Hierarchical Fe_3O_4/TiO_2 hollow microspheres and their applications in photocatalysis and phase-change materials

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Abstract. A novel hierarchical Fe_3O_4/TiO_2 hollow microspheres were prepared by combining sol-gel process, hydrothermal etching technology, and high-temperature calcination. The microspheres displayed excellent performance in the photodegradation of methylene blue under visible light. The Fe_3O_4/TiO_2-$LiNO_3$ composite phase change material showed high latent heat of fusion without leakage of salts. The morphology and properties of the Fe_3O_4/TiO_2 hollow microspheres and the Fe_3O_4/TiO_2-$LiNO_3$ composite phase change material were investigated by field emission scanning electron microscopy (FESEM), Ultraviolet-visible (UV-Vis) spectroscopy and differential scanning calorimetry (DSC). The results show that the hierarchical Fe_3O_4/TiO_2 hollow microspheres have potential applications in energy materials.

Introduction

With the development of energy and environmental research, numerous efforts have been devoted to the construction of high-efficient multifunction materials and energy saving materials [1-4]. As a kind of clean and efficient process, photocatalysis can treat water pollutants and solve environmental problems. As photocatalysts are widely studied recent years, the anatase phase TiO_2 exhibit excellent photocatalytic activities and has attracted much attention [5,6]. In this work, we demonstrate a novel hierarchical hollow Fe_3O_4/anatase phase TiO_2 microspheres as an efficient photocatalyst in the photodegradation of methylene blue visible light. In addition, the magnetic core of the Fe_3O_4/TiO_2 microspheres facilitates the recovery of the catalyst from the system.

Thermal energy storage (TES) is an important technology to improve energy utilization and environmental protection,and phase change materials (PCMs) are functional materials that can store and release latent heat energy through phase change [7,8].The hierarchical hollow microspheres are supposed to be an ideal carrier for phase change materials owing to the novel structure of hollow space and double shells which can accommodate phase change materials without leakage. In this study, we introduce the novel hierarchical hollow Fe_3O_4/TiO_2 microspheres as a favourable carrier to load $LiNO_3$, and the Fe_3O_4/TiO_2-$LiNO_3$ composite phase change material shows high latent heat of fusion, and no leakage of salts were observed.

Experimental

Materials

$FeCl_3 \cdot 6H_2O$, sodium acetate, ethylene glycol, hydrochloric acid (36.5%), ethanol, ammonium hydroxide (28 wt%), tetraethyl orthosilicate (TEOS), tetrabutyl titanate (TBOT) was analytical grade and purchased from Beijing Chemical Reagent Company. Lithium nitrate with purity ≥ 99.0%

was obtained from Tianjin Fu Chen Chemical Reagents Factory, China. All reagents were used as received without further purification.

Preparation methods

The hierarchical Fe_3O_4/TiO_2 hollow microspheres were prepared by combining sol-gel process, hydrothermal etching technology, and high-temperature calcination, which is reported previously [9]. The Fe_3O_4/TiO_2-PCMs material was prepared using solution impregnation method. The typical preparation procedure was as follows: 0.4 g lithium nitrate, 0.6 g Fe_3O_4/TiO_2 microspheres were dissolved in 30 mL ethanol under ultrasound (60% power), then the prepared mixture was soaked at 70 ^oC for 4 h under vigorous stirring. Finally, the product was collected and dried at 80 °C for 24 h.

Photocatalytic performance

The photodegradation of methylene blue was carried out under visible light by removing light below than 420 nm using a filter at room temperature. 100 mL methylene blue aqueous solution (10 mg/L) was mixed with 0.5 g/L catalyst in an optically matched pyrex vessel and the suspension was stirred in the dark for 30 min to ensure the adsorption-desorption equilibrium of the mixture. Samples of solution were taken away every 15 min from the reactor and the catalysts were magnetically removed from the mixture. The concentration of methylene blue was analyzed by a UV-2550 spectrometer and calculated by a calibration curve. Methylene blue solution has a maximum absorption at about 664 nm. At the end of each photodegradation experiment, the photocatalysts were magnetically collected, and then rinsed with water for further use. The photocatalytic reaction can be described simply by $\ln(C_0/C) = kt$, in which C and C_0 are the actual and initial concentration of methylene blue, and k is the apparent degradation rate constant.

Characterization

The surface morphology and structure of the composite materials were examined using field emission scanning electron microscopy (FESEM, ZEISS SUPRA-55). Ultraviolet-visible (UV-Vis) absorption spectra were obtained with a UV-2550 spectrometer. The thermal property of the Fe_3O_4/TiO_2-$LiNO_3$ composite phase change materials were characterized by differential scanning calorimetry (DSC) using a NETZSCH STA449F3 (Germany). The DSC analyses were conducted at a heating rate of 5 ^oC/min and a cooling rate of 5 ^oC/min.

