

Preparation of zinc titanate nanoparticles and their photocatalytic behaviors in the photodegradation of humic acid in water

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Abstract

A series of zinc titanate nanoparticles was successfully synthesized using a simple sol–gel technique. The composites were characterized by thermogravimetric and differential thermal analysis (TG-DTA), X-ray diffraction (XRD) patterns, scanning electron microscope (SEM), X-ray photoelectron spectra (XPS) and UV–vis diffuse reflectance spectra (UV–vis). The photocatalytic activity of samples was investigated by degradation of humic acid (HA) in water under xenon lamp. The sample calcined at 800 °C was found to exhibit much higher photocatalytic activity than the other samples. The investigation of photocatalytic mechanism indicates that the holes (h^+) and \bullet OH radicals may be the major reactive species for the degradation of HA. Meanwhile, the processing parameters such as the light source and the dosage of catalysts play an important role in tuning the photocatalytic activity. The enhancement of photocatalytic activity for the zinc titanate nanoparticles calcined at 800 °C may be attributed to the higher redox ability, coordination of Ti ions and smaller particle size.

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1. Introduction

As the main organic components in nature water body, humic acid (HA) has brought a great influence on the health of human beings and the environment. Humic acid is a key component of humic substances which is derived from the decomposition of plants and animals materials. They are a complex mixture of organic compounds. The presence of humic substances can impart an undesirable taste and colour to drinking water. In addition, it has been confirmed that humic substances are the major precursors of disinfectant by-products during chlorination disinfection and trichloromethane class carcinogenic substance [1]. However, humic acid cannot be self-degraded and is difficult to treat by traditional biodegradation method. Therefore, it is imperative to search an effective and practical technique for removing HA from nature water.

Photocatalytic degradation processes have been widely applied as techniques of destruction of organic pollutants in waste water [2–12]. With an appropriate light irradiation, the photocatalyst generates electron/hole pairs with free electrons produced in the empty conduction band and leaving positive holes in the valence band. These electron/hole pairs are capable of initiating a series of chemical reactions that eventually mineralize the pollutants [13].

Recently some researchers were interested in discussing the photophysical, acoustic-optic, and catalytic properties of the ilmenite-type titanates such as CoTiO_3 , NiTiO_3 and ZnTiO_3 [14,15]. Dulin and Rase [16] reported that there are three compounds exist in the ZnO–TiO_2 system, including Zn_2TiO_4 (cubic), ZnTiO_3 (hexagonal) and $\text{Zn}_2\text{Ti}_3\text{O}_8$ (cubic). ZnTiO_3 with perovskite structure could be a useful candidate for microwave resonator materials, gas sensors, sorbents for the desulfurization of hot coal gases and paint pigments [17–23]. However, there has not been much work on the photocatalytic activity of zinc titanate particles, which may be used as photocatalyst for the degradation of organic pollutants because its band gap is 3.06 eV. The zinc titanate is usually synthesized

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via solid-state reaction at high temperatures [24–26], but this method has some drawbacks such as the prepared sample with large particle size and limited chemical homogeneity. In order to improve the properties of zinc titanate particles, some researchers used sol–gel method [27–30] to synthesis zinc titanate nano-crystal powders. In 2009, Kong et al. [31] used a modified alcoholic method to prepare zinc titanate powder at 800 °C and they also investigated the photocatalytic activity of zinc titanate powders by degradation of the azo dye methyl violet in water under sunlight. So far, to the best of our knowledge, using zinc titanate powders as a photocatalyst in the degradation of HA has not been reported.

In this work, a novel photocatalyst of zinc titanate nanoparticles was first prepared by sol–gel method using citric acid as chelating agent and ethylene glycol as stabilizer. The structure and morphology of the prepared zinc titanate were characterized by various analytical techniques. Then the photocatalytic activity of zinc titanate nanoparticles was investigated by degradation of humic acid in water under xenon lamp. The results indicated that the zinc titanate nanoparticles exhibit good photocatalytic activity on removing humic acid from water. Meanwhile, the possible photodegradation mechanism was also studied by the examination of active species $\bullet\text{OH}$, $\bullet\text{O}_2^-$ and the holes (h^+) through adding their scavengers.

