

## Spontaneous template-free assembly of ordered macroporous titania

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**Spontaneous formation of ordered macroporous titania is achieved by dropwise addition of titanium alkoxides to aqueous ammonia in the absence of auxiliary organic templates.**

Recently, there has been considerable interest in the template-directed synthesis of macroporous materials with pore or channel diameters exceeding 50 nm. Typically, porogens with well-defined size and architecture, such as emulsion droplets,<sup>1</sup> colloidal crystals,<sup>2</sup> virus liquid crystals,<sup>3</sup> bacterial superstructures,<sup>4</sup> polymer<sup>5</sup> and biopolymer<sup>6</sup> sponges, and wood cellular structures<sup>7</sup> have been used in combination with preformed nanoparticles or *in-situ* precipitation reactions to prepare macroporous ceramics.

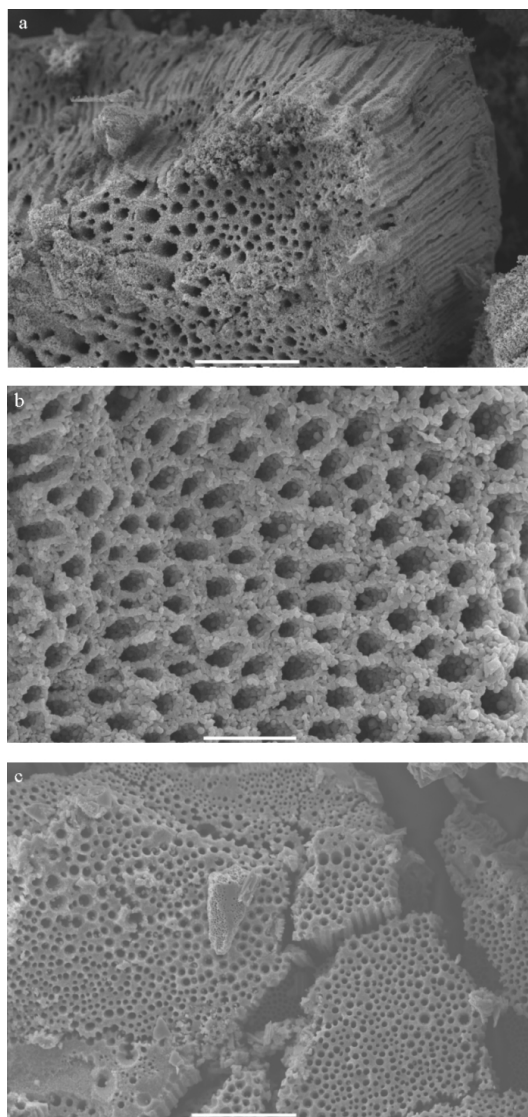
Titania (TiO<sub>2</sub>) is a multifunctional material with a wide variety of potential uses in diverse areas such as photocatalysis and bioactivity. Although titania powders and sols can be readily prepared, synthetic routes to porous titania are less common even though the increased surface area and chemical accessibility associated with such materials offer distinct advantages. Recently, several reports have demonstrated that hierarchically ordered macro/mesoporous materials including titania can be prepared by surfactant templating in which supramolecular aggregates are considered to direct inorganic deposition across a range of length scales.<sup>8–10</sup> However, post-synthetic removal of the template to produce the titania replica requires additional processing steps that can be costly, wasteful and of environmental concern. Clearly, these problems would be circumvented if spatial patterning of the inorganic phase could be achieved in the absence of auxiliary organic templates, for example by coupling the sol–gel reactions with physical phenomena such as microphase separation, transient hydrodynamic gradients or time-dependent diffusion gradients.

