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PAPER

Preparation of multifunctional mesoporous silica particles: the use of an amphiphilic silica precursor with latent amine functionality in selective functionalization of the inner surface

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The mesoporous silica particle has three different areas as a functionalization site, including an outer surface, a silica framework and an inner surface. We functionalized the inner surface selectively using an amphiphilic silica precursor with latent amine functionality and prepared a multifunctional mesoporous silica particle showing fluorescence resonance energy transfer (FRET). An organotriethoxysilane consisting of a pervlene diimide unit and two triethoxysilyl groups was co-condensed with tetraethoxysilane and the amphiphilic organotriethoxysilane [(4-octylphenyl-3-(triethoxysilyl)propylcarbamate)] in the presence of cetyltrimethylammonium bromide under basic conditions. The resulting periodic mesoporous silica particle contained perylene diimide units in a silica framework as a FRET donor. The hydrophobic part of the amphiphile was tethered to the pore wall through a thermally reversible urethane bond. The surfactant molecules were extracted by reflux in a mixture of 1,4-dioxane, HCl and water. In this process, hydrophobic groups in the pore were also removed to produce amino groups on the inner surface. The rhodamine units were introduced into the pore as a FRET acceptor by the reaction of the isothiocyanate group of Rhodamine B isothiocyanate with the amino group on the inner surface, forming a thiourea linkage. The outer surface of the silica particle could be also functionalized by grafting with 3-(trimethoxysilyl)propyl acrylate before extraction of the surfactant molecules. A silica-polymer thin film was prepared where the silica particles were embedded in a poly(2-hydroxyethyl methacrylate) matrix. Both the suspension of the silica particles in ethanol and their polymer composite film showed the efficient FRET effect.

Introduction

Functionalized and ordered mesoporous silica particles have diverse application opportunities in catalysis,¹ separation,² sensing,³ and delivery.⁴ As a functionalization site, the mesoporous silica particle has three different areas including an outer surface, a silica framework and an inner surface. Two approaches have been used for the functionalization: co-condensation of a functional organosilica precursor with a silica precursor, which allows the introduction of functional groups into the silica framework, and grafting, which is widely used for the surface functionalization. These two methods have been used to introduce *various* organic functionalities into the mesoporous silica particle to provide appropriate properties for specific applications, but selectively functionalizing the three areas of the silica particle remains very challenging.

In recent years, several studies on the selective functionalization of the mesoporous silica nanoparticle have been reported.⁵⁻⁷ For example, Bein's group presented the site-selective functionalization by sequential or delayed co-condensation of a functional organosilica precursor and tetraethoxysilane (TEOS). The organosilica precursor participated in the condensation reaction at a different stage of the silica particle growth, resulting in the preferential incorporation of the functional group into the core or the shell of the silica particle. In a different approach, Landry's group used diffusion-based post-reaction for the selective functionalization. Both outer and inner surfaces of mesoporous silica were functionalized with 9-fluorenylmethyloxycarbonyl (Fmoc)-protected aminoalkyl silanes, after which Fmoc groups were removed by the reaction with a piperidine solution to generate an amine functionality. Differential functionalization was achieved by controlling the rate of deprotection.

In this study, we prepared multifunctional periodic mesoporous silica particles, of which three areas were functionalized with a different functional group. In particular, we were able to selectively functionalize the inner surface using an amphiphilic silica precursor with latent amine functionality. Fig. 1 shows a schematic drawing of the multifunctional mesoporous silica particle. The multifunctional silica particle was designed to show fluorescence resonance energy transfer (FRET). FRET is

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Fig. 1 Schematic drawing of the structure of the multifunctional mesoporous silica particle.

a distance-dependent interaction between the electronic excited states of two chromophore molecules. A donor chromophore, initially in its electronic excited state, transfers energy to an acceptor chromophore in proximity through nonradiative dipole-dipole coupling. In the multifunctional silica particle, FRET donor and acceptor moieties were introduced into the silica framework and the pore, respectively. The outer surface of the silica particle was grafted with hydroxyalkyl groups. Here we report the synthesis and FRET activity of the multifunctional silica particle.

