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# Hierarchical mesoporous grape-like titania with superior recyclability and photoactivity

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## Abstract

A novel bubbling-mediated hydrolysis approach has been developed to prepare hierarchically mesoporous titania materials with welldefined grape-like morphology in the presence of a triblock copolymer. The products exhibit superior photocatalytic performance and excellent recyclability in the photochemical degradation of phenol. The photocatalysts were characterized by using X-ray diffraction, Brunauer–Emmett–Teller, scanning electron microscopy, and transmission electron microscopy. The effects of bubbling time and calcination temperature on both physicochemical and photocatalytic properties were investigated. © 2007 Elsevier Inc. All rights reserved.

Keywords: Bubbling-mediated hydrolysis; Hierarchical; Mesoporous titania; Recyclability; Photocatalyst

## 1. Introduction

Recently, heterogeneous photocatalysis has attracted great attention as a promising technology for complete mineralization of various organic pollutants in water treatment [1–5]. Meanwhile, Titanium dioxide has become the most frequently employed photocatalyst in this process owing to its low cost, non-toxicity, and structural stability [6–8]. However, the TiO<sub>2</sub>-based photocatalytic powders are difficult to recycle and they are deactivated easily due to particle agglomeration in a wastewater treatment process [9]. A possible solution to the recyclability problem is to coat or immobilize the nanoscale TiO<sub>2</sub> on various supporting materials [10,11]. Unfortunately, the activity of these supported photocatalysts is greatly compromised due to the loss of contact area. The surface area of a catalyst can be increased by incorporating mesopores in the struc-

\* Corresponding author. *E-mail address:* jimyu@cuhk.edu.hk (J.C. Yu). ture. Mesoporous titanium dioxide receives a lot of attention for its excellent performance in photocatalysis due to the presence of continuous pore channels for efficient transfer of reactants/products and light harvesting [12,13].

Mesoporous TiO<sub>2</sub> with macro-scale dimensions are easier to recycle than the nano-sized photocatalytic powders. Micromoulding processes using emulsion droplets or latex spheres as well as various surfactant-templating methods have been demonstrated to yield hierarchically structured porous titania materials of relatively large particle size (>100 nm in diameter) and with controlled morphology. [14,15]. Nevertheless, to the best of our knowledge, well-crystallized titania photocatalytic materials with tailored structure and morphology that can be easily recycled have never been reported.

In this paper, we present a novel bubbling-mediated hydrolysis approach to the synthesis of hierarchical mesoporous grape-like  $TiO_2$  (HMGT) composed of micro-spherical aggregates. The morphology and high photocatalytic activity are well maintained even after many cycles of repeat uses in an aqueous reaction system.

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# 2. Experiments

## 2.1. Preparation of the samples

The synthesis of HMGT was carried out at 15 °C in the presence of Pluronic P123 triblock copolymer ( $PO_{20}EO_{70}$ - $PO_{20}$ , Mav = 5800, Aldrich) solution. To a Pyrex tube of 50 ml containing 20 ml 100% ethanol, 0.015 mol titanium tert-butoxide (TTB) and 0.7 g P123 were introduced and stirred to form a clear solution. Then humidified nitrogen gas (N<sub>2</sub> passed through a bubbler containing deionized distilled (DD) water) was continuously bubbled at a flow rate of 30 ml/min through a fine glass frit at the bottom of the reactor. The experimental setup is shown in Scheme 1. After a 3–12 h of the bubbling-mediated hydrolysis reaction, the product was filtered, washed with deionized water, and dried in an oven at 100 °C for 12 h. At last, the as-obtained samples were calcined at 400–800 °C for 2 h (ramp of 1 °C min<sup>-1</sup>) to remove the remaining surfactant templates.