Results and discussion

Characterization of morphology of hierarchical Fe_3O_4/TiO_2 hollow microspheres:

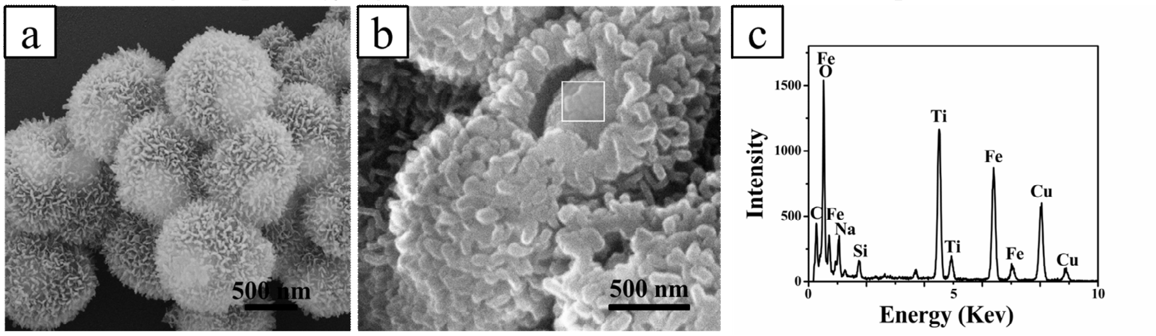

Fig. 1. (a) SEM image of hierarchical Fe_3O_4/TiO_2 hollow microspheres, (b) FESEM image of a broken Fe_3O_4/TiO_2 hollow microspheres, which clearly shows the hierarchical hollow structure, (c) EDS spectra of the Fe_3O_4/TiO_2 hollow microspheres, the Cu and C peaks originate from the carbon-coated copper grid.

The complete morphology of the synthesized hierarchical Fe_3O_4/TiO_2 hollow microspheres was revealed in Fig. 1. The SEM image (Fig. 1a) displayed the sea urchin-like morphology with self-assembly nanofibers on the surface. The diameter of the microspheres was measured to be about 1100 nm. The microspheres have been deliberately broken (grinding with agate mortar) to explore the interior of the structure. Fig. 1b demonstrated clearly the unique structure with central core, hollow cavity and nanofibers-assembled sea urchin-like surface. The integrated EDS (energy dispersive spectrometer) analysis of the Fe_3O_4/TiO_2 hollow microspheres indicated the presence of Ti, Fe, O and negligible amount of Na and Si (Fig. 1c), confirming the presence of magnetic iron oxide core and TiO_2 shells. The XRD pattern of the Fe_3O_4/TiO_2 hollow microspheres were researched in our reported literature, demonstrating the anatase phase in the Fe_3O_4/TiO_2 hollow microspheres (JCPDS card No. 21-1272) [9].

The photocatalytic performance of hierarchical Fe_3O_4/TiO_2 hollow microspheres:

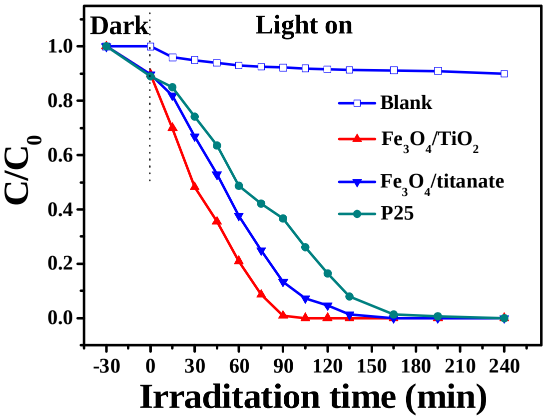

Fig. 2. Photodegradation of methylene blue under visible light (□ = blank, ▲ = Fe_3O_4/TiO_2, ▼ = Fe_3O_4/titanate, ● = P25).

The catalytic activities of the hierarchical Fe_3O_4/TiO_2 hollow microspheres were probed by the photodegradation of methylene blue (MB) under visible light. The degradation of methylene blue in the presence of P25, in the presence of hierarchical Fe_3O_4/titanate hollow microspheres and without catalyst were also tested under identical conditions for comparison, and the results are shown in Fig. 2. The Fe_3O_4/TiO_2 microspheres exhibited the hightest photodegradation efficiency for methylene blue ($0.0298\ min^{-1}$), in comparison to that of Fe_3O_4/titanate ($0.0256\ min^{-1}$) and P25 ($0.0135\ min^{-1}$). Since the peculiar surface morphology of the nanofibers-assembly endows the microspheres with high surface area and porous property, more pollutants substrate molecules have been absorbed after equilibrium, and the substrate molecules can have good contact with the catalysts. Besides, the double-hollow structure enabled the multiple reflections of light source within the interior cavity, leading to the enhancement of light absorbance [5,6]. In general, the results suggest that the unique structure of Fe_3O_4/TiO_2 and Fe_3O_4/titanate contributes to enhancement of their photocatalytic activities. The slight improvement of photodegradation efficiency of Fe_3O_4/TiO_2 to Fe_3O_4/titanate was because of the high crystallinity of the anatase phase obtained after high temperature calcination.

