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Synthesis of phthalocyanine-doped silica mesostructured materials by ferrocenyl surfactant

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Photosensitive copper phthalocyanine-(CuPc) doped silica mesoporous materials (in powder) have been directly synthesized by a self-organizing coassembly process using a functional surfactant, 11-ferrocenyltrimethylundecylammonium (ferrocenyl TMA) molecules. This simple method shows that it is not necessary to dope molecules into mesoporous channels after the pore becomes opened by calcination. X-Ray diffraction patterns (XRD) show the typical hexagonal diffraction pattern of the mesoporous materials. Optical absorption spectra of these powders show the typical band of the CuPc molecule.

Self-assembling organic–inorganic molecules into highly ordered nanostructured architectures has attracted increasing attention because these materials provide a rich source for scientific research and technological applications.[1–6] For example, the mesomaterials derived from mesostructured composites can be used in molecular sieves, catalysts, and host–guest materials.[1,2,7,8] Recently, the production of functional molecules contained in self-assembled mesostructured materials has been a interesting branch of advanced materials research.[9,10] A conducting carbon wire of poly(acrylonitrile) confined in the ordered hexagonal channel has been successfully synthesized[9] by introducing the monomer molecule into the channel and carrying out a radical polymerization reaction therein.

In this work, we have investigated the synthesis of photosensitive mesostructured materials for optical device applications where the photoabsorbing dyes are doped into the mesochannels by a direct self-organizing process of surfactants, not by external doping after the calcination of the channels. If the synthetic path is found to dope functional molecules into mesochannels by a self-organized co-assembly process, it will enable controlled design for the production of functional mesostructured materials for applications such as sensors, photoconversion or luminescent materials.

We report the synthesis of CuPc-doped silica mesostructured materials by using a functional surfactant directly instead of alkyltrimethylammonium salt. In this case, CuPc molecules are, supposedly, embedded and self-assembled among the functional surfactant's hydrophobic tails and organized with a periodic array of the lipid micelle structures. We chose 11-ferrocenyltrimethylundecylammonium (ferrocenyl TMA) bromide as the surfactant in this synthesis process because many organic molecules, such as phthalocyanines, are soluble in ferrocenyl TMA aqueous solution[11,12] by being contained in the micelle or vesicle of ferrocenyl TMA. The ferrocenyl TMA surfactant has a ferrocenyl ligand at the lipid tail with a distance of eleven carbons to the trimethylammonium cation head group. The ferrocenyl TMA (I^0) and its oxidized form I^+ show that the surfactants form redox-active micelles. The isolated molecules have an absorption band at 440 nm which results in the orange color of the surfactants.

Synthesis of MCM-41 (hexagonal structure) has been described by many groups.[1–3] We prepared colored silica-functional surfactant mesostructured materials as follows: 1.0 g 11-ferrocenyltrimethylundecylammonium bromide is dissolved in 50 ml H_2O, followed by stirring for about 30 min to obtain a homogeneous ferrocenyl TMA orange aqueous solution. Copper phthalocyanine (CuPc; 0.08 g) is added to the above aqueous solution. Then, the suspension is sonicated for 5–10 min, and stirred for 3–5 days at room temperature to attain solubilization equilibrium. Undissolved organic compounds in the solution are removed by centrifugation and filtration to give a yellow–green homogeneous ferrocenyl TMA/CuPc aqueous solution. Then, 4.0 g 95% tetraethylorthosilicate (TEOS) is added. Finally, 20 g 35% HCl aqueous solution is added to acidify the above solution, followed by stirring. Then the solution becomes completely colorless because of the precipitation of the colored powders at the bottom of the beaker, which indicates that all of the ferrocenyl TMA/CuPc reacts with silica species to form the mesostructured powder. A schematic diagram of the two new synthetic processes is described in Fig. 1. In this case, acidic synthesis of silica mesostructures through a mediated pathway can form a charged $S^+X^-I^+$ interface: $/\mathrm{CuPc@Fe}\cdots(\mathrm{CH_3})_3\mathrm{N}^+/\mathrm{Br}^-/^+\mathrm{H_2O\text{-}Si\text{-}O}/$, while all of the surfactants have photoabsorbing molecules CuPc at the tail ends. The Pc-doped silica/ferrocenyl

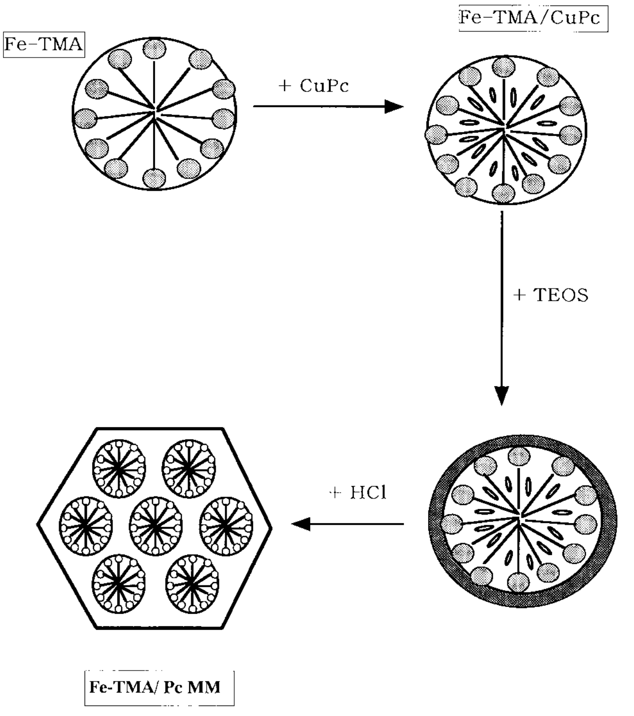

Fig. 1 The self-assembled synthesis method of molecular-doped mesostructured materials by using ferrocenyl TMA surfactants to incorporate CuPc molecules inside the surfactant micelle, assembling with silica (SiO_2) frameworks

TMA mesostructured powder can be obtained after washing and drying in air at room temperature or at temperatures below 60 °C. In this new process, it is not necessary to dope molecules into mesoporous channels after the pores become opened by calcination.

