

Preparation and photocatalytic properties of YVO_4 nanopowders

Haiyan Xu^{a,b}, Hao Wang^{a,*}, Hui Yan^a

^a The College of Materials Science and Engineering, Beijing University of Technology, Beijing 100022, China

^b Department of Materials Science and Engineering, Anhui Institute of Architecture & Industry, Hefei 230022, China

Received 9 August 2006; received in revised form 26 September 2006; accepted 27 September 2006

Available online 1 October 2006

Abstract

YVO_4 photocatalysts with different grain sizes were obtained by annealing the YVO_4 nanopowders synthesized via microwave irradiation. The products were characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), surface area and porosity analyzer, and ultraviolet–visible (UV–vis) spectrophotometer. Photocatalytic measurements showed that the YVO_4 nanopowders with grain size of about 5 nm possess superior photocatalytic properties in decolorization of methyl orange solution.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Photocatalyst; YVO_4 ; Nanopowders

1. Introduction

Photocatalysis using solar energy and semiconductors is of great importance in solving energy and environment issues [1–3]. In the past decade, a great deal of efforts have been devoted to developing novel oxide semiconductor photocatalysts that are applicable to environmental purification and water splitting to generate clean energy hydrogen by light energy conversion [4–6]. Among them, the vanadate such as $InVO_4$, $BiVO_4$, $M_3V_2O_8$ ($M = Mg, Ni, Zn$), etc., catches scientists' attention, due to V 3d orbital electron that can be activated by visible light [7–14]. Zou et al. found that $InVO_4$ with wolframite-type structure, monoclinic system has a much narrower bandgap than that of the $InNbO_4$ and $InTaO_4$ compounds and discovered that it has a prospective photocatalytic production of H_2 from water under visible light irradiation [7,8].

Tetragonal phased YVO_4 has been extensively used as the red phosphor with several rare-earth metal ions as dopant in cathode ray tubes (CRTs) and color television in powder form [15,16]. As an attractive host material, YVO_4 can be excited under the UV light irradiation, and the phonon energy can transfer efficiently from the excited vanadate to the luminescent center, rare-earth metal ions [17]. Recently, some new synthetic methods including solution combustion process [18], hydrolyzed col-

loid reaction (HCR) technique [19], microemulsion-mediated method [20], hydrothermal processing [21], and wet chemical method [22–24], etc. have been developed to synthesize YVO_4 nanopowders in view of its important application in optoelectronic field. However, these methods need longer reaction time and more complicated processing. Our previous paper reported that size-controlled YVO_4 nanopowders with grain size of about 5–18 nm have been synthesized by a rapid microwave irradiation route [25]. The bandgap of YVO_4 is about 3.5 eV, which is wider than that of $InVO_4$, though both of them two have V element in their structure. As heterogeneous Y^{3+} ions are introduced, the crystal structure is modulated consequently to tetragonal zircon-type. Therefore, the electronic structure is also changed, the bandgap is widened. In this work, photocatalytic decolorization of the methyl orange solution using YVO_4 with different grain size obtained by annealing the 5 nm YVO_4 nanopowders at different temperature have been investigated.

2. Experiments

YVO_4 nanopowders with grain size of 5 nm were prepared via a rapid microwave irradiation route as described in Ref. [25]. For investigating the photocatalytic property of YVO_4 powders with different grain size, the YVO_4 nanopowders were annealed at different temperature (200–700 °C) for 2 h.

The X-ray diffraction (XRD) analysis was performed using a Bruker D8 X-ray diffractometer (Cu $K\alpha_1$ radiation,

* Corresponding author. Tel.: +86 10 67392733; fax: +86 10 67392445.
E-mail address: haowang@bjut.edu.cn (H. Wang).

