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Synthesis of Self-Assembled Photosensitive Molecules in Mesostructured Materials

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Self-assembled functional molecules in mesostructured materials (MM) are synthesized directly either by coassembly of dye-bound surfactant of ferrocenyl TMA with silicate or by Pc (phthalocyanine) molecules doped within C_{16}TMA micelles assembled with oxides framework such as vanadia (VO_x), MoO_3, WO_3, and SiO_2 to produce Pc-doped mesostructured materials. The process provides well-organized molecular doped mesostructured materials by a direct and simple procedure.

Introduction

Mesoporous materials invented by scientists of the Mobil Corp. have attracted considerable interest since the first announcement in 1992.[1−4] The formation mechanism of mesoporous materials designated as M41S have been studied by many groups[5−7] and phase change behavior among lamellae, hexagonal, and cubic are understood in terms of charge matching at the interface as well as a free energy argument in the organized organic/inorganic system.[8] The mesoporous products are widely synthesized in silica (SiO_2) framework, and there are interests for extending other oxides such as TiO_2,[9] V_2O_5,[10,13] WO_3,[11−13] and MoO,[13] because their potential applicability to adsorbents and catalytic processes. Hexagonal tungsten, vanadium, and titanium oxides have been successfully produced, and other oxide mesophases were examined in Pb, Fe, Mn, Zn, Al, Co, and Ni to form lamellae structure. Besides extending framework oxides to other classes of transition-metal oxides, it is quite attractive to investigate a novel process of mesoporous film formation. Attempts have been made for silica mesoporous film either on the substrate[14,15] or air−water[16,17] interface. Those films are good for device applications such as optical, electronic, and chemical sensors as well as membranes.

In this work, we have investigated the synthesis of photosensitive mesostructured materials for optical device applications where the photoabsorbing dyes are doped in the mesochannels by a direct self-organizing process of the surfactants, not by external doping after the calcination of the channel. If the synthetic path is found to dope functional molecules to mesochannels by a self-organized coassembly process, it will open a widely controllable design to produce functional mesostructured materials (MM) for applications such as sensors, photoconversion, or luminescent materials.

Experiment and Results

To make self-assembled functional molecules in mesostructured materials (MM), we have investigated two different methods for dye-doped MM. The first one is by using a dye-bound surfactant, Fe−TMA(11-ferrocenylundecylammonium bromide), where the trimethylammonium surfactant has a ferrocenyl dye at the end of the tail. The other is by using C_{16}TMA (hexadecyltrimethylammonium chloride) and the Pc (phthalocyanine ($C_{32}H_{18}N_8$), phthalocyanine blue ($C_{32}H_{16}N_8Cu$)) molecules that are doped in a coassembly within a C_{16}-TMA micelle. In the latter case, Pc molecules are, supposedly, embedded and self-assembled among the C_{16}TMA's hydrophobic tails and organized with a periodic array of the lipid micelle structures. The schematic

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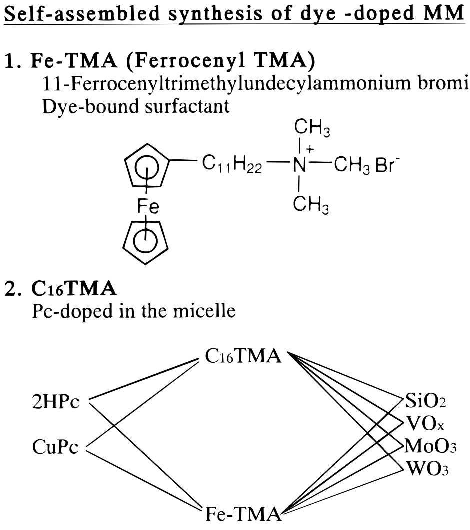

Figure 1. Two different ways of self-assembled synthesis of Pc-doped MM. The former is by using Fe−TMA surfactants and the latter is by using C_{16}TMA surfactants to incorporate Pc molecules in the metal oxides mesostructured channels.

diagram of the two new synthetic process is described in Figure 1. The Fe−TMA surfactant has a ferrocenyl ligand at the lipid tail with a distance of 11 carbons to a headgroup of a trimethylammonium cation. The isolated molecules have an absorption band at 440 nm, which results in a yellow-green color of the surfactants. In the latter case, C_{16}TMA as well as Fe−TMA was used to make Pc-doped mesostructured materials with various metal oxide frameworks where the doping ratio and the mesophase structure was changed by a combination of Pc dyes and framework oxides. In this article, we use the term “mesostructured materials” (MM), not “mesoporous”, to describe the products we have synthesized by our original procedure, because the materials have not been calcined to give an open pore, although the fundamental structure is quite similar to that of M41S materials.

