Su, S.M. Heald, A.M. Tyryshkin, M.K. Bowman, Y. Gao, A.G. Joly, M.L. Balmer, A.C. Kolwaite, K.A. Magrini and D.M. Blake, *J. Am. Chem. Soc.*, 2000, **122**, 5138-5146.

25. T. He and J.N. Yao, *Prog. Mater. Sci.*, 2006, **51**, 810-879.

Figure Captions

Fig.1 TEM images of (a) TiO_2 sol-gel film, (b) Bi_2O_3 nanoparticles, (c) PMoA/TiO_2 and (d) Bi_2O_3/PMoA/TiO_2 composite film.

Fig.2 FT-IR spectra of (a) PMoA, (b) Bi_2O_3, (c) TiO_2 sol-gel film, (d) PMoA/TiO_2, Bi_2O_3/PMoA/ TiO_2 composite film (e) before and (f) after visible light irradiation.

Fig.3 UV-vis spectra of (a) PMoA/TiO_2 and (b) Bi_2O_3/PMoA/TiO_2 composite film.

Fig.4 The kinetic plot of the photochromic process for PMoA/TiO_2 and Bi_2O_3/PMoA/TiO_2 composite film.

Fig.5 Bleaching process of Bi_2O_3/PMoA/TiO_2 composite film after irradiation.

Fig.6 The absorbance change at 730 nm of Bi_2O_3/PMoA/TiO_2 hybrid film during repeated coloration-decoloration process.

Fig.7 UV absorbance edge of PMoA/TiO_2 and Bi_2O_3/PMoA/TiO_2 hybrid film.

Fig.8 Gaussian deconvolution of Mo_{3d} level spectra of (a) PMoA/TiO_2 and (b) Bi_2O_3/PMoA/TiO_2 composite film after irradiation.

Fig.9 (a) Arrangement of the PMoA and TiO_2 valance bands (VB) and conduction bands (CB) for PMoA/TiO_2 composite film. (b) Schematic presenting the electron transfer between PMoA and Bi_2O_3.

