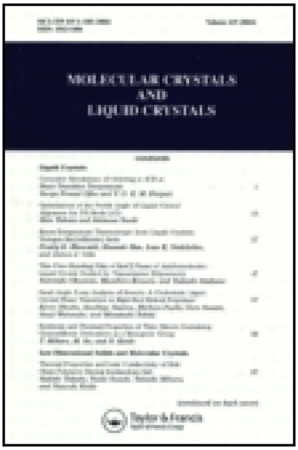

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Preparation of Periodic Mesoporous Organosilicas Using Congo Red Precursor for Potential Optical Applications(I)

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PREPARATION OF PERIODIC MESOPOROUS ORGANOSILICAS USING CONGO RED PRECURSOR FOR POTENTIAL OPTICAL APPLICATIONS(I)

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Congo-red substituted hexagonal mesoporous silica materials (Congo-SBA15) have been synthesized from tetraethoxysilane (TEOS) and Congo-red modified precursor by sol-gel method. In the present investigation, poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) was used as the template to prepare highly ordered mesoporous materials. Well-ordered hexagonal arrays of the mesopores were shown in small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) measurements. The modification of congo-red precursor was proved by FT-IR spectroscopy.

Keywords: block copolymer templating; congo-red; mesoporous organosilica

INTRODUCTION

SBA-15 is a newly discovered mesoporous silica molecular sieve with tunable large uniform pore sizes (up to ~300 Å) which is obtained by use of amphiphilic block copolymer as an organic structure-directing agent. In

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particular, poly(alkylene oxide) triblock copolymers such as poly(ethylene oxide)-*b*-poly(prolylene oxide)-*b*-poly(ethylene oxide)(PEO-PPO-PEO) are good candidates, because of their mesostructural ordering properties, amphiphilic character, low-cost commercial availability, and biodegradability [1]. Using aqueous acidic conditions($pH < 1$) and dilute triblock copolymer concentrations, SBA-15 has been synthesized with a highly ordered two-dimensional(2D) hexagonal (*p6mm*) mesostructure and thick uniform silica walls [1].

Much progress has been made recently in the preparation of a new class of organic-inorganic hybrid materials called periodic mesporous organosilicas(PMOs) through surfactant-templated condensation of organosilanes with two trialkoxysilyl groups bridged by an organic group [2–5]. Not only were a number of new synthesis strategies developed for the preparation of PMOs under a wide range of pHs from highly basic to strongly acidic conditions using cationic, anionic, and neutral surfactants and a variety of commercially available block copolymers, but also several new mesostructrues such as mesoporous benzene-silica [6] with crystal-like pore walls were synthesized. Furthermore, PMOs have already found use as novel catalysts, adsorbents, and hosts for nanocluster synthesis as the porous structures, surface, and framework properties of PMO materials can be finely tuned by changing the bridging organic group incorporated and the synthesis conditions employed.

More recently, mesoporous and mesostructured materials have attracted interest for electronic and optical applications. It has been also recognized that mesoporous systems are promising candidates for the next-generation low-*k* dielectric materials for integrated circuits [7]. Early research in optical properties of mesostructure and mesoporous materials grew on the success of dye doping in polymers, sol-gel inorganic matrices, and molecular sieve materials. Mesostructured materials offer the same rigidity and photostability while at the same time having a well-defined hydrophilic/hydrophobic phase separation allowing for more sophisticated tuning of the dye microenvironment. In this sense, well-ordered mesoporous PMOs with large pores (>4.5 nm) have recently attracted particular interest from the viewpoint of the immobilization and encapsulation of large molecules [1,8].

On the other hand, congo-red is the first successful synthetic direct dye and currently widely used because of it's economics and brightness. However, it is one of the more fugitive direct dyes. Thus, the stabilization of the dyes are necessary for more verstitile applications including colored films. Therefore, we tried to prepare congo-red incorporated PMO where the congo-red can be stabilized by being linked to the silica framework.

Here, we report the synthesis of highly ordered hexagonal PMOs with the aid of inorganic salts under strongly acidic conditions using the nonionic triblock copolymer Pluronic P123[poly(ethylene oxide)-*b*-poly (prolylene oxide)-*b*-poly(ethylene oxide)(PEO-PPO-PEO)] as the template and congo-red precursor as the organically bridged silica source.

