Journal of Alloys and Compounds 551 (2013) 286-292

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

One-step hydrothermal synthesis of C, W-codoped mesoporous TiO₂ with enhanced visible light photocatalytic activity

Qi Xiao *, Lan Gao

School of Resources Processing and Bioengineering, Central South University, Changsha 410083, China

ARTICLE INFO

Article history: Received 15 August 2012 Received in revised form 28 September 2012 Accepted 10 October 2012 Available online 22 October 2012

Keywords: C, W-codoped mesoporous TiO₂ One-step hydrothermal method Photocatalytic activity Visible light

ABSTRACT

C, W-codoped mesoporous TiO₂ is prepared by one-step hydrothermal method and characterized by Xray diffraction (XRD), Raman spectra, transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectra (XPS), Brunauer–Emmett–Teller method (BET), and UV-vis diffuse reflectance spectroscopy (DRS). The C, W-codoped TiO₂ exhibited the highest photocatalytic activity under visible light irradiation compared with undoped TiO₂. C-doped TiO₂ and W-doped TiO₂ because the co-operation of C and W not only led to the much narrowing of the band gap, but also promoted the separation of the photo-generated electrons and holes.

© 2012 Elsevier B.V. All rights reserved.

ALLOYS AND COMPOUNDS

1. Introduction

Mesoporous TiO₂ is attracting increasing attentions for the application as highly efficient photocatalysts and energy-converters due to high specific surface area [1]. However, more widespread applications of mesoporous TiO₂ as photocatalysts are encumbered by its wide band gap (3.2 eV for anatase). Further, photoexcited electron-hole pairs tend to recombine relatively easily in TiO₂. Therefore, it is highly desirable to extend the optical absorption of TiO₂-based mesoporous materials to the visible-light region with a low photogenerated electron-hole recombination rate.

In general, doping is one of the most effective approaches to extend the absorption edge from ultraviolet to the visible light range. Thus, a large number of investigations focusing on doping of TiO_2 with have been reported during the past decade and demonstrated obvious visible-light activity. Many studies have revealed that doping TiO_2 with transition metal [2,3] or nonmetal elements [4–7] can shift its optical response to the visible light region, therefore increasing visible light photocatalytic activity. However, many studies have demonstrated that the monodoping (transition metal [8,9] or nonmetal [10,11]) will generate recombination centers of photogenerated electron-hole inside the TiO_2 , resulting in the reduction of charge carrier quantity and photocatalytic activity [8–11]. Recently, both theoretical calculations [12–18] and experimental results [19–23] indicated that the passivated codoped TiO_2 with both nonmetal anions and metal cations can reduce

the recombination centers because of the neutralization of positive and negative charges inside TiO_2 , which can effectively improve the charge carriers' migration efficiency and then enhance the photocatalytic activity. These results suggest that mesoporous TiO_2 passivated codoped with nonmetal and transition metal elements can have promising visible light photocatalytic properties.

Although numerous reports on mesoporous TiO₂ doped with metal or nonmetals have been presented [24-31], the preparation of C, W-codoped mesoporous TiO₂ has never been reported. According to the previous theoretical calculation results [14], the present work tries to experimentally fabricate the C, W-codoped mesoporous TiO₂ by using a simple one-step hydrothermal method and to evaluate its visible light photocatalytic properties. In the present study, we synthesize the C, W-codoped mesoporous TiO₂ based on the contributions of Dong et al. [31]. C, W-codoped mesoporous TiO₂ with anatase phase are synthesized by simple one-step hydrothermal method with low-cost inorganic Ti(SO₄)₂, glucose, and Na₂WO₄ as precursors. The resulting C, W-codoped mesoporous TiO₂ exhibit enhanced photocatalytic activity compared to C-doped TiO₂ and W-doped TiO₂. To the best of our knowledge, this method is the first report on a one-step green synthetic route for C, W-codoped mesoporous TiO₂ with efficient visible light photocatalytic activity.

2. Experimental

2.1. Preparation of samples

C, W-codoped TiO₂ is synthesized by one-step hydrothermal method. In a typical synthesis, 4.8004 g Ti (SO₄)₂, 0.0396 g glucose and appropriate amount of Na₂WO₄ are mixed in 100 ml of distilled water to form an aqueous solution. The



^{*} Corresponding author. Tel.: +86 731 88830543; fax: +86 731 88879815. *E-mail address*: xiaoqi88@mail.csu.edu.cn (Q. Xiao).

