Facile Synthesis and Characterization of Novel CdS/BiOI Heterojunctions with Enhanced Visible-Light Photocatalytic Performances

SHANSHAN FANG^a, MIN LU^a, MAN ZHOU^a, ZHONGYU LI^{a,b,c,*}, SONG XU^a, YANYAN PENG^c,
QINCHI LI^{a,c} AND DAYONG LU^c

^aChangzhou University, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology,
School of Petrochemical Engineering, Changzhou 213164, PR China

^bAdvanced Catalysis and Green Manufacturing Collaborative Innovation Center,
Changzhou University, Changzhou 213164, PR China

^cJilin Institute of Chemical Technology, Jilin 132022, PR China

(Received September 1, 2016; in final form January 7, 2017)

Novel CdS/BiOI heterojunction photocatalysts were successfully prepared by facile method. The as-prepared samples were characterized by transmission electron microscopy, field-emission scanning electron microscopy, X-ray diffraction, the Raman spectroscopy, UV-vis diffuse reflectance spectra, the Fourier transform infrared spectra, and photoluminescence. It was found that CdS nanoparticles were uniformly distributed on the surface of BiOI microspheres. The photodegradation tests showed that the photocatalytic efficiency was increased at first and then decreased when further increasing CdS content in the nanocomposites. The highest activity was obtained by 3%-CdS/BiOI nanocomposites. The enhanced photocatalytic performances were attributed to the matched band potentials of CdS and BiOI, which resulted in the efficient separation of photogenerated electron-hole pairs. Based on the experimental results, a reasonable photocatalytic mechanism of CdS/BiOI photocatalysts was also proposed.

DOI: [10.12693/APhysPolA.131.263](https://doi.org/10.12693/APhysPolA.131.263)

PACS/topics: CdS/BiOI heterojunctions, visible-light photocatalyst, photocatalytic activity, nanocomposites

1. Introduction

Semiconductor photocatalysts have attracted considerable attention in recent years due to its wide application in pollutant degradation and hydrogen production from splitting water using solar energy [1, 2]. Among various semiconductor materials, TiO₂ semiconductor has been mostly investigated owing to the non-toxicity, low cost, relatively high chemical stability, and strong oxidizing power [3, 4]. However, owing to its wide band gap ($E_g = 3.2$ eV), TiO₂ requires ultraviolet light (UV) instead of more abundant visible light for effective photocatalysis [5]. Hence, developing visible-light-driven semiconductor photocatalysts is one of the most key topics for its application in environmental protection [6–10].

Recently, bismuth oxyhalides BiOX (X = F, Cl, Br, and I) are a new category of promising photocatalysts, which manifests unusual visible-light photocatalytic activity for photocatalytic energy conversion and environment remediation, because of their unique anisotropic layered-structures, the internal static electric field, and strong absorption in the visible light region [11, 12]. Among them, BiOI has the maximum absorption abi-

lity in visible-light region due to its smallest band gap (≈ 1.8 eV) [13]. However, due to the low separation efficiency of photogenerated electrons and holes, the photocatalytic activity of BiOI is very poor [14–16].

A strategy for improving the photocatalytic efficiency of BiOI is to couple it with another semiconductor to form heterojunction at the interface [17]. Such as TiO₂/BiOI [18, 19], ZnO/BiOI [20], Bi₂O₃/BiOI [21], BiOBr/BiOI [22], BiOCl/BiOI [23], Pt/BiOI [24] and AgI/BiOI [25] have been investigated as efficient visible-light photocatalysts. The general concept is that the combined semiconductors should have different band gaps so that charge separation can be enhanced by the internal electric field driving force. CdS is a photocatalytic material with a high visible-light activity, due to its narrow band gap (2.42 eV) [26]. It has been widely used as a sensitizer to improve the visible-light response of wide band gap semiconductors [27]. Using CdS nanoparticles to decorate semiconductor materials can effectively separate the photogenerated electrons and holes, then result in an improvement of the photocatalytic efficiency [28].

