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ScienceDirect

Ceramics International 40 (2014) 3097–3103

CERAMICS INTERNATIONAL

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Porous titania microspheres with uniform wall thickness and high photoactivity

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Received 26 July 2013; received in revised form 28 September 2013; accepted 1 October 2013
Available online 8 October 2013

Abstract

Highly porous titania particles were prepared by depositing thin films of titania, using alternating reactions of $TiCl_4$ and hydrogen peroxide, on poly(styrene-divinylbenzene) (PS-DVB) template particles via atomic layer deposition (ALD) at 77 °C. The composition of the titania films was verified by XPS analysis and the titania films were directly observed by TEM. TGA/DSC was used to study the thermal decomposition of the polymer template. Porous titania particles with uniform wall thicknesses were successfully obtained after the template PS-DVB was removed by oxidation in air at 400 °C for 24 h. Verification of the resulting porous structure of the titania particles was done by cross-sectional SEM and nitrogen adsorption–desorption analysis. Porous titania particles were treated at different temperatures. XRD analysis was used to determine the microstructure and phase transformation of titania at elevated temperatures. The photocatalytic activity of these porous titania particles was studied by methylene blue decomposition under UV light at room temperature and was found to be comparable to that of commercial anatase titania nanoparticles (~20 nm). Depositing Na_2SO_4 on TiO_2 retarded the TiO_2 phase transformation from anatase to rutile during calcination and, thus, greatly increased the photoactivity of the porous titania particles.

Keywords: Atomic layer deposition (ALD); Coating; Titania; Porous; Photoactivity

1. Introduction

Titania (TiO_2) is extensively studied for use in different applications including dye-sensitized solar cells [1], hydrocarbon and hydrogen production [2–5], and CO_2 reduction [6–8], because of its high photoactivity, chemical stability, non-toxicity, and low cost [9]. Titania has a band gap energy of 3–3.2 eV. Under UV light, the energy of a photon is equal to or greater than the band gap energy of titania, and electron–hole pairs can be created in the transition of the excited electrons from valance band to conduction band [9]. This creates hydroxyl radicals as a result of oxidation–reduction reactions that occur on the surface of each particle. Hydroxyl groups and oxygen radicals play an important role in the decomposition of organic compounds on the surfaces of titania particles. Detailed information on the photocatalytic process has been covered in several review articles [9,10].

To increase the efficient usage of titania, high surface area titania nanoparticles are normally used. However, the smaller the particle size, the more difficult it is to separate titania nanoparticles from the reaction system for their re-use. This problem could be readily solved if we used large porous titania particles that had high surface areas. The high photocatalytic activity of these particles can be retained because of their high surface areas, since large particle sizes make recovery and re-use much simplier. These highly porous titania particles can be easily applied to a continuous flow reactor for water treatment or other photocatalytic processes, essentially making the whole system easy to handle and more eco-friendly by recovering the titania particles and reusing them.

A number of articles have been published that document the preparation of titania microspheres. Many techniques have been developed to synthesize meso-microporous titania using facile template methods, such as chemical implantation [11], a sol–precipitation method [12–14], the templating of polymers [15–17], or hydrothermal synthesis [18]. For example, Zhong et al. prepared hollow spheres of TiO_2 by using a sol–gel precursor solution on a crystalline array of a polystyrene

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http://dx.doi.org/10.1016/j.ceramint.2013.10.001

template [13]. Lin et al. successfully developed porous nanocrystalline TiO_2 photocatalysts using a sol–gel technique with polyethylene glycol as the structure directing agent [14]. Sun et al. used carbonaceous polysaccharide microspheres as templates for the fabrication of hollow spheres of titania [17]. Recently, some novel methods have been developed to self-formulate template-free hollow titania materials using continuous spray pyrolysis [19], and a spontaneous self-formation procedure [20], among others [21]. These methods provide different ways of preparing TiO_2 hollow spheres. However, in many cases there are issues with the ability to control the microstructural and morphological of the synthesized particles [10], and there is no control over the wall thicknesses of the titania porous structures. This study provides an alternative to these methods by preparing porous titania particles that have uniform wall thicknesses through the use of atomic layer deposition (ALD).

ALD is a layer-by-layer gas phase deposition technique [22–24]. It provides highly uniform and conformal coating of metal oxides on 3-D structures due to alternating self-limiting saturative surface reactions. The deposition of ALD films can be controlled to a 0.1 nm range. This gives a commanding lead over the control provided by other techniques. Ultra-thin titania films that are deposited via ALD at low temperatures (<100 °C) are amorphous [25,26] and have low photoactivity [26]. Heat treatment, however, can enhance the photoactivity of titania. In this study, we used ALD to deposit titania films (with thicknesses that could be controlled) onto a porous polymer template. Porous titania particles were formed after the polymer template was removed. The porous structure of these particles and the influence of calcination treatment on the phase structures were determined by using various techniques, including SEM, XRD, and nitrogen adsorption and desorption. The photoactivity of the titania particles were studied by methylene blue decomposition under UV light.

