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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 SiMW₁₁-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 SiW₁₂-F and SiMOW₁₁-F microtubes show more similar fluorescent properties than the SiVW₁₁-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.

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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 Keggintype ($XM_{12}O_{40}$, 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 (SiW₁₂-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 -SiMW₁₁-F ($M = W^{VI}$, Mo^{VI} and V^V) microtubes doped with fluorescein dye.

2. Experimental section

2.1. Materials and equipments

Monolacunary tungstosilicate $K_8[\alpha-SiW_{11}O_{39}]$ ($\alpha-SiW_{11}$) was synthesized according to a published procedure [41]. HCl, Na₂MoO₄, NaVO₃, 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 $Na_2SO_4 + H_2SO_4$ solution (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 SiW₁₂-F microtubes

In a typical procedure, 3 g of α -K₈[SiW₁₁O₃₉] 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}(C₂₀H₁₃O₅)_{0.02}[SiW₁₂O₄₀]· 4H₂O 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 SiMoW₁₁-F microtubes

3 g of α -SiW₁₁ (1 mmol) and 0.2 g of Na₂MoO₄ (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}(C₂₀H₁₃O₅)_{0.02}[SiMoW₁₁O₄₀]·3.7H₂O 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 SiVW₁₁-F microtubes

SiVW₁₁-F microtubes were obtained by using the same method as that for SiMoW₁₁-F microtubes, except that Na₂MoO₄ was replaced by NaVO₃ (0.12 g, 1 mmol) in the starting materials (yield: 1.1 g). Anal. Calcd for $K_{4.97}(C_{20}H_{13}O_5)_{0.03}$ [SiVW₁₁O₄₀]·6.5H₂O 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 SiMW₁₁-F microtubes

The SiMW₁₁-F microtubes are prepared by the same method. The starting materials Keggin α -SiW₁₁ anions are metastable in acidic media, and easily transform to more stable Keggin α -SiW₁₂ anions, especially, to form Mo- and V-monosubstituted Keggin α -SiMoW₁₁ and SiVW₁₁ anions in the presence of Mo and V components. FS molecules exist as protonated cations in an acidic solution. Therefore, we deduce that the SiMW₁₁-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 SiW₁₁ species transforms to the saturated Keggin-type SiMW₁₁ species, and FS molecules are protonated to form FCs in the acidic solution. Consequentially, SiMW₁₁ 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 SiMW₁₁-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 SiMW₁₁-F ($M = W^{VI}$, Mo^{VI} and V^V) microtubes.



Fig. 1. (a) The optical micrograph of the SiW12-F microtubes; ESEM of (b) intact and (c) destruct SiW12-F microtubes (the ruler scale was redrawn for clarity).

micrographs of the SiMW₁₁-F microtubes growing in beakers. These microtubes are yellow, but the color of SiVW₁₁-F microtubes is deeper than those of the SiW₁₂-F and SiMoW₁₁-F microtubes. ESEM-FEG images (Figs. 1b, 2b and 3b) reveal that the average lengths are around 3 mm for SiW₁₂-F and SiMoW₁₁-F, and around 2.5 mm for SiVW₁₁-F microtubes. The inner diameters and wall thicknesses of the SiW₁₂-F microtubes are in the ranges of 60–100 and 15–35 μ m, respectively, the SiMoW₁₁-F microtubes are in the ranges of the SiVW₁₁-F microtubes are in the ranges of 45–100 and 10–30 μ m, respectively. The SiVW₁₁-F microtubes grow more slender. The ESEM images (Figs. 1c, 2c and 3c) taken from a deliberately destroyed individual SiMW₁₁-F microtube further prove the hollow structures.

In the FT-IR spectra of SiMW₁₁-F microtubes (Figure S1), the four characteristic vibration absorption bands below 1000 cm⁻¹ are assigned to v_{as} (M-O_d), v_{as} (Si-O_a), v_{as} (M-O_b-M) and v_{as} (M-O_c-M) for the Keggin anions (M = W, Mo, and V), respectively. The quite weak absorption bands in the range of 1200–1500 cm⁻¹ are attributed to those for FC. The FT-IR spectra prove that not only the polyanions possess the saturated Keggin structure, but also the dye molecules have been successfully introduced into the microtubes.

The XRD patterns measured for SiMW₁₁-F microtubes (Figure S2) show some differences compared with each other and with that for SiW₁₂ microtubes, which is expected as the doping of FC and the second metal components, Mo and V, may influence the crystalline morphology of the POM microtubes. Notably, the difference of XRD pattern for SiVW₁₁-F microtubes is obvious perhaps due to different features between Mo/W and V atoms.

