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Preparation of transparent mesoporous silica films by a rapid solvent evaporation method

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Thin films of silica–alkyltrimethylammonium (alkyl = decyl, dodecyl, tetradecyl, hexadecyl and octadecyl) chloride mesostructured materials are synthesized by spin coating the precursor solutions containing prehydrolyzed tetramethoxysilane and alkyltrimethylammonium salts. The films have been converted to transparent porous silica films by calcining in air. Cationic dyes, Methylene Blue, 1,1′-diethyl-2,2′-cyanine, tetrakis(*N*-methyl-4-pyridinio)porphyrin, have been adsorbed on the porous films to give colored films. The preparation of the self-standing film of the silica–hexadecyltrimethylammonium chloride mesostructured material by using poly(methyl methacrylate) coated glass substrate is also reported.

Introduction

Inorganic–organic nanocomposites with ordered structures have been investigated from a wide range of scientific and practical interests. Recently, the preparation of inorganic–organic mesostructured materials by using supramolecular assemblies of surfactants to template the reactions of inorganic species have attracted increasing interest as a biomimetic approach to the fabrication of inorganic/surfactant biphase arrays.[1] The preparation of silica based mesoporous materials by using surfactant aggregates as structure directing agents is a successful example of this synthetic strategy.[2–6] While crystalline microporous materials are used as adsorbents, catalysis and hosts for inclusion compounds,[7] there has been a demand for mesoporous materials with well confined pore structures because of their potential applications such as catalytic conversion of large molecules and hosts for bulky organic species for advanced materials applications.

The preparation of inorganic–surfactant mesostructured materials in a controlled morphology is a key issue for the application of inorganic–organic mesostructured materials.[8–32] The processing of the silica–surfactant mesostructured materials as thin films is a subject of current interest, since the films might be applied to sensors, optical and electronic materials, *etc*., for which powder samples cannot be utilised. Accordingly, thin films of mesoporous silica have been prepared on solid substrates[13,18,21–23] and at an air–water interface.[17]

The preparation of the transparent thin films of silica–alkyltrimethylammonium salt mesostructured materials by simply depositing the solutions containing prehydrolyzed tetramethoxysilane and alkyltrimethylammonium salts has been reported by Ogawa.[11–15] Since the procedure is very simple, the solvent evaporation method is an effective way to prepare silica–surfactant mesostructured materials in a controlled morphology. Thin films,[21–23] hollow spheres and fibers[29] of silica–surfactant mesostructured materials have successfully been prepared by utilizing the solvent evaporation method. In this paper, we report the preparation of transparent mesoporous silica films from the silica–surfactant mesostructured materials. The resulting porous silica films are promising materials in such applications as adsorption, separation, and hosts for large organic species.

Experimental

Materials

Tetramethoxysilane (abbreviated as TMOS) and alkyltrimethylammonium chlorides [$(C_nH_{2n+1})(CH_3)_3NCl$; abbreviated as C_nTAC, where *n* denotes the carbon number in the alkyl chain] were obtained from Tokyo Kasei Industries Co., and used without further purification. Poly(methyl methacrylate) (abbreviated as PMMA; secondary standard, Aldrich) was used as received.

Sample preparation

The silica–surfactant mesostructured materials were prepared as follows: TMOS was partially hydrolyzed by a substoichiometric amount of deionized and distilled water (the molar ratio of TMOS : H_2O was 1 : 10) under acidic conditions for 1 h at room temperature. Initially the mixture was an emulsion but it became homogeneous as the hydrolysis proceeded. Then C_nTAC was added and the mixture was allowed to react at room temperature. The solution was dripped onto a spinning Pyrex glass substrate (with a spinning rate of 6000 rpm) and spread evenly. The films were dried in air at room temperature to remove solvent and to complete condensation of the silica. Thus, transparent thin films formed on the substrates. In order to remove surfactant from the composites, the films were calcined in air at 350–550 °C. The thickness of the films was retained at *ca.* 1 μm throughout this study, since thicker films may be peeled off from the substrate to give very fine particles during drying and calcining.

For the preparation of a self-standing film, a PMMA coated Pyrex glass substrate was prepared by spin coating a chloroform solution of PMMA. The thin films of the silica–surfactant mesostructured materials were deposited on the PMMA coated substrates by spin coating. By immersing the coated plate in acetone, PMMA dissolved and the silica–surfactant mesostructured materials were removed from the substrate.

