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Hybrid microtubes of polyoxometalate and fluorescence dye with tunable photoluminescence†

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Fluorescent microtubes based on α -Keggin tungstosilicate and fluorescein (SiW₁₂-F) have been obtained by using a simple method, which present tunable photoluminescence from sky blue to green to red by variation of excitation light. The SiW₁₂ component can inhibit photobleaching of fluorescein.

Materials with tunable photoluminescence (PL) properties show important technical applications in wavelength conversion, multiplex imaging display and chemical or bio-sensors. Design and preparation of new PL-tunable materials are one of the research focuses in materials chemistry. Examples of PL-tunable materials include size-controlled Si quantum dots with size-dependent photoluminescence,¹ ZnO powders dealt with diverse annealing temperatures² and lanthanide compounds.³ Some MOFs (metal–organic frameworks) also exhibit tunable photoluminescence by variation of excitation light.⁴ However, design and preparation of PL-tunable materials with high performance still remains a challenge.

In recent years, organic fluorescent dyes (OFDs) have attracted great attention due to their potential applications in lighting and optoelectronic devices.⁵ OFDs with a variety of chromophores show excellent optical and fluorescent properties owing to the large planar conjugated π systems. Fluorescein (F) is a common OFD in the yellow green region and has numerous applications.⁶ F may exist as a cation (FC), neutral molecule (FN) or anion (FA), depending on pH, whose PL property is also pH-dependent. This feature can be used to change the output of wavelength or increase the output energy.⁷

Polyoxometalates (POMs) are good candidates for synthesis of inorganic–organic functionalization materials.⁸ Their applications have been involved in the fields of catalysis, medicine, optics, electronic and magnetic materials.⁹ However, the study of POM hybrids functionalized by organic dyes is

still in its infancy.¹⁰ The reports on hybrid materials constructed by POMs and OFDs are rare.¹¹

During the last decade, one-dimensional (1D) micro/nano-tubular materials have attracted a great deal of attention.¹² Meanwhile, various POM-based tubular materials have been obtained.¹³ Tubular architectures may endow the materials with novel properties and versatile technological applications.¹⁴ For instance, Cooper and Cronin have realized a real-time direction control of self-fabricating POM-based microtubes, which could be used as microreactor components.^{13a} Wang and co-workers have obtained Zn_{1.5}PW₁₂O₄₀ nanotubes which have a better performance in dye decolorization.^{13b}

Here, we report the preparation of fluorescent microtubes (designated SiW₁₂-F), which are consisted of α -Keggin tungstosilicate (SiW₁₂) and F dye. The SiW₁₂-F microtubes were obtained from K₈[α -SiW₁₁O₃₉] (SiW₁₁) and sodium fluorescein (FS) in an acidic medium by using a method similar to that reported previously.^{15†}

An optical micrograph of SiW₁₂-F microtubes is shown in Fig. 1(A), and an ESEM-FEG image is shown in Fig. 1(B). The length of SiW₁₂-F microtubes is around 3 mm; the wall thickness and inner diameter are in the range of 15–35 μ m and 60–100 μ m, respectively.

To clarify the mechanism of tube formation, an experiment was done in which SiW₁₂ microtubes were physically dyed with FS (Fig. S1, ESI†). Fig. S1 (ESI†) clearly shows that completely different from the physically fluorescein-dyed SiW₁₂ microtubes (SiW₁₂/F), the as-synthesized SiW₁₂-F microtubes present uniform yellow. The mechanism of tube formation should resemble the SiW₁₂-AA microtubes,^{15b} whereas a two-step

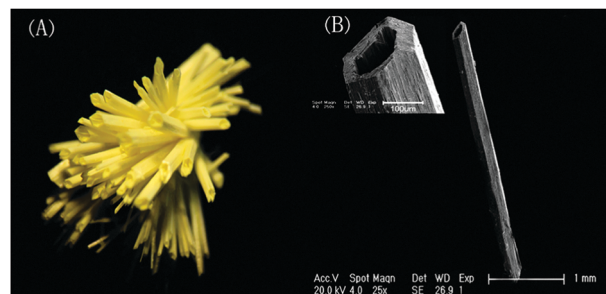
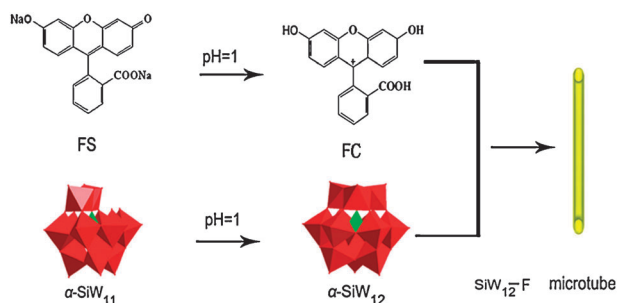


Fig. 1 (A) Optical micrograph and (B) ESEM-FEG image of SiW₁₂-F microtubes.

