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3D flower-like ironphthalocyanine hierarchical microstructures: solvothermal-fabrication and high visible light photocatalytic properties

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Abstract

The three-dimensional flower-like TNFePc hierarchical microstructures were fabricated by a simple solvothermal method. The as-obtained products exhibited high adsorption capacity and excellent simultaneously visible-light-driven photocatalytic performance for Rhodamine B (RB) under visible-light. Repetitive tests showed that the flower-like TNFePc hierarchical microstructures could maintain high catalytic activity over several cycles, and it had a better regeneration capability under mild conditions. Finally, a possible mechanism for the formation of three-dimensional flower-like TNFePc was suggested based on the evolution of morphology as a function of solvothermal time, which involved the initial formation of microparticles followed by their recrystallize to microspheres and transformation into three-dimensional flower-like hierarchical microstructures by mass diffusion and Ostwald ripening.

Keywords: Phthalocyanine; Solvothermal; Microstructures; Photocatalytic activity

1. Introduction

Nowadays, organic pollutants constitute an important family of pollutants of wastewater produced by chemical, petrochemical, food-processing or textile industries. Owing to the urgent need for a clean and comfortable environment, photocatalysis as a "green" technique, offers great potential use for the elimination of toxic chemicals in the environment through its efficiency and broad applicability [1–4]. TiO_2 has been deemed to be an efficient photocatalyst due to its relatively high photocatalytic activity and chemical stability [5–7]. However, a major handicap is its rather large optical band gap (3.2 eV for the anatase phase), which means it can only be activated by ultraviolet (UV) light ($\lambda < 400$ nm). According to the solar spectrum, UV light accounts for only a small fraction (4%) of the incoming solar energy, whereas visible light makes up as large as 43% [8–10]. For the more efficient utilization of incoming light energy, considerable research efforts have been directed toward exploring visible-light photocatalysts [11–14].

Metal phthalocyanines, one of the most promising visible-light photocatalyst has attracted considerable interest in recent years for the intense absorption bands in the longer wavelength region of the visible light in a solar spectrum. So, its photocatalysis might use sunlight as the energy source to degrade organic pollutions and widely used for waste-water treatment [15]. Moreover, since the photocatalytic reactions often take place on the surface of catalysts, the structure and morphology are strongly related to the photocatalytic activity of photocatalysts [16], therefore, for a practical application in photocatalysis, the fabrication of desired morphologies and textures is important as well as control in crystallinity, porosity and composition. Among various microstructures, in particular, three-dimensional (3D) hierarchical microstructures have exhibited very high visible-light photocatalytic activity because of their special hierarchical porous structure, good permeability and large surface area [17,18].

To the best of our knowledge, there are no reports on the synthesis and photocatalytic properties of 3D flower-like

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ironphthalocyanine hierarchical microstructures. Herein, we report the fabrication of a 3D flower-like TNFePc hierarchical microstructure constructed from 2D microplates through a simple template-free and reproducible solvothermal method. And, the visible-light photocatalytic activity of these heterostructures photocatalysts are investigated by measuring the degradation of dyes RB as the test substances.

2. Experimental section

2.1. Synthesis of 3D flower-like TNFePc hierarchical microstructures

In a typical experiment, 4-nitrophthalonitrile (0.100 mmol), Fe $(Ac)_2 \cdot 2H_2O$ (0.025 mmol) and ammonium molybdate (1 mg) were put into a Teflon-lined stainless steel autoclave of 20 mL capacity which containing 17 mL of butanol solution. The mixture was then stirred to form a milk-like suspension, sealed and heated to 160 °C. After reaction for 14 h, the autoclave was cooled down to room temperature. The obtained sample was washed several times with water and ethanol respectively, and then dried under vacuum at 80 °C for 4 h.

2.2. Characterization

Field emission scanning electron microscope (FESEM, XL-30 ESEM FEG, Micro FEI Philips) and high-resolution transmission electron microscopy (HRTEM; JEOL JEM-2100) were used to characterize the morphologies of the products. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku, D/max-2500 X-ray diffractometer. Fourier transform infrared spectra (FT-IR) were obtained on Magna 560 FT-IR spectrometer with a resolution of 1 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was performed on a VG-ESCALAB LKII instrument with Mg KR ADES ($h\nu$=1253.6 eV) source at a residual gas pressure of below 1×10^{-8} Pa. The UV-vis diffuse reflectance (DR) spectroscopy of the samples were recorded on a Cary 500 UV-vis-NIR spectrophotometer.