Characterization

X-Ray diffraction was performed on a RAD IB diffractometer (Rigaku) using monochromatic Cu-Kα radiation. The thickness of the films was determined with a surface profilometer (Kosaka Laboratory Co., SE 1700). Scanning electron micrographs were obtained on a Hitachi S-2840N scanning electron microscope. The nitrogen adsorption isotherm was obtained on a Bell sorp TCV (Bell Japan Inc.) system.

Results and Discussion

By spin coating the mixture containing the prehydrolyzed TMOS and $C_{16}TAC$ (at a molar ratio of $TMOS:C_{16}TAC=7:1$) a transparent thin film formed on the substrate. The X-ray diffraction pattern of the film showed a sharp diffraction peak with a *d* value of 3.8 nm, which accompanied a second order reflection. When alkyltrimethylammonium salts with different alkyl chain lengths (C_{10}, C_{12}, and C_{18}) were used, transparent thin films with different *d* values were obtained. The *d* values determined from the X-ray diffraction patterns are shown in Fig. 1. There is a linear relationship between the carbon number in the alkyl chains and the *d* values, which indicates the formation of silica–surfactant mesostructured materials.

In order to remove surfactant from the substrate to obtain porous silica films, the as-coated films of the silica–surfactant mesostructured materials were calcined in air. Sharp diffraction peaks were observed in the XRD patterns of the calcined films, showing that the ordered microstructures remained even after the removal of surfactant. The *d* values of the calcined films are also shown in Fig. 2. The decrease in the *d* values upon calcination has been observed for silica–surfactant mesostructured materials synthesized under acidic conditions.[33] The condensation of the silica walls during heating may be the reason for the shrinkage. The *d* values decreased gradually with increasing heating temperature, indicating that the porous structure can be controlled by varying the conditions of the thermal treatment.

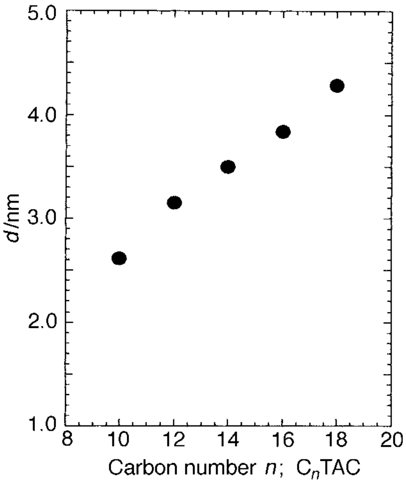


Fig. 1 Variation of the *d* values of the silica–C_nTAC mesostructured materials as a function of alkyl chain length

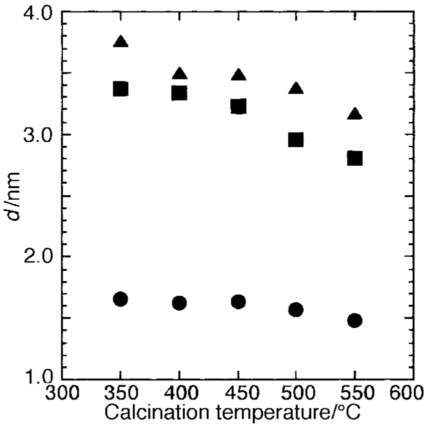


Fig. 2 Change in the *d* values of the silica–C_nTAC mesostructured materials thin films upon calcination; (▲) $C_{18}TAC$, (■) $C_{16}TAC$ and (●) $C_{10}TAC$

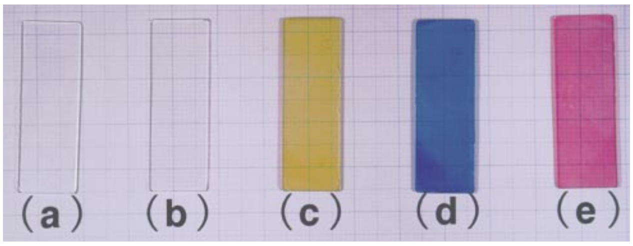


Fig. 3 Photographs of the silica–$C_{16}TAC$ mesostructured materials thin film supported on a Pyrex glass substrate (a) before and (b) after calcination, and (c)–(e) dye impregnated films; (c) TMPyP, (d) MB and (e) PIC

