Multilayered MoS₂ Coated TiO₂ Hollow Spheres for Efficient Photodegradation of Phenol under Visible Light Irradiation

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Abstract:

Multilayered MoS₂ coated hollow TiO₂ heterostructures were fabricated by a two-step hydrothermal process using TiO₂ hollow spheres as precursors. Compared with pure TiO₂, the heterostructures exhibited greatly enhanced visible-light-responsive activity on photodecomposition of colorless phenol, due to the enlargement of visible light absorption and improvement separation efficiency of photogenerated electron-hole pairs. Photocatalytic activity was influenced by the MoS₂/TiO₂ ratio and the optimized composition was obtained with high stability during recycling.

Keywords: Semiconductors; Nanocomposites; TiO₂; MoS₂; Photodecomposition; Photocatalysts

1. Introduction

The global energy crisis and demand for environmental protection promote the research on semiconductor photocatalysts with kinds of nanostructures. Titanium dioxide (TiO₂) is widely recognized as the most excellent candidate for commercial photocatalysts, because it shows high photocatalytic property in the degradation of organic compounds and hydrogen production and long-term stability against photo- and chemical corrosion [1,2]. However, its applications are largely hindered by the low quantum efficiency in photocatalytic reactions and ineffective utilization of visible light, which result from its high recombination of photo-generated electron-hole pairs and wide band gap (~3.3 eV for the anatase phase). Therefore, it is highly desirable to develop photocatalysts with high catalytic activities under the visible light range. To achieve this goal, the design and growth of TiO₂-based heterostructures using a semiconductor with narrow band gap is an effective way to promote the transfer of photo-induced electron and enlarge the light absorption [3-5].

Recently, 2D layered MoS₂ has been widely studied for the potential applications in supercapacitors, solar cell and photocatalysis etc. Layered MoS₂ has been deposited on TiO₂ nanobelts, nanofibers and nanoclusters to enlarge the light absorption and improve the performance of photocatalytic hydrogen generation and photodegradation of hazardous organic pollutants [6-8]. Hollow TiO₂ sphere has been reported with superior photocatalytic activity because of the relatively large surface area compared with nanoparticle [7]. In this work, multi-layered MoS₂ coated TiO₂ hollow spheres were successfully prepared, which exhibits high activity for photodecomposition of colorless phenol.

2. Experimental

Preparation of TiO₂/MoS₂ heterostructures

TiO₂ hollow sphere was synthesized by a facile hydrothermal method [9-12] and the TiO₂/MoS₂ heterostructures were fabricated as follows. Typically, 135 mg of sodium molybdate (Na₂MoO₄•2H₂O) and 90 mg of thioacetamide (C₂H₅NS) were dissolved in 20 mL of deionized water to form a transparent solution. Then, 30 mg, 60 mg, 90 mg and 120 mg of TiO₂ hollow spheres were added into the above solution and stirred to get a suspension and the resulted samples were named TM3, TM6, TM9 and TM12, respectively. The whole mixture was transferred into a Teflon-lined stainless steel autoclave and kept at 220 °C for 24 h to deposit MoS₂ on the surface of TiO₂ spheres. The precipitate was collected, washed and finally dried at 60 °C for 12 h in a vacuum oven to get the TiO₂/MoS₂ heterostructures [13,14].

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Characterization

The composition and phase purity of $\text{TiO}_2/\text{MoS}_2$ were analyzed by a Rigaku D/max-2600/PC X-ray diffractometer (XRD) using Cu-K α radiation. Sample microstructures were revealed by a Hitachi SU-70 scanning electron microscopy (SEM) and a FEI Tecnai G2 F20 transmission electron microscope (TEM). UV-vis diffuse reflectance spectra (DRS) were obtained by a Shimadzu UV-2500 spectrophotometer with a BaSO₄ reflectance standard. Photocatalytic activity was evaluated under visible light irradiation using a 300 W Xe lamp with a cut off filter ($\lambda \geq 420$ nm). The colorless phenol was chosen as a model pollutant to evaluate the photocatalytic activity with a concentration of 10mg/L. 0.01g catalyst was added in the reaction of 60 mL solution and the concentration change was monitored by a Perkin-Elmer Lambda-35 UV-Vis spectrophotometer at the maximum absorption band (269 nm). The photocurrent was measured by a Chenhua CHI 660E electrochemical system in 0.5 M Na₂SO₄ solution using a Pt-calomel electrode.

3. Results and discussion.

Fig. 1 presents the XRD patterns of $\text{TiO}_2/\text{MoS}_2$ heterostructures and pure TiO_2 and MoS_2 . For pure TiO_2 , all the detected peaks coincide with the standard anatase phase of TiO_2 (JCPDS No. 89-4921). As for the pure MoS_2 powder, the diffraction peaks can be clearly assigned to the (003), (101), (104) and (110) planes in the hexagonal phase MoS_2 (JCPDS No. 17-0744) [15]. For the $\text{TiO}_2/\text{MoS}_2$ composites, both phases can be observed and the diffraction peaks intensity of MoS_2 tend to be stronger with the increasing content of MoS_2 . The results show that the $\text{TiO}_2/\text{MoS}_2$ composites are successfully prepared and the component ratios can be easily controlled by varying the TiO_2 adding.

