A spray pyrolysis synthesis of MnFe$_2$O$_4$/SnO$_2$ yolk/shell composites for magnetically recyclable photocatalyst

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Article info
Article history:
Received 27 February 2017
Received in revised form 4 April 2017
Accepted 12 April 2017
Available online 12 April 2017

Keywords:
Composite materials
Magnetic materials
XPS
X-ray techniques
Microstructure

Abstract
The MnFe$_2$O$_4$/SnO$_2$ yolk/shell structured composites were synthesized through an organics assisted spray pyrolysis process. The yolk/shell structure of as-synthesized particles was confirmed by both SEM and TEM, indicating that solid MnFe$_2$O$_4$ particle was captured inside a hollow SnO$_2$ particle. The crystallization was investigated by XRD, which confirmed the existence of both SnO$_2$ and MnFe$_2$O$_4$ phases. The VSM characterization showed that the yolk/shell structure had good magnetic properties. The photocatalytic performance of MnFe$_2$O$_4$/SnO$_2$ yolk/shell particles was investigated through a methyl orange degradation reaction under UV irradiation. The stability of the particles was also investigated by running the reactions in four cycles.

1. Introduction
Tin dioxide (SnO$_2$) is a typical semiconductor material with a wide band gap (3.6 eV) [1]. The research of SnO$_2$ has been a great interest of scientists due to its wide application in gas-sensor devices, water treatment, and energy storage [2–5]. As one of the important applications, SnO$_2$ can be used as a heterogeneous catalyst to degrade the organic pollutants in water through photo-catalytic reactions [6–9]. Many different methods have been proposed to synthesize SnO$_2$, including sol-gel, hydrolysis, electro-chemical oxidation, and chemical precipitation [10], and different morphology of the products, such as nanorods, nanotubes, hollow spheres, and nanodisks [6,8,9,11], are reported. Their photocatalytic activities were evaluated, and some of them are showing high performance for waste water treatment [8,9]. However, to separate the photocatalysts from the water after reaction is currently limited to filtration. This has been a great technical challenge, to a large scale waste water treatment. To solve this problem, Fe$_3$O$_4$/SnO$_2$ yolk/shell structured particles were synthesized by Zhang et al. [12]. Due to the high magnetization of Fe$_3$O$_4$, the catalyst could be easily separated from the water by a magnet. However, this synthesis requires complicated chemical processes, and generates pollutants to the environments. Herein, an environmental friendly, and easy synthesis of MnFe$_2$O$_4$/SnO$_2$ particles was proposed. MnFe$_2$O$_4$ was captured inside hollow SnO$_2$, forming a yolk/shell structure. MnFe$_2$O$_4$ is selected, instead of other spinel ferrites, because its low coercivity, which could prevent magnetic agglomeration, and high magnetization for magnetic separation.

2. Experimental
The synthesis of MnFe$_2$O$_4$ was based on a previous report with little modification [13]. The as-synthesized MnFe$_2$O$_4$ particles (1 g) and 0.05 mol Sn(NO$_3$)$_2$ were dispersed into ethylene glycol (EG, 10 mL) and water (90 mL), and magnetically stirred for 30 min. The MnFe$_2$O$_4$ dispersed solution was then transferred to an ultrasonic nebulizer. The water droplets generated by nebulizer were carried to a horizontal furnace (integral diameter: 10 cm; length: 60 cm) with a gas (Air) flow rate of 5 L/min. The furnace temperature was controlled to be 800 °C. The spray pyrolysis products were finally cooled down to room temperature with a heat exchanger, and collected by a fiber filter. The whole process is simplified in Fig. 1a. As-synthesized products were characterized with various techniques, including SEM, TEM, XRD, VSM, and XPS, and their photocatalytic activities were investigated in a Methyl Orange (MO, 0.1 M) degradation reaction.
3. Results and discussion

The TEM image of as-synthesized MnFe$_2$O$_4$ particles were displayed in Fig. 2a. It can be seen these particles are solid. According to Xu’s previous report [14], the hollowness (shell thickness) of particles generated from spray pyrolysis can be controlled by the concentration of organics in the precursor solution, and the particle size could be controlled by the metal precursor concentration. When 10% volume percentage of EG was introduced into Sn(NO$_3$)$_4$ aqueous solution, hollow SnO$_2$ particles could be generated, as shown in Fig. 2d. This is because the organics were oxidized and gas was produced inside the droplet at high temperature, and metal oxides were precipitated in the outer layer, forming a hollow structure [15]. When MnFe$_2$O$_4$ particles were introduced into Sn(NO$_3$)$_4$ water/ethanol solution, the droplets generated from ultrasonic nebulizer would contain MnFe$_2$O$_4$ particles, as shown in Fig. 1b. When flowing through the furnace, the MnFe$_2$O$_4$ particles were captured into the SnO$_2$ hollow particles, as shown in Fig. 2b and e, forming a yolk/shell structure. The corresponding histogram for MnFe$_2$O$_4$/SnO$_2$ particle size distribution is shown in Fig. 2b inset, and the average size is 432 nm. A Scanning Transmission Electron Microscopy (STEM) image in Fig. 2c clearly shows the yolk/shell structure, and the corresponding elemental mapping is displayed in Fig. 2f, and the different colors of the yolk and shell confirmed that MnFe$_2$O$_4$ was captured inside hollow SnO$_2$ particle.

