



Constructing iron phthalocyanine nanosheets/electrospun carbon nanofibers heterostructures with enhanced photocatalytic activity under visible light irradiation



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ABSTRACT

In this work, a novel heterostructures photocatalyst was constructed by loading 2,9,16,23-tetranitrophthalocyanine iron (II) (TNFePc) nanosheets on one-dimensional carbon nanofibers (CNFs). The coverage density of TNFePc nanosheets could be tailored by changing the precursor concentration for fabrication of TNFePc/CNFs heterostructures. These TNFePc/CNFs heterostructures exhibited enhanced visible light photocatalytic activity than that of pure TNFePc. Photoelectrochemical property test showed TNFePc/CNFs heterostructures exhibited an increased current density, about 1.8 times than that of pure TNFePc, which indicated the recombination of the photogenerated charge carrier was inhibited greatly in the TNFePc/CNFs heterostructures. Notably, the TNFePc/CNFs heterostructures could be easily recycled without a decrease of the photocatalytic activity due to the large length to diameter ratio of the one-dimensional CNFs.

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1. Introduction

Nowadays, a large amount of wastewater containing dyes is discharged without effective treatment in the process of production and use of dyes [1–6], which led to a serious pollution to the environment and harms human health [7]. Since the pioneering reporting photocatalysis on a TiO₂ electrode, photocatalysis is regarded as one of the most effective and economical ways for the treatment of polluted water [8,9]. However, one severe disadvantage of TiO₂ is the large band gap (3.2 eV for anatase form), which could only be excited by a small UV fraction of solar light. Finding photocatalysts with high visible light activity has been a research focus [10–13].

Recent research, including ours, have demonstrated metal phthalocyanines, for the intense absorption bands in the longer wavelength region of the visible light in a solar spectrum, could be referred to attractive alternatives for the visible light induced photocatalytic decomposition of dye compounds [14–18]. Unfortunately, similar to other narrow band gap photocatalysts, some fundamental disadvantage, such as its quick recombination of

electrons and holes, poor electrical conductivity and adsorptive performance, limit its performance in environmental mediation and solar conversion. To overcome these disadvantages, some different methods have been made, including controlling the morphologies forming composite structures or heterojunctions catalysts [19–21].

Most recently, compared with catalysts from a single metal oxide, considerable research efforts have been directed toward the design and synthesis of heterostructures photocatalytic due to their rapid photoinduced charge separation in electron-transfer processes. Therefore, combining metal phthalocyanines with a suitable electron acceptor became an important subject for improving the phthalocyanines-based photocatalysts.

Recently, electrospun carbon nanofibers (CNFs) have been considered as an ideal object, which could efficiently capture and transport of photogenerated electrons through highly conductive long CNFs [22,23]. Moreover, compared with traditional carbon nanofibers obtained by physical and chemical methods, the super long 1D nanostructure of electrospun CNFs have been proved to possess enhanced electronic transport properties [24,25]. Considering the above analysis, combination of 2,9,16,23-tetranitrophthalocyanine iron (II) (TNFePc) and CNFs seems to be ideal for hindering the recombination of electrons and holes and

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improving the visible light photocatalytic efficiency.

To our knowledge, so far, there has been no report on the fabrication of TNFePc/CNFs heterostructures photocatalysts with efficient electron-hole separation ability. Herein, we present the first example to construct a new heterostructured photocatalyst through coupling the two-dimensional (2D) rectangular iron phthalocyanine nanosheets with one-dimensional (1D) electrospun CNFs by combining the electrospinning technique and solvothermal method. In addition, the experimental results showed that the as-obtained TNFePc/CNFs photocatalysts exhibited excellent photocatalytic activity toward the decomposition of Rhodamine B (RB) and Methyl orange (MO), moreover, the TNFePc/CNFs heterostructures could be reclaimed easily by sedimentation without decrease of the photocatalytic activity due to the large length-to-diameter of CNFs. And, a possible mechanisms of photocatalysis enhancement in TNFePc/CNFs heterostructures was proposed.

2. Experimental section

2.1. Preparation of the carbon nanofibers

First, polyacrylonitrile (PAN) (1.5 g, $M_w = 150000$) powders were dissolved in *N,N*-dimethylformamide (10 mL) solution and stirred for 12 h at room temperature, the obtained solutions were pour into a hypodermic syringe for electrospinning. The positive voltage of the tip was 10 kV, and the distance between the collector and the needle tip was 10 cm. The PAN fibers were collected on aluminum foil which was attached on the surface of the collecting plate. Second, carbonization, the as-spun PAN fibers were placed into a tube furnace and stabilized at 270 °C in air for 60 min, then carbonized at a rate of 5 °C min⁻¹ up to 1000 °C in nitrogen atmosphere. Thus, electrospun carbon nanofibers (CNFs) were obtained.

