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Enhanced visible light photocatalytic degradation of methylene blue by F-doped TiO_2

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ABSTRACT

F-doped TiO_2 (F-TiO_2) were successfully synthesized using a modified sol–gel method. The morphologies, structures, and photocatalytic performance in the degradation of methylene blue (MB) were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, UV–vis absorption spectroscopy, and electrochemical impedance spectra, respectively. The results show that F-TiO_2 exhibits an enhanced photocatalytic performance in the degradation of MB with a maximum degradation rate of 91% under visible light irradiation as compared with pure TiO_2 (32%). The excellent photocatalytic activity is due to the contribution from the increased visible light absorption, promoted separation of photo-generated electrons and holes as well as enhanced photocatalytic oxidizing species with the doping of F in TiO_2.

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1. Introduction

Numerous efforts have been made to develop highly effective photocatalysts for the degradation of organic pollutants [1–8], reduction of heavy metals [9–11], air purification and hydrogen production [12–14]. TiO_2 has been proved to be the promising photocatalyst for widespread environment applications due to its electric properties, nontoxicity, biological and chemical inertness, cost effectiveness, strong oxidizing power, and long-term stability against chemical corrosion and photocorrosion [15–20]. However, it can only absorb ultraviolet light due to its wide band gap (3.2 eV), and is not responsive to visible light ($\lambda > 400$ nm), which accounts for around 46% of the total solar energy. Therefore, exploring visible light efficient photocatalysis has been an urgent issue from the viewpoint of using solar energy.

Considerable effort has been made to expand the photoresponse of TiO_2 into the visible light region [21–23]. Doping with nonmetal elements such as N, C, and B revealed a possibility for the utilization of solar light [24–26]. Among these elements, F-doped TiO_2 (F-TiO_2) was demonstrated an effective approach to promote the visible light photocatalytic activity of TiO_2 [27–30]. Up to now, F-TiO_2 was fabricated by various methods such as hydrothermal or solvothermal process, spray pyrolysis, solution combustion method [31,32]. However, these methods are inevitably confronted with several disadvantages, such as long duration of reaction, high energy-consumption or requirement of special conditions. Compared with these methods, the sol–gel method is a simple one-step synthesis method, which usually does not require special equipment and produce toxic products. Dozzi et al. [33] synthesized F-TiO_2 via a sol–gel method in the presence of NH_4F followed by calcination and found that F-TiO_2 exhibited high photocatalytic activity in the degradation of formic acid under visible light irradiation, which is ascribed to highly crystalline pure anatase and reduced the charge carrier recombination. Huang et al. [34] reported that F-TiO_2 photocatalysts fabricated by a modified sol–gel hydrothermal method showed enhanced remarkably photocatalytic activity in the degradation of formaldehyde at concentrations of 0.4 mg m^{-3} (74.5%) under visible light irradiation as compared with pure TiO_2 (62.1%) because the doped F could improve the crystallization and adsorption capacity of TiO_2. Xu et al. [35] revealed that F-TiO_2 film fabricated by a sol–gel method exhibited much higher photocatalytic activity in the degradation of X-3B (82%) under artificial solar light than pure P25, which may be

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due to extrinsic absorption through the creation of oxygen vacancies rather than the excitation of the intrinsic absorption band of bulk TiO_2. Despite the above progress to date, as promising hybrid materials for photocatalysis, the exploration on F-TiO_2 is not nearly enough so far. Especially the photocatalytic efficiency of F-TiO_2 is far away for practical application. Therefore, the photocatalytic efficiency of F-TiO_2 needs to be further improved by optimizing the experimental conditions.

In this work, a one-step synthesis of F-TiO_2 was carried out through the hydrolysis of tetrabutyl titanate in NH_4F solution. The as-prepared F-TiO_2 exhibits an enhanced photocatalytic activity in the degradation of methylene blue (MB) under visible light irradiation as compared with pure TiO_2. A maximum MB degradation rate of 91% was achieved for F-TiO_2 under visible light irradiation.

2. Experimental

Seven milliliter of tetrabutyl titanate was first dissolved in 30 ml of ethanol by stirring for 30 min at room temperature to obtain solution A. A certain amount of NH_4F was dissolved in 28 ml of ethanol, and then 10 ml of acetic acid, 3 ml of deionized water and 1 ml of hydrochloric acid were successively added to the solution with stirring for 30 min at room temperature to obtain solution B. Solution B was then added dropwise into solution A under vigorous stirring. Subsequently, the mixture solution was continuously stirred at room temperature for the hydrolysis of tetrabutyl titanate until a transparent sol was formed. Finally, the sol was dried in air at 100 °C for 24 h, ground and heated at 500 °C for 1 h. The as-synthesized F-TiO_2 samples with 5, 10, 15 wt.% F during the preparation were named as T-5, T-10, and T-15, respectively. The pure TiO_2 was also synthesized using the similar method without adding of NH_4F for comparison. For the electrochemical impedance spectra (EIS) testing, the as-synthesized composites with 5 wt.% cellulose binder were homogenously mixed in terpineol to form a slurry. Then, the resultant slurries were coated on the FTO using a screen-printing approach. Finally, these prepared electrodes were sintered at 500 °C for 30 min.