Photographs of the silica–$C_{16}TAC$ mesostructured materials deposited on a Pyrex substrate before and after calcination at 550 °C are shown in Fig. 3. The calcined film is still transparent. An SEM image of the film surface (data not shown) also indicates that the film is continuous and crack free. A nitrogen adsorption isotherm of the silica–$C_{18}TAC$ film ($d=3.5$ nm) on a glass substrate calcined at 450 °C was type IV, showing that the film is mesoporous. Since the isotherm was obtained for a film supported on a substrate, it was impossible to determine the exact weight of the porous film. Therefore, the surface area and the porosity of the film cannot be determined at present. A powder sample, which was obtained by removing the film from the substrate, showed a highly porous microstructure with a BET surface area of *ca.* 1000 $m^2\ g^{-1}$.[13] Since the *d* value of the powder did not change on removal from the substrate, the supported films are thought to have a similar porosity and BET surface area. From these observations, the calcined films possess a porous structure as schematically shown in Fig. 4.

Since the films were obtained as transparent films, their application as hosts for photoactive species is worth investigating. Alkoxysilane derived sol–gel materials have been used as immobilizing media for organic photoactive species.[34,35] The guest species were dissolved into the starting solutions to obtain dye doped sol–gel materials. In the present system, guest species can be incorporated into the preformed porous silica films by impregnation in a similar way for the introduction of guest species into the crystalline inorganic host materials.[7,36] Host–guest as well as guest–guest interactions in porous silica films are expected to control the states of guest species to lead to novel functional supramolecular systems.

Preliminary experiments into the incorporation of organic dyes were carried out by immersing the calcined silica–$C_{16}TAC$ film in an aqueous solution of dyes. Cationic dyes, Methylene Blue (MB), 1,1′-diethyl-2,2′-cyanine (PIC), tetrakis(*N*-methyl-4-pyridinio)porphyrin (TMPyP; Scheme 1) were adsorbed to give colored films as shown in Fig. 3. The adsorbed amounts of dyes can be controlled by changing the reaction conditions, *i.e.* dye concentration and reaction period.

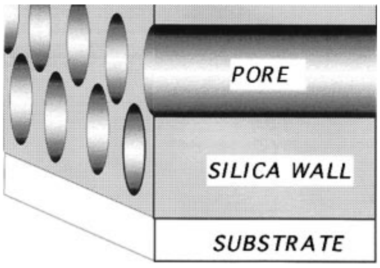
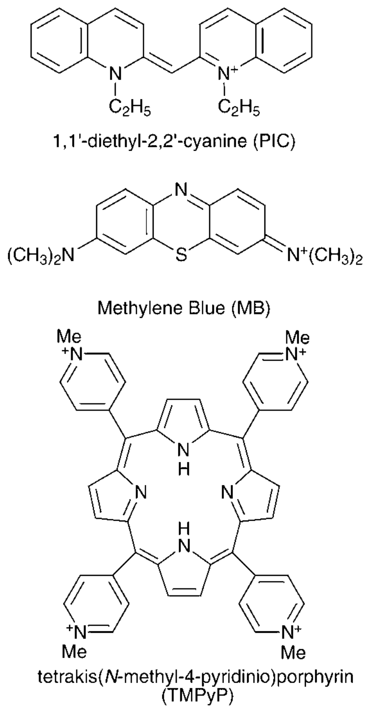


Fig. 4 Schematic drawing for the proposed microstructure of the porous silica films



Scheme 1

The absorption spectrum of the PIC adsorbed films showed an absorption band at around 524 nm due to monomeric PIC,[37] showing that the PIC cations adsorbed molecularly on the surface. On the other hand, the absorption spectra of the TMPyP and MB adsorbed films showed significant spectral shifts depending on the loading amount of the dyes. Since the shape of the pores in the present silica films was thought to be a one-dimensional cylindrical opening, intermolecular interactions between adjacent adsorbed dyes cause the spectral shifts, as well as dye–surface interactions. The loading amounts of the dyes, the pore size and surface modification are expected to affect the photoprocesses of the adsorbed dyes. In order to construct molecularly designed functional host–guest systems from mesoporous silica films, further study on the adsorption of the dyes is now underway and will be reported subsequently.

A self-standing film of the mesostructured material was obtained using a PMMA coated substrate. A silica–C_{16}TAC mesostructured material formed on the PMMA coated substrate as evidenced by the XRD pattern. When the coated film was immersed in acetone, PMMA dissolved to separate the mesostructured materials and substrate. Although the resulting film is brittle and collected as aggregates of small pieces, each piece is a continuous film as revealed by an SEM image of the product calcined at 550 °C (shown in Fig. 5).

