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Keggin POM Microtubes: a Coincident Product of Crystal Growth and Species Transformation[†]

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Microtubes of α-$K_4SiW_{12}O_{40}$ with the length around 1 cm and inner diameter and wall thickness in the ranges of 7–55 μm and 3–15 μm, respectively, were copiously fabricated by a one-step, template-free aqueous synthesis. The formation mechanism is discussed. The discovered tubular structure of the polyoxometalate is believed to be promising for use in templates, as a precursor of tungsten oxide ceramic microtubes, and for other uses associated with tubular structures.

Since the discovery of carbon nanotubes,[1] tubular structures have extended to multiple disciplines for their potential applications in solid-state physics, chemistry, and advanced technology. In the early 1980s, Yager and Schoen first reported the formation of tubules through polymerizable surfactants.[2] Since then, fabricating methods and applications of microtubes have been developing and widening, for example, self-assembled lipid tubules were used as templates to fabricate a field-emissive metal cylinder and as a microvail to release antifouling agents.[3] Increasing attention is being paid to organic and inorganic microtubular structures in recent years because of mesosystem tubular objects' potential applications in containers, microreactors, gas sensors,[4] conductors,[5] etc. Inorganic tubules boast sturdy, inherent electronic transport properties[6] and special photovoltaic properties.[7] They have been successfully synthesized by various methods, such as microemulsion,[8] vapor−liquid−solid (VLS)-assisted synthesis,[9] templating synthesis,[10] a hydrothermal technique,[7b] and a chemical vapor deposition (CVD) route.[7a,11] To consider the use of tubular microstructures, it is important to understand the relations between the morphology and the structure of the molecular building blocks comprising the microstructure. Most tubular structures[12] such as carbon nanotubes, lipid tubules, and tubular crystals of chalcogen compounds are formed by lamellar compounds,[1,13] while few tubular crystals comprise nonlayered microstructures.[7a]

Polyoxometalates (POMs) are an important family of inorganic cluster compounds.[14] Having versatile structures and chemical properties, POMs exhibit potential applications in multifunctional catalysts, antitumor medicines, and high-tech materials.[15] In recent years, POM chemistry has gone from classical inorganic chemistry to 'smart' chemistry and POM-based functional materials with different morphologies have attracted much attention.[16] However, published studies on the tubular structures of POMs are few. It appears to be that only $Ag_4SiW_{12}O_{40}$ microtubes synthesized by the assisting of poly(ethylene glycol) (PEG) in microemulsions[8] and $(HTyr)_3XM_{12}O_{40}$ nanotubes synthesized by solid-state reac-

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[†] Dedicated to the late Professor RuLi Zheng.

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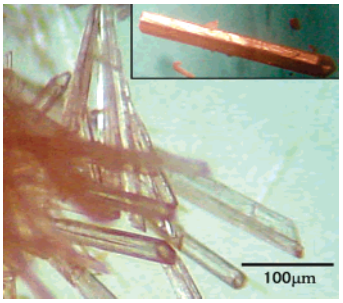

Figure 1. Optical micrograph of the tubules growing in a beaker; the insert shows a single tube.

tion[17] were reported, and there has been no report on POM microtubes synthesized by template-free method in aqueous solution until now. This paper focuses on the study of a facile method and formation mechanism to generate POM microtubes without using templates.

The starting materials to prepare POM tubules involve monolacunary tungstosilicate $K_8[\alpha\text{-}SiW_{11}O_{39}]$ (α-SiW_{11})[18] and common inorganic acids. In a typical process, 3 g of α-SiW_{11} was put in a beaker with a scraped rough surface and 10 mL of distilled water was added under stirring (pH = 4.7). Then, 3 M HCl (or H_3PO_4) was dropped into the beaker until the solid dissolved completely and the pH reached ca. 1. This solution was heated for 15 min in an 80 °C water bath and then cooled at room temperature (25 °C) for about 10 min, when air bubbles adsorbed on the beaker bottom were observable. Once a few tubular clusters appeared, many tubular clusters grew immediately in seconds. The time of the microtubes' appearance is between 5 and 30 min, depending on the concentration of α-SiW_{11}, namely, the higher the concentration, the shorter the time is. Tubular crystals of ca. 1 g were harvested by careful filtration and dried in air. The obtained microtubes were characterized by scanning electron microscopy (SEM), powder X-ray spectroscopy (XRD), IR and NMR spectroscopy, transmission electron microscopy (TEM), and selected-area electron diffraction (SAED). All the samples used for physical measurements were obtained from the reaction solution whose pH was adjusted with H_3PO_4, unless otherwise indicated.