In the first case, we have synthesized Fe−TMA mesostructured materials in a similar way as an acidic synthesis of silica M41S, while C_{16}TMA was replaced by Fe−TMA. The molar ratio of the synthetic precursors were as follows: 1.0 TEOS:9.0 HCl:0.12 Fe−TMA: 130 H_2O, which is the exact same molar ratio as a first acidic hexagonal silica M41S synthesis.[18] The acidic Fe−TMA solution is yellow-greenish colored, but after adding TEOS, 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 surfactants react with silica species to form the mesostructured powder. Despite the lower concentration of the surfactants, hexagonal phases were successfully produced, and the products were colored (yellow-green) by the surfactant’s ferrocenyl ligands. Figure 2a shows a low-angle XRD pattern for Fe−TMA−MM, and the fundamental reflection pattern of the hexagonal mesophase was observed. The powder sample were dispersed at the center of the open-framework Al holder (this is commonly used for XRD measurement) on a metallic stage, and the sustaining clay was pushed from the top side of the holder. So the powders at the bottom has a flat face with clay and the holder for the low-angle XRD measurement. The *d* spacing of the products was 37 Å, which is twice as long as the Fe−TMA surfactant, and those are basically the same products as mesoporous silicates where lipid micelles form the mesochannel structure. A slight shift of the molar ratio of the surfactant to silicate was proved to result in the same hexagonal mesostructured products. Figure 2b shows a transmission electron microscopy (TEM) photograph of the Fe−TMA−MM and the hexagonal array of the mesostructured channels are clearly observed. As far as an eye observation of the whole area of the low magnification view, only the hexagonal phase was produced and other phases such as cubic or lamellae were not observed.

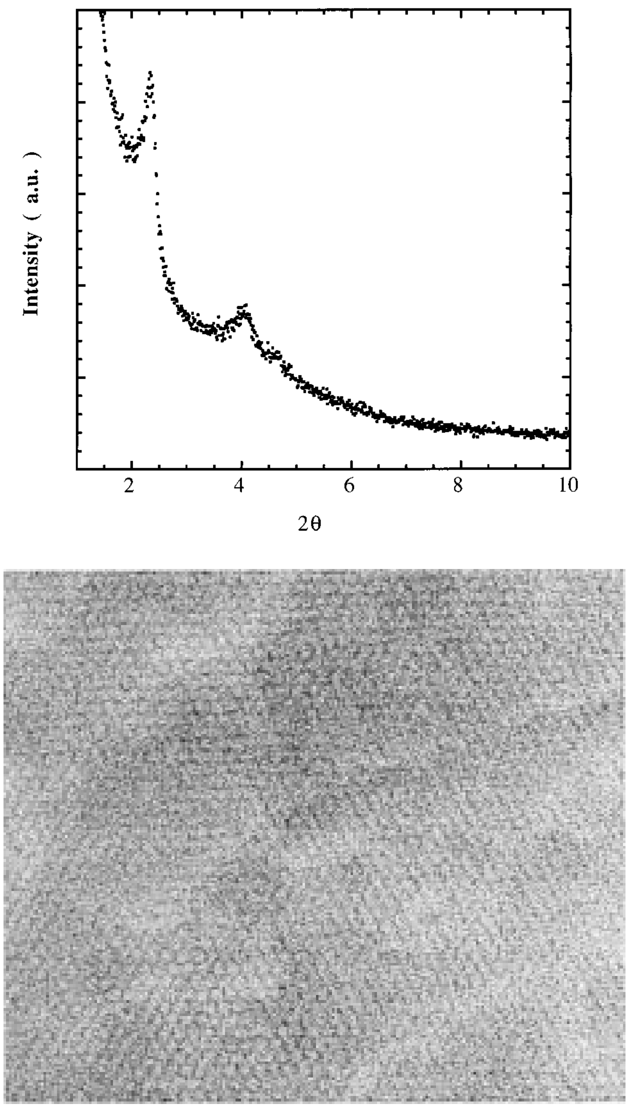

Figure 2. (a, top) Low-angle XRD pattern of Fe−TMA−MM powders. Fundamental reflection (100) as well as satellite peaks (110), (200) from the hexagonal phase is seen. (b, bottom) Transmission electron microscopy (TEM) photographs for Fe−TMA−MM. The hexagonal array of the mesostructure channels with a diameter of 37 Å were clearly observed, which is identical with the LAXRD results.

