Microscopic Structure of Separately Accommodated Porphyrins and Viologens in Mesoporous Silica and Titania Nanosheet Hybrid Films

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The microscopic structures of two nano-structured inorganic films, one based on titania nanosheets (TNS) and the other on mesoporous silica (MPS), were investigated. The clear stacking structure of the TNS and MPS films were observed by the XRD, SEM, and TEM analyses. The selective adsorption of the porphyrin derivatives into the MPS nano-cavities and viologens into the TNS nano-layers was also investigated by absorption and energy-dispersive spectroscopy (EDS).

Key Words: Mesoporous silica, Titania nanosheet, Photoinduced electron transfer, Charge separation

1. INTRODUCTION

Nano-structured inorganic compounds such as mesoporous silicas[1] and layered inorganic materials[2,3] are of great interest for their potential in the development of organic-inorganic hybrid materials, since they can easily accommodate various organic molecules within their nano-sized structure. Organic molecules in nano-structured inorganic compounds exhibit unique physical and chemical properties such as the increased lifetimes of unstable organic species[4], acceleration of electron and energy transfer efficiencies, [5] suppression of back-electron transfers[6], and the control of the structural orientation[7,8], thus, allowing unique, controlled reactions and product distributions[2,3].

We have reported[9,10] on the syntheses of consecutively stacked hybrid thin films of mesoporous silica (MPS) and layered titania nanosheets (TNS)[2b,c,11] and the accommodation of two different photofunctional organic molecules, i.e., cationic metalloporphyrin derivatives (tetrakis (1-methylpyridinium-4-yl) porphyrinatometal (4+) ion (MTMPyP); $M = H_2$, Zn, Co) and 1,1'-dimethyl-4,4'-bipyridinium (methyl viologen; MV^{2+}). The MTMPyP and electron-accepting MV^{2+} were separately incorporated within the MPS nano-cavities and the interlayers of the photocatalytic



Fig. 1. Schematic drawing of an (MV²⁺-TNS)/ (MTMPyP-MPS) hybrid films.

TNS, respectively (Fig. 1). The $(MV^{2+}-TNS)$ film

was stacked on the (MTMPyP-MPS) film to form a (MV²⁺-TNS)/(MTMPyP-MPS) hybrid which exhibited unique photoinduced electron transfer across the interface. The changes observed in the absorption spectra of $(MV^{2+}-TNS)/(H_2TMPyP-MPS)$ upon UV-light irradiation are shown in Fig. 2 as typical examples. Upon irradiation of the TNS within the $(MV^{2+}-TNS)/(H_2TMPyP-MPS)$ films by UV light (TNS excitation), one-electron reduced MV^{2+} radical ions (MV^{++}) were formed at the expense of the one-electron oxidative consumption of the H₂TMPyP ions, i.e., a charge separation (CS) between the two could be achieved. Interestingly, the CS observed within the (TNS)/(MPS) hybrids was thermally stable, even in ambient atmosphere, and this stability was retained even after several hours,[12] although its origin has yet to be clarified. Such unique photoinduced electron transfers and CS may be the result of the microscopic structure of the (MV²⁺-TNS)/(MTMPyP-MPS) films. With regard to the distance between the TNS/MPS interfaces and





MTMPyP molecules within the photonically inactive

MPS nano-cavities, the MTMPyP molecules were found to be concentrated near the TNS/MPS interface or homogenously dispersed in the MPS nano-cavities. In the present work, the microscopic structure of the $(MV^{2+}-TNS) / (MTMPyP-MPS)$ films was investigated by absorption spectroscopy, transmittance electron microscopy (TEM), and energy dispersive spectroscopy (EDS).

