



Preparation and application of L-cysteine-doped Keggin polyoxometalate microtubes

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ABSTRACT

L-cysteine-doped tungstosilicate (Lcys-SiW₁₂) microtubes are prepared, and the amount of L-cysteine doped in the microtubes can be tuned to some extent. The as-prepared Lcys-SiW₁₂ microtubes are sensitive to ammonia gas exhibited through the distinct color change of the microtubes from light purple to dark blue after exposing to ammonia gas. A possible mechanism of the coloration is that the adsorbed ammonia molecules increase the basicity of the Lcys-SiW₁₂ microtubes and promote the redox reaction between L-cysteine and polyoxometalate. This is a pH-dependent solid–solid redox reaction, which is triggered by proton capture agent. The Lcys-SiW₁₂ microtubes show application in chemical sensors for alkaline gases.

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1. Introduction

Inorganic nano- and microtubes, as the focus of intense investigation since the discovery of carbon nanotubes (NTs) in 1991 by Iijima [1] have become one of the most promising candidates in chemical materials due to their unique structures, mechanical and chemical properties [2,3]. Especially, the design and synthesis of tubular molecular materials have attracted special attention [4–6], as the combination of bulk properties and hollow morphology has been found to be important in potential applications in unusual electronic transport [7] and acting as a container to provide a platform for some chemistry reactions [8]. Recently, attention has been paid for constructing tubular architectures based on polyoxometalates (POMs), which are important inorganic clusters, having potential applications in various fields [9,10]. Many efforts have been made for exerting both merits of POMs and hollow architectures. For example, Ag₄SiW₁₂O₄₀ microtubes [11], micrometer-scale tubes based on POM solids [(C₄H₁₀NO)₄₀[W₇₂Mn₁₂O₂₆₈X₇]]_n (X=Si and Ge) [12], tyrosine POM NTs [13], and so on.

We have made an effort to synthesize composite POM microtubes with bio-active components, including ascorbic acid [14] and L-cysteine in this paper. We chose L-cysteine as a doping component to functionalize the POM microtubes based on the following considerations: L-cysteine (C₃H₇NO₂S) is an amino acid containing sulphhydryl groups, which is of importance in biological processes;

L-cysteine has a high chemical reactivity, and can react with mild oxidant readily [15]; the sulphhydryl of L-cysteine easily form S–Au bond, which can be used for biochemical binding with specific proteins [16]. These features may improve biocompatibility of the POM microtubes and expand possible bio-applications. Here we report the preparation of L-cysteine-doped tungstosilicate (Lcys-SiW₁₂) microtubes. The tubular crystals have been designed for the purpose of endowing di-functions of L-cysteine and POM components. An application of the Lcys-SiW₁₂ microtubes is also described.

2. Experimental section

2.1. Chemicals and measurements

K₈[α-SiW₁₁O₃₉] (α-SiW₁₁) was synthesized according to a published procedure [17]. L-cysteine hydrochloride (C₃H₈NO₂SCl), HCl, NH₃, C₂H₅NH₂, (C₂H₅)₂NH, (C₂H₅)₃N, C₆H₅NH₂, HCHO, and KOH were of analytical grade. All the chemicals were used directly without any further purification. All aqueous solutions were made with deionized water.

The elemental analyses were carried out on a Euro Vector EA 3000 and Vario EL instruments. FT-IR spectra were performed on a Rigaku D/MAX-IIIC spectrometer. UV/Vis spectra were recorded on a 756 CRT UV/Vis spectrometer. TG measurements were finished on a Perkin-Elmer TGA7 instrument. SEM images were acquired with XL30 Field Emission Environmental Scanning Electron Microscope (ESEM-FEG). XRD analyses were measured by using a D/max-IIIC diffractometer.