Results and discussion

Our approach to the preparation of the multifunctional mesoporous silica particle is shown in Scheme 1. The overall synthetic strategy was as follows. A FRET donor was introduced into a silica framework by co-condensation of a functional silica precursor bearing a FRET donor moiety, TEOS and amphiphilic organotriethoxysilane having a thermally reversible urethane bond. In the resulting periodic mesoporous silica particle, the hydrophobic part of the amphiphile was tethered to the pore wall through a urethane bond.⁸ After functionalizing the outer



Scheme 1 Preparation of the FRET mesoporous silica particles.

surface, surfactant molecules occupying the pores were removed by heating under acidic conditions. In this process, an amino group was also generated on the inner surface *via* dissociation of the urethane bond. A FRET acceptor was attached covalently to the pore wall by the reaction with the amino group.

Organotriethoxysilane Pervlene-Si, comprised of a pervlene diimide unit and two triethoxysilyl groups, was prepared according to the literature method (Scheme 2).9 and incorporated into a silica framework as a FRET donor by co-condensation with TEOS. Perylene diimides have high fluorescence efficiency and photochemical stability.10 The amphiphilic organotriethoxysilane (OctylPh-Si) was synthesized from octylphenol and 3-(triethoxysilyl)propyl isocyanate. OctylPh-Si could function as a surfactant as well as a monomer for the condensation reaction. The fluorescent mesoporous silica particles (FMS) were prepared by co-condensation of an amphiphilic organotriethoxysilane (OctylPh-Si), a fluorescent organotriethoxysilane (Pervlene-Si), and TEOS in the presence of cetyltrimethylammonium bromide (CTAB) under basic conditions. Both amphiphiles, CTAB and OctylPh-Si, were dissolved in a basic aqueous medium and allowed to form a micellar structure, where hydrophobic portions of the amphiphiles were located inside the pore. The silica precursors, TEOS and Perylene-Si, were allowed to react in this aqueous solution and precipitated silica particles were isolated as reddish solids.

The outer surface of the silica particle as precipitated was functionalized by grafting with 3-(trimethoxysilyl)propyl acrylate. Since the pores of the silica particle were filled with amphiphile molecules, we presume that the grafting reaction occurred preferentially at the outer surface.^{11,12} However, it is still possible that some silyl molecules diffused into the pore. Several studies reported surfactant–silane exchange under similar conditions, resulting in the reaction inside the pore.^{5a,13,14}

Fig. 2 shows SEM images of the mesoporous silica particles as precipitated and the grafted ones. The silica particles had spherical and elliptical morphology with diameters of between 100 nm and 500 nm. Their shapes were unaffected by the grafting reaction.

The surfactant molecules were extracted by reflux in a mixture of 1,4-dioxane, HCl and water. In this process, hydrophobic octylphenoxy groups in the pore and acryl groups on the outer surface were also removed to produce amino and hydroxyl groups, respectively.¹⁵ Extraction was confirmed by the decrease in the characteristic FT-IR absorptions of CTAB in the 3000–2800 cm⁻¹ region (Fig. 3). In addition, the peak around 1735 cm⁻¹ disappeared, supporting the hydrolysis of the urethane and ester bonds.

The structure of **FMS-NH₂** was further investigated by solidstate ¹³C CP/MAS NMR spectroscopy (Fig. 4). The peaks corresponding to three different organic groups were observed as



Scheme 2 Synthesis of organotriethoxysilane molecules.





Fig. 4 ²⁹Si and ¹³C CP/MAS solid NMR spectra of FMS-NH₂.

expected. The peaks for the aminomethylene carbon on the inner surface and the hydroxymethylene carbon on the outer surface appeared at 42 and 64 ppm, respectively. The peak at 163 ppm was assigned to the carbonyl carbon of **Perylene-Si**. The aromatic carbon peaks appeared at 120–135 ppm. The peak for the silylmethylene carbon of the propyl groups appeared at 7 ppm.

