Asian Journal of Chemistry; Vol. 26, No. 24 (2014), 8291-8294

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16792

Quasi-Hexagonal VO_2/Ag_3VO_4 Microcrystals for Photo-Catalytic Degradation of Rhodamine B

XIUCHENG TAO[1,*], QING HONG[1,2], TIANQING WU[1] and FAN LIAO[2,*]

[1]College of Environmental Science and Engineering, Anhui Normal University, Wuhu 241000, Anhui Province, P.R. China
[2]Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-based Functional Materials and Devices, Soochow University, Suzhou 215123, P.R. China

*Corresponding authors: Fax: +86 553 3869303; Tel: +86 553 3869302; E-mail: taoxiuch@mail.ahnu.edu.cn; fliao@suda.edu.cn

Received: 30 November 2013; *Accepted*: 10 April 2014; *Published online*: 1 December 2014; AJC-16348

Quasi-hexagonal VO_2/Ag_3VO_4 heterogeneous photocatalyst was successfully synthesized *via* a hydrothermal method. Detailed characterization was carried out based on X-ray powder diffraction pattern, scanning electron microscopy, UV-visible diffuse-reflectance spectroscopy. The as-prepared samples exhibited strong absorption in the UV-light region and displayed excellent UV-light-driven photocatalytic activities and stabilities in degradation of Rhodamine B under UV-light irradiation ($\lambda = 400$ nm). This enhanced photocatalytic activity might be attributed to the heterogeneous structure.

Keywords: VO_2/Ag_3VO_4, Quasi-hexagon, Heterogeneous structure, Photocatalysts.

INTRODUCTION

Several million tons of dyes were consumed every year by a variety of printing and dyeing industries, which could result in the dangerous accumulation in the environment attribute to dyes and their degradation products' properties, such as toxicit[1], mutagenicity[2] and carcinogenicity[3].

In dye wastewater treatment, photocatalysis is a convenient and environmentally friendly method. Among the photocatalysts, semiconductors have received considerable attention on its great potential to deal with this issue[4-8], since titanium dioxide (TiO_2) was found to be widely used as the photocatalyst for its superior photocatalytic performance, easy availability, low cost, non-toxicity and relatively high chemical stability[9,10].

Recently, there are several non-TiO_2-based photocatalysts, which have also been applied to decompose the organic molecules under light irradiation, such as in MO_4 (M = V, Nb, Ta)[11], $BiVO_4$[12], $AgTaO_3$[13], $AgNbO_3$[13] and $PbBi_2Nb_2O_9$[14]. However, they had long migration distances for excited electron-hole pairs, which could decrease photocatalytic activities.

Simultaneously, silver vanadate has also raised close attention due to its special band structure[15-17]. It has been reported that the silver vanadate crystals with different constituents mainly consist of α-$AgVO_3$, β-$AgVO_3$, $Ag_4V_2O_7$ and Ag_3VO_4, but just the monoclinic Scheelite Ag_3VO_4 shows the best photocatalytic activity[18].

In order to further improve the photocatalytic efficiency, constructing the heterojunction structure is an effective method[19,20]. Recently, the heterogeneous composite photocatalysts such as $MgFe_2O_4/Ag_3VO_4$[21], Gd_2O_3/Ag_3VO_4[22] and Ag_3VO_4/TiO_2/graphene[23], all performed superior photocatalytic activities to pure Ag_3VO_4 under light irradiation.

Until now, several methods have been reported for the synthesis of heterogeneous photocatalyst[24,25]. Yet, it is desirable to use hydrothermal treatment, for numerous advantages, such as controllable particle size, high crystallinity and purity by using mild synthesis temperature and simple process configuration[26,27].

Furthermore, it is well-known that the size and shape of inorganic materials are important factors to determine their electrical, optical and catalytic properties. So much effort has been devoted in obtaining rational control over the size, shape, dimensionality and complexity of nanocrystals[28,29]. Here, we adopted a one-step hydrothermal method to obtain quasi-hexagonal VO_2/Ag_3VO_4 heterogeneous and investigated their photocatalytic activities under UV-light illumination using Rhodamine B (RhB) dye as a model pollutant.