^{0925-8388/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jallcom.2012.10.040

molar ratio of W to Ti is controlled at 10%. The as-prepared samples are labeled as C, W-codoped TiO₂. After stirring for 0.5 h, the solution is poured into a Teflon-lined stainless autoclave with 200 ml capacity. The autoclave is sealed and heated, and then kept at a certain temperature in a range from $150 \,^{\circ}$ C for 12 h. The resulting product is separated by centrifugation, and washed with distilled water and alcohol for several times, respectively, and finally, dried at 80 $^{\circ}$ C for 6 h. For comparison purposes, the samples of pure TiO₂, C-doped TiO₂, and 10% W-doped TiO₂ are also prepared by similar procedures, respectively. The as-prepared samples are labeled as undoped TiO₂, C-doped TiO₂, and W-doped TiO₂, respectively.

2.2. Characterization methods

The X-ray diffraction (XRD) patterns of the synthesized samples are obtained by a Brucker D8-advance X-ray powder diffractometer (XRD) with Cu Kg radiation (λ = 0.15418 nm). Raman spectrum analysis is conducted on a Labram HR800 Laser Raman Spectroscopy made by Jobin Yvon, France, using the 632.8 nm He-Ne ion laser as an excitation source. The laser power on the sample is 10 mW. Transmission electron microscopy (TEM) images are obtained using a JEM-2100F transmission electron microscope. X-ray photoelectron spectra (XPS) measurements are performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum (UHV) chambers using Al Ka radiation (1486.6 eV) to investigate the surface properties. The binding energy of the XPS spectra is calibrated with the reference to the C 1s peak (284.8 eV) arising from adventitious carbon. Ar⁺ sputtering is applied to clean the surface of the samples. Nitrogen adsorption and desorption isotherms are collected at 77 K on a Micromeritic ASAP 2010 instrument. The specific surface areas are calculated using the Brunnauer-Emmett-Teller (BET) equation and the pore size distributions are calculated by applying the Barrett-Joyner-Halenda (BJH) method using the desorption branch of the isotherms. The UV-vis absorption spectra are measured under the diffuse reflection mode using the integrating sphere attached to a Shimadzu 2450 UV-vis spectrometer. The powders are pressed to form a pellet and BaSO₄ is used as a reference.

2.3. Photocatalytic activity measurements

The photocatalytic activities of the samples are evaluated by the degradation of terephthalic acid (TA) in an aqueous solution under visible light irradiation. The analysis of 'OH radical's formation on the sample surface under visible light irradiation is performed by fluorescence technique using terephthalic acid, which readily reacted with OH radicals to produce highly fluorescent product, 2-hydroxyterephthalic acid [32]. The intensity of the peak attributed to 2-hydroxyterephtalic acid is known to be proportional to the amount of 'OH radicals formed [32]. The selected concentration of terephthalic acid solution is 5×10^{-4} M in a diluted NaOH aqueous solution with a concentration of 2×10^{-3} M. It has been proved that at these experimental conditions (low concentration of terephthalic acid, less than 10^{-3} M, room temperature), the hydroxylation reaction of terephthalic acid proceeds mainly by 'OH radicals [32]. Five hundred milligrams of the prepared samples is added to 100 mL of the 5×10^{-4} M terephthalic acid solution in 2×10^{-3} M NaOH under ultrasonic vibration for 10 min. Prior to light irradiation, the reactor is left in the dark for at least 30 min until an adsorption-desorption equilibrium is finally established. A 100 W tungsten lamp fixed at a distance of 150 mm above the surface solution is used as visible light source, and a UV cut-off filter is used to completely remove any radiation below 420 nm to ensure illumination by visible light source only. The average irradiation intensity of 100W tungsten lamp was about 0.7 mW cm⁻². The radiant flux was measured with a power meter from Institute of Electric Light Source (Beijing). Sampling is performed in every 15 min. Solution after filtration through 0.45 µm membrane filter is analyzed on a Hitachi F-4500 fluorescence spectrophotometer. The product of terephthalic acid hydroxylation, 2-hydroxyterephthalic acid, gave a peak at the wavelength of about 425 nm by the excitation with the wavelength of 315 nm.

