



Synthesis of bimodal porous structured TiO₂ microsphere with high photocatalytic activity for water treatment

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ABSTRACT

In this work bimodal structured titanium dioxide (TiO₂) microsphere has been prepared from commercial TiO₂ powder and nano-sized titania gel via sol–gel spray-coating technique. Crystallization and transformation behavior of titania gel were investigated. The results revealed that the crystallization and transformation of anatase particles were substantially affected by the concentration of solvent and calcination temperature. Anatase crystallite size of 10 nm was obtained at mole ratio of solvent/precursor 50/1 and calcination temperature of 450 °C. The prepared nano-sized titania gel was embedded within the core (commercial TiO₂, P25) during the spraying process. The prepared TiO₂ microsphere was characterized using X-ray diffractometer (XRD), scanning electron microscope (SEM), field emission electron microscope (FESEM) and micropore analysis. The photocatalytic activity was monitored by following the degradation of phenol with activity benchmarked against commercial P25 (Degussa). The increase of photocatalytic activity of TiO₂ microsphere was attributed to the nano-sized anatase crystallite which has been incorporated into the TiO₂ microsphere.

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1. Introduction

Semiconductor TiO₂ photocatalyst has been studied by many researchers due to its chemical stability, non-toxicity and reusability for environmental applications [1–4]. It is a clean oxidation reaction process and requires only oxygen and UV light. The most commonly used commercial TiO₂ photocatalyst is Degussa P25 with an anatase to rutile ratio of 70:30 [5]. It has a surface area of 50 ± 15 m²/g and an average particle diameter by number count of 21 nm. It is a high surface area powder which is not thermally stable and loses surface area readily [6,7]. These TiO₂ photocatalyst particles usually do not present individually in aqueous system, but rather as physically unstable primary aggregates ranging from 25 nm to 0.1 μm [5]. These physically unstable aggregates would reduce the surface area and create problems for separation and recovery in engineering application [8–11]. Even though TiO₂ is harmless to environment, the photocatalyst particles must be fil-

tered prior to the discharge of the treated water. On the other hand, photocatalytic activity of TiO₂ is also an important aspect that should not be overlooked. It was suggested that the photocatalytic activity is strongly dependent on its phase composition, crystallite size, especially the BET surface areas and pore structure [12,13].

To resolve this problem, many supported photocatalysts of TiO₂ were prepared by immobilizing or coating a thin film of photocatalysts on the surfaces of many carriers such as glass, fiber or stainless steel [10,14–18]. These novel immobilized durable catalysts are attractive in water treatment applications. Indeed the fabrication of film type TiO₂ photocatalyst is simple, cost effective and practical. The application of film type TiO₂ photocatalyst required a careful reactor design to ensure the accessibility of the catalytic surface to the photons and the reactants [19–22]. In view of this, the overall photocatalytic degradation rate might be lower as compared with the suspended system. Rachel et al. [20] claimed that the efficiency of photoactivity using the immobilized photocatalysts could be drastically declined to only 1/200 of that using TiO₂ slurry. Mobilized type TiO₂ photocatalyst will be attractive if the separation and recovery problem can be overcome. A possibly practical alternative would be maintaining the supported catalyst in a suspension form. In a suspension system, the photocatalyst can be easily fluidized by air bubbling and settled by gravity after

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reaction. Efforts have been devoted in recent years to coat TiO₂ on supports or free carriers such as polystyrene bead [23], carbon [24] and silica [25,26]. However, the advantage of good contact with a light source was still kept to some degree. It was found that the attachment of TiO₂ powder on those free carriers was not strong enough for a long period of operation from an engineering point of view [9].

Some researchers reported the synthesis of submicron hollow TiO₂ microspheres which would possess an effective separation [27–29]. The critical procedure in these methods is the removal of the templates or the usage of two immiscible liquid phases, which results in the complication of the preparation, cracking of microsphere shell and limits of their application. Recently, Li and coworkers described a sol – spraying – calcination method to fabricate a new type of TiO₂ microsphere photocatalyst with a particle size of 30–160 nm [9]. Polymer was used as the template to create a porous structure in the mentioned microsphere photocatalyst. Hence it is still highly desirable to develop an efficient, template-free, and surfactant-free method to prepare TiO₂ microspheres. This study was aimed at developing a TiO₂ microsphere via spray-drying process by controlling the sol–gel conditions, using neither PEG nor polymer templates. A novel TiO₂ microsphere was synthesized by embedding the nano-sized titania gel into a porous matrix or core via sol–gel spray-coating process. The nano-sized titania gel was prepared by sol–gel method under various synthetic conditions using titanium alkoxide. Crystallization and transformation behavior of titania gel was investigated. The obtained TiO₂ microsphere was characterized by scanning electron microscopy, gas adsorption at 77 K and X-ray diffractometer (XRD). The photocatalytic activity of TiO₂ microsphere benchmarked against commercial TiO₂ was reported.

