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Fabrication and characterization of nano TiO_2 thin films at low temperature

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Abstract

Anatase TiO_2 thin films were successfully prepared on glass slide substrates via a sol–gel method from refluxed sol (RS) containing anatase TiO_2 crystals at low temperature of 100 °C. The influences of various refluxing time on crystallinity, morphology and size of the RS sol and dried TiO_2 films particles were discussed. These samples were characterized by infrared absorption spectroscopy (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission-scanning electron microscopy (FE-SEM) and UV–vis absorption spectroscopy (UV–vis). The photocatalytic activities of the TiO_2 thin films were assessed by the degradation of methyl orange in aqueous solution. The results indicated that titania films thus obtained were transparent and their maximal light transmittance exceeded 80% under visible light region. The TiO_2 thin films prepared from RS-6 sol showed the highest photocatalytic activity, when the calcination temperature is higher than 300 °C. The degradation of methyl orange of RS-6 thin films reached 99% after irradiated for 120 min, the results suggested that the TiO_2 thin films prepared from RS sol exhibited high photoactivities.

Keywords: A. Oxides; A. Thin films; B. Sol–gel chemistry; C. X-ray diffraction; D. Catalytic properties

1. Introduction

Nanocrystalline TiO_2, one of the most popular photocatalyst, have long been investigated in environmental purification, decomposition of dyes in wastewater [1,2]. Many researchers have focused on the preparation and characteristics of titanium dioxide nanoparticles as well as their applications [3]. The immobilization of TiO_2 in the form of a thin film provides an advantage over the drawbacks encountered with powder suspensions such as difficult separation of TiO_2 particles from the suspension and easy aggregation of suspended TiO_2 particles. Good photocatalytic activities of the TiO_2 films necessitate efficient photo-induced electron–hole pair generation and efficient charge separation, which requires in turn preparations of well-crystallized TiO_2 films, preferably in the anatase crystalline form [4]. To prepare titanium dioxide thin film, many papers have been published on the preparation of titania films. Physical methods include sputtering [5], CVD [6], MOCVD [7], ion-assisted electronbeam evaporation [8], etc. These methods require a high amount of energy that is reemitted in part as exhaust heat or in the

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exhaust gases, and an annealing post-treatment, usually at 450 °C, is necessary to remove the organics used in the preparation of the colloidal suspension or paste. Recently, efforts have been made to produce TiO_2 thin films through chemical routes, which are less energy consuming and do not require equipment. Among these, the sol–gel method using the peroxotitanic acid solution (PTA) is of great interest because it has neutral pH and low material cost. The study about the formation of TiO_2 film using the PTA has been recently performed by Ichinose et al. [9,10]. Gao et al. [11] have reported the synthesis of anatase TiO_2 thin films using the aqueous peroxotitanate solution obtained by dissolving metatitanic acid (H_2TiO_3) in a mixture of H_2O_2 and ammonia in water. Lee et al. [12] prepared PTA sol using $TiCl_3$ as raw materials. However, the PTA sol contains no anatase crystals, the TiO_2 film on substrate should be calcined at high temperature to obtain anatase structure after the sol was coated on the substrates. It is evident the interest of low-temperature methods for fabrication of crystalline TiO_2 thin films not only from the point of view of energy saving, as annealing post-treatment is avoided, but also as they allow the use of low thermally resistant materials such as plastics, wood or paper as substrates. Furthermore, to make the whole chemical approach environmental friendly, the use of aqueous solutions instead of organic solvents is desired. Recently, our group has accomplished the deposition of anatase TiO_2 films with relative ease and at low temperature using hydrothermal processing method in which crystallization is enhanced by autoclave heating [13,14].

In this paper we show a new method in which anatase TiO_2 thin films are deposited on glass slides substrates by dip-coating method. The refluxed sol (RS) containing needle-like anatase crystals was synthesis by refluxing the PTA sol at relative low temperature and pressure condition, and the TiO_2 thin films were formed on glass slides substrates after dried in air or heated at low temperature.

2. Experimental

For the preparation of the anatase TiO_2 sol, the following materials were used: titanyl sulfate ($TiOSO_4 \cdot nH_2O$, 23.2% TiO_2); hydrogen peroxide (H_2O_2, 30%); ammonia solution ($NH_3 \cdot H_2O$, 3 mol/l); methyl orange.

The anatase TiO_2 sol (RS) was prepared in the following way. Titanyl sulfate (17.3 g) was slowly added to the distilled water at room temperature, then precipitated by adding ammonia solution (NH_4OH, 3 mol/l) resulting the formation of white precipitate [$Ti(OH)_4$]. The white precipitate was filtered and sufficiently washed with distilled water to remove the NH_4^+ and SO_4^{2-} formed in the reaction, and then added 450 ml distilled water to disperse the precipitate homogeneously. The precipitate was peptized in 50 ml aqueous hydrogen (30%), continual magnetic stirring was required to avoid the immediate dense gel formation during dissolution and to keep the reactant mixed uniformly. The obtained transparent sol was kept under reflux condition (around 100 °C) for 2 h. Finally, the pure RS sol with anatase TiO_2 crystals was obtained, which was used to prepare thin films and equivalent powders after dried in air oven. This sample was denoted as sample RS-2. Samples RS-6 and RS-10 were prepared by the same procedure, but the refluxing time was 6 and 10 h, respectively.

Glass slides were used as substrates. Before the deposition, substrates were ultrasonically cleaned in acetone and absolute ethanol for 5 min, respectively. Finally, they were thoroughly rinsed with water. TiO_2 thin films were deposited on substrates by a dip-coating process at room temperature with the withdrawing speed about 5–6 cm/min. Substrates were immersed into the TiO_2 sol for 10 min. Upon withdrawing from the sol, the substrates were dried under infrared light for 30 min, the drying temperature was about 100 °C, the distance between the IR light and samples of TiO_2 thin films was 20 cm. TiO_2 layers on substrates could be thickened by means of consecutive dip-coating processes.

The FT-IR spectra of the dried gel were measured by the KBr pellet method (BIO-RAD FTS-3000). The crystalline structure of the RS particles dried in air and TiO_2 thin films prepared from RS sols were determined by X-ray diffractometer (Rigaka D/max 2500 v/pc, Japan) using graphite monochromatic copper radiation (Cu Kα) at 40 kV, 30 mA over the 2θ range 20–80°. The morphology and size of the RS sol crystals were examined by transmission electron microscopy (JEM-1200 EX II). The adhesion of the dried TiO_2 films was evaluated by ultrasonic washing and weight measuring. The surface morphologies of dried TiO_2 thin films were observed by a field emission-scanning electron microscope (FE-SEM JEDL JSM-6700F) Spectroscopic analysis of the TiO_2 films was performed using UV–vis spectrophotometer (7230G, Shanghai, China) with wave range of 300–800 nm.

The photocatalytic activities of the prepared TiO_2 thin films were evaluated from an analysis of the degradation of methyl orange in an aqueous solution under UV illumination. The main wavelength of the UV lamp was 254 nm and the power of the UV lamp was 25 W. Two pieces of 25 mm × 75 mm glass slides coated with TiO_2 thin films were settled in a watch glass containing 80 ml methyl orange aqueous solution (10 mg/l) and exposed to UV-irradiation. The