To verify the substitution of Mo and V in the POM anions, cyclic voltammetry (CV) measurements of solutions of SiMoW₁₁-F and SiVW₁₁-F microtubes were carried out (Figure S3) [42]. Three reversible couples, II–II', III–III', and IV–IV', with midpoint potentials, E_m , of –155, –438, and –617 mV found for SiMoW₁₁-F microtubes are ascribed to the electrochemistry of the W^{VI}/W^V redox centers. The couple at $E_m = 404$ mV (I–I') is ascribed to the Mo^{VI}/Mo^V redox centers, which supports the existence of Mo in the Keggin anions [43]. Similarly, three reversible couples, II–II', III–III', and IV–IV', with midpoint potentials, E_m , of –152, –440, and –618 mV found for SiVW₁₁-F microtubes are ascribed to the W^{VI}/W^V redox centers, and the couple at $E_m = 517$ mV (I–I') is

ascribed to the V^V/V^{IV} redox centers, which proves the presence of V in the Keggin anions. The CV results show that the oxidizing ability of the V-monosubstituted Keggin POM is stronger than that of the Mo-monosubstituted Keggin POM.

Thermogravimetry (TG) was carried out to measure the contents of crystal water and F in the SiMW₁₁-F microtubes (Figure S4). From the TG curves of SiMW₁₁ microtubes, two steps of mass loss were found below 150 °C and in the range of 420–600 °C, corresponding to the losses of H₂O and F components: 2.09% (4H₂O) and 0.246% (0.02 F), for SiW₁₂-F microtubes; 2.07% (3.7H₂O) and 0.221% (0.02 F), for SiMOW₁₁-F microtubes; 5.366% (6.5H₂O) and 0.452% (0.03 F), for SiVW₁₁-F microtubes. The thermalanalyses are consistent with the element analysis results of carbon and nitrogen, and support the given formula of SiMW₁₁-F.

3.3. The inhibiting effect of the SiMW₁₁ POMs on photobleaching of FS dye

Quite a few reports have demonstrated effect on photocatalytic decolorization of dyes by POMs [44-46]. To check out if FS dye is stable in the preparation process of SiMW₁₁ POM tubes, comparative photobleaching experiments of FS were carried out in the same conditions as in the reaction systems. These experiments were monitored by UV/Vis spectroscopy in a time interval of 10 min. The visible spectra showed that, along with the increase of ultraviolet irradiation time, absorption intensities of a pure FS solution decreased significantly. Contrastively, the absorption intensities of FS solutions did not obviously decrease in the presence of SiMW₁₁ POMs (Figure S5). This fact indicates that FS solutions exhibit more stable against photobleaching in the presence of SiMW₁₁ POM in the reaction systems, that is, all the Keggin SiMW₁₁ POMs have an inhibition effect on photobleaching of FC although oxidation abilities of SiMW₁₁ POMs are different. We deduce that FS molecules are protonated to form FCs in the acidic solutions, thus it becomes more difficult to lose electrons and easier to attach SiMW₁₁ anions for the protonated dye cations, and the electrostatic interaction between the POM anions and protonated dye cations may inhibit the rate of photochemical reaction and configuration change of FC. This inhibiting effect is favorable for obtaining fluorescence dyedoped POM hybrid fluorescent materials.



Fig. 2. (a) The optical micrograph of the SiMoW₁₁-F microtubes; ESEM of (b) intact and (c) destruct Si MoW₁₁-F microtubes (the ruler scales were redrawn for clarity).



Fig. 3. (a) The optical micrograph of the SiVW₁₁-F microtubes; ESEM of (b) intact and (c) destruct SiVW₁₁-F microtubes (the ruler scales were redrawn for clarity).

3.4. Fluorescent properties of the SiMW₁₁-F microtubes

Solid-state fluorescent properties of the SiMW₁₁-F microtubes have been comparably studied. The fluorescence microscopy images reveal that, under irradiation of diverse light sources of violet light, blue light and green light, FS powder fluoresces from orange to green to red (Fig. 4a), whereas an individual SiW₁₂-F microtube fluoresces from sky blue to green to red (Fig. 4b). This result proves that the fluorescence of F is not quenched by SiW₁₂ POM, which is different from those for most reported POMs [47–50]. Furthermore, a new fluorescent feature is generated in blue light region for the SiW₁₂-F microtube. The fluorescence microscopy images of an individual SiMOW₁₁-F microtube show similar behaviors to those of the individual SiW₁₂-F microtube (Fig. 4c). While an individual SiVW₁₁-F microtube weakly fluoresces from kelly to green to red

(Fig. 4d). It is noted that under visible light, the SiVW₁₁-F microtubes are more transparent.

