



Mechanistic insights into TiO₂ thickness in Fe₃O₄@TiO₂-GO composites for enrofloxacin photodegradation



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HIGHLIGHTS

- Fe₃O₄@TiO₂-GO (FTG) composites with different TiO₂ shell thickness were synthesized.
- The photodegradation mechanism of ENR under visible light irradiation was studied.
- The effect of TiO₂ shell thickness on photo-degradation performance was investigated.

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ABSTRACT

Multifunctional Fe₃O₄@TiO₂-GO (FTG) magnetic composites have extensive application potential. However, the effect of TiO₂ shell thickness as well as its underlying mechanism remains murky and motivates our study. Herein, FTG composites with the optimized TiO₂ shell thickness were synthesized. The characterization results show that the FTG photocatalysts had the advantages of easy magnetic separation, extended light absorption range (>600 nm), and efficient charge separation properties. The photocatalytic activity of FTG was performed for photo-degradation of enrofloxacin (ENR) under visible light. The FTG composites with TiO₂ layer thickness of 17 nm exhibited the highest photocatalytic activity, and significant recycle efficiency. The photocatalytic mechanism, as characterized using electrochemistry, ESR, and *in-situ* QXAFS analysis, indicates that this optimal TiO₂ shell thickness delicately balances the generation and effective transport of electrons, and therefore is optimal for the production of hydroxyl radicals. This study provides new insights into the fabrication of TiO₂-based materials and their photocatalytic application.

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1. Introduction

TiO₂-based materials have attracted extensive attention due to the unique photocatalytic capability of TiO₂ [1]. However, the high recombination rate of photo-generated electron-hole pairs in TiO₂ limits its photocatalytic efficiency [2]. In addition, TiO₂ particles encounter intrinsic difficulties in subsequent solid/liquid separation, limiting its application in water treatment [3]. To this end, multifunctional Fe₃O₄@TiO₂-GO nanocomposites have received tremendous interest with their promise of integrating high

photocatalytic activity and magnetic separation properties within a single hybrid material [4]. Magnetic separation is a convenient approach combining active TiO₂ with Fe₃O₄ to create composite materials that are readily separable under modest magnetic fields [3]. On the other hand, GO provides an efficient platform for the adsorption of dyes as well as efficient charge transfer due to its unique two-dimensional planar structure [5].

Previous research suggests that the photocatalytic performance of core-shell composites strongly depends on having shell frameworks with tunable thickness over well-designed functional cores [6,7]. Recently, researchers have become aware of the crucial role of the molar ratio of TiO₂ shell to Fe₃O₄ core in photocatalytic activity, but conclusions on the TiO₂ thickness effect are controversial. For example, the photocatalytic activity of Fe₃O₄@TiO₂ composites was reported to decrease with increasing TiO₂ thickness from 15 nm to 120 nm [6]. In contrast, Jing et al. proposed that the increase in molar ratio of TiO₂ to Fe₃O₄ from 1:1 to 70:1 leads

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to an increase in the photo-degradation efficiency of quinolone from 73.45% to 89.88% [7]. The lack of conformity between many experimental observations suggests that the effect of TiO₂ thickness as well as its underlying mechanism is still not fully understood. Nevertheless, this missing knowledge is critical for developing TiO₂-based materials and their environmental application.

The widespread usage of antibiotics is the matter of increasing concern in recent years. Based on the amounts reported in literature, the concentration of enrofloxacin (ENR) is in the range of few tens of ppb [8]. As designed to interfere with specific biological systems, ENR poses serious threats to the ecosystem and human health even at low concentrations [9]. Conventional approaches including absorption and biodegradation suffer from the drawback of time-consuming [3]. Photocatalytic degradation is one of the more promising removal methods in surface waters [10]. From the perspective of environmental photocatalysis, the search of visible light active photocatalyst is highly indispensable for the purification of wastewater [11].

Here we report the synthesis of FTG multifunctional composites with the optimized TiO₂ shell thickness, which can photocatalytically degrade the organic ENR under visible light. A systematical synthetic strategy and mechanism were reported to fabricate multifunctional Fe₃O₄@TiO₂-GO (FTG) magnetic composites with tunable TiO₂ thickness. Multiple characterization techniques were used including field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS). The photocatalytic performance of FTG composites was tested for the photo-degradation of ENR, and the recycle efficiency of FTG was also tested for seven cycles to ensure the applicability of FTG. In order to clarify the photo-degradation mechanism, ESR, *in-situ* QXAFS, and electrochemistry were conducted, and the ENR degradation pathway was proposed. The insights gained from this study shed new light on the design and fabrication of multifunctional materials and their environmental application in water/wastewater treatment.

2. Experimental section

2.1. Materials

Cetyl trimethyl ammonium bromide (CTAB, 99%), tetrabutyl titanate (TBOT, ≥ 97%), 3-aminopropyltrimethoxysilane (APTMS, 97%), 5,5-dimethyl-1-pyrrolidine-N-oxide (DMPO), and enrofloxacin (ENR, 98%) were purchased from Sigma-Aldrich (St. Louis, US). Ferric chloride (FeCl₃·6H₂O), ammonium acetate (NH₄Ac), sodium citrate (Na₃C₆H₅O₇), aqueous ammonia, sulfuric acid (H₂SO₄, 98%), and sodium nitrate (NaNO₃, ≥99%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were used as received without further purification.