²⁹Si CP/MAS solid NMR spectroscopy also supported the structure of **FMS-NH₂** (Fig. 4). The ²⁹Si CP/MAS NMR spectrum of **FMS-NH₂** exhibited relatively strong two signals at -59 and -68 ppm corresponding to T² [RSi(OSi)₂OH] and T³ [RSi (OSi)₃] resonances, respectively, suggesting that organic groups were covalently attached to the silica framework.¹⁶

The N₂ adsorption/desorption isotherms of **FMS-NH₂** were of type IV, indicating that the pore sizes were in the mesopore range (Fig. 5a). The Barrett–Joyner–Halenda (BJH) pore size distribution function calculated from the adsorption branch of the isotherm is shown in Fig. 5a (inset).¹⁷ The **FMS-NH₂** samples had a Brunauer–Emmett–Teller (BET) surface area of 861 m² g⁻¹ and pore volume of 0.77 cm³ g⁻¹. The narrow BJH pore size



Fig. 5 (a) Nitrogen adsorption-desorption isotherm (inset: pore size distribution), (b) X-ray diffractogram, (c) SEM image and (d) TEM image of FMS-NH₂.

distribution indicated uniform mesopores with a diameter of 3.3 nm. The X-ray diffraction (XRD) pattern of **FMS-NH₂** showed two resolved peaks with *d*-spacings of 46.93 and 27.07 Å, corresponding to (100) and (110) reflections of a hexagonal structure with a lattice parameter of a = 54.19 Å, respectively (Fig. 5b).

The visual images of the multifunctional particles were obtained by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 5c and d). The SEM image showed that the morphology of the silica particles was not altered during the pore modification. The TEM image showed a densely packed hexagonal pore structure with an average pore diameter of about 3 nm, which was in good agreement with the values calculated from the XRD and BJH measurements.

In FMS-NH₂, perylene diimide units were embedded in the silica matrix between the pores as a FRET donor. We chose Rhodamine B isothiocyanate (rhodamine) as a FRET acceptor chromophore because its absorption wavelength was well matched with the emission wavelength of **Perylene-Si** as shown in Fig. 6. A strong overlap of the absorption band of the acceptor with that of the emission band of the donor is required to achieve efficient FRET. In an ethanol solution, **Perylene-Si** showed three intense absorption bands at 454, 488 and 520 nm and



Fig. 6 Normalized UV-vis (dashed-line) and PL (solid-line) spectra of **Perylene-Si** ($\lambda_{ex} = 488 \text{ nm}$) and rhodamine ($\lambda_{ex} = 548 \text{ nm}$) obtained at a concentration of $1 \times 10^{-5} \text{ mol } L^{-1}$ in ethanol.

fluorescence emission bands at 535 and 575 nm when excited at 488 nm. The absorption band of rhodamine appeared around 548 nm.

The rhodamine units were introduced into the pore by the reaction of the isothiocyanate group of Rhodamine B isothiocyanate with the amino group on the inner surface, forming a thiourea linkage.^{5,18} The loading amount of rhodamine was calculated by assuming all the reactions occurred stoichiometrically. The sample was labeled with respect to the molar ratio of rhodamine to the amino functional group on the pore wall as **FMS-NH**₂ (no rhodamine), **FMS-Rh(0.5)** (0.5 molar ratio) and **FMS-Rh(1.0)** (1.0 molar ratio). After introduction of the rhodamine unit, a decrease in a BET surface area was observed. **FMS-Rh(1.0)** showed a BET surface area of 501 m² g⁻¹ and pore volume of 0.60 cm³ g⁻¹.

Fig. 7 shows the PL spectra of the suspension of the silica particles in ethanol. **FMS-Rh** showed absorption bands corresponding to perylene diimide and rhodamine units around 500 and 550 nm, respectively. When excited at 488 nm, the intensity of the perylene diimide emission peak at 543 nm decreased with increasing rhodamine content, while the intensity of the rhodamine emission peak at 575 nm increased. These results strongly suggest that the excitation energy of perylene diimide units in the silica framework was transferred to the rhodamine moieties inside the pore. Similar FRET effects were reported by Inagaki and coworkers, where FRET acceptors were introduced into the pore inside by physical adsorption.¹⁹

We prepared a free standing nanocomposite film in which the functional silica particles were embedded in a poly(2-hydroxyethyl methacrylate) (PHEMA) matrix. Free radical polymerization of a dispersion of **FMS-Rh(1.0)** in 2-hydroxyethyl methacrylate (HEMA) was carried out in between glass plates to yield a film with a thickness of about 260 μ m.²⁰ The film was transparent and slightly reddish (Fig. 8a), indicating a homogeneous dispersion of the silica particles in the polymer matrix. We presume that hydroxypropyl groups located on the outer surface of the silica particle enhanced the compatibility between the silica particle and PHEMA.