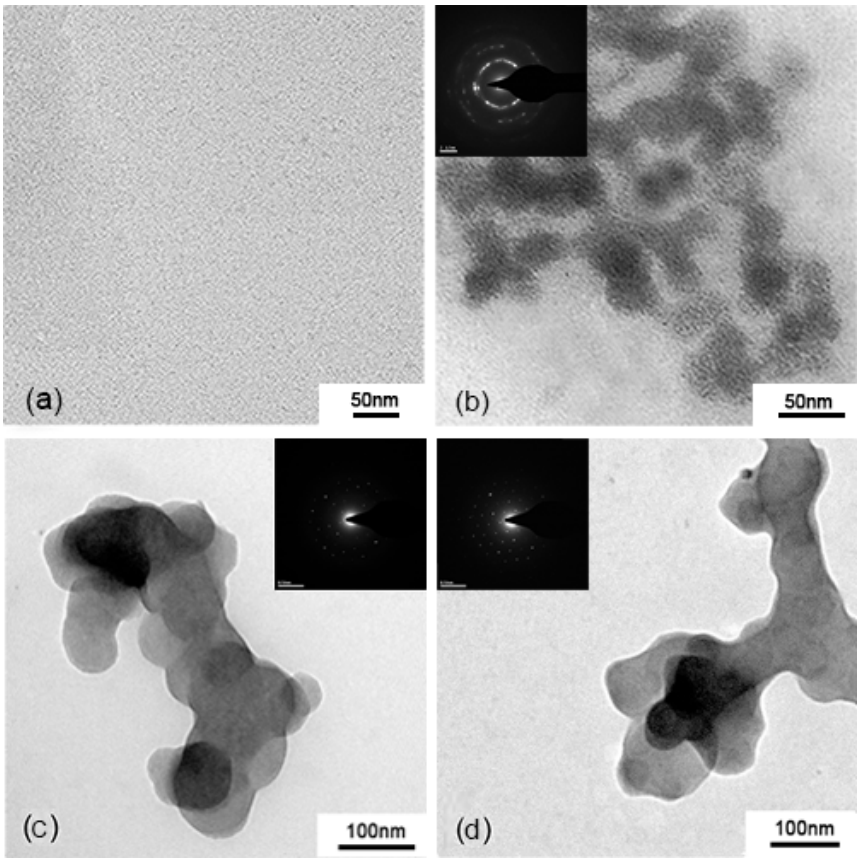

Fig.1

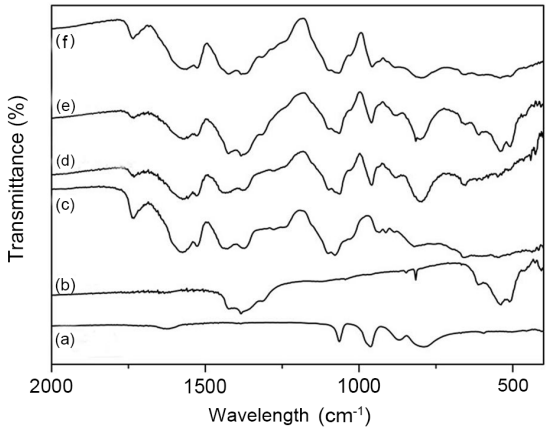

Fig.2

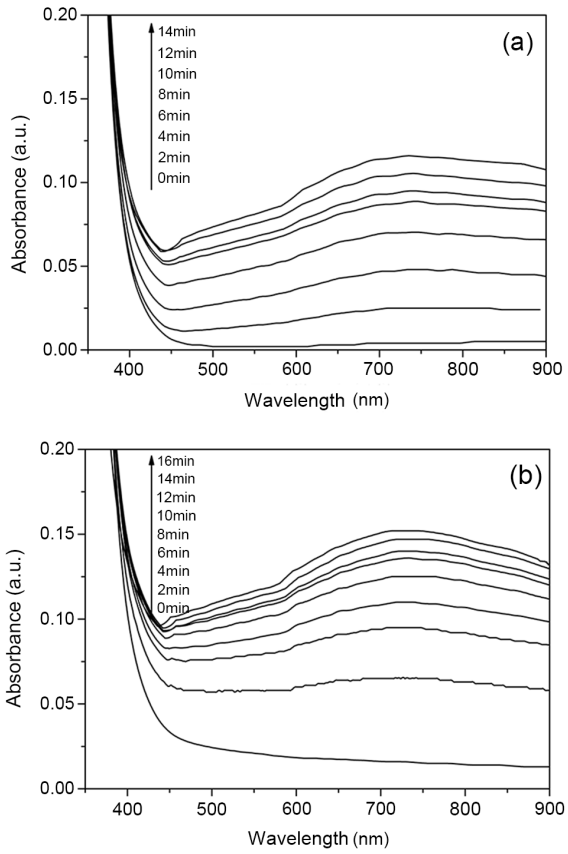

Fig.3

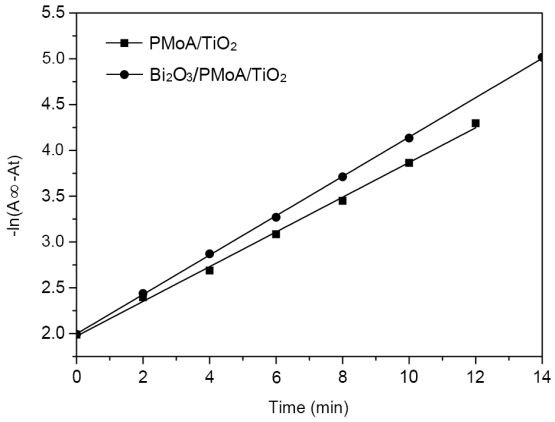

Fig.4

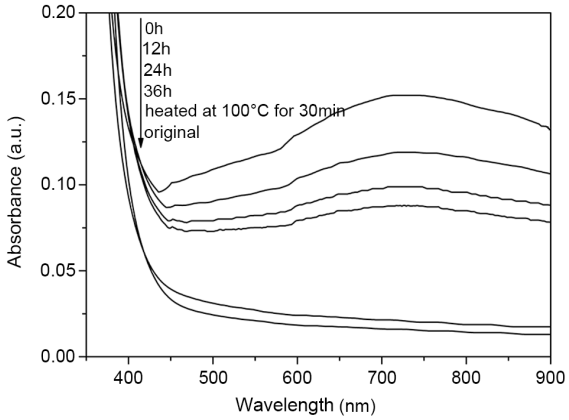

Fig.5

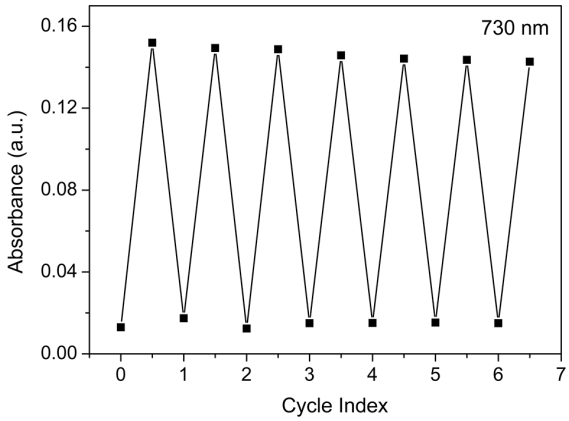

Fig.6

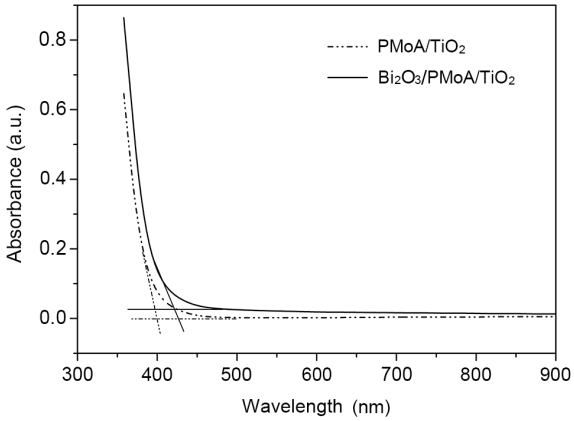

Fig.7

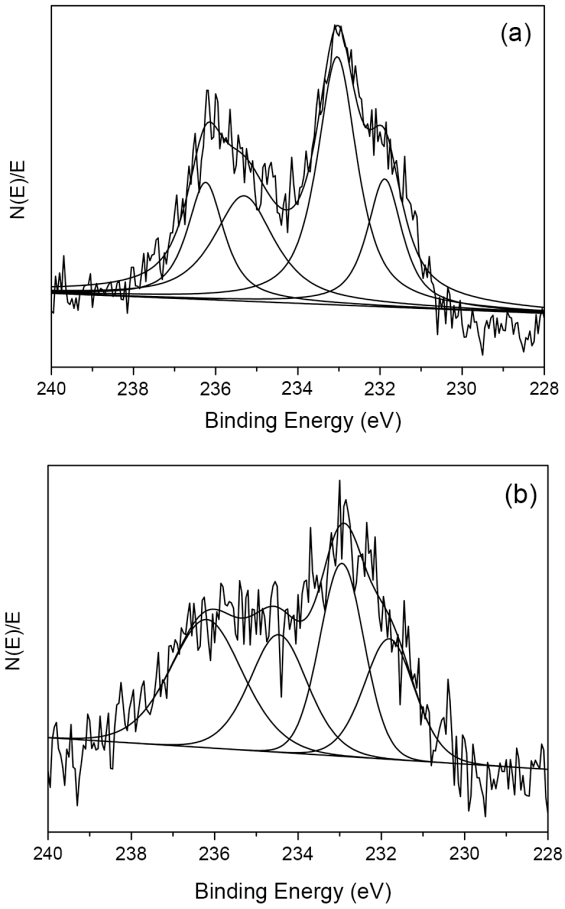

Fig.8