Therefore, in the present study, the BiOI microspheres were synthesized by a facile solvothermal method. The CdS/BiOI heterojunction photocatalysts were prepared by absorbing CdS nanoparticles on the surface of BiOI. The influence of CdS on the photocatalytic activity of BiOI was discussed, and the photocatalytic mechanism was proposed.

*corresponding author; e-mail:
zhongyuli@mail.tsinghua.edu.cn

2. Experimental

2.1. Synthesis of the CdS/BiOI heterojunctions

All the reagents are analytical grade and used without further purification. BiOI powders were synthesized according to Ref. [29]. Briefly, 1.94 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.830 g KI were dissolved in 80 ml ethylene glycol, respectively. Then KI solution was added into $\text{Bi}(\text{NO}_3)_3$ solution and the mixture was stirred for 10 min and then transferred into 200 ml Teflon-lined stainless steel autoclave and maintained at 160 °C for 6 h. The products were washed for one time with ethanol and three times with distilled water and dried at 120 °C for 8 h.

To prepare CdS, 0.5187 g $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 0.1691 g thioacetamide (TAA) were dissolved in 15 ml distilled water, respectively. Then TAA solution was added into $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution and the mixture was stirred for 30 min to get a stable mixture. Then, a certain amount of polyvinylpyrrolidone (PVP) was put into the above mixture under stirring for another an hour and transferred into 50 ml Teflon-lined autoclave. Finally, the autoclave was kept at 100 °C for 12 h and natural cool down to room temperature. The resulting products were centrifuged, washed with ethanol and distilled water several times, and dried at 80 °C for 8 h.

The CdS/BiOI heterojunctions were prepared as following: an appropriate amount of solution containing the CdS was ultrasonicated for 30 min to make CdS totally dispersed. The as-prepared BiOI powder (0.1 g) was added into the above solution and stirred for 24 h. The solvent was evaporated at 80 °C. The obtained powder was CdS/BiOI heterojunctions. The mass ratio of CdS to BiOI was 1%, 3%, and 5%, respectively.

2.2. Characterization

To characterize the synthesized samples, X-ray diffraction (XRD), transmission electron microscope (TEM), field-emission scanning electron microscope (FE-SEM), the Fourier transform infrared spectra (FT-IR), photoluminescence (PL), the Raman and UV-vis absorption spectra were used. The crystalline catalyst was examined by XRD under a Rigaku D/Max-2500PC X-ray diffractometer (Rigaku Co., Japan) employing $\text{Cu } K_\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$ operated at 40 kV and 100 mA. A JEM-2100 TEM and a JSM-6360LA FE-SEM (JEOL, Japan) were used to characterize the morphology of the samples. FT-IR were recorded in the wave number range from 400 to 4000 cm^{-1} by Nicolet (PROTéGé 460) spectrometer. The Raman spectra were measured at room temperature using a LabRAM XploRA Raman spectrometer (Horiba Jobin Yvon, France) with a 532 nm laser focused on a spot about 3 μm diameter. UV-vis diffuse reflectance spectroscopy (DRS) spectra of the photocatalysts were measured by a UV-vis scanning spectrophotometer (Shimadzu UV-2550) using an integrating sphere and BaSO_4 as white standard. The PL spectra were obtained by an F-280 spectrometer (Tianjin Keqi, China).

2.3. Adsorption experiments

Batch experiments were performed by equilibrating 18 mg of adsorbent with 30 ml malachite green (MG) solutions of predetermined initial concentrations. 30 ml of $V(V)$ solutions of concentration ranged from 4.0 to 16.0 mg/l. By adding NaOH and HCl of different concentrations, initial pH of the solutions was maintained at required pH value. The suspensions were shaken for 1 h. MG concentration was determined by UV759 UV-vis spectrophotometer at 617 nm. The equilibrium sorption capacity was calculated using the following equation:

$$q_e = C_0 - C_e V/m,$$

where q_e is the equilibrium amount of $V(V)$ adsorbed per unit mass of adsorbent [$\mu\text{mol/g}$], m is the sorbent mass [g], V is the sample volume [L], C_e is the equilibrium concentration [mg/L] and C_0 is the initial concentration [mg/L].

