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Synthesis and Characterization of Fluorescent Mesoporous Silica(Znq-CMS)with a Zinc Complex of 8-Hydroxyquinoline

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Abstract. This experiment is to prepare fluorescent mesoporous silica and explore its characteristics of the zinc complex of 8-hydroxyquinoline, synthesize CMS-SH by base-catalyzed sol-gel method, and then complex the zinc complex of 8-hydroxyquinoline. Go in and successfully synthesize Znq-CMS. In addition, the particle size and potential of CMS-SH and Znq-CMS were characterized by dynamic scattering (DLS), and the fluorescence characteristics of Znq-CMS were characterized by a fluorescence spectrophotometer and an ultraviolet lamp. The results show that Znq-CMS has good dispersibility and fluorescence effect. The purpose of this study is to explore a new model of drug delivery system for stimulus response.

1. Introduction

Despite the great development of various effective nanomaterial-based drug delivery systems (DDSs), such as liposomes, polymeric micelles, carbon nanotubes, inorganic nanoparticles, and silica-based materials [1], the ideal stimuli-responsive DDSs are still in great challenges to have the following characteristics: (i) identify, label and locate malignant tumor cells Specifically [2], (ii) modulate drug release profiles [3], (iii) Monitoring of Drug Release in vivo. From a certain point of view, mesoporous silica nanoparticles (MSN) with large surface area and microporous volume capacity have obvious advantages. Because of its easy control of internal aperture and high biocompatibility, it is more suitable for biomedical applications such as imaging in vivo, disease diagnosis, sensing, biochemical reaction catalysis, tissue and organ repair, scaffold engineering and drug targeting delivery[4,5]. These ordered pore network systems unique to MSN can make macromolecular groups or nanoparticles loaded with specific substances on the outer surface of MSN molecules in the same pore, thus closing the pore system. Closed MSN can change the speed of drug release by sensing internal or external changes such as temperature, light, magnetic field, pressure, redox potential, etc. [6,7].

In recent years, redox reaction has been widely used to control the release of targeted drugs in vivo. The core of this mechanism is the breaking of disulfide bond in high concentration glutathione (GSH) environment. Generally, the concentration of GSH in plasma and normal cells is low and stable, while the concentration of GSH in tumor cells is 103 times higher than that in normal organisms. At this time, disulfide bond breaks, which opens the pore closure system on the surface of particles, and the targeted therapeutic drugs are successfully released.



Although various stimulating responsive MSNs have been reports for drug delivery, How to use digital signal system to realize real-time detection function will become the next research focus. The continuous upgrading of fluorescence imaging system provides a direction for our research. Zinc is one of the trace elements essential for the human body and plays an important role in regulating the structure and function of enzymes, the transmission of nerve signals and the expression of genes [8]. In addition, 8-hydroxyquinoline (8-Hq) and its derivatives have attracted a great deal of attention because of their tendency to form stable complexes with metal cations [9]. In this paper, a method for synthesizing a fluorescent mesoporous silica with a zinc complex of 8-hydroxyquinoline (Znq-CMS) will be described and characterized (Figure.1).

