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Preparation and photocatalytic performance of transparent titania film from monolayer titania quantum dots

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ABSTRACT

By using monolayer titania quantum dots (MTQDs) colloid, a continuous and transparent ultrathin titania film was prepared simply by drop-cast or spray coating method at room temperature. The formation of this even and ultrathin film was not only because of the very thin thickness of two-dimensional MTQDs, but also because of the suppression of coffee-ring effect. The self-assembly behaviors of MTQDs were examined by AFM and the reason for the suppression of coffee-ring effect was discussed in detail. Furthermore, the photocatalytic performance of this MTQDs film was evaluated and an improvement was achieved by loading graphene. Comparison between MTQDs/graphene composite and sphere-shaped nanoTiO_2/graphene composite indicated that, the face-to-face contact mode between MTQDs and graphene may contribute to the high activity of MTQDs/graphene composite.

1. Introduction

Owing to the inherent excellent photocatalytic, photoelectrical properties, and chemical stability, titania film has been proven as a high efficiency, environmental friendly catalytic film, and can be applied to various applications, such as antibacterial coating, antifogging coating, self-cleaning film, deodorant fiber, gas sensors, photovoltaic devices, and photocatalysis [1–3]. Well-crystallized titania coatings can be prepared by multiple deposition techniques, such as sol–gel [4], sputtering [5], and spray pyrolysis [6]. Since crystalline degree of catalysts strongly affect their catalytic activity, a heating treatment at relatively high temperatures above 400 °C is usually required to obtain sufficient crystallinity in these methods. During the heating process, along with crystallinity, catalyst particles unavoidably grow and aggregate [7], making it difficult to produce an ultrathin and transparent highly crystalline titania film.

In our previous study, monolayer titania quantum dots (MTQDs) with two-dimensional morphology and ~0.4 nm thickness were synthesized by treating titania nanotubes (TNTs) in supercritical water (SCW) [8]. The high crystallinity and special plane morphology of MTQDs, may give us an opportunity to prepare an ultrathin and transparent titania film at room temperature. Furthermore, because MTQDs and graphene both possess a plane morphology, it can be expected that the combination of MTQDs and graphene will in a plane–plane mode instead of a point-plane mode. The enlargement of contact area will be beneficial for electronic transfer, and therefore will facilitate the photocatalytic performance of the composites. It also can be expected that comparing with the combination between sphere-shape TiO_2 particles and paper-like graphene, the stacking of two kinds of two-dimensional particles has more tendency to form a smooth film with ultrathin thickness.

In this article, based on our previous study, the self-assembly behavior of MTQDs was observed by AFM. Taking advantage of the special assembly behaviors of MTQDs, a highly crystallized, ultrathin, and transparent titania film was prepared using MTQDs colloid at room temperature by a simple drop casting method. The photocatalytic performance of the self-assembly film with or without graphene enhancement was discussed. The effect of the special face-to-face contact mode between MTQDs and graphene (which possessing similar two-dimensional morphology) on photocatalytic efficiency was compared with the effect of common point-to-face contact mode between sphere-shaped TiO_2 particles and graphene. To our knowledge, this is the first time to report the self-assembly behavior of the very tiny two-dimensional titania nanosheets and the further thin-film fabrication from them. The comparison of the effect of two different contact modes between titania particles and graphene on photocatalytic efficiency may also provide some useful information for the development of graphene-based composite catalyst.

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2. Materials and methods

All the reaction in SCW was carried out in a 15 mL SCHOELLER 316L SS stainless-steel reactor (caution: the reactor maximum loading is 80% (12 mL), the remaining space is filled with air). All reagents were analytical grade and used without any further purification.

2.1. Synthesis of TNTs

As precious reports [9,10], to prepare the TNTs, 2 g commercially available anatase TiO_2 powder (Aladdin, Shanghai) 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 10 h. After the alkali treatment, the autoclave cooled down naturally to room temperature. The resulting sample was washed with 0.1 M HCl and then with de-ionized water until a pH value near 7 was reached. 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

MTQDs were synthesized by treating TNTs in SCW as reported in our previous study [8]. In a typical procedure, 25 mg as-prepared TNTs powder and 10 mL de-ionized water were mixed and dispersed with ultrasonic agitation (40 kHz, maximum output power 180 W) for 15 min, and then carefully transferred into the reactor. The reactor was sealed and heated in a tube furnace at 400 °C for 20 min, then was cooled rapidly in ice water. The products were transferred into a beaker and dispersed by sonication for 5 min. The resulting solution was further dialyzed in a dialysis bag (retained molecular weight 2000 Da) for 24 h to obtain the MTQDs colloid (see Refs. [8] and [11] for more information.).