2.4. Photocatalytic activity

The photocatalytic activities of as-prepared products were evaluated by the degradation of MG solution. A 1 kW Xe lamp was used to simulate sunlight irradiation and a cutoff filter of 420 nm was used to filter the ultra-violet light. In a typical procedure, 0.03 g of as-prepared photocatalyst was dispersed into 50 ml of MG solution (15 mg/l) and the suspension was magnetically stirred in the dark for 30 min to reach adsorption-desorption equilibrium between MG and photocatalyst. At every intervals of 20 min, 5 ml of the suspension was collected, centrifuged to remove the photocatalyst particles. Finally, the catalyst-free MG solution was analyzed by a UV759 UV-vis spectrometer (Shanghai Precision & Scientific Instrument Co., Ltd., China) to obtain the absorbance of the target contaminant at its maximum absorption wavelength. The decomposition efficiency of the target contaminant was calculated by $D = (1 - C_t/C_0) \times 100\%$, where C_0 and C_t are the equilibrium concentration of the target contaminant before and after visible-light irradiation, respectively.

3. Results and discussion

3.1. XRD patterns

The detailed information on the crystal phase and crystallinity of the as-prepared samples was determined by XRD patterns. Figure 1 presents the XRD patterns of the pure BiOI and CdS/BiOI nanocomposites with different CdS amounts. The pure BiOI displays sharp diffraction peaks (from 10° to 75°) which are indexed to (012), (110), (013), (200), (114), (212), (115), (024), and (220) planes of the tetragonal phase structure (JCPDS card no. 73-2062). The XRD pattern of CdS with peaks around 26.7°, 44.1°, and 52.2° are shown in the inset of Fig. 1. In the diffraction pattern of CdS/BiOI nanocomposites, they exhibit diffraction peaks very similar to those of the pure BiOI powders except for one small

Fig. 1. XRD patterns of pure BiOI and series of CdS/BiOI nanocomposites.

peak at 26.7° which is attributed to the characteristic peak of CdS. It can be clearly seen that the characteristic peaks of CdS become more intense with the increase of its loading amount. No impurity peaks were observed, confirming the high purity of the two products. The XRD results revealed the coexistence of BiOI and CdS in the CdS/BiOI nanocomposites.

3.2. FE-SEM images

The FE-SEM morphologies and microstructures of CdS, BiOI, and CdS/BiOI are presented in Fig. 2. The pure CdS shows very uniform particle morphology, and the particle size is less than 100 nm (Fig. 2a). The pure BiOI had 3-dimensional flower-like hierarchical architecture with the diameter of approximate 6–7 μm (Fig. 2b).

Fig. 2. FE-SEM images of the pure CdS (a), pure BiOI (b), and as-prepared 3%-CdS/BiOI (c, d) nanocomposites.

It is obvious that BiOI hierarchical architecture was further composed of irregular nanoplates with thickness ranging from 50 to 100 nm. It is obvious that BiOI hierarchi-

cal architecture is further composed of irregular nanoplates with thickness ranging from 50 to 100 nm. Figure 2c and d shows the SEM image of the 3%-CdS/BiOI nanocomposite. The CdS nanoparticles were observed to be closely adhered to the surface of BiOI, resulting in intimate contact, which was thought to facilitate the transfer of photogenerated charges. The results indicated that the CdS nanoparticles can be easily attached to the surface of BiOI microspheres.

