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Rod-in-tube nanostructure of MgFe_2O_4 : electrospinning synthesis and photocatalytic activities of tetracycline

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Magnesium ferrite (MgFe_2O_4) nanofibers were synthesized by direct annealing of electrospun precursor fibers using an appropriate heat treatment process. The crystal structure, morphology and surface area of the as-synthesized MgFe_2O_4 nanofibers were investigated by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy, respectively. The optical properties of the as-synthesized products were studied through ultraviolet-visible and photoluminescence spectroscopy. Due to its potential application in photocatalysis, the photocatalytic degradation of tetracycline (TC) was conducted, and the result indicated that MgFe_2O_4 showed a better photocatalytic degradation ratio (1.5 times and 2 times) of TC than the others under visible-light irradiation, which may be due to the unique rod-in-tube structure, and larger specific area and the larger specific surface area could absorb more catalyst and provide more active sites.

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1 Introduction

Environmental problems have undoubtedly become one of the greatest problems and have attracted worldwide attention in the modern society.^{1,2} Tetracycline (TC), a widely used antibiotic, is usually released into the water environment³ and directly affects the environment by disrupting the ecosystem equilibrium.⁴ Natural bacteria exposed to residual antibiotics, such as TC, could modify their genetic information, develop higher antibiotic resistance and result in multi-resistant strains of micro-organisms.⁵ Fortunately, semiconductor-based photocatalysts provide a good tool for the degradation of antibiotics, and much effort has been focused on the degradation of TC by photocatalysis.^{6–8} Conventional photocatalysts such as TiO_2 , CdS, and ZnO have been reported recently,^{9–12} but due to their disadvantages (inability to respond to visible light, poor stability, and poor ability to degrade), their practical application is restricted. Therefore, new-type visible light driven photocatalysts with excellent stability and high efficiency for TC degradation are still desired.

Multi-metal oxides are of particular interest due to their remarkable magnetic, electrical, and optical properties. Among

them, MgFe_2O_4 , a member of spinel family, is found to be a promising visible light photocatalyst due to its narrow band gap (2.0 eV) and corrosion resistance.¹³ In the past few decades, there have been a variety of reports on synthesis of MgFe_2O_4 using methods such as hydrothermal, solvothermal, solid synthesis, sol-gel, and microwave-assisted methods.^{14–18} However, these conventional synthesis methods could not effectively control the morphology and size, therefore, searching a new method for the controllable synthesis of MgFe_2O_4 is urgent.

Among these fabrication methods, the electrospinning technique has been extensively exploited as a simple and versatile controllable synthesis method for generating 1D nanostructures of various different materials.¹⁹ The electrospinning method has demonstrated its capability to prepare a range of interesting structures, such as porous nanofibers,^{20,21} nanotubes,²² nanobelts,²³ core-shell,²⁴ tube-in-tube,²⁵ side-by-side,²⁶ hollow tubes,²⁷ and triaxial structures.²⁸

Herein, we report the synthesis of MgFe_2O_4 by electrospinning and subsequent direct annealing processes. Compared with the above-mentioned methods, only simple electrospinning and calcination are required, without a coating procedure and a special spinner. In our experiments, a mixed ethanol and water solution was used as a solvent instead of the use of toxic solvents such as DMF,^{29,30} avoiding the pollution of the environment. The unique rod-in-tube structure nanofiber morphology and larger specific surface area of MgFe_2O_4 endow it better photocatalytic properties.

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2 Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP, K-90, $M_w = 1\,300\,000$) was purchased from tianjin tiantai Fine Chemical Co., Ltd. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (purchased from Beijing Chemical Reagent Co., Ltd), $\text{Mg}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (purchased from Shanghai Shanpu Chemical Co., Ltd) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%, purchased from tianjin Rionlon BoHua Medical Chemistry Co., Ltd) were used as received. Other reagents were commercially available and were of analytical reagent grade.

2.2. Preparation of MgFe_2O_4 nanofibers

4.04 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1.28 g of $\text{Mg}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were added into a mixture of 2.5 mL of ethanol and 7.5 mL of water, and then 1.3 g of PVP was added into the above solution to increase viscosity. Then the mixture was magnetically stirred for several hours at room temperature (RT) to form a homogeneous precursor solution. In the subsequent electrospinning process, the spinnable precursor sol was loaded into a glass syringe equipped with a stainless steel needle. A high voltage of 25 kV was supplied by a direct-current power supply. The distance between the tip of the needle and the collector was 15 cm. The humidity is about 40–50% and temperature is room temperature (25–30 °C). For the following thermolysis process, the as-spun fibers were placed in a muffle furnace and calcined at a temperature of 500 °C for 2 h to remove PVP and obtain MgFe_2O_4 samples under different conditions of heating treatment.

