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Synthesis and Characterization of Mesoporous Core-Shell Silica with Incorporation of Dye

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We have prepared nano size mesoporous silica using sol-gel reaction and incorporated fluorescent dye inside the silica network, and investigated fluorescent properties of the particles. Monodisperse core silica has been prepared via sol-gel reaction of TEOS (tetraethoxysilane) and water using base catalyst. The SEM images of silica cores showed that most particles were uniform and spherical with particle diameters of 187 nm. Mesoporous core-shell structure of silica with shell was prepared via further reaction with C_{18}-TMS (octadecyltrimethoxysilane) and heat treatment. The SEM image of core-shell silica shows that the average diameter is 305 nm and the thickness of shell is 118 nm. The size of silica particles was measured by electrophoretic light scattering system (ELS-8000, Otsuka). The pore volume and surface area were increased after calcination. A typical value for the specific surface area, calculated according to the BET (Brunauer–Emmett–Teller) method from nitrogen isotherms is $a_s = 400\,m^2/g$. Fluorescein isothiocyanate (FITC) could be incorporated into the silica network by coupling reaction with organic functionalized silane. The optical properties of the particles were characterized with UV/Vis spectrometer and PL spectrometer.

Keywords: FITC; incorporated dye; mesoporous silica

1. INTRODUCTION

Rapid photobleaching is one of the critical problems for organic fluorescent dyes in the process of biological assays. Numerous photochemical reactions occuring in the cellular environment can lead

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to photodegradation of the dye [1]. The encapsulation of the dye in a ceramic matrix is one methodology presently in use to maximize both *in vitro* and *in vivo* stability. The ceramic matrix minimizes oxygen access, increases chemical stability of dyes and allows surface modification of the shell to enhance hydrophilic character and cell uptake. Different techniques that are in use for encapsulation of dye include incorporation in nucleic acid and PNA oligomers [2], lipid micelles [3], polymer matrices, and encapsulation in silica matrix [4].

For these composite systems, the 'dye' encapsulated within the matrix of the nanoparticles is the source of the fluorescence. The encapsulation process may alter the fluorescence emission of the dye marginally but offers many advantages. Capturing of dye within the core prevents the dye from rapid photobleaching as it is prevented or delayed from coming into direct contact with the chemicals in the surrounding environment. Santra *et al.* [5] have recently described a novel fluorescence lifetime-based approach to determine the core-shell structure of FITC-doped silica nanoparticle. It is revealed that approximately 62% of dye molecules remained in the solvated silica shell, while 38% of dye molecules remained in the non-solvated (dry) silica core. This allows imaging process to be performed over extended periods of time. In this paper, we present new approaches to the incorporation of dyes in the pores of the colloidal particles. Fluorescein isothiocyanate (FITC) could be incorporated into the silica network by coupling reaction with organic functionalized silane. The optical properties and size of the particles were characterized with UV/Vis spectrometer, PL spectrometer, FE-SEM, BET, and TEM.

2. EXPERIMENTAL

2.1. Materials

The following chemicals were purchased from various companies and were used without further purification: TEOS (98%, Sigma), C_{18}-TMS (90% tech., Aldrich), ethanol (CARLO ERBA), ammonium hydroxide (NH_4OH, ~28–30%, J. T. Baker), fluorescein isothiocyannate (Fluka), and (3-aminopropyl)triethoxysilane (Sigma).

2.2. Synthesis of Mesoporous Core-Shell Silica

3.14 ml of aqueous ammonia (32 wt.-%) was added into a solution containing 74 ml of ethanol and 10 ml of deionized water. 6 ml of TEOS was added into the mixture at 303 K under vigorous stirring and the reaction mixture was kept stirring for 1 h to yield uniform silica spheres (Stober silica sol). A mixture containing 5 ml of TEOS and

2 ml C_{18}-TMS was added into the colloidal solution containing silica spheres and further reacted for 1 h. The resulting octadecyltrimethoxy-incorporated silica shell/solid core nanocomposites were retrieved by centrifugation, and calcined at 823 K for 6 h under oxygen atmosphere to produce mesoporous core-shell silica material.