3.3. TEM images

Moreover, the crystal structure of the pure BiOI and the 3%-CdS/BiOI heterojunction photocatalyst were further investigated by TEM and the HRTEM. Figure 3a shows the low-magnification TEM image of a single BiOI nanoflower. It can be clearly seen that the nanoflowers are self-assembled of nanosheets, which is consistent with the results of FE-SEM observation. From Fig. 3b, it can be seen that CdS nanoparticles closely adhered to

Fig. 3. TEM images of the pure BiOI (a), 3%-CdS/BiOI (b), and higher magnification TEM image of 3%-CdS/BiOI nanocomposites (c).

the surface of the BiOI. The HRTEM image of the 3%-CdS/BiOI photocatalyst was also displayed, as shown in Fig. 3c. The phase with the lattice fringes (0.282 nm) could be observed, which corresponds to the (110) plane of BiOI while the lattice space of crystallite locating on the BiOI is 0.336 nm, which agrees well the (111) plane of CdS. The TEM result confirms assembling of CdS particles on the surface of the BiOI crystal.

3.4. UV-vis diffuse reflectance spectra

The optimum absorption property of photocatalyst and the migration of the light induced electrons and holes play a vital role in the photocatalytic process. Figure 4 shows the UV-vis DRS spectra of pure CdS, BiOI, and CdS/BiOI heterostructure samples. It can be seen that

all the samples show the intense absorption in the visible-light region, which implies the possibility of photocatalytic activity under visible-light irradiation. For the pure CdS sample, the absorption edge occurs at a wavelength shorter than 570 nm, whereas the absorption intensity of BiOI shows absorption edges at 630 nm. In comparison to CdS and BiOI, the absorption band edge of CdS/BiOI exhibited an apparent red shift. This shift is ascribed to the interaction between CdS and BiOI semiconductors in the heterojunction. The enhanced light absorption of the nanocomposites led to the production of more photogenerated charge carriers and was thought to result in improved photocatalytic performance.

Fig. 4. UV-vis diffuse reflectance spectra of pure CdS, BiOI, and series of CdS/BiOI nanocomposites.

Fig. 5. FT-IR of pure BiOI and CdS/BiOI nanocomposites.

3.5. FT-IR analysis

To investigate the chemical composition and chemical bonding of composites, FT-IR investigation was carried out. Figure 5 displays the FT-IR spectra of pure

BiOI and CdS/BiOI heterostructure samples. The broad bands centered at 3450 cm^{-1} and 1587 cm^{-1} in the spectrum of BiOI corresponded to the stretching and bending vibrations of O–H, respectively. Moreover, the band at 489 cm^{-1} for both samples of pure BiOI and CdS/BiOI nanocomposites was associated with the stretching vibrations of the Bi–O [30]. In comparison with the spectrum of BiOI, the weak absorption band at 618 cm^{-1} could be ascribed to the Cd–S group which was in the spectrum of the CdS/BiOI nanocomposites. The peak ranged from 1120 to 1000 cm^{-1} could be attributed to the C–O of ethanol which might come from the washing process. Absorption bands of CdS and BiOI were apparent in the CdS/BiOI nanocomposites, confirming that CdS and BiOI had been coupled together successfully.

3.6. Raman analysis

The Raman scattering is an effective technique to investigate the crystallization, structure, and defect of nanostructure materials. Figure 6 shows the Raman spectra of CdS, BiOI, and CdS/BiOI nanocomposites. The Raman spectra of CdS and CdS/BiOI nanocomposites displayed one prominent peak around at 148 cm^{-1} .

Fig. 6. Raman spectra of as-prepared BiOI, CdS, and 3%-CdS/BiOI nanocomposites.

BiOI can be recognized based on the characteristic peak position of 148 cm^{-1} due to the E_g internal Bi–I stretching mode. The curves of CdS and CdS/BiOI exhibited two Raman active peaks. One well defined intense peak appeared at 295 cm^{-1} and a low intense peak at around 589 cm^{-1} was attributed to first and second order longitudinal-optical (LO) phonon modes.