The XRD patterns of the yolk/shell particles were shown in Fig. 3a, and the peaks from both SnO$_2$ and MnFe$_2$O$_4$ are presented, indicating that both phases are well crystalized. The magnetic hysteresis loops of MnFe$_2$O$_4$ and MnFe$_2$O$_4$/SnO$_2$ particles are shown in Fig. 3b. Due to the introduction of non-magnetic phase of SnO$_2$, the
magnetization of MnFe₂O₄/SnO₂ particles was decreased to 49 from 69 emu/g in MnFe₂O₄ particles, but still high enough to magnetically separate the particles from the solutions after reaction. Furthermore, it can be seen that both remanent magnetization and coercivity of the yolk/shell particles are almost zero, which could prevent the magnetic agglomeration of the particles, and result in a good dispersion of photocatalytic catalyst in water. XPS characterization of yolk/shell particles are presented in Fig. 3.

Fig. 3. (a). XRD patterns of MnFe₂O₄/SnO₂ yolk/shell particles; (b). Magnetic hysteresis loops of MnFe₂O₄ and MnFe₂O₄/SnO₂ yolk/shell particles; (c). XPS analysis of SnO₂ nanostructure at Sn 3d level; (d). XPS analysis of SnO₂ nanostructure at O 1s level.

Fig. 4. (a). UV–vis spectrum of MO aqueous solution in the presence of MnFe₂O₄/SnO₂ yolk/shell particles under exposure to UV; (b). MO degradation efficiencies with and without MnFe₂O₄/SnO₂ yolk/shell particles; (c). MO degradation efficiencies of MnFe₂O₄/SnO₂ yolk/shell particles in four cycles; (d). STEM images of MnFe₂O₄/SnO₂ yolk/shell particles after four reaction cycles.

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Fig. 3c and d. The two peaks at the binding energy of 495.3 and 486.8 eV in Fig. 2c are from Sn 3d_{3/2} and Sn 3d_{5/2}, respectively. There could be several states of Sn ions (such as Sn^{4+} and Sn^{2+}) in Tin Oxides. The peak presented at 486.8 eV is attributed to Sn^{4+} in the oxide, which shows the photocatalytic activities. The peak at the binding energy of 530.4 eV is from O1s, and this peaks indicates the Sn^{4+-O} binds in the products. In summary, the XPS results confirmed that SnO2 phase is well formed in the synthesis process.

The photocatalytic investigation results of MnFe2O4/SnO2 yolk/shell particles were displayed in Fig. 4. The characteristic absorption of MO at 464 nm was used to monitor the reaction progress. The MO solution containing MnFe2O4/SnO2 particles were mechanically stirred in the dark for 10 min to reach an adsorption/desorption equilibrium before the UV light irradiation. The adsorption-desorption equilibrium was supported by constant MO concentration over time in the dark. The reaction progress was monitored every 10 min, and the results were presented in Fig. 4a. It can be seen that the MO absorption peak intensity decreases with the increase of UV irradiation time, and the peak is almost disappeared after 60 min exposure. To further confirm the photocatalytic effects of MnFe2O4/SnO2 yolk/shell particles, a blank comparison experiment (without MnFe2O4/SnO2 catalysts, but exposed to UV light irradiation) is conducted, and the corresponding results are shown in Fig. 4b. It can be seen that, in the blank comparison experiment, the value of C/C0 (C: instant MO concentration; C0: initial MO concentration) changed very little over time. However, when MnFe2O4/SnO2 particles are presented in the MO solution under UV light irradiation, the value of C/C0 dramatically decreases over time, confirming the catalytic effects of MnFe2O4/SnO2 particles. The catalytic efficiency was defined as (C0−C)/C0 × 100%, and was calculated to be 98% at the end of the experiment. The stability of the catalyst is investigated by repeating above reaction cycle, and the results are presented in Fig. 4c. It can been seen that after four reaction cycles, there is negligible change on the activity, which indicates that the photocatalyst shows a good stability, and photo corrosion resistivity. Usually, hollow structure is more fragile than a solid structure. The mechanical stirring during the reaction could potentially destroy the hollow structure of SnO2. After the four reaction cycles, the STEM image of the MnFe2O4/SnO2 particles is presented in Fig. 4d. It shows that the hollow structure is well maintained after the reaction. It is noted that, due to the short reaction time (a few seconds) during the spray pyrolysis, the photocatalytic performance could be potentially further increased by a post annealing to increase the crystallization. Due to the limited length of this manuscript, further results are not presented.

4. Conclusions

MnFe2O4/SnO2 yolk/shell particles were synthesized through a spray pyrolysis process. The yolk/shell structure was confirmed by both SEM and TEM images. The photocatalytic activity of MnFe2O4/SnO2 particles was investigated through MO degradation reaction under UV light irritation, which showed that the MnFe2−O4/SnO2 catalyst displayed high photocatalytic activity to degrade MO. The stability of catalyst was tested in four continuous tests. The results confirmed that the catalyst has a high performance in photocatalytic reaction, and the yolk/shell structure was well maintained.

Acknowledgements

The authors acknowledge the financial support from the National Natural Science Foundation of China (No. 21477167), the Science and Technology Research Plan Program of Henan Province (No. 172102310712), the Natural Science Research Plan Program of Henan Province Department of Education (No. 17B61009), the Research Funding from the Doctoral Program of Zhoukou Normal University (No. ZKU2014118), and the Research Funding from the School Based Program of Zhoukou Normal University (No. zknubB2201606).

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