2.3. Incorporation of Dye

The fluorescein isothiocyanate (FITC) can be covalently attached to the (3-aminopropyl)triethoxysilane (APTS) by coupling reaction of amine group with isothiocyanate. Typically, 0.14 g of APTS and 0.02 g of FITC were mixed in 1 ml of ethanol and stirred for 24 h. After that, 1 ml of ethanol containing 50 mg of calcinated mesoporous silica particles was added to the FITC mixture. The color of the particles changed from white to orange because of the incorporation of the dye.

2.4. Instrumental Analysis

The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritiecs ASAP 2020 system. Surface areas and pore volumes were determined using BET equation and the BJH method. The pore size distribution curve was obtained from the analysis of the adsorption branch of the nitrogen isotherm. The size of the particles was measured by electrophoretic light scattering system (ELS-8000, Otuska). SEM images were obtained using HITACH S-4700 microscope. TEM analysis was performed using HITACH H7600 (80 kV) microscope. Steady-state fluorescence excitation and emission spectra were obstained by using spectrofluometer luminescence spectrometer (PTI). Fluorescence image was obtained using IM-12005 Ratio Fluorescence Imaging System (Photon Technology International) equipped with xenon lamp which is connected with a fluorescent microscopy (Olympus IX71). The excitation wavelength was served at 488 nm via monochromator with a 520 nm emission filter.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Mesoporous Core-Shell Silica

Monodisperse mesoporous core-shell silica sphere templates were synthesized by using previously reported method, employing a molar ratio of TEOS/C_{18}-TMS = 5.3 [6]. The SEM images of silica cores (Fig. 1a) showed that most particles were uniform and spherical with particle diameters of 187 nm. Mesoporous silica was prepared via

further reaction with C_{18}-TMS (octadecyltrimethoxysilane) and heat treatment. The SEM image of silica core-shells shows that the average diameter is 305 nm and the thickness of shell is 118 nm (Fig. 1b). The size of silica core and core-shell was measured by ELS (Figs. 1c and d) and TEM (Fig. 2a). The pore volume and surface area were increased after calcination. A typical nitrogen isotherm at 77 K of the calcinated mesoporous silica is shown in Figure 2(b). The isotherm shows typical features of colloidal mesoporous material. The isotherm is reversible and does not show hysteresis between the adsorption and desorption branches, which is characteristic for materials with small pores. The nitrogen isotherms indicate a linear increase of the amount of adsorbed nitrogen at low pressures ($P/P_0 = 0.197$). The pore size

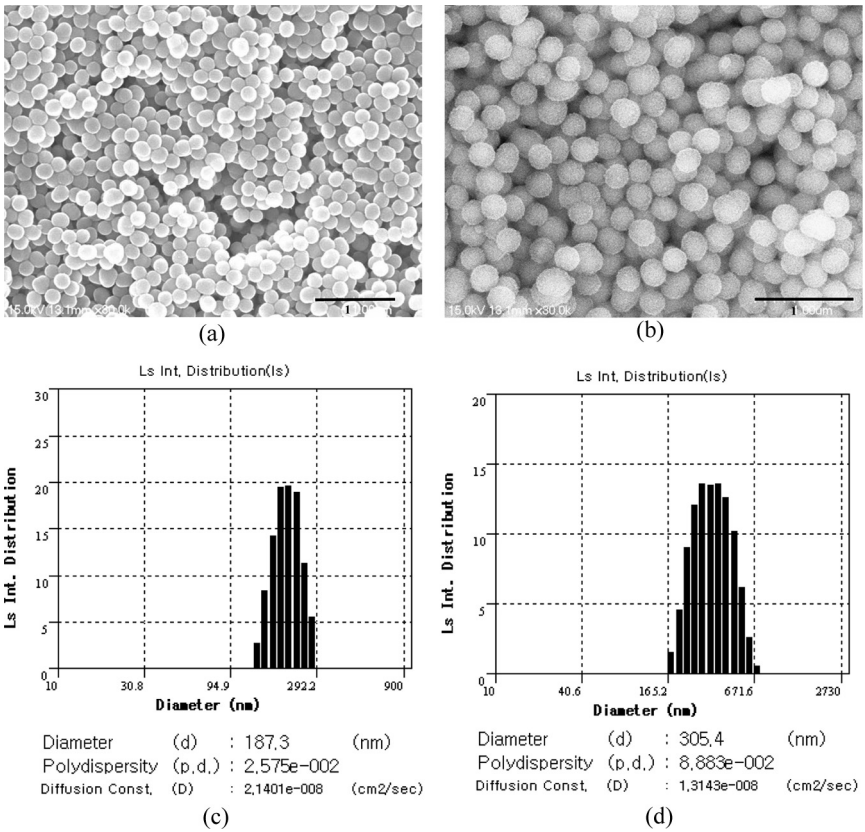
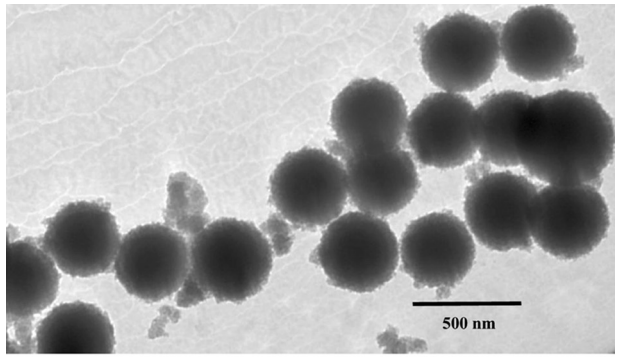
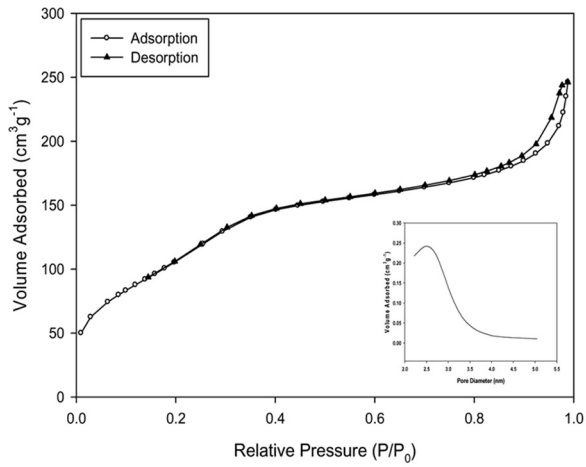


