



A facile and controllable multi-templating approach based on a solo nonionic surfactant to preparing nanocrystalline bimodal meso-mesoporous titania



Dongthanh Nguyen^a, Wei Wang^{a,*}, Haibo Long^a, Weijun Shan^a, Xiaodong Li^a, Ming Fang^b, Mingya Li^c, Xiaoqiang Wang^c, Hongqiang Ru^{a,**}

^a Key Laboratory for Anisotropy and Texture of Materials of Ministry of Education (ATM), Northeastern University, Shenyang, China

^b Tianle New Materials and Technology Ltd., Shengzhou City, 312400, China

^c Institute of New Materials, Northeastern University at Qinhuangdao, 066004, China

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ABSTRACT

In this work, a facile and controllable multi-templating approach based on a solo nonionic surfactant P123 and peroxotitanic acid (PTA) was reported for the preparation of bimodal meso-mesoporous titania (BMM-TiO₂) with high surface area (150–243 m² g⁻¹), high pore volume (0.3–0.6 cm³ g⁻¹), large mesopore sizes spanning from 8 to 16 nm (BJH pore size), and high & tunable crystallinity (Anatase or Anatase + Rutile). The BMM-TiO₂ was shown to be a homogeneous ‘mixture’ of two series of wormhole mesostructures with two modes of mesopore sizes that depend on both the contents of P123 and synthetic conditions. The formation of BMM structures was proposed to arise from both the formation of differentiated micellar structures of P123 (dual soft-templating) and their subsequent different mesostructural shrinkages driven by prolonged drying process (*i.e.*, 100 °C for 12 h) in the presence of PTA. The low-temperature crystallization behaviours of PTA, unusual hard-templating effect of P123 and its carbon derivatives (3rd fold templating), large mesopores relative to the surrounding TiO₂ crystals are all believed to be responsible for the high thermal stability of the obtained BMM-TiO₂. To our knowledge, it is for the first time reported that P123 plays such multiple templating roles (three folds in this work) in the preparation of meso-TiO₂, not to mention that P123 was also confirmed to be a prerequisite for the formation bi-crystalline BMM-TiO₂. In the photodegradation test of Rhodamine B in water by UV irradiation, other than the high surface area and synergistic effect between anatase and rutile phases, the BMM structures were also found to be advantageous to enhance the photocatalytic properties of mesoporous TiO₂.

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1. Introduction

Mesoporous titanium dioxide (meso-TiO₂) materials have received enormous attention due to their promising applications in photocatalysis, antimicrobials, water splitting, sensors, lithium rechargeable batteries and solar cells, as summarized in many excellent literature reviews [1–5]. It is therefore highly desirable to prepare meso-TiO₂ with controllable mesoporous and crystalline structures. Compared with bulk TiO₂, large surface area and

uniform mesopore channels of meso-TiO₂ not only increase the density of active sites, but also facilitate the diffusion of reactants and products. And also, high crystallinity means few defects and therefore enhanced energy conversion efficiency and high stability in many photoelectrochemical applications, compared with its amorphous counterparts [5]. Therefore, the controlled preparation of meso-TiO₂ is still the key to optimizing their performance in applications.

Among the methods reported so far for the preparation of meso-TiO₂, soft-templating method still received much attention, fuelled by the huge success in the preparation of ordered mesoporous silica since 1992 [6]. This method, though is long at mesostructural manipulation and can yield meso-TiO₂, still faces some problems in practice. One known fact is that some of the requirements on the

* Corresponding author.

** Corresponding author.

E-mail address: wangw@atm.neu.edu.cn (W. Wang).

meso-TiO₂ defined by the application are sometimes conflicting each other, which impose high challenges on the synthetic methodologies. For example, thermal treatment processing, which is widely employed to induce/enhance the crystallization and evacuate the pores from the occupation of organic templates, often results in deterioration/collapse of the mesostructures, witnessed by the substantial decrease in surface area [1,5]. The underlying reasons mainly arise from two common aspects.

- (1) The INTRINSIC rigid Ti–O–Ti covalent bond angles, when no longer accommodate the curvature of mesostructures upon crystallization from the amorphous and further crystal growth, will surrender to substantial structural reorganization and often the collapse of the mesostructures [7]. Therefore, to template the pre-synthesized titania nanocrystals into mesostructures based on the same soft-templating principle seemingly can shunt harsh thermal treatment and avoid concomitant structural deterioration, and simultaneously guarantee the high crystallinity even under mild conditions (e.g., at low temperatures) [8–11]. However, the thermal treatment temperature at as low as 300 °C, which was necessary to both consolidate the framework and remove the template, was still found to be detrimental to the mesostructures [8].
- (2) The lack of EXTRINSIC support, for example from organic surfactant templates or their carbon derivatives, is often another reason for the collapse of mesostructures. Previous works based on some special organic templates, such as the lab-made block-copolymers with large molecular weights, therefore, showed to be successful in maintaining the mesostructures, because the *in-situ* generated carbon species can function as hard template after the carbonization of such organic templates. So, the large and carbonizable hydrophobic segments are core to these organic templates [12–21]. However, the syntheses of these block copolymers need further expertise and will add to the complexity of the preparation of meso-TiO₂.

