



Synthesis of hierarchically porous TiO₂ nanomaterials using alginate as soft templates



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ABSTRACT

We herein report a large-scale synthesis of hierarchically porous TiO₂ structures composed of nanoparticles by a facile soft-template method. The natural and abundant biopolymer named alginate acted as sacrificial templates, providing porous structures and controlling the morphology of TiO₂ nanoparticles. The size of the resultant TiO₂ nanoparticles was around 20 nm. The TiO₂ structures were obtained by directly crosslinking Ti⁴⁺ ions to alginate and then burning off the biopolymer templates. Based on the observation of various reactive conditions, we propose that the alginate has two important function in the formation of hierarchically porous TiO₂ structures. One is acting as a template for the nucleation of TiO₂. The other one is to facilitate the formation of porous TiO₂ nanomaterials. The photocatalytic property of hierarchically porous TiO₂ in UV-light-driven degradation of organic dyes was proved to be better than that of commercial available TiO₂.

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1. Introduction

Titanium dioxide (TiO₂) is a very well-known material due to its important applications in photovoltaics, photocatalysis, photonics and sensors [1–3]. Among all these, its photocatalytic properties have been utilized in various environmental fields to remove contaminants from both water and air. The photocatalytic properties of TiO₂ are derived from the formation of photogenerated hole and electron which occurs upon the absorption of ultraviolet (UV) light corresponding to the band gap. The electrons which are excited by the UV light to the conduction band typically react with molecular oxygen in the air to produce superoxide radical anions. Meanwhile, the holes in the valence band diffuse to the surface of TiO₂ and react with the adsorbed water molecules to form hydroxyl radicals, which can oxidize nearby organic compounds into simple molecules [4,5].

It has been well-known that many factors can exert significant influence on the photocatalytic property of TiO₂, such as the size, morphology, exposed lattice planes, and crystalline phase [6,7]. Nanostructured TiO₂ showed higher adsorption capacity and

charge carrier mobility owing to the increased contact surface area and shortened path length for diffusion of carrier [8]. Recently, it has been reported that the introduction of porosity into TiO₂ nanomaterials can further enhance the photocatalytic performance because of excellent incident light scattering within the structures, and high organic dye or pollutant adsorption [9,10].

In order to fabricate the porous TiO₂ nanostructure with high performance, many controllable synthesis methods have been employed to produce TiO₂ nanomaterials with controllable sizes and morphologies [11]. The templating technique is one of the versatile and efficient methods to adjust both the external (shape and size) and internal (porosity) properties of the final products. Although the common sacrificial templates like metal foams, solid nanostructure particles, and surfactant assemblies or emulsions are effective [12–14], they have suffered from high cost and complex fabrication. Therefore, it is still a significant challenge to develop low-cost, easy-operation and shape-controlled template methods for the formation of hierarchically porous TiO₂ materials.

Alginate, which is extracted from brown seaweed, is attractive for synthesizing structured materials on a large scale because of its non-toxicity and ability to form hydrogels under mild conditions. Alginate as a kind of natural biopolymer, consists of linear chains of (1–4)-linked monomers of β-D-mannuronic acid and α-L-guluronic acid which can be crosslinked to multivalent metal cations by strong electrostatic bonds [15–17]. This reaction binds guluronic

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blocks from two different chains tightly together. In this way, the biopolymer forms an extended gel network with metal cations dispersed throughout the structure. The gelation property of alginate is recently used for the preparation of metal oxides by dripping the alginate solution into the calcium ions (Ca^{2+})-containing solution, which can bind to the hydroxyl and carboxyl groups of the guluronic sites to achieve the Ca-alginate template [18–20]. Although the hierarchical structure of TiO_2 has been produced in the two-step method as described above [21–23], few studies are focused on Ti^{4+} ions directly crosslinked to alginate without the help of Ca^{2+} . The one-step method of preparing hierarchically porous TiO_2 nanomaterials is more effective and facile for controlling the morphology and structure of the products than the Ca-alginate template method.

Herein, we introduce alginate as sacrificial templates to synthesize hierarchically porous TiO_2 nanomaterials with tunable pore volumes and nanoparticle sizes. For the sake of precise control of the hierarchical structure, alginate was employed as soft-templates and binded to Ti^{4+} ions directly. The hierarchically porous TiO_2 nanomaterials composed of TiO_2 nanoparticles were formed after burning off the templates. The effects of the concentration of alginate on the properties of TiO_2 structures, such as pore volumes and nanoparticle sizes were examined. Additionally, the as-prepared TiO_2 nanomaterials with promising performance for photocatalysis were also investigated.

2. Experimental section

All chemicals were of analytical grade and purchased from Chinese domestic suppliers.