$\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM) image of samples was obtained with a Hitachi model S-3500N scanning electron microscope. Transmission electron microscopy (TEM) image was taken on a JEOL-JEM 2000 transmission electron microscope, using an accelerating voltage of 160 kV. The surface areas of the grains were determined by a Micromeritics ASAP 2020 surface area and porosity analyzer in the method of Brunauer–Emmett–Teller (BET) nitrogen adsorption and desorption. Optical adsorption studies were carried out using a UV–vis–NIR spectrophotometer (Shimadzu UV-3101PC).

The photocatalytic property of the products was tested in our home-made instruments. At first, 0.2 g product was dispersed into five beakers, which were filled with 100 ml 10 mg/l methyl orange solution separately. Prior to irradiation, the suspensions were ultrasonically sonicated for 10 min and then magnetically stirred in a dark condition for 30 min to establish adsorption/degradation equilibrium. The suspensions were then irradiated under the UV light. A 400 W high-pressure Hg lamp with a maximum emission at about 360 nm was used as the light source. The concentrations of methyl orange solution were determined by measuring the absorbance at 464 nm with the UV–vis spectroscopy.

3. Results and discussion

Fig. 1 shows the XRD patterns of YVO_4 nanopowders and annealed products at 200, 400, 500 and 700 °C, respectively. The five patterns in Fig. 1 are found to be consistent with the tetragonal zircon-type structure of YVO_4 (JCPDS card no. 17-0341). As anneal temperature increased, the diffraction peaks of products become gradually narrow and sharp, and the phenomenon of peak merging relieves by degrees. It indicates that the crystallinity of the as-annealed products increased, and the grain size grew with increasing the annealing temperature. The mean grain size can be roughly determined from the broadening of the peaks by using the Scherrer formula. By fitting the full width at half maximum (FWHM) of (2 0 0) peaks to this

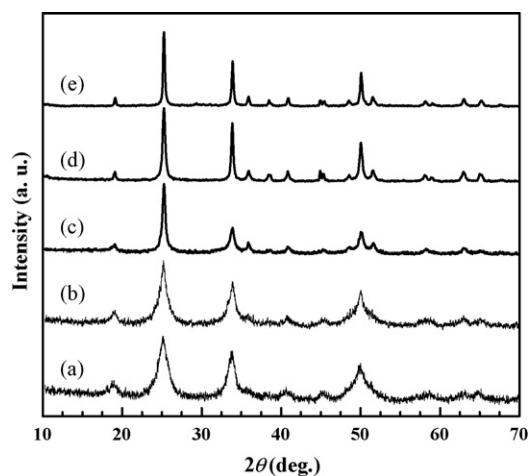


Fig. 1. XRD patterns of (a) YVO_4 nanopowder synthesized by microwave irradiation and the products annealed at (b) 200 °C, (c) 400 °C, (d) 500 °C and (e) 700 °C.

Table 1
BET surface areas of the samples annealed at different temperature

Annealing temperature (°C)	BET surface area (m ² /g)
0	92.3541
200	89.6588
400	81.7302
500	27.1527
700	5.1347

formula, the mean size of YVO_4 nanopowders and the products obtained at different annealing temperature (200, 400, 500 and 700 °C) is 5, 20, 50, 160 and 350 nm, respectively.

The surface areas of products are illustrated in Table 1. The surface area of YVO_4 nanopowders obtained directly via microwave irradiation is approximately 92 m²/g. With increasing the annealing temperature, the surface area of the annealed products reduces greatly from 89 at 200 °C to 5 m²/g at 700 °C. It can be seen that the surface area reduces slowly when temperature increasing from 200 to 400 °C, however, it sharply reduces from 82 to 27 m²/g at temperature above 500 °C.

