Journal of Materials Chemistry A

COMMUNICATION

RSCPublishing

View Article Online View Journal | View Issue

Cite this: J. Mater. Chem. A, 2013, 1, 2406

Received 2nd November 2012 Accepted 14th December 2012

DOI: 10.1039/c2ta00942k

www.rsc.org/MaterialsA

Photocatalytic properties of hierarchical structures based on Fe-doped BiOBr hollow microspheres†

Guohua Jiang,^{*ab} Xiaohong Wang,^{ab} Zhen Wei,^{ab} Xia Li,^{ab} Xiaoguang Xi,^{ab} Ruanbing Hu,^{ab} Bolin Tang,^{ab} Rijing Wang,^{ab} Sheng Wang,^{ab} Tao Wang^{ab} and Wenxing Chen^{*ab}

Fe-doped BiOBr hollow microspheres were successfully prepared by a simple solvothermal method. The as-prepared samples exhibit excellent photocatalytic activity and electrochemical behaviour, attributed to the unique hollow structure and Fe doping, which is favorable for transfer of photogenerated carriers and enhancement of photoadsorption.

In recent years, many studies have been devoted to the arrangement of micro- and nanostructured building blocks into hierarchical structures. During this process, different building blocks, such as nanoparticles, nanofibres, and nanosheets, could self-assemble into higher level sophisticated architectures due to hydrogen bonding, electrostatic, and van der Waals forces.1-5 Among the hierarchical structures, hollow structures with remarkable interior space and shell have attracted extensive attention owning to their high specific area, low density and good permeation, and widespread potential applications in chemical reactors,6 sensors,7 catalysis8-11 and various new application fields.12-14 Numerous synthetic methods have been exploited to accelerate the realization of hollow microstructures, including conventional templating methods as well as newly emerging template-free methods.¹⁵⁻¹⁷ The templateassisted approach has been demonstrated to be very effective for the fabrication of hollow structures. However, this approach tends to be rather complicated, with the obvious drawback that the template removal process may damage the structural integrity of the final products, thereby increasing the complexity, and one-pot rational control of the hollow

architectures still remains a challenge.^{18,19} Therefore, new template-free approaches are emerging and some attractive attempts have been made in the controllable synthesis of hollow structured materials through simple ionic-mediated processes.^{20–22}

Semiconductor photocatalysis and electrochemical processes have been regarded as an effective resolution to organic pollutant removal and supercapacitor research.23-28 The conventional semiconductors (e.g. TiO2 and ZnO) are restricted by their deficient visible light absorption or high recombination rate of the photogenerated carriers.^{29,30} As a group of V-VI-VII semiconductors, bismuth oxyhalides are of great importance because of their optical properties and promising industrial applications, such as in photocatalysis, ferroelectric materials, pigments etc. 31-33 In particular BiOBr has received much interest because of its considerable visible light photocatalytic activity. It crystallizes in the tetragonal matlockite (PbFCl) structure, which comprises a layer of [Bi2O2] slabs interleaved by double slabs of halogen atoms.^{34,35} Although many efforts have been made for the enhancement of the photodegradation ability of BiOBr,^{22,32,33,36} the photocatalytic activity of BiOBr is far from efficient for practical applications and it is necessary to boost the photocatalytic efficiency and exploit the other properties.

Herein, a facile one-pot solvothermal method was used to achieve tuning of the structure and bandgap of the BiOBr semiconductor by Fe doping in a mixture of 2-methoxyethanol and iron chloride hexahydrate (FeCl₃·6H₂O), which not only acts as Fe doping source, but also plays a key role in the formation of the hollow structure. Time-dependent evolution of the crystal structure and morphology was investigated by XRD and FE-SEM in detail in order to elucidate the growth mechanism of the uniform Fe-doped BiOBr hollow microsphere structure. These Fe-doped BiOBr hollow microspheres exhibit highly efficient photocatalytic activity in the degradation of RhB and electrochemical characteristics in KCl solution, which is supposed to be associated with enhancement of the photoadsorption and the effective transfer of the photogenerated carriers.