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2.2. Preparation of the Lcys-SiW₁₂ microtubes

α -K₈[SiW₁₁O₃₉] (3 g, 1 mmol) was added in deionized water (10 mL) under stirring, accompanied by dropwise adding HCl (3 mol L⁻¹) until the solid dissolved completely and pH reached to 1. This solution was then heated in a water bath of 80 °C for 15 min, into which L-cysteine hydrochloride was added. Different amounts of L-cysteine hydrochloride were used to harvest differently doped Lcys-SiW₁₂ microtubes, and the amounts of L-cysteine hydrochloride added were: 0.3 g, 0.19 mol L⁻¹ (Lcys-SiW₁₂-1); 0.6 g, 0.38 mol L⁻¹ (Lcys-SiW₁₂-2); 0.9 g, 0.57 mol L⁻¹ (Lcys-SiW₁₂-3); 1.2 g, 0.76 mol L⁻¹ (Lcys-SiW₁₂-4). The resulting solution was heated for 5 min more. Light purple cluster tubes grew rapidly on the beaker bottom after cooling to room temperature (25 °C) for about 10 min. The Lcys-SiW₁₂ microtubes were isolated by careful filtration and dried in air (yield, 1.5 g).

2.3. Elemental analyses of the Lcys-SiW₁₂-i (i=1–4) microtubes

Elemental analysis calcd (%) for K_{3.3}(C₃H₇NO₂S)_{0.7}H_{0.7}SiW₁₂O₄₀·2H₂O (Lcys-SiW₁₂O₄₀-1): K 4.13, C 0.81, Si 0.90, W 70.60; found: K 4.09, C 0.84, Si 0.89, W 70.51; calcd (%) for K_{2.8}(C₃H₇NO₂S)_{1.2}H_{1.2}SiW₁₂O₄₀·2H₂O (Lcys-SiW₁₂O₄₀-2): K 3.46, C 1.37, Si 0.89, W 69.67; found: K 3.70, C 1.30, Si 0.87, W 69.79; calcd (%) for K_{2.5}(C₃H₇NO₂S)_{1.5}H_{1.5}SiW₁₂O₄₀·2H₂O (Lcys-SiW₁₂O₄₀-3): K 3.06, C 1.69, Si 0.88, W 69.13; found: K 3.14, C 1.64, Si 0.86, W 69.32; calcd (%) for K_{2.2}(C₃H₇NO₂S)_{1.8}H_{1.8}SiW₁₂O₄₀·2H₂O (Lcys-SiW₁₂O₄₀-4): K 2.67, C 2.02, Si 0.87, W 68.60; found: K 2.61, C 1.98, Si 0.85, W 68.78.

3. Results and discussion

3.1. Doping amount of the Lcys-SiW₁₂ microtubes

In order to know how many L-cysteine could be doped into the microtubes, four different amounts of L-cysteine had been used in the parallel experiments to harvest the Lcys-SiW₁₂-i (i=1–4) microtubes. Thermogravimetry (TG) (Fig. 1a) and elemental analyses were carried out to measure the content of L-cysteine in the Lcys-SiW₁₂-i (i=1–4) microtubes. A mass loss ranging from 1.01% to 1.26% was observed in the TG curves below 200 °C, approximately corresponding to two H₂O molecules. The mass losses in 150–650 °C corresponded to the L-cysteine component: 2.81% for Lcys-SiW₁₂-1, 4.35% for Lcys-SiW₁₂-2, 5.50% for Lcys-

SiW₁₂-3, and 6.76% for Lcys-SiW₁₂-4. The thermal analyses are consistent with the element analysis results of carbon and nitrogen. Based on the TG and element analysis results, a general formula of Lcys-SiW₁₂-i (i=1–4) microtubes can be given as α -K_{4-x}(C₃H₇NO₂S)_xH_x[SiW₁₂O₄₀]·2H₂O (x=0.7–1.8). The number of L-cysteine doped in the POM microtubes was increased as the augment of the amount of L-cysteine added in the starting materials (Fig. 1b). Lcys-SiW₁₂-4 represents the Lcys-SiW₁₂ microtubes with a maximum doping amount of L-cysteine, as excess L-cysteine would restrain the formation of the microtubes.