3.7. Adsorption experiments

The adsorption isotherms of MG dye onto heterojunction surface was studied by taking solutions in the concentration ranging from 4.0 to 16.0 mg/l and the results are shown in Fig. 7. With increase of initial concentration of MG from 4.0 to 16.0 mg/l , the adsorption capacity increased, indicating that MG adsorption depends on initial concentration. The result suggests that

Fig. 7. Adsorption isotherms of MG on the CdS, BiOI, and 3%-CdS/BiOI surfaces.

the doing of CdS could improve its adsorption abilities. The enhanced dye removal efficiency was attributed to the synergetic effects of the adsorption and photodegradation [31, 32].

3.8. Photocatalytic activity of CdS/BiOI nanocomposites

The photocatalytic activities of CdS/BiOI samples were measured by the degradation of MG under visible light irradiation. Figure 8a shows the change of absorption peak spectra of MG solution exposed to visible light as a function of time in the presence of 3%-CdS/BiOI sample. During the photodegradation process, the intensity of the typical adsorption peak of MG at 617 nm decreased gradually as the photocatalytic reaction time increased, indicating the excellent photocatalytic activity of 3%-CdS/BiOI nanocomposites for the MG degradation under visible-light irradiation. The larger part (92%) of MG could be discolored by 3%-CdS/BiOI nanocomposites within 100 min of visible-light irradiation. No new absorption bands appeared, indicating the complete photocatalytic degradation of MG during that reaction.

Figure 8b shows the MG photodegradation over pure CdS, BiOI, and CdS/BiOI heterostructures. It can be seen that the single CdS and pure BiOI exhibit weak degrade efficiency of 31.5% and 25.3% after 100 min of visible-light illumination and all of the CdS/BiOI heterostructures exhibited superior photocatalytic activity. With increasing CdS content, the photocatalytic activity enhanced gradually and then decreased. As the content of CdS was 3%, the highest photocatalytic activity could be achieved. These results suggest that 3% CdS is the optimal sample among the CdS/BiOI nanocomposites, which can be mainly ascribed to the heterojunction structure between CdS and BiOI. With increasing CdS content, more CdS/BiOI heterojunctions interface will be formed, which suppresses the recombination of photo-induced electron-hole pairs. However, the excessive CdS

Fig. 8. (a) Temporal evolution of the spectra during the photodegradation of MG over 3%-CdS/BiOI sample, (b) photodegradation of MG with pure CdS, BiOI and CdS/BiOI nanocomposites under visible light irradiation, (c) kinetic data for the degradation of MG in the presence of different photocatalysts.

content will lead to the decrease of heterojunction interface and function as recombination centers of electron-hole pairs. Consequently, suitable content of CdS could improve the photocatalytic activity.

Figure 8c reveals that the photocatalytic degradation of MG on different catalysts fits pseudo-first-order kine-

tics, $\ln(C_0/C_t) = k_{app}t$, where t is the irradiation time and k_{app} is the rate constant. Moreover, the k_{app} for MG degradation with CdS, BiOI, 1%-CdS/BiOI, 3%-CdS/BiOI and 5%-CdS/BiOI were estimated to be 0.004, 0.002, 0.011, 0.024, and 0.010 min^{-1} , respectively. It is worth mentioning that the MG degradation rate constant of the CdS/BiOI nanocomposites is much higher than that of CdS and BiOI. Remarkably, the rate constant of the 3%-CdS/BiOI nanocomposite is 12 times as high as that of pure BiOI under the same experimental conditions, which indicates that the coupling of CdS could enhance the photocatalytic capability of BiOI under the visible-light irradiation.

3.9. Photoluminescence analysis

PL spectra are usually used to estimate the separation efficiency of photoinduced charge carriers for semiconductors. A higher intensity of PL indicates a faster recombination of charge carriers. Figure 9 shows the PL spectra of the as-prepared samples at an excitation wavelength of 300 nm. Pure CdS, BiOI, and CdS/BiOI nanocomposites exhibit the similar peak shape and peak position, but the intensities of peaks are different with each other. In contrast, the emission intensity from CdS/BiOI nanocomposites is clearly reduced, which suggests that the recombination of photogenerated electrons and holes is effectively inhibited. The intensity of the 3%-CdS/BiOI nanocomposites photocatalyst was the lowest than other photocatalysts, which indicated that the 3%-CdS/BiOI nanocomposites had a lowest recombination rate of photo-generated charge carriers. Therefore, the heterostructured CdS/BiOI nanocomposites are highly favorable for the efficient separation of the photo-induced charge carriers during the photocatalytic reactions.

