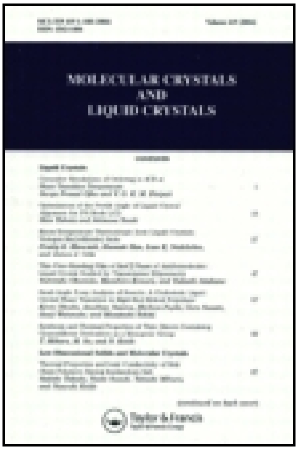

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Synthesis and Properties of Periodic Mesoporous Organosilicas Using Carbazole Precursor for Potential Optical Applications

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Synthesis and Properties of Periodic Mesoporous Organosilicas Using Carbazole Precursor for Potential Optical Applications

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Carbazole-substituted hexagonal mesoporous silica was synthesized using tetraethoxysilane (TEOS) and carbazole modified silica precursor as silica source and triblock copolymer as structure-directing agent based on surfactant assembly. The excitation spectrum of the carbazole modified silica precursor exhibited a blue shift as compared to pure carbazole. The carbazole modified silica precursor was characterized by time resolved spectroscopy, absorption and photoluminescence spectra. Well-ordered hexagonal arrays of the mesopores were investigated using transmission electron microscopy (TEM) and N_2 isotherm.

Keywords: carbazole; mesoporous organosilica; sol-gel reaction; time resolved spectroscopy

INTRODUCTION

Since hybrid organic-inorganic nanocomposites present several advantages for designing materials for optical applications, numerous silica- and siloxane-based hybrid organic-inorganic materials have been developed in the past few years [1]. Much progress has been done in the preparation of a new class of organic-inorganic hybrid materials called periodic mesoporous organosilicas (PMOs) through

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surfactant-templated condensation of organosilanes with two trialkoxysilyl groups bridged by an organic group [2]. Framework properties of PMO materials can be finely tuned by changing the bridging organic group incorporated and the synthesis conditions employed. Therefore, incorporation of dyes into the sol-gel matrix is a useful strategy for preparing waveguides [3], lasers [4], sensors [5], LEDs [6], and nonlinear optical (NLO) materials [7]. The use of a dye molecule as a bridging group provides exceptionally high loading of chromophore and prevents leaching and/or phase separation of the dye molecule. Bridged polysilsesquioxanes also offer a novel chemical approach to produce nanosized particles doped in transparent hybrid glass materials [8]. These complex materials may have utility for electro-optical devices, as supported catalysts, and as catalytic membrane materials. Nanosized CdS particles have been deposited by external doping, that is, treating porous bridged polysilsesquioxanes with successive washes of $CdNO_3$ and Na_2S. The optoelectronic properties of carbazole derivatives have generated a great deal of interest. Organic oligomer and polymer containing carbazole units have proved to be useful in organic photorefractive [9], light emitting devices and solar cell [10]. Morais *et al.* [11] have shown the ability of the sol-gel technique to produce multilayer devices comprising two or three hybrid layers exhibiting different functionalities. These layers have been prepared from silane precursors modified with hole- or electron-transporting units and with light-emitting species. Also, composites of organic dye derivatives and inorganic materials have been studied from a variety of perspectives. For example, the process of energy transport in organic dye has been studied by inclusion of the dye within an oriented porous silica host [12]. Charge transfer in photovoltaic cell has also been studied by forming nanocomposites of organic dye [13], porous TiO_2 and SnO_2. Mesoporous molecular sieves comprise an important class of inorganic materials and have been widely studied for their tunable pore size and morphology. The potential application in catalysis, separations, chemical sensors, dielectric coatings, and a wide variety of other areas drive this research.

In this paper, we describes novel, deep-blue chromophore doped silica precursor, which provides us with a basic structure for color tuning within the 390–450 nm spectral region. In addition, 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(prolyene oxide)-*b*-poly(ethylene oxide)(PEO_{20}-PPO_{70}-PEO_{20})] as the template and carbazole precursor as the organically briged silica source.

