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Original Research Paper

Study on crystallinity and morphology controlling of titania using acrylamide gel method and their photocatalytic properties

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ABSTRACT

In this study, polyacrylamide gel method was used for preparation of pure and mixed phase TiO_2 nanoparticles. The influence of synthesis conditions on the physicochemical properties of products was investigated. It was found that the type of acid, which was used for acidifying the precursor solution together with calcination temperature can affect the phase structure, crystalline size, morphology and thereby photocatalytic activity of obtained TiO_2 nanoparticles. Different trends were observed during the phase transformation, particle growth, shift in energy of band gap with the change in tensile strain to compressive strain of the prepared TiO_2 nanomaterial. X-ray diffraction (XRD) showed that prepared nanocrystals, which were calcined at 450 °C have pure anatase and anatase–rutile mixed structures. The prepared samples having crystallite size between 5 nm and 60 nm were observed at different calcination temperatures. In addition, the photocatalytic activities of the prepared samples were evaluated by monitoring the degradation of Cresol Red (CR). The results show that the photocatalyst (TEC_1), exhibits the highest photocatalytic efficiency where 94.7% of CR can be decomposed after UV exposure for 75 min.

1. Introduction

In recent years, semiconductor-based photocatalysis is a very promising technique for decomposition of organic pollutants. Among various semiconductors, due to good chemical stability, absence of toxicity and relative low price, TiO_2 has attracted growing scientific interest in photocatalytic oxidation of organic molecules [1,2]. Moreover, since the photochemical sterilization of *Escherichia coli* using Pt–TiO_2 was first reported by Ref. [3], many photocatalytic disinfection studies using TiO_2 have been performed in order to improve understanding of the disinfection mechanism responsible for the inactivation of the microorganism [4,5]. It has been shown that the photocatalytic activity of TiO_2 is influenced by crystal structure, surface area, crystallinity and porosity [6].

Many approaches have been used to obtain nano-sized titania samples with anatase phase, such as chemical vapor synthesis [6], the sol–gel method [7,8] and the hydrothermal [9,10] or solvothermal methods [11]. Recently, the polyacrylamide gel has been demonstrated to be an efficient and cost-effective tool for easy synthesis of ultrafine oxide powders [12,13]. In this method, direct pyrolysis of polymeric network without separate drying step yields ultrafine and highly dispersed powders [14]. This method is time-saving in comparison with the Pechini method because in this method the formation of the gel at low temperatures is more rapid than the Pechini method [15]. This method has been successfully applied in the synthesis of a considerable number of ultrafine powders and there are few reports about the synthesis of TiO_2 nanoparticles with this method.

The main objective of the present work was the synthesis of the titania nanoparticles via polyacrylamide gel method. In addition, the effect of different condition of the synthesis process was investigated, and the obtained samples were characterized by using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and UV–Vis diffuse reflectance spectroscopy analysis. Finally photocatalytic properties of the prepared samples were investigated by monitoring the degradation of Cresol Red and inactivation of *E. coli* bacteria.

2. Experimental

2.1. Chemicals

Tetraethylorthotitanate, absolute ethanol, acrylamide, 2,2′-azoisobutyronitrile (AIBN) were obtained from Merck Company.

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Cresol Red was obtained from the Fluka Company. The structure of the dye is shown in Fig. 1.

