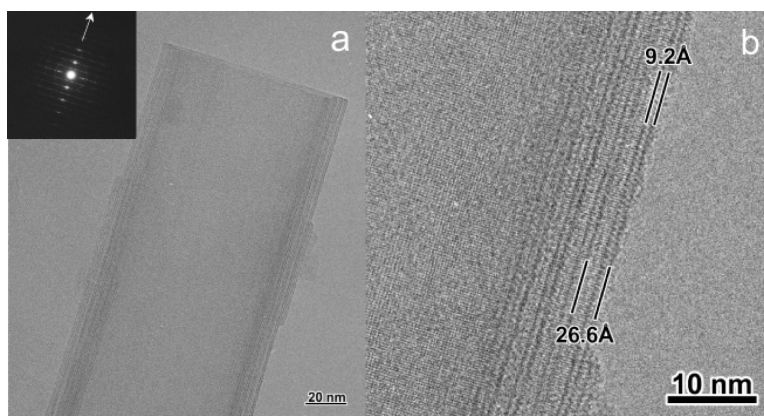


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J. Am. Chem. Soc., **2004**, 126 (29), 8882-8883 • DOI: 10.1021/ja047684l • Publication Date (Web): 01 July 2004

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Microemulsion-Based Synthesis of Titanium Phosphate Nanotubes via Amine Extraction System

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Since the discovery of $\text{AlPO}_4\text{-}n$ molecular sieves at the beginning of the 1980s,¹ open-framework metallophosphates have attracted considerable attention not only because of their rich compositional and structural diversity but also because of their potential applications in catalysis, separation, as well as in environmental and advanced functional materials.^{2–4} The morphology of metal phosphates is important, which may affect their performance significantly. As a consequence, there has been considerable interest in developing new strategies to tailor the morphology of these metallophosphate materials.^{5–7}

Soon after the discovery of carbon nanotubes in 1991,⁸ one-dimensional (1D) nanostructured materials sparked worldwide interest because of their unique electronic, optical, and mechanical properties.⁹ Nanotubes, in particular, can act as macroporous materials¹⁰ for macromolecular catalysis. In the past few years, several methods have been developed for the preparation of 1D inorganic nanotubes. By using a high-temperature process as well as soft-chemistry techniques, nanotubes of metals, metal chalcogenides, metal oxides, BN, NiCl_2 , etc. have been prepared.^{11–16} Not yet seen, however, is the preparation of metal phosphates with tubular structures. In this work, a simple route to the synthesis of metallophosphate nanotubes has been reported. The first uniform titanium phosphate nanotubes have been successfully prepared via microemulsion-based solvothermal synthesis in an amine extraction system.

In a typical synthesis, a certain amount of trioctylamine (TOA) in benzene was first acidified with phosphoric acid to obtain a reverse microemulsion of TOA/ H_3PO_4 . A calculated amount of titanium butoxide was added dropwise to the above microemulsion. The corresponding molar ratio of Ti:P:TOA is 1:5.1:10.2. The mixture was stirred at room temperature for a few minutes, after which a slightly viscous and optically transparent single-phase liquid was formed; this was then transferred into a Teflon-lined autoclave and sealed before being heated in an oven at 180–200 °C for 1–7 days statically. After cooling, the solid product was separated by centrifugation and further washed using benzene and anhydrous ethanol repeatedly. The product was dried in an oven at 60 °C for 24 h.

X-ray powder diffraction (XRD) analyses of the products were carried out on a Siemens D5005 X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The XRD patterns of the as-synthesized TiPO samples are shown in Figure 1. Except for the reflections below 7°, all diffraction peaks in Figure 1b were indexed to the layered $\text{Ti}(\text{HPO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ phase (JCPDS 33-1380). The presence of two peaks at lower 2θ angles (Figure 1a), suggests that some newly organized structure due to the assembly of nanostructured TiPO materials (*vide infra*) might be formed.

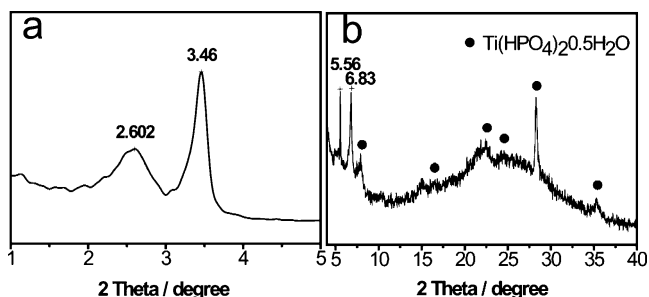


Figure 1. XRD patterns for the as-synthesized TiPO nanotubes after 3 days of synthesis. Peaks marked with dots are indexed to the layered $\text{Ti}(\text{HPO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ phase (JCPDS 33-1380).

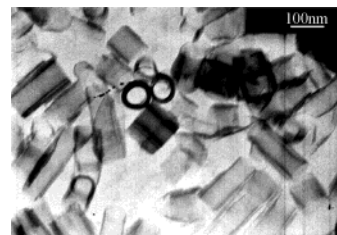


Figure 2. TEM image of the TiPO nanotubes after 3 days of synthesis.

The composition of the as-made product was determined as $[\text{Ti}(\text{HPO}_4)_2 \cdot 0.5\text{H}_2\text{O}] \cdot 0.27[(\text{C}_8\text{H}_{17})_3\text{N}]$ on the basis of the elemental and TG analyses. This formula suggests that the TOA ($(\text{C}_8\text{H}_{17})_3\text{N}$) molecules are intact and incorporated into the nanostructured $\text{Ti}(\text{HPO}_4)_2 \cdot 0.5\text{H}_2\text{O}$.

