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A new strategy towards ultra stable mesoporous titania with nanosized anatase walls

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A new and generally applicable synthesis procedure is developed in order to synthesise micelle-templated mesoporous titania built up of nanosized anatase walls with thermal stability up to 600 °C.

The successful combination of sol–gel chemistry and self-assembly in the synthesis of ordered mesoporous silica[1,2] resulted in a very impressive effort devoted to the extension of the surfactant templating process to the formation of non-silica mesoporous oxides since these compounds display very interesting and promising functionality for electrochemical applications and high surface area catalysis. As one of the most important oxides, titania has been widely used in which many of the possible applications arise from the semiconductive nature of titania and the photoactivity of its anatase crystal phase.[3–5] Different synthetic strategies have been developed using a variety of templates[6–16] where most reports focused on the adequate balance between the hydrolysis–condensation processes of the titanium precursor on the one hand and the self-assembling reactions occurring between the resulting hydrolysed supramolecular species and the template on the other. Furthermore, controlled thermal treatment upon removal of the template as well as nucleation and growth of anatase domains is crucial since high porosity and a crystalline character of the TiO_2 particles are indispensable for most applications. However, in spite of the high specific surface areas and pore volumes after calcination at 350 °C, a further temperature increment to transform the amorphous titania walls into nanosized anatase walls mostly results in a total collapse of the pore system. Only in the case of titania directed with poly(ethylene oxide)-based templates, could higher temperatures be reached without collapse of the mesophase.[12–16]

As most reports have focused on the control of the different processes during synthesis, we developed a new post-synthesis step in order to govern the processes during calcination. This method, which is generally applicable to all surfactant-assembled titania hybrids, extends the templating of titania mesophases consisting of amorphous walls to stable, ordered mesostructures with high surface areas composed of walls built up of anatase nano crystallites and further leads to titania materials with greatly enhanced thermal stability.

Two recently described pathways towards titania-hybrids were chosen, in particular titania prepared by using cetyl trimethyl ammonium bromide[8] (CTAB) and hexadecyl amine[11] (HA) templates. The titania hybrid assembled by the CTAB-pathway was synthesised by the addition of titanium isopropoxide ($Ti(O^iPr)_4$) (Aldrich) to an ethanolic (Merck) HCl (Acros) solution. An ethanolic solution of CTAB (Acros) was added and the hybrid was formed in an open Petri dish at 60 °C for 7 d. The molar ratios were Ti : CTAB : HCl : H_2O : EtOH = 1 : 0.16 : 1.4 : 17 : 20. Amine-templated titania was prepared by adding H_2O and 0.1 M HCl to a mixture of HA (Acros) and ($Ti(O^iPr)_4$). The mixture, with molar ratios Ti : HA : HCl : H_2O = 1 : 0.5 : 0.06 : 79, was aged at 60 °C for 4 d, filtered and dried. Part of the samples was post-treated with NH_3. 1 g of titania-hybrid was added to 50 ml of an aqueous NH_3 (Merck) solution with a pH of 9 to 10. The solution was refluxed for 48 hours and the pH was kept between 9 and 10. Titania hybrids were then filtered, dried and are further denoted as Ti-CTAB-NH_3 and Ti-HA-NH_3 while the calcined template-free titania samples are designated as Ti-CTAB-NH_3-C and Ti-HA-NH_3-C.

The N_2 isotherms (Fig. 1A) and XRD-patterns (Fig. 1B) of post-treated titania samples are very similar to those of materials prepared by conventional procedures. In order to assess the upper limits of their thermal stability, samples were heated at various temperatures for 4 h starting from a calcination temperature of 300 °C. As expected, non-treated samples are totally destroyed upon calcination at 400 °C. In contrast, a large part of the mesoscale order is conserved as Ti-HA-NH_3-C exhibits isotherms with a well-developed capillary condensation step and a clear d_{100}-reflection up to a temperature of at least 500 °C. Moreover, Ti-CTAB-NH_3-C even shows a thermal stability to at least 600 °C. These observations are further supported by the physical data provided in Table 1. Ti-CTAB-NH_3-C retains more than 65% of its surface area and framework pore volume at 600 °C. Similar beneficial effects were observed by Sanchez *et al.*[13] after treatment of titania hybrids with gaseous NH_3.

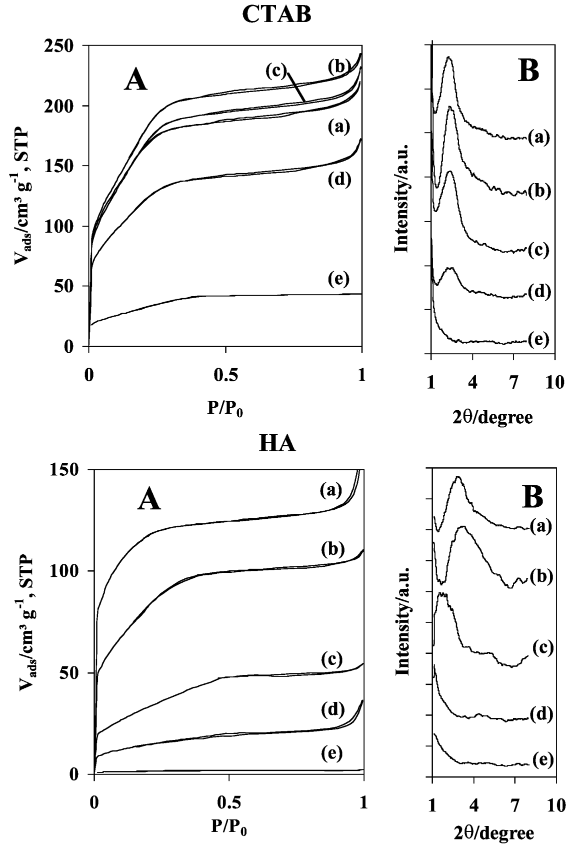

Fig. 1 N_2 adsorption–desorption isotherms (A) and XRD patterns (B) of titania samples treated with NH_3 and calcined at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C for 4 h and (e) non-treated titania calcined at 400 °C for 4 h.

