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# Efficient visible-light-induced photocatalytic activity over the novel Ti-doped BiOBr microspheres

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### ABSTRACT

A novel and efficient visible-light-induced Ti-doped BiOBr photocatalyst was successfully obtained by double self-assemble method. The resultant samples were characterized by XRD, FE-SEM, HR-TEM, EDS, and UV-vis adsorption spectra. The possible formation process of the as-prepared samples and titanium doping in the lattice of BiOBr were investigated in this paper. The Ti-doped BiOBr microspheres exhibited higher visible-light-induced photocatalytic activity for the degradation of rhodamine B (RhB) than BiOBr due to the synergetic effect of the unique structure and the titanium doping as well as larger specific surface area, which effectively improved photogenerated electrons and holes transferring.

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# 1. Introduction

Currently, the science and technology progress rapidly. Yet, at the same time, the environment problems have arisen, such as an increasing amount of waste water and exhausted gas. Thus, it is of importance to develop simple and effective methods to address these issues. Among these promising strategies, photocatalysis has drawn widespread attention owing to its ability to degrade organic contaminant at a relatively effective rate [1–5]. In particular, TiO<sub>2</sub> has been the focus in this field due to its unique physical and chemical properties, including high efficiency, good stability, nontoxicity, etc. [6–9]. However, it exhibits photocatalytic activity under UV light ( $\lambda$ <387 nm), whose energy exceeds its band gap, resulting in its limited practical applications [10–12]. Therefore, the exploitation of visible-light-driven photocatalytic system.

Aiming at effectively utilizing visible light, a great deal of effort has been devoted to the hierarchical structure development and band gap regulation because shape and band energy of photocatalysts play vital influence on their physical/chemical properties [13–17]. As a group of V-VI-VII semiconductors, bismuth oxyhalide compounds have attracted considerable attention due to their remarkable photocatalytic activities under visible-light illumination. Bismuth oxyhalides crystals possess the tetragonal matlockite structure, a layered structure composed of  $[Bi_2O_2]^{2+}$  layers interleaved with double Br layers [18–21]. To date, a variety of bismuth oxyhalide nano- and micro-structures, including nanoplates, nanobelts, and microspheres prepared by numerous methods, has been used as photocatalysts to degrade organic contaminant [22-25]. For instance, Feng et al. reported the synthesis of mesoporous BiOBr 3D microspheres by a facile solvothermal method with high photodecomposition ability under UV and UV-vis light irradiation [26]. Wang and co-workers reported a new class of oxyhalide photocatalysts xBiOBr–(1-x)BiOI with high visible light-catalytic activity prepared by a soft chemical method [27]. However, the photodegradation ability of BiOBr is far from efficient for practical application, and it is necessary to enhance its photocatalytic activity by modification.

Several studies have reported that the optical properties of photocatalysts can be modified by incorporation of the highly reactive component, such as cation, anion, and metal oxides [28–31]. Based on titanium is an archetype for highly reactive element; in our work, a facile and rapid solvothermal method has been successfully developed to prepare visible light-activated Ti-doped BiOBr microspheres using 2-methoxyethanol as the solvent. Based on characterization results, the possible formation mechanism of  $Ti_{0.22}BiO_{1.48}Br$  flower-like microspheres was studied and the differences between the  $Ti_{0.22}BiO_{1.48}Br$ and BiOBr were also proposed. Moreover, the photocatalytic activity of

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Fig. 1. XRD patterns of the as-prepared BiOBr and Ti-doped BiOBr samples prepared at 160  $^\circ\text{C}$  for 24 h.

the as-prepared samples was evaluated by the degradation of rhodamine B (RhB) and compared with that of BiOBr and P-25 under visible light (11 W daylight lamp) irradiation.

# 2. Experimental

## 2.1. Materials and reagents

Bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O), cetyltrimethylammonium bromide (CTAB), and 2-methoxyethanol, tetrabutyl orthotitanate (TBOT) were all purchased from Shanghai Chemical Co., Ltd. Pure TiO<sub>2</sub> (P-25) was purchased from Degussa Co. Ltd. All the reagents were analytical grade and used without further purification.