The result shows that the Fe−TMA surfactants can synthesize hexagonal mesophase in a way similar to

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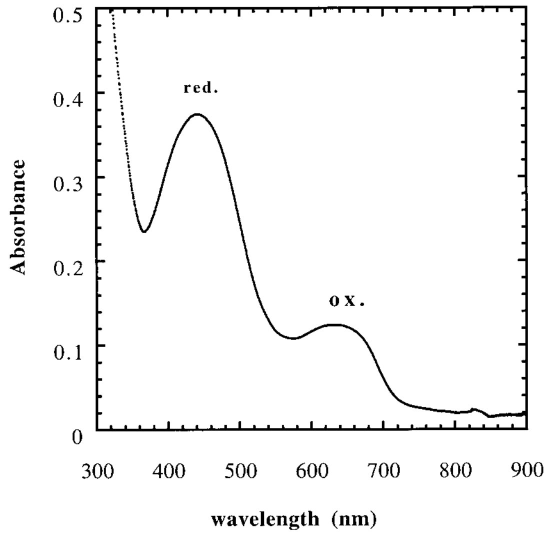

Figure 3. Optical absorption spectrum for Fe–TMA–MM powders measured by diffuse reflectance method. The absorption band at around 650 nm is ascribed to an oxidized state of the ferrocenyl ligands.

that for mesoporous silicates, and this is the first complete synthesis of the M41S-type products through ferrocenyl surfactants. As an Fe–TMA surfactant carries ferrocenyl dye at the end of the lipid tail, the as-prepared products possess an optical absorption band in a visible light wavelength region, and those are colored in light green or yellow green. The absorption spectra were obtained by the diffuse reflection method, which is commonly used for getting powder sample spectra although the absolute absorption intensity is not so quantitative by light scattering. Figure 3 shows an absorption spectrum of Fe–TMA-mesostructured powders and two absorption band at 440 and 640 nm were clearly seen. The absorption at 440 nm was ascribed to a reduced state (original state) of the ferrocenyl ligand of Fe–TMA 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's center. The absorption band of 440 nm is a reduced state and identical to the absorption of isolated Fe–TMA molecules in the solution, while the one at 640 nm, an oxidized state, appeared by the reaction with air (oxygen) as well as moisture after the synthesis. As the products are exposed to air at ambient temperature, the relative absorption intensity ratio of 640 to 440 nm increases with time. The increase of the absorption intensity ratio indicates an oxidation of the sample by aging. In this new process, it is not necessary to dope molecules into mesoporous channels after the pore becomes open by calcination. The process provides economic and more efficient ways to dope heavily in the mesochannels. The molar ratio of ferrocenyl dye to silica is as high as 12%, which is a higher doping ratio than other conventional doping method to silicate glassy materials.

Pc-doped mesostructured vanadia

$Pc/C_{16}TMA$ (molar ratio)	0	1/20	1/10	1/5	1/2.5
Pc	0.0 g	0.043 g	0.085 g	0.17 g	0.34 g
C_{16} TMA	0.54 g	0.54 g	0.54 g	0.54 g	0.54 g
NH_4VO_3	1.0 g	1.0 g	1.0 g	1.0 g	1.0 g
H_2O	18 g	18 g	18 g	18 g	18 g

Synthetic process

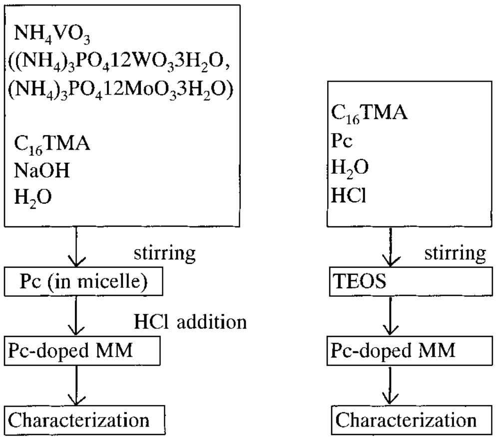

Figure 4. Synthetic pathways for Pc-doped MM (bottom) and the synthetic conditions for various Pc-doped MM (top).