^aKey Laboratory of Advanced Textile Materials and Manufacturing Technology (ATMT), Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China

^bDepartment of Materials Engineering, College of Materials and Textile, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China. E-mail: polymer_jiang@hotmail.com; wxchen@zstu.edu.cn; Tel: +86 571 86843527

 $[\]dagger$ Electronic supplementary information (ESI) available: Experimental section, XRD patterns, FE-SEM images, EDS spectra, N₂ adsorption–desorption, CV curves, and cycle degradation rate. See DOI: 10.1039/c2ta00942k

Fig. 1 presents typical field emission scanning electron microscopy (FE-SEM) images of Fe-doped BiOBr samples prepared at 160 °C for 24 h. As-prepared samples were found to contain intact microspheres as well as broken microspheres of 1–4 μ m in size (inset in Fig. 1A). The higher magnification microscopy image (Fig. 1A) shows the surface of the hollow microspheres, which are constructed by numerous interlaced nanosheets with thickness of about 20 nm. In addition, the shell of the hollow structure is confirmed by Fig. 1B, showing a hollow structure with a shell thickness of about 450 nm. The HR-TEM image of Fe-doped BiOBr shows a well-defined crystallinity of BiOBr with a lattice spacing of 2.77 Å, which is consistent with the *d*-spacing of the [110] reflection (see Fig. S1 in ESI⁺).

The crystallographic structure of Fe-doped BiOBr was further characterized by X-ray diffraction (XRD, Fig. 1C). All the diffraction peaks can be indexed to the tetragonal phase BiOBr whose lattice parameters are a = 3.915 Å, c = 8.076 Å (space group: P4/nmm, JCPDS 73-2061) before and after Fe doping (2θ \approx 25.26, 32.31, 39.43, 46.35, 47.77, 53.51, 57.31, 67.63, and 76.96° correspond well to (011), (110), (112), (020), (201), (211), (212), (220), and (130)). However, it is worth noting that all the characteristic peaks of Fe-doped BiOBr samples have a slight shift compared to those of BiOBr, which may attributed to the substitution of the Bi^{3+} ions ($r_{\text{Bi}} = 1.03$ Å) with the smaller radius Fe^{3+} ions ($r_{\text{Fe}} = 0.79$ Å).³⁶ Moreover, the characteristic peaks of Fe hybrid are not detected due to the high dispersion and low content of the Fe compound. The energy-dispersive X-ray spectroscopy (EDS) spectra (see Fig. S2 in ESI⁺) reveal the presence of Fe, Bi, O, and Br elements and the content of Fe doping is about 5 wt% (compared to BiOBr, see Table S1 in ESI[†]). In addition, the optical absorption properties of the as-prepared samples were determined by UV/Vis diffuse reflectance spectroscopy (Fig. 1D), revealing that Fe doping effectively increases the absorption under visible light. The bandgap of the as-prepared samples is estimated to be 1.67 eV by fitting to a



Fig. 1 (A) FE-SEM images, (B) the corresponding higher magnification image, (C) XRD patterns, and (D) UV/Vis diffuse reflectance spectra of the as-prepared Fe-doped BiOBr samples.

plot of Kubelka–Munk function *versus* energy (see Fig. S3 in ESI[†]). Furthermore, the porous structure of the Fe-doped BiOBr was also characterized by N₂ absorption analysis, which shows that the adsorbed volume of Fe-doped BiOBr sample is comparatively high (see Fig. S4 in ESI[†]). The BET specific surface area of the Fe-doped BiOBr sample was calculated to be $32.3 \text{ m}^2 \text{ g}^{-1}$, which is much larger than the value ($8.0 \text{ m}^2 \text{ g}^{-1}$) of BiOBr, due to the hollow structure of the former. The corresponding pore size distribution curve of the hollow microspheres displays a pore size distribution from 3 to 45 nm, centered at *ca.* 15 nm, which confirmed that the as-prepared samples are mesoporous (see inset in Fig. S4 in ESI[†]).

To investigate the formation mechanism of Fe-doped BiOBr hollow microspheres, the evolution process was examined thoroughly by XRD and FE-SEM. The crystallographic structures of the resultant samples collected at different reaction steps are presented in Fig. S5 in ESI.[†] It is found that all the samples are crystallized and the crystallization is improved by prolonging the reaction time. As the reaction times increase to 24 h, the emergent BiBr1.167, Bi2O3, FeCl3 and BiCl3 diffraction peaks gradually disappear and all the peaks can be assigned to tetragonal phase BiOBr. Moreover, the morphological transformations of nanosheets to hollow microspheres under varying reaction times can be clearly observed in Fig. 2. Before the solvothermal reaction, the main morphology of the product is nanosheets with organic coating (Fig. 2A). As shown in Fig. 2B, the coating is gone and irregular aggregations of nanosheets are the main yield, when the reaction is prolonged to 10 min. The nanosheets self-assemble to construct the flower-like microspheres after 15 min of thermal treatment (Fig. 2C). By prolonging the reaction time to 20 min, the hollowing process takes place in the inner core of the microsphere (Fig. 2D). Then an obvious hollowing effect is observed with a longer reaction time of 1 h, which is confirmed by Fig. 2E. When the reaction time exceeds 1.5 h, the prefect hollow microspheres are formed. No apparent increase in size for the microsphere when the reaction time is further extended to 24 h from the FE-SEM observation (Fig. 2F). Comparing to our preliminary investigation of BiOBr,32 the structure transformations of solid microspheres to hollow microspheres reveal the introduction of Fe is critical to the formation of hollow structures. The influences of the Fe-doped content on the structure of the final samples were also investigated (see Fig. S7 in ESI⁺). The results show that the asprepared products with the lowest Fe-doped content exhibit hollow microspheres and nanosheets. However, when the concentration of Fe doping was increased to 15%, the hollow microsphere structure was destroyed. Therefore, the concentration of iron chloride hexahydrate plays a key role in the formation of the perfect hollow microsphere structure. But the specific mechanism is not clear, remaining for further study.