## 2.2. Preparation of BiOBr and Ti-doped BiOBr flower-like microspheres

In the typical preparation, 0.6 g of  $Bi(NO_3)_3 \cdot 5H_2O$  was dissolved in 60 mL of 2-methoxyethanol to from a clean solution, and then 1.2 g of CTAB and 0.3 mL of TBOT were added slowly to the solution with sonication. Next, the resultant solution was transferred into a Teflon-lined stainless steel autoclave, followed by a solvothermal treatment at 160 °C for 0–24 h. After cooling to room temperature, the precipitates were washed with deionized water and ethanol six times, and dried in a vacuum oven at 60 °C for 12 h. The BiOBr microspheres were also prepared by the same method without TBOT being added (details in Appendix A).

# 2.3. Characterization

Microstructures of the as-prepared samples were analyzed with a SIEMENS Diffraktometer D5000 X-ray diffractometer using Cu K $\alpha$  radiation source at 35 kV, with a scan rate of 0.02° s<sup>-1</sup> in the 2 $\theta$  range of 20–80°. The morphologies were investigated by ULTRA-55 field-emission scanning electron microscopy (FE-SEM) and JSM-2100 transmission electron microscopy (TEM) equipped with an energy dispersive X-ray spectrum (EDS, Inca Energy-200) at an accelerating voltage of 200 kV. The Brunauer–Emmet–Teller (BET) specific surface area of the samples were determined by a high speed automated area and pore size analyzer (F-Sorb3400, China). UV–vis adsorption spectra were recorded with a UV–vis spectrometer (U-3010, Hitachi).

### 2.4. Measurement of photocatalytic activity

The photocatalytic activity of P-25 and the as-prepared samples was investigated by the photo-degradation of RhB. The photo-degradation experiments were carried out under visible light irradiation whose source was an 11 W daylight lamp (25 Hz) equipped with UV cutoff filter to provide visible light ( $\lambda \ge 400$  nm). Fifty milligrams



Fig. 2. (A) and (B) FE-SEM images, (C) TEM image, and (D) HR-TEM image, together with SAED pattern of the as-prepared Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br microspheres prepared at 160 °C for 24 h.

#### Table 1

The BET specific surface area, pore volume, band gap ( $E_{\rm g}$ ) and photodegradation rate constants ( $k_{\rm RhB}$ ) of BiOBr and Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br photocatalyst.

Photocatalyst	BET specific surface area $(m^2 g^{-1})$	Pore volume $(mL g^{-1})$	Band gap <sup>a</sup> (eV)	${k_{\mathrm{RhB}}}^{\mathrm{b}}$ $(\mathrm{h}^{-1})$
BiOBr	8.0	0.72	2.66	0.53
Ti <sub>0.22</sub> BiO <sub>1.48</sub> Br	27.1	0.77	2.54	0.82

<sup>a</sup> Band gap was derived from  $E_g = 1239.8/\lambda_g$ , where  $\lambda_g$  is the absorption edge in the UV-vis spectra [34].

<sup>b</sup> The RhB self-degradation (in the absence of the catalysts) is negligible.

of the as-prepared catalysts was suspended in 50 mL RhB aqueous solution ( $C_0 = 10 \text{ mg} \cdot \text{L}^{-1}$ ) with constant stirring. Prior to irradiation, the suspensions were stirred in the dark for 1 h to ensure the adsorption–desorption equilibrium. The temperature of suspensions was maintained below 283 K by a flow of cooling water during the reaction. The change of RhB concentrations (*C*) in accordance with the irradiation time was measured by JASCO V-570 UV/vis/NIR spectrophotometer (Japan).

## 3. Results and discussion

The crystallographic structure of the resultant samples was confirmed by XRD patterns (Fig. 1). For the BiOBr sample, all the diffraction peaks can be well indexed to the tetragonal phase whose lattice parameters are a = 3.915, c = 8.076 Å (space group: P4/nmm, JCPDS) 73-2061). Moreover, the (110) and (020) peaks are sharper compared to others, which are assigned to the preferential attachment along the (110) plane and related self-assembly [32,33]. In the regarding of Ti-doped BiOBr, however, two stronger peaks at  $2\theta = 25.3^{\circ}$  and  $31.8^{\circ}$  can be observed as well as the reduction of the BiOBr peaks after doped with titanium. Meantime, no other diffraction peaks assigned to titanium hybrids are observed, probably due to its low content and high dispersity. In addition, the crystal phase of BiOBr was almost not affected by the incorporation of titanium. According to the content of their constituent elements from EDS results (Table S1), the chemical formula Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br also can be used to denote the Ti-doped BiOBr samples.