The second method to make self-assembled molecules in a mesostructured materials is by mixing dye molecules among the surfactant's hydrophobic tails where the dye molecules are inserted in a periodic manner within a mesostructured channels. In the present work, we have chosen Pc (phthalocyanine ($C_{32}H_{18}N_8$), phthalocyanine blue ($C_{32}H_{16}N_8Cu$)) molecules as dopants and metal oxides of vanadia, WO_3, MoO_3, and SiO_2 were chosen as mesostructure frameworks. The synthetic procedures of Pc-doped mesostructured materials by C_{16}-TMA surfactant are schematically drawn in Figure 4. For example, in the Pc-doped mesostructured vanadia case, the process is as follows: the ammonium vanadate (NH_4VO_3, 1.0 g) was first dissolved in aqueous water (18 g) with addition of an amount of NaOH (1.2 g) to be solvated completely at high pH. And the C_{16}TMA (0.54 g) are dissolved in the above solution with no precipitation at this high pH condition. And, the various amount of Pc (0.043–0.34 g) were added to the above solution and stirred for 1 h. Surprisingly, the Pc molecules were solvated quite well in the surfactant solution, which becomes completely blue because the Pc molecules are well dissolved within the surfactant micelles. In the present experiment, the molar ratio of Pc to C_{16}TMA was changed from 0.0 to $^1/_{2.5}$, so that, in the heavy doping case, Pc are inserted into every several surfactant molecule. After stirring $Pc/C_{16}TMA$ solution, HCl (5 N) is added dropwise to gradually decrease a solution's pH to around 1.0. As HCl is added, passing the neutral point, vanadia starts precipitating at the surface of the micelle, and mesostructured vanadia with Pc molecules doped in the mesochannel was formed. After precipitation of the Pc-doped mesostructured vanadia at the bottom of the beaker, the solution becomes completely colorless, indicating that all of the photoabsorbing Pc molecules are completely doped in the precipitating products. Similarly, Pc-doped WO_3–MM as well as Pc-doped MoO_3–MM were produced; the ammonium tungstate parapentahydrate ($(NH_4)_{16}W_{12}O_{41}\cdot 5H_2O$) was dissolved in water with C_{16}TMA at high pH, and Pc was well solvated in the above surfactant

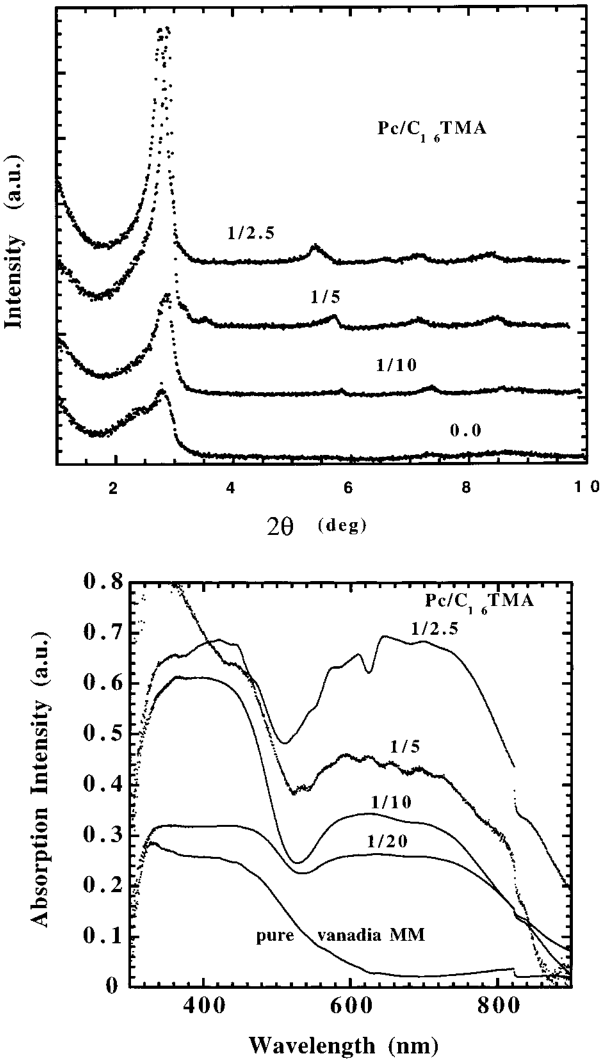

Figure 5. (a, top) Low-angle XRD pattern for Pc-doped vanadia mesostructured material. The reflection pattern shifts with a doping. (b, bottom) Optical absorption spectra for Pc-doped vanadia mesostructured material and the absorption from Pc molecules was measured through vanadia framework oxides.

