

Preparation, characterisation and enhanced photocatalytic activities of Fe,F co-doped TiO₂ nanotubes

Zhuanni Yu, Jing Lan, Qiang Wang ✉

College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao 266109, People's Republic of China

✉ E-mail: 13954283108@139.com

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Fe,F co-doped TiO₂ nanotubes (Fe,F/TiO₂ NTs) were synthesised by the combination of hydrothermal process and impregnation method. The structure and composition of prepared catalysts were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). XRD results confirmed only the presence of the anatase phase in Fe,F/TiO₂ NTs. Well-defined TiO₂ NTs with nearly uniform diameters could be seen from the TEM images. Also, the high-resolution XPS spectra of Fe 2P and F 1s showed that Fe³⁺ and F⁻ existed in TiO₂ lattice and on the surface of TiO₂, respectively. The photocatalytic performances of Fe/TiO₂ NTs and Fe,F/TiO₂ NTs with different Fe concentrations were evaluated by photo-degrading aqueous methyl orange under visible light irradiation, and the results showed that the photoactivity of Fe and F co-doped TiO₂ NTs was enhanced obviously compared with Fe mono-doped TiO₂ NTs and the 0.5% Fe,F/TiO₂ NTs presented the best photocatalytic performance.

1. Introduction: Since titanate nanotubes (NTs) fabricated through the hydrothermal process were reported by Kasuga [1], a number of research studies have focused on the characterisation and modification of this kind of NT owing to its special shape, size confinement effect in the radial-direction and larger specific surface area [2–4]. However, the practical application of TiO₂, as a semiconductor, is limited because of its low photocatalytic efficiency. Doping with appropriate transitional metals and non-metals have been attempted to enhance its photocatalytic performance [5–9].

More recently, ion co-doping becomes a prospective strategy to further improve the photocatalytic efficiency of TiO₂. This property can be due to the synergetic action of ion co-doping [10]. Shen *et al.* have prepared N and Fe co-doped titania photocatalysts by a sol-gel method which exhibited significantly enhanced photocatalytic activity for the degradation of metal oxide (MO) in comparison with the commercial TiO₂ (Degussa P25) [11]. Yang *et al.* have synthesised F and N co-doped titania nanocrystals with higher photocatalytic performance partly due to the synergetic effect of F and N co-doping [12]. As has been reported, fluorine or ferrum mono-doping can improve the photocatalytic performance of TiO₂ [5, 6, 9]. Therefore, it is essential to prepare tubular TiO₂ photocatalysts co-doped with F and Fe and investigate their photocatalytic activity, to the best of our knowledge, which has been few reported up to now.

In this Letter, Fe,F co-doped TiO₂ NTs (Fe,F/TiO₂ NTs) were prepared by the impregnation method using Fe/TiO₂ NTs as precursors, which were synthesised by the combination of the sol-gel process and hydrothermal treatment. The Fe,F/TiO₂ NTs were characterised by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The photocatalytic performances of Fe/TiO₂ NTs and Fe,F/TiO₂ NTs with different Fe content under visible-light irradiation were evaluated by the degradation of methyl orange.

2. Experimental: All the reagents were of analytical grade and used without any further purification.

2.1. Preparation of Fe,F/TiO₂ NTs: The Fe-doped TiO₂ powder was prepared by the sol-gel method using tetrabutyl titanate as a titanium source and ferric nitrate as the dopant. Under continuous

stirring, an ethanol solution of tetrabutyl titanate was added dropwise to the ethanol solution of ferric nitrate. After the mixture was hydrolysed at room temperature for 2 h under strong stirring, the transparent sol was obtained. When the sol was aged for 12 h at room temperature, the gel was obtained. The resulting gel was dried at 80°C for 12 h to remove the solvents and then calcined at 500°C in air for 3 h to obtain Fe-doped TiO₂ nanoparticles. Then, Fe-doped TiO₂ NTs were synthesised by a hydrothermal method [1]. 1 g Fe-doped TiO₂ nanoparticles and 50 ml 10 mol/l NaOH solution were mixed in a Teflon vessel, being kept at 150°C for 12 h. 0.1 mol/l HNO₃ solution and distilled water were used in turn to wash the obtained materials. Also, Fe-doped TiO₂ NTs were obtained after drying at 80°C overnight. The doping concentrations of Fe are expressed as wt.%.