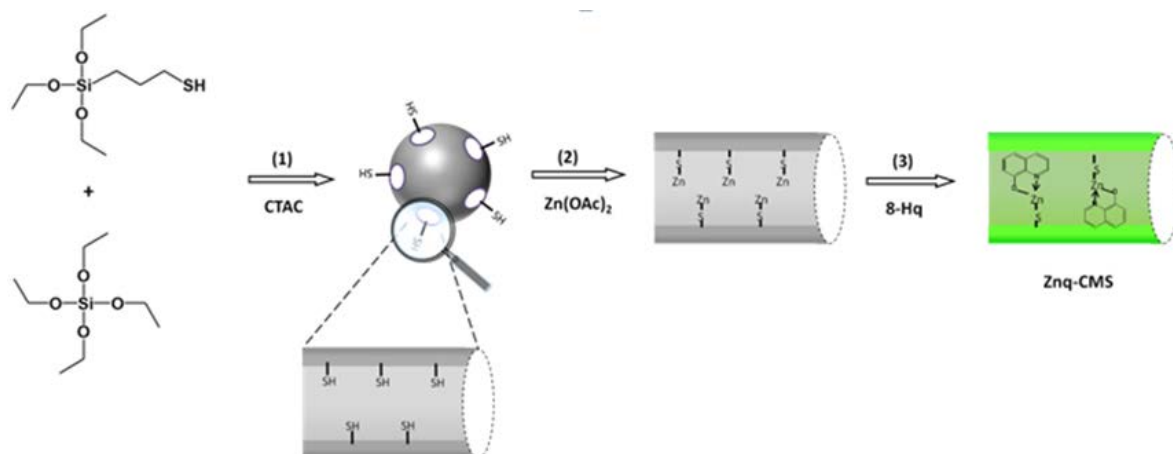


Figure 1. Schematic illustration of the synthesis route of Znq-CMS

2. Experimental Section

2.1. Materials

Hexadecyl trimethyl ammonium chloride (CTAC), Tetraethoxysilane (TEOS), triethylamine (TEA), 3-mercaptopropyl-trimethoxysilane (MPTES) were all purchased from Aladdin Chemistry Co. (Shanghai). 8-Hydroxyquinoline (Hq), hydrochloric acid, acetic acid, absolute ethanol, were purchased from Sinopharm Chemical Reagent Co. (China).

2.2. Preparation of mesoporous silica nanoparticles (CMS-SH)

The preparation method is based on the alkali catalyzed sol-gel method recommended by previous literatures. At room temperature of 25 °C, 10.4 ml 25 wt% CTAC, 64 ml water and 10.5 ml ethanol were fully mixed and stirred evenly (10 min). Then, 4.125 ml triethanolamine was added to the mixing system and stirred for 15 minutes. The 20 ml oil bath of the above solution was heated to 60 °C, and 1.45 ml TEOS and 0.163 ml MPTES were added into the solution rapidly. Then the mixture was stirred continuously for 2 hours in 60 °C nitrogen atmosphere. The mixed liquid was put into a normal temperature centrifuge for 30 minutes at 10000 rpm/separation center. The precipitation was washed twice with absolute ethanol. The product was then refluxed twice in a mixture of 15 ml hydrochloric acid and 140 ml anhydrous ethanol at 60 °C for 2 hours. Finally, CMS-SH surfactant was removed by high-speed centrifugation. The product was washed repeatedly with distilled water and ethanol and then put into ethanol solution (5 mg/ml).

2.3. Synthesis of Znq-CMS

20 ml CMS-SH was removed and centrifuged in a high-speed centrifuge (10000 rpm/min). The product was washed with ultra-pure water. Subsequently, the precipitates were centrifuged and dispersed in 9.5 ml 0.05 mol/L zinc (AC) 2 solution at low speed. The mixed products were stirred in a room temperature container for 12 hours. Finally, the mixture was centrifuged in a centrifuge (8000 rpm/min), centrifuged for 10 minutes, washed with ethanol three times, and then dispersed in

pure water. 9.7 mg of 8-hydroxyquinoline (8-Hq) dissolved in 25 mL of ethanol was added dropwise to 20 mL of 5mg/mL the above solution at room temperature under stirring for 48 h. The resulting solids of fluorescent mesoporous silica nanoparticles (Znq-CMS) were centrifuged at 10000 r/min for 15 min and washed with ethanol until the supernatant was colorless, and finally dispersed in ethanol (Fig. 1A). Note: The reaction starts at 18:00-19:30 in the evening, and the obtained silicon spheres can be dispensed without quantification. Each batch is directly dispersed in 20 ml of water for the next reaction.