Fluorescence emission spectra were measured with excitation light at 380 nm, 458 nm and 550 nm, corresponding to the light sources of violet, blue, and green light, respectively, in the fluorescence microscopy images (Fig. 5). The fluorescence emission spectra match well with the fluorescence microscopy images of FS and SiMW₁₁-F microtube. It is found from Fig. 5 that the solid-state fluorescence emission spectra obtained from SiMW₁₁-F microtubes are the same as that from FS under excitation at 550 nm light, and are rather similar to each other under excitation at 458 nm light. But the fluorescence emission spectra of FS and SiMW₁₁-F microtubes under excitation at 380 nm light: A broad emission band covering a wavelength range from 550 to 750 nm with a maximum at ca. 600 nm is observed for FS



Fig. 4. Fluorescence microscopy images of a powder sample of FS (a) and an individual SiW₁₂-F microtube (b), SiMoW₁₁-F microtube (c), SiVW₁₁-F microtube (d). The light source in the order from left to right is visible, violet, blue and green light. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Solid-state fluorescence emission spectra obtained from the powder sample of FS (a) and the SiW₁₂-F (b), SiMoW₁₁-F (c), SiVW₁₁-F microtubes (d) at room temperature by variation of excitation light (E_x). From left to right: $E_x = 380$ nm; $E_x = 458$ nm; $E_x = 550$ nm, corresponding to the light sources of violet, blue, and green light, respectively, in the fluorescence microscopy images.

(Fig. 5a). Whereas, a broad emission band covering a wavelength range from 400 to 600 nm is observed for SiMW₁₁-F microtubes (Fig. 5b–d). It is noted that the broad emission bands of SiW₁₂-F (a maximum at ca. 500 nm) are more similar with that of SiMOW₁₁-F microtubes (a maximum at ca. 490 nm), which corresponds to blue fluorescence. While two divided peaks with max values at ca. 440 nm and 550 nm, corresponding to blue and green fluorescence, are observed for SiVW₁₁-F microtubes, and an obvious hypsochromic shift of the maximum absorption peak in the blue light region is observed. This phenomenon suggests that two different emission centers perhaps be generated in the SiVW₁₁-F microtubes.

PL lifetimes were obtained under the conditions of the most effective excitation and emission: excitation at 350 nm and emission at 650 nm for FS; excitation at 380 nm and emission at 508 nm for SiW₁₂-F microtubes; excitation at 380 nm and emission at 490 nm for SiMoW₁₁-F; excitation at 380 nm and emission at 440 nm for SiVW₁₁-F microtubes. The emissions follow a biexponential decay pattern with: average value of τ is 11.398 µs for FS, 12.073 µs for SiW₁₂-F microtubes, 9.827 µs for SiMoW₁₁-F microtubes, and 10.569 µs for SiVW₁₁-F microtubes. The slightly increase in the τ value for SiW₁₂-F microtubes is perhaps because SiW₁₂ heteropolyanions are more rigid.



Fig. 6. Time-scan fluorescence spectra obtained from FS (excitation at 350 nm, emission at 650 nm for FS); SiW_{12} -F microtubes (excitation at 380 nm, emission at 508 nm); $SiMoW_{11}$ -F microtubes (excitation at 380 nm, emission at 490 nm) and $SiVW_{11}$ -F (excitation at 380 nm, emission at 440 nm).

Stability is one of the most important issues for PL materials. PL stabilities were studied with time-scan fluorescence spectra (Fig. 6). Fig. 6 shows that the emission-intensity of FS and SiVW₁₁-F microtubes are almost unchanged during the given period, while a gradual increase in emission-intensity of SiW₁₂-F and SiMOW₁₁-F microtubes are observed. This phenomenon may attribute to the different surface defect states of the POM microtubes.

The different fluorescent features between FS and SiMW₁₁-F microtubes in the blue light region imply that new fluorophores are generated in the SiMW₁₁-F microtubes. The similar and different fluorescent behaviors among the SiMW₁₁-F microtubes should be attributed to the different natures of the POMs. In SiW₁₂ and SiMOW₁₁ polyanions, W(VI) and Mo(VI) have similar radiuses and the same oxidation state, which make the SiW₁₂-F and SiMOW₁₁-F microtubes more similar in structure, thus more semblable in fluorescent behavior. Whereas V(V) has a smaller radius and a lower oxidation state, these differences lead to a more negative charge and a stronger oxidizing ability for the SiVW₁₁ heteropolyanions than for the SiW₁₂ and SiMOW₁₁ heteropolyanions. So it is reasonable that SiVW₁₁-F microtubes show obvious diverse appearance and different fluorescent behavior compared with SiW₁₂-F and SiMOW₁₁-F microtubes.

4. Conclusions

Three new kinds of fluorescent hybrid microtubes based on the Keggin POMs and F dye have been synthesized through a two-step chemical reaction mechanism, namely, a reaction of POM species transition and a doping reaction of organic dye F. The fluorescent hybrid POM microtubes exhibit different luminescent emission properties compared with F dye in the blue spectral region, which suggests that different luminescence centers may be formed in the POM microtubes. Comparative studies on fluorescent properties have been carried out for the SiMW₁₁-F microtubes by adjusting the polyanions with a second transition metal, Mo and V. The SiW₁₂-F and SiMoW₁₁-F microtubes show more similar fluorescent properties than the SiVW $_{11}$ -F microtubes, due to the differences in radius and oxidation state between W/Mo and V. The fluorescent hybrid microtubes based on the Keggin POMs show potential in chemical sensor, wavelength converter and display materials. And this work provides a simple approach to functionalize the POMs with fluorescent dyes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.03.020.

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