EXPERIMENTAL

Synthesis of VO_2/Ag_3VO_4 quasi-hexagonal crystals: Ammonium vanadate (NH_4VO_3), silver nitrate ($AgNO_3$) and sodium hydroxide (NaOH) were of analytical grade and used without further purification.

Quasi-hexagonal crystals were prepared by a simple hydrothermal process. Typically, 0.1 M $AgNO_3$ (20 mL)

solution was added dropwise to 0.1 M NH_4VO_3 (10 mL) solution under constant stirring for 0.5 h to obtain yellow precipitate. The pH value of the mixture was adjusted to 8 using NaOH solution. After stirring for 5 h with a constant rate at room temperature, the mixture was transferred into a 50 mL teflon-lined stainless autoclave and maintained at 160 °C for 6 h. The autoclave was allowed to cool to room temperature naturally. The brown products were collected by centrifugation, washed with deionized water and anhydrous ethanol for several times and dried at 60 °C.

The phase and crystallography of the products were characterized by X-ray diffraction (XRD, Philips X'pert PRO MPD diffractometer) equipped with CuK_α radiation (λ = 0.15406 nm). A scanning rate of 0.05 % was applied to record the pattern in the 2θ range of 10-85°. The size and morphology of samples and their energy dispersive X-ray spectroscopy (EDS) were examined by scanning electron microscopy (SEM, FEI-quanta 200 scanning electron microscope) with acceleration voltage of 20 kV. Transmission electron microscope (TEM) images were recorded using a FEI Tecnai F20 transmission electron microscope with accelerating voltage of 200 kV. UV-visible absorption spectra were obtained using a Lambda 750 UV-visible spectrophotometer at room temperature under ambient condition.

Photocatalytic activity measurements: The photocatalytic reactivity of the as-prepared samples was estimated by photocatalytic oxidation of aqueous solution of Rhodamine-B at ambient temperature. Experimental details were as follows: First, 50 mg VO_2/Ag_3VO_4 crystals were added into 50 mL aqueous solution of Rhodamine-B with concentration of 1 × 10^{-5} mol/L in a beaker. After establishment of an adsorption/desorption equilibrium by magnetically stirring in the dark for 4 h, a 5 W UV lamp was used as a light source to trigger the photocatalytic reaction. During the irradiation procedure, the reaction samples were collected at 10 min intervals and centrifuged to remove photocatalyst particles. The UV-visible absorption spectra of the supernatant were then collected. The photocatalytic degradation efficiency (E) of Rhodamine-B was calculated by the formula

$$E = \frac{C_0 - C}{C_0} \times 100\ \% = \frac{A_0 - A}{A_0} \times 100\ \%$$

C_0 is the adsorption equilibrium concentration of Rhodamine-B, C is the concentration of Rhodamine-B solution at time t and A_0 and A are the corresponding values for the absorbance.

RESULTS AND DISCUSSION

The SEM images reveal that the as-prepared micropieces are nearly monodispersed (Figs-1a,b). It can be observed that the shape of the sample is a quasi-hexagon with side length of ca. 3.5 μm (Fig. 1c) and thickness in the range of 500-700 nm (Fig. 1d).

The composition of this catalyst is further analyzed with EDS as shown in Fig. 2. From the EDS spectrum in Fig. 2a, the peaks of the Ag, V and O elements were detected; other peaks assign to silicon and carbon from substrate and air, respectively. The ratio of peak indicates the atomic ratio of Ag/V in the structure of the sample is 36.74: 19.69, which is