Fe,F/TiO₂ NTs were synthesised by the impregnation treatment. Fe/TiO₂ NTs were immersed into an aqueous NH₄F solution for 24 h and the NTs were doped with fluorine. The obtained powders were centrifuged and dried in air at 80°C for 12 h. Then the powders were calcined at 300°C for 2 h.

2.2. Samples characterisation: The powder XRD experiments were performed at room temperature by using a Rigaku D/Max-2500 X-ray diffractometer (Cu K α λ = 0.154 nm) to identify the crystal phase of samples. A Philips T20ST transmission electron microscope working at 200 kV was used to obtain the TEM images. The composition of Fe,F/TiO₂ NTs at the surface was characterised by XPS with an Al X-ray source (Al K α -150 W, Kratos Axis Ultra DLD).

2.3. Photoactivity measurement: The photocatalytic activity of the as-prepared catalysts under visible irradiation was evaluated by the residual ratio of methyl orange (10 mg/l) in an aqueous solution (100 ml) including 50 mg of sample. After being ultrasonically dispersed for 30 min in the dark, the reaction mixture was irradiated through a 300 W high-pressure mercury lamp with a 420 nm cutoff filter to remove the ultraviolet (UV) lights. The suspension was withdrawn and centrifuged after 3 h of irradiation. The obtained solution was then measured to check the residual concentration of methyl orange through a UV-visible (vis) spectrophotometer (TU-1901) at the wavelength of 464 nm. The results were corrected based on the decomposition of methyl

orange in the absence of a catalyst and the adsorption of methyl orange in the presence of catalysts.

3. Results and discussion: XRD analyses were performed to identify crystal phases of the prepared catalysts. Fig. 1 shows the XRD patterns of 0.5% Fe/TiO₂ NTs and 0.5% Fe,F/TiO₂ NTs. It could be observed that the diffraction peaks at 25.3°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7°, 68.8°, 70.3°, and 75.0° in the two samples corresponded well to (101), (004), (200), (105), (211), (204), (116), (220), and (215) lattice planes of anatase TiO₂ (JCPDS Card No. 21-1272), indicating no influence on the phase of TiO₂ by the introduction of F and Fe species [13]. Also, no typical reflections of F or Fe, F containing phases were observed in Fe,F/TiO₂ NTs, indicating that ferrum and fluorine were well-dispersed in TiO₂ or the changes for TiO₂ were too minor to be detected by XRD [14]. In comparison with Fe/TiO₂ NTs, the diffraction peaks of Fe,F/TiO₂ NTs clearly weakened and slightly broadened, indicating that the growth of TiO₂ crystallite was restrained after the introduction of F ions [15].

Fig. 2 shows TEM images of 0.5% Fe,F/TiO₂ NTs. It could be observed from Fig. 2 that the well-defined NTs constructed during the hydrothermal process [4, 16] were hollow and open-ended (see the small black circles in Fig. 2b), which were more than 100 nm in length with nearly uniform diameters. Also, the average outer and inner diameters of the Fe,F/TiO₂ NTs were about 10 and 2 nm, respectively.

To reveal the states of the co-doped F and Fe, 0.5% Fe,F/TiO₂ NTs were analysed by XPS. Fig. 3 shows its XPS survey spectra and the relevant elements' high-resolution XPS spectra. It could