3.2. Characterization of the Lcys-SiW₁₂ microtubes

The Lcys-SiW₁₂-1 microtubes are taken as a typical example of characterization. The optical micrograph and ESEM image are shown in Fig. 2. The basic length of the Lcys-SiW₁₂ microtubes is around 2 mm, the inner diameter in the range of 50–100 μm, the wall thickness in the range of 20–40 μm.

In the FT-IR spectrum of the Lcys-SiW₁₂ microtubes (Fig. S1), the characteristic absorption peaks of L-cysteine are observed at 1606 cm⁻¹ for $\nu_{\text{C=O}}$, 1724 cm⁻¹ for $\nu_{\text{C=O}}$, 1227 cm⁻¹ for $\nu_{\text{C-O}}$, 3436 cm⁻¹ for $\nu_{\text{N-H}}$, 1492 cm⁻¹ for $\nu_{\text{NH}_3^+}$ and 2560 cm⁻¹ for $\nu_{\text{S-H}}$. The characteristic absorption peaks of Keggin SiW₁₂ are distinguishable at 975, 928, 878, and 775 cm⁻¹. The FT-IR spectrum indicates that L-cysteine component has been integrated into the POM microtubes and the POM component maintains the α -Keggin structure.

3.3. Formation mechanism of the Lcys-SiW₁₂ microtubes

The formation of the microtubes involved two processes (Scheme 1): One process was a chemical transformation of the monolacunary Keggin-type [α -SiW₁₁O₃₉]⁸⁻ anions to the saturated Keggin-type [α -SiW₁₂O₄₀]⁴⁻ anions under the low pH condition [18]. The other one was a crystallization of the potassium salt of the saturated Keggin-type [α -SiW₁₂O₄₀]⁴⁻, which further packed to form hollow crystalline. Meanwhile, L-cysteine molecules were doped during the growth of the microtubes. This formation mechanism is supported by X-ray powder diffraction (XRD) (Fig. 3), which can reveal their inner architectures. The diffraction pattern of the Lcys-SiW₁₂ microtubes is in good agreement with that of the SiW₁₂ microtubes, which can be attributed to the orthorhombic phase of K₄SiW₁₂O₄₀ (Powder Diffraction File entry 01-070-1714). This result verifies that the

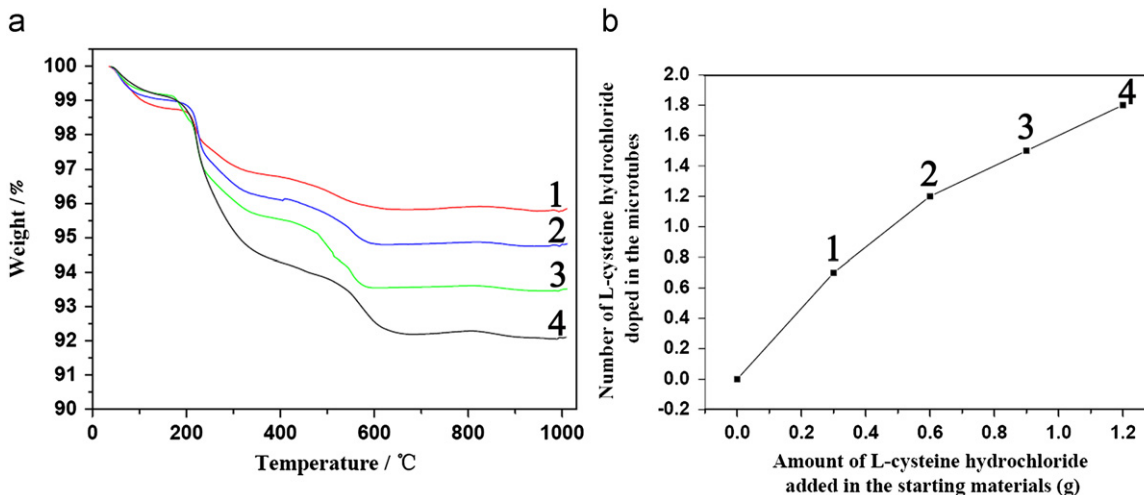


Fig. 1. (a) TG curves of Lcys-SiW₁₂-i (i=1–4) microtubes and (b) plot of the number of L-cysteine doped in Lcys-SiW₁₂-i (i=1–4) microtube vs the amount of L-cysteine added in the parallel experiments.

