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 TiO_2 thickness as well as its underlying mechanism is still not fully understood. Nevertheless, this missing knowledge is critical for developing TiO_2 -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 TiO_2 shell thickness, which can photocatalytically degrade the organic ENR under visible light. A systematical synthetic strategy and mechanism were reported to fabricate multifunctional $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-GO}$ (FTG) magnetic composites with tunable TiO_2 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, $\geq 97\%$), 3-aminopropyltrimethoxysilane (APTMS, 97%), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), and enrofloxacin (ENR, 98%) were purchased from Sigma-Aldrich (St. Louis, US). Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ammonium acetate (NH_4Ac), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), aqueous ammonia, sulfuric acid (H_2SO_4 , 98%), and sodium nitrate (NaNO_3 , $\geq 99\%$) 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, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, sodium citrate and ammonium acetate were dissolved in ethylene glycol to synthesize the Fe_3O_4 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 Fe_3O_4 -APTMS dispersed solution to synthesize the $\text{Fe}_3\text{O}_4/\text{TiO}_2$ particles. CTAB was also added to improve the dispersibility of particles. After calcining at 450°C , as-prepared $\text{Fe}_3\text{O}_4/\text{TiO}_2$ 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 $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-GO}$ com-

posites with molar ratios of TiO_2 to Fe_3O_4 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 $\text{Cu K}\alpha$ 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 $\text{Al K}\alpha$ X-ray radiation at 1486.8 eV. The ESR signal of $\cdot\text{OH}$ 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, $\text{pH} = 7$) 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 ($\lambda = 420$ 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 $\text{Fe}_3\text{O}_4/\text{TiO}_2$ spheres synthesized with tunable molar ratios of TiO_2 to Fe_3O_4 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 Fe_3O_4 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 TiO_2 to Fe_3O_4 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 $\text{TiO}_2/\text{Fe}_3\text{O}_4$ (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 $\text{TiO}_2/\text{Fe}_3\text{O}_4 > 10$.

The TEM images clearly illustrate that $\text{Fe}_3\text{O}_4/\text{TiO}_2$ particles with a well-defined core/shell structure are distributed on the graphene sheets (Fig. 1C2–C6). In addition, the thickness of the TiO_2 shell can be effectively tuned by varying the $\text{TiO}_2/\text{Fe}_3\text{O}_4$ molar ratio during the synthetic process. In agreement with a previous report [4,14], the formation of the TiO_2 shell occurs in three stages: when $\text{TiO}_2/\text{Fe}_3\text{O}_4 < 1$, heterogenous nucleation of TiO_2 takes place on the surface of the Fe_3O_4 cores, resulting in a thin TiO_2 shell (< 10 nm, Fig. S2). Once $\text{TiO}_2/\text{Fe}_3\text{O}_4 > 5$, uniform TiO_2 shells (17 nm) are constructed on the surface of the Fe_3O_4 spheres. When $\text{TiO}_2/\text{Fe}_3\text{O}_4 > 10$,

Scheme 1. Schematic illustration of the synthesis process of the $\text{Fe}_3\text{O}_4@\text{TiO}_2\text{-GO}$ (FTG).

Fig. 1. SEM images of Fe_3O_4 (A1) and FTG with different molar ratios of TiO_2 to Fe_3O_4 0.5:1 (A2), 1:1 (A3), 5:1 (A4), 10:1 (A5), and 20:1 (A6). B1–B6 show the particle size distributions obtained with DLS of as-prepared samples A1–A6, respectively. TEM images of Fe_3O_4 (C1) and FTG with the molar ratios of TiO_2 to Fe_3O_4 0.5:1 (C2), 1:1 (C3), 5:1 (C4), 10:1 (C5), and 20:1 (C6), and the corresponding EDS spectra D1–D6.

however, the presence of an appreciable amount of titanium oligomers enables TiO_2 shells to grow rapidly in thickness (>45 nm). At this stage, heterogeneous and homogeneous nucleation occur simultaneously, leading to the observed aggregated structures. Notably, the relative intensity of Ti in the EDS spectra increased from 0.4% to 12% (Fig. 1D1–D6), in line with the SEM and TEM conclusion. As expected, the FTG samples exhibited a good magnetic property [4], with saturation magnetization of 27 emu g^{-1} , and good thermal stability, with 30% weight loss from room temperature to 1000°C (Fig. S3).

