

Preparation and Characterization of Fluorescent SiO₂ Microspheres

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Abstract. Fluorescent compound without typical fluorophores was synthesized with citric acid (CA) and aminopropyltriethoxysilane (APTS) firstly, and then it was grafted to the surface of the prepared SiO₂ microspheres by chemical reaction. The fluorescent SiO₂ microspheres with good fluorescent properties were obtained by optimizing the reaction conditions. And the morphology and structure of the fluorescent SiO₂ microspheres have been characterized by scanning electron microscopy (SEM) and fourier transform infrared (FTIR) spectroscopy. The results showed that the preparation of fluorescent SiO₂ microspheres have good monodispersity and narrow particle size distribution. Moreover, the fluorescent SiO₂ microspheres can be applied to detect Fe³⁺ in aqueous solution, prepare fluorescent SiO₂ rubber, and have potential to be applied in the fluorescent labeling and fingerprint appearing technique fields.

1. Introduction

Fluorescent microspheres are a kind of solid fluorescent nanoparticles which can emit fluorescence when stimulated by external energy. In recent years, with the development of biotechnology, the convergence of nanotechnology and biotechnology has been promoted [1-3]. Fluorescent microspheres have great potential in molecular tracing, drug screening and other fields due to their unique fluorescence properties and material properties [4-6]. Silica microspheres are very important inorganic nanomaterials which have high specific surface area, good physical chemical stability, good light transmission and low biological toxicity [7-9]. Therefore, it is a good choice to use silica microspheres as a carrier to prepare fluorescent microspheres. Generally, there are two methods to prepare fluorescent silica microspheres. One is physical method [10, 11]. That is adding the silica microspheres into the solution that containing fluorescent materials, the fluorescent materials can deposited on the surface of the microspheres by physical adsorption. The other is chemical method [12], which means the fluorescent substance grafted to the surface of the silica microspheres by the reaction of active groups. In this paper, we synthesis a kind of fluorescent compound with citric acid (CA) and aminopropyltriethoxysilane (APTS) to use as the fluorochrome. And then the compounds were grafted to the surface of prepared silica microspheres by chemical bonding. The obtained fluorescent microspheres have good fluorescent performance and water-soluble. Moreover, they can be used to detect Fe³⁺ ions in aqueous solution, could be doped into silicone rubber to produce fluorescent silicone rubber, and could be used as one of the fluorescence indicator and fingerprints luminescent dye reagent.



2. Experiments

2.1. Chemicals and Devices

Citric acid, thionyl chloride and γ -aminopropyl trimethoxy silane was all purchased from Aladdin Industrial Corporation (China). Tetrahydrofuran (THF), alcohol and N-hexane were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. All reagents are of analytical reagent grade and used as received. The solution of different ions (10^{-3} mol L $^{-1}$) were prepared in deionized water from the respective salts of NaCl, CaCl $_2$, CuCl $_2 \cdot 2H_2O$, FeCl $_3 \cdot 6H_2O$, HgCl $_2$, NiCl $_2 \cdot 6H_2O$, CoCl $_3 \cdot 6H_2O$, and ZnCl $_2$.

Ultraviolet-Visible and Photoluminescence spectra were recorded by a Shimadzu UV2550 spectrophotometer and a Fluoromax-4 spectrophotometer (Horiba JY, France). Fourier transformed infrared spectroscopy (FTIR) spectra were carried out on a Nicolet 380 FTIR (Thermo Nicolet). Spectrometer with the KBr pellet technique. The morphology of the products were observed on a QUANTAN FEG250 scanning electron microscope (SEM).

2.2. Synthesis

The synthesis routes of the fluorescent compound (CA-APTS) and the fluorescent SiO $_2$ microspheres are shown in figure 1. And the detailed prepared processes are described followed.

