Materials Letters 181 (2016) 216–219

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Supersaturation-controlled growth of polyhedra-assembled anatase TiO_2 hollow nanospheres

Juanjuan Ge [a], Yang Ping [a], Guiwu Liu [a], Guanjun Qiao [a], Eui Jung Kim [b,*], Mingsong Wang [a,*]

[a] School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China
[b] Department of Chemical Engineering, University of Ulsan, Ulsan 680-749, South Korea

ARTICLE INFO

Article history:
Received 2 April 2016
Received in revised form
9 June 2016
Accepted 10 June 2016
Available online 11 June 2016

Keywords:
Tio_2
Anatase single crystals
Nanocrystalline materials
Crystal growth

ABSTRACT

TiO_2 hollow nanospheres assembled with single-crystalline anatase polyhedra have been prepared by a facile hydrothermal method. The supersaturation is found to significantly affect the crystallization habit of TiO_2. Larger polyhedral single crystals are obtained at lower supersaturation, while higher supersaturation results in the formation of hollow nanospheres assembled with anatase polyhedra. The photocatalytic performance of produced TiO_2 crystals with various morphologies is tested for the photodecomposition of methylene blue. TiO_2 hollow nanospheres with higher surface area exhibit enhanced photocatalytic activity.

1. Introduction

Titanium dioxide (TiO_2) has been extensively investigated as a wide band gap semiconductor due to its abundance, nontoxicity, long-term stability and high efficiency in various applications [1–3]. TiO_2 in the form of hollow spheres exhibits excellent photocatalytic activity [4,5], photovoltaic property [6], and electrochemical performance [7]. Various strategies such as Ostwald ripening [8], self-template transformation [9], and templating methods involving hard colloidal spheres [10,11] or soft emulsion droplets [12,13] have been developed for the preparation of TiO_2 hollow spheres. Among these methods, Ostwald ripening starts from solid aggregate spheres and the hollowing is driven by the dissolution of the inner particles with higher free energy and the growth of the lower-free-energy particles distributed on the outer radius [14], while the self-template method usually begins with the formation of amorphous precursor spheres. The surface of the formed spheres is subsequently crystallized and the inside of the spheres, however, is gradually removed under hydrothermal conditions [15]. Although the straightforward template strategies have the merits of recovering the shape of the templates and realizing size tunable preparation, they suffer from many disadvantages such as high cost, tedious procedure and the collapse of the hollow structure when removing the templates [16]. Therefore, it is still a challenge to develop a facile method for the preparation of uniform hollow spheres.

Herein, supersaturation-controlled growth of narrow size distribution TiO_2 hollow nanospheres has been demonstrated. Assembled with anatase TiO_2 nano-polyhedra, the as-prepared hollow nanospheres are observed to exhibit enhanced photocatalytic activity.

2. Experimental

One-pot synthesis of anatase TiO_2 hollow nanospheres was modified from a previous work [17]. Typically, 0.1 g of Ti powder (200 mesh, 99.9% purity) was dissolved in a solvent containing 54 mL of H_2O, 6 mL of H_2O_2 (30%, A. R.) and 0.2 mL of hydrofluoric acid (40 wt%). The solution became yellowish after stirring overnight. It was then transferred to a 100 mL Teflon-lined autoclave and hydrothermally treated at 180 °C for 10 h. After the solution was cooled to room temperature, the precipitate was collected by centrifugation, which was followed by washing with deionized water and ethanol for several times and drying at 60 °C overnight. The crystal structure of the as-prepared products was analyzed using an X-ray diffractometer (XRD, Bruker Axs D8 Advance) with Cu Kα radiation. Sample morphology was examined by a JEOL JSM-7001F field emission scanning electron microscope (SEM) operated at 10 kV and a JEOL JEM-2100F high-resolution transmission electron microscope (TEM) operated at 200 kV.

* Corresponding authors.
E-mail addresses: ejkim@ulsan.ac.kr (E.J. Kim), wangms@mail.ujs.edu.cn (M. Wang).

http://dx.doi.org/10.1016/j.matlet.2016.06.042

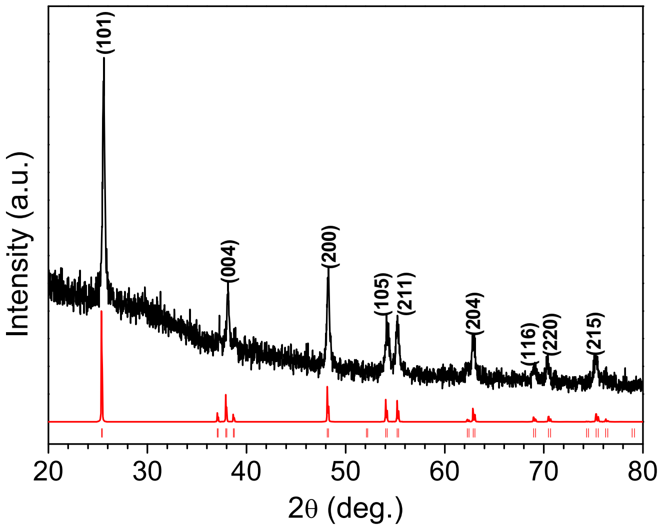

Fig. 1. Typical XRD pattern of TiO_2 hollow nanospheres. The red line is a simulated pattern of anatase TiO_2 based on ICSD # 202243. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

Fig. 1 presents the XRD pattern of the as-prepared TiO_2 hollow nanospheres. All diffraction peaks are indexed to anatase TiO_2. No impurity phase such as rutile or brookite is detected, indicating that the as-synthesized TiO_2 hollow nanospheres have pure anatase structure. The crystallite size determined from the (101) reflection of the XRD pattern using Scherrer formula is found to be ca. 34 nm.