2.3. Characterization

To analyze the crystal structures of the samples, the X-ray diffraction (XRD) measurements were conducted on an X-ray diffractometer using $\text{Cu-K}\alpha$ radiation (XRD, Panalytical X'Pert Pro) from 10 to 80°. The morphology and microstructures of the as-spun fibers and calcined samples were analyzed using a field emission scanning electron microscope (FESEM, Hitachi S-4800) and a transmission electron microscope (TEM, Hitachi JEM-2010). The BET surface area was calculated from N_2 adsorption–desorption measurements by using a Beesd instrument technology (Beijing) Co., Ltd 3H-2000PM2 Surface Area & Pore Size analyzer. In addition, UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrometer. Photoluminescence spectra were recorded on a QuantaMaster & TimeMaster Spectrofluorometer. The room-temperature photoluminescence spectrum (PL) was collected using a Hitachi F-4500 spectrofluorometer with an excitation wavelength of 440 nm.

2.4. Photocatalytic activity measurement

The photodegradative reaction for TC was carried out at room temperature under visible light. The photochemical reactor contained 10 mg of the sample and 50 mL of TC solution (10 mg L^{-1}). To determine the initial absorbency of samples, the reactor was kept in darkness for 60 min to reach absorption equilibrium. The photochemical reactor was irradiated with a 150 W Xenon lamp which was located with a distance of 8 cm at one side of the containing solution. UV light with wavelengths less than 420 nm was removed using a UV-cutoff filter.

The sampling analysis was conducted at 15 min intervals. The photocatalytic degradation ratio (DR) was calculated by the following formula:

$$\text{DR} = \left(1 - \frac{A_i}{A_0}\right) \times 100\%$$

A_0 is the initial absorbency of TC that reached absorption equilibrium, while A_i is the absorbency after the sampling analysis. The TC concentration was measured using a UV-vis spectrophotometer with the maximum absorption wavelength at 357 nm.

3 Result and discussion

3.1. Morphology and structure

The phase of the synthesized MgFe_2O_4 nanofibers is identified by XRD characterization. Fig. 1 shows the XRD patterns of precursor fibers after annealing at different heating rates. As shown in Fig. 1, all diffraction peaks of the three samples can be indexed to spinel MgFe_2O_4 . When the heating rate increases, the diffraction peaks gradually enhance, which indicates the enhanced crystallinity and the growth of MgFe_2O_4 nanocrystals. No other crystalline impurities are detected, which indicates that all the products are in correspondence with pure MgFe_2O_4 (JCPDS 36-0398).

The morphology and microstructure of the samples were obtained by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), Fig. 2 shows the SEM and TEM images of the prepared samples. Uniform nanofibers and nanobelts, which are *ca.* 400 nm in diameter and from several to ten of micrometers in length, are shown in Fig. 2a. Fig. 2b shows that the rough nanofibers are rod-in-tube nanostructures and there exists nanorod in them. The formation of a rough surface is attributed to the growth of MgFe_2O_4 nanocrystals at the higher heating rate in the second step. The average length is up to tens of micrometers with the average diameter of *ca.* 450 nm. In Fig. 2c, a nanobelt is coating onto the nanofibers, and several other nanofibers are smooth without any nanobelt. The TEM images in Fig. 2d–f further revealed the internal structure of the obtained products. Fig. 2d shows a solid nanofiber structure. As shown in Fig. 2e and f, in the intensive

Fig. 1 Typical XRD pattern of the prepared MgFe_2O_4 nanofibers: (a) at the heating rate of 1 °C min^{-1} to 500 °C, (b) at the heating rate of 1 °C min^{-1} to 400 °C and 5 °C min^{-1} to 500 °C, and (c) at the heating rate of 5 °C min^{-1} to 500 °C.