solution with stirring. The WO_3–MM was formed by dropwise addition of HCl, and green-blue Pc-doped MM powder was precipitated. In the case of Pc–MoO_3–MM, ammonium phosphomolybdate trihydrate ($(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 3H_2O$) was used as a precursor chemical for the products. In the silica (SiO_2) case, Pc was first dissolved in a C_{16}TMA surfactant solution at a low pH (acidic) condition, and TEOS (tetraethoxysilane) was added to precipitate Pc-doped MM powders. The molar ratio of Pc to C_{16}TMA was changed from 0 to $^1/_{2.5}$, and the products were characterized by transmission electron microscope (TEM), scanning electron microscope (SEM), low-angle XRD, and optical absorption measurements. The change of *d* spacing as well as mesophase structural change induced by the Pc doping was examined.

Figure 5a shows a low-angle XRD (LAXRD) scan for Pc-doped vanadia MM with a variation of Pc-doping ratios. LAXRD of the pure vanadia MM was also shown in the figure (Pc/C_{16}TMA = 0). The pure vanadia mesostructured products without Pc doping are amorphous mesostructures, which is confirmed by a broad fundamental reflection at about 2.5–3.0°.[10,13] The

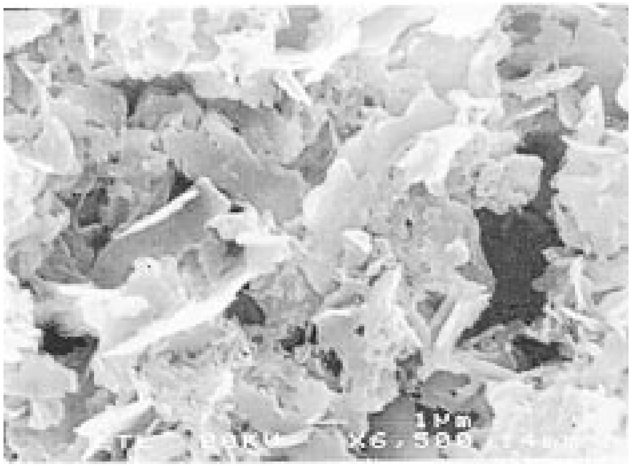

Figure 6. Scanning electron microscope (SEM) photograph for Pc-doped vanadia mesostructured material and flakelike powders with a size around 1–10 μm can be observed.

amorphous structure in this case means that the material has a mesoporous structure, but the pores are not regularly arranged, not forming crystalline symmetry of the channel's array. The vanadia mesostructure is built from a crystalline unit cell, but Pc insertion to vanadia framework induces the mesostructural change which is apparent in the change of the LAXRD pattern with doping Pc molecules to the vanadia mesostructured materials. In the vanadia case, as the Pc-doping ratio increases, the initial phase becomes unstable, especially, at the Pc/C_{16}TMA ratio of around $^1/_{20}$, where the initial (pure vanadia) amorphous structure changes and the LAXRD pattern shifts by minor experimental conditions. A further increase of the Pc doping makes the mesostructure stable and a symmetrical mesophase appeared that is different from the initial amorphous phase. In other words, the insertion of Pc molecules in the mesochannel stabilizes a crystalline phase possibly because of the modification of the channel wall shape. The material has a long-range structural ordering. Supposedly, because of the inversion, Pc modifies the channel structure, and the metal oxides building unit can be arranged to have the proper position to form a symmetrical mesophase.

It is also observed that the peak position of the fundamental reflection of the mesophase shifts toward a low angle with the Pc doping, i.e., the *d* spacing of the vanadia mesostructured materials becomes slightly larger by the expansion of the mesochannel. The *d* spacing is 30.55 Å at a Pc/C_{16}TMA ratio of $^1/_5$ and shifts to 31.87 Å at the ratio of $^1/_{2.5}$. Although there is a small expansion from the pure vanadia mesostructured to Pc-doped MM, the main peak position does not change significantly, which indicates that the Pc molecules are doped, perhaps among the surfactants hydrophobic tails of the lipid micelle and not in the center position of the micelle as in the expander molecules of trimethylbenzene (TMB).[6,19] Pc molecules inserted between the surfactant expand slightly the channel size and, at the same time, stabilize the vanadia framework. Figure 5b shows an optical absorption spectra for Pc-doped vanadia MM, and the absorption from the doped Pc was clearly seen. The powder is green, and as the doping