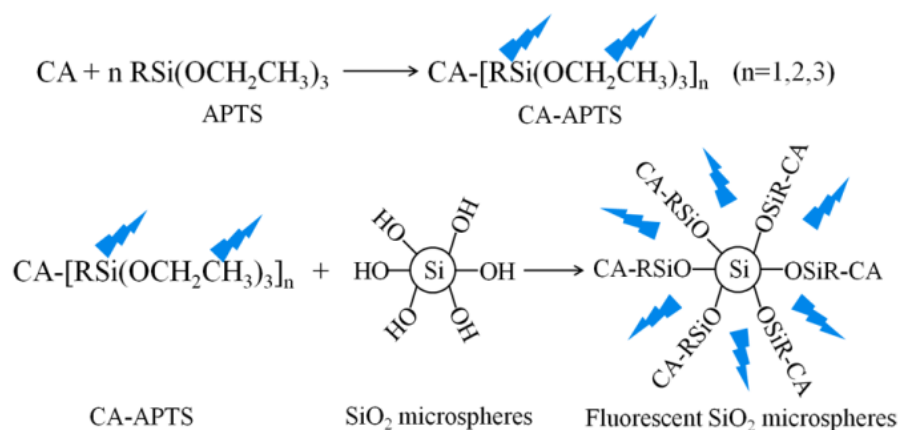


Figure 1. The synthesis routes of the CA-APTS and fluorescent SiO $_2$ microspheres.

2.2.1. Synthesis of fluorescent small molecules. Firstly, 1 g CA was dissolved in 15 mL THF, 1.2 mL thionyl chloride was added and kept in an ice bath under stirring overnight. Next, the mixture above was rotary evaporated for three times to remove impurities and byproducts, and the product (CAC) was resolved in 10 mL THF. Next, 1 mL APTS was added to the CAC solution and kept stirring at room temperature for 3 h. Finally, the CA-APTS was obtained after purification.

2.2.2. Synthesis of SiO $_2$ microspheres. The silica microspheres were prepared by Stober method [13]. Briefly, 500 mL ethyl alcohol, 50 mL water and 15 mL ammonia were added into the 1000 mL beaker. The mixture was stirring at room temperature for 30 minutes. Then 5 mL ethyl silicate was dripped into the above solution, and stirred for 6 h to reach the full reaction. After that, the solution was centrifuged to obtain the settling out and then the precipitates were washed with deionized water repeatedly. Finally the SiO $_2$ microspheres can be obtained after drying in vacuum less than 50 °C.

2.2.3. Synthesis of fluorescent SiO $_2$ microspheres. 0.2 g silica microspheres were put into 100 mL beaker with 40 mL tetrahydrofuran, stirring well and then adding suitable amount of prepared fluorescent compound (0.002 to 0.032 g). The reaction temperature is -10 °C, 10 °C and 30 °C respectively, and the aging time was varied from 1 to 24 h. Then the mixture was centrifuged to obtain the precipitates and the it was washed with deionized water repeatedly until the fluorescence cannot be detected in the washing liquid. Finally, the fluorescent SiO $_2$ microspheres can be obtained after drying

in vacuum under 50 °C. The best weight ratio, temperature and time were obtained by comparing the fluorescence intensity of the products.

3. Results and Discussion

With the increasing weight of CA-APTS, the fluorescence intensity of the prepared fluorescent SiO₂ microspheres is increased until the weight reaches to 0.016 g and then the intensity remains unchanged when the weight is over 0.016 g (Figure 2a). That is, the optimal weight ratio of SiO₂ microspheres to CA-APTS is 0.2: 0.016. Figure 2b shows that the fluorescence intensity is increased significantly when the temperature rises from -10 °C to 10 °C. However, when the temperature continues to rise to 30 °C, the fluorescence intensity is increased slightly, which means that the fluorescence intensity of the fluorescent SiO₂ microspheres can reach to the maximum at 30 °C. From figure 2c, we can draw that the optimum reaction time is 12 h, because the fluorescence intensity of the fluorescent SiO₂ microspheres is increased continuously before the time came to 12 h, and then stays the same. So far, the best condition for the preparation of the fluorescent SiO₂ microspheres is obtained. Next, the morphology and structure characterization and application of the fluorescent SiO₂ microspheres prepared under the optimal condition are studied.