Fig. 2 shows the Raman spectra of YVO_4 nanopowders and annealed products at 200, 400, 500 and 700 °C, respectively. As the annealing temperature increased, the peaks in Raman spectra become narrow and sharp; moreover, the symmetry of the peaks increases gradually. It indicates that the crystallinity increases, the particle grows up, and the surface area decreases, after the YVO_4 nanopowders were annealed at 200–700 °C. It is notable that the position and width of the Raman peaks annealed at different temperature varies clearly with annealing temperature as well as grain size. As can be seen from Fig. 3, the width of the peak decreases, and the position shows obviously blue shift with increasing temperature. In a word, the Raman spectra display usual anharmonic effects as the grain size decreases. Broadening, peak merging, and frequency shifting are observed, which are the typical character of nanosystem [26].

The morphology and grain size of the YVO_4 powders were characterized by TEM and SEM. Fig. 4 shows the TEM image of

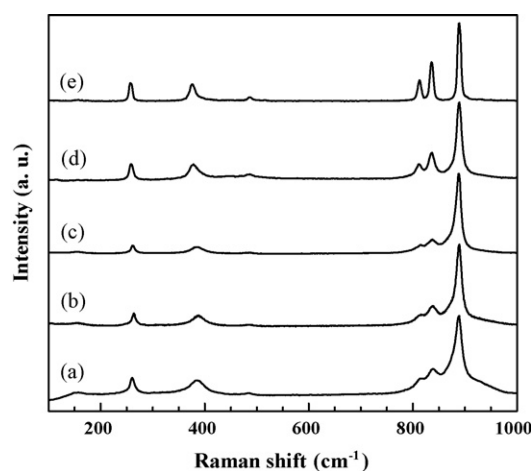


Fig. 2. Raman spectra of (a) YVO_4 nanopowder synthesized by microwave irradiation and the products annealed at (b) 200 °C, (c) 400 °C, (d) 500 °C and (e) 700 °C.

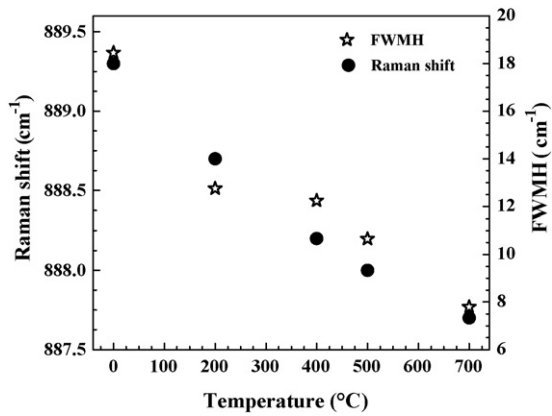


Fig. 3. Variation of Raman shift and FWHM of products with different annealed temperature.

the YVO_4 nanopowders directly obtained via microwave irradiation and SEM image of the product annealed 700°C for 2 h. It is clear that the mean grain size of spherical YVO_4 powders produced directly by microwave irradiation and that of the product annealed at 700°C is about 5 and 300 nm, respectively, which is consisted with the results calculated by Scherrer formula from the XRD patterns. The ED pattern taken from several nanoparticles shows that the nanoparticles are YVO_4 crystallites with tetragonal zircon-type structure. It provides the powerful and direct evidence that the powders of annealing products grow up greatly. The YVO_4 products annealed at the other temperatures have the similar characteristic, the images of which are not shown here.

Fig. 5 shows the UV–vis spectra of YVO_4 nanopowders and annealed products at 200, 400, 500 and 700°C , respectively. Obviously, the absorbance edges of YVO_4 products varied regularly. With the increase of annealing temperature, products grain size increases, and the absorbance edge of products moves gradually to long wavelength. In other words, when the grain size decreases, the blue shift occurs, which is the typical phenomenon mainly resulted from quantum size effect of nano-system.

