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Towards flexible inorganic “mesomaterials”: one-pot low temperature synthesis of mesostructured nanocrystalline titania†

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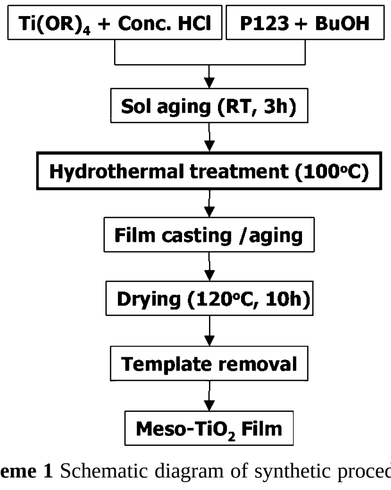
We hereby report a simple route for the low temperature synthesis of mesoporous nanocrystalline titania involving brief hydrothermal treatment of butanolic precursors and non-ionic tri-block-copolymer surfactant at 100 °C, followed by evaporation induced self assembly to make a crack-free flexible film. At no time in the film-forming process is a temperature of more than 120 °C reached, thereby permitting the use of substrates that are not stable to higher temperatures.

Mesoporous titania (meso-TiO_2) materials are of considerable interest as they usually show higher surface areas and much more uniform and controllable pore size and pore morphologies compared with randomly organized forms of nanocrystalline titania. The nanocrystalline (nc) form has been widely studied with respect to potential applications in electrochromic devices, photoconductors, photocatalysts and sensors, in addition to photovoltaics.[1,2] These applications rely upon the intrinsic properties of titania, which are governed by the extent and nature of its crystalline phase. Therefore, crystallite growth within the mesostructured inorganic framework should be considered the most important step in the synthesis of meso-TiO_2. Unfortunately, the most common way to impart crystallinity upon titania is calcination at over 350 °C, and this is often too severe a treatment to conserve the mesostructure as assembled before the calcination.[1] In addition, the need for high-temperature sintering limits the choice of substrates to heat-resistant materials, which are not flexible as required for various device applications of meso-TiO_2. From this point of view, a low temperature synthetic route towards meso-TiO_2 with nanocrystalline pore walls is of high demand. There have been two reports for low-temperature syntheses of mesoporous nanocrystalline titania,[3,4] however, the first uses a 2-step process where the “anatase sol” is generated prior to adding the surfactant template to organize the structure, and the second uses a one-step autoclave treatment but results in a poorly defined material with very little mesostructural order. Neither report gives electron microscopy evidence for nanocrystallinity within the channel framework. Herein we introduce a novel low temperature synthetic route to mesoporous nanocrystalline titania, denoted meso-nc-TiO_2, using mild (100 °C) hydrothermal conditions, which have already been applied to the low temperature synthesis of randomly organised forms of nc-TiO_2.[5–8]

Our synthetic route is described in the flow chart of Scheme 1. The stock solution was prepared with 3.5 g of titanium butoxide (Aldrich) as an inorganic precursor, 6 g of 1-butanol (ACP) as a solvent, 2 g of P123 (BASF) as a template, and 1.3 ml of conc. HCl (Fluka) as a stabilizing agent. 1-Butanol is chosen as a solvent because it leads to an enhanced microphase separation between the template and the inorganic precursor and allows for the formation of a more condensed inorganic framework.[9] The prepared solution was stirred for 3 h and treated hydrothermally at 100 °C in an autoclave for 1–2 h. This hydrothermal treatment step produces anatase nanocrystallites in the stock solution and allows for the mesoporous titania assembled afterwards to contain anatase nanocrystallites embedded within the inorganic framework without requiring further severe thermal treatment. The hydrothermally treated solution was (a) dropped onto a glass substrate to form a bulk gel, which was achieved by aging the sol for two days in a humidity chamber at 40 °C/50% relative humidity or (b) spin-coated on a glass slide at 2400 rpm for 20 s, which was aged in the humidity chamber for 2 days at 20 °C/80%RH. Aged samples were thermally treated at 120 °C for 10 h to achieve full condensation of the titania framework. Templates were successfully removed by exposing the sample to UV irradiation for 2 days (thin films) or by solvent extraction using 1 : 1 diethylether–acetone mixture for 3 days (bulk gels). IR spectra (Fig. S1†) of the titania samples before and after template removal clearly showed that the C–O–C stretching vibrational band ($\sim 1100\ cm^{-1}$) and C–H stretching vibrational band ($\sim 2800\ cm^{-1}$) from P123 disappeared after UV irradiation or solvent extraction.

