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Supercritical hydrothermal synthesis of titanium dioxide nanostructures with controlled phase and morphology

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ABSTRACT

A novel template- and organic-free synthesis of TiO_2 nanostructures with controlled phase and morphology was realized through batch supercritical hydrothermal treatment (400 °C) of titanate nanotubes (TNTs) with H_2O_2 in NaOH aqueous solution. Well-defined 3D titanate hierarchical spheres (THSs), 2D multilayered titanate nanosheets (TNSs), and 1D monodisperse anatase nanorods (ANRs) exposing (0 1 0) facets were prepared in 15 min by slightly varying the NaOH solution pH. Specifically, the obtained Na/H-THSs (without/with HCl neutralization) exhibited highly porous structures with large specific surface area (109 $m^2 g^{-1}$ and 196 $m^2 g^{-1}$, respectively). Temperature-dependent phase and morphology evolutions of products under subcritical condition (200 and 300 °C) were investigated. The formation of the TiO_2 nanostructures from TNTs was proposed mainly following a dissolution–nucleation-growth mechanism, suggesting that both supercritical temperature and NaOH solution pH were determinant factors governing the nucleation and growth process and thus the phase and morphology.

1. Introduction

In modern era, nanoscience and nanotechnology to tailor material's properties at nanoscale is a very important and promising scientific field, in which significant advancements have been achieved to synthesize different inorganic nanostructured architectures [1]. In particular, TiO_2 (titania/titanate) nanostructures have been widely investigated owing to their distinctive semiconducting and catalytic properties, low cost, and nontoxicity [2].

Among various methods to synthesize TiO_2 nanostructures [3,4], alkaline hydrothermal reaction was most widely used because of its remarkable efficiency, reliability, and selectivity. Generally, one-dimensional (1D) titanate nanostructures including nanotubes, nanowires, and nanobelts were the usual final products by alkaline hydrothermal treatments of TiO_2 polymorphs [4]. Interestingly, they were thermodynamically metastable and easily transformed into more stable TiO_2 nanomaterials. So these 1D primary titanate nanostructures themselves were proper titanium precursors and templates to synthesize other secondary TiO_2 nanostructures [5,6].

In the past few years, much attention has been devoted to synthesizing three-dimensional (3D) TiO_2 hierarchical spheres (HSs) with 0–2D building blocks, which take the advantages of both nanosized building blocks and their micro- or submicrosized ensembles [7], e.g., highly porous structure, low density, high surface area, and high delivering ability. Some research groups have synthesized 3D TiO_2 HSs by solvothermal reactions of titanium alkoxides such as titanium butoxide [8,9], tetrabutyl titanate [10–12], and titanium isopropoxide [13,14]. Tang et al. [15,16] reported the synthesis of 3D TiO_2 HSs through an ultrafast electrochemical spark discharge spallation on the surface of titanium foil. Mao et al. [17] as well as Wang et al. [18] prepared 3D TiO_2 HSs by alkaline hydrothermal treatments of titanium foil or powder in the presence of H_2O_2. Very recently, Li et al. [19] successfully synthesized 3D TiO_2 HSs through the hydrothermal reaction with titanate nanotubes (TNTs) being titanium precursors. Besides this report, however, few studies have been conducted to investigate possible synthesis of 3D TiO_2 HSs from 1D titanate nanostructure precursors. And it is still a great challenge to synthesize 3D TiO_2 HSs during minutes instead of hours (12 h for reaction in ref [19]). Moreover, it is significant to investigate how different reaction conditions such as changing the solution pH and hydrothermal temperature affect the final products.

It is well known that supercritical hydrothermal reaction has proven to be an excellent method to synthesize nanomaterials [20]. While the critical temperature is reached, high temperature and pressure can take up water in its supercritical state (T_c = 374.2 °C, P_c = 22.1 MPa), then the supercritical water (SCW) will possess

