Synthesis of TiO₂ Nanocrystals by Nonhydrolytic Solution-Based Reactions

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Nanocrystalline metal oxides have potential or demonstrated application in many technologies, including solar energy conversion,[1−3] batteries,[4] catalysis,[5,6] and ductile ceramics.[7,8] The solution-phase chemistries used to make nanocrystalline oxides, in particular titania, employ hydrolysis of metal alkoxides or halides. Particles obtained from such preparations have fully hydroxylated surfaces unless extreme heat treatments or chemical dehydroxylation reactions are applied,[9] and these hydroxyls influence material properties. For example, hydroxylated titania surfaces are less strongly reducing than their dehydroxylated counterparts,[10] and interfacial electron-transfer rates can be enhanced when hydroxyl bound surface traps are eliminated.[11] Also, sintering rates are influenced by the presence of polar surface hydroxyls and adsorbed water.[9,12] Given the significant effects that chemisorbed and physisorbed water have on the properties of nanoscale oxides, there would be potential scientific as well as technological value in the development of synthetic strategies that create oxides in the absence of water.

In this work we describe a nonhydrolytic preparation of titania nanocrystals that should be general for many metal oxides.[13] The reactions occur at high temperatures in anhydrous organic solvents providing nanocrystals with no surface hydroxyl groups. Control of average particle size by variation of reactants has been demonstrated, as has some morphological control. These particles are highly dispersible in hydrocarbon solvents due to the coordination of surface titanium atoms to passivating agents employed during the reaction. The use of coordination chemistry to stabilize the nanocrystals allows for ready exchange of surface capping groups which should provide control over the surface and consequently over properties.

Recent developments in the synthesis of II−VI semiconductor clusters illustrate the potential of using the rapid thermal decomposition of molecular precursors in the presence of strong coordinating agents to create high-quality nanocrystals.[16,17] To extend this strategy to oxides, we employed chemistry known to produce amorphous Ti−O networks at low temperatures. TiCl₄ reacts with titanium alkoxides (eq 1) or ethers (eq 2) with the resultant elimination of alkyl halides.[14,15]

$$TiX_4 + Ti(OR)_4 \rightarrow 2TiO_2 + 4RX \quad (1)$$

$$TiX_4 + 2ROR \rightarrow TiO_2 + 4RX \quad (2)$$
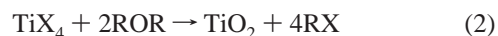
These reactions are well suited for our purposes as their by-products are volatile and thus easily removed at high temperatures; also, they do not rely on hydrolysis for the creation of Ti−O bonds which makes it possible to use coordinating species to control solubility. A typical procedure for making nanocrystalline materials was as follows. A titanium halide (2 mmol) was mixed with distilled trioctylphosphine oxide (TOPO, 6.5 mmol) in heptadecane (17.5 g) and heated to 300 °C under dry nitrogen. A metal alkoxide (2 mmol) was then rapidly injected into the hot solution. Reactions were completed within 5 min. High reactant concentrations led to the formation of off-white precipitates which could be recovered as powders while lower reactant concentrations (0.2 mmol TiX₄) gave clear, orange solutions. The reaction precipitates were isolated by centrifugation and subsequently washed with acetone to remove involatile heptadecane. The yields were low, less than 50% of theory for pure TiO₂, because much of the product remained dispersed in solution. This dispersed product could be partially precipitated by the addition of reagent grade acetone, providing material that redispersed in heptane. Reactions conducted in the absence of TOPO gave quantitative precipitate yields, and we believe the reactions conducted with TOPO proceed to completion as well.

The powders obtained were confirmed to be anatase TiO₂ by X-ray diffraction (XRD), and analysis of diffraction line widths indicated that the crystalline domains were under 10 nm in diameter (Figure 1).[18] Particle sizes observed by transmission electron microscopy (TEM) appeared in general agreement with the XRD determinations, though there was considerable distribution in size (Figure 2). Many particles exhibited irregular shapes, but crystalline perfection was high. Redispersed nanocrystals obtained from low concentration reactions appeared isolated or only very loosely aggregated depending on TEM sample preparation, while precipitated products were somewhat more agglomerated. The degree of agglomeration is the only difference that has been discerned between precipitated products and particles that remained in solution. FTIR spectra of products showed that particle surfaces were not covered with water or titanol,[19] and Raman spectroscopy indicated that very few oxygen vacancies were present.[20] Characterization of molecular products by GC mass spectrometry indicated that eq 1 was indeed an appropriate description in the presence of TOPO.

The rate of the alkyl halide elimination reaction may influence the nucleation and growth of titania nanocrystals and thereby determine the particle sizes and size distributions. Consequently, we systematically varied the substituents X and R (eq 1) to affect control over the reaction rate. If nucleophilic attack of the halide at the alkoxide carbon proceeds by an S_N1 mechanism, then