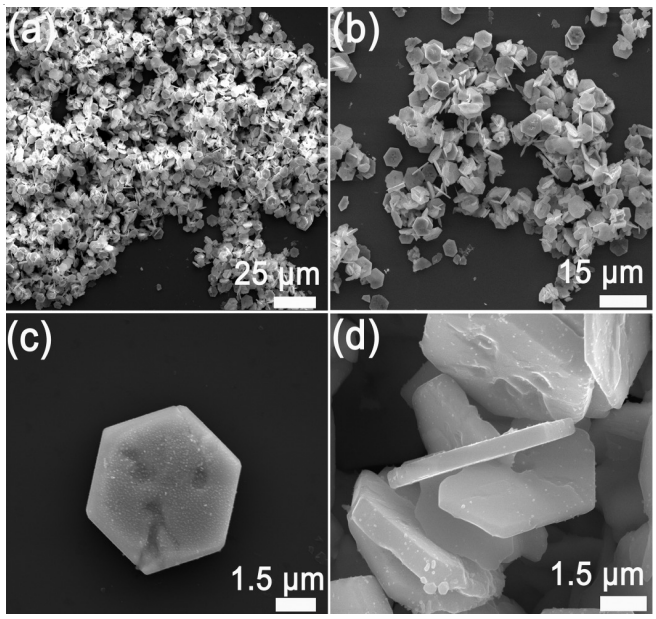

Fig. 1. SEM images of the VO_2/Ag_3VO_4 quasi-hexagons in different magnification

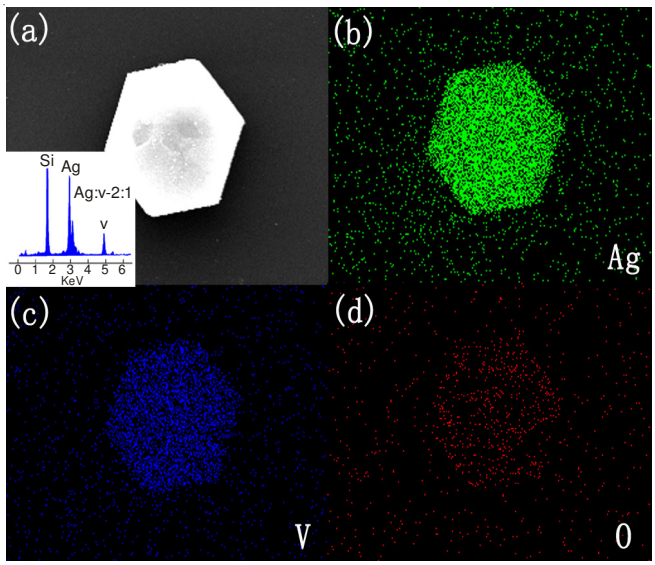

Fig. 2. VO_2/Ag_3VO_4 quasi-hexagon: (a) SEM image, and EDS element mapping data of (b) Ag, (c) V and (d) O elements

close to the ideal value of 2:1. In addition, the other pictures are the EDS element mapping of VO_2/Ag_3VO_4 microcrystal, which shows that the Ag, V and O elements mapping images (Fig. 2b-d) are in conformity with the corresponding SEM image (Fig. 2a). All above mentioned indicates that elements Ag, V and O are uniformly dispersed in the microcrystal.

The XRD pattern of the sample is shown in Fig. 3a. Two kinds of peaks could be indexed as the monoclinic phase of Ag_3VO_4 (JCPDS No. 43-0542) and the tetragonal phase of VO_2 (JCPDS No. 82-1074). In details, 2θ peaks at 19.08°, 30.74°, 32.21°, 33.21° and 38.46° were corresponded to (011), (-121), (121), (212) and (022) planes of Ag_3VO_4; and the other peaks to the planes of VO_2. The cell parameters of Ag_3VO_4 are calculated to be a = 0.8767 ± 0.0020, b = 0.6687 ± 0.0025, c = 0.6580 ± 0.0035 nm and β = 95.4433 ± 2.9610° corresponding to the monoclinic lattice parameters from the standard card of

a = 0.8734, b = 0.6707, c = 0.6514 nm and β = 95.36°. And VO_2's are calculated to be a = 0.8536 ± 0.0032 and c = 0.7572 ± 0.0047 nm corresponding to the tetragonal lattice parameters from the standard card of a = 0.8483 and c = 0.7615 nm.

