

Photocatalytic photodegradation of xanthate over C, N, S-tridoped TiO₂ nanotubes under visible light irradiation

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ABSTRACT

C, N, S-tridoped TiO₂ nanotubes were synthesized via hydrothermal synthesis and post-treatment, and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS), the Brunauer–Emmett–Teller method (BET), and UV–vis diffuse reflectance spectroscopy (DRS). The UV–diffuse reflectance spectra of all the C, N, S-tridoped TiO₂ nanotubes greatly extended the absorption edge to the visible light region, and the absorbance in the visible region increased with increasing molar ratio of thiourea to Ti (*R*), which could be attributed to C, N, S-tridoping in the form of cation C-doping, interstitial N-doping, cation S-doping, and adsorbed SO₄²⁻ ions' states. The photocatalytic activity of C, N, S-tridoped TiO₂ nanotubes was evaluated by photocatalytic photodegradation of potassium ethyl xanthate (KEX) under visible light irradiation. It was found that the photocatalytic activity of the prepared samples increased with increasing molar ratio of thiourea to Ti (*R*). At *R*=6, the photocatalytic activity of the tridoped sample TNTS-6 reached a maximum value. With further increase in *R*, photocatalytic activity of the sample decreased, which could be attributed to the high visible light activity resulting from the balance between visible light absorption and recombination of electron/hole pairs.

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1. Introduction

Xanthates are widely used in flotation of sulphide minerals [1]. Although most of the xanthates enter into the foam product, the residual concentration of xanthate in flotation tailings may have environmental consequences as xanthate is toxic for biota [2]. Various types of methods for the removal of residual xanthate such as chemical [2], adsorption [3], biological [4], etc. have been used in the past decades. These methods have advantages and disadvantages. For example, the chemical method produces secondary pollution and the main disadvantage of the biological method is that it requires much more time. Therefore, it was urgent to develop new methods for degradation of residual xanthate in the flotation effluent.

The TiO₂ photocatalyst has attracted a great deal of attention in environmental wastewater treatment in the past decade, because it generates highly oxidative hydroxyl free radicals (*OH) resulting in complete mineralization of many toxic and non-biodegradable organics [5,6]. Recently, TiO₂ nanotubes for photocatalysis and photoelectrocatalysis have attracted much attention owing to their multiwalled nanotubular structure, together with the outstanding stability and oxidative capability of TiO₂ [7–9]. However, only a

small UV fraction of solar light (3–5%) could be utilized because of the wide band gap of TiO₂ [10]. One of the most important approaches was to dope TiO₂ with non-metal elements such as N, S, and C, which would extend the absorption range of TiO₂ nanotubes from ultraviolet (UV) to visible light region [11–19].

To the best of our knowledge, although there was some research related to the photocatalytic activity of C, N, S-tridoped TiO₂ photocatalysts [20–23], photocatalytic activity of C, N, S-tridoped TiO₂ nanotubes has not been reported. In this work, C, N, S-tridoped TiO₂ nanotubes were synthesized and photocatalytic photodegradation of potassium ethyl xanthate (KEX) was carried out under visible light irradiation.

2. Experimental

2.1. Sample preparation

2.1.1. Preparation of TiO₂ powder

TiO₂ powder was synthesized by the hydrothermal method. In a typical synthesis, 10 g Ti (SO₄)₂ was added to 120 ml of distilled water to form an aqueous solution. After stirring for 0.5 h, the solution was poured into a Teflon-lined stainless autoclave with 200 ml capacity. The autoclave was sealed and heated, and then kept at 150 °C for 4 h. The resulting product was separated by

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centrifugation and washed with distilled water and alcohol several times and finally dried at 80 °C for 6 h.

2.1.2. Preparation of titanate nanotubes (TNTs)

Titanate nanotubes (TNTs) were prepared by the alkaline hydrothermal method [24]. In a typical preparation, 2.0 g TiO₂ powder was mixed with 120 ml of 10 M NaOH solution followed by hydrothermal treatment of the mixture at 150 °C in a 200 ml Teflon-lined autoclave for 24 h. After the hydrothermal reaction, the precipitate was separated by filtration and washed with a 0.1 M HCl solution and distilled water until the pH value of the rinsing solution reached ca 7.0. The washed samples were dried at 80 °C for 6 h to get TNTs.

2.1.3. Preparation of C, N, S-tridoped TiO₂ nanotubes

The TNT precursor was mixed with a certain amount of thiourea and stirred for 1 h in ethanol. The mixture was dried and further calcined at 350 °C for 2 h in air. The molar ratio of thiourea to Ti (*R*) was controlled at 0, 2, 3, 4, 5, 6, and 7 and the samples obtained were labeled as TNTS-0, TNTS-2, TNTS-3, TNTS-4, TNTS-5, TNTS-6, and TNTS-7, respectively.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the synthesized samples were obtained by a Bruker D8-advance X-ray powder diffractometer (XRD) with Cu K_α radiation ($\lambda = 0.15418$ nm). Transmission electron microscopy (TEM) images were obtained using a JEM 3010 transmission electron microscope. X-ray photoelectron spectra (XPS) measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum (UHV) chambers using Al K_α radiation (1486.6 eV). The XPS binding energies were calibrated with respect to the C 1s peak from a carbon tape at 284.6 eV. The Brunauer–Emmett–Teller (BET) surface area was determined by nitrogen adsorption–desorption isotherm measurements at 77 K with a Micromeritics ASAP 2000 Analyzer. The diffuse reflectance spectra (DRS) of samples in the wavelength range of 200–900 nm were obtained using a UV–vis scanning spectrophotometer (Shimadzu UV-2450), while BaSO₄ was used as a reference.

