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# A sonochemical approach to hierarchical porous titania spheres with enhanced photocatalytic activity†

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**A novel sonochemical approach has been developed to prepare hierarchical porous titania spheres in the presence of a triblock copolymer; it was found that textural meso- and macro-porosity could enhance the photocatalytic activity of mesoporous $TiO_2$.**

Chemical reactions can occur more easily when the transport paths through which molecules move into or out of the nanostructured materials are included as an integral part of the architectural design.[1] These transport paths may be realized through a hierarchical combination of independently controlled, well-connected smaller and larger meso- and macro-pores. The transport of small molecules in media featuring large mesopores ($>10$ nm) and macropores ($>50$ nm) can approach rates of diffusion comparable to those in open medium.[1]

It is known that hexagonal mesoporous silica (HMS) consists of smaller domain size with short channels and larger textural mesoporosity.[2] The importance of textural mesopores in enhancing the catalytic activity of HMS materials relative to unimodal mesoporous MCM-41 has been demonstrated for several reactions.[2] For instance, $Fe^{3+}$ exchanged Al-HMS exhibits a higher activity for the selective catalytic reduction of NO by $NH_3$ than does its MCM-41 analog.[2] Unfortunately, current studies on the preparation of hierarchical (or bimodal) mesoporous materials appear to be focused on silica.[3] As silica does not possess variable oxidation states like the transition metals, it is a rather poor catalytic material. Moreover, the preparation of spherical mesoporous particles in the micrometer- and submicrometer-size range is more attractive because of their broad applications in chromatography, bioseparation, and nanotechnology.[4] Here, we present a sonochemical approach to the synthesis of hierarchical porous titania (HPT) spheres. The hierarchical porous structure was preserved after calcination, and the calcined materials exhibited high photocatalytic activity.

The synthesis of HPT was performed in the presence of poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) ($PO_{20}EO_{70}PO_{20}$, $M$ = 5 800, Aldrich, denotes as P123). 0.032 mol titanium isopropoxide (TIP), 3.2 g P123, and 0.016 mol glacial acetic acid were dissolved in 20 mL absolute ethanol. After stirring for 1 h, the resulting solution was added dropwise to 100 mL deionised water under sonication in air. During the whole process, the sonication cell was water-cooled to avoid overheating. The suspension was sonicated for 3 h (3 seconds on, 1 second off, Amplitude 95%) by a high-intensity probe with 13 mm diameter (Sonics and Materials, VC750, 20 KHz). The powder was collected by centrifugation, washed with deionised water, and dried in an oven at 100 °C. The as-washed sample was calcined at 400 °C for 1 h. For comparison, a sample (denotes as SMT) was prepared in the absence of P123 according to a similar procedure described in our previous study.[5]

An XRD peak is observed in the low angle region for the as-washed and calcined HPT, suggesting the existence of wormhole-like mesopores (Fig. S1 in ESI). The peak of the calcined samples in the low angle region shifts to lower 2 theta positions, indicating the enlargement of the mesopores. This may be due to the removal of surfactant. The as-washed HPT is amorphous in nature, and it transforms into anatase $TiO_2$ with average crystalline size of about 8.8 nm (calculated by Scherrer equation) after calcination (inset of Fig. S1 in ESI).

Two distinct capillary condensation steps can be clearly seen on the $N_2$ adsorption–desorption isotherms of the as-washed and calcined HPT (Fig. S2 in ESI). These confirm the hierarchical combination of independently controlled, well-connected smaller and larger meso- and macro-pores. The first hysteresis loops of the as-washed and calcined HPT are at $0.38 < P/P_0 < 0.55$ and $0.35 < P/P_0 < 0.65$, corresponding to the filling of the framework confined mesopores formed between intra-agglomerated primary particles.[6] The second hysteresis loops are at $0.85 < P/P_0 < 1$ and $0.9 < P/P_0 < 1$, corresponding to the filling of textural meso- and macro-pores produced by interaggregated secondary particles.[2] The surface areas of the as-washed and calcined HPT are 622 and 145 $m^2\ g^{-1}$, respectively, as calculated from the linear part of the BET plot.

The hierarchical porous structure of HPT is confirmed by its SEM and TEM images. The aggregates of well-defined spheres with unsmooth surfaces are shown in Fig. 1a. The TEM image in Fig. 1c reveals that the spheres possess wormhole-like mesopores of several nanometers in size, which are produced by the ultrasound-induced agglomeration of the small primary nanoparticles.[5] The sizes of the mesoporous spheres are about 100 nm. Large textural meso- and macro-pores are produced by the interaggregation of the mesoporous spheres. Meanwhile, connections between the mesoporous spheres are also observed. We attribute these connections to the turbulent flow and shock waves produced by acoustic cavitation, which forces the metal particles together at sufficiently high velocities.[7] It is known