FIGURE 1 SEM images for (a) silica cores, and (b) calcinated silica core-shells, and then ELS plots of (c) silica cores and (d) calcinated silica core-shells.



(a)



(b)

FIGURE 2 Characterization of mesoporous silica with core diameter of 187 nm and shell thickness of 118 nm: (a) TEM image, and (b) N_2 adsorption/desorption isotherms and the corresponding pore size distribution (inset).

distribution data calculated from the adsorption branches of nitrogen isotherms showed that pores are uniform and centered at 2.5 nm. The meosoporous silica exhibited a BET surface area of $400\,m^2g^{-1}$ and a total pore volume of $0.33\,cm^3g^{-1}$. Their corresponding pore size distribution data calculated from the adsorption branches of nitrogen isotherms showed that the BJH adsorption average pore diameter is $4\,V/A = 4.017$ nm.

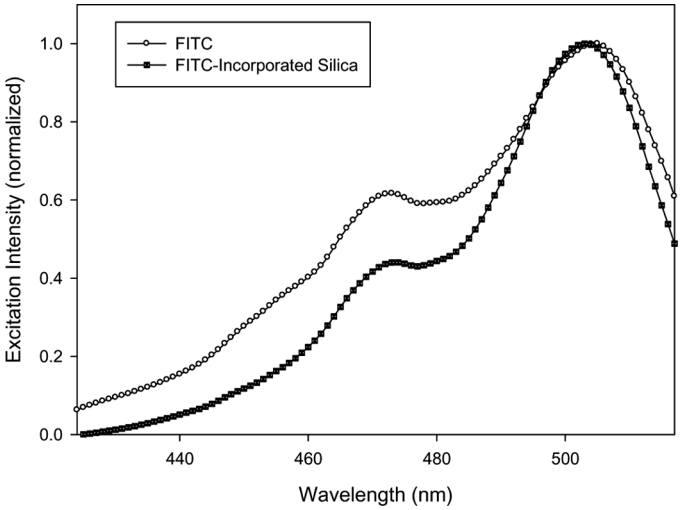


FIGURE 3 Fluorescence excitation spectra of FITC and FITC-incorporated silica in absolute ethanol. Emission wavelength is 520 nm.