Thermal property of Fe_3O_4/TiO_2-PCMs:

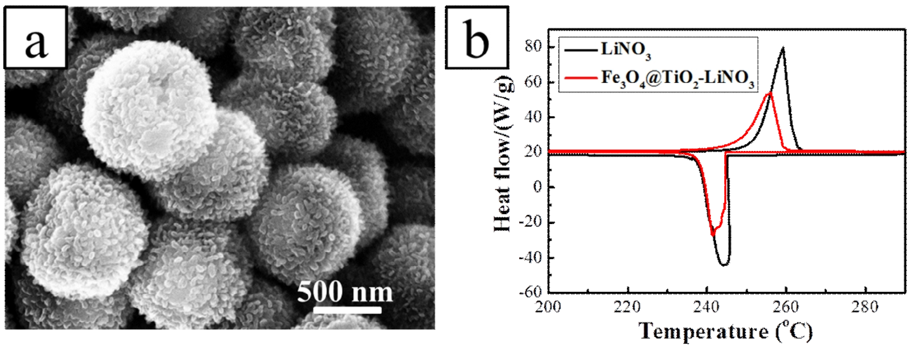

Fig. 3. Fe_3O_4/TiO_2-$LiNO_3$ composite phase change material: (a) SEM image, (b) DSC thermograms.

The Fe_3O_4/TiO_2 microspheres are supposed to be potential carriers of phase change materials owing to their unique hierarchical hollow structure. Lithium nitrate was chosen as the core material because of its high heat of fusion and the Fe_3O_4/TiO_2-$LiNO_3$ composite phase change materials were synthesized by solution impregnation method [7]. The SEM image of the Fe_3O_4/TiO_2-$LiNO_3$ composite phase change material shows that no leakage of salts can be observed on the surface of the composites (Fig. 3a). The impregnation efficiency of 40% was investigated as a model sample and the phase change behavior of the Fe_3O_4/TiO_2-PCMs were investigated by DSC (Fig. 3b). The latent heat of fusion of Fe_3O_4/TiO_2-$LiNO_3$ composite phase change material was 139 J/g, approximately 38% of pure $LiNO_3$, which further confirms the absence of salts leakage. Since the hierarchical Fe_3O_4/TiO_2 hollow microspheres can efficiently load phase change material without salts leakage, we look forward to taking advantage of this multifunctional hollow microspheres and applying them in new energy materials.

Conclusions

In summary, we have successfully synthesized the hierarchical Fe_3O_4/TiO_2 hollow microspheres, which exhibit excellent performance in the photodegradation of methylene blue under visible light. The anatase Fe_3O_4/TiO_2 displayed better efficiency in comparison to Fe_3O_4/titanate because of higher crystallinity. Furthermore, the unique hierarchical hollow structure endows the Fe_3O_4/TiO_2 microspheres with potential applications in energy materials. The Fe_3O_4/TiO_2-$LiNO_3$ composite phase change material shows high latent heat of fusion, and no leakage of salts were observed. These observations are of importance to the development of energy and the environment.

Acknowledgments

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References

[1] S. Y. Yu, X. D. Wang, D. Z. Wu. Appl. Energ. 114 (2014) 632-643.
[2] F. Khakzad, Z. Alinejad, A. R. Shirin-Abadi, M. Ghasemi, A. R. Mahdavian. Colloid Polym. Sci. 292 (2014) 355-368.
[3] W. D. Liang, G. D. Zhang, H. X. Sun, Z. Q. Zhu, A. Li. RSC Adv. 3 (2013) 18022-18027.
[4] Y. Konuklu, M. Unal, H. O.Paksoy. Sol. Energ. Mat. Sol. C. 120 (2014) 536-542.
[5] H. X. Li, Z. F. Bian, J. Zhu, D. Q. Zhang, G. S. Li, Y. N. Huo, H. Li, Y. F. Lu. J. Am. Chem. Soc. 129 (2007) 8406-8407.
[6] Y. Zeng, X. Wang, H. Wang, Y. Dong, Y. Ma, J. N. Yao. Chem. Commun. 46 (2010) 4312-4314.
[7] L. M. Zhong, X. W. Zhang, Y. Luan, G. Wang, Y. H. Feng, D. L. Feng. Sol. Energy. 107 (2014) 63-73.
[8] B. T. Tang, M. G. Qiu, S. F. Zhang. Sol. Energ. Mat. Sol. C. 105 (2012) 242-248.
[9] J. Li, L. Tan, G. Wang, M. Yang. Nanotechnology 26 (2015) 095601.