HRTEM combined with EDX elemental mapping allows a direct view of the surface features and crystal structure of FTG (Fig. 2). Clearly, the lattice fringe spacing of 0.25 nm in the spherical parti-

cles was consistent with the (311) plane of Fe_3O_4 (Fig. 2B) [15]. Meanwhile, the TiO_2 layer exhibited a set of apparent lattice fringes with an inter-planar distance of 0.35 nm (Fig. 2C), which is indexed to the (101) plane of anatase TiO_2 [16]. The corresponding selected-area electron diffraction (SAED) pattern (Fig. 2D) revealed the (101), (004), (200) and (204) planes of anatase TiO_2 , indicating the polycrystalline nature of the FTG composites.

The elemental composition and distribution of FTG were characterized with EDX mapping (Fig. 2E–H). The predominant elements were Fe, Ti, and O, with Fe (yellow dots) in the core, Ti (orange dots) uniformly around the core, and O (red spots) throughout the whole field. This EDX mapping result confirms that the composites have a core/shell structure and are well-dispersed

Fig. 2. TEM (A), high-voltage TEM image of Fe_3O_4 (B) and the as-prepared FTG-5 (C–E), and the corresponding EDX mapping images of oxygen (F), titanium (G), and iron (H) elements. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

on the GO sheets. In this study, $\text{Fe}_3\text{O}_4@\text{TiO}_2$ was synthesized using ATPMS modification of the Fe_3O_4 surface, which promoted the subsequent chemical grafting of TiO_2 onto the surface of Fe_3O_4 [12]. In contrast to reported strategies using SiO_2 as an intermediate shell connecting Fe_3O_4 and TiO_2 , our approach allows facile growth of TiO_2 over Fe_3O_4 colloids without the use of any bridging shells [17]. Moreover, the intimate connection between $\text{Fe}_3\text{O}_4@\text{TiO}_2$ particles and GO sheets facilitates the transfer of photo-induced electrons during the photoexcitation process [18].

The successful incorporation of $\text{Fe}_3\text{O}_4@\text{TiO}_2$ onto GO sheets was confirmed by XRD analysis (Fig. 3A). Five well-defined diffraction peaks at 25.3, 37.9, 48.0, 54.0, 55.0 and 62.8° were indexed to the (101), (004), (200), (105), (211) and (204) planes of anatase TiO_2 (JCPDS 21-1272), respectively. In addition, five peaks at 30.1, 35.4, 43.0, 56.9, and 62.5° were assigned respectively to the (220), (311), (400), (511) and (440) planes of spinel structure Fe_3O_4 (JCPDS 65-3107). Notably, the characteristic peak of GO corresponding to the (100) plane shifted from 42.0° on GO to 41.0° on FTG, implying the formation of $\text{Fe}_3\text{O}_4@\text{TiO}_2$ -modified graphene sheets [17]. FTG exhibited several peaks at 33.9, 50.0 and 63.0° due to Fe_2O_3 , indicating the oxidation of Fe_3O_4 at high temperature [19]. However, the peak intensities of Fe_2O_3 relative to Fe_3O_4 gradually diminished with increasing TiO_2 thickness (Table S1), suggesting that the TiO_2 shell protects the Fe_3O_4 core from oxidation.