2.2. Fabrication of TNFePc/CNFs heterostructures

In a typical procedure, 0.025 mmol FeCl₂·4H₂O, 0.100 mmol 4-nitrophthalonitrile, 1 mg ammonium molybdate and 15 mg CNFs were put into a 25 mL autoclave with ethylene glycol up to 80% of the total volume. The autoclave was heated at 160 °C for 12 h and then cooled to room temperature naturally. The obtained samples were then washed with distilled water under ultrasound, and dried for 8 h at 50 °C. The sample FPC1 was obtained. By increasing the precursor concentration for synthesizing TNFePc to 2 and 4 times, two other samples of TNFePc/CNFs were fabricated, which were named as FPC2 and FPC3, respectively. The pure TNFePc (FP) was obtained in the absence of CNFs and ready for further test.

2.3. Characterization

The morphologies of TNFePc/CNFs heterostructures were characterized using field emission scanning electron microscope (FESEM, XL-30 ESEM FEG, Micro FEI Philips) and high resolution transmission electron microscopy (HRTEM; JEOL JEM-2100). X-ray diffraction (XRD) patterns of the samples were carried out using a D/max 2500 XRD spectrometer (Rigaku). Fourier transform infrared (FTIR) spectra were recorded on Magna 560 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) was performed with a VG-ESCALAB LKII instrument. The UV–vis diffuse reflectance (DR) spectroscopy was performed using a Cary 500 UV–vis–NIR spectrophotometer. The conventional three electrodes setup, which connected to an electrochemical station (CHI600E Chenhua Shanghai, China) was used to characterize the photoelectrochemical property. This assembly had TNFePc/FTO and

TNFePc/CNFs/FTO as working electrodes, a saturated calomel electrode and a Pt wire were used as the reference electrode and counter electrode, respectively. 0.5 M Na₂SO₄ aqueous solution was used as the electrolyte, and A 200 W xenon lamp with a cutoff filter ($\lambda > 420$ nm) was used as the visible light source.

2.4. Photocatalytic test

The experiments were carried out in a photoreaction apparatus, which was designed with an internal xenon lamp (XHA 200 W) surrounded by a water-cooling quartz jacket to cool the lamp. 0.05 g solid catalyst was dispersed into 100 mL of RB and MO aqueous solution (concentration: 10 mg/L). The solution was stirred in the dark for 30 min. Then, exposed to a 200 W Xe lamp. At given intervals of illumination, 3 mL supernatants were collected, the concentration of RB and MO in the separated supernatant was determined at 554 nm using a UV–vis spectrophotometer.

3. Results and discussion

3.1. Characterization

SEM was used to investigate the morphology of samples, which was shown in Fig. 1. As shown in Fig. 1A, before solvothermal treatment, CNFs had a relatively smooth surface without secondary nanostructures. The diameter of CNFs was about 150–250 nm. The EDX spectrum (Fig. 1B) indicated the high purity of CNFs. After solvothermal treatment (Fig. 1C), the morphology of sample FPC1 remained as non-woven nanofibers. However, the surface of the CNFs was no longer smooth, it could be observed that the secondary 2D TNFePc nanosheets were uniformly distributed across the surface of each fibers without aggregation, offering the high level exposure of the nanosheets' surface. The more detailed structural characteristic of the heterostructures was revealed in Fig. 1D, we could see TNFePc nanosheets closely attaching onto the surface of the CNFs. The edge length of these nanosheets was in the range of 500 × 600 nm. Fig. 1B, and E were the energy-dispersive X-ray (EDX) spectra of the samples CNFs and FPC1, respectively. It was confirmed that pure CNFs was composed of C and O elements, while the TNFePc/CNFs heterostructures was composed of C, O, N and Fe. The EDX spectrum further confirmed that the TNFePc/CNFs heterostructures were successfully fabricated.

The further structural characterization of the as-obtained the 2D rectangular TNFePc nanosheets/CNFs heterostructures was further analyzed using TEM and HRTEM. Fig. 2 provided clear TEM and HRTEM images of sample FPC1. As it could be seen in Fig. 2A. The TNFePc nanosheets did not fall off the CNFs during the sample preparation for TEM measurements in vigorous ultrasonic progress, it indicated that TNFePc nanosheets had been successfully grown onto the surface of CNFs. As the photocatalytic reactions often took place on the surface of catalysts, these nanosheets might improve the photocatalytic activity of TNFePc. These thin nanosheets could be exposed to the organic pollution with the highest surface area, and thus the structure might result in a high photocatalytic activity. Moreover, it could be observed that the diameter of CNFs was about 180 nm, which was in agreement with the SEM analysis above. The TNFePc nanosheets possessed the average size length about 500 × 600 nm, coinciding with the results from the FESEM observation. The corresponding high-resolution TEM image was shown in Fig. 2B. From the HRTEM, we could see that the sample was arranged in lamellar structure with the fringe spacing of 0.36 nm. A selected-area electron diffraction (SAED) pattern (inset) from a single nanosheet clearly demonstrated the polycrystalline configuration of the TNFePc nanosheets.

The X-ray diffraction (XRD) patterns of FP, FPC1 and CNFs were

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