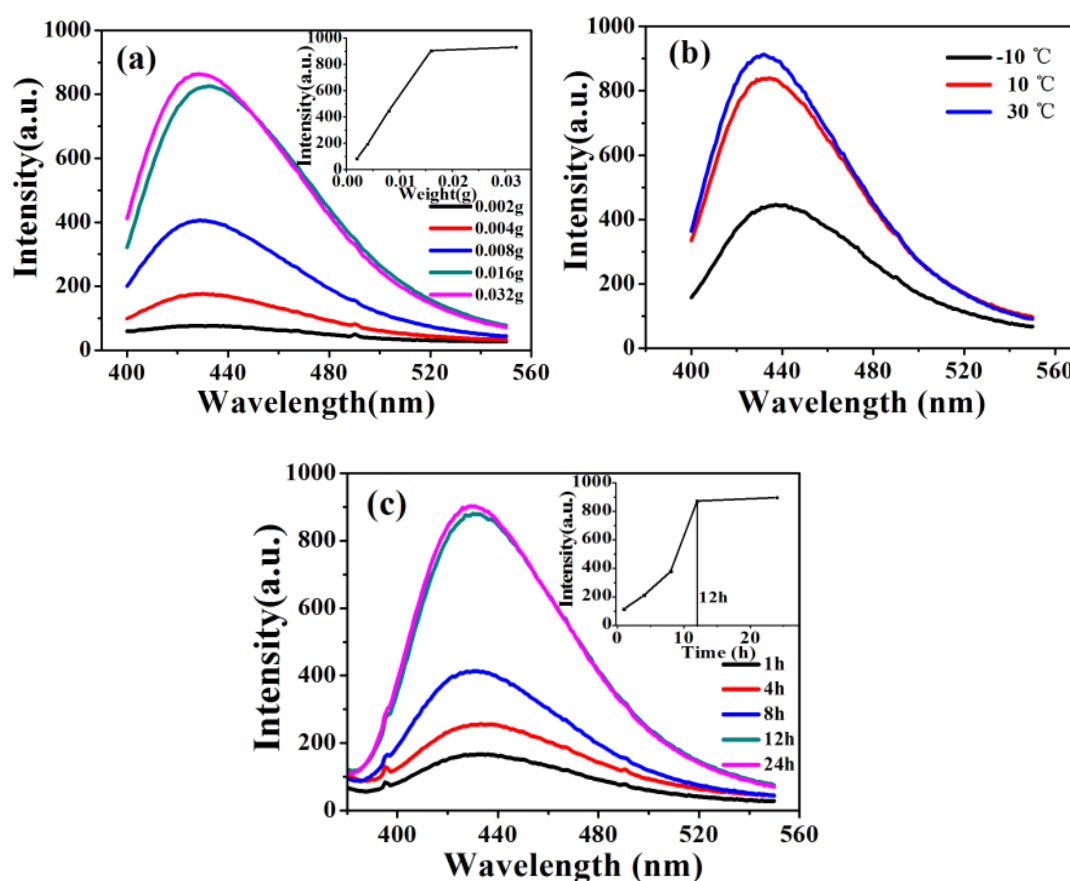


Figure 2. The Variation of fluorescence spectra of fluorescent SiO₂ microspheres prepared under different conditions: (a) different weight ratio; (b) different temperature; and (c) different time.

Figure 3 shows the SEM images of the SiO₂ microspheres and fluorescent SiO₂ microspheres. It can be seen from the figure that they have good monodispersity and narrow particle size distribution. And the particle size of the microspheres has been changed after grafted with CA-APTS. The distribution of the particle size of silica microspheres is from 114 to 152 nm, while it of fluorescent SiO₂ microspheres is from 120 to 157 nm.

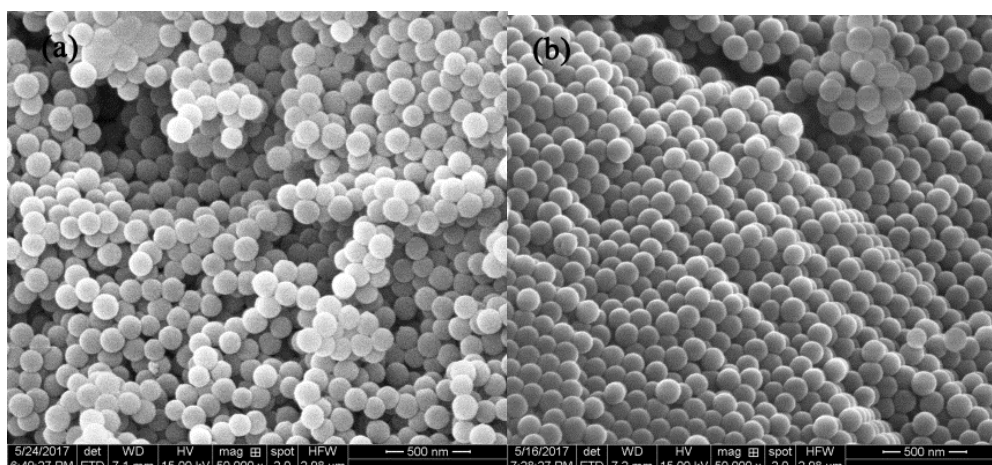


Figure 3. The SEM images of SiO₂ microspheres (a) and fluorescent SiO₂ microspheres (b).

