Hexafluorotitanate salts containing organic cations: use as a reaction medium and precursor to the synthesis of titanium dioxide†

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The straightforward modification of commercial hexafluorotitanic acid with organic derivatives containing a tetraalkylammonium cation produced stable precursor solutions with only a small fraction of water, which were then used as a reaction medium for the synthesis of nanocrystalline TiO_2.

In the search for low cost and easy to implement methods to prepare nanocrystalline titanium dioxide (TiO_2), we are exploring the use of new techniques that avoid the use of organic solvents and/or controlled atmospheres. TiO_2 is a strategic material, with numerous applications in the areas of coatings and sensors. Its use in photocatalysis and dye-sensitized solar cells (DSSCs) is especially relevant to the solution of several problems, such as water contamination and energy supply. Hence, the search for new preparation methods that allow control over the microstructural and morphological parameters, and thus the properties of TiO_2, is encouraged. In this Communication, we describe how the simple modification of commercial hexafluorotitanic acid (HFTA) (60 wt% in water, Aldrich) with organic derivatives containing a tetraalkylammonium cation produces stable precursor solutions that include only a small fraction of water. These titania precursors, after reacting with boric acid (a common fluoride scavenger) at low temperature (85 °C), were quantitatively transformed into nanocrystalline TiO_2.

Ionic liquids (ILs) are new tools for designing alternative strategies in chemical synthesis and separation processes. Several advantages have also been established for materials preparation.[1] For instance, ILs can stabilize nanoparticles, they work as templates in zeolite crystallization and allow materials that are usually produced under hydrothermal conditions to be prepared in non-pressurized reactors.[1,2] The direct crystallization of TiO_2 at low temperature with complex morphologies like microspheres, in presence of ILs based on the butylmethylimidazole cation, has been reported.[3]

Other described materials preparation methods are based on ILs with a metal center, which simultaneously act as a solvent, molecular precursor and crystal growth driving agent.[4] This attractive "all-in-one" synthesis strategy, never reported before for TiO_2 preparation, has been pursued in this work. The use of salts containing a hexafluorotitanate anion and a tetraalkylammonium cation, present in numerous ILs, has been explored. These salts were prepared from commercial, low cost and easy to handle chemicals such as HFTA[5] and two organic derivatives: betaine (Bet; $Me_3N^+–CH_2–CO_2^-$) and choline (Cho^+; $Me_3N^+–CH_2–CH_2OH$) chloride.

Betaine, which can act as a base, forming the $HBet^+$ cation after carboxylate protonation, was firstly chosen for assay. In a typical synthesis procedure, 2.93 g (24.9 mmol) of Bet was dissolved in 3.35 g (12.2 mmol) of a 60 wt% HFTA solution in an exothermic reaction. The container was a plastic bottle, internally covered with Teflon and heated in a double boiler. The obtained viscous $(HBet)_2TiF_6$ solution, containing only 21 wt% of water, was stable over 60 °C. Due to the low proportion of water present, the obtained medium can be considered similar to that of ILs, and especially close to those formed from hydrated transition metal salts.[6] The concentration of ions was also higher than in previously described TiO_2 preparation procedures, in which ILs were used only as minor components of the initial reaction mixture.[3a,b,e]

HFTA and, most frequently, the derived ammonium salt are used to produce TiO_2 films by the Liquid Phase Deposition (LPD) method.[7,8] In this process, boric acid is employed as a fluoride scavenger, allowing a controlled hydrolysis of the precursor. In this work, a similar procedure was used to transform the new $(HBet)_2TiF_6$ precursor into TiO_2. 1.5 equivalents of boric acid, with respect to Ti, were added to the solution. The mixture was aged at 85 °C over 18 h, and gradually acquired a white paste texture. The sample did not evolve after this aging period. It was then dispersed in water, and the solid part was separated by centrifugation and thoroughly washed with water. The TiO_2 yield was almost 100%. The non-dried samples formed a colloidal aqueous suspension, which was easily stabilized against aggregation by the addition of a diluted base ($N(C_4H_9)_4OH$) or acid (HCl, $HClO_4$).

Characterization by high-resolution transmission electron microscopy (HR-TEM; Fig. 1a) showed that the obtained material consisted of nanocrystals (5–7 nm) with a narrow size distribution. A selected-area electron diffraction analysis of the sample (Fig 1b) pointed to the anatase crystal phase.