Fig. 9. PL spectra of pure CdS, pure BiOI and series of CdS/BiOI nanocomposites.

3.10. Photocatalytic mechanism

The reusability and durability are important parameters to explore real applications of catalysts. As a result, 3%-CdS/BiOI nanocomposites were specifically chosen

for successive catalytic estimations in Fig. 10. There is no obvious decrease of photocatalytic efficiency over MG for five cycling runs under visible light, possibly linking to the well-maintained chemical composition and phase structures.

Fig. 10. The stability of 3%-CdS/BiOI photocatalyst over MG degradation.

Fig. 11. Effects of different scavengers on the degradation of MG in the presence of 3%-CdS/BiOI under visible-light irradiation.

In the photodegradation process of organic pollutants, reactive species as superoxide radical ($\cdot\text{O}_2^-$), hole (h^+) and hydroxyl radical ($\cdot\text{OH}$) acted as a bridge, playing the role of photocatalysts under the light irradiation, therefore, it is necessary to determine the main reactive species for the degradation of MG in this study. Some sacrificial agents, such as iso-propyl alcohol (IPA), disodium ethylenediaminetetraacetate (EDTA) and 1,4-benzoquinone (BQ) were used as the scavengers of $\cdot\text{OH}$, h^+ and $\cdot\text{O}_2^-$, respectively. Figure 11 shows that the photodegradation efficiency of MG over 3%-CdS/BiOI is not affected by the addition of IPA, indicating that almost no superoxide radicals ($\cdot\text{OH}$) were involved in the degradation of MG. When EDTA was added, the photodegradation efficiency of MG obviously decreased, which revealed the existence of h^+ radical species. Besides, the photocatalytic activity was thoroughly suppressed by addition of BQ, suggesting that the $\cdot\text{O}_2^-$ pathways play a crucial role in the process of MG degradation. These results indicated that the h^+ and $\cdot\text{O}_2^-$ were the main active species in the MG photodegradation process.

The E_g values of pure BiOI and CdS were estimated to be 1.8 eV and 2.42 eV in the optical property section.

The valence band (VB) edge potential of a semiconductor can be predicted by the following empirical equation [33–35]:

$$E_{CB} = X - E^e - 0.5E_g,$$

where X is the absolute electronegativity of the semiconductor, E^e is the energy of free electrons on the hydrogen scale (4.5 eV), E_g is the band gap of the semiconductor. The E_{VB} value could be deduced from the equation [36]:

$$E_{VB} = E_{CB} + E_g.$$

It could be seen that the calculated positions of CB and VB edge potentials of BiOI were determined to be 0.6 eV and 2.4 eV, respectively. For CdS, the CB and VB potentials of CdS were determined to be −0.5 eV and 1.92 eV, respectively.

Fig. 12. Proposed mechanism for the photodegradation of MG over CdS/BiOI nanocomposites under visible light irradiation.

Based on the above analysis, the possible mechanism for the photocatalytic activity enhancement of 3%-CdS/BiOI nanocomposite is proposed in Fig. 12. Under visible-light irradiation, CdS and BiOI would be excited simultaneously and generate electron–hole pairs. On the one hand, the CB electrons (CdS) easily flow into the CB edge of BiOI through the interface because the CB edge of CdS is higher than that of BiOI. On the other hand, because the VB edge level of BiOI is lower than that of CdS, holes in the VB edge of BiOI will transfer to that of CdS by the control of the interface. In such way, photo-induced electron–hole pairs could be separated efficiently at the interface of two semiconductors. Consequently, the photogenerated electrons could easily transfer from the reformed CB of CdS to that of BiOI, and then react with O_2 to generate reactive $\cdot O_2^-$ radicals. Meanwhile the holes can also move in the opposite direction from the VB of BiOI to that of CdS. Therefore the h^+ and $\cdot O_2^-$ radicals were beneficial for the MG degradation. As a result, efficient separation of photogenerated electron–hole pairs is achieved by the distribution of electrons and holes on different semiconductors and thus enhanced the corresponding photocatalytic performance.