Raman analysis, as shown in Fig. 3B, resolved two characteristic peaks at 1340 cm^{-1} and 1596 cm^{-1} , which are attributed to the disordered sp^3 -carbon (D band) and graphitic sp^2 -carbon (G band), respectively [20]. The intensity ratio of D and G bands (I_D/I_G) is usually used to evaluate the crystal structure, disorder and defects of carbons [21]. Compared with the original GO ($I_D/I_G = 0.84$), increased I_D/I_G values were observed for FTG-0.5 (1.15), FTG-1 (1.35), FTG-5 (1.63), FTG-10 (1.71), and FTG-20 (1.80), indicating the reduction of GO when it bonds with $\text{Fe}_3\text{O}_4@\text{TiO}_2$ particles. The high I_D/I_G value also implies that a variety of defects are present in the GO sheets, which efficiently increases the electron density and extends the lifetime of electrons [22]. As shown in the Fig. 4, the Raman shifts of Fe_3O_4 at 219, 284, and 391 cm^{-1} and of TiO_2 at 150 (E_g), 377 (B_{1g}), 511 ($B_{1g} + A_{1g}$) and 638 cm^{-1} (E_g) were resolved [21], in line with our XRD results.

XPS was used to study the surface chemical bonding, and the results are presented in Fig. 3C and Table S2. The C1s spectra of

GO and FTG were deconvoluted into three components, C–C/C=C, C–O, and C=O. The shift of the C–O peak in FTG-5 (286.4 eV) with respect to the pristine GO (287 eV) demonstrated the successful incorporation of $\text{Fe}_3\text{O}_4@\text{TiO}_2$ on the GO sheets. Meanwhile, compared with the pristine GO, the peak intensities of the C–O group in FTG decreased substantially, suggesting the reduction of GO and the formation of rGO [23]. In the hydrothermal process, supercritical water as the reducing agent partly removes the oxygen-containing functional groups on GO, and leads to the reduction of GO. Due to the two-dimensional π -conjugation structure, rGO provides a better platform for adsorption and charge transfer [5]. Notably, the formation of a TiO_2 shell on the surface of Fe_3O_4 cores was clearly evidenced by the Ti 2p XPS spectra. Importantly, the Ti 2p_{3/2} peak (458.8 eV) on FTG was shifted to lower energy with respect to that on FT (459.0 eV). This energy shift demonstrates the presence of Ti^{3+} on FTG, and agrees well with the chemical shift of Ti^{3+} -doped TiO_2 as reported in the literature [24]. Ti^{3+} captures photoelectrons, promotes the segregation of electrons and cavities, and ultimately reduces the bandgap of TiO_2 [25]. The slightly increased percentage (approximately 1%, Table S2) of Ti^{3+} may be attributed to positively-charged oxygen vacancies with accompanying charge-compensating electrons. With the increase of oxygen vacancy, the electronic band gap of the as-prepared FTG composites was substantially reduced to 1.78 (in FTG-20 and FTG-10), 1.71 (FTG-5), 1.77 (FTG-1), and 1.76 (FTG-0.5) eV (Fig. S5). Compared with crystalline TiO_2 (3.2 eV) and Fe_3O_4 (1.84 eV), this narrowing of the band gap was attributed to the introduction of Fe_3O_4 and GO, which is significant for improving solar energy conversion [26].

3.2. Photocatalytic performance

To explore the effect of TiO_2 thickness on the photocatalytic activity of FTG, photo-degradation experiments were conducted. FTG-5 exhibited the highest photocatalytic efficiency, as evidenced by its MO removal (87.7%) and pseudo-first-order rate constant (0.039 min^{-1}), which were the highest among all FTG samples (Fig. S6). Then, the photo-degradation of ENR was conducted using FTG-5 as photocatalysts. The adsorption kinetics for FTG-5 and P25 have been analyzed by the pseudo-second-order model (Fig. 4A). During dark adsorption experiment, the equilibrium adsorption

Fig. 3. (A) XRD patterns of (a) GO, (b) Fe₃O₄, (c) TiO₂-GO, FTG prepared with different molar ratios of TiO₂ to Fe₃O₄ (d) 0.5:1, (e) 1:1, (f) 5:1, (g) 10:1, (h) 20:1. (B) Raman spectra of (a) GO, (b) FTG-0.5, (c) FTG-1, (d) FTG-5, (e) FTG-10, and (f) FTG-20. (C) High-resolution XPS spectra of the C 1s peaks of GO and FTG-5, the Ti 2p peaks of FT and FTG-5.