2.2. Preparation of materials

2.2.1. Preparation TiO_2 samples

In a typical synthesis, 4.5 ml of tetraethylorthotitanate and 7 ml of absolute ethanol were mixed and slightly heated until a clear solution has been obtained. Afterwards, the solution has cooled down to room temperature and stirred for another 0.5 h, followed by adjusting the pH value within the range of 3–4 by using a concentrated acid, and stirring was continued. Subsequently, the monomer of acrylamide (6 g) was added into the clear solution. The resulting solution was heated in a water bath and during the whole process, the system was continuously stirred. The solution became gradually transparent with temperature rising. When the temperature reached about 80 °C, a small amount of initiator AIBN ($C_8H_{12}N_4$) was added to the solution, and polymerization occurred quickly and the gel started swelling until it reached its equilibrium degree of swelling. Thus transparent polymeric resin was obtained without any precipitation. At last, the gel was dried at 110 °C for 12 h to yield a xerogel (as shown in Fig. 2). The obtained xerogel was homogenized using mortar and pestle and submitted to one subsequent thermal treatment. The grinded xerogel was sintered up to 450 °C, meanwhile, kept at 250 °C and 350 °C for 1 h, and at 450 °C for 5 h respectively, to gain the TiO_2 powders and also small amounts of the obtained powder samples were calcinated for 2 h at temperature of 700 °C. These products are referred to as TE series and the letter after TE is related to the kind of used acid: A, C, N, PC, S for acetic acid, hydrochloric acid, nitric acid, perchloric acid, sulfuric acid, respectively. Moreover, the subscript letter as I or II is referred to the calcination process; the subscript letter "I" was dedicated to the conventional samples which were calcined at 450 °C and also in the case of performing additional calcination at 700 °C, the letter "II" was used as subscript.

2.3. Characterization

The crystalline phase of photocatalysts was identified with a D500 Siemens diffractometer. UV–vis spectra was recorded on a Shimadzu MPC-2200 spectrometer. Electronic microscopic studies (SEM and TEM) were carried out with the use of the LEO 440i and a model FEG CM 200 Philips instrument, respectively. The SEM sample was gold coated prior to examination, and SEM was operated at 15 kV. The specimens for TEM were made by evaporating one drop of solution of sample in ethanol onto carboncoated copper grids. Grids were blotted dry on filter paper and investigated without further treatment.

2.4. Bacterial culture

Lyophilized *E. coli* (ATCC 43894) was used as model microorganism for the disinfection experiments. A nutrient broth

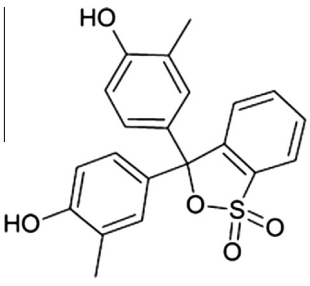

Fig. 1. Structure of Cresol Red.

Fig. 2. The xerogel of TEN sample.

(Merck/Germany) culture medium of pH 7.4 was prepared by dissolving 37 g of nutrient broth (5 g peptone; 3 g meat extracts) in 1 L of distilled water followed by sterilization in an autoclave at 121 °C. Eosin Methylene Blue Agar (10 g peptone, 5 g lactose, 5 g sucrose, 2 g dipotassium phosphate, 0.04 g Eosin Y, 0.06 g methylene blue, 13.5 g agar) solution in 1 L boiling distilled water was prepared and sterilized in an autoclave at 121 °C and poured into Petri dish. Fresh bacterial cultures of around 109 CFU/mL of stationary concentration were prepared by inoculation of 20 mL of nutrient broth and aerobic incubation at 37 °C for 24 h. Five mL of this culture was centrifuged and rinsed twice with sterile PBS before diluting 1 mL of the resultant bacterial suspension to 1 L to prepare the reacting suspension, with an initial concentration of viable bacteria around 106 CFU/mL.

2.5. Evaluation of photocatalytic activity

2.5.1. Degradation of Cresol Red

An aqueous solution of Cresol Red (CR) was used as a model contaminant for studying the photocatalytic activity of prepared TiO_2 samples. This evaluation was performed by measuring the decrease in concentration of the dye in the reaction solution. The concentration of the photocatalyst was chosen as the minimum concentration to obtain full absorption of the incident photon flux. So 0.2 g of catalyst and 100 ml of Cresol Red solution with a typical concentration of 10^{-5} M were mixed in an open Pyrex reactor with a diameter of 10 cm and a height of 5 cm.

Prior to commencing illumination, the suspension was stirred continuously for 30 min in the dark, to ensure the establishment of adsorption/desorption equilibrium of the specific substrate on the surface of the catalysts. Then the suspension was exposed to UV light under a 30 W (UV-C) lamp. The distance between the UV lamp and the surface of the solute was adjusted at 25 cm. A 5 mL aliquot of sample was withdrawn by syringe from the irradiated solution at an interval of 30 min and then; the catalyst