3. Results and discussion

3.1. XRD, Raman spectroscopy and TEM analysis

Fig. 1 shows the XRD patterns of the as-prepared samples. The diffraction peaks of each sample can be indexed to anatase phase with lattice parameters a = b = 0.37852 nm, c = 0.95139 nm, and space group $I4_1/amd$ (141) (JCPDS No. 21-1272). No traces of impurity peaks other than TiO₂ are observed. In the case of XRD of C-doped or C, W-codoped TiO₂, no characteristic peak from carbon was detected in XRD, indicating that C ion has been substituted into the crystal lattice sites of the titania or amorphous carbon exists over the titania surface. It is worth noting that no WO₃ phase can be observed in all the XRD patterns of C, W-doped TiO₂ and W-doped TiO₂. On the basis of this, it can be inferred that either the W ion has been substituted into the crystal lattice sites of the site of the crystal lattice sites of the site of the crystal lattice sites of the crystal la



Fig. 1. The XRD patterns of the as-prepared samples. (a) undoped TiO_2 ; (b) C-doped TiO_2 ; (c) C, W-codoped TiO_2 ; (d) W-doped TiO_2 .

titania or the tungsten oxide species exist as a highly dispersed polymeric form over the titania surface, which could not be detected by XRD. The averaged crystallite sizes *D* is determined according to the Scherrer equation $D = k\lambda/\beta\cos\theta$ [33], where *k* is a constant (shape factor, about 0.9), λ is the X-ray wavelength (0.15418 nm), β is the full width at half maximum (FWHM) of the diffraction line, and θ is the diffraction angle. The values of β and θ of anatase are taken from anatase (101) diffraction line. The calculated averaged crystallite sizes of the as-prepared samples are shown in Table 1. It is found that the crystallite sizes of the as-prepared samples are about 12–14 nm.

Fig. 2 shows the Raman spectra of the as-prepared samples. It is found that the typical Raman peaks of anatase are detected in each sample, which reports that the characteristic Raman peaks of anatase locate at 144 cm⁻¹ (E_g), 399 cm⁻¹ (B_{1g}), 515 cm⁻¹ (A_{1g}) and 639 cm^{-1} (E_{σ}) [34]. The characteristic Raman peaks for WO₃ were observed by Daniel et al. at 807, 715, 324, 293, and 270 cm⁻¹ [35]. Interestingly, the Raman spectra in the present work did not show any trace of WO₃, implying that WO₃ does not exist as a separate crystalline oxide phase. There is also a significant decrease in the intensity of the Raman peaks with the increase of the W doping concentration. On the basis of these Raman spectroscopic observations, it can be inferred that the W ion is doped in the titania lattice, which is in agreement with the XRD results. In addition, the main peak intensity (146 cm^{-1}) of C-doped TiO₂ with no change in the peak position decreases compared with that of undoped TiO₂, which can be inferred that carbon is doped in the TiO₂ lattice [36].

The structure and morphology of the sample are further examined by transmission electron microscopy (TEM) and highresolution transmission electron microscopy (HRTEM). The TEM and corresponding HRTEM images of the C, W-codoped TiO₂ sample are presented in Fig. 3. It can be seen that the primary crystallite size is about 13 ± 1 nm (Fig. 3a), which is in agreement with the value of the crystallite size determined by XRD (as shown in Table 1). Fig. 3b shows clear lattice fringes of primary crystallite (0.35 nm corresponding to) of the same sample. The HRTEM image (Fig. 3b) shows that the fringe spacing is 0.35 nm, which corresponds to the (101) crystallographic plane of anatase, and the HRTEM picture and its corresponding FFT (inset in Fig. 3b) further demonstrates that the particle is single crystalline in nature, and there are no indications of secondary phases or impurities visible in the HRTEM pictures, suggesting that all dopant atoms are homogeneously incorporated into the TiO₂ nanocrystallines.

288	
Table	1

The c	haracteristics	of the	as_nrenared	samples
THE C	Indiduceristics	or the	as-prepareu	samples.