2.3. Synthesis of graphene in SCW

The procedure of graphene producing in supercritical fluid was described in our previous research in detail [12]. Typically, expandable graphite powder (Qingdao Tianhe Graphite Co., Ltd., China) was added in DMF (Sinopharm Chemical Reagent Co., Ltd.) and dispersed by sonication for 15 min, and then transferred into the stainless-steel reactor. The reactor was sealed and heated in a tube furnace at 400 °C for 30 min, then was cooled rapidly in ice water. The obtained production was centrifuged in 6000 rpm for 10 min, suspension was then filtered through film (PVDF) and washed several times with fresh solvent. The resulting products were vacuum dried overnight at 100 °C to obtain graphene.

2.4. Synthesis of graphene/MTQDs composite

To prepare graphene/MTQDs suspension, MTQDs colloid and graphene were mixed together in different proportions and sonicated for 15 min to obtain stable composite colloid. After filtration and drying, graphene/MTQDs particles were obtained.

2.5. Synthesis of sphere nanoTiO$_2$ and nanoTiO$_2$/graphene composite

Based on our previous report [13], 5 mL $Ti(OBu)_4$ (Sinopharm Chemical Reagent Co., Ltd.) and 1 mL PrOH were added in 50 mL de-ionized water and kept under reflux condition at 75 °C for 24 h to obtain nanoTiO$_2$ colloid. The as-prepared nanoTiO$_2$ colloid was subject to dialysis in water to remove the residual PrOH. For preparing nanoTiO$_2$/graphene colloid, graphene solution instead of pure de-ionized water was add in for the reflux treatment. After flocculation, filtration, and drying, the composite particles were obtained.

2.6. Material characterization

The surface morphology 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. Atomic force microscopy (AFM) measurements were carried out with an E-sweep/NanoNavi Station (SII Nanotechnology, Inc., Tokyo, Japan). The resistant measurement was performed by a Honeytek DT9205 digital multimeter. Transient photocurrents test was performed on a CHI660C electrochemical workstation (Chenhua Instruments Co., Shanghai, China).

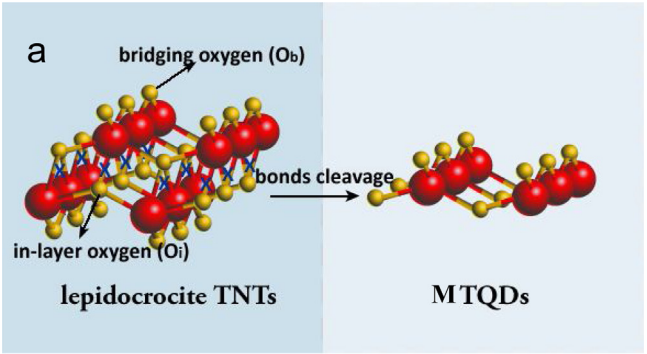
2.7. Photocatalytic performance test

Dye concentration in the aqueous solution after irradiation was measured by a SHIMADZU UV-2450 spectrophotometer. Catalyst/dye solution was irradiated with a 350 W Xe-lamp.

3. Results and discussion

3.1. Morphology and structure of MTQDs

While temperature and pressure get to the critical point of water, wide-range hydrogen bonding network breaks down into small water clusters which possess special characteristics such as



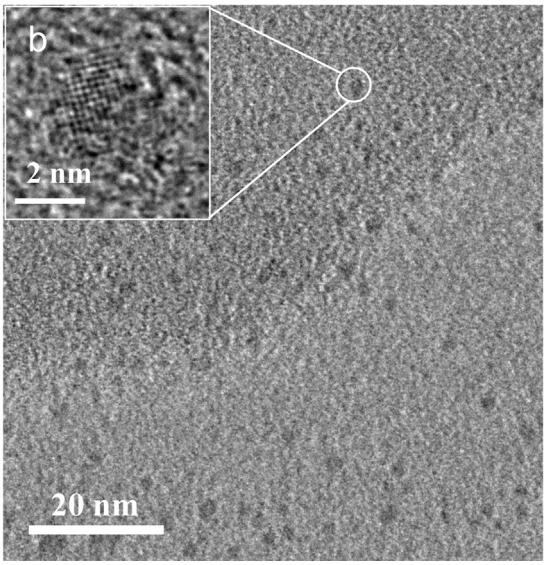


Fig. 1. (a) Chemical structure of lepidocrocite TNTs and MTQDs. (b) TEM and HRTEM images of discrete MTQDs.