On the basis of the above results, it is proposed that both oriented attachment and Ostwald ripening should play major roles in the formation of the nanosheet-assembled hollow microspheres and the evolution process is illustrated in Fig. 2G. At the first stage, BiOBr nanosheets were obtained when the CTAB was added into the solution containing Bi³⁺, Fe³⁺, and self-assembled to form microspheres *via* oriented attachment to



Fig. 2 FE-SEM images and the corresponding magnified images of the asprepared Fe-doped BiOBr samples at different stages: (A) 0 h, (B) 10 min, (C) 15 min, (D) 20 min, (E) 1 h and (F) 24 h; (G) schematic illustration of the possible formation process of a Fe-doped BiOBr hollow microsphere.

minimize their surface energy. As a solid microsphere composed of numerous nanosheets, the sheets in the inner core can be visualized as smaller spheres with higher curvature compared to those on the outer surface. Therefore, at the second stage, they could dissolve and merge into sheets on the outer surface because of the higher surface energy, resulting in the formation of hollow flower-like structures.^{7,21,37} Moreover, the carbonization of the organic coating on the surface of the nanosheets might also contribute to the formation the hollow structures in the solvothermal reaction.

Cyclic voltammetry (CV) measurement was used to investigate the electrochemical properties of the samples. As shown in Fig. 3A, Fe-doped BiOBr samples show high re/oxidative current peaks, while BiOBr do not display any peaks. This phenomenon reveals that Fe-doped BiOBr may exhibit better re/oxidative ability and electron transfer rate than BiOBr during chemical reaction.³⁸ In addition, the CV curves of the as-prepared Fedoped BiOBr microspheres recorded at different scan rates from



Fig. 3 (A) Cyclic voltammograms of Fe-doped BiOBr and BiOBr samples in KCI solution at a known scan rate (50 mV s⁻¹), (B) photocatalytic degradation of RhB over Fe-doped BiOBr, BiOBr, Ti-doped BiOBr, Ag/Ti-doped BiOBr samples.

20 mV s⁻¹ to 100 mV s⁻¹ over the potential range of -1.0 to 0.5 V (see Fig. S7 in ESI[†]) show the anodic peaks shifted towards positive potential and the cathodic peaks shifted towards negative potential. This result reveals that the as-prepared samples may exhibit pseudocapacitive behavior.27,39 In order to study the photoinduced charge separation efficiency of the as-prepared Fe-doped BiOBr samples, photocurrent transient response and Nyquist impedance experiments were carried out under visible light irradiation. Comparing to BiOBr, the produced photocurrent of Fe-doped BiOBr is much higher (Fig. S8 in ESI⁺). A higher photocurrent means that photoinduced electrons have transferred more effectively. Moreover, Nyquist impedance plots show the arc radius for the Fe-doped BiOBr electrode was much smaller than that of the BiOBr electrode, which further demonstrated that the Fe-doped BiOBr electrode displayed a much higher separation efficiency of photogenerated electron-hole pairs and faster charge-transfer than the BiOBr electrode at the solid-liquid interface. Therefore, doping Fe into BiOBr could improve the photocatalytic efficiency.