Samples dried at 85 °C presented a candy-like aspect due to particle aggregation. The small size and clean surface of the obtained nanoparticles facilitated their sintering at very low temperatures. According to ATR-FTIR characterization (not shown), the obtained TiO_2 contained only traces of organic species; below 1.5% according elemental analysis (C, N). XRD analysis (Fig. 2a) confirmed that the precipitated solid was anatase.

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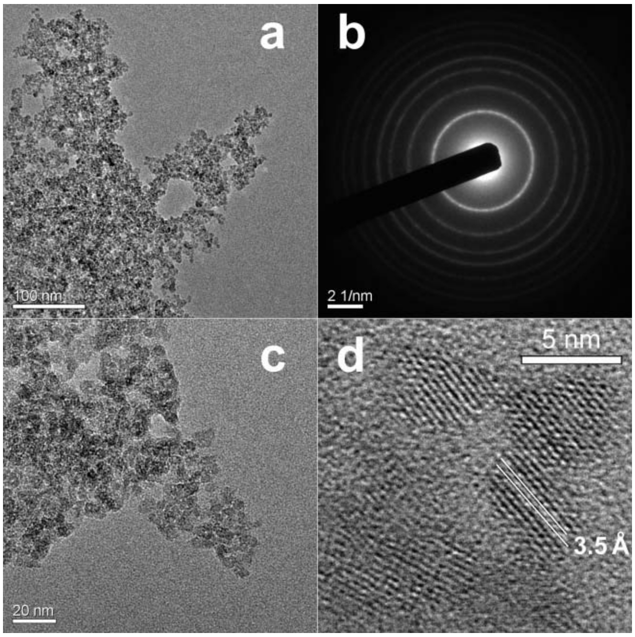

Fig. 1 Representative HR-TEM photographs.

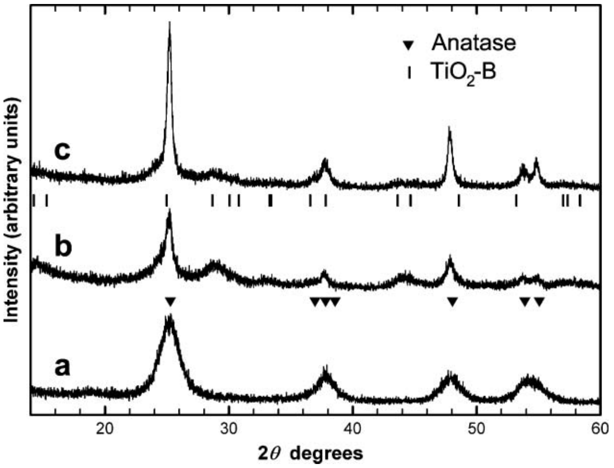

Fig. 2 XRD patterns of TiO_2 samples obtained from (a) $(HBet)_2TiF_6$ and from (b,c) $(Cho)_2TiF_6$. Symbols between traces signal the positions of the peaks corresponding to anatase (▼) and TiO_2–B (|).

The size of the nanoparticles, estimated from the peak width (Scherrer equation) of the XRD pattern, agreed with the value obtained from TEM characterization. Preferential growth of (004) is usually observed in anatase grown by LPD.[9] However, this preferential growth was not observed in the prepared samples, denoting that the growth medium used differed significantly from that of a diluted aqueous solution. The low temperature N_2 gas adsorption/desorption isotherm (BET analysis) of the TiO_2 nanoparticles showed a H2 type hysteresis loop, characteristic of mesoporous materials (Fig. 3a). The pore size distribution, calculated from the adsorption branch (Fig. 3b),[10] denoted the presence of pores in the 3–8 nm range. The estimated value of the specific surface area (S_a) was around 200 $m^2\ g^{-1}$.