The surface morphology, structure and composition of the samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800), high-resolution transmission electron microscopy (HRTEM, JEOL-2010), energy dispersive X-ray spectroscopy (EDX, JEM-2100) and X-ray diffraction (XRD, Holland Panalytical PRO PW3040/60) with Cu Kα radiation ($V = 30$ kV, $I = 25$ mA), respectively. The UV–vis absorption spectra were recorded using a Hitachi U-3900 UV–vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurement was performed on an Imaging Photoelectron Spectrometer (Axis Ultra, Kratos Analytical Ltd.) with a monochromatic Al Kα X-ray source. Brunauer–Emmett–Teller (BET) surface area was analyzed by nitrogen adsorption in a Micrometitics ASAP 2020 nitrogen adsorption apparatus. The adsorption isotherm was used to determine the pore size distribution using the Barret–Joyner–Halender (BJH) method. EIS measurements were carried out on an electrochemical workstation (AUTOLAB PGSTAT302N) under dark conditions using a three electrode configuration with the as-prepared films as working electrode, a Pt foil as counter electrode and a standard calomel electrode as reference electrode. The electrolyte was 10 mg l^{-1} MB aqueous solution. EIS were recorded in the frequency range of 0.005 Hz^{-1} MHz, and the applied bias voltage and ac amplitude were set at open-circuit voltage and 10 mV.

The photocatalytic performance of the as-prepared samples was evaluated by photocatalytic degradation of MB under visible light irradiation. The samples (2 g l^{-1}) were added into 80 ml MB aqueous solutions (10 mg l^{-1}). The mixed suspension was magnetically stirred in the dark for 0.5 h to reach an adsorption–desorption equilibrium. Under stirring, the mixed suspension was exposed to the visible irradiation ($\lambda > 400$ nm) produced by a 400 W metal halogen lamp with cut off filter. At certain time intervals, 2 ml of the mixed suspension was extracted and centrifugated to remove the photocatalyst. The filtrates were analyzed by recording the UV–vis spectra of MB using a Hitachi U-3900 UV–vis spectrophotometer.

The formation of hydroxyl radicals at the photocatalyst/water interface under visible light irradiation was detected by a photoluminescence (PL) technique using coumarin as probe molecule,

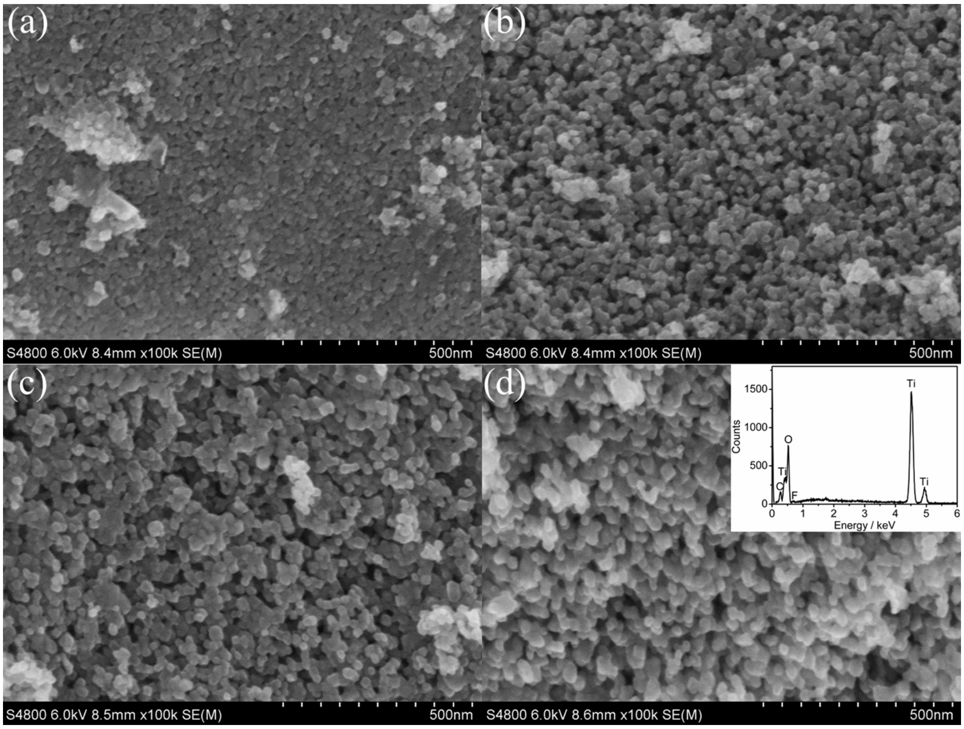

Fig. 1. Surface morphologies of (a) TiO_2, (b) T-5, (c) T-10, and (d) T-15; Inset is EDX spectrum of T-10.

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