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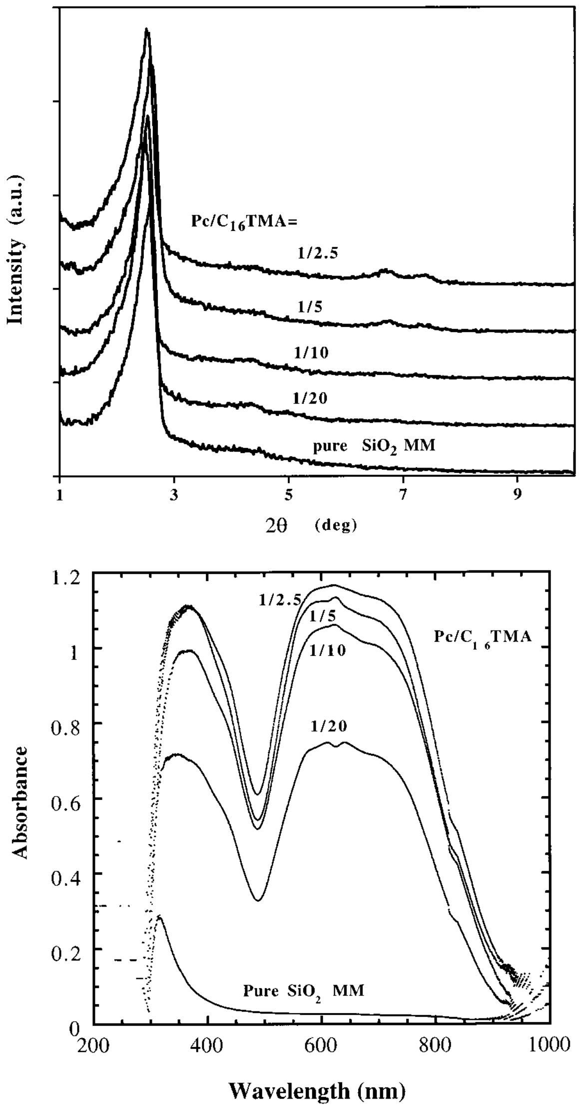

Figure 7. (a, top) Low-angle XRD pattern for Pc-doped SiO_2 MM with a variation of doping concentrations and the reflection pattern shifts with the doping concentration. (b, bottom) Optical absorption spectra for Pc-doped SiO_2 MM and the Pc molecular absorption was clearly seen through transparent SiO_2 framework.