EXPERIMENTAL

Synthesis of Carbazole Modified Silica Precursor

3,6-diaminocarbazole powder and 3-isocyanatopropyltriethoxsilane were purchased from Tokyo Kansei Kogyo co., Ltd. (Japan) and Sigma-Aldrich (95+ %), respectively, and used without further purification. 1.5 g of carbazole and 2.3 g of 3-iscyanatopropyltriethoxysilane were dissolved respectively in 40 mL and 20 mL of tetrahydrofuran (THF) for 1 h at room temperature. The two solutions were mixed and the mixture was heated at 60°C for 8 h under nitrogen atmosphere. Figure 1 show the chemical structure of the carbazole modified silica precursor synthesized in this work. More details of synthesis and characterization of this carbazole modified silica precursor will be reported elsewhere.

Synthesis of Carbazole-SBA 15 PMO

In a typical synthesis, 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. 1.26 g of carbazole modified silica precursor was dissolved in 10 g of THF. To this homogeneous solution was added 3.26 g of tetraeaethoxysilane (TEOS) and carbazole modified silica precursor solution. Then the mixture was stirred for 42 h at the same temperature. The product

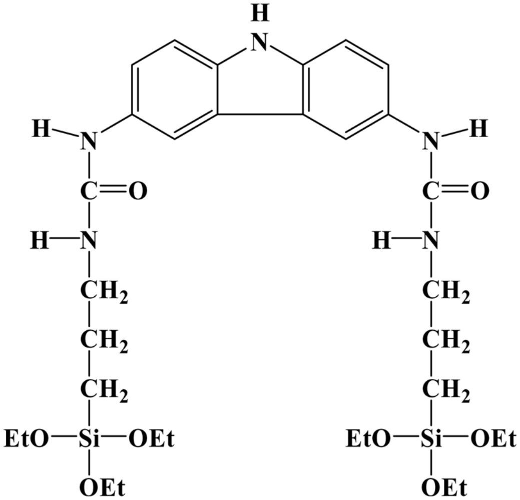

FIGURE 1 Chemical structure of carbazole modified silica precursor used in the work.

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 dried in air at 60°C. This extraction procedure was repeated to remove the surfactant completely. Since the typical synthesis method follows the preparation of the SBA-15, we designated the carbazole-incorporated mesoporous silica as the carbazole-SBA 15 PMO.

Measurements

An ultraviolet-visible spectrophotometer (UV-vis, CARY 5E, Varian Co.) was used for the measurement of the optical absorption spectra of the pure carbazole solution and carbazole modified silica precursor solution in THF. A photoluminescent (PL) spectrum was measured with a spectroscopy system (JOBIN-YVON 270 M, SPEX Instruments Inc.) equipped with a monochromator. The luminescence signal was collected at 90 from the laser (Nd:YAG, Quantel YG681) beam direction using a 0.5 m monochromator (Spex 500 M) equipped with a cooled PMT (Hammamatsu R928). The signal from the PMT was digitized with transient digitizer (Tektronix 7912 HB). Transmission electron microscopy (TEM) image was acquired with JEOL 2010 electron microscope operating at 200 kV. The adsorption and desorption isotherms of nitrogen at –196°C were measured using a Qunatachrome Nova 4000e instrument. Sample was outgassed at 150°C for 12 h under vacuum ($p < 5 \times 10^{-6}$ Torr) in the degas port of the adsorption analyzer. The pore size distribution curve was obtained from an analysis of the desorption branch by using the Barrett-Joyner-Halenda (BJH) method.

RESULTS AND DISCUSSION

The carbazole absorbed ultraviolet light and emit blue light. Figure 2 shows the absorption spectrum of the pure carbazole and the carbazole modified silica precursor. For the pristine carbazole, three main absorption bands appeared at 288 nm, 325 nm, and 393 nm. For the carbazole modified silica precursor, three peaks were blue shifted to 284 nm, 317 nm, and 368 nm by about 24 nm (from 393 to 368 nm) shifts. This could be suggested as the decrease of interchain electron delocalization in a well-stretched configuration of the carbazole modified silica precursor resulting in decreased π-π stacking, thereby shifting the emission to higher energy [14]. The excitation photoluminescence spectra with the