The X-ray diffraction pattern of the self-standing film of the silica–C_{16}TAC mesostructured material is shown in Fig. 6. A very sharp X-ray diffraction peak with a *d* value of 3.8 nm was observed for the self-standing film, showing that the mesostructure was retained even after the removal from the substrate. The infrared spectrum of the film showed absorption bands characteristic of silica (such as Si—O—Si symmetric stretching vibrations at around 1230 and 1080 cm^{-1} and Si—O—Si bending vibration at around 460 cm^{-1}) along with those ascribable to C_{16}TAC (such as C—H stretching vibrations of CH_2 groups at 2927 and 2854 cm^{-1}). The bands due to C_{16}TAC disappeared in the infrared spectrum of the film calcined at 550 °C, indicating that the C_{16}TAC decomposed as a result of calcination. A very sharp diffraction peak with a *d* value of 3.3 nm was observed in the X-ray diffraction pattern of the calcined film (Fig. 6), showing that the calcined film possessed a periodic structure. Thus, an unsupported film of the silica–surfactant mesostructured material has successfully been prepared by using a PMMA coated substrate. For the practical application of the films of the mesostructured materials as catalysis and separation membranes, the preparation of unsupported films with controlled thickness, size and mechanical strength is required.

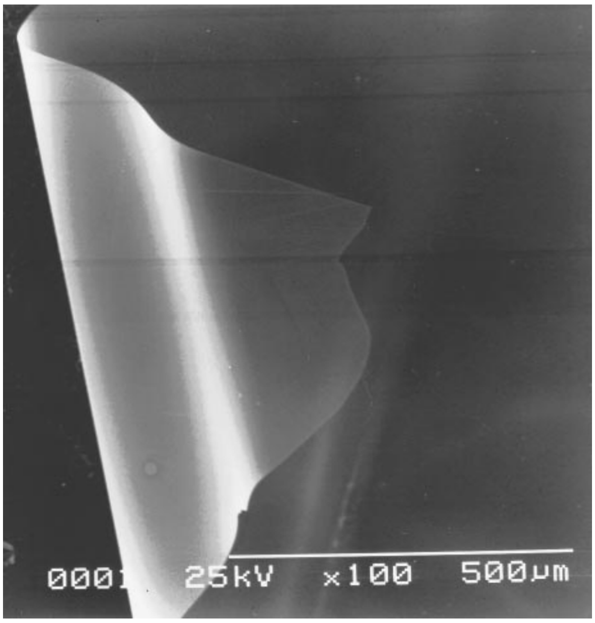


Fig. 5 Scanning electron microscope image of the self-standing film of the silica–C_{16}TAC mesostructured material film calcined at 550 °C

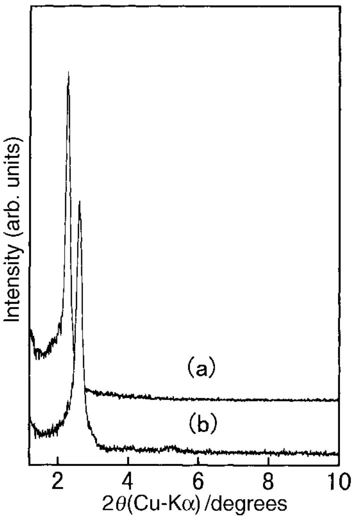


Fig. 6 X-Ray diffraction patterns of the self-standing film of the silica–C_{16}TAC mesostructured material, (a) before and (b) after calcination at 550 °C

Conclusions

Thin films of silica–alkyltrimethylammonium (alkyl = decyl, dodecyl, tetradecyl, hexadecyl and octadecyl) chloride mesostructured materials are synthesized by spin coating the precursor solutions containing prehydrolyzed tetramethoxysilane and alkyltrimethylammonium salts. The films have been converted to transparent porous silica films by calcining in air. The porous films can host cationic organic dyes, Methylene Blue, 1,1′-diethyl-2,2′-cyanine and tetrakis(*N*-methyl-4-pyridinio)porphyrin, by immersing the film in a dye solution.

An unsupported film of a silica–hexadecyltrimethylammonium chloride mesostructured material has been obtained by removing the spin coated film from poly(methyl methacrylate) coated glass substrate.

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