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† Electronic supplementary information (ESI) available: Control experiment; TG; IR; XRD; solid-state fluorescence emission spectra; optical micrograph images; time-scan fluorescence spectra; UV-Vis spectra. See DOI: 10.1039/c2cc00132b



Scheme 1 Fabrication of SiW₁₂-F microtubes *via* a two-step process.

process is deduced (Scheme 1). Firstly, two parallel reactions occur in an HCl solution of pH = 1: Keggin-type SiW₁₁ anions, which are unstable in acidic media, transform to saturated Keggin-type SiW₁₂ anions; dopant FS dye is protonated to form FC in the acidic solution. Secondly, FCs combine with SiW₁₂ anions through electrostatic interaction, and are doped finally into the hollow crystals, in the growing process of tubes. This approach has proved highly effective for synthesis of other fluorescent dye-doped microtubes (Fig. S2, ESI†).

The FT-IR spectrum of the SiW₁₂-F microtubes (Fig. S3, ESI†) contains four characteristic absorption bands of $\nu_{\text{as}}(\text{W}-\text{O}-\text{W})$, $\nu_{\text{as}}(\text{Si}-\text{O}-\text{a})$, $\nu_{\text{as}}(\text{W}=\text{O})$ and $\nu_{\text{as}}(\text{W}-\text{O}-\text{b}-\text{W})$ between 500 and 1000 cm⁻¹ expected for α -Keggin polyoxoanions,¹⁶ with shifts of 10–20 cm⁻¹ compared with those of pure SiW₁₂ species due to incorporation of FCs along with SiW₁₂ anions. The absorption bands in the range of 1400–1800 cm⁻¹ and 3000–3500 cm⁻¹ are from F.

The XRD patterns found for SiW₁₂-F microtubes are similar to those found for SiW₁₂ microtubes (Fig. S4, ESI†), with the latter being indexed to the orthorhombic phase of K₄SiW₁₂O₄₀ (JCPDS 70-1714). These results verify that the structure of crystalline K₄SiW₁₂O₄₀ is maintained in the SiW₁₂-F microtubes. Integrating the results of IR, XRD, TG (Fig. S5, ESI†) and element analysis measurements, a formula K_{3.98}(C₂₀H₁₃O₅)_{0.02}[SiW₁₂O₄₀]·4H₂O is established for SiW₁₂-F microtubes.

The solid UV-Vis spectrum obtained from SiW₁₂-F microtubes presents not only the characteristic O → W charge transfer (CT) transition band of the POM at 263 nm but also a new absorption band at 443 nm attributable to the dopant F, as the maximum absorption of FS in the visible region appears at 506 nm (Fig. S6, ESI†). A hypsochromic shift of *ca.* 60 nm is reasonably ascribed to the formation of counterion pairs between [α-SiW₁₂O₄₀]⁴⁻ and FC in SiW₁₂-F microtubes.

Comparative studies on solid-state fluorescent properties of SiW₁₂-F microtubes and FS have been made. Fluorescence microscopy images reveal that an individual SiW₁₂-F microtube fluoresces visibly from sky blue to green to red, while FS powder fluoresces from orange to green to red, under irradiation of diverse light sources from violet light to blue light to green light, respectively (Fig. 2). This difference implies that new fluorophores are generated in SiW₁₂-F microtubes.

This conclusion is verified by fluorescence emission spectra, when excited with 380 nm light which corresponds to violet light. In the fluorescence emission spectra, a broad emission band with a maximum around 500 nm is observed for SiW₁₂-F microtubes, which corresponds to blue–green fluorescence; in