2.3. Photocatalytic test

The photoreactor was designed with an internal xenon lamp (XHA 150 W and the average intensity was 28 mW/cm^2) equipped with a cut-off glass filter transmitting $\lambda > 400$ nm surrounded by a water-cooling quartz jacket to cool the lamp, where a 100 mL of the RB solution with an initial concentration of 10 mg L^{-1} in the presence of solid catalyst (0.05 g). The solution was stirred in the dark for 30 min to obtain a good dispersion and reach adsorption-desorption equilibrium between the organic molecules and the catalyst surface. Decreases in the concentrations of dyes were analyzed by a Cary 500 UV-vis-NIR spectrophotometer at λ=554 nm. At given intervals of illumination, 3 mL aliquots were collected from the suspension and immediately centrifuged, the concentration of RB after illumination was determined at 554 nm using a UV–vis spectrophotometer.

3. Results and discussion

The morphologies of the as-synthesized products were examined by SEM. A large number of uniform flower-like hierarchical microstructures of TNFePc with an average diameter of 8 μm could be clearly observed in Fig. 1a. No single microplate could be found, showing that almost all of the plates had been self-assembled into a flower-like hierarchical microstructures. More detailed morphologies were displayed in Fig. 1b, which showed that the flower-like hierarchical microstructure was made up of numerous two-dimensional microplates with a thickness of about 150 nm. More importantly, many pores of different diameters were found among the microplates in the hierarchical microstructures. Further structural characterization of the TNFePc hierarchical microstructures was achieved using transmission electron microscopy (TEM). Fig. 1c showed typical TEM images of the 3D flower-like hierarchical microstructures, revealing that the entire flower was built from thin microplates, which was in accordance with the SEM images. As the photocatalytic reactions often took place on the surface of catalysts, these microplates might improve the photocatalytic activity of TNFePc. These thin microplates could be exposed to the organic pollutions with the highest surface area, and thus the structure might result in a high photocatalytic activity. The corresponding high-resolution TEM image was shown in Fig. 1d. From the HRTEM, we could see that the sample was arranged in lamellar structure with the fringe spacing of 0.36 nm. The insert of Fig. 1d showed the corresponding selected area electron diffraction (SAED) pattern, indicating the polycrystalline configuration of the TNFePc hierarchical microstructures, Moreover, all of the flower-like hierarchical microstructures maintained their integrity after vigorous ultrasonic processing during the sample preparation for TEM measurements, showing the structural stability of the product.

Fig. 2 showed the X-ray diffraction pattern (XRD) and Fourier transform infrared (FT-IR) spectrum of the hierarchical microstructures. As observed in Fig. 2a, four main reflection peaks appeared at $2\theta = 11.8°$, 17.7° and 27.1° could be indexed to the diffraction peaks of TNFePc, respectively [19]. The FT-IR spectrum of flower-like TNFePc hierarchical microstructures was shown in Fig. 2b, it was observed that the flower-like TNFePc hierarchical microstructures appeared several absorption peaks at around 727, 755, 910, 1090, 1141 and 1605 cm^{-1}, which might be assigned to phthalocyanine skeletal and metal-ligand vibrations, respectively [20]. And, the other absorption peaks at 1521, 1337 and 850 cm^{-1} might be assigned to the asymmetric N-O stretching, symmetric N-O stretching and C-NO_2 stretching due to the nitro groups present in the structure of the TNFePc molecule [21].

Additionally, the chemical composition and purity of the flower-like TNFePc hierarchical microstructures were studied by XPS analysis. The fully scanned spectrum in Fig. 3a demonstrated that C, N, O, and Fe elements existed in the flower-like TNFePc hierarchical microstructures, respectively. The XPS spectrum of N 1s was shown in Fig. 3b, the lower binding energy component at 398.4 eV was attributed to the