The SAED pattern inserted at Fig. 3b also confirms the high crystallinity of tetragonal system VO_2, which can obtain a quasi-hexagonal diffraction pattern corresponding to lattice plane of (-2 -2 0), (0- 2 2), (-2 0 2) from [111] zone axis. Because the values of the cell parameters a and c have only slightly difference, the micropieces of VO_2 with growing direction of [111] will become to quasi-hexagonal morphology. There are also some disorder diffraction dots in the SEAD pattern (marked with red arrows), which may be attributed to Ag_3VO_4. Therefore, the quasi-hexagon has the heterogeneous structure composed of single crystal VO_2 and polycrystalline Ag_3VO_4.

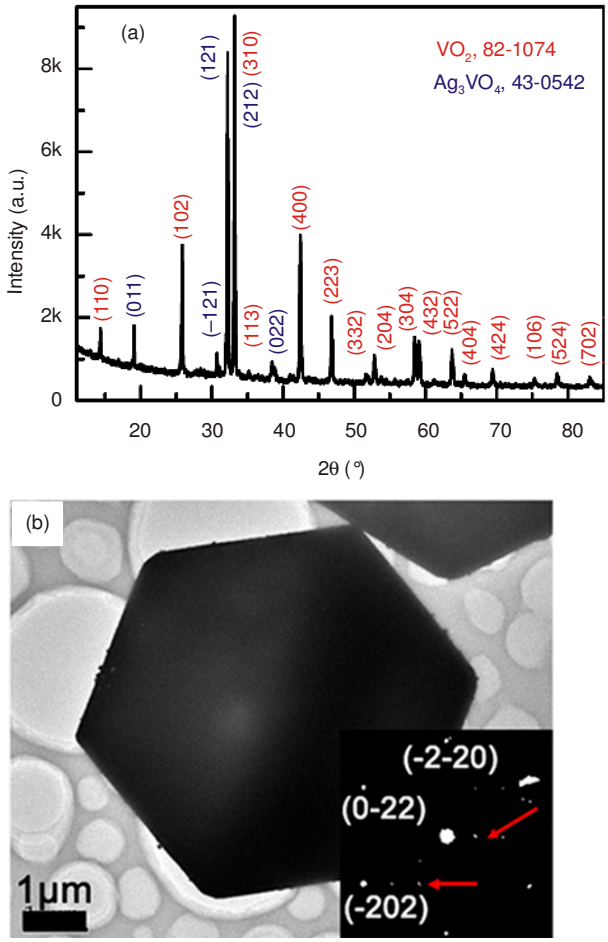

Fig. 3. (a) XRD pattern and (b) TEM pattern of the VO_2/Ag_3VO_4

The UV-visible diffuse reflectance spectrum of the quasi-hexagonal sample is shown in Fig. 4. The sample shows strong absorption in the ultraviolet region of 200-300 nm and an absorption peak at about 420 nm, which may be attributed to Ag_3VO_4[30].

Photocatalysis: The photocatalytic activity and stability of the as-prepared VO_2/Ag_3VO_4 photocatalysts were evaluated by photodegradating Rhodamine B dye under UV-light irradiation. Total concentrations of aqueous solution of Rhodamine-B were simply determined from the maximum absorption (λ