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Table 1 Textural properties of titania samples before and after NH_3-treatment calcined at different temperatures

Calc. T/°C	S_{BET}/m² g⁻¹	D_{BJH}/nm	V_p/cm³ g⁻¹
CTAB[a]			
300	585 (466)	1.85 (—)[b]	0.28 (0.19)
400	613 (112)	1.90 (—)[c]	0.32 (0.06)
500	576 (8)	1.89 (—)[c]	0.29 (—)[c]
600	420	1.86	0.21
HA[a]			
300	435 (393)	— [b]	0.19 (0.16)
400	291 (5)	1.96 (—)[c]	0.16 (—)[c]
500	123	2.07	0.08
600	52	2.15	0.03

[a] Values of corresponding non-treated samples are displayed in parentheses. [b] The pores are too small to use the BJH method. [c] No mesoporosity is observed.

The unique outstanding thermal stability of post-treated titania hybrids is governed by the intermediate formation of nanosized crystalline domains in the walls before the template is thermally removed. On increasing the temperature from 300 to 400 °C, the disappearance of the d_{100} diffraction line of non-treated samples is accompanied by the appearance of single peak at $2\theta = 25.5°$, assigned to the massive formation of crystalline anatase. Based on XRD, anatase or any other crystal phase could not be observed for the NH_3-treated samples calcined at 400 °C. However, Raman spectroscopy is a much more sensitive technique for the detection of small 'nanosized' crystalline domains. The *in situ* Raman spectra (Fig. 2) of non-treated HA-assembled titania do not display any peaks up to 350 °C. In accordance with the XRD pattern, three clear bands at 399, 519 and 638 cm⁻¹, characteristic for anatase,[17] appear at 400 °C. For the sample treated with NH_3, two lines at 442 and 611 cm⁻¹, ascribed to the rutile crystal phase,[17] can be observed between 200 and 300 °C. However, on further increases to 350 °C, the Raman lines related to the rutile phase disappear and the three characteristic anatase bands at 399, 519 and 638 cm⁻¹, can be identified.

According to the results above, the thermal processes occurring in the conventional synthesised titania mesophases are different compared to the NH_3-treated titania hybrids and can be described as follows: Based on thermogravimetric analysis, the combustion of the template is the first process occurring at temperatures between 220 and 300 °C. At 300 °C, a template-free mesostructure with an array of amorphous TiO_2-walls is formed. However, between 350 and 400 °C, a crystallographic reorganisation from amorphous titania to anatase takes place in the absence of template and therefore, no medium is available to 'freeze' or 'block' the nuclei growth. As such, the nano building blocks have a free hand in the uncontrolled growth to robust anatase crystals and thus, the mesoporous amorphous titania is transformed to a non-porous anatase crystal phase. In contrast, the calcination of NH_3-treated samples occurs in a much more controlled way. Before the template is thermally removed (220–300 °C), the NH_3 adsorbed in the pore channels promotes the transformation of the amorphous titania walls into nanosized rutile domains. The templates preserve the meso-organized network and govern the crystallisation process to form a rutile hybrid assembly. Extended crystallisation to robust large crystal grains is therefore avoided and the walls are from now on built up of small individual meso-organised rutile domains. Upon further heating to 300 °C, the template is burned out of the rutile hybrid in such a way that no extensive growth of the rutile nano building blocks into large crystal grains takes place. By a subsequent increase of temperature, a rutile to anatase phase transformation occurs in such a way that this crystallographic rearrangement is accompanied by a retention of the pore structure as still clear d_{100} diffraction lines can be observed. In contrast to the conventional samples thermally treated at 400 °C, no anatase peak appears in the X-ray diffractogram which, together with the preservation of the porosity characteristics, indicates that the transformation of rutile to anatase was carefully performed.

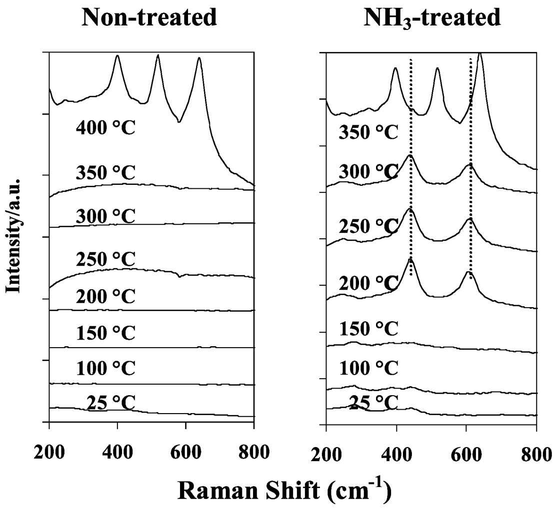

Fig. 2 *In situ* Raman spectra of non-treated and NH_3-treated HA-assembled titania as a function of calcination temperature. Samples were heated in an *in situ* cell with a rate of 5 °C min⁻¹ under a 50 cm³ min⁻¹ flow of air.

This study illustrates a simple post-treatment that allows the preparation of mesoporous titania with walls built up of nanosized anatase domains and leads to highly porous titania materials with remarkably enhanced thermal stability. This successful method can be easily extended to all surfactant-assembled titania materials and opens a new area in the synthesis and applications of titania materials.

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