Synthesis of Chlorophyll Doped Silica-mesostructure Materials

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The photosynthetic molecule chlorophyll(Chl) doping silica mesostructure material can be directly synthesized by self-organized co-assembly of mixing Chl with hexadecyltrimethylammonium chloride (C_{16}-TMA) surfactant, successfully. X-ray diffraction pattern (XRD) shows a typical hexagonal diffraction pattern of the mesoporous materials with d_{100} about 35.3 Å. The optical absorption spectra show the typical band (located at about 680 nm) of Chl.

Self-assembled organic-inorganic molecules into highly ordered nanostructure architecture have attracted increasing attention because these materials provide a rich source available for scientific researches and technological applications.[1-3] Recently, the production of functional molecule containing self-assembling mesostructure material has been a interesting branch of the advanced mesomaterials research.[4]

In this work, we have investigated the synthesis of photosynthetic mesostructure materials (in powder) for optical device applications where Chl is doped in the mesochannels by direct self-organizing process of C_{16}-TMA surfactant, not by external doping after the calcination of the channel. In this case, Chl molecules are, supposedly, embedded and self-assembled among the C_{16}-TMA surfactant's hydrophobic tails and organized with a periodic array of a lipid micellar structures. Chl was chosen as a functional molecule because much attention are given for the electronic and optical properties of Chl on the possibility of producing useful solar cells.[5,6]

Synthesis of the MCM-41 (hexagonal structure) has been described by many groups.[1-3] Chl doping silica-functional surfactant mesostructure material was prepared as follow: C_{16}-TMA 1.0 g was dissolved in 60 ml H_2O, then stirring for about 30 min to obtain homogeneous C_{16}-TMA aqueous solution. Chl 0.0015 g was added to this aqueous solution. The suspension was sonicated for 5-10 min and then stirred for 3-5 h at room temperature to attain solubilization equilibrium. A green homogeneous C_{16}-TMA/Chl aqueous solution was obtained, and 4.0 g 95% tetraethyl orthosilicate (TEOS) was added. Finally, HCl aqueous solution was added to make the solution acidic. Then, the mixture was stirred for about 15 min. After stirring, the solution became completely colorless because of precipitation of the green powders at the bottom of a beaker, which indicated that all of the C_{16}-TMA/Chl reacted with silica species to generate the mesostructured powder. In this case, an acidic synthesis of silica mesostructure through a mediated pathway can form a charged $S^+X^-I^+$ interface; /Chl@C_{16}-----$(CH_3)_3N^+/Cl^-/^+H_2O$-Si-O/. The Chl doping silica mesostructure powder can be obtained after washing and drying in air. All the operations with Chl molecule were carried out at room temperature under dim green light. After drying, Chl is stable even in VIS light. In this new process, it is not necessary to dope molecules into mesoporous after the channels became open by calcination.

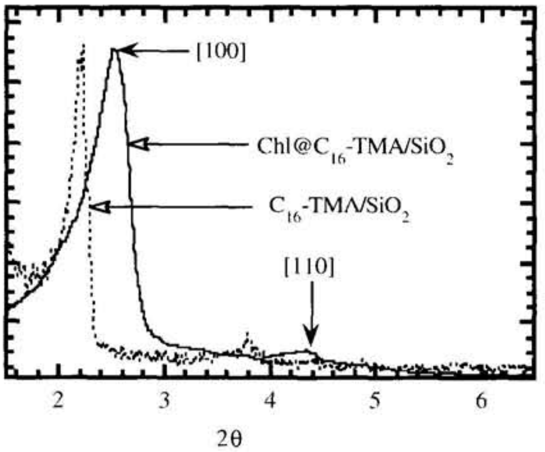

Figure 1. The X ray diffraction pattern of the Chl doped silica mesoporous materials. The interplanar distance d_{100} of the hexagonal unit cell is 35.3Å and that (d_{110}) is 21.0Å. The d_{200} is very weak.