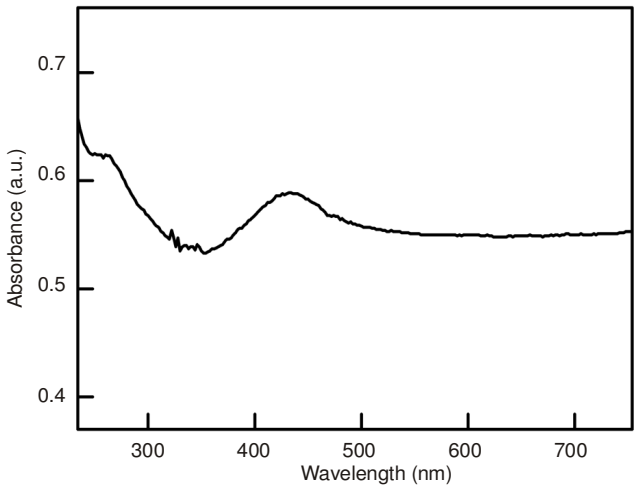

Fig. 4. UV-visible diffuse-reflectance spectrum of the VO_2/Ag_3VO_4

= 554 nm) measurements by UV-visible spectra. C/C_0 was used to describe the degree of the degradation, which stands for the concentration ratio during a certain period of reaction time.

As shown in Fig. 5, VO_2/Ag_3VO_4 displayed a superior photocatalytic activity and about 73.2 % of Rhodamine-B molecules were degraded only in 90 min. The characteristic absorption band of Rhodamine-B at 554 nm diminishes quickly, accompaning by a slightly concomitant blue shift from 554 to 514 nm of the maximum absorption. This hypsochromic shift

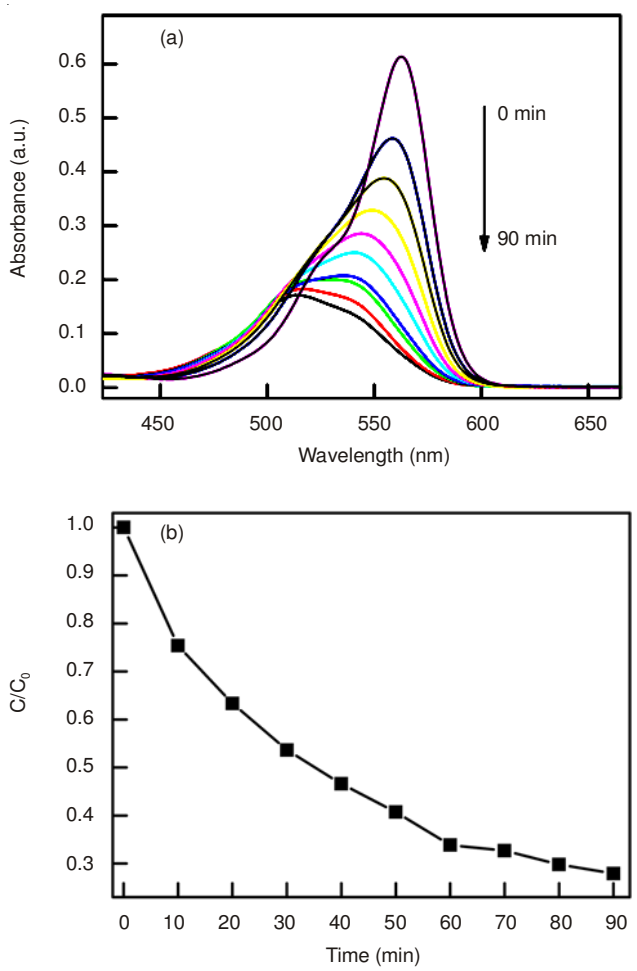

Fig. 5. (a) Successive UV-visible spectra and (b) curve of concentrations *vs.* time using the VO_2/Ag_3VO_4 as catalysts

of the major absorption peak has been attributed to a step-by-step de-ethylation derivative generated from the Rhodamine-B reduction process[31,32]. To quantitatively evaluate catalysts, the turn over frequency (TOF) was calculated according to the following equation:

$$TOF = r/W\ g_{RhB}\cdot(g_{cata}\cdot h)^{-1}$$

where r is the degradation rate and W is the mass of catalyst. From the above equation, the TOF of the catalyst could be calculated to be $[g_{RhB}\cdot(g_{cata}\cdot h)^{-1}]$. The TOF of the VO_2/Ag_3VO_4 catalyst was calculated to be 0.05148 $g_{RhB}/(g_{cata}\cdot h)$.