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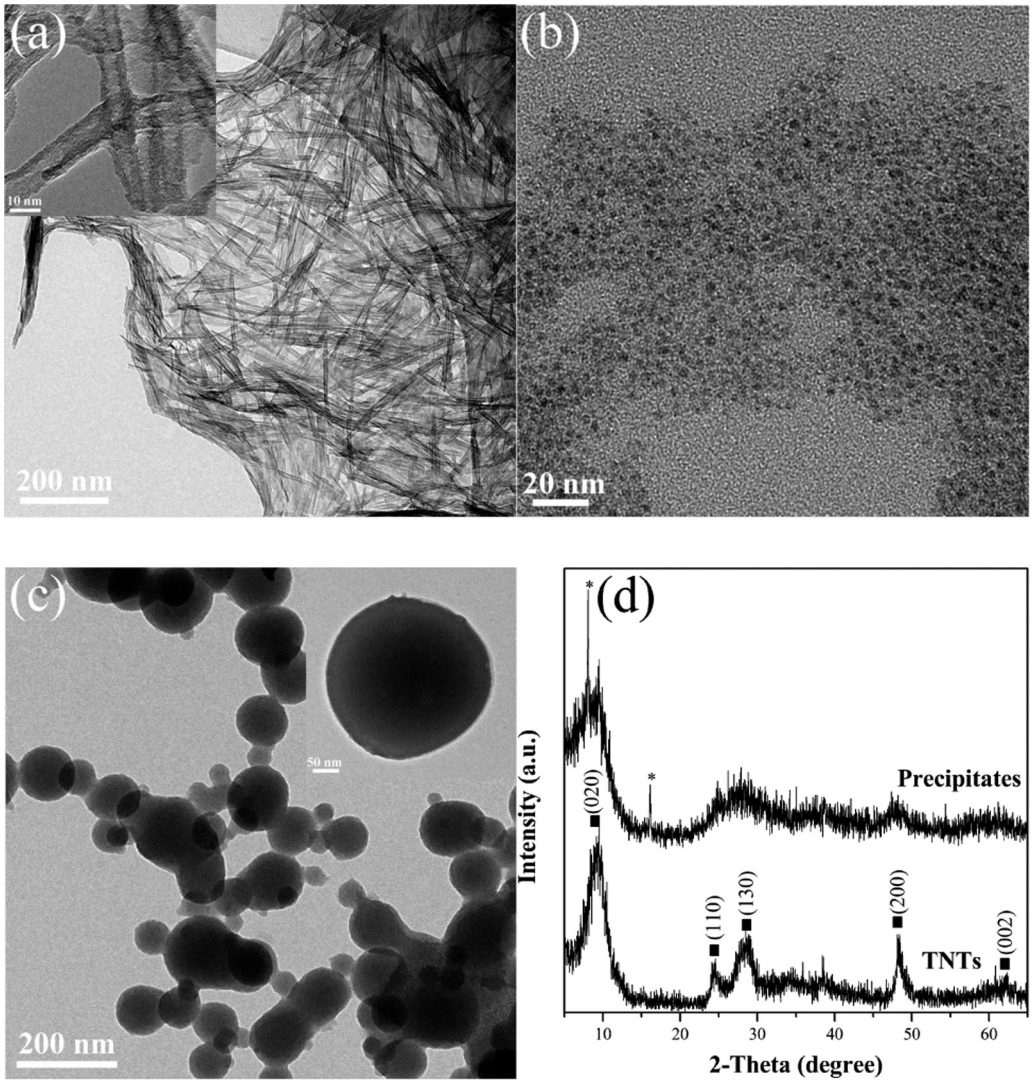

Fig. 1. TEM images of (a) hydrothermally prepared TNTs, and (b) and (c) Ti-complex precipitates formed by naturally placing peroxotitanate complex (intermediate B) for 48 h. And (d) XRD patterns of TNTs and precipitates. The insets in (a) and (c) are the magnified TEM images.

some specific properties such as high solvating power, low viscosity, and high diffusivity [6,20,21], which can significantly accelerate the hydrothermal reaction.

To explore the possibility of synthesizing 3D TiO_2 HSs from 1D titanate nanostructure precursors in a much shorter duration, in this work, we conducted supercritical hydrothermal experiments by using 1D TNTs as precursors. 3D titanate hierarchical spheres (THSs) were successfully prepared within 15 min. We also found that 2D multilayered titanate nanosheets (TNSs) and 1D monodisperse anatase nanorods (ANRs) exposing (0 1 0) facets were prepared by slightly varying the NaOH solution pH. Moreover, the effect of subcritical temperatures (200–300 °C) on the phase and morphology evolution of products was studied. And a possible mechanism for this controlled supercritical hydrothermal synthesis was discussed.

2. Experimental

2.1. Synthesis of TNTs

A simple hydrothermal reaction described by Kasuga et al. [22] was used to synthesize TNTs with commercially available P25 powder (Degussa AG, Germany) as the starting material. In a typical procedure, 2 g of P25 powder was dispersed in 70 ml of 10 M NaOH aqueous solution by ultrasonication for 5 min and then charged into a 100 ml Teflon-lined stainless steel autoclave. The sealed autoclave was subsequently heated at 130 °C for 16 h. The resulting precipitate was separated by filtration, washed with de-ionized water three times to remove excess NaOH, and then oven-dried at 60 °C for 12 h.

2.2. Sub/supercritical hydrothermal synthesis of products from TNTs

50 mg of TNTs and 0.45 ml of H_2O_2 (30%) were dispersed in 9.5 ml of NaOH aqueous solution at different pH (14.1, 13.2, and 12.4, respectively). After ultrasonication for 6 min, TNTs were completely dissolved in NaOH solution at pH 14.1 and 13.2, and partly dissolved in NaOH solution at pH 12.4, to form a colorless solution (intermediate A), a pale yellow solution (intermediate B), and a yellow suspension (intermediate C), respectively. The solution pH of the formed intermediate A, B, and C was 13.8, 10.3, and 9.0, respectively.

Referred to our previous reports [6,21,23], sub/supercritical hydrothermal reactions were carried out in a 20 ml stainless-steel batch type reactor made of Swagelok tube and adaptor. Typically,