The hexagonal mesostructures of CuPc-doped silica mesoporous material powders were confirmed by XRD (Fig. 2). In spite of the lower concentration of surfactants, the hexagonal phase was successfully produced and the products were colored (yellow–green) by the surfactant's ferrocenyl ligands and CuPc molecules.

Fig. 2 shows a typical hexagonal diffraction pattern of the mesoporous materials. The two peaks were observed in the low-angle region for [100] and [110]. The interplanar distance $d_{100} = 36.4$ Å, which is twice as long as the ferrocenyl TMA surfactant molecule, is basically the same as those of silica MCM products where lipid micelles form the mesochannel structure. The hexagonal unit cell length $a = 2d_{100}/\sqrt{3} = 42.3$ Å.

The XRD shows that the interplanar distance and hexagonal unit cell length of CuPc-doped silica mesostructured materials are the same as those of undoped materials.[13] This phenomenon can be explained by part of a CuPc molecule inserting in between the self-assembled ferrocenyl TMA surfactants' hydrophobic tails in a periodical manner within a mesostructured channel. Therefore, it is unlikely that CuPc molecules are located in the center of the ferrocenyl TMA micelle, which would expand the micelle size very much.[11,12] CuPc molecules inserted between ferrocenyl TMA hydrophobic tails would slightly enlarge the channel size, and may stabilize the silica (SiO_2) framework. In the case of silica, because of the amorphous nature of the Si–O networks, a curved interior surface such as in the hexagonal phase is possible even in Pc-doped mesostructured materials. This is why ferrocenyl TMA/SiO_2 shows a hexagonal phase.

Fig. 3 shows the absorption spectrum of a undoped ferrocenyl TMA/SiO_2 powder,[13] and two absorption bands at 440 nm and 640 nm were clearly seen. The absorption at 440 nm was ascribed to the reduced state (original state) of the ferrocenyl ligand and the one at 640 nm was an oxidized state. Because the ferrocenyl dyes are incorporated in the channel by a self-assembly process, the absorption of the products comes from concentrated dyes at the channel center. The absorption band at 440 nm is a reduced state and is identical to the absorption of isolated Fe-TMA molecules in the solution, while the one at 640 nm, an oxidized state, arose from reaction with air (oxygen) as well as moisture after the synthesis. As the products are exposed to air at about 100 °C, the relative absorption intensity ratio of the 640 nm and 440 nm bands increases with time. The increase of the absorption intensity ratio indicates oxidation of the sample by heat aging.

Fig. 3 also shows the absorption spectra of Pc-doped silica mesoporous materials including the ferrocenyl TMA surfactant. The absorption bands located at about 730 nm and 660 nm result from the phthalocyanine chromophore. It displays the typical absorption band of phthalocyanines, which is slightly broader than that of the CuPc molecule only in organic solvent. This phenomenon results from interaction between the CuPc molecules. Because phthalocyanine aggregation results in a much broader absorption band, an only slightly broadened absorption band indicates that the CuPc molecules lie among the functional surfactant's hydrophobic tails and are organized with a periodic array of the lipid micelle structures, not an aggregated CuPc cluster in the center of the ferrocenyl TMA micelle.

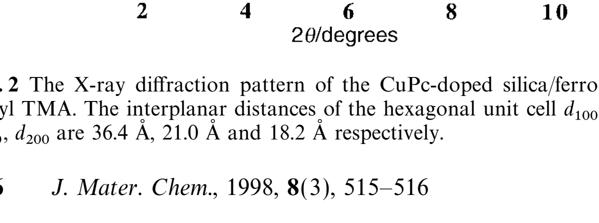

Fig. 2 The X-ray diffraction pattern of the CuPc-doped silica/ferrocenyl TMA. The interplanar distances of the hexagonal unit cell d_{100}, d_{110}, d_{200} are 36.4 Å, 21.0 Å and 18.2 Å respectively.

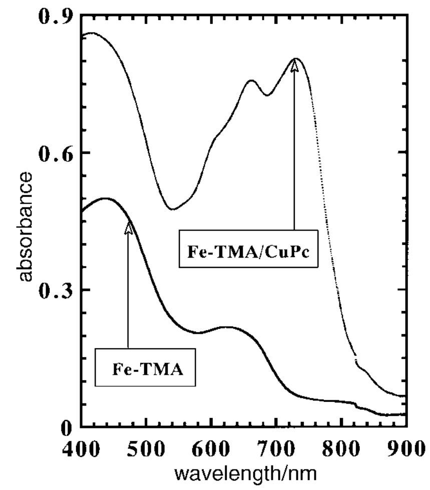

Fig. 3 Absorption spectra of silica/ferrocenyl TMA mesostructured materials and CuPc-doped silica/ferrocenyl TMA mesostructured materials

We directly synthesized CuPc-doped silica mesostructured materials. The mesostructure has been investigated and proved by X-ray diffraction. This communication reports a new and simple method for the preparation of functional molecular-doped silica-functional mesostructured materials. Because many organic molecules are soluble in surfactant aqueous solution by being contained in the micelle or vesicle of the surfactant, efforts are being made to synthesize films of functional mesostructured composite materials for optical device applications.

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