Optical micrographs of the tubular crystals are shown in Figure 1. The lengths of the tubes are around 1 cm, the inner diameter in the range of 7−55 μm, and wall thickness in the range of 3−15 μm. IR spectra of the tubes exhibit four character absorption bands between 700 and 1100 cm^{-1} distinguishable from the starting material α-SiW_{11}[19] (see Figure S1). The bands at ~980, ~924, ~877, and ~778 cm^{-1} are respectively assigned to the asymmetric stretching vibrations of W−Od, Si−Oa, W−Ob−W, and W−Oc−W bands, in accordance with those for complete Keggin α-$K_4SiW_{12}O_{40}$(α-SiW_{12}).[20]

The ^{183}W NMR spectrum of the redissolved tubules in D_2O (pD = 4.5) gives a single signal at a chemical shift value of −105 ppm attributed also to the $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ anion (see Figure S2).[21] The crystalline phase of the tubes is verified by powder XRD. The diffraction patterns in $2\theta = 5-45°$ are in good agreement with the standard values of the pure crystal $K_4SiW_{12}O_{40}$ orthorhombic phase [space group *Pnma*] with lattice constants $a = 20.62$ Å, $b = 15.57$ Å, and $c = 12.95$ Å (JCPDS 70-1714) (see Figure S3). SAED pattern of a single tube verifies a crystal orthorhombic phase (see Figure S4). All these results indicate unambiguously that the component of the tubes is $K_4[\alpha\text{-}SiW_{12}O_{40}]$.

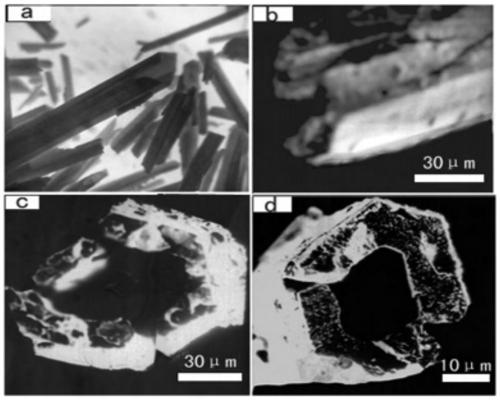

Figure 2. Optical micrograph (a) and SEM images (b−d) of incomplete microtubes.

Because the precursor is monolacunary a tungstosilicate, $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$, transformation of α-SiW_{11} into α-SiW_{12} certainly occurs accompanying the growth of the α-SiW_{12} microtubes under the reaction conditions, namely, a process of reconstitution of the complete Keggin structure from lacunary anion α-SiW_{11} in acidic media. Such transformation reactions in eq 1 on acidification have been known for some time.[22]

$$[\alpha\text{-}SiW_{11}O_{39}]^{8-} + WO_4^{2-} + 6H^+ \rightarrow [\alpha\text{-}SiW_{12}O_{40}]^{4-} + 3H_2O \quad (1)$$

The microtubes are found to be made of individual microplanks through the observation of optical micrographs (see Figure 2a). SEM images further confirm that the tubes are hollow unions of solid multiprisms (see Figure 2b−d). The orthorhombic phase of the tubes indicated by XRD and SAED strongly suggests that they are formed by coalescence of cubic plank crystals of α-SiW_{12}. Experimental effort to understand the formation mechanism of the tubes has been made from the following three aspects.

First, we scraped a 'λ' on the bottom of a new beaker for the reaction. Bunches of microtubes grew along with the trace of the scraped 'λ', while no obvious growth was seen in other areas (see Figure 3). Furthermore, when a new beaker was used for this reaction, only rod crystals grew (see Figure S5). This means that the rough surface of the substrate

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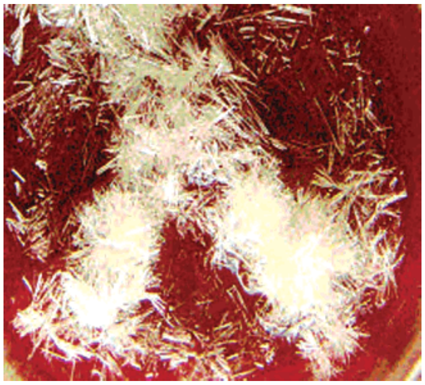
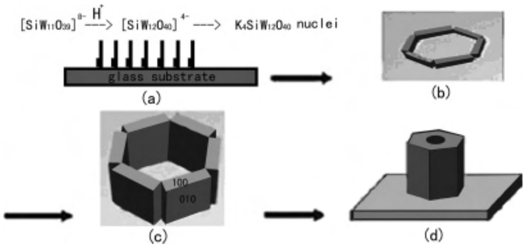


Figure 3. Optical micrograph of bunches of tubules growing on the scraped "λ" surface of the beaker.