Fig. 2 SEM and TEM images of the prepared MgFe_2O_4 nanofibers: (a) and (d) at the heating rate of $1\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$, (b) and (e) at the heating rate of $1\text{ }^\circ\text{C min}^{-1}$ to $400\text{ }^\circ\text{C}$ and $5\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$, and (c) and (f) at the heating rate of $5\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$.

contrast between the dark center and the dark edges, there exists light space, which demonstrates that the obtained fibers are rod-in-tube nanostructures, which is consistent with the SEM results. Moreover, it is clear that the wall of the rod-in-tube structure is assembled by irregular nanoparticles.

Based on the experiment data and analyses above, a possible formation mechanism of the MgFe_2O_4 rod-in-tube produced in this study is proposed, whose schematic diagrams are shown in Scheme 1. Initially, a sol-gel composed of PVP, ethanol/deionized water, iron nitrate, and magnesium nitrate was prepared for electrospinning. After the electrospinning process, nanorods and nanobelts were formed when the nanofibers were collected on the collector. At the heating rate of $1\text{ }^\circ\text{C min}^{-1}$, due to the slow heating rate, the morphology remained unchanged, and nanofibers and nanobelts were smooth on the surface (entry a in Fig. 2). When the

heating rate increased to $5\text{ }^\circ\text{C min}^{-1}$, the nanobelts gradually coated on the surface of the nanofibers and in the meantime the nanoparticles which formed the nanobelts gradually became large so the surface of the rod-in-tube nanostructure is rough (entry b in Fig. 2). In the end, the unique rod-in-tube structure was formed. If the heating rate was $5\text{ }^\circ\text{C min}^{-1}$ from initial, a large number of nanobelts will reunite to form a rod-like structure, so the nanobelts disappeared, which was not conducive to the formation of a rod-in-tube structure, and therefore the structure of rod-in-tube decreased (entry c in Fig. 2).

3.2. UV-vis diffuse reflectance spectra

The optical absorption properties of the photocatalysts are one of the most important parameters in the field of photocatalysis. The diffuse reflectance spectrum (DRS) of the as-prepared MgFe_2O_4 nanofiber samples is shown in Fig. 3. The absorbance in the 400–600 nm range is observed. From Fig. 3, it is obvious that MgFe_2O_4 samples respond to visible

Scheme 1 Schematic diagram illustrating the possible formation and growth mechanism of the unique MgFe_2O_4 rod-in-tube structure.

Fig. 3 UV-vis absorption spectra of MgFe_2O_4 nanofibers: (a) at the heating rate of $1\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$, (b) at the heating rate of $1\text{ }^\circ\text{C min}^{-1}$ to $400\text{ }^\circ\text{C}$ and $5\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$, and (c) at the heating rate of $5\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$.

Fig. 4 Photocatalytic degradation ratios (detection wavelength is 357 nm) of MgFe_2O_4 under visible light: (a) at the heating rate of $1\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$, (b) at the heating rate of $1\text{ }^\circ\text{C min}^{-1}$ to $400\text{ }^\circ\text{C}$ and $5\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$, and (c) at the heating rate of $5\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$.

light, which is due to their narrow band (2.0 eV). They all share the similar UV-vis curves, and sample b has superior absorption spectroscopy compared to the others, which may be attributed to its unique structure. Besides they also exhibit the magnetic properties. These two properties (absorption in the visible range and magnetism) exhibited by MgFe_2O_4 make this material attractive for magnetically separable and recyclable photocatalyst materials.³¹

3.3. Photocatalytic properties

Antibiotics are widely used in human life. It was usually released into the water environment and directly affects the

environment by disrupting the ecosystem equilibrium. TC, a popular broad-spectrum antibacterial agent, has been widely applied in bacterial infection treatment. Therefore, there are serious threats to the ecosystem and human health if TC is released into the environment. So, the degradation of TC has been established to be one of the most promising technologies for environmental remediation.³²

Based on the interesting absorption spectra and unique structure, the photocatalytic activity of MgFe_2O_4 was studied on degradation of TC in an aqueous solution (10 mg L^{-1}). During the process of photo-degradation, the major absorbance (ca. 357 nm) from TC in the solution gradually decreased under visible light ($\lambda > 420\text{ nm}$) for 2 h, which suggested the significant photodegradation of TC by MgFe_2O_4 .