Samples	Crystal size D ₍₁₀₁₎ (nm)	$S_{\rm BET} ({ m m}^2{ m g}^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore size (nm)	Rate contant k (min ⁻¹)
Undoped TiO ₂	11.9	170.2	0.220	3.000	0
W-doped TiO ₂	12.3	120.9	0.178	3.582	5.89841
C-doped TiO ₂	12.5	117.4	0.15	3.591	4.16586
C, W-codoped TiO ₂	13.3	111.9	0.14	4.64	11.54337



Fig. 2. The Raman spectra of the as-prepared samples. (a) undoped TiO_2 ; (b) C-doped TiO_2 ; (c) C, W-codoped TiO_2 ; (d) W-doped TiO_2 .

3.2. XPS studies

The X-ray photoelectron spectroscopy (XPS) survey spectrum (Fig. 4) shows that C, W-codoped TiO₂ contains only Ti, O, C, and W, in which the chemical binding energies for Ti $2p_{3/2}$, O 1s, C 1s, and W 4d were 459.1, 530.5, 284.8, and 247.8 eV, respectively.

Fig. 5 shows the high-resolution Ti 2p XPS spectra of asprepared samples. The Ti 2p3/2 peak is composed of a single signal at 459.1 eV, typical of the Ti⁴⁺ oxidation state [37]. The shape and position of the Ti 2p signal clearly excludes the existence of other oxidation states. Fig. 6a shows the high-resolution O 1s XPS spectra of as-prepared samples. The peak at around 530.5 eV was resolved into two peaks centered at 530.4 and 531.5 eV (shown in Fig. 6b). The first peak at 530.5 eV can be ascribed to an oxygen atom (O²⁻) in the lattice of TiO₂ [38]. The second peak at 531.5 eV can be assigned to the hydroxyl groups (–OH) resulting mainly from the chemisorbed water [39].

In the present work, two energy levels of tungsten are measured in the W4d and W4f regions. Fig. 7 shows the high-resolution W 4d XPS spectra of as-prepared samples. The examination on the W 4d core levels confirms the element W exists in both W-doped TiO₂ and C, W-codoped TiO₂ samples. However, the W4d peak is broad and cannot be used to determine the oxidation state of tungsten, so we analyze the W4f region as shown in Fig. 8a. It is found that the W4f region of both undoped TiO₂ and C-doped TiO₂ samples contains only one peak at binding energies of 37.5 eV, and the W4f region of both W-doped TiO₂ and C, W-codoped TiO₂ samples contains two peaks at binding energies of 35.9 and 37.9 eV, in which the W 4f doublet of the W-doped TiO₂ and C, W-codoped TiO₂ samples shows an unusual asymmetry due to overlapping with the Ti 3p component. In order to determine the valence of W element from the position of the W4f level, the spectra at the W 4f region of W-doped TiO₂ (shown in Fig. 8b) are then fitted with one doublet (W $4f_{7/2}$ (35.8 eV) and W $4f_{5/2}$ (38.1 eV)) and a single peak corresponding to Ti 3p (37.3 eV) [40]. The chemical binding energies of W $4f_{7/2}$ was 35.8 eV, corresponding to a W⁶⁺ oxidation state [41]. Combined with the XRD and Raman results without WO₃ phase, it can be inferred that the element W has been doped into anatase TiO₂ lattice of the W-doped TiO₂ and C, W-codoped TiO₂ samples as a W⁶⁺.

Fig. 9 shows the high-resolution C 1s XPS spectra of as-prepared samples. It can be seen that the C 1s spectra of both undoped TiO_2 (Fig. 9a) and W-doped TiO_2 (Fig. 9b) samples can be well resolved into three peaks centered at 284.8, 286.2, and 288.4 eV, which can be assigned to adventitious hydrocarbon from the XPS instrument itself. The C 1s spectra of C-doped TiO_2 (Fig. 9c) and C, W-codoped TiO_2 (Fig. 9d) samples can be well resolved into four peaks centered at 282.6 eV, 284.8 eV, 286.2 eV, and 288.4 eV. The first peak at 282.7 eV can be ascribed to carbon substituting for an oxygen atom in the lattice of TiO_2 , forming an O–Ti–C bond [30,31,42,43]. The other three peaks at 284.8 eV, 286.2 eV, and 288.4 eV for all of the samples can be assigned to adventitious hydrocarbon from the XPS instrument itself.