In order to explain the enhanced photocatalytic activity of the VO_2/Ag_3VO_4 composite, a mechanism is proposed as follows: tetragonal phase VO_2 has good conductivity, which can be served as electron sink that accumulates photoelectrons generated from the Ag_3VO_4 and further transfers them into solution. As a result, the recombination of induced electrons and holes is subsequently reduced and thus the photocatalytic activity is enhanced.

In addition to photocatalytic activity, the stability of photocatalysts is another important issue for their practical applications. Therefore, the cycling experiments were carried out by evaluating the decreased concentration of Rhodamine-B under UV-light irradiation with all experimental parameters kept unchanged during the cycling tests. As shown in Fig. 6, VO_2/Ag_3VO_4 catalysts for the degradation of Rhodamine-B show a slight decline after three cycling experiments tests: the degradation efficiency degreases from 73.2 to 71 % after three recycles, confirming that our heterostructured VO_2/Ag_3VO_4 photocatalysts are stable enough during the photocatalytic process.

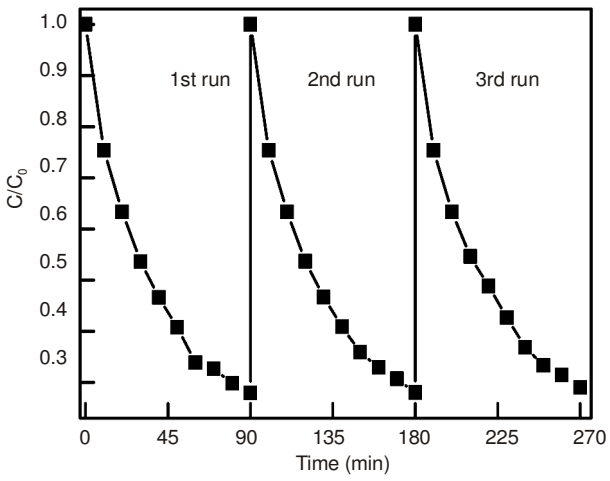

Fig. 6. Cycling runs in the photodegradation of Rhodamine-B in the presence of VO_2/Ag_3VO_4 under UV-light irradiation

Conclusion

In summary, we have successfully synthesized quasi-hexagonal VO_2/Ag_3VO_4 photocatalysts *via* hydrothermal reaction, which showed a better photocatalysis in the degradation of Rhodamine-B. The enhanced photocatalysis mechanism of VO_2/Ag_3VO_4 photocatalysts was worth to be further studied in the future.