To illustrate this approach, in this paper we describe the spontaneous formation of ordered macroporous titania by simple dropwise addition of titanium alkoxides to a 5 wt% ammonia solution without stirring in the absence of surfactant molecules.† In each case, base-catalysed hydrolysis and condensation of the alkoxide precursors gave a white powdery precipitate almost immediately after addition of the reactants. Scanning electron microscopy (SEM) studies of the products revealed a polydisperse distribution of millimetre-sized, irregularly shaped titania grains that appeared to be fragments of larger particles. Remarkably, the fragments consisted of a pseudo-hexagonally ordered porous interior of co-aligned channels that radiated inwards from a smooth and curved particle surface (Fig. 1(a), (b)). The channels were typically up to 100 μm in length and 1 to 10 μm across. Corresponding powder XRD experiments indicated that the wall structures comprised amorphous titania.

Comparisons between the porous micro-architectures produced by different titanium alkoxide precursors indicated that increased levels of channel ordering, as well as smaller channel diameters, were associated with slower rates of hydrolysis. The particles recovered using Ti(OEt)<sub>4</sub> showed only localised regions of ordered macroporosity, whereas samples prepared from Ti(OPr)<sub>4</sub> (Fig. 1(a)) and Ti(OPr)<sub>4</sub> had increased levels of macroporosity with heterogeneous channel dimensions (7–10 and 5–8 μm, respectively) and wall thickness (typically 3–6 μm). In contrast, macroporous titania from Ti(OBu)<sub>4</sub> (Fig. 1(b)) exhibited long range periodicity and regularity in channel diameter (*ca.* 1.5 μm) and wall thickness (600–800 nm). In this case, the thin walls were composed of closely

packed titania nanoparticles, *ca.* 350 nm in size, and typically only two particles wide. Lowering the concentration of the ammonia catalyst solution retarded the rate of precipitation, with the consequence that the extent of macroporosity was reduced and channel disorder increased.

Controlled heating of the precipitates converted the amorphous titania wall structures to a mixture of crystalline anatase and rutile, with full or partial retention of the macroporous architecture. The calcined material prepared from Ti(OBu)<sub>4</sub> showed a partially collapsed ordered macrostructure, presumably due to the small pore

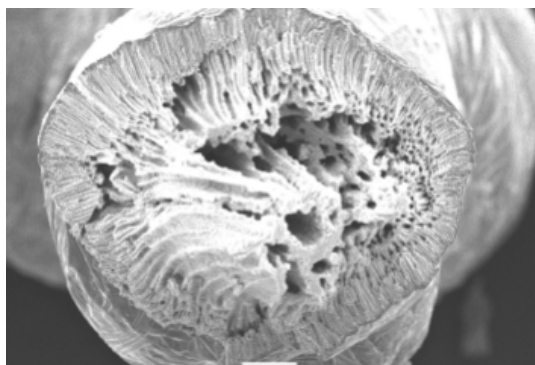


**Fig. 1** SEM images of spontaneously assembled macroporous titania prepared from (a) Ti(OPr)<sub>4</sub>, scale bar = 100 μm, and (b) Ti(OBu)<sub>4</sub>, scale bar = 5 μm; (c) macroporous titania prepared from Ti(OPr)<sub>4</sub> after calcination, scale bar = 100 μm.

diameter and thin walls associated with the initial precipitate. In contrast, SEM studies of samples prepared by calcination of  $\text{Ti}(\text{OPr}^i)_4$ -derived titania showed intact macroporosity with regular ordering of co-aligned channels with similar size distributions to those obtained from the uncalcined material (Fig. 1(c)). The BET total surface area of the as synthesized powder was  $368 \text{ m}^2 \text{ g}^{-1}$  with a micropore area of  $270 \text{ m}^2 \text{ g}^{-1}$ . The pore size distribution determined by the BJH method is centred at about 1.5 nm. After calcination the total surface area decreased to  $92 \text{ m}^2 \text{ g}^{-1}$  due to sintering of the titania particles in the channel walls during heat treatment. BJH methods showed an increase in pore size, with a distribution of mesopores with an average diameter of 3.5 nm.