Synthesis of hierarchically porous TiO_2 nanomaterials

2.1. Synthesis of hierarchically porous TiO_2 nanomaterials

In a typical synthesis of TiO_2 nanoparticles, a transparent solution containing 2.0 g sodium alginate (NaAlg) powder dissolved in 100 mL deionized water was added to a 200 mL beaker under constant electromagnetic stirring. The mixture was stirred overnight to ensure complete dissolution. Then 20 mL of titanium disulfate ($\text{Ti}(\text{SO}_4)_2$) aqueous solution at concentration of 0.4 M was prepared in another 200 mL beaker. Prior to TiO_2 bead formation, the $\text{Ti}(\text{SO}_4)_2$ solution was added to 0.25 mL of dilute hydrochloric acid (HCl, 0.5 M) to avoid possible hydrolysis to form hydrous titanium oxides. The NaAlg solution was manually dripped into $\text{Ti}(\text{SO}_4)_2$ aqueous solution without stirring. Prior to washing with water, the beads remained in the $\text{Ti}(\text{SO}_4)_2$ solution and cured for 24 h at room temperature. The resultant Ti/template composite beads were dried in a freeze dryer for 24 h and in an oven at 50°C for 3 h. The organic template was removed by sintering the beads in muffle furnace at 600°C for 3 h under air atmosphere.

2.2. Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Focus diffractometer with $\text{Cu K}\alpha$ radiation and a Lynx Eye detector at a scanning rate of $2^\circ/\text{min}$. Field emission scanning electron microscopy (FESEM) images and scanning electron microscopy with an energy dispersive X-ray analytical system (SEM-EDX) were taken using Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) images were taken using an FEI Tecnai F20 transmission electron microscope operated at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a SDTQ-600 thermal analyzer from room temperature to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ under air flow. The nitrogen adsorption-desorption

isotherm was obtained on AutoSorb iQ-C TCD analyzer (BET). The UV–vis spectra were recorded by using a Hitachi U–3900H UV–visible spectrophotometer.

2.3. Photocatalytic measurements

For the photocatalytic measurement, 20 mg TiO_2 nanoparticles were completely dispersed into 200 mL of rhodamine B (RhB) aqueous solution (10 mg/L). The sample was firstly magnetically stirred in the dark for 1 h to ensure absorption equilibrium of MB onto the surface of TiO_2 nanoparticles. A 300 W xenon lamp providing UV–vis light with intensity $90\text{ mW}/\text{cm}^2$ was used as the UV light source. After given time intervals, 3 mL solution were taken out and centrifuged to remove the photocatalyst. The RhB concentration in the irradiated solution was monitored by measuring the absorption intensity of the supernatant at 553 nm. The degradation degree was evaluated according to $C/C_0 \times 100\%$, where C_0 and C represent the absorbance of the RhB solution before and after irradiation, respectively.

3. Results and discussion

3.1. Characterization results

The preparation of hierarchically mesoporous TiO_2 nanomaterials can be divided into three steps as shown in Fig. 1. The first step is the formation of a gel through crosslinking of the polymer by addition of the NaAlg solution to the $\text{Ti}(\text{SO}_4)_2$ aqueous solution. It is worthwhile to mention that the addition method has a great impact on the macroscopic shape of the gel. The dropwise addition of the NaAlg solution forms spheres of Ti-alginate gel with a diameter of about 5 mm, while extruding the NaAlg solution continuously results in noodle shapes of Ti-alginate gel. The resultant Ti-alginate gel is translucent because of the permeation of water or air in it (Fig. 1a). The following step is to dry the gel in a freeze dryer, and then obtain the substance with a volume shrinkage of 60% (Fig. 1b). Finally, hierarchically mesoporous TiO_2 materials are prepared after calcination in muffle furnace. Moreover, this sintering step induces an additional 50% volume shrinkage of Ti-alginate substance (Fig. 1c).

The representative SEM image in Fig. 2a indicates the as-prepared TiO_2 materials possess sponge-like hierarchically mesoporous structures with a broad pore size distribution. A close-up observation of the open framework in Fig. 2b reveals the macropores are formed by the agglomeration of TiO_2 nanoparticles. These TiO_2 nanoparticles with uniform size and morphology are closely connected, which is also confirmed by TEM characterization in Fig. 2c. It can be observed that the hierarchical structure composed of TiO_2 nanoparticles with an average size of about 20 nm. In order to further explore the detailed crystalline structures of the nanoparticles, high-resolution TEM (HRTEM) was carried out. The clear lattice fringes of the nanoparticles with a lattice of 0.35 nm correspond to the spacing for the (1 0 1) planes of anatase TiO_2 (Fig. 2d).

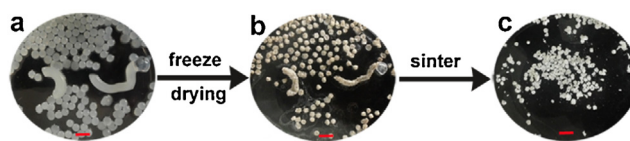


Fig. 1. Optical images of Ti-alginate gel (a), Ti-alginate substance (b) and TiO_2 after calcination (c). The scale bars (red colour) equal 10 mm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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