# 2.2. Measurement of photocatalytic degradation of phenol

The photocatalytic degradation of phenol was carried out in an aqueous solution at ambient temperature. Briefly, in a 100 ml beaker, 0.05 g of the hierarchical mesoporous grape-like titania (HMGT) or P25 was mixed with a 50 ml aqueous solution containing 200 ppm phenol with a pH value of 7.0. The mixture was stirred for 1 h until reaching adsorption equilibrium. The photocatalytic degradation of phenol was initiated by irradiating the reaction mixture with a commercial 24 W UV light with a wavelength of 365 nm. During the photoreaction, air bubbles were continuously introduced to the reaction system at a flow rate of 100 ml/min. Photodegradation efficiency was monitored by measuring the absorbance of the phenol at its maximum with a UV–vis spectrophotometer (Shimadzu, UV-2450) [16].

#### 2.3. Characterization

The wide-angle X-ray diffraction measurements were carried out in a parallel mode ( $\omega = 0.5^{\circ}$ ,  $2\theta$  varied from  $20^{\circ}$  to  $60^{\circ}$ ) using a Bruker D8 advance X-ray diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5406$  Å). The crystal size was estimated by applying the Scherrer equation to the fwhm of

the (101) peak of anatase-TiO<sub>2</sub>, with silicon as a standard of the instrumental line broadening. The N<sub>2</sub>-sorption isotherms were recorded at -196 °C in a Micromeritics Tri-Star system. All the samples were degassed at 150 °C and  $1.33 \times 10^{-4}$  Pa prior to the measurement. The Brunauer-Emmett-Teller approach was used for the determination of the surface area. Standard transmission electron microscopy images and high-resolution transmission electron microscopy (HRTEM) images were recorded using a Gatan slow-scan charge-coupled device (CCD) camera on a JEOL 2011 electron microscope operating at 200 kV. The electron microscopy samples were prepared by grinding and dispersing the powder in acetone with ultrasonication for 5 min. Carbon-coated copper grids were used as sample holders. The morphology of the HMGT materials was recorded by a scanning electron microscopy (SEM) (Cambridge S-360).

#### 3. Results and discussion

SEM and TEM measurements confirm the hierarchical mesoporous structure and grape-like morphology of the as-prepared HMGT. Fig. 1a shows the macrostructured grape-like titania aggregates with dimensions from 25 to 30 µm composed of interconnected microspheres. The average size of the mesoporous microspheres is estimated to be about 3 µm (as shown in the inset of Fig. 1a). The TEM image in Fig. 1b reveals that the microspheres possess wormhole-like mesopores of several nanometers in diameter. These mesoporous structured pores are produced by the continuous bubbling-mediated hydrolysis condensation of TTB in alcohol solution in the presence of P123. The inset of Fig. 1b presents the selected area electron diffraction (SAED) pattern taken from the HMGT sample. The presence of diffusion rings suggests the sample is composed of highly crystalline anatase, which plays an important role in the photocatalytic reaction of mesoporous TiO<sub>2</sub> [13]. The HRTEM of the sample (Fig. 1c) also confirms the nanocrystalline nature. Furthermore, the X-ray diffraction characterization in Fig. 1d further reveals that the HMGT sample is composed of well-crystallized anatase TiO<sub>2</sub> with average crystalline size of about 6.2 nm (calculated by Scherrer equation).

Fig. 1e gives the nitrogen adsorption-desorption isotherm of the 400  $^{\circ}$ C calcined sample. It shows type IV-like



Scheme 1. The typical bubbling-mediated hydrolysis experimental setup.



Fig. 1. (a) SEM image of the HMGT material obtained by bubbling-mediated hydrolysis for 8 h and calcined at 400 °C for 2 h. (b) TEM image showing the mesoporous structure for (a). Inset of (b), the SAED pattern of anatase crystalline. (c) HRTEM image showing the crystal lattice fringes of anatase for (a). (d) Wide angle XRD pattern for (a). (e) Nitrogen adsorption/desorption isotherms and the corresponding pore size distribution (inset) for (a).

isotherm with an inflection of nitrogen adsorbed volume at  $P/P_0 = 0.45$  (type H<sub>2</sub> hysteresis loop), indicating the presence of well-developed mesoporosity in the HMGT sample. Typical value for the specific surface area according to the BET method is 115.7 m<sup>2</sup>/g (Micromeritics TriStar System), which is much higher than the 27 m<sup>2</sup>/g for the reference sample prepared in the absence of P123. The inset of Fig. 1e shows the pore-size distribution plots calculated using the BJH (Barrett–Joyner–Halenda) equation from the adsorption branch of the isotherm. The pore-size distribution (PSD) measurements show that the HMGT sample has pronounced mesoporosity of a very narrow pore-size distribution with an average pore diameter at ca. 3.5 nm. This is in good agreement with the well-defined mesoporous structure of the HMGT sample as revealed by TEM analysis. Such mesoporous architecture, with a large surface area and connected pore system, could accelerate the molecular transport of reactants and products to enhance catalytic activity [12].