Scheme 1. Proposed Formation Mechanism of the Tubules[a]



[a] (a) Synchro process of the transformation of α-SiW_{11} into α-SiW_{12} and the formation of $K_4SiW_{12}O_{40}$ nuclei in acidic conditions; (b−d) growth process of α-$K_4SiW_{12}O_{40}$ tubular crystals.

provides crystal seeds and nucleation causes rapid crystallization of the microtubes.

Second, different POMs as starting materials were used for comparison, including a Keggin-type unsaturated series α-SiW_{11} and $K_8[\gamma\text{-}SiW_{10}O_{36}]$ (γ-SiW_{10}), and saturated a series α-SiW_{12}, and "tungstate-Y" $K_4W_{10}O_{32}$, which is not structurally related to Keggin POMs (their polyhedral structures are presented in Figure S6). In the case of an unsaturated species, either α-SiW_{11} series or γ-SiW_{10} series, crystal microtubes were harvested (see Figure S7), while crystals of the saturated species α-SiW_{12} and the tungstate-Y grew only in a solid rod phase.

Third, different sorts of protic acids, pH values, concentrations of starting materials, and reaction time frames were screened for growing microtubes from α-SiW_{11}. From these experimental results, we found that any kind of protic acid could be used; suitable concentrations of α-SiW_{11} were in the range 0.06−0.12 M (see Table S1); suitable pH values were between 0.1 and 3.0 (see Figure S8); if the growth time of the tubules was prolonged, the openings of the tubes would be closed (see Figure S9), and eventually all the tubes grew into solid rods.

These lines of evidence suggest that the formation of the tubules is a synchro process of the transformation of a vacant tungstosilicate into a saturated one and the crystal growth of the saturated tungstosilicate shown in Scheme 1. At the beginning, crystal nuclei of α-SiW_{12} are generated from the transformation of α-SiW_{11}, which is a metastable species in acidic media and prone to decomposition, and reassembly into more stable α-SiW_{12} anion. Accompanying the crystal growth of α-SiW_{12} on the rough substrate (see Scheme 1a), the α-SiW_{11} species continuously converts into the α-SiW_{12} species, providing growth units for the orthorhombic crystals of α-SiW_{12}. In the end, the cubic plank crystals α-SiW_{12} aggregate into hollow coalescence with visual tubular morphology (see Scheme 1b−d).

IR spectroscopy and ^{183}W NMR should be helpful to analyze the reaction solution and shed more light on the supposed mechanism. The IR spectrum of white precipitate (**M**), which was extracted by absolute ethanol from the reaction solution in just the beginning of microtube growth, was recorded (see Figure S10). It can be seen from the IR spectrum that the characteristic vibration peaks of Keggin-type α-11-series anions dominate the finger area, suggesting that the main species in the beginning of microtube growth is α-SiW_{11}. To measure the ^{183}W NMR spectrum, deuterium oxide was used in the preparation of microtubes. The ^{183}W NMR of the reaction solution in the beginning of microtube growth was recorded (see Figure S11). Unfortunately, the ^{183}W NMR spectrum is not good enough to distinguish all species present in the mother liquid due to low concentrations of species,[23] whereas a signal at −105 ppm is obviously observed after 24 h of data collection, which can be attributed to Keggin-type α-12-series anions. These results strongly support the occurrence of POM species transformation from α-11-series to α-12-series during the process of microtube growth.

The collective ^{183}W NMR, IR, and XRD data and SEM and optical images provide evidence establishing that the formation of α-SiW_{12} microtubes depends on the matched rates of transformation of lacunary tungstosilicate into complete tungstosilicate and the crystal growth of complete tungstosilicate.

In summary, microtubes of α-SiW_{12} were fabricated by a template-free simple aqueous reaction. The growth of the tubular crystals depends on the concentration of starting materials, the crystallization time, and perhaps the surface roughness of the container. The formation of the tubes results from a dynamical match of the transformation process of Keggin-type α-11-series into α-12-series and the crystal growth of the 12-series. This is an interesting phenomenon observed for the first time. Hopefully, this process will be generalized to other POMs. The newly discovered tubular structure of the POM in this work is believed to be promising for use in the application fields of microreactor, template, gas storage and sensors, biosensors, radiator, separation, etc. Further studies are underway on the possibility of preparing the POM tubes in nanoscale by this simple method and on potential applications of the POM microtubes. We are also attempting to extend this method to grow other POM tubes.

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Supporting Information Available: Physical measurements and characterization of $K_4[\alpha\text{-}SiW_{12}O_{40}]$ microtubes. This material is available free of charge via the Internet at http://pubs.acs.org.

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