3.3. Nitrogen adsorption

The nitrogen adsorption-desorption isotherm and BJH pore size distribution curve of the as-prepared samples are measured. The Brunauer-Emmett-Teller (BET) specific surface areas and pore volumes are summarized in Table 1. It is found that the surface area and pore volume decrease with the increase of W doping concentration.



Fig. 3. (a) TEM images and (b) HRTEM images and the corresponding FFT analysis (inset).



Fig. 4. XPS survey spectrum of the as-prepared samples. (a) C, W-codoped TiO_2 ; (b) C-doped TiO_2 ; (c) undoped TiO_2 and (d) W-doped TiO_2 .



Fig. 5. The high-resolution Ti 2p XPS spectra of as-prepared samples. (a) C, W-codoped TiO_2 ; (b) undoped TiO_2 ; (c) C-doped TiO_2 and (d) W-doped TiO_2 .

3.4. UV-vis spectra

Fig. 10 shows the diffuse reflectance spectra (DRS) of the asprepared samples. It is found that undoped TiO_2 had no absorption



Fig. 7. The high-resolution W 4d XPS spectra of as-prepared samples. (a) Undoped TiO₂; (b) C-doped TiO₂; (c) C, W-codoped TiO₂ and (d) W-doped TiO₂.

in the visible region (>400 nm). Comparing with the undoped TiO₂, C-doped TiO₂ has a little red shift (8 nm) of the spectrum onset, while both W-doped TiO₂ and C, W-codoped TiO₂ have more red shift (30 nm) of the spectrum onset. In addition, both C-doped TiO₂ and C, W-codoped TiO₂ have a stronger absorption in the visible light range (400–700 nm). The enhancement of absorbance in the UV-vis region increases the number of photogenerated electrons and holes to participate in the photocatalytic reaction, which can enhance the photocatalytic activity of TiO₂ [44]. Lettmann et al. [45] reported that there is a good correlation between the light absorption properties and the photocatalytic activity, so it is a good way to obtain high visible photocatalytic activity by improving its photoabsorption.

3.5. Photocatalytic activity

Fig. 11 shows the plots of increase in fluorescence intensity against illumination time at 425 nm. The fluorescence intensity under visible light illumination in terephthalic acid solutions increased almost linearly against time. Consequently, we can conclude that 'OH radicals formed at the TiO₂ interface are in proportional to the light illumination time obeying zero-order reaction rate kinetics. The formation rate of the 'OH radicals k_{OH} can be expressed by the slop of these lines shown in Fig. 11. It is found that the order of the formation rate of 'OH radicals k_{OH}



Fig. 6. (a) The high-resolution O 1s XPS spectra of as-prepared samples and (b) peak-fitting XPS spectrum of O 1s.



Fig. 8. (a) The high-resolution W 4f XPS spectra of as-prepared samples and (b) peak-fitting XPS spectrum of W 4f.



Fig. 9. The high-resolution C 1s XPS spectra of as-prepared samples. (a) undoped TiO₂; (b) W-doped TiO₂; (c) C-doped TiO₂ and (d) C, W-codoped TiO₂.

formed on the as-prepared TiO₂ samples is as following: C, W-codoped TiO₂ > W-doped TiO₂ > C-doped TiO₂ > undoped TiO₂, which suggested that the C, W-codoping could effectively enhance the formation rate of \cdot OH radicals k_{OH} .

Some studies indicated that the photocatalytic activity of TiO₂ catalysts depends strongly on two factors: specific surface areas and the separation efficiency of electron–hole pairs [46,47]. On the one hand, the increase of the specific surface area generally would lead to improvement of the photocatalytic activity [48,49]. According to the BET analysis (shown in Table 1), the order of the specific surface areas of the catalysts is as following: W-doped TiO₂ > C-doped TiO₂ > C, W-codoped TiO₂ decreased from 120.9 m² g⁻¹ for W-doped TiO₂ to 110.9 m² g⁻¹ for C, W-codoped

TiO₂ sample. The reduction of surface area would lead to the decrease of active sites on which the reactants can adsorb, and the C, W-codoping apparently seemed to be not helpful for the photocatalytic activity. In order to remove the influence of the surfacearea reduction on the photocatalytic activity, the rate constants (k_{OH}) per unit surface area of the as-prepared samples are shown in Fig. 12. It is found that the order of the rate constant (k_{OH}) per unit surface area is as following: C, W-codoped TiO₂ > W-doped TiO₂ > C-doped TiO₂, and the C, W-codoped TiO₂ exhibited the highest photocatalytic activity under visible light irradiation. On the other hand, both theoretical calculations [12–18] and experimental results [19–23] indicated that the passivated codoped TiO₂ with both nonmetal anions and metal cations can reduce



Fig. 10. UV-vis absorption spectra of the as-prepared samples.