2.4. Characterizations

Malvern Zetasizer Nano ZS90 can be used to measure the particle size and zeta potential. UV-Vis absorption spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer. Fourier transform infrared (FT-IR) spectrum was noted on Nicolet Nexus 470. Fluorescence emission spectra were measured on a Perkin Elmer LS-55 fluorescence spectrophotometry.

3. Results and Discussions

Figure 2 shows FT-IR spectroscopic analysis of Znq-CMS and CMS-SH. Compared with the infrared spectrum of CMS-SH, the characteristic peak of mercapto group disappeared at 2561 cm^{-1} after doping the metallo-quinolates (Znq) complex by in-situ method and the appearance of peaks at 1500 cm^{-1} , 1465 cm^{-1} and 1384 cm^{-1} and 1322 cm^{-1} was the vibrational peaks of the pyridyl and phenyl groups of Znq, indicating the formation of the coordination compounds with the mercapto and 8-hydroxyquinoline incorporated in the channels of CMS-SH.

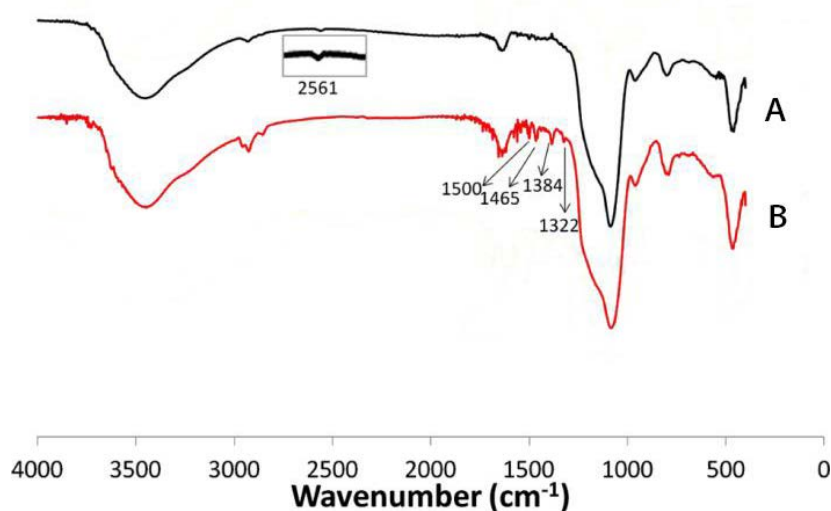


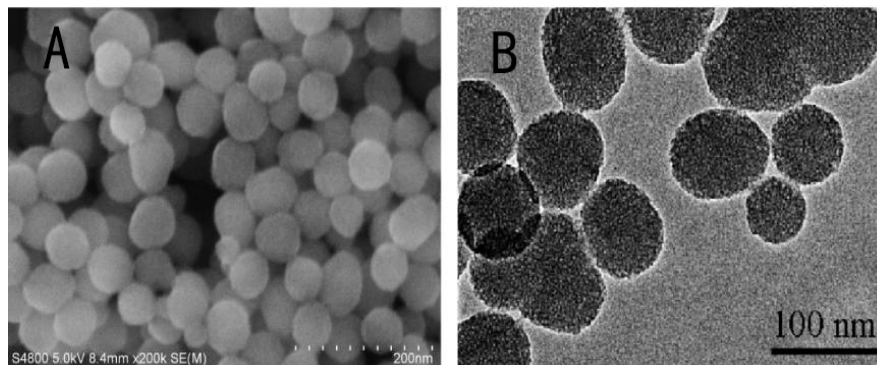
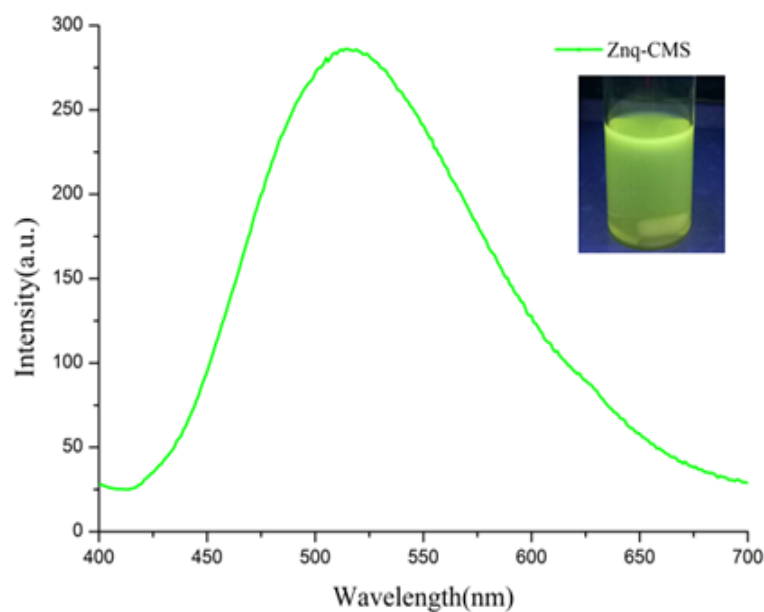
Figure 2. FT-IR spectra of CMS-SH (A) and Znq-CMS (B)