Fig. 4. (A) Adsorption of ENR by FTG-5 and P25 as a function of contact time. The solid line is the fit to the 2st kinetics model. The inset shows parameters of the kinetics model for adsorption of ENR on FTG-5 and P25. (B) Photocatalytic degradation of ENR with and without photocatalysts under visible light. (C) Variation in the efficiency of the FTG-5 for the photocatalysis of ENR with cycling. The exposure time in each cycle was 120 min.

capacity of ENR on FTG-5 and P25 was 5.3 and 3.1 mg·g⁻¹, respectively. The results are line with the comparison of their BET surface area, the FTG-5 (47.1 m²·g⁻¹) has higher specific surface area than the P25 particles (38.7 m²·g⁻¹). The kinetics studies indicated that the adsorption of ENR on the FTG-5 and P25 particles follows the pseudo-second-order kinetics model with higher correlation coefficients (Fig. S9). The rate constant for ENR adsorption was found to be 0.062 and 0.017 g mg⁻¹·min⁻¹ using FTG-5 and P25, respectively. This superior adsorption performance of FTG-5 can be attributed to facile adsorption of ENR onto the planar surface of rGO with an offset face-to-face orientation via π - π stacking [11].

The adsorption measurements highlight the importance of GO by not only enhancing the water-dispersion of FTG but also providing adsorption sites for the inclusion of the ENR molecules [3].

The photocatalytic degradation of ENR was carried out under visible light ($\lambda = 420$ nm) in the presence of FTG-5 and P25. For comparison, blank experiments were observed under direct photolysis without photocatalysts. It may be seen from Fig. 4B that ENR was not susceptible to photodegradation under 420 nm illumination. Under visible light, 96.0 and 48.2% of ENR was removed in 240 min by FTG-5 and P25, respectively. Compared to P25 particles, FTG-5 showed higher photocatalytic performance for ENR

degradation. The advancement of FTG-5 in photocatalytic activity should be first attributed to the superior adsorptivity, which facilitates the initial oxidation step of the photocatalytic reaction [5]. The change in COD and TOC during the degradation process was analyzed to investigate the extent of ENR mineralization (Fig. S10). The results indicated that during photo-degradation process, 76.8% COD and 79.1% TOC removal were attained for ENR degradation using FTG. It is noteworthy that the absorption range of light plays an important role in the visible light photocatalysis. Then FTG has the potential to significantly improve solar energy conversion, facilitating its use in practical environmental remediation.

The separation and reusability of the photocatalysts are important consideration for their application in practical water remediation. The initial concentration of ENR was 100 ppb, based on the actual ENR concentration in the range of few tens of ppb [27]. The FTG-5 was magnetically separated after the photocatalytic degradation of ENR, and then reused for the photocatalysis of a freshly prepared ENR solution. The efficiency of the FTG-5 for the photocatalytic degradation of ENR is shown in Fig. 4C, even after 7 cycles 90% efficiency maintained as compared to the first use efficiency. As presented in Fig. S12, the XRD spectra of FTG-5 showed no significant change before and after photo-degradation. These results clearly demonstrated the stability of FTG composites during ENR mineralization process.