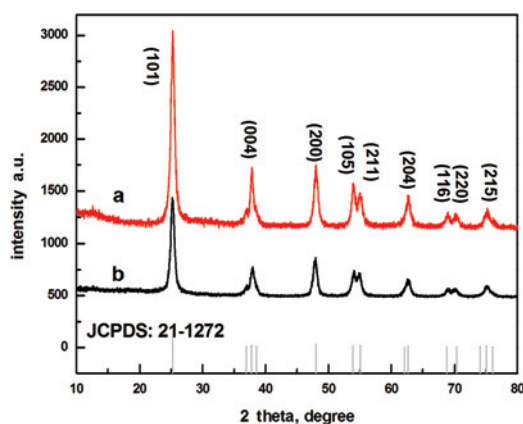


Fig. 1 XRD patterns of
a 0.5% Fe/TiO₂ NTs
b 0.5% Fe,F/TiO₂ NTs

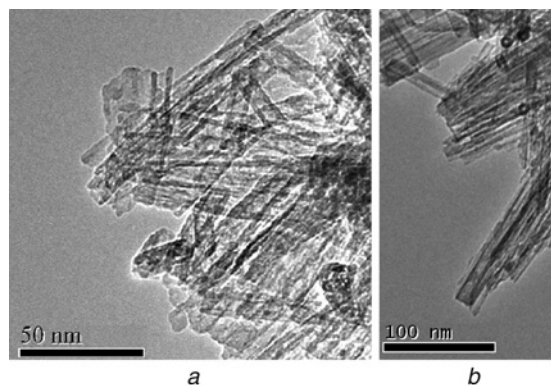


Fig. 2 TEM images of 0.5% Fe,F/TiO₂ NTs

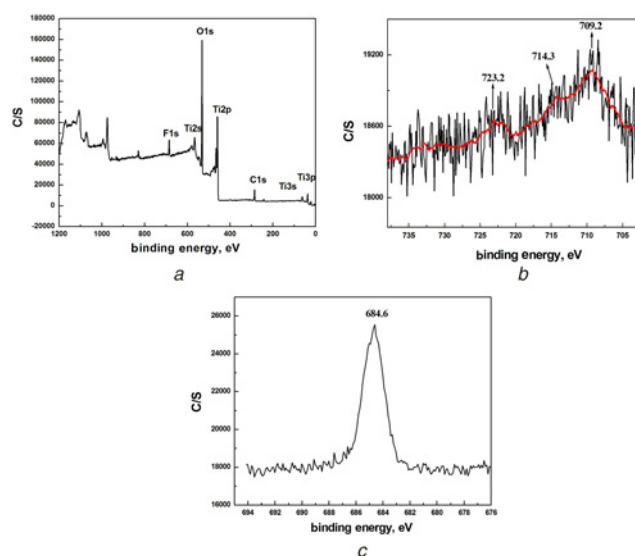


Fig. 3 XPS survey spectra and high-resolution XPS spectra of 0.5% Fe,F/TiO₂ NTs

a Survey Spectra,
b Fe 2p,
c F 1s

be seen from Fig. 3a that the prepared sample included Ti, O, F, and C elements. The peak centred at 285.8 eV belonged to C 1s, which may be the result of the adventitious hydrocarbon from XPS itself. Nevertheless, the typical peaks of Fe were not noticeably observed possibly due to the small Fe amount. Even though, the high-resolution XPS spectrum of Fe 2p could give the relevant information of its chemical states (Fig. 3b). It could be seen from Fig. 3b that the peaks at 709.2 and 723.3 eV corresponded to the binding energies of Fe 2p_{3/2} and Fe 2p_{1/2}, respectively, indicating the presence of Fe³⁺ in TiO₂ lattice [14, 17]. The peak at 714.3 eV indicated the presence of Fe²⁺, which was detected possibly because of the photocatalytic reduction from Fe³⁺ to Fe²⁺ during XPS measurement in vacuum [18].

The high-resolution XPS spectrum of F 1s (Fig. 3c) showed that the peak at 684.6 eV belonged to F adsorbed on TiO₂, which originated from the surface fluoride (≡Ti-F) due to the ligand exchange between F⁻ and a hydroxyl group on the surface of TiO₂ [19]. Moreover, no noticeable sign of F ions (688 eV) in the lattice was found.