The PL spectrum of the film (Fig. 8b) showed a similar pattern of emission to that of the **FMS-Rh(1.0)** suspension in ethanol with a little red shift of about 16 nm. Fig. 9 shows the confocal laser scanning microscopy (CLSM) images of **FMS-Rh(1.0)**



Fig. 7 PL spectra of FMS-Rh suspended in ethanol (1 mg per 10 mL) ($\lambda_{ex} = 488$ nm).



Fig. 8 (a) Photograph of the **FMS-Rh(1.0)**-embedded PHEMA film and (b) PL spectra of the film and the **FMS-Rh(1.0)** suspension in ethanol ($\lambda_{ex} = 488$ nm).



Fig. 9 Confocal laser scanning microscopy (CLSM) images of the **FMS-Rh(1.0)**-PHEMA film. Images (a) and (b) were obtained by detecting the emission at 505–530 nm and above 560 nm, respectively.

dispersed in the PHMMA film obtained by using the 488 nm line of an argon-ion laser for excitation. The emission was detected at 505–530 nm and above 560 nm. At 505–530 nm, weak green fluorescence was observed from perylene diimide units in the silica particles (Fig. 9a). When detected above 560 nm, the distinct red fluorescent particle image was obtained, indicating the strong emission of rhodamine units due to the FRET effect (Fig. 9b).

Conclusions

We investigated the synthesis of multifunctional mesoporous silica particles by selective and sequential functionalization. The designed multifunctional silica particle contained FRET donor and acceptor moieties inside the silica framework and the pore, respectively, and hydroxypropyl groups at the outer surface. A free standing, multifunctional, silica–polymer thin film was prepared where the silica particles were embedded in the PHEMA matrix. Both the suspension of the silica particles in ethanol and their polymer composite film showed the efficient FRET effect. We believe that this selective and sequential functionalization method will help in synthesizing advanced multifunctional mesoporous silica materials for diverse applications.

Experimental

Measurements

¹H and ¹³C NMR spectra were recorded on a Bruker Avance DPX-300 (300 MHz) and an Avance 500 (125 MHz)

spectrometer, respectively. Solid-state ¹³C CP/MAS and ²⁹Si CP/ MAS NMR spectra were obtained on a Bruker Avance DSX-400 (400 MHz) spectrometer equipped with the CP-MAS probe. Samples were spun in air at approximately 7 kHz. Powder X-ray diffractograms were obtained with the use of a Bruker Nanostar Small Angle X-Ray Scattering (SAXS) system (Cu Ka radiation, $\lambda = 1.54$ Å). SEM images were obtained by using a JEOL JSM-6330F microscope. Transmission electron microscopy (TEM) images were obtained by a Tecnai F20 operating at 200 kV. TEM samples were dispersed in chloroform and a drop of the mixture was placed on a carbon-coated copper TEM grid. N2 adsorption/ desorption measurements were carried out using Belsorp-Max (BEL Japan, Inc.), and the pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) model on the adsorption branch. Fluorescence measurements were performed using a Shimadzu RF-5301PC spectrofluorometer. Fluorescence images were obtained by using Carl Zeiss-LSM510 confocal laser scanning microscope. UV-vis spectra were obtained with the use of a SCINCO S-3150.

