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Synthesis and characterization of Fe, N and C tri-doped polymorphic TiO_2 and the visible light photocatalytic reduction of Cr(VI)

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ABSTRACT

The (Fe, N and C) tri-coped polymorphic TiO_2 (Fe-N-C-TiO_2), containing anatase, rutile and brookite phase, were synthesized by a hydrothermal method. The tri-coped polymorphic TiO_2 were characterized in detail by several techniques in terms of their structure, composition, optics, morphology, surface area, and so on. The photocatalytic activities of Fe-N-C-TiO_2 nano-materials were examined under visible light illumination using Cr(VI) as target pollutant. The results showed that Fe/Ti weight ratio crucially determines the photocatalytic activity of Fe-N-C-TiO_2 nano-materials. Fe-N-C-TiO_2 nano-materials with Fe/Ti weight ratio of 0.30% exhibits highest photocatalytic activity than that of the other nano-materials under visible light irradiation, which can be attributed to the synergic effect of the higher BET surface area, separation rate of electron-hole pairs, more number of surface absorbed hydroxyl groups (—OH), stronger absorption in the visible-light region and optimum Fe/Ti weight ratio.

1. Introduction

Cr(VI) is the one among the highly carcinogenic and mutagenic inorganic contaminants found in industrial effluents, which is extensively used in electroplating, metallurgy, leather tanning industry and pigments [1–3]. Consequently, effective treatment of Cr(VI) in natural water and effluent, is of extreme importance for environmental safety and public health. Usually, Cr(VI) can efficiently be converted into Cr(III) by photocatalytic reduction on semiconductor photocatalyst, which shows lower mobility and toxicity in the environment [2–4]. Of the semiconductor photocatalyst employed, TiO_2 is the most widely researched and used in various applications. However, due to large band-gap (3.0–3.2 eV for rutile and anatase, respectively), TiO_2 can absorb only UV light and is limited as a visible light-driven photocatalyst.

Many efforts have been made in the past few decades in order to extend absorption edge of TiO_2 into the visible light region. One of approaches is to co-dope with nonmetal, such as C-N [5,6], N-I [7], N-S [8,9], N-F [10,11], B-N [12], B-N-F [12], N, S and C [13] and so on, has been proved as an effective method to narrow the band-gap and extend absorption to visible light region. Giannakas et al. [7] reported that N-I co-doped TiO_2 exhibits enhanced photocatalytic activity under visible light irradiation, which is possibly ascribed to the synergistic effect between nitrogen and iodine, leading to the narrowing of band gap. Moreover, few reports are focused in tri-doped TiO_2 photocatalysts [12,13]. Giannakas et al. [12] reported that B-N-F tri-doped TiO_2 showed higher reduction and oxidation rates than N doped and N-F co-doped TiO_2 under UV–visible light irradiation due to the higher specific surface area and lower mean pore diameter. On the other hand, lots of investigations have proved that metal ions doping (such as Fe, Cr and Mn) is one of the typical methods to inhibit the recombination of electron-hole pairs and extend its photoresponse to visible region [14–16]. Among various metal ions, Fe^{3+} ions is considered to be an appropriate dopant, which yields following benefits [14,17–19]: (i) the radii of Ti^{4+}(78.5 pm) and Fe^{3+}(74.5 pm) ions are similar and the electronegativity of Ti^{4+}(1.5) and Fe^{3+}(1.96) ions are considerably approximate, so Fe^{3+} ions can enter into the structure of TiO_2 and locate at interstices or occupy some of the lattice sites of TiO_2; (ii) Fe^{3+} ions act as trap for electron-hole pairs and

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enhance the separation of charge carriers, and thereby improve the photocatalytic activity of TiO_2. In the study by Kim et al. [20] Fe, N co-doped TiO_2 prepared by a sonochemical method revealed higher photocatalytic activity for indigo carmine dye degradation under visible light irradiation, possessing two absorption edges around 385 nm and 550 nm. Consequently, co-doping with non-metal and metal (e.g. Fe-N) could not only enhance light absorbance intensity in the visible-light region, but also accelerate the separation rate of photo-induced charge carriers, and thus enhance the photocatalytic activity of TiO_2 under the visible-light irradiation [18,20–22]. However, the available publication on photocatalytic reduction of Cr(VI) by the multi-nonmetal and metal ions co-doped TiO_2 nano-materials under UV or visible light radiation is still very limited. So in this paper, we present a comparative study on the photocatalytic reduction of Cr(VI) by TiO_2 and Fe, N and C tri-doped TiO_2 nano-materials prepared by hydrothermal method with butyl titanate as the titanium source and ferric nitrate as the doping agent, and the enhanced photocatalytic performance of Fe, N and C tri-doped TiO_2 nano-materials is demonstrated. The influence of Fe/Ti weight ratio on the crystal structure, morphology, surface area, optical and luminescent properties were studied in detail. The reasons for the enhanced photocatalytic activities of Fe, N and C tri-doped TiO_2 nano-materials with different Fe/Ti weight ratio were also studied.