EXPERIMENTAL

Synthesis of Congo-red Modified Organosilica Precursor [Congo-red Precursor]

2.788 g of congo-red and 2.01 g of 3-isocyanatopropyltriethoxysilane were dissolved respectively in 40 ml and 20 ml of dimethylformamide(DMF) for 5 minute at room temperature. The two solutions were mixed and the mixture was heated at 85°C for 8 h under nitrogen atmosphere. Figure 1 shows the chemical structure of the congo-red modified organosilica precursor synthesized in this work.

Synthesis of Congo-SBA15 PMO

Table 1 shows experiential conditions to synthesize congo-red modified periodic mesoporous organosilicas, Congo-SBA15. In a typical synthesis (for Congo5-SBA15), 1.2 g of P123 and 3.5 g of NaCl were dissolved in 10 g of water and 30 g of 2.0 M HCl solution with stirring at 40°C. The mixture was further stirred for 4 h at ambient temperature. 0.279 g of congo-red precursor was dissolved in 9.44 g of DMF. To this homogeneous solution was added 3.269 g of tetreaethoxysilane(TEOS) and congo-red

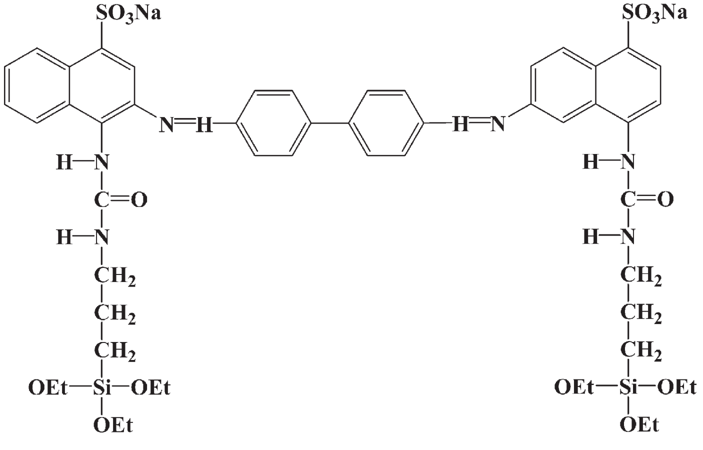


FIGURE 1 Chemical structure of Congo-red modified organosilica precursor used in this work.

TABLE 1 Experimental Conditions to Synthesize Congo-red Modified Periodic Mesoporous Organosilicas.

	Precursors			
Symbol	TEOS	Congo-red Precursor	Surfactant (P123, mol)	Catalyst 2M HCl
Congo5-SBA15	1	0.025	0.013	3.82
Congo10-SBA15	1	0.050	0.013	3.82

precursor solution. Then the mixture was stirred for 42 h at the same temperature. The final reactant molar composition was 1.0 TEOS/0.013 P123/3.82 HCl/3.82 NaCl/0.025 congo-red precursor/8.223 DMF/134 H_2O. The product was filtered, washed by neutral aqueous solution and dried in air at 80°C. The surfactant was removed by stirring 5.0 g of as-synthesized sample in 100 ml of ethanol with 7.0 g of 35% HCl aqueous solution at 60°C for 12 h. The resulting solid was recovered by filtration, washed with ethanol, and dired in air. This extraction procedure was repeated to remove the surfactant completely. In this way, we have synthesized two congo-red modified SBA-15 with two different contents of congo-red precursors, Congo5-SBA15(0.05 mol% of congo-red) and Congo10-SBA15(0.10 mol% of congo-red) as well as the pristine SBA-15 without congo-red.

Measurements

Small angle X-ray scattering (SAXS) were performed at Pohang Accelerator Laboratory (PAL), POSTECH, Korea using Co- Kα ($\lambda = 1.608$Å) radiation with the energy range of 4-16 keV (Energy resolution : $E/E = 5 \times 10^{-4}$, Photon flux : 1010–1011 ph/s, Beam size : $< 1\,\mathrm{mm}^2$) over the scan range $0.2° < 2\theta < 3.5°$ [9]. FT-IR spectra were recorded between 4000 and 400 cm^{-1} by a Recollect impact 400D spectrometer using the KBr pellet technique. TEM images were acquired with JEOL 2010 electron microscope operating at 200 kV. Samples were prepared by crushing the sample particles and dispersing the powder products in methanol with vibrating of ultrasonic wave. Powders were deposited and dried on holey carbon file on a Cu grid. Images were recorded at magnification of 250,000X.

