Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Preparation, characterization and visible-light-driven photocatalytic activity of a novel Fe(III) porphyrin-sensitized TiO_2 nanotube photocatalyst

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ARTICLE INFO

Article history:
Received 22 April 2016
Received in revised form 24 May 2016
Accepted 29 May 2016
Available online xxx

Keywords:
Metalloporphyrin
TiO_2 nanotube
Visible-light driven photocatalyst
Nanocomposite
Electron transfer

ABSTRACT

Iron(III) *meso*-tetra(4-carboxyphenyl) porphyrin (FeTCPP) loaded on the surface of TiO_2 nanotubes (TNTs) has been successfully prepared through improved hydrothermal and heating reflux process. The new photocatalyst has been characterized and analyzed by TEM/EDS, BET, XRD, FT-IR, DRS, PL, XPS and EPR. The photocatalytic activity of FeTCPP/TNT nanocomposite was evaluated by the photodegradation of MB under visible light irradiation. The degradation results showed a purification of more than 90% MB in simulating wastewater, and confirmed that the prepared FeTCPP/TNT nanocomposite has acquired superior photocatalytic activitiy. The 6 times cycled results suggested the great stability of the photocatalyst. These results confirmed the FeTCPP played an important role in capturing photons and expanding the absorption wavelength to the visible light region, and the FeTCPP/TNT photocatalyst is also beneficial for the electron transfer and long-distance transmission, and could efficiently increase the separation of the electron-hole pairs, and accelerate the decomposition of organic pollutants. In addition, nano-sized structures can increase adsorption capability.

1. Introduction

As we all known, the global environment pollution and energy related issues have been regarded as the two main problems in the 21st century, which are becoming increasingly severe. And semiconductor photocatalysts have been regarded as one of the most ideal photocatalysts for energy and environment applications [1]. Among these research fields, heterogeneous photocatalysis by using solar energy has drawn much attention during the past decades because it was a promising mean to address both global energy crises and environmental pollution, especially for nano-sized TiO_2 [1,2]. That is because of its simple preparation, high catalytic activity and stability. Importantly, TiO_2 is economical, versatile, stable, non-toxic and environmentally friendly. The nano-sized TiO_2 was widely used in the area of catalysis. In general, TiO_2 can produce electronic transition under UV irradiation, then various active radicals are formed in the process. These active radicals play an important role in the area of catalysis [2,3]. Thus, it has the broad prospect for photocatalytic degradation to alleviate the increasingly serious environmental pollution problems. However, it still exists some questions in practical applications, such as only in the ultraviolet light absorption wavelength, wide band gap, not too long separation of electronic-hole pairs and low utilization efficiency of sunlight [2]. In theory, the band gap width of TiO_2 is 3.2 eV [2]. So its application and development in the field of environmental protection were severely limited [1–3]. Therefore, extensive research efforts have been made to improve its absorption ability of visible light and photocatalytic efficiency via all kinds of modification methods [3,4].

To date, various methods have been developed to modify nanosized TiO_2, such as physical methods [4,5], metals doped [6,10] and sensitization modified [3,7]. Among these methods, the sensitization method can effectively extend the range of visible light absorption, and improve the photocatalytic efficiency for TiO_2 [7,8]. In addition, metalporphyrin was a special compound which contains macrocyclic aromatic conjugation system. The central metal can also improve the symmetry of porphyrin molecule. It will have a stronger absorption band in the visible light, and its light and temperature stability is good [8–10]. The various functional groups on the surface of TiO_2 and metalporphyrin sensitizers were regarded as the great approach to

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http://dx.doi.org/10.1016/j.apsusc.2016.05.161
0169-4332/

combine them with each other. Then They played an important role in various chemical processes, including catalytic oxidation, light-capturing, electron transfer, oxygen-carrying and so on. So, it have been regarded as the promising sensitizer, and attracted the wide attention of the research community [10,11]. For example, Chang have employed nickel-porphyrin sensitized TiO_2 to handle 2,4-dichlorophenol under visible light irradiation, and the maximum degradation rate was 81% within 4 h [12]. In addition, Murphy has employed 4-(4-carboxyphenyl) porphyrin to improve the catalytic activity of TiO_2. The degradation result also showed it can efficiently degrade pharmaceutical Famotidine under visible light irradiation [13]. These phenomena confirmed that those porphyrins or metalloporphyrin-sensitized TiO_2 catalysts could improve the visible-light photocatalytic performance of TiO_2. But there were no reports of TNTs sensitized by FeTCPP as the promising visible-light photocatalyst nanocomposite.

It is well-known that TNTs have been studied by many researchers for the decontamination of industrial wastewater and municipal wastewater [11,12–14]. Here, we prepared TNTs sensitized by FeTCPP as a visible-light photocatalyst that we call FeTCPP/TNTs. The novel photocatalysts have been characterized and analyzed by TEM/EDS, BET, XRD, FT-IR, DRS, PL, XPS and EPR in this work. Then the physical structure and chemical composition of FeTCPP/TNTs and bare TNTs were investigated systematically. The results showed that TNTs sensitized by FeTCPP can efficiently enlarge the wavelength response range, then it can increase the separation of electron-hole pairs. Therefore, it will enhance the photocatalytic activity under visible light irradiation. Meanwhile, the photocatalytic activity and stability of the prepared samples were evaluated by the degradation of MB solution under visible light irradiation.