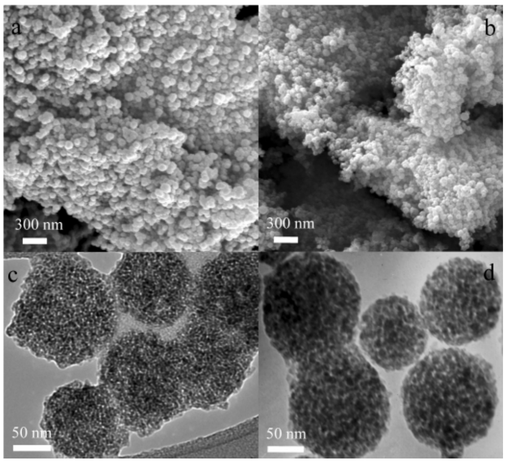

**Fig. 1** SEM images of the as-washed (a) and calcined (b) HPT; TEM images of the as-washed (c) and calcined (d) HPT.

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† Electronic Supplementary Information (ESI) available: XRD patterns, nitrogen adsorption/desorption isotherms, pore size distribution curves, photocatalytic activities and physicochemical properties of HPT and SMT. See http://www.rsc.org/suppdata/cc/b3/b306013f/

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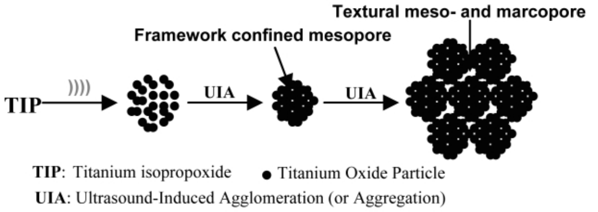
that a high-speed collision driven by high intensity ultrasound irradiation can generate localized high temperature regions. This can enhance the condensation reactions among hydroxyl groups on adjacent mesoporous spherical particles, to produce the agglomerates of spherical particles. After calcination, the spherical morphology of HPT and the mesopores in the spheres are preserved (Fig. 1b and Fig. 1d). This is in agreement with the hierarchical porous structure of the calcined HPT as revealed by nitrogen adsorption analysis.

The formation of HPT can be illustrated in Scheme 1. First, monodispersed titanium oxide sol particles are formed by the slow hydrolysis and condensation of acetic acid modified TIP. These sol particles are then agglomerated to produce mesoporous secondary spheres under high intensity ultrasound irradiation.[5] Finally, textural meso- and macro-porosity are produced through the interaggregation (or interagglomeration) of these mesoporous titania spheres under sonication.

The use of acetic acid to slow down the hydrolysis of TIP was found to be crucial for the formation of HPT. Without the modification of acetic acid, the hydrolysis of TIP resulted in a unimodal mesopore titania with a bicrystalline framework under high intensity ultrasound irradiation.[8] In the absence of P123, the secondary titania spheres obtained under high intensity ultrasound irradiation were far from uniform and the size of the spheres was larger than that obtained in this study.[5] Meanwhile the textural meso- and macro-porosity would decrease (Fig. S3 in ESI). It is obvious that P123 micelles inhibit the growth of the secondary titania spheres, and favour the formation of more uniform mesoporous titania spheres. The textural mesoporosity is enhanced through the interaggregation (or agglomeration) of these mesoporous titania spheres. Besides these two factors, high intensity ultrasound irradiation is believed to assist the formation of hierarchical porous structure. For comparison, a unimodal mesoporous titania with mean pore size of 3.8 nm and surface area of 580 $m^2 g^{-1}$ was obtained by the hydrolysis of acetic acid modified TIP in the presence of P123 under magnetic stirring instead of high intensity ultrasound irradiation.

The as-washed HPT has negligible photocatalytic activity due to its amorphous nature. However, the photocatalytic activity of the calcined HPT is about 50% higher than that of commercial nonporous photocatalyst P25 (as-received sample) on the photodegradation of n-pentane in air.[8] This can be attributed to the high surface area of the calcined HPT and the interconnection of mesopores in it.[5] Moreover, it is interesting to note that the calcined HPT shows about 15% higher activity than the calcined SMT (ESI). Both calcined HPT and SMT have about the same surface area and crystalline size as well as an identical crystalline phase (anatase). The only difference is that the textural meso- and macro-porosity of the calcined HPT (35%) is higher than that of the calcined SMT (23%). We believe that the presence of extra large textural meso- and macro-pores provides more efficient transport channels for the reactant molecules to get to the reactive sites on the framework walls of the small mesopores. The beneficial effect of textural meso- and macro-porosity on catalysis has been reported by Pinnavaia.[2] To the best of our knowledge, however, this is the first evidence of a similar effect for photocatalytic reactions.



**Scheme 1** Schematic illustration of the formation of hierarchical porous titania spheres under high intensity ultrasound irradiation.

In summary, a sonochemical approach has been developed to prepare hierarchical porous titania spheres. The calcined materials show high photocatalytic activity on the degradation of a volatile organic compound in air. We also demonstrate that textural meso- and macro-porosity enhance the photocatalytic activity of mesoporous $TiO_2$. We think that the spherical porous titania may also be used as an efficient column packing material for chromatographic separation.

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