Comparing the FTIR spectra (Figure 4) of silica microspheres and fluorescent SiO₂ microsphere, obvious changes can be observed. The peak at 1100 cm⁻¹ is assigned to the stretching vibration peak of Si-O-Si skeleton. Signals at 3440 cm⁻¹ and 948 cm⁻¹ are attributed to the stretching vibration and bending vibration of Si-OH groups, respectively. The peak at 795 cm⁻¹ and 460 cm⁻¹ are the symmetric stretching vibration and bending vibration of Si-O, suggesting that both microspheres are composed of Si-O-Si network structure. However, compared with the SiO₂ microspheres, the peak of Si-OH of the fluorescent SiO₂ microspheres is weakened and the peak of Si-O-Si become more stronger, because the CA-APTS reacted with Si-OH and formed Si-O-Si structure. And the signal at 2834-2946 cm⁻¹ of the fluorescent SiO₂ microsphere are attributed to methylene of APTS. The above changes prove that the modification is successful.

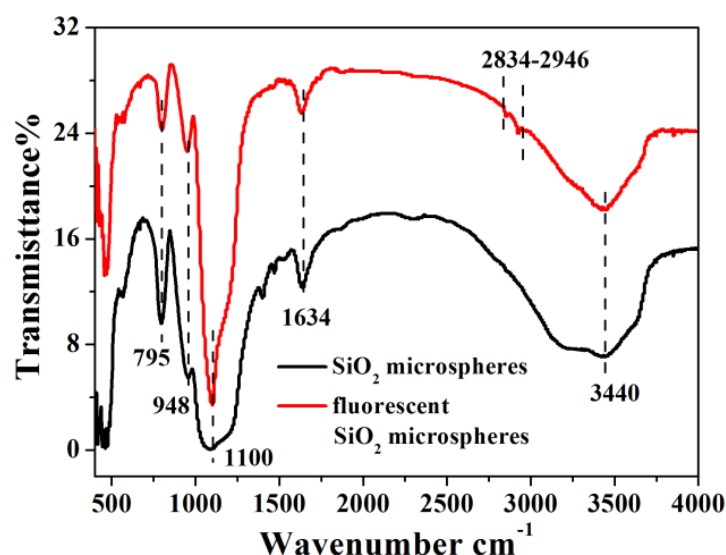


Figure 4. FTIR spectra of SiO₂ microspheres and fluorescent SiO₂ microspheres.

Furthermore, the fluorescent SiO₂ microspheres can be used to detect Fe³⁺ ions in aqueous solution. Each of the ions, including Ni²⁺, Ca²⁺, Cu²⁺, Co³⁺, Hg²⁺, Na⁺, Zn²⁺, and Fe³⁺, was added into the aqueous solutions of fluorescent SiO₂ microspheres (6 μg mL⁻¹; final concentration of ions: 10⁻⁵ mol L⁻¹). Figure 5 shows that among the ions tested, Fe³⁺ ions has the greatest effect on fluorescence quenching, while the other ions have only a slight effect which is negligible. And when the concentration of the Fe³⁺ reached to 70 μM, the fluorescence of the solution was almost completely quenched.

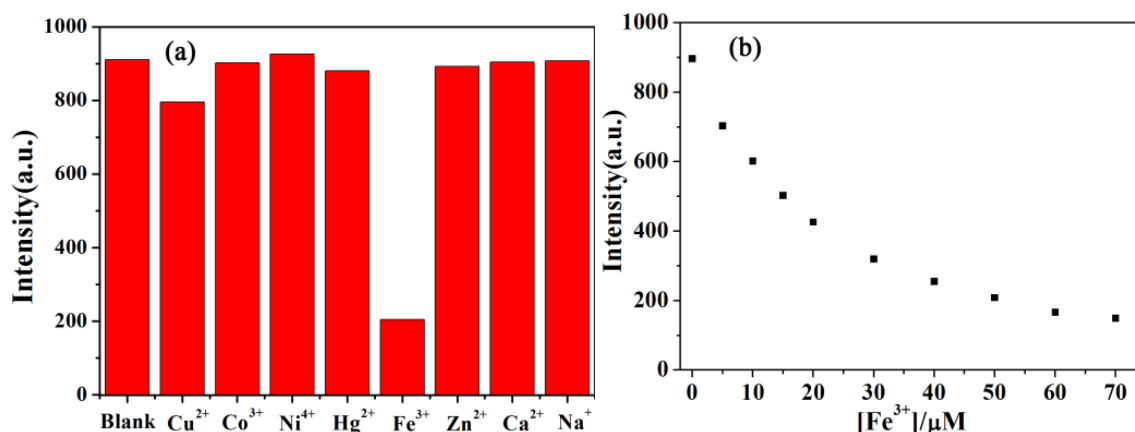


Figure 5. (a) Fluorescence intensity of the fluorescent SiO₂ microspheres aqueous solution in the presence of 50 μM of various metal ions with $\lambda_{\text{ex}}=350$ nm. (b) The changes of the fluorescence intensity in the presence of increasing concentration of Fe³⁺.

