

Microwave Synthesis of Monodisperse TiO₂ Quantum Dots and Enhanced Visible-Light Photocatalytic Properties

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Abstract. Semiconductor TiO₂ quantum dots sized 2-3 nm have been first synthesized by a simple and facile microwave method. The low/high-magnification TEM images illustrate these TiO₂ quantum dots are monodisperse. The TiO₂ quantum dots were deposited in acetone quickly and then dissolved in water well, exhibiting reversible process between in water and acetone. We further investigated the enhanced photocatalytic properties in degradation of organic dye under visible light.

Keywords: TiO₂ quantum dots, microwave synthesis, monodisperse, photocatalytic properties.

1. Introduction (Use “Header 1” Style)

It has been a challenging goal for chemists to transform chemicals efficiently with solar energy. TiO₂-based materials, as one of the most important photocatalysts, has demonstrated a great potential in significant redox reactions under light irradiation, e.g. photocatalytic treatment of wastewater and water splitting to generate H₂ and O₂ [1]. Recent studies have shown that the morphologies of TiO₂ particles and surface properties, such as crystalline structure, exposed facets, particle size, shape and dopants, can affect the photocatalytic activities significantly [2-7]. The photocatalytic activities of TiO₂ photocatalyst can be enhanced by the other semiconductor quantum dots embedded or sensitized TiO₂, e.g. CdTe quantum dots-sensitized TiO₂ [8] and TiO₂ sensitized by CuInS₂ quantum dots [9]. The unique optical properties of semiconductor quantum dots are size dependent based on quantum confinement [10]. Cernuto *et al.* investigated methylene blue decomposition by TiO₂ nanoparticles sized from 4 to 10 nm and employed the total scattering technique to obtain the effects of the particle size and shape on the photo-oxidation efficiency [11].

It is important to be able to fabricate TiO₂ quantum dots and control their size and shape. However, by using simple and facile method, the preparation of TiO₂ quantum dots with smaller diameter, i.e. less than 5 nm, is still a challenging task. In this investigation, we fabricated 2-3-nm monodispersed TiO₂ quantum dots by facile and effective microwave method. We further studied photocatalytic effect under visible-light and the corresponding mechanisms of removing the organic pollutants.

2. Material Fabrication and Characterization

In the synthesis procedure, all chemicals used were purchased from Sigma-Aldrich company. Titanium tetrachloride (TiCl₄) (0.05 mL) was added into 10-mL ethylene glycol under stirring at room temperature. After dissolving completely, the solution was transferred into a 50-ml cell for microwave treatment at 160°C and 800 W for 10 min. After reaction, the microwave system was cooled to room temperature and the as-prepared clear and transparent solution was obtained (Fig. 1).

The TEM and HRTEM images (Figs. 2) show that many small particles in this clear solution were obtained after the microwave treatment. And these small particles with the diameter of 2-3 nm (Fig. 2c) are monodisperse. After adding some acetone, white precipitates were collected

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immediately. Then, the powder was washed for 3 times using acetone and dried at 60°C in air for 12 h. The XRD spectrum of the powder revealed the formation of titanium dioxide with anatase (JCPDS 21-1272). The results indicated that the as-prepared small TiO₂ particles in the as-prepared clear solution were quantum dots.

Interestingly, the as-prepared TiO₂ quantum dots powder obtained are able to gradually dissolve in water and become clear again after ultrasonic treatment for 20 min (Fig. 1e), while the commercial anatase titanium dioxide (P25) powder has no such phenomenon (Fig. 1d). Moreover, the TEM images show that the morphology of TiO₂ QDs in water is significantly different from that in the as-prepared clear and transparent solution. The particles were unfolded and connected with each other, forming a very thin multiporous sheet structure, like graphene seen from the TEM images (Fig. 2d). The HRTEM image and FFT pattern (Figs. 2e and 2f, respectively) showing the lattice spaces of 0.35 nm and 0.38 nm are corresponding to (101), (200) facets, respectively. Thus, the crystallinity of the TiO₂ QDs has been improved significantly without calcination due to re-dissolving into aqueous medium.

Although the white TiO₂ QDs powder was dissolved in water and became clear solution forming a thin sheet graphene-like structure, the thin sheet folded immediately, gathered and precipitated quickly once acetone was dropped in this water solution. The TiO₂ QDs precipitates were separated out from solvent (Fig. 1f). Consequently, the as-prepared TiO₂ QDs powder presents a dissolving reversible process between acetone and water solvents. Moreover, the recovery and recycling of this TiO₂ material would become much easier, compared with centrifuging method.