2. Experimental

2.1. Materials

Ethanol, zinc acetate, tetrabutyl titanate, ethylene glycol, citric acid, isopropanol, sodium bicarbonate and humic acid were purchased from Tianjin Chemical Reagent Factory. Deionized water was used throughout all the experiments. All the chemicals were obtained as analytical grade reagents and used without further purification.

2.2. Synthesis of zinc titanate

Zinc titanate nanoparticles were prepared by the following method. A stoichiometric amount of zinc acetate and tetrabutyl titanate with cationic ratio of Zn: Ti = 1:1 were separately dissolved in water and ethanol (marked as A and B solution separately). Citric acid was then put into the B solution under constant stirring to get a transparency solution (marked as C solution). When the A solution was mixed with the C solution, a small amount of ethylene glycol was added to the solution as a stabilizing agent. The mixed solution was kept stirring at 80 °C for 1 h to form a homogeneous sol. Then the homogeneous sol was aged in an oven in air at 80 °C for 6 h to evaporate excess solvent. Finally, the gel was calcined at 600, 700, 800 and 900 °C in air for 2 h with a heating rate of 5 °C/min, respectively.

2.3. Preparation of humic acid solution

A HA suspension was prepared by adding the HA chemicals into deionized water and gently heating up to 60 °C under

magnetic stirring in order to accelerate the dissolution of HA. After the supersaturated HA suspension was cooled down to room temperature, the suspension was filtered by Millipore filter paper. The HA residue on the filter was dried in an oven at 85 °C until the weight stabilized. The HA concentration in the clear solution (filtrate) was calculated by the gravimetric method. The HA solution was stored as a stock solution in a refrigerator at 4 °C for further use.

2.4. Evaluation of photocatalytic activity

Experiment equipment of photocatalytic experiments consists of three parts. The first part is a 500 W xenon lamp in an empty chamber. The second part is a thimble for cooling the xenon lamp by running water. Owing to the continuous cooling, the temperature of the reaction solution is maintained at approximately 32 °C. The third part is a special cylindrical quartz photoreactor with effective reactive volume of 50 mL. The distance between light source and cylindrical quartz photoreactor was about 1.5 cm. The intensity of light was 165,000 lx, measured by a Luxmeter (XYI-III All Digital Luxmeter). At the start of the experiment, the prepared HA solution with initial concentration of 10 mg/L and appropriate amount of photocatalyst were put into the photoreactor. During the photocatalytic reaction, the photocatalytic powder was dispersed by an air bubbler. Portions of approximately 4 mL solutions were taken at selected time intervals and centrifuged at 3000 rpm for 10 min. The concentration of HA in the supernatants was measured with a UV–vis spectrophotometer (Varian Cary 50) at wavelengths of 254 nm. The degradation rate of HA solution was defined according to the equation:

$$D = \left[\frac{A_0 - A_t}{A_0} \right] \times 100\%$$

where A_0 was the absorbance value of initial HA solution, A_t was the absorbance value of degraded HA solution at photocatalytic reaction time “ t ”.

2.5. Characterization

Thermal behavior examination of Zn–Ti-complexed precursor was performed by TG-DTA Analyzer (America PERKEN ELMER 1700) in air to investigate the calcination temperature and possible phase transformation from 20 °C to 1000 °C with a heating rate of 30 °C/min. The resultant phase and crystal structure of the photocatalyst were identified by Rigaku X-ray diffraction ($D/\text{max-2500}$) with monochromated Cu K α radiation at accelerating voltage and applied current are 40 kV and 100 mA, respectively. The data was collected with a scan rate of 8°/min in the range of $2\theta = 20\text{--}70^\circ$. The microstructure was examined by scanning electron microscopy (SEM, XL30, Philips). The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a spectrometer (XSAM-800, KRATOS Co.) with an Mg K α anticathode, 12 kV, 11 mA, FRR mode. The UV–vis diffuse reflectance

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