2. EXPERIMENTS

The $(MV^{2+}-TNS)/(MTMPyP-MPS)$ hybrid films were synthesized as reported in previous literature, as follows:[9] An aqueous MPS precursor gel suspension of a cationic surfactant, i.e., CTAC (cetyltrimethylammonium chloride), was spin-coated on a quartz substrate and then calcined at 500°C for 3 hrs. The thin films were soaked for 1.0 hr in an aqueous $9.7 \times 10^{-5} M$ solution of MTMPyP at ambient temperature, leading to the formation of brownish colored films. The MTMPyP/MPS films were then hybridized with TNS by casting deposition and were soaked in an aqueous $2.1 \times 10^{-4} M$ solution of MV²⁺ for 4 hrs at ambient temperature. The $(MV^{2+}-TNS)/(MTMPyP-MPS)$ hybrid films

were irradiated with a 300-W Xe lamp (XDS-301S, WACOM, Co.) as the light source at a distance of 10 cm under ambient atmosphere. A combination of two cut-off filters, UTVAF-50S and UTVAF-43U (HOYA), was used for UV light irradiation of 270-380 nm. Under these conditions, TNS was observed to function as a photocatalyst and almost all of the incident light (> 99%) could be absorbed. Scanning electron micrograph (SEM) images were recorded on a JSM-5600 apparatus (JEOL) operating at 20 kV for the Au-coated samples. Transmittance electron micrographs (TEM) and energy dispersive spectroscopic (EDS) elemental analyses were carried out on a JEM-2010FEF (JEOL) apparatus operating at 200 kV and 1.0 nA. The scanning time and energy range for the EDS analysis were set at 17 s and 0-20 keV, respectively. Powder X-ray diffraction analysis (XRD) was carried out with a Rigaku RINT-2100 XRD apparatus operating at 40 kV and 40 mA with Ni-filtered CuK_a radiation of 0.154 nm The UV-visible absorption spectra wavelength. were recorded in the transmittance mode with a JASCO type V-550 spectrometer. The fluorescence spectra were recorded on a JASCO FP-750 fluorescence spectrophotometer.

RESULTS AND DISCUSSION

The structures of the mesoporous silica/titania nanosheet [(MPS)/(TNS)] hybrid films were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD).[9b] SEM analyses revealed that (MV²⁺-TNS)/(MTMPyP-MPS) exhibits clear a [substrate-MPS-TN] tri-layer structure. XRD studies showed two characteristic diffraction peaks for the (MV²⁺-TNS)/(MTMPyP-MPS) hybrid film. The diffraction peaks at $2\theta = 2.8 \text{ deg} (d_{210} = 3.3 \text{ nm})$ and $2\theta = 4.9 \text{ deg} (d_{001} = 1.1 \text{ nm})$ were attributed to the MPS nano-cavities and MV²⁺-containing TNS layer structures, respectively. These results clearly indicate that the TNS/MPS hybrid films were independently stacked on the substrate without any peeling or disorientation of the films.

The MPS films were soaked in $[MV^{2+}] = 2.1 \times$

 10^{-4} M aqueous solution, however, the MV²⁺ molecules were not adsorbed into the MPS nano-cavities. This may be the result of the strong hydrophilicity of the MV²⁺ molecules as well as the incompatibility of the molecular size of MV²⁺ and pore size of the MPS nano-cavities.

The selective adsorption of MTPMyP into the MPS nano-cavities was also investigated. When the MTMPyP molecules were intercalated within the stacked clay interlayers, a 50-60 nm red shift was observed, as compared to aqueous solution, due to a leveling off or flattening of the methylpyridinium ring.[7] The adsorbed state of MTMPyP was estimated by analysis of the Soret absorption maxima and the absorption maxima of MTMPyP for the three different systems: (A) in aqueous solution; (B) the $(MV^{2+}-TNS)/$ (MTMPyP-MPS) hybrid films; and (C) intercalated in the stacked TNS interlayers. The results are summarized in Table 1 and the absorption spectra (MV²⁺-TNS)/(MTMPyP-MPS) the of and (MTPMyP-TNS) hybrid films are shown in Figs. 3(a) and (b), respectively.

 Table I:
 Soret Absorption Maxima (nm) of MTMPyP in Various Systems^a

System	MTMPyP		
	H ₂	Zn	Co
(A) aqueous solution	421	435	428
(B)(MV ²⁺ -TNS)/(MTMPyP-MPS)	433	450	441
(C) (MTPMyP-TNS)	475	462	462

^a Reported values in Ref. 9b



Fig. 3. Absorption spectra of (a) $(MV^{2+}-TNS)$ /(H₂TMPyP-MPS) and (b) (H₂TPMyP-TNS) hybrid films.