RESULTS AND DISCUSSION

Figure 2 shows the SAXS patterns of Congo5-SBA15, Congo10-SBA15 and SBA15. In the low 2θ region of 0.5–3.5°, SBA15 shows three peaks indexed

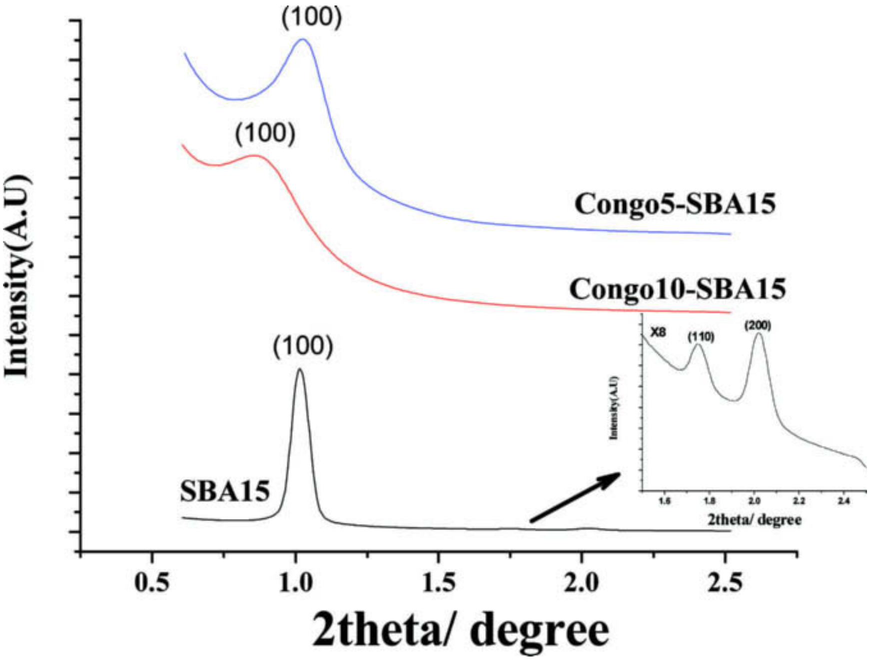


FIGURE 2 Small angle X-ray scattering (SAXS) patterns of Congo5-SBA15, Congo10-SBA15 and SBA15.

as (100), (110) and (200), which is indicative of hexagonal lattice structure. However, SAXS patterns of congo-red modified mesporous organosilicas with 0.05 and 0.10 Si mole ratio of congo-red precursor/TEOS exhibit only one peak indexed as (100). The absence of a resolved secondary feature indicates that there is no long-range order in the structures of these PMOs [10]. The SAXS peaks indicated that the d(100)-spacing for the congo-red modified organosilicas is 89.9Å and 107.8Å for Congo5-SBA15 and Congo10-SBA15, respectively. It is interesting to note that the d(100)-spacing of the SBA-15 was increased by increasing the congo-red contents due to its bulky size of the congo-red.

FT-IR spectroscopy is a reliable technique to study the chemical change in materials, specially for the sol-gel processing of silica based materials since one can get information about the backbone structure of the network as well as the organic side groups attached to it. Figure 3 shows the representative IR spectra of SBA15 and Congo5-SBA15. The IR spectra of the two mesoporous samples show characteristic adsorption bands at ca. 1068 and 808 cm^{-1} corresponding to the Si-O-Si asymmetric stretching