In order to characterize both the mesostructural order and crystalline phase of the obtained samples, small angle X-ray scattering (SAXS, Bruker Nanostar with GADDS) and wide-angle X-ray scattering (WAXS, Siemens D5000) experiments were carried out. Fig. 1 shows SAXS (A) and WAXS patterns (B) of the ground bulk gels synthesized using hydrothermal treatment times from 1 to 2 h. The sample made from the solution hydrothermally treated for 1 h showed two distinct peaks in SAXS representing the first and second order (h00) reflections with d_{100} = 131 Å. (Fig. 1A, solid line). With increasing hydrothermal treatment time, the obtained films gradually loose their mesoscopic order (Fig. 1A, dashed line). WAXS patterns obtained from those samples shown in Fig. 1B reveal that they are composed of both nanocrystalline anatase and amorphous titania. As expected, longer hydrothermal treatment leads to progressively more intense anatase peaks in the WAXS patterns. The measured crystallinity (WAXS patterns) varies between 10–23% depending on the time of treatment. The microstructural properties of the nanocrystalline anatase were measured using Topas[10] profile fitting software. The volume weighted average crystallite size was found to be independent of the hydrothermal treatment time and is within the range 57–65 Å. Interestingly, the lattice disorder (measured as an average strain, e_0)



Scheme 1 Schematic diagram of synthetic procedure.

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† Electronic supplementary information (ESI) available: IR spectra and SEM image of mesoporous nanocrystalline titania. See http://www.rsc.org/suppdata/cc/b4/b403607g/

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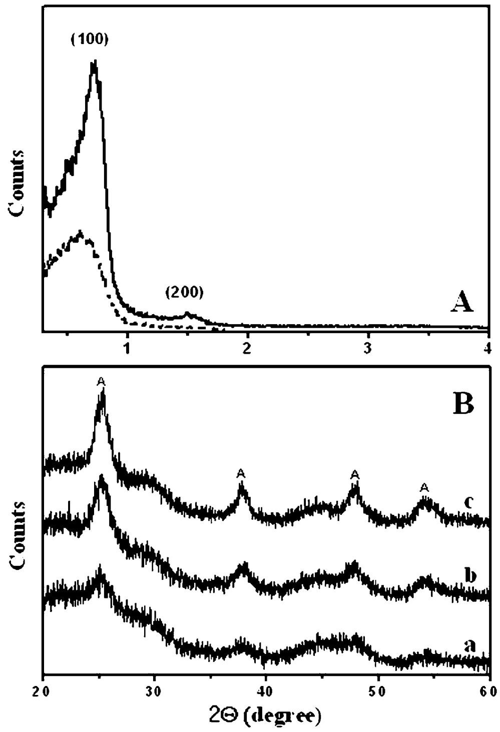

Fig. 1 Integrated SAXS patterns (A) ground bulk gels made of solutions hydrothermally treated for 1 h (solid line), and 1.5 h (dashed line), and WAXS patterns (B) ground bulk gels made of solutions hydrothermally treated for 1 h (a), 1.5 h (b), and 2 h (c).