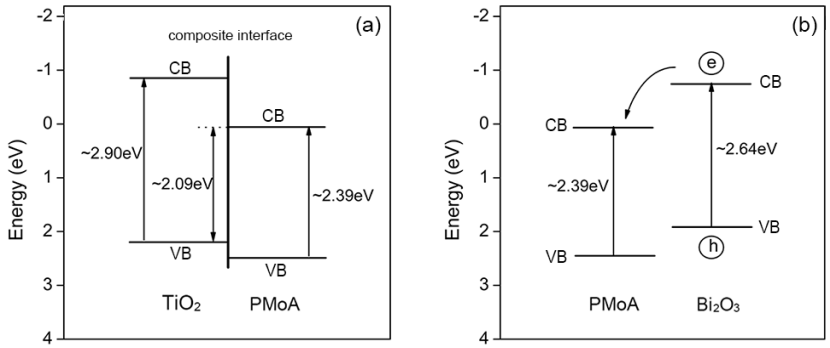

Fig.9

Table 1 Binding energies of Mo_{3d} energy level and Mo^{5+}/Mo ratios of $PMoA/TiO_2$ and $Bi_2O_3/PMoA/TiO_2$ composite film after irradiation.

Sample	Mo^{5+}		Mo^{6+}		Mo^{5+}/Mo Ratios
	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	
$PMoA/TiO_2$	235.31	231.88	236.25	233.04	0.38
$PMoA/TiO_2/Bi_2O_3$	234.46	231.71	236.19	232.94	0.49