Fig. 2 shows the morphologies of HMGT prepared with different bubbling time. A critical dependence of the average diameter of the HMGT materials as a function of the bubbling time in the reaction system is well observed. The formation of HMGT is believed to be produced by a



Fig. 2. SEM images of the HMGT material obtained by a bubbling-mediated hydrolysis for different times. (calcined at 400 °C for 2 h).

two-step polycondensation of the titania species during the bubbling-mediated hydrolysis process. Initially, monodispersed titanium oxide microspheres are formed by the slow hydrolysis and condensation of P123 modified titania sol species. These microspheres are then agglomerated to produce grape-like aggregates through the inter-aggregation (or inter-agglomeration) of these mesoporous titania microspheres under the subsequent polycondensation step. In addition, the use of P123 as a template agent is crucial for the final formation of grape-like titania aggregates with well-developed mesoporosity. In the absence of P123, the secondary titania aggregates cannot be obtained (see Fig. 1b of supporting information) and the mesoporosity would decrease significantly. Only normal fine TiO<sub>2</sub> powders were formed. It is obvious that the P123 micelles promote the interconnection of the titania microspheres, and favor the formation of hierarchically mesostructured grape-like titania aggregates. Besides the factors mentioned above, higher bubbling reaction temperature is also believed to assist the formation of grape-like structure. For comparison, a super large grape-like titania aggregate with ca. 100 µm in diameter was obtained in 3 h by the bubbling-mediated hydrolysis of P123 modified TTB at 25 °C (see Fig. 2 of supporting information).

A thermal treatment at temperatures above 400  $^{\circ}$ C is required to remove the copolymer template and to crystallize the walls into nanocrystalline anatase. The thermogravimetric analysis shows that the polymer is completely decomposed at 400  $^{\circ}$ C in air. XRD patterns in Fig. 3 reveal that well-crystallized anatase has been formed at 400  $^{\circ}$ C and no other crystalline phases (brookite or rutile) are



Fig. 3. Wide angle XRD patterns for HMGT material obtained by bubbling-mediated hydrolysis for 8 h calcined at different temperatures.

observed at the temperature of 500 °C. Even at 600 °C, only a very small peak corresponding to rutile phase is observed. This confirms the very high stability of anatase within the scaffold. The anatase to rutile phase transformation requires temperature as high as 800 °C.

Table 1 shows that the HMGT sample prepared with a bubbling time of 8 h and annealed at 400 °C has the largest surface area of  $115.7 \text{ m}^2 \text{ g}^{-1}$  and a pore volume of 0.150 cm<sup>3</sup> g<sup>-1</sup>. The surface area and pore volume decrease slowly with the increase of the calcination temperature from 400 °C to 600 °C. At 800 °C, the mesoporous struc-

Table 1	
Physicochemical parameters of the as-prepared HMGT samples	

Sample	Bubbling time (h)	Calcined temperature (°C)	$\frac{S_{\rm BET}}{(\rm m^2 g^{-1})}^{\rm a}$	Pore size <sup>b</sup> (nm)	$\frac{V_{\rm P}^{\rm c}}{\rm (cm^3 g^{-1})}$
Ti-8-400	8	400	115.7	4.3	0.150
Ti-8-500	8	500	97.2	5.5	0.121
Ti-8-600	8	600	63.3	9.1	0.072
Ti-8-800	8	800	4	_	_
Ti-3-400	3	400	121.0	4.2	0.161
Ti-5-400	5	400	118.1	4.3	0.149
Ti-12-400	12	400	100.5	4.8	0.132

<sup>a</sup> BET surface area calculated from the linear part of the BET plot  $(P/P_0 = 0.1-0.2)$ .