The morphologies and structures of the samples prepared by solvothermal method were characterized by FE-SEM and HR-TEM images. Fig. 2A presents a typical FE-SEM image of the Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br heterostructures prepared at 160 °C for 24 h, clearly showing that these structures exhibit uniform microspheres of 1–3 µm in size. The magnified image of an individual sphere is showed in Fig. 2B, which indicates that the flower-like microspheres are assembled by nanoplates with the thickness of about 15 nm. Comparing with Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br, BiOBr with loose hierarchical microspheres of 1-2 µm in size and consisting of larger nanoplates are observed (see Fig. S1 in the Appendix A). Moreover, the nanoplate of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br is comprised of the nanoparticles, confirmed by Fig. 2C. Furthermore, high-resolution TEM (HRTEM) image (Fig. 2D) reveals the lattice spacing is 0.351 nm corresponding to the (011) plane of BiOBr. It is worth noting that BiOBr successfully doped by titanium can be confirmed by the distortion of lattice (the selected area of inset in Fig. 2D). Therefore, the selfassembly of the nanoplates to obtained flower-like Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br microspheres is different from that of BiOBr microspheres, attributed to the variation of exposed (011) plane. In addition, the SAED pattern reveals that the sample has poly-crystalline nature of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br.

 $N_2$  absorption analysis is carried to further characterize the porous structure of the as-prepared samples (Fig. S2 in Appendix A). The Brunauer–Emmett–Teller (BET) specific surface areas and pore volumes of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br and BiOBr are summarized in Table 1. The former specific surface area (27.07 m<sup>2</sup> g<sup>-1</sup>) is almost 3.4 times compared with latter due to the more interlaced nanoplates on the surface of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br structure. Then, the UV–vis absorption spectra were used to characterize physical properties of the samples, which are shown in Fig. 3. The UV–vis



Fig. 3. UV-vis adsorption spectra of the as-prepared BiOBr and  $\rm Ti_{0.22}BiO_{1.48}Br$  samples prepared at 160 °C for 24 h.

absorption edges of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br have an appreciable red shift. Moreover, the Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br samples show a stronger absorption in the visible light range than that of BiOBr because of titanium doping. The adsorption edges of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br and BiOBr are approximately 487 nm (corresponding to 2.54 eV) and 466 nm (corresponding to 2.66 eV) (Table 1), respectively. The narrowed band gap is induced by a sub-band-gap transition, which originated from titanium doping in the lattice of BiOBr [10,28].

To study the formation mechanism of the  $Ti_{0.22}BiO_{1.48}Br$  microspheres under solvothermal conditions, time-dependent experiments were conducted and the resultant samples collected at different steps were analyzed by XRD, FE-SEM, and EDS. Fig. 4 are the XRD patterns of  $Ti_{0.22}BiO_{1.48}Br$  powders collected at different reaction steps, indicating that all the samples are well crystallized. Interestingly, the crystal can be obtained without the solvothermal treatment [27], and the diffraction peaks can be assigned to the tetragonal phase of BiOBr, BiBr<sub>3</sub> and TiBr<sub>4</sub>. When the reaction time increases to 0.25 h or more, the phases of BiBr<sub>3</sub> and TiBr<sub>4</sub> disappear and all the diffraction peaks can be indexed to the tetragonal phase of BiOBr (JCPDS 73-2061).

Based on the FE-SEM images of the samples prepared at certain reaction time intervals, the structure growth processes were further investigated. During the pretreatment, the reagents react with each other to form nanoplates, and these nanoplates are interfaced because



Fig. 4. XRD patterns of the as-prepared  $\rm Ti_{0.22}BiO_{1.48}Br$  microspheres under different stages.