2.3. Photocatalytic activity measurements

Photocatalytic activities of the samples were evaluated by the degradation of potassium ethyl xanthate (KEX) in an aqueous solution. 50 mg of the photocatalyst was added to 100 ml of the 20 mg/l potassium ethyl xanthate (KEX) aqueous solution. The photocatalysts were dispersed under ultrasonic vibration for 10 min. Prior to light irradiation, the reactor was left in the dark for at least 30 min until an adsorption–desorption equilibrium was finally established. A 100 W tungsten lamp fixed at a distance of 150 mm above the surface solution was used as the visible light source, and a UV cut-off filter was used to completely remove any radiation below 420 nm to ensure illumination by visible light source only. During irradiation, about 5 ml of the suspension was continually taken from the reaction cell at given time intervals for potassium ethyl xanthate (KEX) concentration analysis using the UV–vis spectrometer (Shimadzu UV-3101). The UV spectrometer was set to measure absorbance at 301 nm, where xanthates in aqueous solution have an absorbance maximum (shown in Fig. 1).

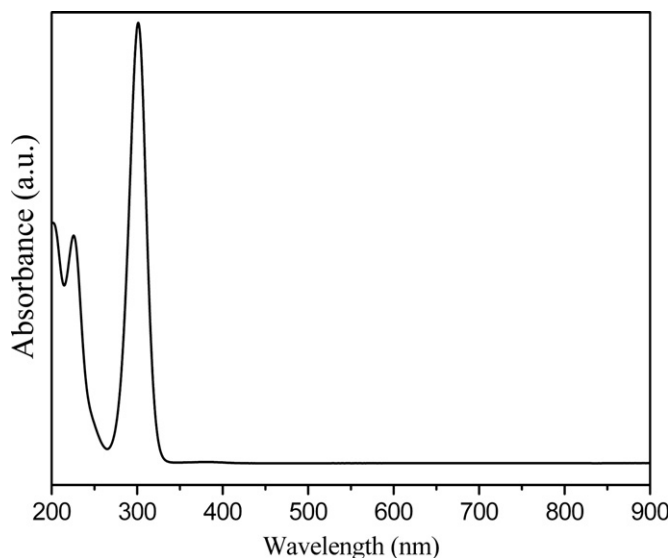


Fig. 1. UV–vis absorption spectra of xanthate.

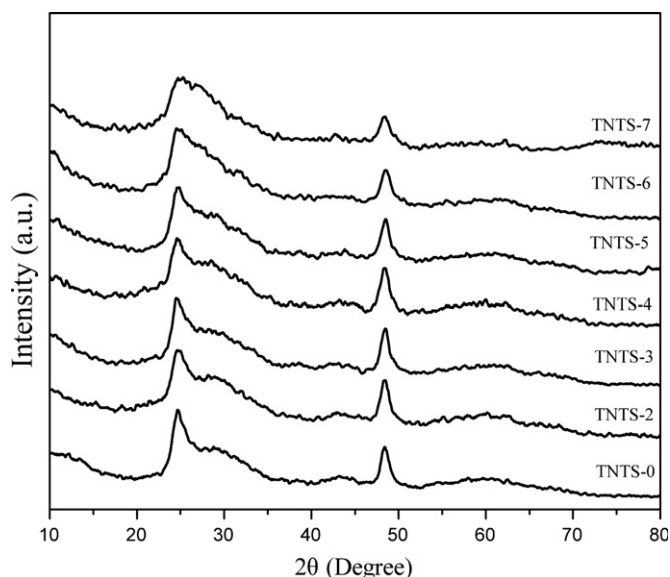


Fig. 2. XRD patterns of the as-prepared samples.

3. Results and discussion

3.1. XRD analysis

XRD was used to investigate the phase structure of the as-prepared samples calcined at 350 °C for 2 h in air. Fig. 2 shows the effects of *R* on phase structures of the samples. Diffraction peaks of each sample are well in agreement with the anatase phase (JCPDS 21-1272). No traces of impurity peaks were observed other than the peaks of TiO₂.

3.2. TEM analysis

Fig. 3(a) and (b) shows a representative TEM image of sample TNTS-0 and TNTS-6, respectively. It was found that both TNTS-0 and TNTS-6 showed almost the same nanotubular structure. All the tubes were open-ended and the inner diameter, outer diameter, and length of nanotubes were approximately 5, 10, and 150–200 nm, respectively. Fig. 3(c) and (d) shows the EDX of samples TNTS-0 and TNTS-6,

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