Whereas the above approach gave macroporous titania in powder form, intact fibrous structures with ordered macroporosity could be prepared by fast injection of the Ti alkoxides into the catalysis solution. For example, this method was used to prepare fibres 0.5–1 mm in width and several mm in length using  $\text{Ti}(\text{OPr}^i)_4$ . SEM images of transverse and longitudinal cross-sections of the titania fibres revealed a smooth outer surface and macroporous interior consisting of radially arranged channels that originated at the outer membrane and progressively curved in the direction of hydrodynamic flow of the injected reaction fluid such that they became disordered within the central lumen (Fig. 2). The curved channels were 50–100  $\mu\text{m}$  in length and 7–9  $\mu\text{m}$  across. The presence of the disordered central lumen suggests that shear associated with the flow of alkoxide disrupts the radial patterning. This is consistent with other observations, which showed that under normal reaction conditions the highest degree of macroporosity was obtained in the absence of stirring.

Based on the above observations, our data clearly indicate that ordered macroporous structures of titania can be prepared by spontaneous assembly in alkoxide–water solutions without the intervention of surfactant templates. Our results indicate that ordered macroporosity is dependent on the Ti alkoxides and catalyst solutions used, suggesting that the rates of hydrolysis/condensation or nature of the alcohol by-product, or both, could be important factors in controlling pattern formation. We propose therefore a model based on synergistic coupling between the above factors and the induction of microphase-separated domains within the incipient deposit. Contact between the added titanium alkoxide droplets and aqueous ammonia immediately produces a thin, dense semi-permeable titania membrane at the droplet interface, which compartmentalises the subsequent hydrolysis and condensation reactions. The reaction front then proceeds inwardly, and approximately perpendicular to the external surface, as the catalyst solution diffuses through the spherical outer membrane. This produces microphase-separated regions of  $\text{TiO}_2$  nanoparticles and water/alcohol channels within the alkoxide droplets that undergo



**Fig. 2** SEM image of a fibrous macroporous structure produced by fast injection of  $\text{Ti}(\text{OPr}^i)_4$  into aqueous  $\text{NH}_3$ , scale bar = 100  $\mu\text{m}$ .

spontaneous radial patterning due to hydrodynamic flow of the solvent. This mechanism may also be applicable to some of the previously reported macrostructures prepared in the presence of surfactants.<sup>8–10</sup> In these studies, addition of surfactants could enhance the stability of microphase separated interfaces, rather than serve as self-assembled templates for macropore formation as originally proposed.

In the case of fibre formation, the reagent stream and shear associated with rapid injection of the liquid alkoxide augments the above patterning process. Under these conditions, the rate of precipitation is slower than the flow of the alkoxide, resulting in the observed curvature of the channel pores. Thus, by varying the rate of alkoxide injection it should be possible to control the alignment of the pores within the fibres. In addition, the fibre-like structures appear to be partially stabilized, whereas spontaneously ordering and assembly within individual droplets results in fragmentation rather than intact spheroids. In both cases, the patterning process continues towards the centre of each reaction droplet until the alkoxide precursor is consumed. Further studies are under way to investigate the photocatalytic and bioinductive properties of the above macroporous titania materials, as well as the use of spontaneous microphase separation to spatially pattern the hydrolysis/condensation reactions of transition metal alkoxides in general.

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## Notes and references

† Titanium alkoxides (ethoxide, propoxide, isopropoxide, butoxide) were used as supplied from Aldrich with no further purification. A 5 wt% solution of ammonia was prepared by dilution of a 35 wt% stock solution (Aldrich) with deionized water. In a typical synthesis 2 mL of alkoxide was added to 20 mL of the ammonia solution without stirring. Precipitates were removed, rinsed with distilled water then left to dry on filter paper for 24 h. Samples were calcined by heating to 800 °C at a heating rate of 5K  $\text{min}^{-1}$ . Fibrous structures were produced by fast injection of the alkoxide from a 5 mL autopipette held vertically with the tip close to the surface of the catalyst solution. SEM images, acquired using a JEOL 5600 LV instrument, were imported into AnalySIS image analysis software. Samples were also characterized by PXRD (Siemens D500) and BET surface area measurements (Quantachrome Autosorb-1).

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