2. Experiment

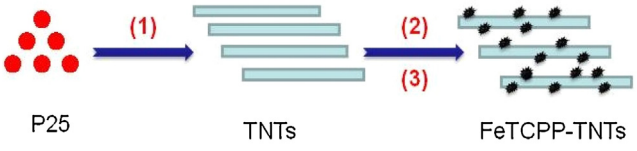
2.1. Chemicals and materials

TiO_2 nanoparticles (P25, d = ai.30 nm) were bought from EVONIK-DEGUSSA Co., Germany. MB, Dimethyl Formamide (DMF) (C_3H_7NO, 99.9%, AR) and Ethanol (C_2H_5OH, 99.7%, AR) were analytical reagent grade quality. FeTCPP was bought from the company called J&K Scientific, Ltd. Other chemicals were analytical grade. They were used without another purification in the process of experiment. And the solutions were prepared with deionized (DI) water.

2.2. Preparation of TNT and FeTCPP-TNT samples

TNTs were prepared by hydrothermal treatment [11]. 2 g of P25 nanoparticle was added into 50 mL 10 M NaOH solution. The solution was mixed thoroughly, then put into a 100 mL Teflon-lined flask. The flask was kept at 135 °C for 24 h in the oven and cooled naturally to room temperature (RT). Next, the precipitate of solution was washed by 0.1 M HCl until the pH value of the filtrate reached around 1.5. Another 24 h stirring was followed. Then the solution was ultrasound-treated for about 0.5 h to avoid agglomeration. Then, the solution was filtrated by pumping. Its precipitate was washed with DI water for about 6 recycled times until the pH value of the solution was neutral. Finally, the precipitate was dried at 60 °C for 24 h in the oven, and it was tagged as TNTs (as shown in Scheme.1).

The FeTCPP/TNTs were prepared as shown below (as shown in Scheme.1): 1 g of TNTs was added into 100 mL of DMF of FeTCPP with different loadings ranging from 10 mg to 50 mg, respectively. Then the mixture was heated to reflux for 6 h at 120 °C in the dark. The solids was washed with DMF until the filtrate was colorless.



(1) for hydrothermal treatment; (2) for heated reflux; (3) for FeTCPP.

Scheme 1. Preparation of TNTs and FeTCPP/TNTs samples.
(1) for hydrothermal treatment; (2) for heated reflux; (3) for FeTCPP.

Then it was washed with DI water for 10 times and dried for 8 h at 60 °C in the oven. It was taged as FeTCPP/TNTs.

2.3. Characterizations

TEM/EDS was characterized by a Tecnai G2 instrument. It was operated at 120 kV condition. Prepared samples were mixed and dissolved in ethanol before ultrasonic vibrations for 10 min. Next, two or three drops of the suspension were deposited on C-film coated copper grids, and it was ensured dry before analysis. In addition, an ordinary EDS instrument was used to detect the change of the atomic mass percent of the samples before and after loading. The specific surface areas and pore volume of the samples were estimated by BET (Micromeritics, ASAP 2020) with nitrogen adsorption at 77 K condition. X-ray diffraction (XRD) characterization was performed by a Rigaku Ultima IV X-ray diffractometer at RT, and operated at 40 kV and 44 mA condition, and scanned with a step length of 0.02 at 1°/min in the scope of $2\theta = 10°–90°$. Diffuse reflectance UV–vis spectrum (DRS) was characterized by a Varian Cary-500 UV–vis NIR spectrophotometer (USA). Photoluminescence (PL) spectra was carried out on Horiba Jobin Yvon-Fluoromax-4 equipment. The excitation wavelength was 325 nm. The emission was detected in the range of 400–700 nm. The EPR signals were acquired by A Bruker A300 spectrometer at RT under the following parameters: center field of 3400 G, sweep width of 2000 G, microwave frequency of 9.87 GHz, modulation frequency of 100 kHz and power of 20 mW.

2.4. Measurement of photocatalytic activity

The photocatalytic behavior of the samples was surveyed by the degradation of MB under visible light irradiation. The light source can provide by a 500 W halogen lamp with a 390 nm cut-off filter. The average value of luminous intensity on the samples surface was about 650 mW cm^{-2}. The temperature within the reaction system was maintained at 25 °C with a circle of running water, which could be used to hold the whole system in balance. The photo-degradation experiment was implemented through a Model XPA-VII photocatalytic reactor. The reacting suspension consisting of 1 L 10 mg/L MB and 100 mg catalysts, then it was stirred with a magnetic rod for 30 min to achieve complete incorporation before testing its adsorbability or photocatalytic activity. 5 mL of solutions was withdrawn from the suspension at interval time (20 min) to test its adsorbability or photocatalytic activity. Then, the photocatalysts were parted from the solution by centrifugation at 10,000 rpm for 5–10 min. Finally, the quantitative determination of degradation MB was detected by measuring its absorption at 665 nm through a UV–vis spectrophotometer. In addition, TNTs were also tested for reference. Importantly, these samples were separated from solution through centrifugal filtration at 10^4 rpm. Then the precipitate was reused for another 5 cycles to test its chemical stability.

Please cite this article in press as: M. Wei, et al., Preparation, characterization and visible-light-driven photocatalytic activity of a novel Fe(III) porphyrin-sensitized TiO_2 nanotube photocatalyst, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.05.161