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Preparation and fluorescent properties of the all-W and Mo/V-monosubstituted Keggin-tungstosilicate microtubes doped with fluorescein dye

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ABSTRACT

Three new dye-doped inorganic-organic hybrid microtubes, $SiMW_{11}$-F (M = W, Mo and V; F = fluorescein), have been obtained and characterized by X-ray diffraction, ultraviolet/visible spectroscopy, elemental analysis, thermogravimetric analysis. Comparative studies have been carried out on fluorescent properties of the three $SiMW_{11}$-F microtubes and fluorescein. These fluorescent hybrid microtubes exhibit luminescent emission properties which are different from raw material fluorescein in the blue spectral region, which is suggests that different luminescence centers may be formed in the hybrid microtubes. The SiW_{12}-F and $SiMoW_{11}$-F microtubes show more similar fluorescent properties than the $SiVW_{11}$-F microtubes, due to the differences in ionic radius and oxidation state between W/Mo and V. Furthermore, the three polyoxometalate components in the microtubes exhibit an inhibiting effect on photobleaching of fluorescence dye in the reaction system.

1. Introduction

Polyoxometalate (POM) chemistry, having hundreds' history, is boosting developments either in structural diversities or in multiple applications in recent decades [1–14]. Especially, the Keggin-type ($XM_{12}O_{40}$, X = Si, Ge, P, As; M = Mo, W) POM family is the best known and most studied one. However, it still raises interest in the Keggin-type $XM_{12}O_{40}$ heteropolyanions, the X and M components can be alternated by many elements, thus their chemical properties can be adjusted [15–19].

Organic fluorescent molecules have shown significance in the technological applications such as lighting and optoelectronic devices, fluorescent chemical sensors, DNA diagnosis, and so on [20–24]. However, fluorescent solid materials of organic small molecules are usually prone to fluorescence quenching or integration in some hybrid fluorescent materials. To synthesize new fluorescent solid materials with good performance and overcoming the shortcomings is a challenging work [25].

Tubular structures exhibit potential applications in catalysis, microreactors, templates, gas storage and sensing [26–34]. Taking a combination of POMs and organic fluorescent molecules into a tubular structure is of significance related to an integration of morphology and functionalization for POM-based materials. Therefore it is worthy of making effort to create such new materials. Fluorescein (F) is a common organic fluorescent dyes in the yellow green region, and has numerous applications in optoelectronic devices, serologic identification, immunology, and so on [35–38]. F may exist as a cation (FC), a neutral molecule (FN) or an anion (FA), depending on pH. The photoluminescence (PL) property of F is also pH-dependent [39]. These features can be used to synthesize fluorescent hybrid materials which integrate POMs and organic fluorescent dye. Recently, we communicated the microtubes (SiW_{12}-F) composed of the all-W α-Keggin tungstosilicate and fluorescein, which showed tunable photoluminescence from sky blue to green to red by variation of excitation light [40]. In this paper, we systematically report the preparation and fluorescent properties of the

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Keggin-type α-$SiMW_{11}$-F ($M = W^{VI}$, Mo^{VI} and V^{V}) microtubes doped with fluorescein dye.

2. Experimental section

2.1. Materials and equipments

Monolacunary tungstosilicate $K_8[\alpha\text{-}SiW_{11}O_{39}]$ (α-SiW_{11}) was synthesized according to a published procedure [41]. HCl, Na_2MoO_4, $NaVO_3$, and fluorescein sodium (FS) were of analytical grade and were used directly without any further purification. All aqueous solutions were made with deionized water. Fourier transform infrared (FT-IR) spectra were recorded on a D/MAX-IIIC instrument, elemental analyses were carried out on a Euro Vector EA 3000 and Vario EL instruments, environmental scanning electron microscopy (ESEM) images were acquired with an XL30 field emission environmental scanning electron microscope (ESEM-FEG), powder X-ray diffraction (PXRD) patterns were obtained with a D/max-IIIC diffractometer, thermogravimetric analysis measurements (TG) were performed with a Perkin–Elmer TGA7 instrument, visible spectra were recorded on a 756 CRT ultraviolet/visible (UV/Vis) spectrometer. Cyclic voltammograms (CV) were obtained with a CHI 660 electrochemical workstation at room temperature. A three-electrode system was employed, with a platinum foil counter electrode, a saturated calomel reference electrode, and a glassy carbon working electrode. The POM microtubes were dissolved in 0.25 M Na_2SO_4 + H_2SO_4solution (pH = 1) for electrochemical measurements. Fluorescence spectra were measured on an FLSP920 Edinburgh Fluorescence Spectrometer. Fluorescence microscopy images were obtained with an Olympus FV-1000 confocal laser scanning microscope with mercury lamp as excitation source, using CCD scanning (objective lens 20 times). The fluorescent stability was performed with a HITACHI F-7000 fluorescence spectrophotometer.