The photocatalytic activities of the as-prepared samples were evaluated by the degradation of the antibiotic under visible light irradiation. TC was chosen as a representative hazardous antibiotic to evaluate the photocatalytic performance. Fig. 4 shows the photocatalytic performance of the synthesized MgFe_2O_4 under different conditions of heating treatment under visible light ($\lambda > 420\text{ nm}$). As shown in Fig. 4, sample b exhibits an excellent photocatalytic degradation ratio of TC (64.4%) after irradiation for 2 h under visible light, which is 50% more than the others under the same conditions. This may be ascribed to the special rod-in-tube nanostructure, which has superior absorption spectroscopy. In order to check the stability of the catalyst, we have made an error bar analysis. Fig. 4 indicates that the error range is small, which confirms that it is relatively stable.

Fig. 5 Nitrogen adsorption-desorption isotherms and pore size distribution (a) at the heating rate of $1\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$, (b) at the heating rate of $1\text{ }^\circ\text{C min}^{-1}$ to $400\text{ }^\circ\text{C}$ and $5\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$, and (c) at the heating rate of $5\text{ }^\circ\text{C min}^{-1}$ to $500\text{ }^\circ\text{C}$.

Table 1 Specific surface area (S_{BET}), total pore volume (V_{pore}) and average pore width (d_{pore}) of the as-prepared products

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ($\text{cm}^3 \text{g}^{-1}$)	d_{pore} (nm)
a	15.0933	0.2115	17.38
b	19.0752	0.2093	17.61
c	16.3916	0.1839	15.30

3.4. BET and PL properties of the MgFe_2O_4 samples

Fig. 5 shows the N_2 absorption–desorption isotherms and pore size distribution. The materials exhibit absorption–desorption isotherms which can be attributed to type IV according to the classification of IUPAC³³ with a small hysteresis loop (type H3) due to the capillary condensation process in the mesopores.³⁴ The specific surface area of each sample is estimated according to the BET method. The pore size distributions are obtained from the Barrett–Joyner–Halenda (BJH) method. According to the calculation, the results are summarized in Table 1. From Table 1 we could see that the specific surface areas, total pore volume and average pore width of all the samples are nearly the same. From the data above, we could see that the special structure cannot alter the specific surface areas much, but the slightly changed specific surface areas do affect the photocatalytic performance and the larger specific area do enhance its photocatalytic activity.

To further understand the higher photocatalytic activity of sample b for the degradation of TC than the other two, we probe into a possible reason on the basis of experimental analysis. Fig. 6 shows photoluminescence (PL) spectra of the samples. The fluorescence intensity is directly proportional to the electron hole recombination probability,³⁵ and the lower PL intensity indicates the decrease in the recombination rate. The results shown in Fig. 6 indicate that sample b shares the lowest fluorescence intensity when compared with the others, which may be due to the unique rod-in-tube structure, leading to the enhancement of electron and hole separation and improving the photocatalytic performance.

For further understanding the role of photogenerated radical species and the underlying reaction mechanism for the degradation of TC under visible light irradiation, a series of controlled

Fig. 7 Controlled experiments using different radical scavengers for the photocatalytic degradation of TC; (a) reaction in the absence of radical scavengers, (b) reaction with AgNO_3 as a radical scavenger for photo-generated electrons, (c) reaction with isopropanol as a radical for hydroxyl scavengers, and (d) reaction with triethanolamine as a scavenger for photogenerated holes under visible light irradiation for 2 h.

experiments were conducted. Fig. 7 shows the results of adding different radical scavengers over the MgFe_2O_4 photocatalyst reaction system under visible light irradiation. When the radical scavenger, isopropanol, for hydroxyl is added into the reaction system, the degradation rate of TC is inhibited (entry c in Fig. 7). A significant inhibition phenomenon for the photocatalytic reaction is observed when the triethanolamine scavenger for holes is added (entry d in Fig. 7), while when the AgNO_3 scavenger for electrons is added into the reaction system, it almost remains the same but rises a little (entry b in Fig. 7), which may be due to the fact that part of electrons are captured by AgNO_3 and therefore inhibit the recombination of electron and hole pairs and increase the numbers of holes. These results clearly suggest that the photocatalytic degradation of TC over MgFe_2O_4 is primarily driven by photogenerated holes and hydroxyl.