The morphology of the as-made product was investigated with JEM-100CXII transmission electron microscopy (TEM). It was revealed that the as-made products were nanotubes as shown in the TEM image in Figure 2. The nanotubes synthesized with 3 days of solvothermal reactions have about 50 nm in inner diameter, 10 nm in tube-wall thickness, and 100–200 nm in length. With increasing the reaction time, there is no significant increase in the tube diameter and wall thickness, but an obvious increase in length of the tubes was observed. It increased from 100 nm for the samples synthesized in 3 days to 600 nm for those synthesized in 7 days. This results in an unusually small aspect ratio.

Further investigation of the fine tubular structure was made with high-resolution transmission electron microscopy (HRTEM) on JEOL-3010 at an acceleration voltage of 300 kV. It was revealed that the TiPO nanotubes were multiwalled with highly ordered open ends (Figure 3a). The corresponding electron diffraction (ED) pattern (inset) showed diffraction spots indicative of a single-crystalline structure. The orientation of the growth axis of any other nanotubes corresponds to the direction of the arrow indicated in the ED pattern in Figure 3. The magnified image of the nanotube wall in Figure 3b shows parallel dark and bright lines. The dark

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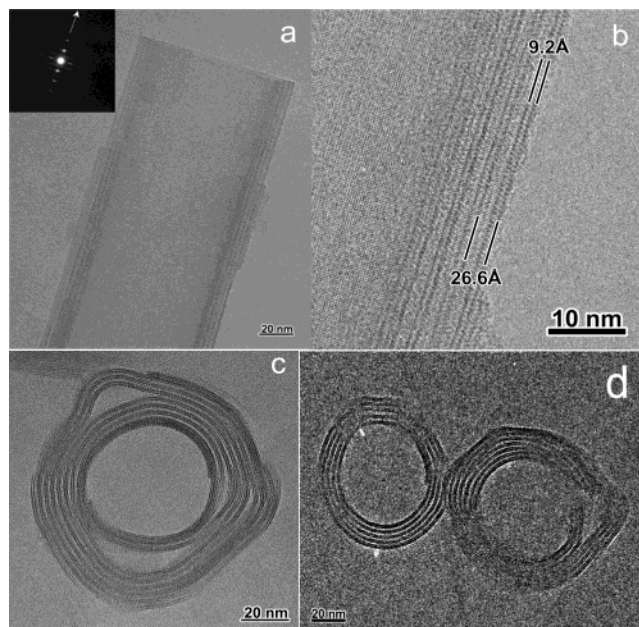


Figure 3. HRTEM images of (a) a single nanotube, inset is its SAED pattern; (b) a magnified image of the tube wall corresponding to (a); (c) the cross section of a single tube; and (d) the cross section of a twin nanotube.

lines correspond to the crystalline TiPO layers. Remarkably, the bright lines are of different width due to the presence of two different spacings occurring in a regular alternating way. The shorter spacing of about 9.2 Å corresponds to the TiPO layers separated by the intercalated H₂O molecules, while the larger spacing of 17.4 Å (26.6–9.2 = 17.4 Å) accommodates the TOA molecules between the TiPO layers. The 26.6 Å distance is very close to the *d*-spacing of the broad peak at $2\theta = 3.5^\circ$ ($d = 25.2$ Å) in the XRD pattern (Figure 1), and as mentioned above, the peak does not belong to the bulk phase Ti(HPO₄)₂·0.5H₂O. It is noted that the larger spacing of 17.4 Å is smaller than the calculated double length of the TOA molecules, implying that either a considerable overlap of the aliphatic tails or a certain tilt angle must be present.

Images c and d of Figure 3 show the cross section of a single nanotube and a twin nanotube. The cross sections reveal that the tubes are composed of rolled-up sheets of some layered structure. The sheets bend and roll upon themselves to form the tubes, much like a rolled-up tube of paper. The tubules, however, are formed from loose wrapping of the sheets, leaving gaps between the sheets on the walls of the tubules, as in the case of VO_x nanotubes.^{14b} This modulation in the distance between the double-layered sheets results in the lower-angle diffraction peaks of the XRD pattern to be weak and broad. Interestingly, in Figure 3d, a twin nanotube is formed by sharing the same pair of short layers. This phenomenon suggests that the twin nanotube probably comes from the same wraps of the layers.

The nanotubes discussed above appear to form from the wrapping of long and narrow sheets, as suggested by Figure 4. It shows the morphology of the sample obtained after 1 day of solvothermal reaction. The curved nanobelts, along with some already rolled-up tubes (appearing as circles) strongly support the scrolling formation

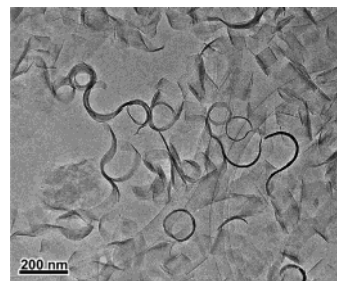


Figure 4. TEM image of samples after 1 day of synthesis, showing the nanobelts along with the already rolled-up tubes.

mechanism of the nanotubes, which has been proposed previously.^{14a,b} Further investigation on the detailed formation process of TiPO nanotubes is ongoing.

In summary, the first titanium phosphate nanotubes with alternating interlayer spacings have been successfully prepared and characterized. The synthesis is accomplished in a reverse micro-emulsion formed in an amine extraction system. TEM data from samples made after different times of reaction suggest a scrolling formation mechanism. The uniform TiPO nanotubes may have interesting properties as macroporous materials, which is an area of our current study. Additionally, this simple route should be applicable to the synthesis of a variety of metallophosphates with 1D nanotube structure.

Acknowledgment. This work is supported by the National Natural Science Foundation of China, the State Basic Research Project of China, and CREST, JST.

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JA047684L