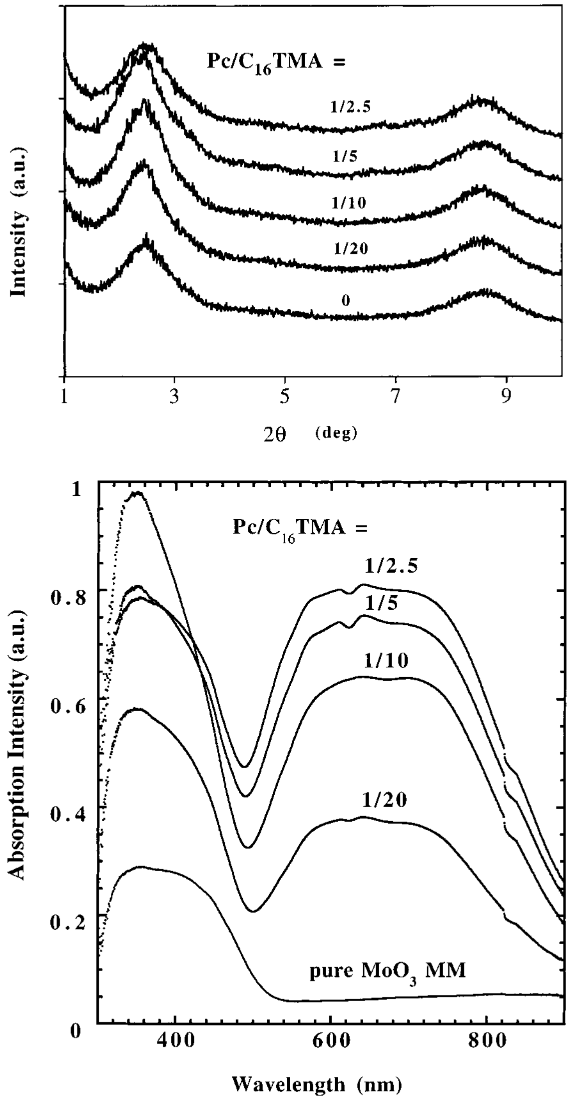

Figure 8. (a, top) Low-angle XRD pattern of Pc-doped MoO_3 MM and diffuse fundamental reflections from amorphous mesostructure are seen for various Pc-doping concentrations. (b, bottom) Optical absorption spectra for Pc-doped MM and the absorption of Pc molecules is observed through transparent MoO_3 frameworks. The powder is greenish and the color becomes intense with a doping.

ratio increases, the absorption intensity increases and the powder becomes more greenish. The absorption at short wavelength region is coming from the interband transition of vanadia framework.

Figure 6 shows a SEM photograph for Pc-doped vanadia MM, and powders of a size around 1−10 μm were clearly seen. The shape of them seems like a flake or sheet, which is a typical feature of the vanadia materials. The shape of the materials is identical with the results of XRD, in which a lamellae pattern was observed for doped vanadia mesostructured materials. The Pc molecules are doped between the lamellae vanadia sheets and do not act as an expander molecule, perhaps inserted among the C_{16}TMA surfactant tail in the micelles.

The Pc-doped SiO_2 mesostructured materials were similarly synthesized and characterized. Figure 7a shows LAXRD for Pc-doped SiO_2 MM, and the mesostructure was examined by the diffraction peaks at low angles. In pure SiO_2 MM, supposedly, hexagonal phase was formed and the addition of the Pc molecules shifts the mesostructure and at the Pc/C_{16}TMA ratio of $^1/_5$, from there, (110) as well as (200) reflections become small and other reflections at around 7° appear; the changes are significant if comparing between pure SiO_2 MM and Pc/C_{16}TMA ratio of $^1/_{2.5}$. It is very interesting to note that the mesostructure channel size is not expanding by heavy doping of Pc molecules while a half-width of the fundamental reflection increases with doping, which indicates that the mesostructure is distorted. The peaks at around 7° appear at a high Pc-doping ratio, and those are correlated with a stacking of Pc molecules where the *d* value is equivalent to a crystalline form of Pc molecules. Figure 7b shows the absorption spectra of Pc-doped SiO_2 MM, and absorption from Pc molecules is clearly seen through a transparent SiO_2 framework. The absorption becomes intense with doping concentration, and the Pc molecules are concentrated in the mesochannels without expanding its size.