In addition, Rhodamine B (RhB), which is a typical fluorescent dye, was used as a model contamination to evaluate the photocatalytic activity of the samples. According to our

preliminary investigation,32,40 RhB self-photodegradation is almost negligible. The photocatalytic degradation of RhB over various photocatalysts based on BiOBr is shown in Fig. 3B. As observed, the hollow Fe-doped BiOBr samples display highly efficient photocatalytic activity, in which about 75% of RhB is degraded under daylight lamp irradiation (11 W and 25 Hz) for only 30 min, and all are catalyzed within 45 min. For comparison, Ag/Ti-doped BiOBr, Ti-doped BiOBr and BiOBr, which were obtained by a solvothermal method, could only degrade about 80%, 62% and 55%, respectively, of RhB after irradiation for 45 min. Provided that the photodegradation process is a pseudo-first-order reaction, the RhB degradation rate of Fedoped BiOBr (1.01 h⁻¹) is faster than those of Ag/Ti-doped BiOBr (0.82 h^{-1}), Ti-doped BiOBr (0.31 h^{-1}) and BiOBr (0.23 h^{-1}), which is attributed to the hollow architecture and Fe doping. The Fe doping sites and unique hollow structure of Fedoped BiOBr microspheres, which consist of numerous interlaced nanosheets with preferential orientation, are favorable for transfer of photogenerated carriers.^{36,40} Moreover, the higher BET surface area and mesopores provide more active sites for photocatalytic reaction. Besides the higher activity, durability is also indispensable for photocatalysts. In the recycling experiment of RhB photodegradation, Fe-doped BiOBr samples are mechanically robust, which can be reused five times with no significant decrease in activity (see Fig. S9 in ESI⁺).

In summary, a novel Fe-doped BiOBr photocatalyst with hollow microsphere structure was prepared by a simple solvothermal reaction. The Fe ions play a key role in Fe doping and the self-assembly process of the hollow structures. The asprepared samples exhibit excellent photocatalytic ability in the photodegradation of RhB, which is attributed to the hollow structure and Fe doping, which are favorable for transfer of photogenerated carriers and enhance photoadsorption. Moreover, electrochemical measurement confirmed that Fe-doped BiOBr may have bright prospects in the field of supercapacitor materials.

Acknowledgements

This work was financially supported by the Qianjiang Talents Project of Zhejiang Province (2010R10023), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, the State Education Ministry (1001603-C), the Natural Science Foundation of Zhejiang Province (Y4100045), Training Foundation for the Excellent Young Talents by the Key Laboratory of Advanced Textile Materials and Manufacturing Technology (ATMT), Ministry of Education (2011QN04) and the National Natural Science Foundation of China (51133006).

Notes and references

- 1 X. W. Lou, L. A. Archer and Z. Yang, *Adv. Mater.*, 2008, **20**, 3987.
- 2 M. Yang, H. You, Y. Zheng, K. Liu, G. Jia, Y. Song, Y. Huang, L. Zhang and H. Zhang, *Inorg. Chem.*, 2009, **48**, 11559.
- 3 C. Sun, S. Rajasekhara, J. B. Goodenough and F. Zhou, *J. Am. Chem. Soc.*, 2011, **133**, 2132.