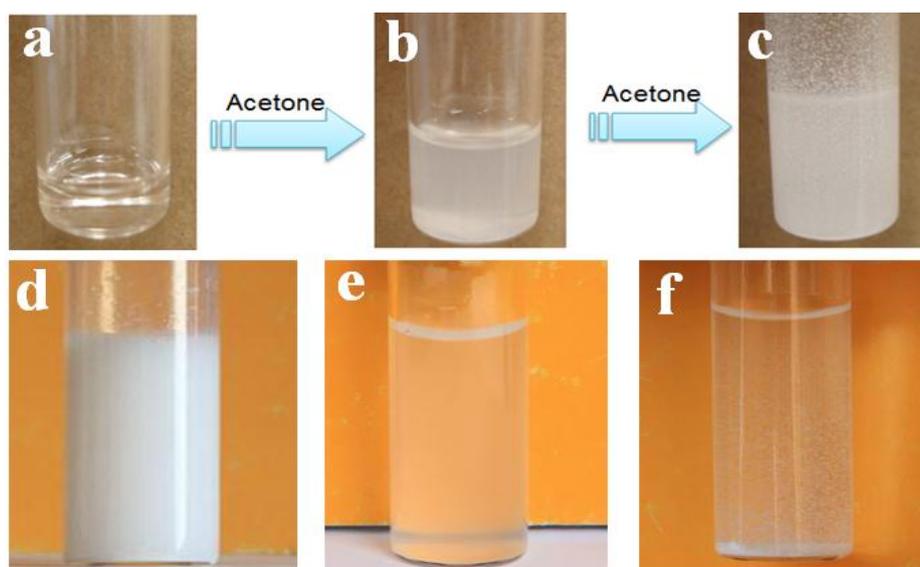


Fig. 1: Photos of TiO₂ quantum dots: (a) as-prepared clear solution with small TiO₂ quantum dots after microwave treatment; (b) white TiO₂ quantum dots powder starting to precipitate after dropping little acetone immediately; (c) white TiO₂ quantum dots powder were separated out after acetone was added; (d) commercial P25 TiO₂ in water; (e) the as-prepared TiO₂ QDs powder obtained by acetone washing in water; (f) as-prepared TiO₂ quantum dots powder precipitates again after dropping into some acetone.

3. Experimental Study

The enhanced photocatalytic performance of as-prepared TiO₂ quantum dots was measured in degradation of organic dye pollutant Rhodamine B. The commercial Titanium dioxide P25 powder was also tested for comparison. Figure 3 presents the measured photocatalytic effect of TiO₂ quantum dots under visible-light irradiation ($\lambda > 420$ nm).

As shown in Fig. 3, the as-prepared TiO₂ QDs adsorbed dye better than the commercial P25. The P25 TiO₂ was not able to respond to visible light, whereas the as-prepared TiO₂ QDs had extended the absorption edge to visible light region. As a result, the as-prepared TiO₂ QDs exhibited better photocatalytic activity to degrade the organic pollutant dye RhB. The RhB adsorption saturation on the surface of TiO₂ QDs and P25 could be reached after 40 min in dark condition without light

irradiation. After turning on the light, the RhB dye was nearly completely removed after 60 min. From the experimental results, we conclude that the visible-light photocatalytic activity of TiO₂ was effectively enhanced by quantum dot mechanisms.

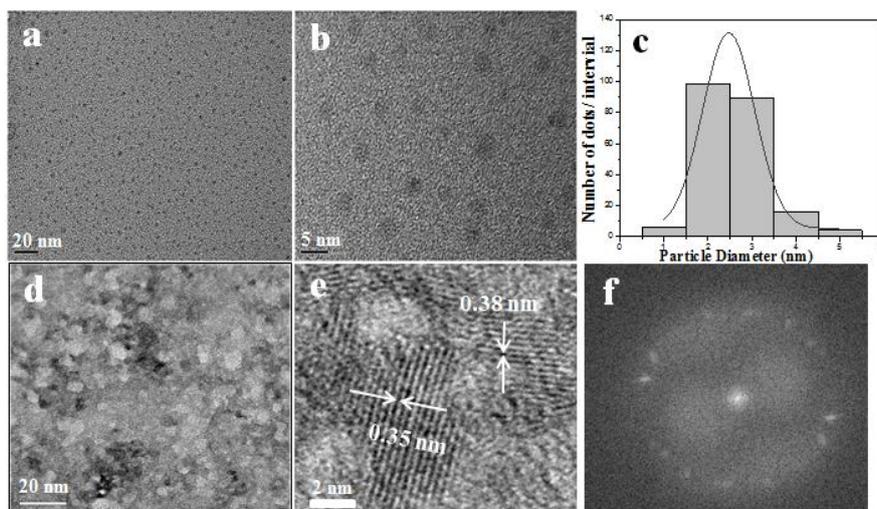


Fig. 2: As-prepare clear solution with small TiO₂ quantum dots after microwave treatment: (a) TEM, (b) HRTEM images and (c) the size distribution of the small particles; as-prepared TiO₂ QDs powder obtained by acetone washing in water: (d) TEM, (e) HRTEM, and (f) corresponding FFT images.