3.2. Characterization of Dye-Incorporated Silica

Steady-state fluorescence excitation (Fig. 3) and fluorescence emission (Fig. 4) spectra of FITC and FITC-incorporated silica were obtained by

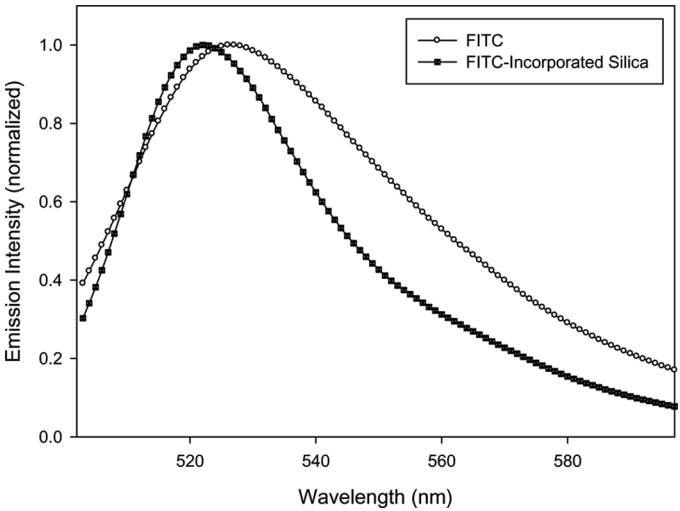
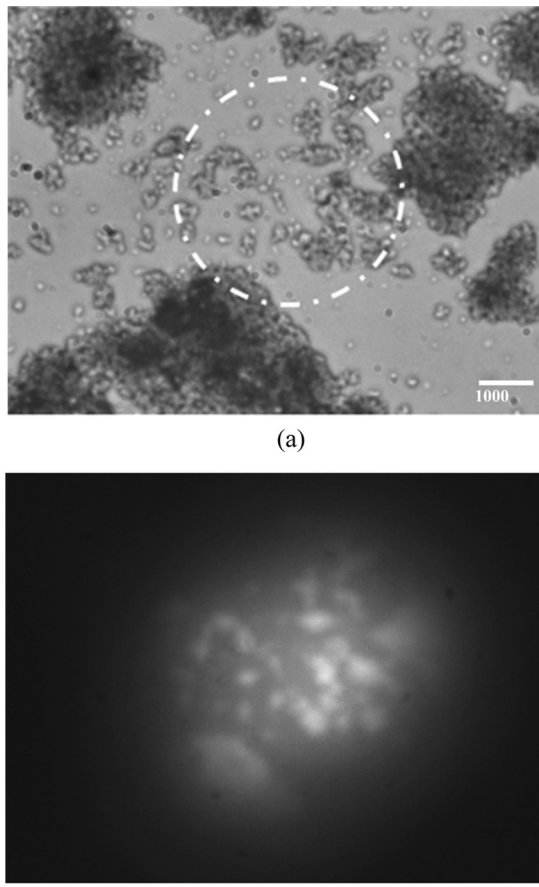


FIGURE 4 Fluorescence emission spectra of FITC and FITC-incorporated silica in absolute ethanol. Excitation wavelength is 502 nm.

using spectrofluorometer (PTI). All measurements were performed at room temperature and all experimental solutions were prepared in absolute ethanol. Fluorescence excitation (Fig. 3) and emission spectra (Fig. 4) for FITC and FITC-incorporated silica showed the presence of strong peaks at around 502 and 522 nm, respectively. The excitation wavelength of 502 nm was used by incorporating dye into silica network, both fluorescence spectra show blue shift which is observed when it is compared with the pure FITC in the solution. This is due to the presence of silica network surrounding the dye, and the blue shift could be explained as the result of the decrease of



(a)

(b)

FIGURE 5 The microscopy image (a), and the fluorescence image (b) of FITC-incorporated silica.

microenvironment by confinement into the silica network. Moreover, in order to verify incorporation of dye, FITC-incorporated silica was separated by centrifuge, washed by using alcohol, and then its fluorescence images were measured. The fluorescence microscopy image (Figs. 5a and b) show that the dye was incorporated only in mesoporous silica.

4. CONCLUSION

Core-shell structure of mesoporous was prepared by using sol-gel process with organic modified silanes. The SEM image of the silica shows uniform size distribution, and BET analysis shows typical features of colloidal mesoporous material. FITC was incorporated into the silica network via coupling reaction with amine group containing silanes, and this was confirmed by fluorescence spectra.

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