REFERENCES

1. A. Dellai, D. Dridi, V. Lemorvan, J. Robert, A. Cherif, R. Mosrati and H.B. Mansour, *Environ. Sci. Pollut. Res*, **20**, 5790 (2013).
2. S. Unal and D. Murat, *Energy Educ. Sci. Tech. A*, **30**, 397 (2012).
3. M. Arslan, S. Sayin and M. Yilmaz, *Water Air Soil Pollut*., **224**, 1527 (2013).
4. M.W. Shao, L. Cheng, X.H. Zhang, D.D.D. Ma and S.T. Lee, *J. Am. Chem. Soc*., **131**, 17738 (2009).
5. Y.C. Chen, X.H. Tao, Y.L. Min and F.C. Zheng, *J. Mater. Sci. Mater. Electron*., **24**, 1319 (2013).
6. H.C. Zhang, H. Huang, H. Ming, H.T. Li, L.L. Zhang, Y. Liu and Z.H. Kang, *J. Mater. Chem*., **22**, 10501 (2012).
7. B. Liu, Z.R. Wang, Y. Dong, Y.G. Zhu, Y. Gong, S.H. Ran, Z. Liu, J. Xu, Z. Xie, D. Chen and G.Z. Shen, *J. Mater. Chem*., **22**, 9379 (2012).
8. P. Li, Z. Wei, T. Wu, Q. Peng and Y.D. Li, *J. Am. Chem. Soc*., **133**, 5660 (2011).
9. A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).
10. X.B. Chen, S.H. Shen, L.J. Guo and S.S. Mao, *Chem. Rev*., **110**, 6503 (2010).
11. J. Ye, Z. Zou, H. Arakawa, M. Oshikiri, M. Shimoda, A. Matsushita and T. Shishido, *J. Photochem. Photobiol. A*, **148**, 79 (2002).
12. X. Zhang, Z.H. Ai, F.L. Jia, L.Z. Zhang, X.X. Fan and Z.G. Zou, *Mater. Chem. Phys*., **103**, 162 (2007).
13. H. Kato, H. Kobayashi and A. Kudo, *J. Phys. Chem. B*, **106**, 12441 (2002).
14. H.G. Kim, D.W. Hwang and J.S. Lee, *J. Am. Chem. Soc*., **126**, 8912 (2004).
15. X.X. Hu and C. Hu, *J. Solid State Chem*., **180**, 725 (2007).
16. M.W. Shao, L. Lu, H. Wang, S. Wang, M.L. Zhang, D.D.D. Ma and S.T. Lee, *Chem. Commun.*, **20**, 2310 (2008).
17. Q. Zhu, W.S. Wang, L. Lin, G.Q. Gao, H.L. Guo, H. Du and A.W. Xu, *J. Phys. Chem. C*, **117**, 5894 (2013).
18. R. Konta, H. Kato, H. Kobayashi and A. Kudo, *Phys. Chem. Chem. Phys*., **5**, 3061 (2003).
19. D.B. Ingram, P. Christopher, J.L. Bauer and S. Linic, *ACS Catal*, **1**, 1441 (2011).
20. K. Yin, M.W. Shao, Z.S. Zhang and Z.Q. Lin, *Mater. Res. Bull*., **47**, 3704 (2012).
21. L. Zhang, Y.M. He, P. Ye, Y. Wu and T.H. Wu, *Catal. Commun*., **30**, 14 (2013).
22. G.S. Sun, H. Xu, H.M. Li, H.M. Shu, C.T. Liu and Q. Zhang, *React. Kinet. Mech. Catal*., **99**, 471 (2010).
23. J.X. Wang, P.X. Wang, Y.T. Cao, J. Chen, W.J. Li, Y. Shao, Y. Zheng and D.Z. Li, *Appl. Catal. B*, **136-137**, 94 (2013).
24. S. Kittaka, S. Nishida and T. Ohtani, *J. Solid State Chem*., **169**, 139 (2002).
25. N. Fischer, M. Minnermann, M. Baeumer, E.V. Steen and M. Claeys, *Catal. Lett*., **142**, 830 (2012).
26. G.D. Yang, B.L. Yang, T.C. Xiao and Z.F. Yan, *Appl. Surf. Sci*., **283**, 402 (2013).
27. W.Z. Wang, X.W. Huang, S. Wu, Y.X. Zhou, L.J. Wang, H.L. Shi, Y.J. Liang and B. Zou, *Appl. Catal. B*, **134-135**, 293 (2013).
28. F. Wang, M. Shao, L. Cheng, D. Chen, Y. Fu and D.D.D. Ma, *Mater. Res. Bull*., **44**, 126 (2009).
29. S.Q. Liu, N. Zhang, Z.R. Tang and Y.J. Xu, *ACS Appl. Mater. Interfaces*, **4**, 6378 (2012).
30. G. Wang, Y. Ren, G.J. Zhou, J.P. Wang, H.F. Cheng, Z.Y. Wang, J. Zhan, B.B. Huang and M.H. Jiang, *Surf. Coat. Tech*., **228**, S283 (2013).
31. W.J. Li, D.Z. Li, S.G. Meng, W. Chen, X.Z. Fu and Y. Shao, *Environ. Sci. Technol*., **45**, 2987 (2011).
32. W.G. Wang, B. Cheng, J.G. Yu, G. Liu and W.H. Fan, *Chem. Asian J*., 7, 1902 (2012).