Therefore, in order to achieve high-surface-area meso-TiO₂, two above-mentioned intrinsic and extrinsic aspects have to be taken into consideration. So far, it is still a challenge in controllably integrating well-defined mesostructures (high surface area/pore volumes, and adjustable mesopore size in a wide range) with high and tunable crystallinity in one meso-TiO₂ simultaneously. Additionally, the titanium chloride and alkoxides are currently extensively used to prepare meso-TiO₂. These precursors are highly reactive and moisture sensitive, so the control over their sol-gel reaction and following self-assembly process with surfactant demands special care in the synthesis.

In our recent work, the peroxotitanic acid (PTA) was chosen as the easy-handling inorganic building species and then coupled with the nonionic surfactant P123 to form a simple ternary templating system (i.e., PTA/P123/H₂O), whereby meso-TiO₂ can be facily prepared with ultra-large mesopores and high surface area/pore volumes [22]. In this work, addressing the above-mentioned synthetic issues as well as aiming to exploit the potential of such templating system, we go one step further and demonstrate that the bimodal meso-mesoporous TiO₂ (designated as BMM-TiO₂) with controllable mesoporous and crystalline structures can be facily obtained, interestingly, *via* a modified approach with a prolonged drying process. Nonetheless, in such a seemingly 'simple' modified approach, a 'sophisticated' multi-templating (three folds) mechanism based on a solo nonionic surfactant P123 was for the first time unveiled to play the roles in directing the formation of thermally stable BMM-TiO₂. It should also be pointed out here that

the preparation of bimodal meso-mesoporous materials (e.g., titania [18,19,23–25], silicas [26–33]) often involves the employment of dual or multiple templates, including surfactant plus hard template [19,23,24], or surfactant plus surfactant [18,25–33]. For example, Sallard and co-workers paired poly(isobutylene)-*b*-poly(ethylene oxide) (i.e., PIB-PEO) with the ionic liquid as complex templates to prepare BMM-TiO₂ [18]. But so far, the works on BMM-TiO₂ are still very limited [18,19,23–25], especially those based on a solo nonionic surfactant [34], as reported in this work. Moreover, the photocatalytic test of meso-TiO₂ in degrading Rhodamine B in water showed that, other than the high surface area and synergistic effect between anatase and rutile phase, the BMM structures were also demonstrated to be advantageous to enhance the photocatalytic performance of meso-TiO₂. This synthetic approach thus constitutes a novel, facile synthesis protocol for the design and fabrication of BMM-TiO₂, and is believed to be able to further promote the application of meso-TiO₂.

2. Experimental

2.1. Chemicals

Titanyl sulphate (TiOSO₄·xH₂O) and Pluronic PEO₂₀–P–PO₇₀–PEO₂₀ (P123 with Mn = 5800) were purchased from Aldrich. Ammonia (NH₃·H₂O, 35% in H₂O) and hydrogen peroxide (H₂O₂, 30% in H₂O) were purchased from the Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used as received.

2.2. Preparation of meso-TiO₂

The detailed procedure of the preparation of PTA sol can be found in our previous work [22]. In a typical preparation of mesoporous titania, PTA sol (10.0 g) was mixed with P123 solution (6.0 g, 10% w/w) to form a homogeneous solution, which was transferred to an uncapped bottle and then directly dried in 100 °C oven for prolonged time up to 12 h. The obtained PTA/P123 bulk materials were subject to calcination at 450 °C in air for 2 h with the heating ramp of 1.5 °C/min to both crystallize the titania and burn off the organic template. The eventually obtained mesoporous titania was designated as P6/450, where 'P6' denotes relative amounts of P123 solution with respect to PTA sol, and '450' for the calcination temperature. Other naming can be deduced by analogy.

2.3. Structural characterization

Powder wide angle XRD patterns with 2θ angles from 15° to 80° were recorded on a Bruker D8 diffractometer using Cu Kr radiation (40 kV, 120 mA). The phase contents of anatase (X_A) and rutile (X_R) in meso-TiO₂ can be calculated based on the integrated intensities of anatase (101) and rutile (110), respectively according to Zhang et al. [35]. The crystal size of nanocrystalline TiO₂ was estimated by applying the Scherrer equation [36]. TEM and high-resolution TEM (HR-TEM) measurements were performed using a JEM2100F instrument operated at 200 kV. FE-SEM images were recorded using scanning electron microscope (Hitachi, S-4800) on samples without any conductive coating. The low operation acceleration voltage and height between detector and sample were used to guarantee quality imaging. TGA-DTA analyses (NETZSCH STA 449F3) were carried out in air with heat ramp of 10 °Cmin⁻¹ from room temperature to 800 °C. Nitrogen adsorption isotherms were measured at –196 °C using Autosorb iQ Station 1 analyzers manufactured by Quantachrome Instruments. The specific surface areas of the samples were calculated using the BET method. The pore size distributions (PSDs) of the cell pore and window pore were determined based on the adsorption and desorption branches

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