On the basis of the experimental results, we have proposed a possible mechanistic pathway. As depicted in Fig. 8, when the visible light irradiates onto the catalyst, e^- changes from the ground state to the excited state, and transfers from the valence band to the conduction band, which is the separation of

Fig. 6 Photoluminescence (PL) spectra of the photocatalysts (excitation wavelength = 440 nm) (a) at the heating rate of 1°C min^{-1} to 500°C , (b) at the heating rate of 1°C min^{-1} to 400°C and 5°C min^{-1} to 500°C , and (c) at the heating rate of 5°C min^{-1} to 500°C .

Fig. 8 Illustration of the proposed possible reaction mechanism for the photocatalytic degradation of TC over MgFe_2O_4 under visible light irradiation.

electron hole pairs. The excited e^- which is transferred to the conduction band reacts with O_2 and produces $\bullet OH$ radicals. The as-produced $\bullet OH$ radicals can then degrade the TC molecules into CO_2 and H_2O . Meanwhile h^+ in the valence band can directly degrade the TC molecules into CO_2 and H_2O and a small amount of h^+ produces $\bullet OH$ to degrade TC.^{36–39} From the analyses above, it can be concluded that h^+ and $\bullet OH$ are the main active species of $MgFe_2O_4$ in aqueous solution under visible light irradiation.

4 Conclusions

In summary, $MgFe_2O_4$ nanofibers have been successfully fabricated by direct annealing of electrospun precursor fibers. Compared with other methods for preparing nanofibers by electrospinning, no toxic substance such as DMF is used and only environmentally friendly ethanol and deionized water are required, which provide a potential application in synthesis. The photocatalytic degradation of tetracycline under visible light is conducted. The as-obtained products which have a unique rod-in-tube nanostructure exhibited a better photocatalytic degradation ratio (64.4%) of tetracycline than the others under visible light irradiation, which may be due to the unique rod-in-tube structure, small diameter in size and large specific area. Furthermore, we study the degradation process of the as-obtained products and propose possible reaction mechanisms. The results show that holes and hydroxyl are the main active species of $MgFe_2O_4$ in the process of degradation TC under visible light irradiation. Our work provides a potential application in fabricating special structure nanomaterials in a facial and environmentally friendly way.