3.3. Photocatalytic mechanism

To further clarify the photocatalytic mechanism of enrofloxacin by FTG, the ESR signal spin-trapped with DMPO was carried out. As shown in Fig. 5A, a 4-fold characteristic peak with an intensity ratio of 1:2:2:1 was observed for DMPO- $\cdot\text{OH}$, and FTG-5 resulted

in the highest $\cdot\text{OH}$ signal intensity. Generally, the formation of $\cdot\text{OH}$ depends on the efficient generation, separation and transfer of photo-induced electrons [15]. Then, how would these photo-generated electrons transfer? In theory, according to the valence band (VB) energy-levels of Fe_3O_4 and TiO_2 [28] (Fig. 5B), electrons may transfer from TiO_2 (VB = -7.41 eV) to Fe_3O_4 (VB = -7.43 eV). However, our *in-situ* Fe-edge XAFS result shown in Fig. 5C indicated that the oxidation state of Fe in FTG-5 remained unchanged upon light irradiation, the three normalized K-edge peaks detected at 7112.2, 7130.9 and 7146.9 eV did not shift. Simultaneously, the EIS spectra (Fig. 5D) demonstrated that with the introduction of GO, the EIS semicircle became smaller, indicating that the existence of GO causes a decrease in the charge transfer resistance on the surface [29,30]. The results suggest that GO is an acceptor and transporter of the generated electrons by TiO_2 shell, which could contribute to the suppression of charge recombination.

In the following, the transformation pathway in the photocatalysis of ENR was proposed, and the structures of three major photo-products, namely P1-P3, were identified by HPLC-Q-TOF-MS (Fig. 6). The proposed pathway is that $\cdot\text{OH}$ broke the C=C bond by the electrophilic attack, opening the piperazine ring to generate P2. The headmost of ethyl group of ENR approached to the FTG surfaces by the electrostatic interactions between protonated ethyl group and negatively charged FTG surfaces ($\text{pH}_{\text{pzc}} = 4.9$) in the investigated conditions (Fig. S13). As a short-lived and high-reactive oxidizing agent, $\cdot\text{OH}$ broke the adjacent C=C position with the highest electron density in the ring [9]. Then the piperazine ring was readily opened by the further reactions including N-dealkylation and C-hydroxylation [31]. The amine with functional group of $-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$ will be further oxidized and decaronylated to $-\text{NH}_2$ [31]. Another possible ENR transformation pathway was that the ENR dealkylation led to the intermediate

Fig. 5. (A) ESR spectra of radical adducts trapped by DMPO in FTG-0.5, FTG-1, FTG-5, FTG-10 and FTG-20. (B) Energy-level diagram of TiO_2 and Fe_3O_4 . (C) The Normalized Fe K-edge XANES spectra of FTG-5. (D) EIS changes of FT-5 and FTG-5 electrodes. The electrochemical measurements were performed in the presence of 2.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ as a redox probe in 0.1 M KCl aqueous electrolyte.

Fig. 6. Degradation paths and byproducts in the photocatalysis of ENR under visible light irradiation.

product P1. Thus, the reactive site and reaction pathways can be determined by both the surface adsorption and the electron density in the target molecules.

4. Conclusion

A multifunctional $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-GO}$ (FTG) photocatalyst with high performance has been successfully synthesized by a hydrothermal method. The superparamagnetic Fe_3O_4 core of FTG allowed efficient separation once photo-degradation was completed. GO provided a good platform for adsorption and charge transport, enhancing the photo-degradation rate. The TiO_2 layer thickness was found to affect the photocatalytic activity. When the TiO_2 layer thickness was 17 nm, superior photocatalytic efficiency and good magnetic separation properties were reached. This optimized TiO_2 thickness delicately balanced both electron generation and transport. The photocatalytic activity of FTG to ENR molecules has been demonstrated. The superior adsorptivity and the narrowing of the band gap of FTG make the photodegradation efficiencies far superior to that of bare TiO_2 particles. Another attractive feature of FTG is that they can be reused with little or no loss of photocatalytic activity. Overall, the insights gained from this study provide the principles to design TiO_2 -based photocatalysts with core/shell structures, which have great potential for environmental applications.

Associated content

Supporting Information available: Experimental details for the fabrication of FTG composites with tunable TiO_2 thickness, VSM, TGA, XPS, UV-vis DRS, CV and EIS characterization of FTG.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. *These authors contributed equally.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2017.05.092>.

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