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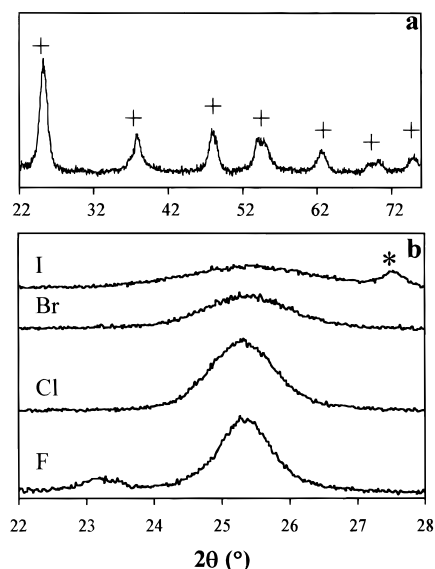(15) Vioux, A. *Chem. Mater.* **1997**, *9*, 2292.
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Figure 1. XRD patterns of reaction products. (a) TiO$_2$ (anatase, 7.3 nm) obtained from reaction of TiCl$_4$ and TIOT in TOPO/heptadecane (300 °C). (b) Patterns showing anatase (101) line broadening due to size variation with halide (X) for the reaction of TiX$_4$ and TIOT in TOPO/heptadecane at 300 °C (F = 9.2 nm, Cl = 7.3 nm, Br = 6.1 nm, I = 3.8 nm). Anatase is designated by + and rutile by *.
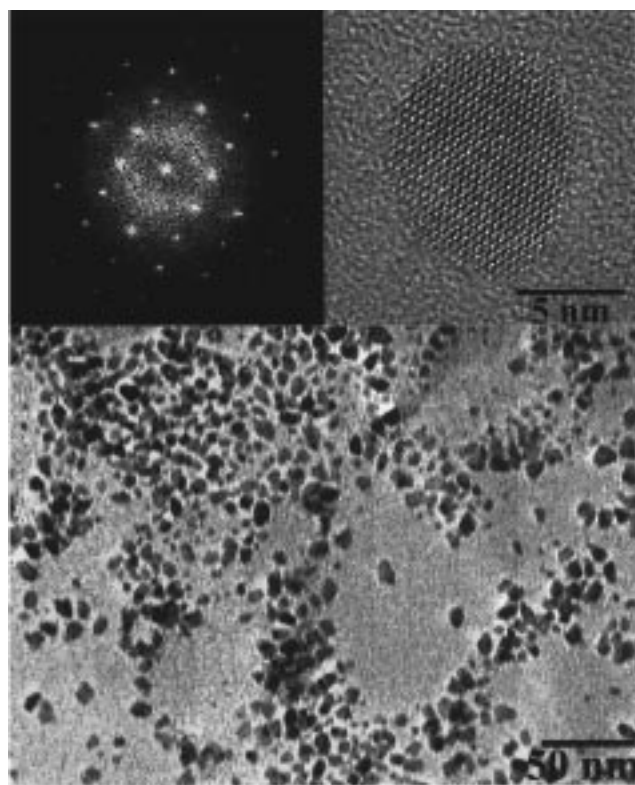

Figure 2. TEM image of titania nanoparticles derived from reaction of TiCl$_4$ and TIOT in TOPO/heptadecane at 300 °C (bottom). A high-resolution TEM image of a single particle illustrates the defect free nature of these nanocrystals (top right). FFT of the particle shown verified the anatase structure and established that the image was taken down the [100] zone axis (top left).

reaction rates would increase with increased branching of R (1° to 3°) and be little influenced by the identity of the halide (X). Observations (onset of precipitation and vigor of byproduct evolution) for a series of alkyl substituents including methyl, ethyl,

isopropyl, and *tert*-butyl indicated that reaction rate did dramatically increase with greater branching of R. This is consistent with similar low-temperature reactions for which observations also indicated an S$_N$1 mechanism.[15,21] Despite the clear variation in reaction rate with R, however, average particle sizes were relatively unaffected. On the other hand, variation of X did not yield a discernible trend in reaction rate, but a clear trend in average particle size was apparent. Increased nucleophilicity (or size) of the halide resulted in smaller anatase crystals. Average sizes ranged from 9.2 nm for TiF$_4$ to 3.8 nm for TiI$_4$ (Figure 1b). Note that some larger rutile particles were present in the case of TiI$_4$, indicating that with proper control of parameters it may be possible to control the crystal structure obtained.

The amount of passivating agent (TOPO) present in the reaction also clearly influences the chemistry. Reactions lacking TOPO were completed in seconds and yielded mixtures of brookite, rutile, and anatase possessing average particle sizes greater than 10 nm. Conversely, reaction in pure TOPO was slower (~5 min) and resulted in smaller particles (5.5 nm) than when heptadecane was present to serve as a diluent (7.3 nm). Other parameters have been examined, including temperature, duration of heating, and TiX$_4$/Ti(OR)$_4$ ratio, but only modest effects on particle size have been observed.

Crystalline titania is not the required product of reactions 1 and 2. Rather, amorphous Ti–O networks can be derived from these reactions, and indeed are obtained at lower temperatures. We propose that nanocrystalline products are obtained at elevated temperatures because TiX$_4$ serves as a crystallization agent as well as a reactant in reactions 1 and 2. TiX$_4$ functions as a reactant when X attacks the electrophilic, oxygen-bound carbon of the titanium alkoxide, which results in alkyl halide elimination and Ti–O bond formation. However, X may also attack the electrophilic titanium center of the alkoxide precursor or of a partially formed titania network. This would result in halide/alkoxy or halide/titanyl exchange, and therefore in Ti–O bond breaking and forming—in essence, a chemical reversibility that would erase defects incorporated into a growing titania crystal. Halide/alkoxy ligand exchange is known to be facile at room temperature,[14,22] and it is conceivable that halide/titanyl exchange would be sufficient under the vigorous reaction conditions of this work to compete with the alkyl halide elimination mechanism and thereby ensure crystalline product. We have observed that some crystallization of amorphous titania precipitated by thermal decomposition of titanium(IV) isopropoxide (TIOT) can be effected by reheating at 300 °C in heptadecane in the presence of TiCl$_4$. Therefore, it is plausible that TiX$_4$ causes crystallization in the manner described.

Work is in progress to better control particle size distributions and morphologies as well as to extend the reactions to other oxide systems. The absence of surface hydroxyls has permitted the exploration of new types of surface derivitization, and the properties of these particles in comparison to hydrolytically derived titania particles are the subject of current investigation.

Supporting Information Available: GC mass spectrometry, FTIR, Raman, and UV–vis data for nano-titania samples (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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