Fig. 6 shows the decolorization curves of methyl orange solutions with the addition of YVO_4 nanopowders with grain size of 5 nm under ultraviolet light. Curve e shows the decolorization

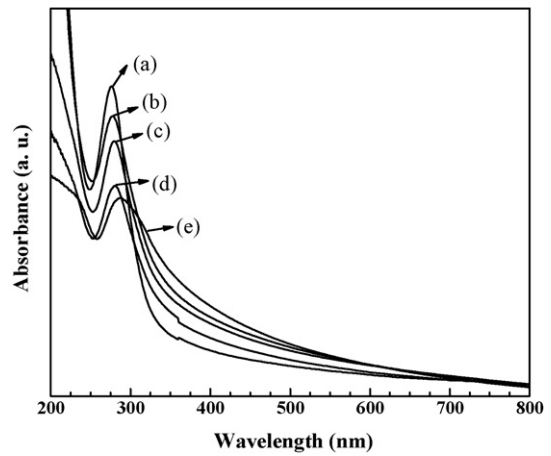


Fig. 5. UV–vis spectra of (a) YVO_4 nanopowder synthesized by microwave irradiation and the products annealed at (b) 200°C , (c) 400°C , (d) 500°C and (e) 700°C .

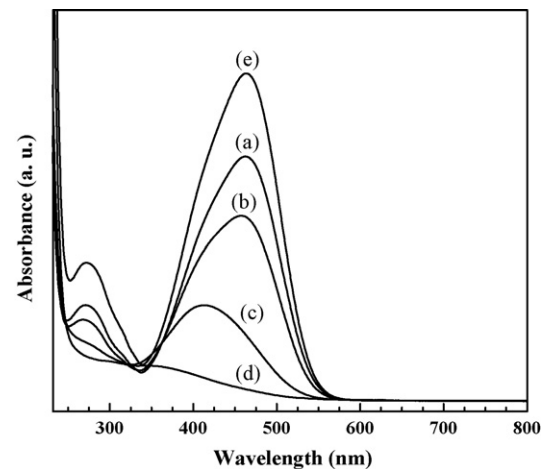


Fig. 6. Depigmentation curves of methyl orange solutions with addition of YVO_4 nanopowders with grain size of 5 nm under ultraviolet light at (a) 20 min, (b) 30 min, (c) 40 min, (d) 50 min and (e) without addition YVO_4 at 50 min.

curve of absolute methyl orange solution without any YVO_4 nanopowders irradiated under ultraviolet light for 50 min, while other curves denote methyl orange solution with 2 g/l YVO_4 nanopowders irradiated under ultraviolet light for different time

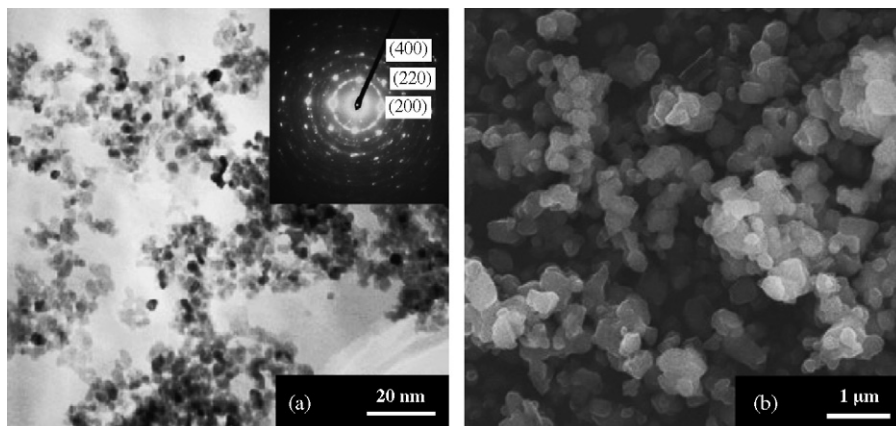


Fig. 4. TEM and SEM images of products (a) before and (b) after annealed 700°C . Insert shows ED pattern taken from several nanoparticles.

