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Colloidal monolayer titania quantum dots prepared by hydrothermal synthesis in supercritical water

Hanyang Gao[a], Guoxin Hu[b,*], Wenfeng Shangguan[a,**], Kunxu Zhu[b]

[a] Research Center for Combustion and Environment Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China
[b] School of Mechanical and Power Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

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ABSTRACT

Two-dimensional monolayer titania quantum dots (MTQDs) with ~0.4 nm thickness and ~2 nm lateral size are synthesized by supercritical water (SCW) treatment of titania nanotubes (TNTs). The morphology, chemical characteristics and the structure of MTQDs are studied. The formation mechanism of the MTQDs and the differences between SCW and low-temperature hydrothermal treatment are discussed. During the reaction, the high temperature, high pressure and high H^+/OH^- concentration of SCW dissolved TNTs into MTQDs, and the intercalation property of the "active" water clusters formed from the broken hydrogen bonding network facilitated the detachment of the MTQDs from the TNTs. The above two reasons lead to the capture of the dissolved tiny particles, which could hardly preserved in low-temperature hydrothermal treatment. The MTQDs may be the minimum constituent unit existing in the reality of the anatase TiO_2. As a new member of the monolayer family, this new kind of 2D material may shed new light on the study of the monolayer materials.

1. Introduction

The two-dimensional (2D) materials have become a focus of scientific research recently. The 2D materials are attractive for use because they are the basis for the complex nanostructures and usually possess many special physical and chemical properties [1,2]. However, due to the strict synthesis, the number of the 2D family members is quite small.

When viewed perpendicular to the (0 0 1) plane, anatase can be considered constituting by the stacked (0 0 1) slabs, which is consisted by edge sharing TiO_6 octahedral unit cells with Ti atom occupying the center, along the [0 0 1] direction in an ABCD staggered fashion [3]. Theoretically, the monolayer (0 0 1) nanosheets (one slab of thickness) can be cut from the (0 0 1) surface of anatase TiO_2 [4,5]. Although some computer simulation studies have been carried out on this monolayer titania sheet [4–6], the experimental research of the synthesis and characterization are hardly found. When the number of (0 0 1) slabs down to only two layers, bilayer of (0 0 1) oriented anatase slabs convert to lepidocrocite nanosheets by allowing the upper slab further slide half a unit cell over the lower one [6,7]. The titania nanotubes (TNTs) are the rolling form of these lepidocrocite nanosheets. It is reported that, under low-temperature hydrothermal conditions (usually 120–200 °C), the TNTs would transform into anatase TiO_2, and one of the plausible route of the phase changing is dissolution–reconstruction [8–11]. In this mechanism, the TNTs dissolute into a kind of crystal seeds and then followed by an orientated crystal growth during the hydrothermal treatment. This mechanism has been widely recognized, because the crystal seeds would easily attach on the sidewall of TNTs by attractive van der Waals forces (the "hit-and-stick" scenario) [10] and then change into anatase. However, the crystal seeds could hardly be captured and preserved.

In this research, instead of low-temperature hydrothermal treatment, the supercritical water (SCW) hydrothermal method is used to treat the TNTs. While the temperature is raised to 400 °C, high temperature and high pressure take up water in its supercritical status, and they possess some features such as high solvating power, low interfacial tension and high diffusion coefficient [12,13]. It was found in our experiments that, the dissolution–reconstruction mechanism is also suitable to the SCW hydrothermal treatment. During the process, the monolayer titania quantum dots (MTQDs) with the thickness of around 0.4 nm are generated as the crystal seeds from the dissolution of the TNTs. Furthermore, owing to the special intercalation property of the SCW, the MTQDs could detach from the TNTs wall and disperse in the SCW.

* Corresponding author. Tel.: +86 021 34206569.
** Corresponding author.
E-mail addresses: hugx@sjtu.edu.cn (G. Hu), shangguan@sjtu.edu.cn (W. Shangguan).

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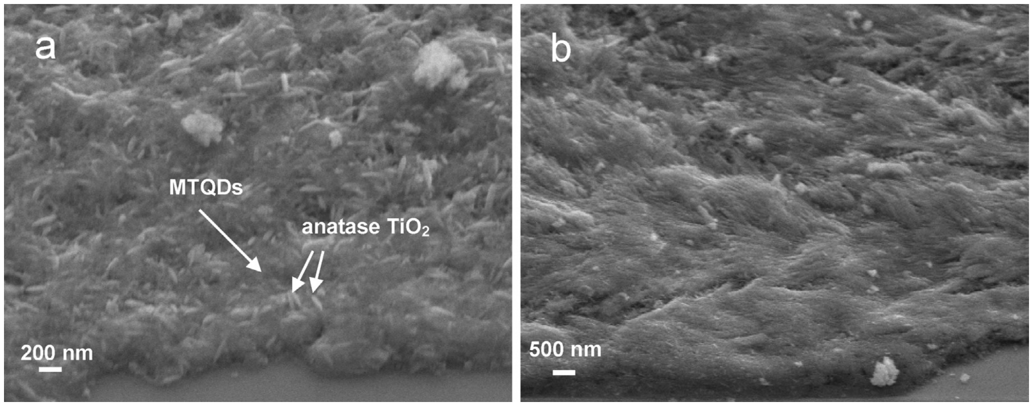

Fig. 1. SEM images of the products prepared in SCW (a) preceding and (b) after dialysis.