Fig. 2 illustrates the SEM and TEM images of the anatase TiO_2 hollow nanospheres. As is seen in Fig. 2(a)–(c), the as-prepared TiO_2 nanospheres are narrow size-distributed, with a diameter ranging from ca. 400 to 600 nm. It is evident from Fig. 2(c) that all nanospheres possess a hollow structure; the inner diameter of the hollow sphere is about 200–300 nm. Close observation reveals that the TiO_2 hollow nanospheres are assembled with single-crystalline anatase polyhedra (Fig. 2(d)). The shell thickness, as indicated in Fig. 2(d), is around 110 nm. This value is much higher than the crystallite size of 34 nm determined from XRD, implying that the shell of the TiO_2 hollow spheres is assembled with several layers of anatase polyhedra. The selected-area electron diffraction (SAED) pattern of the corresponding nanosphere in Fig. 2(d) confirms the single-crystalline anatase phase of the constituent polyhedra.

To elucidate the formation mechanism of the anatase TiO_2 hollow nanospheres, we vary the precursor (Ti) concentration while keeping other experimental conditions unchanged. As presented in Fig. 3(a) and (b), faceted microspheres as well as nanospheres are formed as the amount of Ti powder employed in the synthesis is reduced to 0.04 g. A further reduction in the amount of Ti to 0.02 g results in the formation of microsized anatase decahedron single crystals, although an intergrowth of some individual single crystals is observed (Fig. 3(c) and (d)). These decahedron single crystals are enclosed by eight {101} side facets, one (001) top surface, and one (00−1) bottom surface [18]. Thus, we have demonstrated the controlled growth of TiO_2 hollow nanospheres and single crystals by simply tuning the precursor concentration.

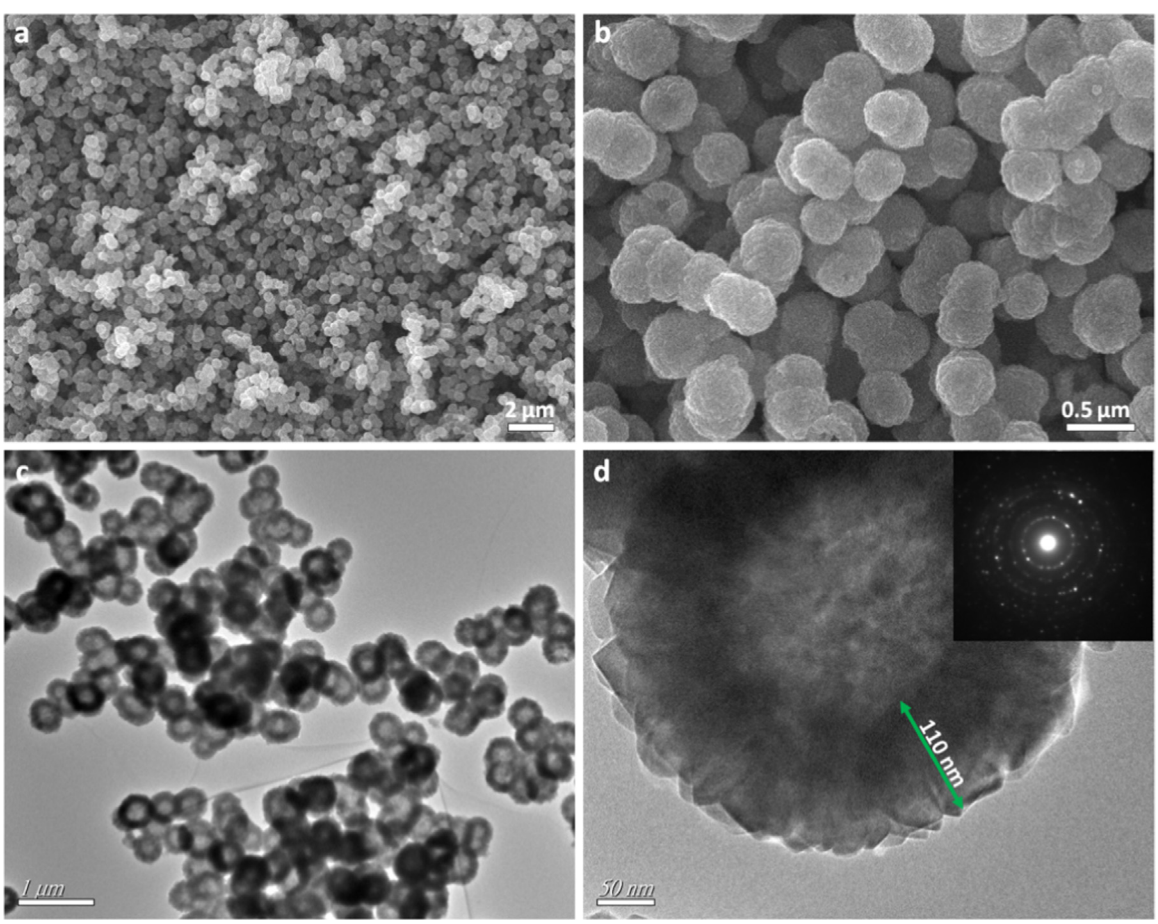

Fig. 2. SEM (a, b) and TEM (c, d) images of TiO_2 hollow nanospheres. The inset in (d) is a SAED pattern of the corresponding TiO_2 nanosphere.