<sup>b</sup> Average pore diameter, estimated using the desorption branch of the isotherm and the Barrett–Joyner–Halenda (BJH) formula.

<sup>c</sup> Total pore volume, taken from the volume of N<sub>2</sub> adsorbed at  $P/P_0 = 0.995$ .

ture of the HMGT disappears owing to the vigorous crystallization of the pore wall under high temperature treatment. The BET results also demonstrate that the HMGT materials have a quite uniform pore-size distribution in the range of 4–9 nm.

Table 1 also shows the effect of the bubbling time on the pore structure parameters of HMGT samples. The effect of the bubbling time on the morphology of the HMGT samples is illustrated by the SEM images in Fig. 2. It is interesting that the pore structures, such as the pore size, pore volume, and surface area, do not change with the bubbling time. This means that HMGT samples of specific size (from ca. 5  $\mu$ m to ca. 50  $\mu$ m) can be synthesized while maintaining the mesoporous structures.

Fig. 4a shows the effect of annealed temperatures and surface area on the photoactivity of photo-degrading aqueous phenol of HMGT samples with the same bubbling time of 8 h. The sample annealed at 400 °C exhibits the highest photocatalytic efficiency because of its large surface area (ca.  $115 \text{ m}^2/\text{g}$ ) and big pore volume (ca.  $0.15 \text{ cm}^3/\text{g}$ ). As is known, the large surface area can not only efficiently increase the adsorption of reactants, but also enhance the light harvesting to capture more light to generate more electron and hole pairs in the photocatalytic reaction [13]. On the other hand, the well-structured mesoporous pore channels are also favourable to the transportation of the reactant and product molecules [12]. Upon thermal treatment at very high temperatures, from 500 °C to 800 °C, the mesoporous structure is destroyed gradually, due to the crystallization of the channel walls that breaks up the long-range order mesoporous structure [17]. The surface area of the HMGT sample decreases from 115 to  $4 \text{ m}^2/\text{g}$ while the temperature is increased from 400 °C to 800 °C. Besides the surface area, the degree of crystallization also affects the activity of a photocatalyst [18,19]. The XRD patterns in Fig. 3 show that the characteristic peak corresponding to anatase phase of HMGT calcined at 400 °C is much weaker and broader than that of the sample calcined at 500 °C. This suggests that the degree of crystalliza-



Fig. 4. (a) Photoactivity and  $S_{BET}$  of HMGT samples calcined at different temperatures for 2 h with the same bubbling time of 8 h. (b) The effect of the bubbling time on the photoactivity of HMGT samples calcined at 400 °C for 2 h. (c) The recycle experiment of HMGT (8 h of bubbling and calcined at 400 °C for 2 h) and P25 photocatalysts. Note that HMGT samples were easily recovered through a gravitational settling, while the nanocrystalline P25 was recovered via centrifugation.

tion in Ti-8-500 is much better than that in Ti-8-400. This is why the photocatalytic activity of Ti-8-500 is higher than its BET value would suggest.

At the same calcined temperature, we also studied the effect of the bubbling time on the samples' photoactivity. As shown in Fig. 4b, the photoactivities of HGMT samples prepared with bubbling times of 3 h, 5 h and 8 h are all

higher than that of Degussa P25. The recycling of P25 from a solution system is the recycled catalyst often suffers from rapid deactivation. The HMGT maintains its high photocatalytic activity even after ten cycles as shown in Fig. 4c. Moreover, the grape-like morphology does not change after repeated use (see Fig. 3 of supporting information).

# 4. Conclusions

In summary, we have successfully demonstrated a bubbling-mediated hydrolysis method for the preparation of hierarchically mesostructured titania materials with very large surface area and unique grape-like morphology. Owing to its large specific area, good anatase crystallinity, structural stability and macroscale dimensions, the products exhibit superior photocatalytic efficiency and recyclability.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso. 2007.03.018.

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