In addition, the XRD patterns of the sample before and after the reaction (Fig. 13) showed that the crystal structure had little change and no additional band appeared during the photodegradation process. These suggest that

Fig. 13. XRD pattern of the 3%-CdS/BiOI before and after the long time experiment.

the nanocomposite was not photocorroded and presented relatively high stability.

4. Conclusion

CdS/BiOI heterojunctions have been successfully prepared by a facile method. The CdS nanoparticles were uniformly distributed on the surface of BiOI microspheres. The nanocomposites exhibited good visible-light absorption. The PL results revealed that the recombination of photogenerated electrons and holes was inhibited. The highest activity was obtained by 3%-CdS/BiOI heterojunctions. The enhanced photocatalytic performance was ascribed to the improved photogenerated carrier separation efficiency caused by the coupling effects of the two semiconductors. The as-prepared CdS/BiOI heterostructure photocatalysts might have potential in environmental remediation applications.

Acknowledgments

This work was financially supported by Open Fund of Key Laboratory of Regional Environment and Eco-remediation of Ministry of Education, China (SYU-KF-E-12), Open Fund of Key Laboratory of Contaminated Environment Control and Regional Ecology Safety, Shenyang University (SYU-KF-L-12), Natural Science Foundation of Jiangsu Province, China (No. BK20150259) and Natural Science Foundation of Changzhou City (CJ20140053).

References

- [1] C.C. Chen, W.H. Ma, J.C. Zhao, *Chem. Soc. Rev.* **39**, 4206 (2010).
- [2] F. Zhao, Q.F. Lu, Z.L. Xiu, C.F. Zhu, *Nano* **11**, 1650048 (2016).
- [3] H. Liu, T. Lv, C.K. Zhu, X. Su, Z.F. Zhu, *J. Mol. Catal. A Chem.* **396**, 136 (2015).
- [4] B. Zeng, X.H. Chen, X.T. Ning, C.S. Chen, H. Long, *Nano* **8**, 1350052 (2013).
- [5] Q.J. Xiang, J.G. Yu, W.G. Wang, M. Jaroniec, *Chem. Commun.* **47**, 6906 (2011).
- [6] Y.J. Wang, R. Shi, J. Lin, Y.F. Zhu, *Energy Environ. Sci.* **4**, 2922 (2011).