2.2. Preparation of SiW_{12}-F microtubes

In a typical procedure, 3 g of α-$K_8[SiW_{11}O_{39}]$ was dissolved in 10 mL of deionized water in a beaker, along with stirring and adjusting pH to 1.0 by 3 M HCl. The solution was heated in a water bath at 85 °C for 15 min, 0.0114 g of fluorescein sodium was then added. After cooling to room temperature (25 °C) over a 10 min period, yellow microtubes crystallized and were collected by filtration, dried under air for 24 h (yield: 1.2 g). Elemental analyses give the percentage of C, H, and K in $K_{3.98}(C_{20}H_{13}O_5)_{0.02}[SiW_{12}O_{40}]\cdot 4H_2O$ microtubes, which were obtained from a mother liquor adding the max quantity of FS: anal. calcd for microtubes (%): K, 5.01; Si, 0.903; W, 70.97; C, 0.15. Found (%): K, 4.32; Si, 0.897; W, 68.98; C, 0.20.

2.3. Preparation of $SiMoW_{11}$-F microtubes

3 g of α-SiW_{11} (1 mmol) and 0.2 g of Na_2MoO_4 (1 mmol) were placed in a beaker, 10 mL of water was added with stirring. And then HCl (3 M) was added dropwise until the solid dissolved completely and the pH value reached 1, temporality, the solution changed from colorless to light yellow. This solution was heated in an 85 °C water bath for 15 min, 0.0110 g of fluorescein sodium was then added. After cooling to room temperature over a period of 10 min, yellow microtubes crystallized and were collected by filtration, dried under air for 24 h (yield: 1.2 g). Anal. Calcd for $K_{3.98}(C_{20}H_{13}O_5)_{0.02}[SiMoW_{11}O_{40}]\cdot 3.7H_2O$ microtubes (%): K, 5.16; Si, 0.93; W, 67.07; Mo, 3.18; C, 0.159. Found (%): K, 4.98; Si, 0.91; W, 66.83; Mo, 3.11; C, 0.151.

2.4. Preparation of $SiVW_{11}$-F microtubes

$SiVW_{11}$-F microtubes were obtained by using the same method as that for $SiMoW_{11}$-F microtubes, except that Na_2MoO_4 was replaced by $NaVO_3$ (0.12 g, 1 mmol) in the starting materials (yield: 1.1 g). Anal. Calcd for $K_{4.97}(C_{20}H_{13}O_5)_{0.03}[SiVW_{11}O_{40}]\cdot 6.5H_2O$ microtubes (%): K, 6.35; Si, 0.92; W, 66.08; V, 1.66; C, 0.24. Found (%): K, 6.21; Si, 0.82; W, 65.96; V, 1.57; C, 0.19.

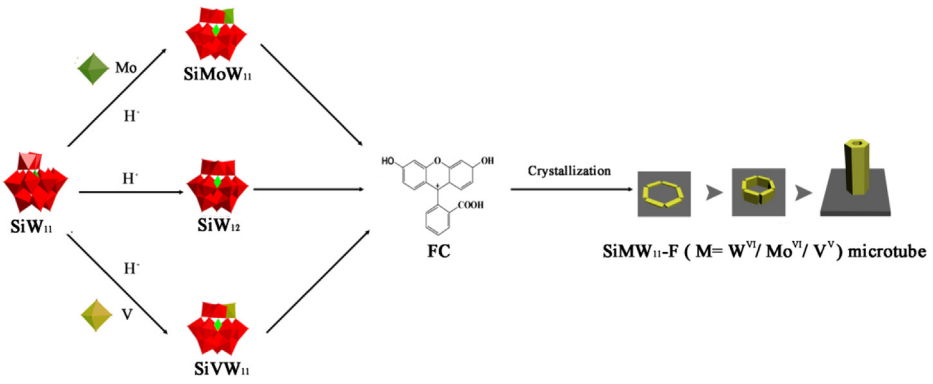
3. Results and discussion

3.1. Formation mechanism of $SiMW_{11}$-F microtubes

The $SiMW_{11}$-F microtubes are prepared by the same method. The starting materials Keggin α-SiW_{11} anions are metastable in acidic media, and easily transform to more stable Keggin α-SiW_{12} anions, especially, to form Mo- and V-monosubstituted Keggin α-$SiMoW_{11}$ and $SiVW_{11}$ anions in the presence of Mo and V components. FS molecules exist as protonated cations in an acidic solution. Therefore, we deduce that the $SiMW_{11}$-F microtubes have the same formation mechanism, which involves two processes of species transformation and tubular crystalline growth. Firstly, two parallel reactions occur in the mother liquor of pH = 1, that is, the monovacancy α-Keggin SiW_{11} species transforms to the saturated Keggin-type $SiMW_{11}$ species, and FS molecules are protonated to form FCs in the acidic solution. Consequentially, $SiMW_{11}$ anions can combine with FCs through electrostatic interaction. Secondly, the FC-doped POM compounds crystallize in microplank phase and finally form tubular morphology (Scheme 1).

3.2. Characterizations of $SiMW_{11}$-F microtubes

The morphologies of the $SiMW_{11}$-F microtubes are well observed by optical micrographs. Figs. 1a, 2a and 3a show the optical



Scheme 1. Preparation processes of the $SiMW_{11}$-F (M = W^{VI}, Mo^{VI} and V^{V}) microtubes.