Fig. 2 presents the typical SEM images of pure TiO_2 , MoS_2 and the $\text{TiO}_2/\text{MoS}_2$ heterostructures. Pure TiO_2 sphere, formed via an ostwald ripening process (Fig. 2a), shows coarse surface, which is made up by many TiO_2 nanocrystalline. Pure MoS_2 exhibits sheet-like morphology with a slightly bending at the edge (Fig. 2b). After the hydrothermal process with the adding of 30 mg TiO_2 , the $\text{TiO}_2/\text{MoS}_2$ composite maintains the sphere ball morphology with fluffy MoS_2 decorated on surface. The broken sphere covered by MoS_2 in Fig. 2c proves its hollow structure. As the quantity of TiO_2 increasing, the $\text{TiO}_2/\text{MoS}_2$ composites kept hollow sphere structure, while the content of MoS_2 deposited on the rough surface is gradually reduced in Fig. 2d,e and f. Thus, the ratio of MoS_2 deposited on TiO_2 can be easily tuned by adjusting the TiO_2 content.

To further observe of the heterostructure microstructure, typical TEM images of $\text{TiO}_2/\text{MoS}_2$ (TM9) are shown in Fig. 3. Obviously, the hollow structure is relative uniform with a diameter about 600 nm (Fig. 3a). An enlarged view in Fig. 3b shows that the thickness of $\text{TiO}_2/\text{MoS}_2$ shell is no more than 100 nm. Moreover, the hollow structure present high porosity, which would provide with high surface area for the photoreactions. High resolution TEM image in Fig. 3c gives the crystalline structure from the selected rectangle area. The shell displayed two types of clear lattice fringes. The fringes spacing of 0.35 nm is corresponding to the (101) plane of the anatase TiO_2 [16]. On the other hand, the spacing of a few layer MoS_2 sheets was observed and measured as 0.75 nm, which is in accordance with the reported value [8]. The selected area electron diffraction (SAED) in Fig. 3d gives the values of R1 and R2 of 0.3510 and 0.2712 nm, respectively. According to the Bragg equation, the calculated d1 and d2 are 0.3509 nm for TiO_2 (101) and 0.2710 nm for MoS_2 (101), respectively, confirming the formation of $\text{TiO}_2/\text{MoS}_2$ heterostructure.

The UV-vis DRS are shown in Fig. 4a. The light absorption of TiO_2 starts from 380 nm and the band gap energy is about 3.25 eV. With the decreasing of TiO_2 adding, the light absorption range of the $\text{TiO}_2/\text{MoS}_2$ heterostructures is greatly enlarged in the visible range, due to the light absorption of MoS_2 . Clearly, the ability of light absorption of $\text{TiO}_2/\text{MoS}_2$ composites is enhanced comparing with pure TiO_2 . Although the absorption properties of heterostructure are weaker than that of the pure MoS_2 , the superior photocatalytic performance is obtained for the composite photocatalysts.

Fig.4b gives the variation of phenol concentration (C/C_0) with the photodegradation time over different photocatalysts. All the $\text{TiO}_2/\text{MoS}_2$ composites exhibit higher activity than that of pure TiO_2 and MoS_2 . With the increasing of TiO_2 content, the photocatalytic activity is enhanced at first and then decreased. The TM9 photocatalyst presents the best performance and the phenol was decomposed 78% after 150 min irradiation. According to the Langmuir-Hinshelwood (L-H) kinetics model, the apparent pseudo-first-order rate constant (h^{-1}) of $\text{TiO}_2/\text{MoS}_2$ composites of TM3, TM6, TM9, TM12 and MoS_2 were calculated to be 0.005, 0.003, 0.010, 0.004 and 0.001 h^{-1} , respectively. Obviously, TM9 shows the fastest decomposition rate for phenol among all the samples and no obvious self-degradation of phenol was observed.

To better elucidate the role of MoS_2 on the generation and separation of photogenerated charge carriers, photocurrent measurements were carried out and compared. As shown in Fig. 4c, the TM9 heterostructure exhibits higher photocurrent density than that of pure TiO_2 and MoS_2 , indicating the heterostructure is much more beneficial to promote effective charges transfer and easy electrons collection [15-20]. Cycling result in photodecomposition of phenol using TM9 photocatalyst is shown in Fig. 4d. It is clear that the TM9 shows the stable performance on the decomposition of phenol after 4 times usage, revealing the high stability of the composites. XRD pattern of the TM9 photocatalyst after recycling in Fig. S1 shows that no additional diffraction peaks were detected, indicating the high phase stability of photocatalyst during the cycling.

4. Conclusion

Multilayered MoS_2 coated hollow TiO_2 heterostructures were fabricated via a two-step hydrothermal method. XRD, SEM and TEM results confirmed the formation of $\text{MoS}_2/\text{TiO}_2$ heterostructures, which exhibited superior visible light photocatalytic activity towards photodegradation of phenol. The higher activity of heterostructures was attributed to improved light absorption and faster transfer of photoinduced charge carriers. The TM9 heterostructure also exhibited stable performance during recycling.

Acknowledgments

This work was supported by the National Science Foundation of Heilongjiang province (A2015005), the Outstanding Youth Science Foundation of Harbin Normal University (XKYQ201303), Innovative Talents Fund of Harbin (2014RFQXJ085).

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Figure Captions

Fig. 1. XRD patterns of pure TiO₂, pure MoS₂ and MoS₂/TiO₂ heterostructures.

Fig. 2. SEM images of (a) pure TiO₂, (b) pure MoS₂, (c) TM3, (d) TM6, (e) TM9 and (f) TM12.

Fig. 3. Low-magnification TEM images of (a) TM9, (b) an enlarged view, (c) HRTEM images of the selected area from the rectangle of (b), and (d) the selected area electron diffraction patterns.

Fig. 4. (a) UV-vis DRS of pure TiO₂, MoS₂, and TiO₂/MoS₂ heterostructures. (b) Photodegradation of phenol over TiO₂/MoS₂ heterostructures, TiO₂ hollow balls and MoS₂ nanoplates. (c) Transient photocurrent responses of TM9 and pure TiO₂ under simulated sun light irradiation. (d) Cycling test in photocatalytic decomposition of phenol using TM9 photocatalyst for 4 times.