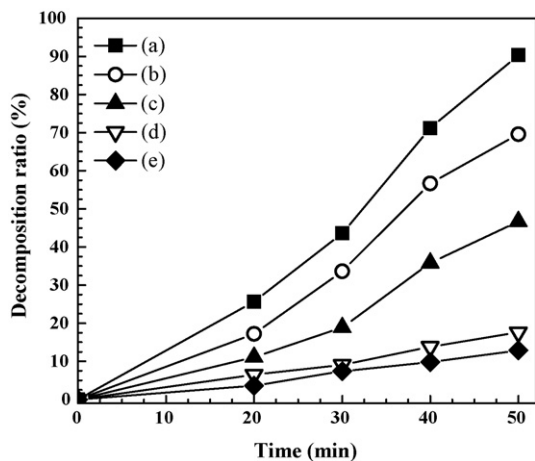


Fig. 7. Decomposition ratio of methyl orange solution with the role of (a) YVO_4 nanopowder synthesized by microwave irradiation and the products annealed at (b) 200 °C, (c) 400 °C, (d) 500 °C and (e) 700 °C under ultraviolet light.

(a: 20 min, b: 30 min, c: 40 min, d: 50 min). It is clear that the solutions with YVO_4 nanopowders decolorized gradually and were almost decolorized totally when the irradiated time was up to 50 min. However, the solution without YVO_4 was always orange for 50 min. The solid powders were collected and characterized by XRD after photocatalytic reaction. The XRD analysis showed that the crystal structure of the collected powders was identical with that of the original YVO_4 nanopowders. It indicates that YVO_4 nanopowders played the role of photocatalyst in the process of decolorization of methyl orange solution.

Fig. 7 shows the decomposition ratio of methyl orange solution with the role of YVO_4 products with different grain size under ultraviolet light for different time. The solutions decolorized gradually with elonged irradiation time. After 50 min, the decomposition ratio of methyl orange solution with 5 nm YVO_4 nanopowders reached to 90%. Comparatively, the decomposition ratio is just about 70, 47, 18 and 13% for the samples annealed at 200, 400, 500 and 700 °C, respectively. It may be resulted from the reduction of the surface areas of the samples which leads to the decrease of the active sites on the surface of particles.

The preceding UV–vis spectra showed that the absorbance edge of YVO_4 products located in the range of 320–380 nm, which indicates that YVO_4 can be excited by ultraviolet light, and generated the electron–hole pair. The mechanism for photocatalytic degradation of organic pollution on the solid catalysis always depicted as follows: a continuous band-gap irradiation of aqueous semiconductor dispersion excites an electron from the valence band to the conduction band, creating an electron–hole pair. The photogenerated holes are considered capable of directly oxidizing many organic compounds. However, the recombination of the electron–hole pairs will decrease the photocatalytic activity. At first, in our experiments, when the grain size is as small as 5 nm, the photogenerated carrier diffuses quickly from center to the surface [27], resulting in the higher separation efficiency photogenerated electron–hole pairs and the higher photocatalytic activity of particles. Secondly, the increasing of specific surface area leads to the increasing of adsorption ability

to organics, and then heightens the photocatalytic degradation ability to organics. Therefore, as the grain size of YVO_4 particles decreases, the specific surface area increases consequently, and then the photocatalytic degradation property of YVO_4 is improved.

4. Conclusions

In summary, the nanosized YVO_4 with the grain size from 5 to 300 nm have been obtained by annealing the YVO_4 nanopowders synthesized via microwave irradiation. The blue shift phenomena depended on size the nanopowders were observed in the UV–vis spectra of the as-synthesized YVO_4 products. Photocatalytic measurements through the photo-decolorization of methyl orange solution showed YVO_4 nanocrystals with grain size of about 5 nm possess well photocatalytic properties in water purification and may find potential application in related fields.

Acknowledgement

The authors are grateful to the Project of New Star of Science & Technology of Beijing for financial support.