Silica microsphere is a common modified padding of silicone rubber which can enhance their mechanical properties and thermal stability. As figure 6 depicted, we doped different amount of the fluorescent SiO₂ microspheres (0.05-0.2%) in the silicone rubber, and obtained the fluorescent silicone rubber with different strength and different fluorescent intensity.

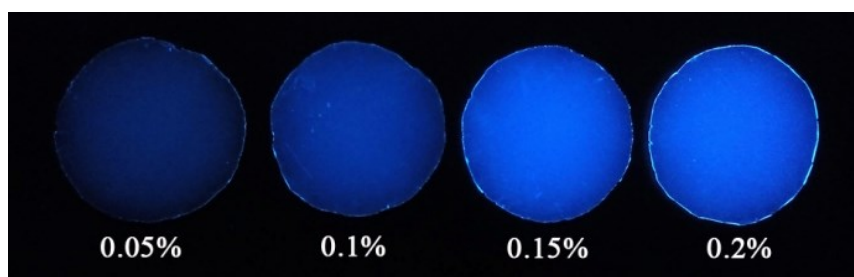


Figure 6. The photograph of prepared fluorescent silicone rubber Doped with different amount of fluorescent SiO₂ microspheres.

Interestingly, the fluorescent SiO₂ microspheres also have potential to be applied in the fluorescent labeling and fingerprint appearing technique fields. As Figure 7a and b showed, there is no fluorescence of cotton fibers itself, but after stained by the fluorescent SiO₂ microspheres solution and drying, they emit bright blue fluorescence under the UV light. It indicates that the fluorescent SiO₂ microspheres can be used in the fluorescent labelling field. What's more, fluorescent powder is one of the commonly selection to marked the fingerprint in criminal cases' detection. Figure 7c, d and e displayed that after sprinkling the fluorescent SiO₂ microspheres on the filter membrane with fingerprints, the pattern of fingerprints is appeared under UV light while there is nothing under nature light. It suggests that the fluorescent SiO₂ microspheres can be used as one of the fingerprints luminescent dye reagent.

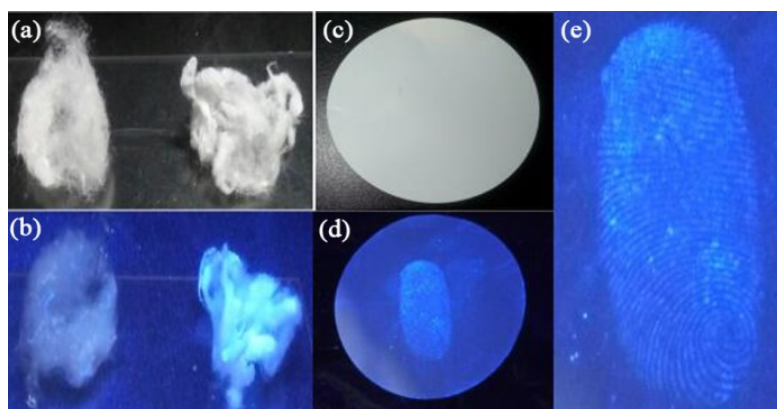


Figure 7. The photograph of cotton fibrils before and after stained by the solution of fluorescent SiO₂ microspheres under nature (a) and UV light (b); And the photograph of fingerprints appeared by the fluorescent SiO₂ microspheres under nature light (c) and UV light (d) and (e).

4. Conclusion

We prepared a kind of fluorescent SiO₂ microspheres with good fluorescent properties using CA-APTS and silica microspheres. The FTIR spectra indicate that the modification is successful. And the SEM images suggest that the fluorescent SiO₂ microspheres have good monodispersity and narrow particle size distribution. Moreover, the fluorescent SiO₂ microspheres can be applied to detect Fe³⁺ in aqueous solution, prepare fluorescent silicon rubber, and could be applied as fluorescence indicator and fingerprints luminescent dye reagent.

5. Acknowledgments

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6. References

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