The absorption maxima for the Soret band of MTMPyP in the $(MV^{2+}-TNS)/(MTMPyP-MPS)$ hybrid films showed red shifts of 12-15 nm, as compared to those in aqueous solution. The Soret band maxima of the porphyrins are known to be sensitive to the polarity of the solvent used, i.e., in a less polar solvent environment, the absorption maximum shifts toward longer wavelengths.[13] The observed red shift indicates a decrease in the polarity of the environment surrounding the MTMPyP within the MPS nano-cavities. However, for the layered TNS systems, the Soret bands showed a red shift (27-54 nm) as compared to aqueous solution. Spectroscopic investigations showed the adsorbed MTMPyP molecules to be level or flat against the TNS layer, in a manner similar to porphyrins incorporated in layered clay systems.[7] Moreover, the fluorescence spectra of the porphyrins showed dramatic changes, i.e., a substantial broadening and change in the spectral shape due to the formation of molecular aggregates. However, the emission spectra of MTMPyP in MPS were similar to those for the monomeric MTMPyP in aqueous solution and, thus, the MTMPyP molecules may exist in an isolated form within the MPS nano-cavities.

The microscopic structure of TNS/MPS and microscopic distribution of MTMPyP in the MPS nano-cavities were investigated by TEM and EDS techniques. To obtain clear EDS spectra, CoTMPyP was used as a representative MTMPyP molecule. Cross-sectional TEM analyses (Fig. 4) showed that the $(MV^{2+}-TNS)/(CoTMPyP-MPS)$ films exhibit a clear [TNS-MPS-substrate] tri-layer structure, and the estimated film thicknesses for TNS and MPS were estimated to be ca. 500 and 200 nm, respectively. These results are in good accordance with the SEM and XRD analyses described above.



Fig. 4. Cross-sectional TEM image of the $(MV^{2+}-TNS)/(CoTMPyP-MPS)$ hybrid film. Two selected areas (A and B) for EDS analyses are shown as rectangles.

EDS analyses were carried out on the (MV²⁺-TNS)/(CoTMPyP-MPS) films in two different selected areas, i.e., (CoMTMPyP-MPS) is directly attached to the TNS layer for Area A (Fig. 4) while, for Area B (Fig. 4), it is detached from TNS. The EDS spectra exhibited intense signals at 0.5, 1.7, and 8.0 keV, characteristic of the SiO₂ in the MPS framework, as shown in Fig. 5. The relative intensities of 0.5/1.7 keV are almost similar to Figs. 5(a) and (b). Moreover, weak but clear signals from the cobalt atoms were observed at around 6.8 keV, indicating that the CoTMPyP molecules were MPS accommodated in the nano-cavities. Interestingly, the signal intensities (ca. 20 counts) from the cobalt atoms were almost the same between the selected areas A and B, indicating that the adsorbed amounts of CoTMPyP were almost the same. On the other hand, the CoTMPyP molecules were homogeneously distributed within the MPS films.

Upon 90 min UV-irradiation, almost all of the MTMPyP molecules in the MPS nano-cavities, i.e., both the MTMPyP molecules directly attached as well as detached from the TNS layers were oxidized (Fig. 2). These results indicate the formation of stable negative charge carriers (electrons) and long distance migrations within the TNS/MPS hybrid systems. Tatsuma *et al.* have reported the remote photocatalytic oxidation of organic molecules by stable, photochemically generated H_2O_2 .[14] Detailed studies on the reaction mechanisms and



Fig. 5. EDS spectra of a $(MV^{2+}-TNS)/(CoTMPyP-MPS)$ film in two different selected areas: (CoMTMPyP-MPS) was (a) directly attached to the TNS layer (Area A, Fig. 4); and (b) detached from the TNS layer (Area B, Fig. 4).

carrier migration within the (MV²⁺-TNS)/(CoTMPyP-MPS) hybrid systems are now underway.

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