Therefore, in our research, the 2D MTQDs colloid is obtained from the TNTs by SCW hydrothermal treatment. This tiny monolayer sheet may be the minimum constituent unit existing in the reality of the anatase TiO_2. As a new member of the monolayer family, this new kind of 2D material may shed new light for the study of the monolayer materials. Furthermore, the MTQDs are coated without surfactant or organic molecular, this ligand-free characteristic and the special morphology would make the MTQDs good building blocks for self-assembly higher order nanoarchitectures.

2. Experimental

2.1. Synthesis of TNTs

As precious reports to prepare the TNTs [14,15], 2 g P25 powder was added in 70 mL 10 M NaOH aqueous solution, the mixture was then held at 130 °C in a 100 mL Teflon-lined autoclave for 24 h. After the alkali treatment, the autoclave cooled down naturally to room temperature. The resulting sample was neutralized with 0.1 M HCl solution for removing the residual NaOH and then washed with deionized water until a pH value reached 7. After filtered and dried in the drying oven at 60 °C for 24 h, the TNTs white powder was obtained.

2.2. Synthesis of MTQDs

2.2.1. Caution

High-pressure experiments with compressed gases are potentially dangerous and must be carried out with suitable equipment under appropriate safety regulation only. The reactor maximum loading of water and the heating time of the reactor should be limited.

In the SCFs procedure, a pressure-resistant SCHOELLER 316L SS vessel with 15 cm^3 volume was used as the SCFs reactor and deionized water was used as the solvent. In a typical experiment, 25 mg as-prepared TNTs powder was mixed with 10 mL de-ionized water in a beaker. After ultrasonic dispersed in an ultrasonic cleaner (40 kHz, maximum output power 180 W) for 15 min, the mixture was then carefully transferred into the reactor. After sealed, the reactor was heated in a tube furnace at 400 °C for 10 min. In heating process, the output power of the furnace during the heating period was changed and controlled by an electronic control program, and the temperature of the reactor was measured to be ca. 375 °C at 6 min and ca. 400 °C at 10 min by a thermocouple spot-welded to the reactor. The reaction time of TNTs in SCW includes the ramping time. The pressure value of water with a constant specific volume (e.g. it is 0.0015 m^3/kg in our experiments) at different temperature could be calculated by using diagrams of properties of water and steam [16]. After heat treatment, cool the vessel rapidly in ice-cold water and transferred the products into a beaker. Wash out any remaining products from the reactor vessel with de-ionized water. After dispersed the product using sonication for 5 min, the product solution was further dialyzed in a dialysis bag with 2000 Da retained molecular weight for 24 h to obtain the MTQDs colloid.

2.3. Characterization of TNTs, anatase TiO_2 and MTQDs

The surface morphology and EDS was examined by a JEM-2100F high resolution-transmission electron microscope (HRTEM) operated at 200 kV with a point-to-point resolution of 0.19 nm. X-ray diffraction patterns (XRD) were measured on a Rigaku D/Max-2200/PC X-ray diffractometer. UV–visible absorption spectra were made with a SHIMADZU UV-2450 spectrophotometer. Unpolarized micro-Raman mapping was performed on a Senterra R200-L micro-Raman spectrometer (laser excitation 532 nm, Bruker Optics, Germany) at room temperature. The photoluminescence (PL) was checked by a LS 50B (Perkin Elmer, USA). Scanning tunneling microscope (STM) imaging and manipulation were carried out using an ambient AFM/STM (Multimode Nanoscope III, from Veeco, Santa Barbara, CA). Atomic force microscopy (AFM) measurements were carried out with an E-sweep/NanoNavi Station (SII Nanotechnology, Inc., Tokyo, Japan). The Zeta potential was examined by a Zetasizer Nano ZS90 (Marlvern, UK).

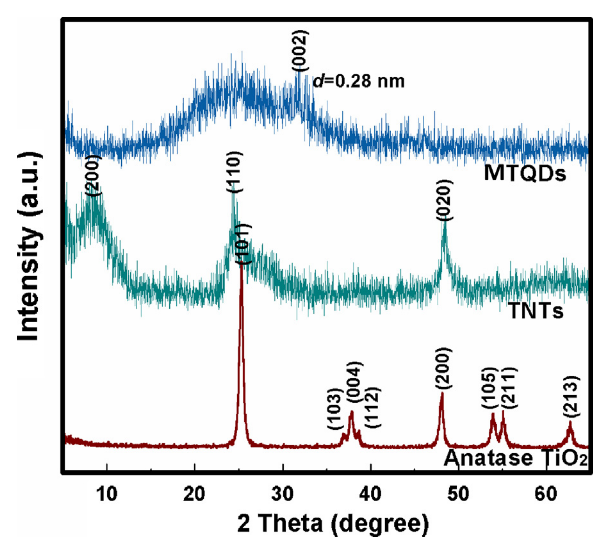

Fig. 2. XRD pattern of anatase TiO_2, TNTs and MTQDs.