Fig. 5. FE-SEM images (scale bar 2  $\mu$ m) and the corresponding magnified images (scale bar 1  $\mu$ m) of the as-prepared Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br microspheres under different stages. (A) 0 h, (B) 0.25 h, (C) 0.5 h, and (D) 1 h.

they preferentially form along (011) plane of the structure (Fig. 5A) [35]. Owing to the high temperature and vapor pressure environment in Teflon vessel, the size of the interlaced nanoplates become smaller and self-assemble to construct the loosely attached aggregates after 0.25 h of thermal treatment (Fig. 5B). Moreover, a reassembly process occurs in the internal structure of these aggregates that is confirmed by the emergence of the microspheres. As shown in Fig. 5C, with the reaction time increasing, the excess segment of nanoplates is detached along the surface of the densely structure to form a mature microsphere when the crystal reformation and reassembly processes are completed, which is in accordance with the results of XRD. After 1 h of solvothermal treatment, the detachment of the excess segment almost complete and the prefect hierarchical flower-like microspheres are successfully obtained (Fig. 5D). No significant changes in the microspheres' dimensions are observed when the reaction time is further extended to 24 h. Moreover, the chemical elemental components of the samples during the reaction span are characterized by EDS, which indicates that the samples are composed of the elements Ti, O, Br, and Bi (Fig. 6). Besides, the solvent plays a key role in the self-assembly processing. In the case of water and ethanol, only nanoplates can be observed instead of flower-like structure (Fig. S3 in Appendix A). This attributes to the special physical/chemical properties of 2-methoxyethanol, especially the limited miscibility of CTAB and 2-methoxyethanol [32]. As to CTAB, it acts not only as the source of Br but also as surfactants that induce the incorporation of titanium.

On the basis of aforementioned discussion, the formation mechanism of the  $Ti_{0.22}BiO_{1.48}Br$  microspheres could be proposed in Fig. 7. It might be divided into four stages: (a) the formation of nanoplates, consisting of BiBr<sub>3</sub>, TiBr<sub>4</sub>, and BiOBr nanoparticles; (b) in the sequence stage, the BiBr<sub>3</sub> and TiBr<sub>4</sub> completely transfer to the BiOBr nanoplates and assemble to the aggregates containing titanium species in the initial step of solvothermal treatment; (c) then the internal of these aggregates undergoes the reassembly process to form the mature microspheres with excess segments on their surface. (d) Finally, these excess segments are detached to form the perfect flower-like  $Ti_{0.22}BiO_{1.48}Br$  microspheres.

The photodegradation of rhodamine B (RhB) is used to evaluate the photocatalytic properties of  $Ti_{0.22}BiO_{1.48}Br$ . As shown in Fig. 8, the adsorption–desorption equilibrium for  $Ti_{0.22}BiO_{1.48}Br$  and BiOBr can be reached after stirred for 1 h under dark condition. The adsorption equilibrium value for all the samples is almost the same (20%). As



Fig. 6. EDS spectra and the corresponding FE-SEM images (scale bar 1 µm) of the as-prepared Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br microspheres under different stages. (A) 0.25 h, (B) 0.5 h, and (C) 1 h.



Fig. 7. Schematic illustration of the possible formation process of the Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br microspheres.

observed, the photocatalytic process of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br and BiOBr follows a pseudo-first-order reaction. The photogradation rate for each photocatalyst is listed in Table 1. It is worth noting that the amount of RhB degradation increases with irradiation time for P-25, BiOBr and Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br samples, and insert of Fig. 8 shows the corresponding color changes of RhB solutions. In the case of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br, the RhB molecules are almost completely degraded comparing with about 75% for the BiOBr sample and 14% for P-25 under visible irradiation for 3 h. The relatively higher photocatalytic activity of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br originates mainly from the following aspects: at first, that the BiOBr is doped by titanium extends the visible light response range and facilitates the electron transport across the sites of titanium, which effectively reduces the charge combination of the photogenerated electrons and holes [10,36,37]. Moreover, the hierarchical flower-like structure of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br provides more spaces, which is beneficial to the transfer of photoexcited carriers [38]. In addition, the higher BET surface specific area and the pore volume endow Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br with more accessible active sites for catalytic reaction [39]. The process of the photocatalytic degradation of RhB is as follows: the photogenerated electron-hole pairs are formed on the valence band of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br under daylight lamp irradiation. The electrons would migrate to the conduction band of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br, which can be trapped by oxygen in solution to form oxidative species. These oxidative species will result in the degradation of RhB. Meanwhile, the photoinduced holes could directly oxide the RhB [22,23].