The typical hexagonal diffraction patterns of C_{16}-TMA/SiO_2 and C_{16}-TMA@Chl/SiO_2 mesoporous structure were confirmed by XRD as shown in Figure 1. Two peaks observed in the low-angle region were [100], and [110]. The interplanar distance d_{100}=35.3 Å of C_{16}-TMA@Chl/SiO_2 which is less than that one (about 39.5 Å) in the C_{16}-TMA/SiO_2 under the same experimental condition. The hexagonal unit cell length of C_{16}-TMA@Chl/SiO_2 is about $2d_{100}/\sqrt{3}=40.8$ Å. The same phenomenon which d-space of [100] decreases after functional molecule doping also appeared in phthalocyanine doped mesostructure materials.[7,8] This phenomena can be explained that Chl molecule piece is inserted into the pieces of the self-assembled hydrophobic tails of C_{16}-TMA in a periodical manner within a mesostructured channel. Chl molecules are scarcely located in the center position of the C_{16}-TMA micelle which should expand micelle size. Chl molecules inserted between C_{16}-TMA's hydrophobic tails extracted slightly the channel size, maybe it stabilize the silica (SiO_2) framework. If Chl is inserted into C_{16}-TMA surfactant's hydrophobic tails one by piece, it increases the interfacial area (A_S) per surfactant molecule effectively. For hexagonal phase, the A_S can be written in: $A_S=2V_S/[d/(\sqrt{3})-w/2]$,[9] here V_S, d and w stand for the volume of one surfactant molecule, the repeat spacing and the width of the silica walls, respectively. V_S should be constant for the same surfactant, After Chl-doping, the increase of A_S just means the decrease of d, that's why [100] peak's position of C_{16}-TMA@Chl/SiO_2 goes shift to high angle. But, the doping mol ratio (Chl : C_{16}-TMA) is very low about 0.0006. Such slightly Chl doping shifts d-space about 4 Å and makes x-Ray peak's

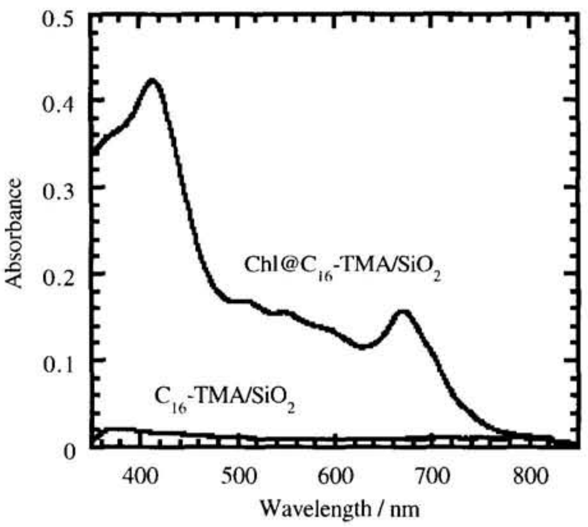

Figure 2. Absorption spectra of silica/C_{16}-TMA mesostructure materials and Chl doped silica/C_{16}-TMA mesostructure materials.

width broad, which shows that doped Chl takes a very important role in C_{16}-TMA@Chl/SiO_2 synthesis process.

Since the silica system exhibits amorphous properties of the Si-O networks, a curved interior surface such in the hexagonal phase is possible even in Chl doping mesostructure materials. That's why C_{16}-TMA@Chl/SiO_2 show a hexagonal phase.

Figure 2 shows the absorption spectra of Chl doped silica-mesoporous materials. The absorption bands located at about 680 nm, and 420 nm result from Chl molecules chromophore, which is broader than those of Chl molecules in organic solvent. It results from the interaction between the Chl molecules arranged in surfactant molecules. In comparison with absorption spectra of C_{16}-TMA/SiO_2, the high absorbance coefficient of Chl can be found because a slightly doping (mole ratio 0.0006) gives very strong absorption spectra. The photosynthetic electron-transfer mechanism is so-called z-scheme. There are two parts involved which move an electron from a low level (donor, ex. water: H_2O---> O_2+H^++e^-) through two successive quantum acts to reach a high level (acceptor, ex. water: H^++e^- --->H_2). Therefore, it is necessary to dope Chl molecule in a redox-active surfactant for a solar cell application.

The Chl-doping silica-mesostructured materials can be directly synthesized. But, for a solar cell and other optical application, it is very important to control the phase from powder to thin film on substrate,[10-12] and to use a redox-active surfactant for mesostructured film. The synthesis procedure of Chl-doping self-organization redox-active meso-structure thin film on ITO substrate is on the way.

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