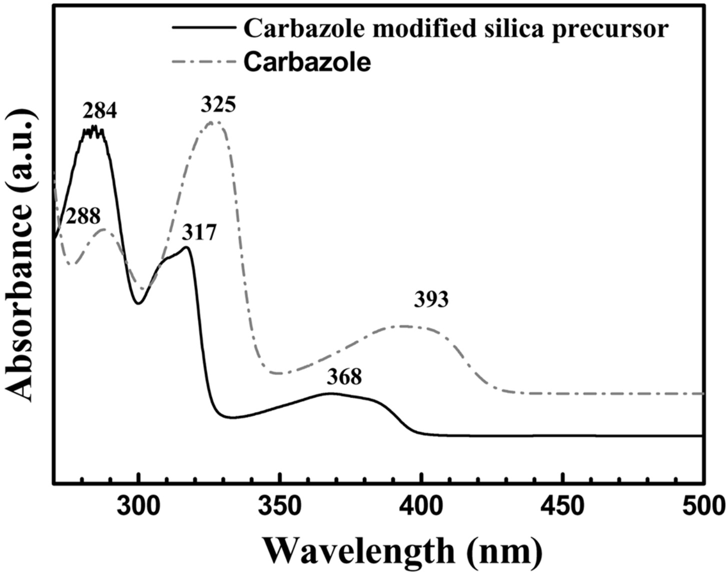

FIGURE 2 The absorption spectra of the carbzole and the carbazole modified silica precursor.

variation of the carbazole and carbazole modified silica precursor are shown in Figure 3. The main emission band of the carbazole is located at 430 nm. For the carbazole modified silica precursor, the main emission band is located at 397 nm, with a shoulder at 415 nm. The shift in the emission peak was also observed by including silica precursor. This evolution is compatible with that observed in the UV-vis absorption spectra. The high energy of the 397 nm and 415 nm peak may indicate that the segments of the silica precursors are involved in the emission process. Therefore, the shift in emission peak reflects the formation of new segments resulted from a variation of the carbazoles upon introduction of the silica precursors. This explanation is in agreement with the result obtained from UV-vis absorption experiments. The photoluminescence behavior of the carbazole and the carbazole modified silica precursor are thus reasonably inferred, by which silica precursor can be said to tailor optical properties of the carbazole. Time resolved PL response is shown in Figure 4. The majority of the PL from the carbazole and the cabazole modified silica precursor displays a first-order exponential decay. The lifetime of the carbazole and carbazole modified silica precursor were found to be 10.7 ns (emission peak at 430 nm) and 7.0 ns (emission peak at 396 and 415 nm), respectively. The results in Figure 4 show that a first-order contribution dominates

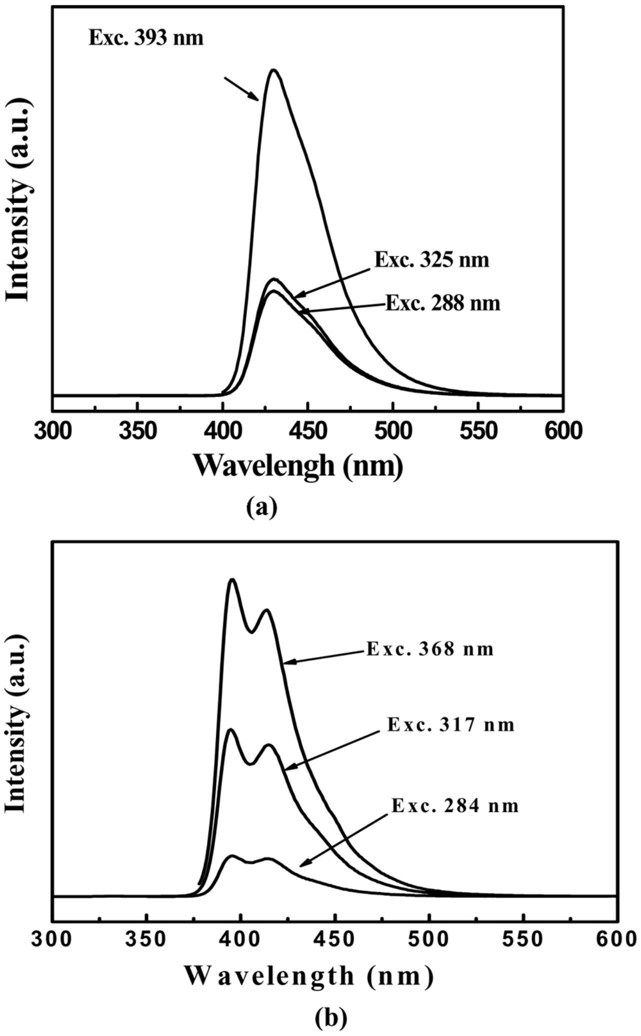

FIGURE 3 Emission spectra of the carbazole (a) and the carbazole modified silica precursor (b).

the luminescence decay kinetics, further corroborating the conclusion reached from the luminescence spectra in Figure 3. This indicates that the source of the emission most likely emanates from silica precursor within carbazole. It never dominates the luminescence intensity. The carbazole modified silica precursor could also display such short nanosecond radiative lifetime due to the specificity of bandgap form of the bulk silica precursor.