- [7] H.C. Zhang, H. Huang, H. Ming, H.T. Li, L.L. Zhang, Y. Liu, Z.H. Kang, *J. Mater. Chem.* **22**, 10501 (2012).
- [8] R. Azimirad, S. Safa, O. Akhavan, *Acta Phys. Pol. A* **127**, 1727 (2015).
- [9] A. Naldoni, M. Allieta, S. Santangelo, M. Marelli, F. Fabbri, S. Cappelli, C.L. Bianchi, R. Psaro, V.D. Santo, *J. Am. Chem. Soc.* **134**, 7600 (2012).
- [10] M.A. Ischay, M.E. Anzovino, J. Du, T.P. Yoon, *J. Am. Chem. Soc.* **130**, 12886 (2008).
- [11] J. Li, Y. Yu, L.Z. Zhang, *Nanoscale* **6**, 8473 (2014).
- [12] T. Yan, H.Y. Liu, P.C. Gao, M. Sun, Q. Wei, W.G. Xu, X.D. Wang, B. Du, *New J. Chem.* **39**, 3964 (2015).
- [13] X.F. Chang, J. Huang, Q.Y. Tan, M. Wang, G.B. Ji, S.B. Deng, G. Yu, *Catal. Commun.* **10**, 1957 (2009).
- [14] J. Cao, B.Y. Xu, H.L. Lin, S.F. Chen, *Chem. Eng. J.* **228**, 482 (2013).
- [15] J. Cao, B.Y. Xu, H.L. Lin, B.D. Luo, S.F. Chen, *Dalton Trans.* **41**, 11482 (2012).
- [16] H.Q. Li, Y.M. Cui, W.S. Hong, *Appl. Surf. Sci.* **264**, 581 (2013).
- [17] Z.K. Cui, M.M. Si, Z. Zheng, L.W. Mi, W.J. Fa, H.M. Jia, *Catal. Commun.* **42**, 121 (2013).
- [18] X. Zhang, L.Z. Zhang, T.F. Xie, D.J. Wang, *J. Phys. Chem. C* **113**, 7371 (2009).
- [19] G.P. Dai, J.G. Yu, G. Liu, *J. Phys. Chem. C* **115**, 7339 (2011).
- [20] J. Jiang, X. Zhang, P.B. Sun, L.Z. Zhang, *J. Phys. Chem. C* **115**, 20555 (2011).
- [21] Y.Y. Li, J.S. Wang, H.C. Yao, L.Y. Dang, Z.J. Li, *Catal. Commun.* **12**, 660 (2011).
- [22] J. Cao, B.Y. Xu, B.D. Luo, H.L. Lin, S.F. Chen, *Catal. Commun.* **13**, 63 (2011).
- [23] T.B. Li, G. Chen, C. Zhou, Z.Y. Shen, R.C. Jin, J.X. Sun, *Dalton Trans.* **40**, 6751 (2011).
- [24] C.L. Yu, J.C. Yu, C.F. Fan, H.R. Wen, S.J. Hu, *Mater. Sci. Eng. B* **166**, 213 (2010).
- [25] H.F. Cheng, B.B. Huang, Y. Dai, X.Y. Qin, X.Y. Zhang, *Langmuir* **26**, 6618 (2010).
- [26] D.W. Jing, L.J. Guo, *J. Phys. Chem. C* **111**, 13437 (2007).
- [27] D.W. Jing, L.J. Guo, *J. Phys. Chem. B* **110**, 11139 (2006).
- [28] N.Z. Bao, L.M. Shen, T. Takata, K. Domen, *Chem. Mater.* **20**, 110 (2008).
- [29] Y.F. Liu, W.Q. Yao, D. Liu, R.L. Zong, M. Zhang, X.G. Ma, Y.F. Zhu, *Appl. Catal. B* **163**, 547 (2015).
- [30] H.L. Lin, C.C. Zhou, J. Cao, S.F. Chen, *Chin. Sci. Bull.* **59**, 3420 (2014).
- [31] A. Turki, C. Guillard, F. Dappozze, Z. Ksibi, G. Berhault, H. Kochkar, *Appl. Catal. B* **163**, 404 (2015).
- [32] T.S. Anirudhan, F.J. Christa, *J. Hazard. Mater.* **324**, 117 (2017).
- [33] C. Chang, L. Zhu, S. Wang, X. Chu, L. Yue, *ACS Appl. Mater. Interf.* **6**, 5083 (2014).
- [34] Y. Sun, W. Zhang, T. Xiong, Z. Zhao, F. Dong, R. Wang, W. Ho, 0.1016/j.jcis.2013.12.037 *J. Coll. Interf. Sci.* **418**, 317 (2014).
- [35] F. Chang, C.L. Li, J. Chen, J. Wang, J.R. Luo, Y.C. Xie, B.Q. Deng, X.F. Hu, *Superlatt. Microstruct.* **76**, 90 (2014).
- [36] Z.C. Yang, J. Li, F.X. Cheng, Z. Chen, X.P. Dong, *J. Alloys Comp.* **634**, 215 (2015).