Fig. 11. The plots of increase in fluorescence intensity against illumination time at 425 nm.

the recombination centers because of the neutralization of positive and negative charges inside TiO₂, which can effectively improve the charge carriers' migration efficiency and then enhance the photocatalytic activity. So, the C, W-codoped TiO₂ exhibited the highest photocatalytic activity under visible light irradiation because the W + C codoping could effectively avoid the generation of the carrier recombination centers [14].

4. Conclusion

In this study, C, W-codoped mesoporous TiO₂ is synthesized by one-step hydrothermal method. The UV-diffuse reflectance spectra of the entire C, W-codoped TiO₂ samples shift remarkably to the visible light region and the absorption enhance significantly. The photocatalytic activities of the as-prepared samples are investigated under visible light irradiation. It is found that the C, Wcodoped TiO₂ exhibited the highest photocatalytic activity under visible light irradiation compared with undoped TiO₂, C-doped TiO₂ and W-doped TiO₂ because the co-operation of C and W not only led to the much narrowing of the band gap, but also promoted the separation of the photo-generated electrons and holes.



Fig. 12. The rate constant per unit surface area of the as-prepared samples.

References

- [1] H. Shibata, T. Ogura, T. Mukai, T. Ohkubo, H. Sakai, M. Abe, I. Am. Chem. Soc. 127 (2005) 16396
- [2] H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, B. Neppolian, M. Anpo, Catal. Today 84 (2003) 191
- D.H. Kim, S.I. Woo, S.H. Moom, H.D. Kim, B.Y. Kim, J.H. Cho, Y.G. Joh, E.C. Kim, [3] Solid State Commun. 136 (2005) 554.
- R. Asashi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269.
- [5]
- S.U.M. Khan, M. Al-Shahry, W.B. Ingler Jr., Science 297 (2002) 2243. T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, Appl. Phys. Lett. 81 (2002) 454. [6] X.T. Hong, Z.P. Wang, W.M. Cai, F. Lu, J. Zhang, Y.Z. Yang, N. Ma, Y.J. Liu, Chem. [7] Mater, 17 (2005) 1548.
- W. Mu, J.M. Herrmann, P. Pichat, Catal. Lett. 3 (1989) 73-75. [8]
- T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, J. Phys. Chem. Solids 63 (2002) [9] 1909-1920
- [10] H. Irie, Y. Watanabe, K. Hashimoto, J. Phys. Chem. B 107 (2003) 5483-5486.
- [11] Z. Lin, A. Orlov, R.M. Lambert, M.C. Payne, J. Phys. Chem. B 109 (2005) 20948-
- 20952 [12] K.S. Ahn, Y. Yan, S. Shet, T. Deutsch, J. Turner, M. Al-Jassim, Appl. Phys. Lett. 91 (2007) 231909
- [13] Y.O. Gai, I.B. Li, S.S. Li, I.B. Xia, S.H. Wei, Phys. Rev. Lett. 102 (2009) 036402.
- [14] Dan Wang, Yanhong Zou, Shuangchun Wen, Dianyuan Fan, Appl. Phys. Lett. 95 (2009) 012106.
- R. Long, N.J. English, Appl. Phys. Lett. 94 (2009) 132102. [15]
- [16] Run Long, Niall J. English, Chem. Phys. Lett. 478 (2009) 175-179.
- [17] Run Long, Niall J. English, Chem. Mater. 22 (2010) 1616-1623.