2. Experimental

2.1. ALD of titania films

Porous poly(styrene-divinylbenzene) (PS-DVB) particles were synthesized by the copolymerization of styrene and divinylbenzene [27]. The size of the particles was ~450 μm (Fig. 1), with a porosity of ~80%, a bulk density of ~0.07 g/cm^3, and a surface area of 42 m^2/g. The titania ALD coating process was carried out in a fluidized bed reactor, which was similar to the one previously described in detail [28]. The fluidized bed system consisted of a reactor column, a vibration generation system, a gas flow control system, and a data acquisition and control system with LabView®. High-purity nitrogen gas was used as the fluidization gas and purge gas. The flow of nitrogen gas was maintained using a mass flow controller from MKS Instruments. All valves used to provide the transient dosing were automatically controlled by LabView® and pressure measurements were recorded to monitor the progress of each dosing cycle. The system was operated at reduced pressures. $TiCl_4$ (ReagentPlus®, 99.9% trace metals basis, Sigma Aldrich) and concentrated H_2O_2 (30–32 wt% in water, semiconductor grade, 99.999% trace metals basis, Sigma Aldrich) were used as reactants for TiO_2 ALD at 77 °C. Since corrosive HCl is one of the byproducts, a liquid nitrogen cold trap was connected to the inlet of the vacuum pump to condense the HCl byproduct. One gram of porous polymer particles was loaded into the reactor and the minimum pressure was ~10 Pa inside the reactor. The minimum fluidization superficial gas velocity was 0.8 cm/s. Precursors were fed separately through the distributor plate at the base of the reactor using their room-temperature vapor pressures as the driving force. A typical coating cycle used the following sequence: $TiCl_4$ dose (180 s), N_2 purge (1200 s), evacuation (120 s); H_2O_2 dose (240 s), N_2 purge (1200 s), evacuation (120 s). 200 cycles of titania ALD were applied.

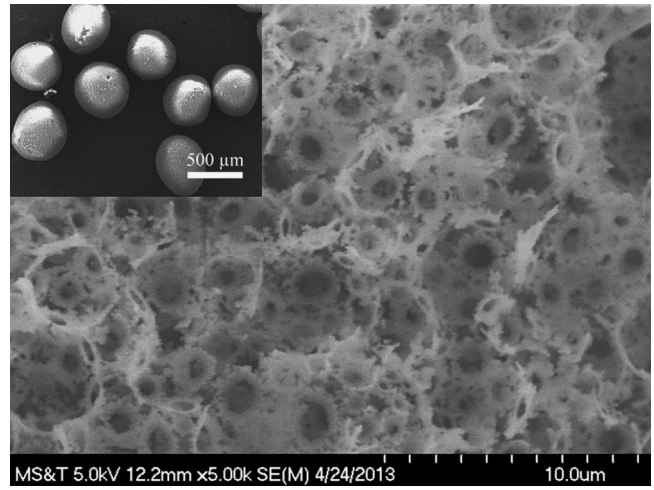

Fig. 1. Cross-sectional SEM image of PS-DVB porous particles. The inset image shows the size of the PS-DVB particles.

2.2. Formation of titania microspheres

To remove the organic constituent after ALD, the titania-coated PS–DVB particles were heated in air at 400 °C for 24 h. Almost all of the organic constituent had been removed, since the particles were white after oxidation. To study the phase transition and thermal stability of titania nanoparticles, calcination was also conducted at 600 °C and 800 °C for an additional 2 h, at a heating rate of 10 °C/min. It was reported that depositing Na_2SO_4 on TiO_2 could significantly retard the TiO_2 phase transformation from anatase to rutile during calcination at elevated temperatures [29]. To obtain sulfated TiO_2 (TiO_2–SO_4^{2-}) with 1 wt% of SO_4^{2-}, the porous titania particles obtained at 400 °C were soaked in a certain amount of Na_2SO_4 solution, air dried, and then calcined at 800 °C for 2 h.

2.3. Characterization

X-ray photoelectron spectroscopy (XPS) (Kratos Axis 165) was used to verify the composition of titania films by employing Al K (a) excitation, operated at 150 W and 15 kV. The coated PS-DVB particles were visualized with an FEI Tecnai F20 field emission gun high resolution TEM/STEM equipped with an energy dispersive X-ray spectrometer