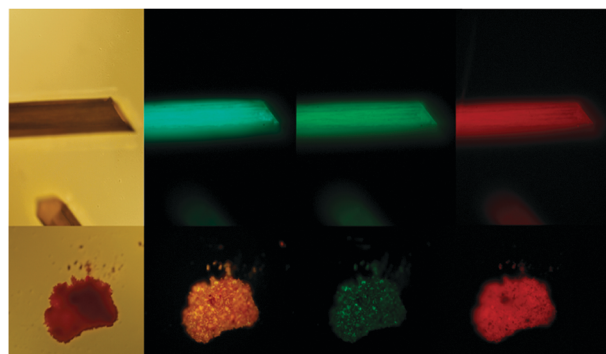


Fig. 2 Fluorescence microscopy images of an individual SiW₁₂-F microtube (up) and a powder sample of FS (bottom). The light source in the order from left to right is visible, violet, blue and green light.

contrast, a broad emission band covering a wavelength range from yellow to red region with a maximum at *ca.* 600 nm is observed for FS (Fig. 3 and Fig. S7, ESI†). This result proves that fluorescence of F is not quenched by SiW₁₂, which is different from the most reported POMs,¹⁷ whereas new fluorophores fluoresce visibly in sky blue color.

PL lifetimes were obtained under the conditions of most effective excitation and emission (excitation at 380 nm and emission at 508 nm for SiW₁₂-F microtubes; excitation at 350 nm and emission at 650 nm for FS). The emissions follow a biexponential decay pattern with τ_1 of 0.9 s (3.12%) and τ_2 of 12.1 s (96.88%) for SiW₁₂-F microtubes; τ_1 of 1.7 s (12.43%) and τ_2 of 11.6 s (87.57%) for FS. The value of τ_2 of SiW₁₂-F microtubes slightly increases because the non-radiative decay process is suppressed by SiW₁₂.

PL stability was studied with time-scan fluorescence spectra (Fig. S8, ESI†). Fig. S8 (ESI†) shows that the emission-intensity of FS is almost unchanged during the given period, while a gradual increase in emission-intensity of SiW₁₂-F microtubes is observed, perhaps owing to the elimination of defect states in SiW₁₂-F microtubes by UV-radiation.¹⁸ This result proves that the PL of SiW₁₂-F microtubes is stable during the measuring period.

Photobleaching experiments of FS in the presence of diverse quantities of SiW₁₂ were conducted to understand if SiW₁₂ had an effect on photocatalytic decolorization of dyes as most

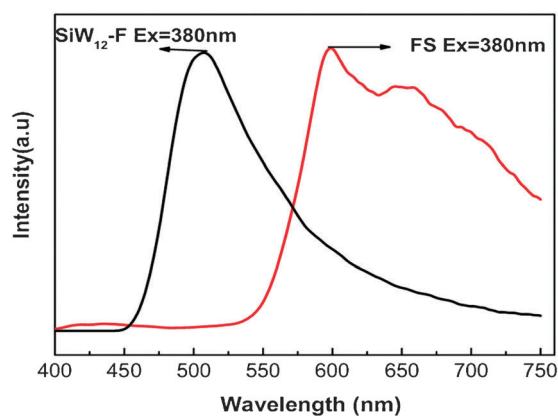


Fig. 3 Solid-state fluorescence emission spectra obtained from SiW₁₂-F microtubes, FC and FS powder at room temperature (Ex = excitation).

of the reported POMs¹⁹ or just had an electrostatic interaction with the F dye molecules. These experiments were monitored by UV-Vis spectroscopy. The visible spectra showed that, along with the increase in SiW₁₂ content, absorption intensity of FS enhanced gradually upon irradiation with daylight (Fig. S8, ESI†). This fact means that SiW₁₂ has an inhibiting effect on photobleaching FS dye through electrostatic interaction.

In summary, SiW₁₂-F microtubes have been prepared by a simple approach through a two-step chemical reaction route. This method can be extended to the synthesis of other fluorescence dye-doped SiW₁₂ microtubes. In the SiW₁₂-F microtubes, new luminescence centres are formed, and the microtubes exhibit tunable PL from sky blue to green to red by variation of excitation light. Additionally, in SiW₁₂-F microtubes, the POM component does not play a role of fluorescence quencher; in contrast, it can inhibit photobleaching of F. These results indicate that microtubes based on polyoxometalate and fluorescence dye hold potential in chemo- and biosensors, wavelength converter and display materials.

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Notes and references

† Synthesis of SiW₁₂-F microtubes: in a typical procedure, 3 g of α -SiW₁₁ was dissolved in 10 mL of deionized water in a beaker having an internal scratched bottom, 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 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 SiW₁₂-F microtubes, which were obtained from a mother liquor containing a max quantity of FS: anal. calcd for (%) C, 0.15; H, 0.27; K, 5.01; found for (%) C, 0.20; H, 0.23; K, 4.32.

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