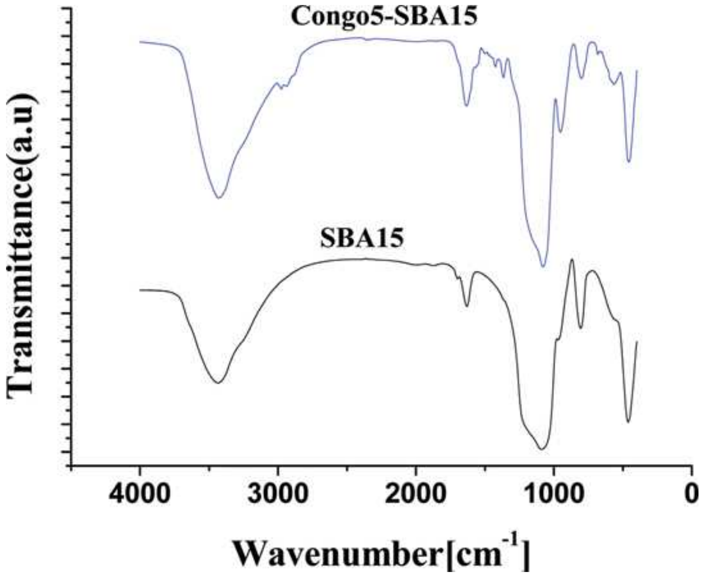
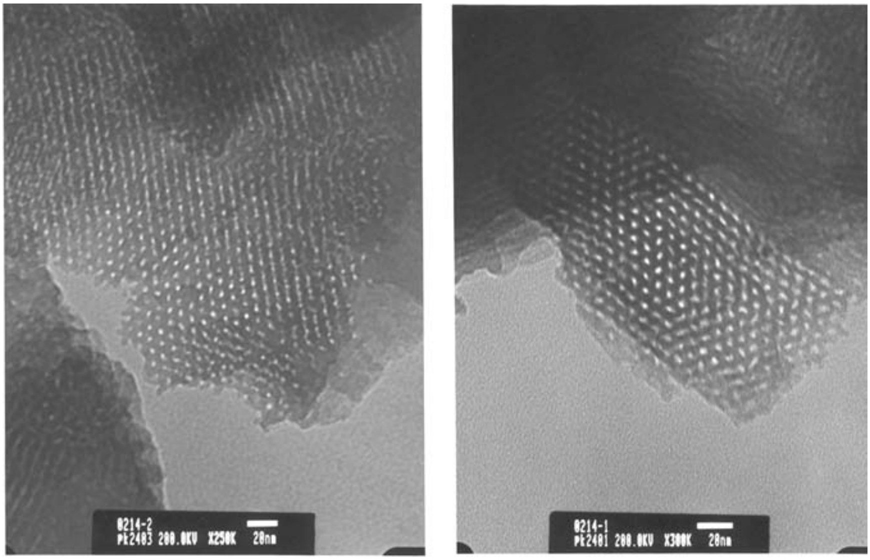


FIGURE 3 FT-IR spectra of Congo5-SBA15 and SBA15.

and the Si-O-Si symmetric stretching vibration, and 460 cm^{-1} corresponding to the Si-O-Si bond bending vibration, respectively. In the FT-IR spectrum of the Congo5-SBA15, two bands were newly appeared at 2976 and 2938 cm^{-1} due to the CH_2 asymmetric and symmetric vibrations. And the bands near at 1362 and 681 cm^{-1} are assigned to the C=C stretching and in-plane ring vibration of the naphthalene. This confirms that the congo-red modified precursor was covalently linked in the channels of the PMOs.

TEM can serve as a unique technique for the studies of mesoporous materials, revealing the morphologies of particles and the local structures in a nanometer resolution. Figure 4 shows TEM images of the SBA15 and the Congo5-SBA15. It is clearly shown in Figure 4 that these samples have ordered hexagonal array uniform channels. The average pore size of the SBA15 and the Congo5-SBA15 were estimated as 5.0 and 7.0 nm, respectively. In the TEM images, a dark field image was observed and it is assumed that particles may be overlapped. The TEM images also show that the pore size of the Congo5-SBA15 is slightly larger than that of the SBA15, which is in accordance with the SAXS results shown in Figure 2.

Further detailed studies are now under way to investigate the optical properties of the Congo-red modified mesoporous organosilicas for their optical applications.



(a) (b)

FIGURE 4 Transmission electron microscopy(TEM) images of (a) SBA15 and (b) Congo-SBA15.

CONCLUSIONS

Congo-red modified mesoporous organosilica materials of SBA-15 type (Congo5-SBA15 and Congo10-SBA15) were successfully prepared by sol-gel method using a triblock copolymer(P123) as the template. SAXS and TEM analyses showed that the mesoporous materials possess hexagonal arrays. FT-IR spectroscopy proved that the congo-red was covalently linked to the framework.

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