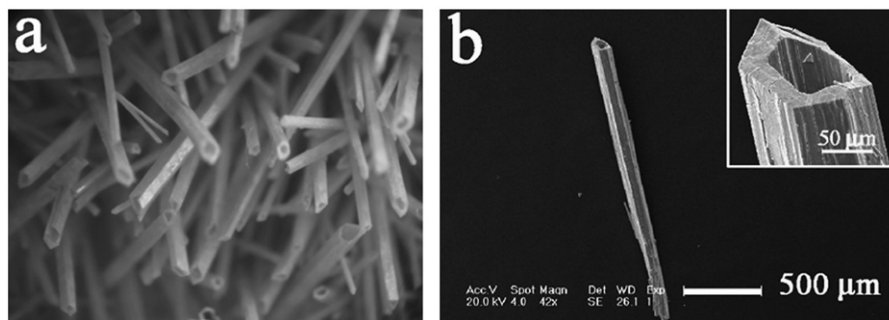
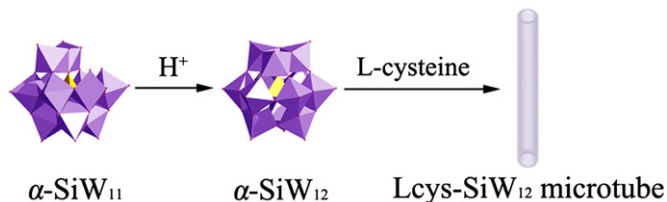


Fig. 2. Optical micrograph (a) and ESEM image (b) of the Lcys-SiW₁₂ microtubes.



Scheme 1. Formation process of the Lcys-SiW₁₂ microtubes.

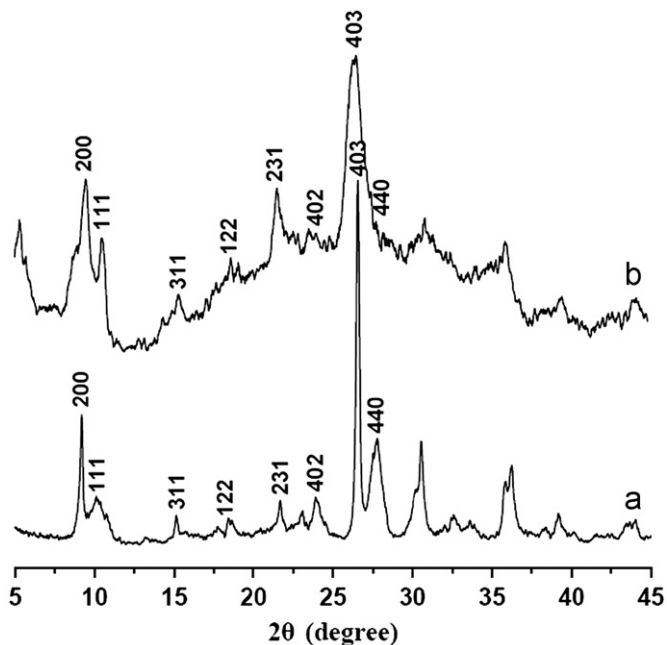


Fig. 3. XRD patterns of SiW₁₂ (a) and Lcys-SiW₁₂ (b) microtubes.

crystal phase structure of the SiW₁₂ microtubes is maintained intact in the Lcys-SiW₁₂ microtubes, although the doping of L-cysteine may disturb it to some extent.

3.4. Application of the Lcys-SiW₁₂ microtubes

We found that the freshly prepared Lcys-SiW₁₂ microtubes could change their color from light purple to dark blue in ammonia gas immediately (Fig. 4).