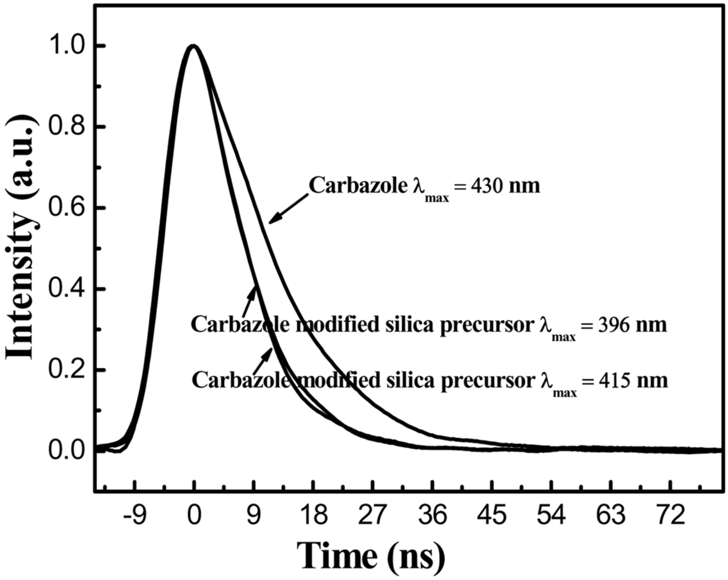

FIGURE 4 Emission lifetime measurements obtained at 396 nm, 415 nm (carbazole modified silica precursor), and 430 nm (carbazole). The photoluminescence decay curve can be fit to a first-order exponential decay.

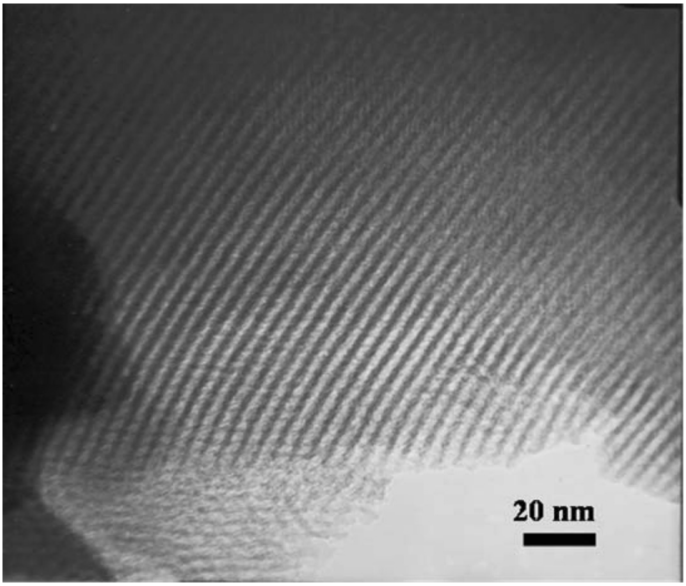

FIGURE 5 Transmission electron microscopy (TEM) image of the carbzole-SBA 15.

The 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 5 shows the TEM image of the carbazole-SBA 15. It is clearly shown in Figure 5 that this sample has well-ordered hexagonal array uniform channels. The average pore size of this material was estimated as 5.3 nm using Barrett-Joyner-Halenda (BJH) method. This preliminary discovery is a first step towards a simple, fast, and economical process for making silica precursor based LEDs useful for optoelectronics and photonics. Further detailed studies are now way under to investigate the optical properties of the carbazole modified mesoporous organosilicas for their optical applications.

CONCLUSIONS

We have found that the excitation spectrum of the carbazole modified silica precursor exhibit a blue shift as compared to pure carbazole. In addition, the carbazole modified silica precursor was characterized by time resolved spectroscopy, absorption and photoluminescence spectra. The carbazole modified mesoporous organosilicas materials of SBA 15 type was successfully prepared by sol-gel method using a triblock copolymer (P123) as the template. Well-ordered hexagonal arrays of the mesopores were investigated using TEM and N_2 isotherm.

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