As shown in Figure 3(A), the SEM image of Znq-CMS had a good spherical morphology with relatively uniform particle size and an average particle diameter. As shown in Figure 3(B), The TEM image of Znq-CMS displayed a spherical morphology and uniform distribution with a wormhole arrangement of the mesopores. The mesoporous structure of Znq-CMS became almost invisible due to the combination of the mesoporous silica nanoparticles by the fluorescent 8-Hydroxyquinoline (Hq). Because of the existence of hydration layer, the particle diameter measured by TEM is found to be lower than that measured by DLS.

The data of particle diameter and zeta potential measured by DLS. As shown in table 1, The sulfhydryl-modified mesoporous silica has a particle size of 117.5 nm and a PDI of 0.102, and has good dispersibility and a potential of -28.3 mV. The negative charge is mainly due to the presence of a large amount of silanol hydroxyl groups on the mesoporous silica surface. After doping with Zn^{2+} and 8-hydroxyquinoline, the potential increase may be the result of the interaction of Zn^{2+} with the surface hydroxyl groups of some nanoparticles, and PDI 0.06 exhibits good dispersibility.

Table 1. DLS measurements of CMS-SH, Znq-CMS

	Size (nm)	PDI	Zeta (mV)
CMS-SH	117.5	0.102	-28.3
Znq-CMS	140.4	0.06	-18

**Figure 3.** SEM (A) and TEM (B) of Znq-CMS, respectively.**Figure 4.** The fluorescence spectra of Znq-CMS in ethanol solution (excited at 380 nm, the inset is the fluorescence photographs under 365 nm UV light).

Meanwhile, The fluorescence properties were investigated on the fluorescence spectrophotometer, As shown in Figure 4, the ethanol dispersion of Znq-CMS had a strong green fluorescence under UV light irradiation, with a fluorescence emission wavelength of 510 nm at an excitation wavelength of 380 nm and a slit of 10 nm.

4. Conclusions

In this paper, fluorescent mesoporous silica with 8-hydroxyquinoline zinc complex was successfully prepared and characterized. The CMS-SH was synthesized by a base-catalyzed sol-gel method, and then Znq-CM was synthesized. In addition, CMS-SH and Znq-CMS were characterized by dynamic

scattering (DLS) and FT-IR, and the fluorescence characteristics of Znq-CMS were characterized by fluorescence spectrophotometer and UV lamp. In terms of data, Znq-CMS has good dispersibility. In terms of phenomena, Znq-CMS has a good fluorescence effect. The results obtained prove that Znq-CMS has excellent prospects in real-time monitoring of drug release and drug delivery.

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