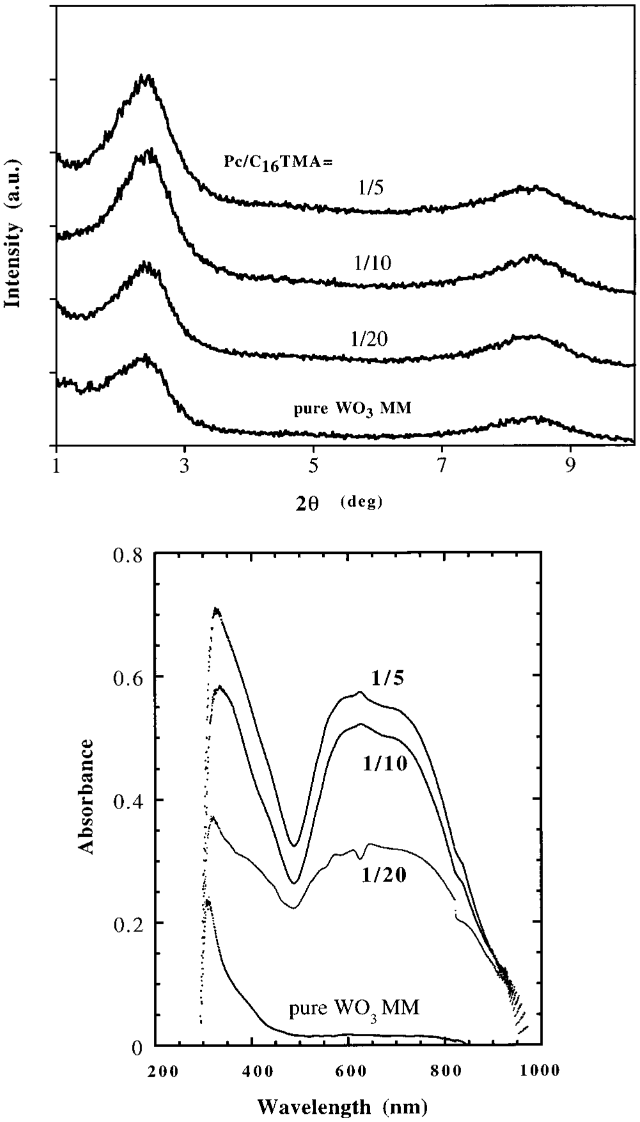

Figure 9. (a, top) Low-angle XRD pattern of Pc-doped WO_3 MM and diffuse fundamental reflections from the amorphous mesostructures are observed for various Pc-doping ratio. (b, bottom) Optical absorption spectra for Pc-doped WO_3 MM; the spectra are similar to other doped metal oxides MM in this work.

We have also investigated structures of Pc-doped MoO_3−MM and MoO_3−MM. The doped MoO_3 mesostructure was made in a manner similar to that for vanadia MM. Figure 8a shows a low-angle XRD scan of Pc-doped MoO_3−MM with a variation of the Pc-doping molar ratio (Pc/C_{16}TMA) from 0.0 (pure MoO_3 MM) to $^1/_{2.5}$. In the materials, the mesostructure was amorphous, lacking in symmetry of the channels' array despite the whole Pc-doping ratio, while diffraction peaks were broad with two diffuse reflections at 2° and 9°, which is quite different from the results of vanadia−MM. In this case, the incorporated Pc molecules do not act as stabilizer molecules for the crystalline hexagonal phase. In the amorphous mesophase, the average pore spacing estimated by broad reflections at LAXRD was not changed so much by Pc doping and, at the same time, the random structure was not changed. The difference presumably comes from a shape difference of the primarily metal oxides building units, in forming an interior surface of the mesochannels. The structural analysis of the primary building units should be the next step for understanding a difference of the mesostructure. Figure 8b shows absorption spectra of the doped MoO_3−MM, and the absorption of Pc was observed through a transparent MoO_3 framework from 500 to 900 nm wavelength region. As the doping ratio in the material increases, the absorption intensity increases without a shift of the spectrum's shape, although the absorption intensity in not so quantitative obtained by the diffuse reflection measurement. Additionally, Pc-doped WO_3−MM was successfully synthesized, and the amorphous mesophase structure was obtained despite the Pc doping ratio, similar to the MoO_3−MM case.

Figure 9 shows LAXRD and optical absorption spectra of the Pc-doped WO_3−MM products. The amorphous mesostructure was clear by the diffuse reflections at 2° and 8°, which is completely similar to MoO_3 MM. The optical absorption for Pc-doped WO_3−MM, shown in Figure 9b, is almost the same as that of MoO_3−MM. The absorption of molecules in the channels can be seen through a transparent metal oxide framework.

So, in the present work, there are two types for Pc-doped MM from a mesoscale structural point of view. The mesophase phase forming system is a vanadia and SiO_2 MM and they have either lamellae or disordered hexagonal phase even in a Pc-doping case; however, an amorphous mesostructure was formed in both MoO_3 and WO_3 MM case with Pc-molecules doping. The origin of the differences is not clear at the moment, but presumably, the building oxides unit-cell structure is responsible for the phase formation of these materials. In the silica (SiO_2) case, because of the amorphous nature of the Si−O networks, a curved interior surface such as for the hexagonal phase is possible even in Pc-doping MM case, but in the MoO_3 and WO_3 case, the well-curved interior surface is inhibited by the crystalline nature of the building-unit metal oxides in the frameworks. The differences among these Pc-doped metal oxides MM were under continuous investigation in relation to the mechanism of formation of the doped mesostructure materials.

Conclusions

We have successfully synthesized Pc-doped metal oxides mesostructured materials in vanadia, MoO_3, WO_3, and SiO_2 framework materials by direct synthetic pathways of dye-doped surfactants micelles coassembling with metal oxide precursors. As an alternative way, dye-doped mesostructured materials were synthesized through a coassembly of ferrocenyl TMA surfactants. The Pc molecules are incorporated and organized inside mesochannels to form mesostructured materials with various mesophase symmetry, and optical adsorptions from those incorporated molecules are measured through transparent metal oxides frameworks.

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