2. Methodologies and materials

2.1. Preparation of nano-sized titania gel

The titania gel was prepared by dissolving tetra-*n*-butylorthotitanate [Ti(OC₄H₉)₄], obtained from Merck, in absolute alcohol (CH₃CH₂OH), obtained from Fluka. A uniform TiO₂ sol was formed under vigorous mixing. During this process, pH was monitored and kept around 3 by the addition of concentrated hydrochloric acid (HCl). The sol was aged for at least 24 h before use. The mole ratio of EtOH to titanium precursor (*R*) was varied in the range of 4, 10, 25, 50, to 100 by fixing the concentration of titanium precursor at 1. For the titania gel analysis, the sol was dried at room temperature for 24 h in order to vaporize water into the gel and was then ground into fine powders to obtain dry gel samples. The dried gel samples were calcined at 450 °C in air for 3 h for crystallite size study. The dried gel samples were further calcined at elevated temperatures from 300 °C to 750 °C for crystallite size and phase composition study.

2.2. Spray-coating process

Titania gel was used as component A and the commercial TiO₂ powder, P25 (anatase = 70%, surface area = 50 m²/g, and crystal size = 30 nm) supplied by Degussa, Germany, was used as component B. Component A was mixed with component B at a gel: powder ratio of 5:1 by weight to form a slurry. Then the slurry was put into a spray dryer (capacity 1500 mL/h) with inlet air at 30 °C and outlet air at 30 °C. In the spray dryer, the TiO₂ powder aggregated to form semisolid microspheres. Finally the semisolid microspheres were calcined at higher temperature of 450 °C for 3–6 h to form solid TiO₂ microspheres.

2.3. Characterization of titania gel and TiO₂ microsphere

Thermogravimetric Analysis TGA 7 was used to determine the temperature of decomposition and phase change of titania gel. The samples were heated at the rate of 10 °C/min from 30 °C to 800 °C. Brukers D8 Advanced powder X-ray diffraction (XRD) was employed for studies of phase composition and crystallite size of titania gel. The crystallite size of titania gel was determined by using the TOPAS refinement software from Brukers. The Micropore system Autosorb-1 by Quantachrome, Italy, was used to measure the BET surface area, pore size distribution and total pore volume of the samples. The particle size of the TiO₂ microsphere was observed by scanning electron microscope (SEM) (Leica stereoscan 420). The surface morphology of all the samples was observed by field emission scanning electron microscope (FESEM) on a JEOL JSM 6340F model, Japan.

2.4. Experimental procedure

Photodegradation study was carried out in a photoreactor. The photoreactor consisted of an outer cylindrical PVC casing fitted with an air distributor at the bottom. The UV lamp used was an 18.4-W low pressure mercury UV lamp (NEC). The major emission of the UV lamp was 253.7 nm. Although this type of lamp is generally used for disinfection process, it will provide more efficient treatment. An air pump was used to supply oxygen and create air bubbles for suspensions. TiO₂ samples were suspended in 1000 mL phenol solution at 100 mg/L in dark for 2 h to attain adsorption equilibrium. Samples were taken at different time interval after UV light was turned on. All samples were filtered through 0.45 μm cellulose acetate membrane filters prior to analysis.

2.5. Chemical analyses

The phenol concentration was analyzed by high performance liquid chromatography (HPLC PerkinElmer, Series 200). The HPLC column used was C-18 (PerkinElmer, Brownlee Columns) with mobile phase of a mixture of 40% methanol and 60% of 1%-acetic acid solution. Standard curve was prepared by diluting phenol (analytical grade) at different concentration. The detection wavelength was set at 280 nm for phenol analysis. The retention time for phenol peak under these conditions was recorded at 1.9 min.

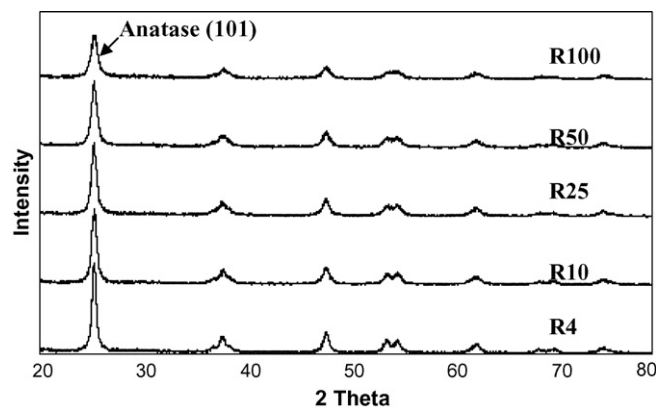


Fig. 1. XRD patterns of titania dried gel at different mole ratio of solvent/titanium precursor (calcined at 450 °C for 3 h).

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