- 4 S. Zhang and H. C. Zeng, Chem. Mater., 2009, 21, 871.
- 5 J. S. Moore and M. L. Kraft, Science, 2008, 320, 620.
- 6 M. R. Kim and D. -J. Jang, Chem. Commun., 2008, 5218.
- 7 P. Hu, X. Zhang, N. Han, W. Xiang, Y. Cao and F. Yuan, *Cryst. Growth Des.*, 2011, **11**, 1520.
- 8 J. Yu and J. Zhang, Dalton Trans., 2010, 39, 5860.
- 9 J. Xia, S. Yin, H. Li, H. Xu, Y. Yan and Q. Zhang, *Langmuir*, 2011, 27, 1200.
- 10 F. Bai, Z. Sun, H. Wu, R. E. Haddad, X. Xiao and H. Fan, *Nano Lett.*, 2011, 11, 3759.
- 11 F. Kong, M. Li, X. Yao, J. Xu, A. Wang, Z. Liu and G. Li, *CrystEngComm*, 2012, 14, 3858.
- 12 Y. Wang, X. Su and S. Lu, J. Mater. Chem., 2012, 22, 1969.
- 13 P. Hu, L. Yu, A. Zuo, C. Guo and F. Yuan, *J. Phys. Chem. C*, 2009, **113**, 900.
- 14 M. -F. Lin, V. K. Thankur, E. J. Tan and P. S. Lee, *J. Mater. Chem.*, 2011, **21**, 16500.
- 15 C. Cao, Z. Cui, C. Chen, W. Song and W. J. Cai, *J. Phys. Chem. C*, 2010, **114**, 9865.
- 16 Z. Wang, J. Hou, S. Jiao, K. Huang and H. Zhu, *J. Mater. Chem.*, 2012, 22, 21972.
- 17 G. Chen, C. Xu, X. Song, S. Xu, Y. Ding and S. Sun, *Cryst. Growth Des.*, 2008, **8**, 4449.
- 18 X. Wang, M. Liao, Y. Zhong, J. Y. Zheng, W. Tian, T. Zhai, C. Zhi, Y. Ma, J. Yao, Y. Bando and D. Golberg, *Adv. Mater.*, 2012, 24, 3421.
- 19 X. W. Lou, C. Yuan, E. Rhoades, Q. Zhang and L. A. Archer, *Adv. Funct. Mater.*, 2006, **16**, 1679.
- 20 J. Xia, S. Yin, H. Li, H. Xu, Y. Yan and Q. Zhang, *Langmuir*, 2011, 27, 1200.
- 21 W. Cai, J. Yu, S. Gu and M. Jaroniec, *Cryst. Growth Des.*, 2010, **10**, 3977.
- 22 H. Cheng, B. Huang, Z. Wang, X. Qin, X. Zhang and Y. Dai, *Chem.-Eur. J.*, 2011, **17**, 8039.
- 23 H. S. Hafez, Mater. Lett., 2009, 63, 1471.
- 24 M. Zou, M. Du, H. Zhu, C. Xu and Y. Fu, *J. Phys. D: Appl. Phys.*, 2012, **45**, 325302.
- 25 G. Jiang, X. Zheng, Y. Wang, T. Li and X. Sun, *Powder Technol.*, 2011, **207**, 465.
- 26 R. Wang, G. Jiang, Y. Ding, Y. Wang, X. Sun, X. Wang and W. Chen, *ACS Appl. Mater. Interfaces*, 2011, 3, 4154.
- 27 (a) Q. Wang, B. Liu, X. Wang, S. Ran, L. Wang, D. Chen and G. Shen, J. Mater. Chem., 2012, 22, 21647; (b) R. Wang, X. Wang, X. Xi, R. Hu and G. Jiang, Adv. Mater. Sci. Eng., 2012, 409379; (c) Y. Fang, R. Wang, G. Jiang, H. Jin, Y. Wang, X. Sun, S. Wang and T. Wang, Bull. Mater. Sci., 2012, 35, 495; (d) G. Jiang, X. Wang, Y. Zhou, R. Wang, R. Hu, X. Xi and W. Chen, Mater. Lett., 2012, 89, 59; (e) L. Tan, S. Chai and A. R. Mohamed, ChemSusChem, 2012, 5, 1868.
- 28 L. Zhao, L. Fan, M. Zhou, H. Guan, S. Qiao, M. Antonietti and M. Titirici, *Adv. Mater.*, 2010, 22, 5202.
- 29 G. Jiang, R. Wang, H. Jin, Y. Wang, X. Sun, S. Wang and T. Wang, *Powder Technol.*, 2011, 212, 284.
- 30 H. Qin, W. Li, Y. Xia and T. He, *ACS Appl. Mater. Interfaces*, 2011, 3, 3152.

- 31 M. Shang, W. Wang and L. Zhang, J. Hazard. Mater., 2009, 167, 803.
- 32 R. Wang, G. Jiang, X. Wang, R. Hu, X. Xi, S. Bao, Y. Zhou, T. Tong, S. Wang, T. Wang and W. Chen, *Powder Technol.*, 2012, **228**, 258.
- 33 H. Cheng, B. Huang, P. Wang, Z. Wang, Z. Lou, J. Wang, X. Qin, X. Zhang and Y. Dai, *Chem. Commun.*, 2011, 47, 7054.
- 34 W. Wang, F. Huang, X. Lin and J. Yang, *Catal. Commun.*, 2008, **9**, 8.
- 35 Y. Feng, L. Li, J. Li, J. Wang and L. Liu, *J. Hazard. Mater.*, 2011, **192**, 538.

- 36 G. Jiang, R. Wang, X. Wang, X. Xi, R. Hu, Y. Zhou, S. Wang, T. Wang and W. Chen, ACS Appl. Mater. Interfaces, 2012, 4, 4440.
- 37 L. Han, D. Wang, Y. Lu, T. Jiang, B. Liu and Y. Lin, J. Phys. Chem. C, 2011, 115, 22939.
- 38 L. Zhou, W. Wang, H. Xu and S. Sun, Cryst. Growth Des., 2008, 8, 3595.
- 39 H. Ming, H. Zhang, Z. Ma, H. Huang, S. Lian, Y. Wei, Y. Liu and Z. Kang, *Appl. Surf. Sci.*, 2012, **258**, 3846.
- 40 S. George, S. Pokhrel, Z. Ji, B. L. Henderson, T. Xia, L. Li, J. I. Zink, A. E. Nel and L. M\u00e4dler, *J. Am. Chem. Soc.*, 2011, 133, 11270.