In addition to efficiency, the durability of the photocatalyst is also very important for its practical application. As a result, the recycling degradation tests were applied to evaluate the durability of Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br photocatalyst. After the RhB molecules are completely decomposed,



**Fig. 8.** Photocatalytic degradation of RhB over P-25, BiOBr and  $Ti_{0.22}BiO_{1.48}Br$  samples prepared at 160 °C for 24 h with 11 W daylight lamp (25 Hz) irradiation.

centrifuging the solution enables  $Ti_{0.22}BiO_{1.48}Br$  to be collected and advances another new run. As shown in Fig. 9, the RhB molecules even can be completely degraded after 6 runs (3 h for each run), indicating this photocatalyst displays good durability.

## 4. Conclusion

In summary, the Ti doped BiOBr microspheres as a novel and efficient visible-light-induced photocatalyst was successfully prepared by double self-assembly method. The formation process of the resultant samples and titanium doping in the lattice of BiOBr were characterized in this paper. According to the content of the constituent elements from EDS results, the atom ratio of Ti doped BiOBr can be calculated as Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br. The as-prepared microspheres exhibited much higher photocatalytic activity for degradation of RhB compared with BiOBr attribute to the corporation of the unique structure and the effect of doping as well as larger specific surface area, which effectively improved the photogenerated electrons and holes transferring. Therefore, the higher efficiency endows this material with a bright perspective in purification of waste water and exhausted gas.

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Fig. 9. Cycling runs for the photodegradation of RhB over as-prepared Ti<sub>0.22</sub>BiO<sub>1.48</sub>Br microspheres prepared at 160 °C for 24 h.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.powtec.2012.05.028.

#### References

- [1] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269-271.
- [2] S.S. Soni, M.J. Henderson, J.-F. Bardeau, A. Gibaud, Advanced Materials 20 (2008) 1493–1498.
- [3] Z. Zou, J. Ye, K. Sayama, H. Arakawa, Nature 414 (2001) 625-627.
- [4] R. Wang, G. Jiang, Y. Ding, Y. Wang, X. Sun, X. Wang, W. Chen, ACS Applied Materials & Interfaces 3 (2011) 4154–4158.
- [5] Y. Zhang, Z.-R. Tang, X. Fu, Y.-J. Xu, ACS Nano 4 (2010) 7303–7314.
- [6] G. Jiang, X. Zheng, Y. Wang, T. Li, X. Sun, Powder Technology 207 (2011) 465-469.
  [7] S. Wang, T. Wang, W. Chen, T. Hori, Chemical Communications (2008) 3756-3758.
- [8] S. Yin, Y. Aita, M. Komatsu, J. Wang, Q. Tang, T. Sato, Journal of Materials Chemistry 15 (2005) 674–682.
- [9] E. Wang, T. He, L. Zhao, Y. Chen, Y. Cao, Journal of Materials Chemistry 21 (2011) 144–150.
- [10] S. Yin, B. Liu, P. Zhang, T. Morikawa, K. Yamanaka, T. Sato, Journal of Physical Chemistry C 112 (2008) 12425–12431.
- [11] Y. Ide, M. Matsuoka, M. Ogawa, Journal of the American Chemical Society 132 (2010) 16762–16764.
- [12] G. Jiang, R. Wang, H. Jin, Y. Wang, X. Sun, S. Wang, T. Wang, Powder Technology 212 (2011) 284–288.
- [13] Q. Zhang, D.Q. Lima, I. Lee, F. Zaera, M. Chi, Y. Yin, Angewandte Chemie, International Edition 50 (2011) 7088–7092.
- [14] X. Qiu, M. Miyauchi, H. Yu, H. Irie, K. Hashimoto, Journal of the American Chemical Society 132 (2010) 15259–15267.
- [15] U. Sulaeman, S. Yin, T. Sato, Applied Physics Letters 97 (2010) 103102.
- [16] J. Yu, X. Yu, B. Huang, X. Zhang, Y. Dai, Crystal Growth and Design 9 (2009) 1474-1480.
- [17] Q. Zhang, J. Wang, S. Yin, T. Sato, F. Saito, Journal of the American Ceramic Society 87 (2004) 1161–1163.