2.2. Synthesis of FTG nanocomposites

The ternary composite FTG was synthesized by a hydrothermal method. In a typical synthesis procedure, FeCl₃·6H₂O, sodium citrate and ammonium acetate were dissolved in ethylene glycol to synthesize the Fe₃O₄ particles by a modified solvothermal reaction [12,13]. Then, 0.05, 0.1, 0.5, 1.0 or 2.0 mL TBOT as the Ti source was added dropwise into the Fe₃O₄-APTMS dispersed solution to synthesize the Fe₃O₄@TiO₂ particles. CTAB was also added to improve the dispersibility of particles. After calcining at 450 °C, as-prepared Fe₃O₄@TiO₂ particles were mixed with GO and then maintained at 180 °C for 18 h. The final product was washed with ethanol and dried in a vacuum at 50 °C. The Fe₃O₄@TiO₂-GO com-

posites with molar ratios of TiO₂ to Fe₃O₄ of 0.5:1, 1:1, 5:1, 10:1, and 20:1 were denoted as FTG-0.5, FTG-1, FTG-5, FTG-10 and FTG-20, respectively. The assumed formation procedure of FTG can be schematically illustrated as shown in Scheme 1, and the details of the synthesis of the composites are given in Supporting Information (SI).

2.3. Characterization

The surface morphology was characterized by using an FE-SEM with an Oxford energy-dispersive X-ray spectrum (EDS) analyzer (S-3000 N, Hitachi). The crystal morphology was recorded using an HR-TEM (F20, FEI). The crystal structure was characterized by XRD using an X'Pert PRO MPO diffractometer (PANalytical, Netherlands) with Cu Kα radiation. The particle size distribution was measured using a Malvern Zetasizer Nano ZS (Malvern Instruments, U.K.). Raman spectra were recorded on a laser confocal microscopy Raman spectrometer (LabRAM HR Evolution, HORIBA, JPN) with excitation wavelength at 532 nm. XPS patterns were analyzed on a Thermo SCIENTIFIC ESCALAB 250 spectrometer with Al Kα X-ray radiation at 1486.8 eV. The ESR signal of ·OH radicals was recorded on a Bruker EMX plus spectrometer (LOT-Oriel GmbH&Co. KG, Germany). The QXAFS was analyzed on beamline 14W1 at the Shanghai Synchrotron Radiation Facility (SSRF, China).

2.4. Photocatalytic experiments

In the visible light photocatalysis, ENR aqueous solution (2 ppm, 50 mL, pH = 7) was stirred with 20 mg photocatalysts and equilibrated prior to irradiation. The photodegradation was constructed with a 500 W Xe lamp and a cutoff filter equipped as the light source (λ = 420 nm). The concentration of ENR was estimated as the area of the peak obtained in the liquid chromatogram. The details of sample analysis by HPLC-ESI-Q-TOF-MS are provided in the SI.

3. Results and discussion

3.1. FTG synthesis and characterization

Fig. 1 summarizes the morphology, composition, and size distribution of FTG samples. As revealed by FE-SEM images, uniform Fe₃O₄@TiO₂ spheres synthesized with tunable molar ratios of TiO₂ to Fe₃O₄ were evenly distributed on the GO sheets with a high density (Fig. 1A1–A6). The detailed fabrication process is described in the Experimental Section. The particle size of Fe₃O₄ spheres was 530 ± 27 nm (Fig. 1A1). The size of FTG increased from 534 ± 23, 552 ± 19, 564 ± 20, 623 ± 23, to 668 ± 17 nm with increasing TiO₂ to Fe₃O₄ molar ratios from 0.5:1, 1:1, 5:1, 10:1, to 20:1, respectively (Fig. 1A2–A6). In agreement with our SEM results, the FTG size distribution exhibited the same increasing trend as a function of TiO₂/Fe₃O₄ (Fig. 1B2–B6). Compared with SEM results (530–668 nm), FTG size distribution resolved slight larger diameters (531–1106 nm) due to colloidal aggregation, which is pronounced at ratios of TiO₂/Fe₃O₄ >10.

The TEM images clearly illustrate that Fe₃O₄@TiO₂ particles with a well-defined core/shell structure are distributed on the graphene sheets (Fig. 1C2–C6). In addition, the thickness of the TiO₂ shell can be effectively tuned by varying the TiO₂/Fe₃O₄ molar ratio during the synthetic process. In agreement with a previous report [4,14], the formation of the TiO₂ shell occurs in three stages: when TiO₂/Fe₃O₄ <1, heterogenous nucleation of TiO₂ takes place on the surface of the Fe₃O₄ cores, resulting in a thin TiO₂ shell (<10 nm, Fig. S2). Once TiO₂/Fe₃O₄ >5, uniform TiO₂ shells (17 nm) are constructed on the surface of the Fe₃O₄ spheres. When TiO₂/Fe₃O₄ >10,

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