- [18] Xinguo Ma, Ling Miao, Shaowei Bie, Jianjun Jiang, Solid State Commun. 150 (2010) 689-692
- [19] B.F. Gao, Y. Ma, Y.A. Cao, W.S. Yang, J.N. Yao, J. Phys. Chem. B 110 (2006) 14391-14397
- [20] O. Teruhisa, M. Zenta, N. Kazumoto, K. Hidekazu, X. Feng, Appl. Catal. A 302 (2006) 62-68
- Y.F. Shen, T.Y. Xiong, T.F. Li, K. Yang, Appl. Catal. B 83 (2008) 177-185.
- Keqi Tan, Huarong Zhang, Chaofei Xie, Haiwu Zheng, Gu Yuzong, W.F. Zhang, [22] Catal. Commun. 11 (2010) 331-335.
- [23] Jun Zhang, Chunxu Pan, Pengfei Fang, Jianhong Wei, Rui Xiong, Appl. Mater. Interfaces 2 (2010) 1173-1176.
- [24] J.R. Xiao, T.Y. Peng, R. Li, Z.H. Peng, C.H. Yan, J. Solid State Chem. 179 (2006)
- 1161–1170. [25] A.R. Gandhe, S.P. Naik, J.B. Fernandes, Micropor. Mesopor. Mater. 87 (2005) 103 - 109
- M.H. Zhou, J.G. Yu, B. Cheng, H.G. Yu, Mater. Chem. Phys. 93 (2005) 159-163.
- [27] T.Y. Peng, D. Zhao, H.B. Song, C.H. Yan, J. Mol. Catal. 238 (2005) 119-126.
- [28] B. Chi, L. Zhao, T. Jin, J. Phys. Chem. C 111 (2007) 6189.
- [29] W. Ren, Z. Ai, F. Jia, L. Zhang, X. Fan, Z. Zou, Appl. Catal. B: Environ. 69 (2007) 138.
- [30] Gu De-en, Lu Yun, Yang Bang-chao, Hu Yong-da, Chem. Commun. (2008) 2453.
- [31] Fan Dong, Haiqiang Wang, Zhongbiao Wu, J. Phys. Chem. C 113 (2009) 16717-16723.
- [32] K. Ishibashi, A. Fujishima, T. Watanabe, K. Hashimoto, Electrochem. Commun. 2 (2000) 207.
- [33] H.P. Klong, L.F. Alexander, X-ray Diffraction Procedures for Crystalline and Amorphous Materials, Wiley, New York, 1954.
- [34] U. Balachandran, N.G. Eror, J. Solid State Chem. 42 (1982) 276.
- [35] M.F. Daniel, B. Desbat, J. Lassegues, B. Gerand, M. Figlarz, J. Solid State Chem. 67 (1987) 235
- [36] K. Bhattacharyya, S. Varma, A.K. Tripathi, S.R. Bharadwaj, A.K. Tyagi, J. Phys. Chem. C 112 (2008) 19102.
- L. Zhang, R.V. Koka, Mater. Chem. Phys. 57 (1998) 23.
- [38] Anna Kubacka, Belén Bachiller-Baeza, Gerardo ColÓn, Marcos Fernández-García, Appl. Catal. B: Environ. 93 (2010) 274–281.
- [39] J.G. Yu, G.H. Wang, B. Cheng, M.H. Zhou, Appl. Catal. B 69 (2007) 171.

- [40] A. Scholz, B. Schnyder, A. Wokaun, J. Mol. Catal. A 138 (1999) 249.
 [41] A. Chica, A. Corma, M.E. Domine, J. Catal. 242 (2006) 299.
 [42] Y. Huang, W.K. Ho, S.C. Lee, L.Z. Zhang, G.S. Li, J.C. Yu, Langmuir 24 (2008) 3510.
 [43] F. Dong, W.R. Zhao, Z.B. Wu, Nanotechnology 19 (2008) 365607–365716.
 [44] D. Li, H. Haneda, S. Hishita, N. Ohashi, Mater. Sci. Eng. B 117 (2005) 67–75.
 [45] C. Lettmann, K. Hildenbrand, H. Kisch, W. Macyk, W.F. Maier, Appl. Catal. B 32 (2001) 215–227.
- [46] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobio. C: Photochem. Rev. 1 (2000) 1. [47] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995)
- 69.
 [48] A.T. Bell, Science 299 (2003) 1688.
 [49] J. Tang, Z. Zou, J. Ye, Angew. Chem. Int. Ed. 43 (2004) 4463.