2. Experimental procedure

2.1. Preparation of Fe-N-C-TiO_2 nano-materials

Firstly, butyl titanate, used as TiO_2 precursor was added dropwise to absolute ethyl alcohol to form solution A, and 5 ml of absolute ethyl alcohol were dripped into deionized water to form solution B, with the operation under magnetic force stirring. And then, the solution A was slowly dripped into solution B to form solution C. Further, a desired mass of ferric nitrate (the weight ratio of Fe/Ti = 0.03%, 0.06%, 0.18%, 0.3%, 0.6%, 0.72%) was added dropwise to solution C, which was then under magnetic force stirring for 30 min. The pH of solution C was maintained $\leqslant 1$ by addition of 36.5% HCl. The resulting solution was then placed in a Teflon lined stainless steel autoclave and heated in an oven at 180 °C for 6 h. After the autoclave was cooled to room temperature, the obtained precipitates were then centrifuged and washed several times with distilled water and ethanol. After proper washing, the obtained products were dried overnight in an electric oven at 50 °C. All the dried products were then ground to get fine powders. The samples thus, obtained with weight ratio of Fe/Ti = 0.03%, 0.06%, 0.18%, 0.3%, 0.6%, 0.72% were designated as 0.03wt%Fe-N-C-TiO_2, 0.06wt%Fe-N-C-TiO_2, 0.18wt%Fe-N-C-TiO_2, 0.30wt%Fe-N-C-TiO_2, 0.60wt%Fe-N-C-TiO_2 and 0.72wt%Fe-N-C-TiO_2, respectively. For comparison, C-doped and N-C co-doped TiO_2 was also prepared by the same method and labeled as C-TiO_2 and N-C-TiO_2 (sodium nitrate as the nitrogen precursor).

2.2. Photocatalytic experiments

The photocatalytic experiments were performed in a multi-tube mixing reaction apparatus. The experimental procedure for the photocatalytic reduction of Cr(VI) was similar to our previous reports [23]. The photocatalytic activity of Fe-N-C-TiO_2 nano-materials was studied for the photocatalytic reduction of Cr(VI) (20 mg/L, pH = 2) with photocatalyst loading of 0.2 g/L. Solution pH was adjusted using 20% or 50% H_2SO_4. In order to reach adsorption-desorption equilibrium, the suspensions was magnetically stirred in dark for 30 min. A 500 W xenon lamp was used as a visible light source ($\lambda > 420$ nm). At regular intervals, a 10.0 ml aliquot of the suspensions was withdrawn. The absorption spectrum of the centrifuged solution was recorded using a Shimazu UV-2500 UV–vis spectrophotometer. The Cr(VI) concentration was determined colorimetrically at 540 nm using diphenylcarbazide as colour agent. All the experiments ran in the same conditions of flow rate and volume.

2.3. Characterization of Fe-N-C-TiO_2 nano-materials

The X-ray diffraction (XRD) patterns of Fe-N-C-TiO_2 nano-materials were obtained by using Philips X'pert X-ray diffractormeter with Cu Kα radiation ($\lambda = 1.541874$ Å). X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5000 C ESCA System with Mg K, source operating at 14.0 kV and 25 mA. All the binding energies were referenced to the contaminant C 1s peak at 284.6 eV of the surface of adventitious carbon. UV–vis absorption spectrum was measured by a Shimazu UV-2500 spectrophotometer with $BaSO_4$ as the reference sample. Photoluminescence (PL) spectra were measured at room temperature on a Hitachi F-7000 Fluorescence Spectrophotometer. Morphology of Fe-N-C-TiO_2 nano-materials was recorded by a Zeiss SUPRA-55 scanning electron microscopy (SEM). High resolution image was observed by JEOL JEM-2200FS transmission electron microscope (TEM). N_2 adsorption-desorption isotherms over Fe-N-C-TiO_2 nano-materials were obtained at −196 °C using a Quantachrome Autosorb-1C instrument. Surface areas were determined by BET equation in 0.05–0.35 partial pressure range. Pore volumes, average pore diameters and pore size distributions were determined by Barrett-Joyner-Halenda (BJH) method from the desorption branches of the isotherms. The change in dissolved Fe concentration during the photocatalytic reaction was measured by a Shimazu AA-6800 Atomic Absorption Spectrophotometer (AAS).

3. Results and discussion

3.1. Physicochemical properties of Fe-N-C-TiO_2 nano-materials

Fig. 1 shows XRD patterns of C-TiO_2, N-C-TiO_2 and Fe-N-C-TiO_2 nano-materials, demonstrating that all the prepared nano-materials are composed of anatase, rutile and brookite. Comparing the peaks of C-TiO_2, N-C-TiO_2 and Fe-N-C-TiO_2 nano-materials, the positions and intensities basically keep no change. It indicates that Fe, N and C tri-doping does not affect the crystalline structure of TiO_2. It can be noted from Fig. 1 that all Fe-N-C-TiO_2 nano-materials show trace amount of brookite. According to the work

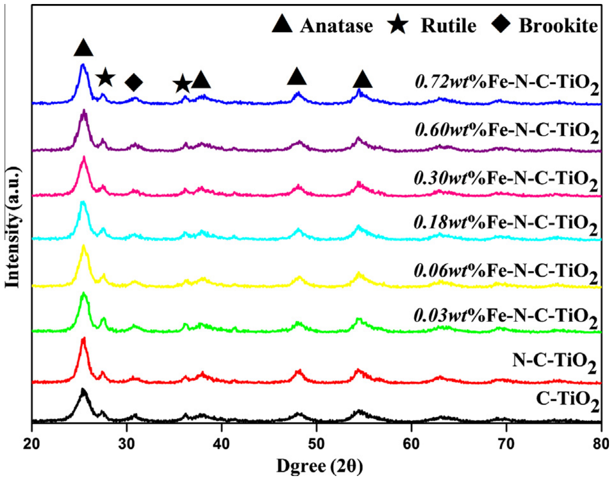

Fig. 1. XRD patterns of C-TiO_2, N-C-TiO_2 and Fe-N-C-TiO_2 nano-materials.