Synthesis

4-Octylphenyl-3-(triethoxysilyl)propylcarbamate (OctylPh-Si). To a solution of 4-octylphenol (4.13 g, 20 mmol) in tetrahydrofuran (10 mL) were added 3-(triethoxysilyl)propyl isocyanate (14.84 g, 60 mmol) and DBDU (2 mL) at room temperature. The reaction mixture was stirred for 24 h at 75 °C. After evaporation, the product was isolated by column chromatography on silica gel (ethyl acetate : *n*-hexane = 1 : 14 v/v): yield: 71%. ¹H NMR (DMSO-*d*₆, 300 MHz): δ 7.14 (d, *J* = 8.3 Hz, Ar–H, 4H), 6.97 (d, J = 8.3 Hz, Ar–H, 4H), 7.72 (t, J = 5.6 Hz, NH), 3.74 (q, J =7.0 Hz, 6H), 3.03 (q, J = 6.7 Hz, 2H), 2.54 (t, J = 7.4 Hz, 2H), 1.49–1.57 (m, 4H), 1.26 (m, 10H), 1.15 (m, 9H), 0.85 (t, J =6.2 Hz, 3H), 0.57 (t, J = 8.5 Hz, 2H); ¹³C NMR (DMSO- d_6 , 125 MHz): δ 154.4, 149.1, 138.6, 128.5, 121.4, 57.6, 43.1, 34.5, 31.3, 28.7, 22.8, 18.1, 13.7, 7.2; IR (KBr, cm⁻¹): 3342, 2973, 2857, 1732, 1538, 1501, 1457, 1390, 1218, 1080, 1020, 956, 785, 641. Anal. Calcd for C₂₄H₄₃NO₅Si: C, 63.54; H, 9.55; N, 3.09. Found: 63.37; H, 9.61; N, 2.94%.

N,N'-Bis[3-(triethoxysilyl)propyl]perylene-3,4,9,10-tetracarboxylic diimide (Perylene-Si). This compound was prepared according to the literature procedure.⁹

Synthesis of fluorescent mesoporous silica particle (FMS). NaOH (aq) (2.00 M, 3.50 mL) was added to a solution of CTAB (0.94 g, 2.59 mmol) in deionized water (480 mL). A solution of **OctylPh-Si** (0.068 g, 0.15 mmol) in THF (5 mL) was added slowly to the solution and then a solution of TEOS (5.12 g, 24.5 mmol) and **Perylene-Si** (0.24 g, 0.30 mmol) in THF (50 mL) was added dropwise. The reaction mixture was stirred for 3 h at 60 °C. The precipitated product was filtered, washed with deionized water, methanol, chloroform and acetone, and dried in a vacuum oven at 25 °C for 3 days.

FMS-Acr. FMS (1.0 g) was dispersed in ethanol (35 mL). An aqueous ammonia solution (28%, 13.9 g) and ethanol (155 mL) were added to the suspension. After stirring for 2 h at 40 $^{\circ}$ C, 3-(trimethoxysilyl)propyl acrylate (1.12 g, 4.8 mmol) dissolved in

ethanol was added and the reaction mixture was continuously stirred for another 48 h at 40 °C. Grafted silica particles (**FMS-Acr**) were isolated by filtration, washed with ethanol several times, and dried in a vacuum oven at 25 °C for 3 days.

FMS-NH₂. FMS-Acr (0.6 g) was stirred in a mixture of HCl (35 wt%, 10 g), deionized water (50 g) and dioxane (150 g) at 120 °C for 24 h. The product was filtered, washed with dioxane, methanol and acetone, and dried in a vacuum oven at 25 °C for 3 days.

FMS-Rh. A certain molar ratio of Rhodamine B isothiocyanate to the amino functional group on the pore wall was introduced into **FMS-NH₂** according to the method in the literature.^{5,18} A typical procedure is as follows: **FMS-NH₂** (50 mg, 2.44×10^{-3} mmol of NH₂) was suspended in ethanol (10 mL). Rhodamine B isothiocyanate (1.51 mg, 2.82×10^{-3} mmol) in EtOH (15 mL) and a catalytic amount of triethylamine were added to the suspension. After stirring the reaction mixture in the dark for 24 h at room temperature, the product was isolated by filtration and washed with ethanol several times to remove the unreacted dye.

Composite film. FMS-Rh(1.0) (2 mg) was dispersed in 2-hydroxyethyl methacrylate (5 mL), and then ADMV (1 wt%) was added to the suspension. A free standing film was prepared by polymerization between glass plates at 40 °C for 2 days.

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