To evaluate the effect of Fe and F co-doping, a set of experiments were performed through the photodegradation of aqueous methyl orange under visible light irradiation. Fig. 4 shows the UV-vis

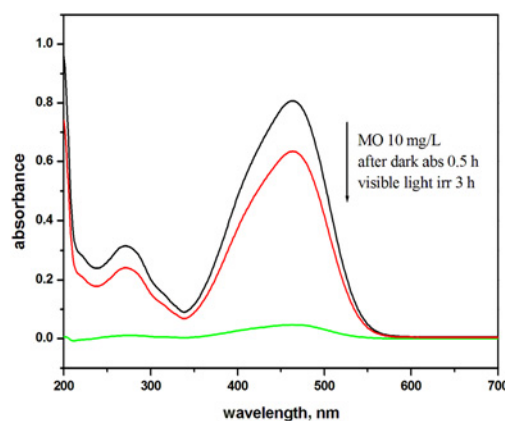


Fig. 4 UV-vis spectra of 10 mg/L MO solution before and after visible-light irradiation in the presence of 0.5% Fe,F/TiO₂ NTs

Table 1 Effect of Fe concentration on the degradation rate of MO by Fe/TiO₂ NTs and Fe,F/TiO₂ NTs, respectively

Samples	0.25% Fe/TiO ₂ NTs	0.5% Fe/TiO ₂ NTs	0.75% Fe/TiO ₂ NTs	0.25% Fe,F/TiO ₂ NTs	0.5% Fe,F/TiO ₂ NTs	0.75% Fe,F/TiO ₂ NTs
mean degradation rate (% , n = 3)	35	67	34	82	91	85

spectra of MO solution before and after visible-light irradiation in the presence of 0.5% Fe,F/TiO₂ NTs. The characteristic absorption band of MO at 464 nm decreased slightly after the MO solution was kept in the dark for 0.5 h (the red line in Fig. 4) and then decreased obviously after visible light irradiation, and the absorbance value at the wavelength of 464 nm was close to 0 after 3 h irradiation (the green line in Fig. 4), indicating that MO has almost been degraded completely. Table 1 summarises the effect of Fe concentration on the degradation rate of MO by Fe/TiO₂ NTs and Fe, F/TiO₂ NTs, respectively. It could be seen that compared with pure TiO₂ NTs, whose degradation rate was nearly 0 under visible light irradiation, both Fe/TiO₂ NTs and Fe,F/TiO₂ NTs presented enhanced photocatalytic activity and the Fe concentration had obvious effects on the photocatalytic performance of Fe/TiO₂ NTs and Fe,F/TiO₂ NTs. When Fe concentration was 0.5%, these two photocatalysts achieved the highest photoactivity, which was attributed to the appropriate amount of Fe³⁺, leading to the formation of Fe²⁺ and Fe⁴⁺ ions by trapping both electron and hole and then suppressing the recombination of charge carriers. However, when the amount of Fe³⁺ continued to increase, it might become the recombination centres of the photogenerated electron-hole pairs and reduce the photocatalytic performance [14, 20]. It also could be observed from Table 1 that the photocatalytic performance of Fe and F co-doped TiO₂ NTs was obviously superior to that of Fe mono-doped TiO₂ NTs, which might be attributed to the fact that the surface doped-F on TiO₂ promoted the formation of movable free ·OH radicals formed by photogenerated holes and then decomposed the organic substances [21]. Therefore, the maximum degradation rate of 91% after 3 h of visible-light irradiation was obtained when the doped Fe content was 0.5% in Fe,F/TiO₂ NTs.

4. Conclusion: Fe,F/TiO₂ NTs were synthesised by the combination of hydrothermal treatment and impregnation method. Fe,F/TiO₂ NTs possessed only the anatase phase. The well-defined NTs with nearly uniform diameters were hollow and open-ended. The doped ferrum and fluorine existed in TiO₂ lattice and on the surface of TiO₂, respectively. When the amount of Fe³⁺ was appropriate, the recombination of photo-induced carriers could be inhibited, and 0.5% Fe,F/TiO₂ NTs presented the highest photoactivity, which was enhanced obviously compared with 0.5% Fe/TiO₂ NTs. Due to the high-photocatalytic performance of Fe,F/TiO₂ NTs, the preparation of TiO₂ NTs co-doped with other ions will be continued.

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6 References

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