Visible spectrum of the Lcys-SiW₁₂ microtubes treated with ammonia gas (Fig. S2) indicates that new absorption bands appear at 500 and 750 nm, attributed to the d–d transition and the $W^{(V)} \rightarrow W^{(VI)}$ intervalence-charge transfer [19], which is a powerful evidence for the reduction of Lcys-SiW₁₂ to the corresponding heteropoly blue (HPB).

IR spectrum of the Lcys-SiW₁₂ microtubes after coloration (Fig. S3) shows the characteristic vibration absorption peaks of $\alpha\text{-SiW}_{12}$ with slight shifts, which indicates that the Keggin structure is still maintained. Another key information obtained from the IR spectrum is the appearance of a new vibration absorption peak at 1406 cm^{-1} attributable to $\nu_{\text{N-H}}$ of NH_4^+ cations [20], which are transferred from the NH_3 molecules adopted in the Lcys-SiW₁₂ microtubes. Additionally, the $\nu_{\text{S-H}}$ of L-cysteine is disappeared, indicating that L-cysteine have been oxidized to L-cystine under the alkaline environment (Scheme 1) [21].

To understand possible mechanism of the coloration process, visible spectroscopy was used to monitor a 5 mL solution containing 1 g Lcys-SiW₁₂-1 microtubes during addition of an ammonia solution ($V_{\text{NH}_3} : V_{\text{H}_2\text{O}} = 1 : 5$) drop by drop (Fig. 5I). Fig. 5I shows that the intensities of the characteristic absorption bands of Keggin HPB enhance along with the increase of the ammonia solution. Furthermore, a plot of maximum absorbances versus pH (Fig. 5II) was made to investigate the influence of the pH on the redox reaction between SiW₁₂ and L-cysteine, which reveals that the redox reaction is speeded up along with the increase of pH, and is accelerated obviously when the pH is greater than 5.2. Alternately, KOH was used, which also confirmed the proposed pH-dependent mechanism (Fig. S4). Other kinds of gases such as H₂, HCl, H₂S, and HCHO were also tested, however, no coloration happened.

A control experiment was performed for a sample of physically mixed L-cysteine and $\alpha\text{-SiW}_{12}$ microtubes through grinding, which showed no color change in an ammonia atmosphere. We drew a conclusion from the above experiments that the redox reaction between L-cysteine and SiW₁₂ was difficult under the acidic condition for growth of the Lcys-SiW₁₂ microtubes ($\text{pH} < 3$). When the Lcys-SiW₁₂ microtubes were exposed to ammonia gas, the adsorbed ammonia molecules acted as a proton acceptor to increase the basicity of the Lcys-SiW₁₂ microtubes and promoted the redox reaction. This was a proton capture agent-triggered solid–solid redox reaction. The sensitivity of the Lcys-SiW₁₂ microtubes to ammonia gas could be applied in a chemical sensor for alkaline gases. However, the Lcys-SiW₁₂ microtubes cannot be recycled because the redox reaction is irreversible.

4. Conclusion

This work presents the preparation of the L-cysteine-doped tungstosilicate microtubes through the doping-tunable methodology, which is the first example of sulphydryl-containing organic molecules doped POM microtubes. By utilizing the reduction reactivity of L-cysteine, the POM microtubes can be used as a gas sensor of ammonia. Furthermore, the L-cysteine component will play a functional role in bio-applications of the Lcys-SiW₁₂