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References

- 1 P. M. Martins, V. Gomez, A. C. Lopes, C. J. Tavares, G. Botelho, S. Irueta and S. Lanceros-Mendez, *J. Phys. Chem. C*, 2014, **118**, 27944.
- 2 J. G. Yu, S. H. Wang, J. X. Low and W. Xiao, *Phys. Chem. Chem. Phys.*, 2013, **15**, 16883.
- 3 F. Baquero, J. L. Martinez and R. Canton, *Curr. Opin. Biotechnol.*, 2008, **19**, 260.
- 4 C. Tixier, H. P. Singer, S. Oellers and S. R. Müller, *Environ. Sci. Technol.*, 2003, **37**, 1061.
- 5 D. M. Bila and M. Dezotti, *Quím. Nova*, 2003, **26**, 523.
- 6 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37.
- 7 R. Hao, X. Xiao, X. X. Zuo, J. M. Nan and W. D. Zhang, *J. Hazard. Mater.*, 2012, **209**, 137.
- 8 M. Brigante and P. C. Schulz, *J. Hazard. Mater.*, 2011, **192**, 1597.
- 9 X. D. Zhu, Y. J. Wang, R. J. Sun and D. M. Zhou, *Chemosphere*, 2013, **92**, 925.
- 10 B. Sun, A. V. Vorontsov and P. G. Smirniotis, *J. Hazard. Mater.*, 2011, **186**, 1147.
- 11 Y. B. Liu, X. J. Gan, B. X. Zhou, B. T. Xiong, J. H. Li, C. P. Dong, J. Bai and W. M. Cai, *J. Hazard. Mater.*, 2009, **171**, 678.
- 12 R. A. Palominos, M. A. Mondaca, A. Giraldo, G. Peñuela, M. Pérez-Moya and H. D. Mansilla, *Catal. Today*, 2009, **144**, 100.
- 13 H. G. Kim, P. H. Borse, J. S. Jang, E. D. Jeong, O. S. Jung, Y. J. Suh and J. S. Lee, *Chem. Commun.*, 2009, 5889.
- 14 Y. H. Yin, B. Zhang, X. T. Zhang, J. J. Xu and S. T. Yang, *J. Sol-Gel Sci. Technol.*, 2013, **66**, 540.
- 15 M. G. Naseri, M. H. M. Ara, E. B. Saion and A. S. Halim, *J. Magn. Magn. Mater.*, 2014, **350**, 141.
- 16 M. R. Barati, C. Selomulya and K. Suzuki, *J. Appl. Phys.*, 2014, **115**, 17.
- 17 H. W. Liu and H. F. Liu, *J. Electron. Mater.*, 2014, **43**, 2553.
- 18 S. Ilhan, S. G. Izotova and A. A. Komlev, *Ceram. Interfaces*, 2015, **41**, 577.
- 19 D. Li and Y. N. Xia, *Adv. Mater.*, 2004, **16**, 1151.
- 20 Y. Z. Zhang, Y. Feng, Z. M. Huang, S. Ramakrishna and C. T. Lim, *Nanotechnology*, 2006, **17**, 901.
- 21 X. Zhang, V. Thavasi, S. G. Mhaisalkar and S. Ramakrishna, *Nanoscale*, 2012, **4**, 1707.
- 22 W. Wang, J. Y. Zhou, S. S. Zhang, J. Song, H. G. Duan, M. Zhou, C. S. Gong, Z. Bao, B. A. Lu, X. D. Li, W. Lan and E. Q. Xie, *J. Mater. Chem.*, 2010, **20**, 9068.
- 23 Y. Wang, Y. R. Su, L. Qiao, L. X. Liu, Q. Su, C. Q. Zhu and X. Q. Liu, *Nanotechnology*, 2011, **22**, 225702.
- 24 Z. Sun, E. Zussman, A. L. Yarin, J. H. Wendorff and A. Greiner, *Adv. Mater.*, 2003, **15**, 1929.
- 25 L. Lang, D. Wu and Z. Xu, *Chem. – Eur. J.*, 2012, **18**, 10661.
- 26 S. Jiang, Q. Jin and S. Agarwal, *Macromol. Mater. Eng.*, 2014, **299**, 1298.
- 27 D. Li and Y. Xia, *Nano Lett.*, 2004, **4**, 933.
- 28 S. Jiang, G. Duan, E. Zussman, A. Greiner and S. Agarwal, *ACS Appl. Mater. Interfaces*, 2014, **6**, 5918.
- 29 S. Maensiri, M. Sangmanee and A. Wiengmoon, *Nanoscale Res. Lett.*, 2009, **4**, 221.
- 30 R. Dom, R. Subasri, K. Radha and P. H. Borse, *Solid State Commun.*, 2011, **151**, 470.
- 31 S. Muhammad, J. L. Liu, A. Zahid, S. Imran, F. W. Muhammad, P. Riffat and N. Muhammad, *Mater. Chem. Phys.*, 2013, **139**, 566.
- 32 X. Xiao, R. P. Hu, C. Liu, C. L. Xing, X. X. Zuo, J. M. Nan and L. S. Wang, *Chem. Eng. J.*, 2013, **225**, 790.
- 33 S. Lowell, J. E. Shields, M. A. Thomas and M. Thommes, *J. Am. Chem. Soc.*, 2005, **127**, 14117.

- 34 L. V. C. Lima, M. Rodriguez, V. A. A. Freitas, T. E. Souza, A. E. H. Machado, A. O. T. Patrocinio, J. D. Fabris, L. C. A. Oliveira and M. C. Pereira, *Appl. Catal., B*, 2015, **165**, 579.
- 35 E. C. Su, B. S. Huang, C. C. Liu and M. Y. Wey, *Renew. Energy*, 2015, **75**, 266.
- 36 S. Q. Liu, N. Zhang, Z. R. Tang and Y. J. Xu, *ACS Appl. Mater. Interfaces*, 2012, **4**, 6378.
- 37 G. H. Zhang, W. S. Guan, H. Shen, X. Zhang, W. Q. Fan, C. Y. Lu, H. Y. Bai, L. S. Xiao, W. Gu and W. D. Shi, *Ind. Eng. Chem. Res.*, 2014, **53**, 5443.
- 38 P. Li, C. B. Liu, G. L. Wu, Y. Heng, S. Lin, A. Ren, K. H. Lv, L. S. Xiao and W. D. Shi, *RSC Adv.*, 2014, **4**, 47615.
- 39 M. Q. Yang, N. Zhang and Y. J. Xu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1156.