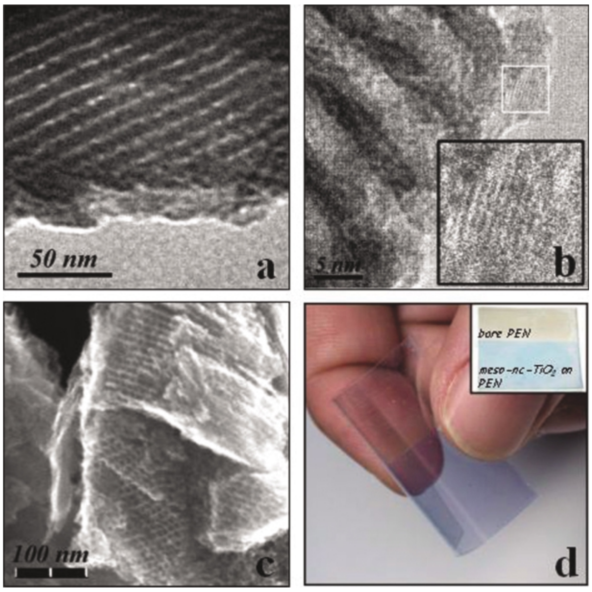

Fig. 2 TEM (a, b) and SEM (c) images obtained from the samples (a, b, and c: ground bulk gel after template removal) made from the solution hydrothermally treated for 1 h and a photograph of a flexible crack-free meso-nc-TiO_2 film, which was deposited on a PEN substrate and dyed with methylene blue in order to distinguish the film from the substrate (d).

is greater for longer treated samples despite the overall increase in the percentage of nanocrystalline anatase. Based upon our results, the quantity of anatase (the crystalline portion of the WAXS patterns) in the samples can be vastly improved by lengthening the hydrothermal treatment time, however, this also causes the titania to precipitate in the sol, thereby hindering formation of the mesostructure. The solution hydrothermally treated for 1 h was found to result in the best samples in terms of balancing the degree of mesostructural order and nanocrystallinity.

Scanning and Transmission Electron Microscopy (SEM, Hitachi S5200; TEM, FEI Technai 20) investigations support our SAXS/WAXS results. In the case of the samples made of the solution hydrothermally treated for 1 h, a very well ordered 2D hexagonal structure as shown in Fig. 2c was easily observed in both bulk gels and thin films. The pore size and wall thickness estimated with HRTEM are *ca.* 70 Å and 40 Å respectively, and the estimated crystallite size is in the range 40–60 Å. These correspond well with our SAXS and WAXS results. The solutions hydrothermally treated for longer than 1 h gave rise to samples having less ordered wormhole like structures or poorly organized nanocrystallite aggregates as expected from SAXS and WAXS data. The inset of Fig. 2b shows conclusive evidence for anatase nanocrystallites embedded within the mesostructure framework.

In order to test the flexibility of our meso-nc-TiO_2, films were deposited on an ITO coated polyethylene naphthalate (PEN, Sheldahl) substrate utilizing the method mentioned above. As shown in Fig. 2d, a fully condensed crack-free film (Fig. S2†) was easily bent without resulting in any damage to the film. This suggests considerable potential for the use of meso-nc-TiO_2 films prepared through our hydrothermal synthetic route in applications where flexibility is required.

In conclusion, we have reported a novel, one-pot synthetic route to make mesoporous nanocrystalline titania films using a mild hydrothermal procedure in combination with the well-known EISA[11] approach. As illustrated, the samples synthesized by this route show a well-defined 2D hexagonal mesostructure with *ca.* 60 Å sized anatase nanocrystallites embedded in the inorganic framework. This is the first conclusive report of a successful low temperature synthesis of mesoporous nanocrystalline titania in the form of a crack-free flexible film. We hope this approach can extend the applicable area of mesoporous inorganic materials to the field of flexible "inorganic" devices. An investigation of the optical, electrical and mechanical properties of our meso-materials is on-going, together with steps aimed at optimising the synthesis and film forming conditions.

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