- [18] W. Su, J. Wang, Y. Huang, W. Wang, L. Wu, X. Wang, P. Liu, Scripta Materialia 62 (2010) 345–348.
- [19] J. Xu, W. Meng, Y. Zhang, L. Li, C. Guo, Applied Catalysis B: Environmental 107 (2011) 355–362.
- [20] X. Zhang, Z. Ai, F. Jia, L. Zhang, Journal of Physical Chemistry C 112 (2008) 747-753.
- [21] Z. Ai, W. Ho, S. Lee, L. Zhang, Environmental Science and Technology 43 (2009) 4143–4150.
- [22] M.A. Gondal, X. Chang, M.A. Ali, A.H. Yamani, Q. Zhou, G. Ji, Applied Catalysis A: General 397 (2011) 192–200.
- [23] H. Cheng, B. Huang, P. Wang, Z. Wang, Z. Lou, J. Wang, X. Qin, X. Zhang, Y. Dai, Chemical Communications (2011) 7054–7056.
- [24] Y. Fang, Y. Huang, J. Yang, P. Wang, G. Cheng, Environmental Science and Technology 45 (2011) 1593–1600.
- [25] T. Li, G. Chen, C. Zhou, Z. Shen, R. Jin, J. Sun, Dalton Transactions 40 (2011) 6751–6758.
- [26] W. Wang, F. Huang, X. Lin, J. Yang, Catalysis Communications 9 (2008) 8-12.
- [27] Y. Feng, L. Li, J. Li, J. Wang, L. Liu, Journal of Hazardous Materials 192 (2011) 538–544.
- [28] M. Rangus, M. Mazaj, I. Arčon, G. Mali, V. Kaučič, Chemistry of Materials 23 (2011) 1337–1346.
- [29] S.P. Webb, M.S. Gordon, Journal of the American Chemical Society 121 (1999) 2552–2560.
- [30] Z. Shan, W. Wang, X. Lin, H. Ding, F. Huang, Journal of Solid State Chemistry 181 (2008) 1361–1366.
- [31] A. Léon, G. Yalovega, A. Soldatov, M. Fichtner, Journal of Physical Chemistry C 112 (2008) 12545–12549.
- [32] H. Cheng, B. Huang, Z. Wang, X. Qin, X. Zhang, Y. Dai, Chemistry A European Journal 17 (2011) 8039-8043.
- [33] X. Han, M. Jin, S. Xie, Q. Kuang, Z. Jiang, Y. Jiang, Z. Xie, L. Zheng, Angewandte Chemie, International Edition 121 (2009) 9344–9347.
- [34] L. Kong, Z. Jiang, T. Xiao, L. Lu, M.O. Jones, P.P. Edwards, Chemical Communications (2011) 5512–5514.
- [35] H. Cölfen, M. Antonietti, Angewandte Chemie, International Edition 44 (2005) 5576–5591.
- [36] S. Tian, J. Liu, T. Zhu, W. Knoll, Chemistry of Materials 16 (2004) 4103–4108.
- [37] J. Liu, H. Bai, Y. Wang, Z. Liu, X. Zhang, D.D. Sun, Advanced Functional Materials 20 (2010) 4175–4181.
- [38] Z. Bian, J. Zhu, J. Wang, S. Xiao, C. Nuckolls, H. Li, Journal of the American Chemical Society 134 (2012) 2325–2331.
- [39] F. Dong, W. Kei, H.S.C. Lee, Z. Wu, M. Fu, S. Zou, Y. Huang, Journal of Materials Chemistry 21 (2011) 12428–12436.