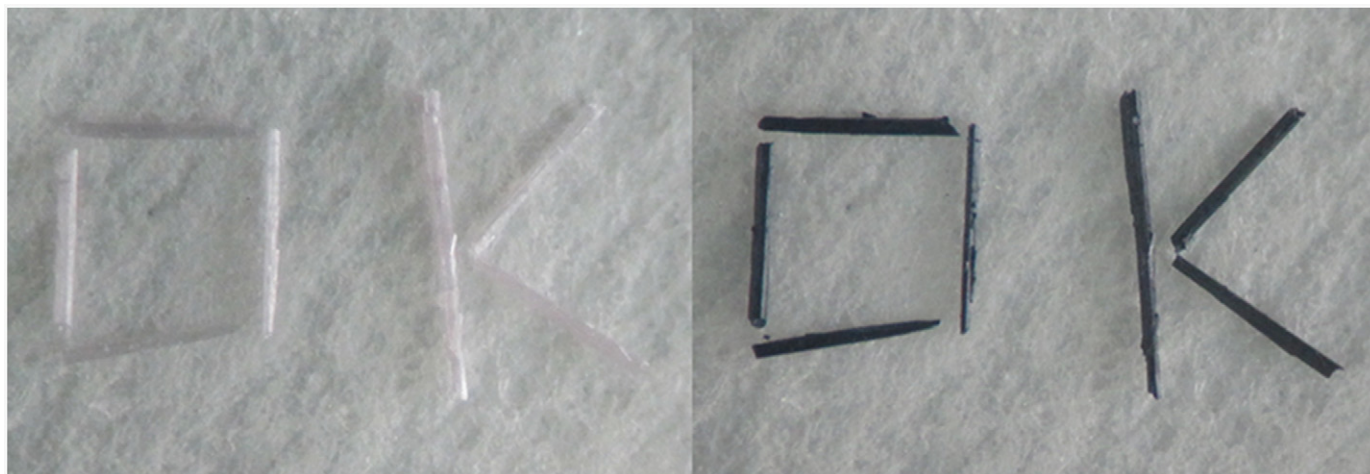


Fig. 4. Optical micrograph of the Lcys-SiW₁₂ microtubes before (left) and after (right) exposure to an ammonia atmosphere. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

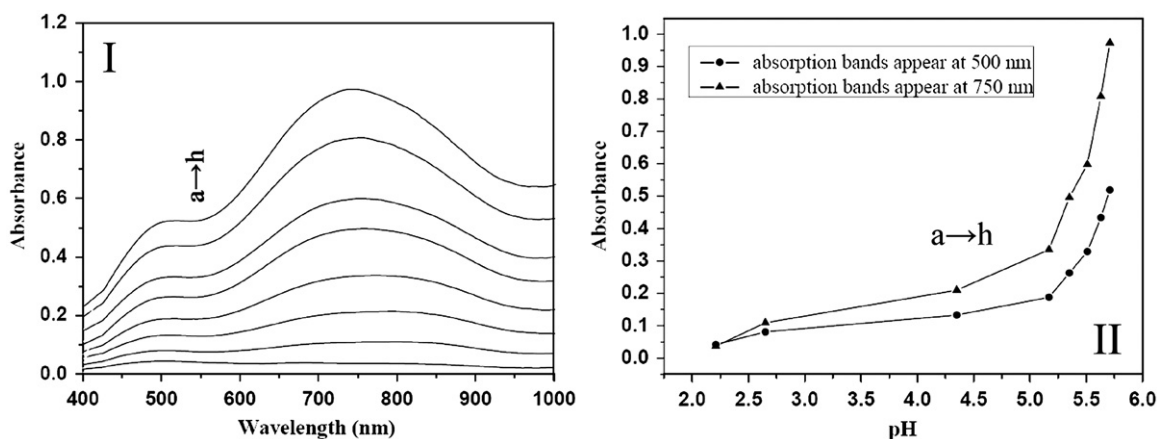


Fig. 5. (I) Visible spectra of the solution (5 mL solution containing 1 g Lcys-SiW₁₂-1 microtubes) recorded during adding an ammonia solution ($V_{\text{NH}_3}:V_{\text{H}_2\text{O}}=1:5$) drop by drop, and the direction $a \rightarrow h$ presents the increase of ammonia. (II) Plot of the maximum absorbances versus pH ($a \rightarrow h$).

microtubes, for example, an expected application for biochemical binding with specific proteins by Au-modified sulphhydryl of L-cysteine. Further study is underway.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2011.10.048](https://doi.org/10.1016/j.jssc.2011.10.048).

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