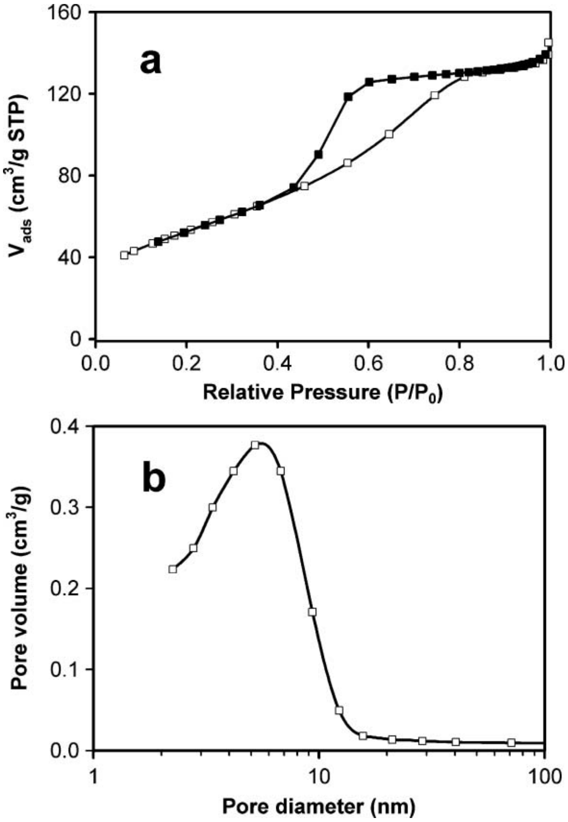

Fig. 3 (a) The N_2 gas adsorption (□)/desorption (■) isotherm and (b) the pore size distribution calculated from the adsorption branch of the isotherm of TiO_2 samples obtained from $(HBet)_2TiF_6$.

Under similar experimental conditions, but in the absence of the $HBet^+$ organic cation, the reaction between concentrated HFTA and boric acid (initially only partially dissolved) produced a titanium oxyfluoride. This compound could be described as $HTiOF_3$ according to the similarities between its XRD pattern and that of the corresponding $(NH_4)TiOF_3$ and other structurally related compounds (Fig. S1†).[11] It should be taken into account that, in our experiments, there was no ammonium source. $HTiOF_3$ is considered to be a product of the thermal decomposition of $(NH_4)TiOF_3$, although no direct preparation method has been described.[12] Therefore, it can be concluded that the $HBet^+$ cation enhanced the solubility of boric acid in the concentrated HFTA solution, allowing complete defluorination of the precursor and simultaneous control of the size of the precipitated particles. This fact is considered to be critical for the formation of nanocrystalline anatase.

In a second assay, the synthesis of TiO_2 was performed under similar experimental conditions, but using the Cho^+ cation instead of Bet. A $(Cho)_2TiF_6$ solution was prepared from HFTA and ChoCl, and HCl was liberated as a gas. This path was preferable to the reaction between HFTA and choline hydroxide, which is highly exothermic and produces additional water. The obtained viscous $(Cho)_2TiF_6$ solution was stable, even at room temperature. After the addition of boric acid and thermal treatment at 85 °C over an aging period of 18 h, a mixture of anatase and TiO_2–B polymorphs was obtained (Fig. 2b). Upon increasing the reaction time to 90 h, almost pure anatase was obtained (Fig. 2c). HR-TEM (Fig. S2†) confirmed the coexistence of TiO_2–B and anatase after 18 h. The TiO_2 particles obtained after 90 h were larger and more irregular than those obtained using the $HBet^+$ cation, which led to a wider pore size distribution and lower S_a.

In summary, nanocrystalline TiO_2 was produced by adding organic derivatives, such as betaine or choline chloride, to commercial solutions of HFTA and using boric acid as a defluorinating agent. Although precautions should be taken due to the toxicity and corrosive character of both the precursor and fluorides, the method presents numerous advantages: all chemicals used are low cost, no organic solvent is needed, neither an inert atmosphere nor pressurized reactors are required, and the by-products can be washed with water. The ratio between TiO_2 yield and the required reaction volume is also advantageous. The aim of this Communication has been to describe a generic method for the preparation of nanometric crystals of TiO_2. A key advantage of this method is its versatility, since the crystal size and structure of the final product can be modified by careful choice of organic cation. Due to its high ionic content, the precursor mixture is, remarkably, able to absorb MW radiation, and using this heating procedure, the time necessary to produce the nanoparticles can be significantly reduced from hours to minutes. The method can also be used to prepare organic capped nanoparticles in a single step, *e.g.* by adding an enediol, such as catechol, to the initial solution. A comprehensive study will be reported elsewhere.

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