References

- [1] K. Honda, A. Fujishima, *Nature* 238 (1972) 37.
- [2] A.L. Linsebigler, G. Lu, J.T. Yates Jr., *Chem. Rev.* 95 (1995) 735.
- [3] Z. Zou, J. Ye, K. Sayama, H. Arakawa, *Nature* 414 (2001) 625.
- [4] Y.I.I. Kim, S. Salim, M.J. Huq, T.E. Mallouk, *J. Am. Chem. Soc.* 113 (1991) 9561.
- [5] J. Yoshimure, Y. Ebina, J. Kondo, K. Domen, *J. Phys. Chem.* 97 (1993) 1970.
- [6] Z.Q. Song, H.Y. Xu, K.W. Li, H. Wang, H. Yan, *J. Mol. Catal. A: Chem.* 239 (2005) 87.
- [7] J. Ye, Z. Zou, H. Arakawa, M. Oshikiri, M. Shimoda, A. Matsushita, T. Shishido, *J. Photochem. Photobiol. A* 148 (2002) 79.
- [8] J. Ye, Z. Zou, M. Oshikiri, A. Matsushita, M. Shimoda, M. Imai, T. Shishido, *Chem. Phys. Lett.* 356 (2002) 221.
- [9] K. Sayama, A. Nomura, Z. Zou, R. Abe, Y. Abe, H. Arakawa, *Chem. Commun.* (2003) 2908.
- [10] A. Kudo, K. Omori, H. Kato, *J. Am. Chem. Soc.* 121 (1999) 11459.
- [11] L. Zhang, D. Chen, X. Jiao, *J. Phys. Chem. B* 110 (2006) 2668.
- [12] S. Kohtani, M. Koshiko, A. Kudo, K. Tokumura, Y. Ishigaki, A. Toriba, K. Hayakawa, R. Nakagaki, *Appl. Catal. B: Environ.* 46 (2003) 573.
- [13] D. Wang, Z. Zou, J. Ye, *Catal. Today* 93–95 (2004) 891.
- [14] D. Wang, J. Tang, Z. Zou, J. Ye, *Chem. Mater.* 17 (2005) 5177.
- [15] A.K. Levine, F.C. Palilla, *Appl. Phys. Lett.* 5 (1964) 118.
- [16] A.K. Levine, F.C. Papilla, *Electrochem. Technol.* 4 (1996) 16.
- [17] A. Huignard, V. Buissette, A.-C. Franville, T. Gacoin, J.-P. Boilot, *J. Phys. Chem. B* 107 (2003) 6754.
- [18] S. Ekambaram, K.C. Patil, *J. Alloys Compd.* 217 (1995) 104.
- [19] S. Erdei, *J. Mater. Sci.* 30 (1995) 4950.
- [20] L.D. Sun, Y.X. Zhang, J. Zhang, C.H. Yan, C.S. Liao, Y.Q. Lu, *Solid State Commun.* 124 (2002) 35.
- [21] K. Riwozki, M. Haase, *J. Phys. Chem. B* 102 (1998) 10129.
- [22] H. Wu, H. Xu, Q. Su, T. Chen, M. Wu, *J. Mater. Chem.* 13 (2003) 1223.
- [23] A. Huignard, T. Gacoin, J.P. Boilot, *Chem. Mater.* 12 (2000) 1090.
- [24] A. Huignard, V. Buissette, G. Laurent, T. Gacoin, J.P. Boilot, *Chem. Mater.* 14 (2002) 2264.
- [25] H.Y. Xu, H. Wang, Y.Q. Meng, H. Yan, *Solid State Commun.* 130 (2004) 465.
- [26] K.N. Yu, Y. Xiong, Y. Liu, C. Xiong, *Phys. Rev. B* 55 (1997) 2666.
- [27] G. Rothenberger, J. Moser, M. Graetzel, N. Serpone, D.K. Sharma, *J. Am. Chem. Soc.* 107 (1985) 8054.