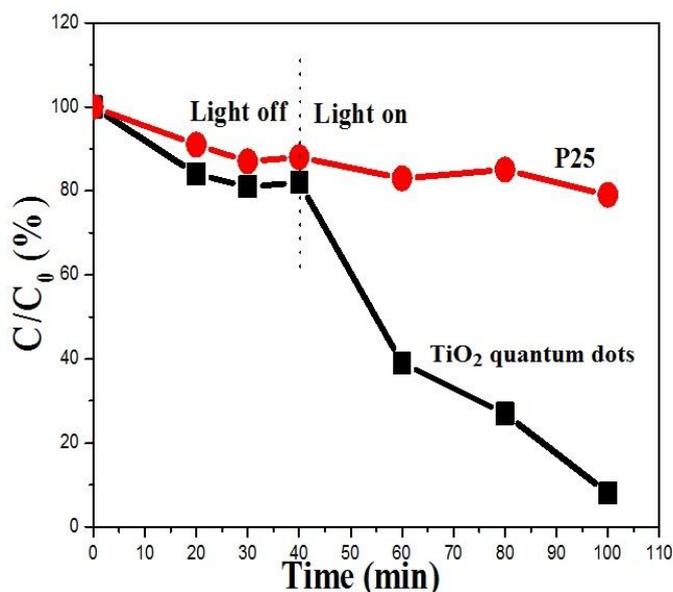


Fig. 3: Photocatalytic effect of visible-light activated as-prepared TiO₂ quantum dots on degradation of Rhodamine B (RhB) dye.

There are a number of key factors contributing to the improved performance. First, the as-prepared TiO₂ quantum dots adsorb organic compound at a higher rate for the surface photocatalytic phenomenon. The XPS data we obtained could illustrate this attribute. The XPS spectra of as-prepared TiO₂ QDs reflect that the Ti region was regular, and the binding energy at 458.9 eV is indicative of Ti⁴⁺ (TiO₂), which is slightly higher than the range of 458.1- 458.5 eV [12], because of a possible contribution from the adsorption of chloride ions and titanium chloride [13] on the surface of TiO₂. The ionic radius of Cl⁻ ion is larger than that of O²⁻ (1.81 Å versus 1.40 Å). The lattice O²⁻ in TiO₂ cannot be substituted by Cl⁻ during the reactions [14,15]. The peak of Cl2p3/2 at 198.0 eV is so similar to that of Cl2p3/2 in TiCl₄ (198.2 eV). The Cl⁻ ions should be located on the TiO₂ surface via the coordination with the unsaturated Ti⁴⁺ sites [16]. In addition, the peak of O1s the Cl elements could replace some OH of O-Ti-OH on the surface of as-prepared TiO₂ QDs,

producing O-Ti-Cl structures and oxygen vacancy sites. Thus, the oxygen vacancy sites produced by chloride element on the surface of TiO₂ QDs could effectively drive the TiO₂ QDs to the visible light range for photocatalysis.

Second, the special structures of as-prepared TiO₂ QDs in aqueous solution highly improve the photocatalytic performance. The hydroxyl radicals (OH species) present on the surface of TiO₂ QDs (O-Ti-OH) enable rapid reactivity in organic solvent based on compatible principle, e.g., acetone dissolved in water forming thin sheets connected with other like graphene structure. As the TEM images in Figs. 2d and 2e show the morphology of TiO₂ quantum dots in water is graphene-like thin sheets with some multiporous structure instead of small particles.

Three potential aspect benefits of this thin sheet structure for the photocatalysis have been proposed for significant improvement in pollutant degradation. Firstly, the thin sheet structure with larger surface areas and multiporous structure improves the activities that this TiO₂ contacts oxygen and pollutants in waste water during the photocatalytic activities. Secondly, high efficiency of separation rate between electrons and holes produced by irradiation during the photocatalytic process on the thin sheet structure is improved significantly since the electrons could move around the surface of this thin structure, like the electrons on the surface of graphene sheet. For the third aspect, the TiO₂ QDs in aqueous medium with graphene-like morphology of thin sheet has highly crystalline intensity (Figs. 2e and 2f), which could greatly improve the property of photocatalysis.

4. Summary

In summary, this work for the first time represents a simple and novel microwave method for the preparation of TiO₂ quantum dots with anatase and enhanced photocatalytic effect on degradation of organic pollutants Rhodamine B dye. The as-prepared TiO₂ quantum dots with microwave treatment are considerably monodisperse, the diameter is 2-3 nm. Moreover, the special performance on reversible dissolving process of TiO₂ material between in water and acetone exhibits different morphologies of as-prepared TiO₂ QDs, thin sheet and graphene-like structures with multi-pores, and small particles, respectively. Some special aspects of mechanisms and reasons of enhanced photocatalytic properties also have been further proposed as follows:

(i) The as-prepared TiO₂ quantum dots yield photocatalytic activities on other chemical species. It is found some OH radical is replaced by Cl element on the surface of TiO₂ material, owing to the adsorption, producing oxygen vacancy sites that drive the TiO₂ QDs to the visible light range and improve the effectiveness and efficiency of photocatalytic activities.

(ii) The special structures of as-prepared TiO₂ quantum dots with thin graphene-like sheet and multi-pores significantly improve the efficiency of the photocatalytic properties. The separation of electrons and holes produced by light irradiation is enhanced by the graphene material. Moreover, this graphene-like structures increase the specific surface area of TiO₂ quantum dots for increasing contacts with the pollutants molecules. More oxygen dissolved in aqueous solution produces more O₂⁻ and OH species.

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6. References

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