

## Nanospace Confinement of Conducting Polymers using Mesoporous Silica and Organosilica

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### Introduction

Conducting polymers with unidirectionally aligned polymer chain, such as those confined in one-dimensional nanoscale channels of mesoporous materials, are expected to lead the novel applications for electroconductive and optoelectronic devices. [1] Although many approaches have been proposed for the confinement of polymers into the pores of mesoporous materials, only insufficient amount of polymers for these applications was confined. In this study, we investigated an adsorption behavior of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) on organically surface-modified mesoporous silica (FSM-16) and mesoporous organosilica. We evaluated the amount of the confined polymers and the UV-vis absorption spectrum of the confined MEH-PPV.

### Experimental

**Preparation of the mesoporous materials.** Mesoporous silica (FSM-16) and mesoporous organosilica were prepared by the previously reported procedures [2-3]. Pore surface of the FSM-16 was modified by using silane coupling agents to obtain mercapt propyl trimethoxy silane grafted FSM-16 (MPTMS-FSM-16) and dimethyl phenyl chloro silane grafted FSM-16 (DMPCS-FSM-16).

**Adsorption of MEH-PPV on the mesoporous materials.** The prepared each mesoporous material (150 mg) was dispersed in the chlorobenzene (CB) solution (30 ml) that dissolved a given amount of MEH-PPV (2, 25 or 100 mg of MEH-PPV in 1L of CB). The solution was stirred for 3 days in air atmosphere at room temperature. The dispersed powder was filtered out, washed three times with chlorobenzene and dried for 1 day at 353 K in air.

**Characterization of the MEH-PPV/mesoporous material composites.** We measured XRD patterns,  $N_2$  adsorption isotherms and TG-DTA curves for the prepared composites in order to evaluate the amount of the MEH-PPV confined in the pore of the mesoporous materials. We also measured UV-vis adsorption spectra of the composites.

### Results and discussion

**Adsorption behavior of MEH-PPV on mesoporous materials.** Figure 1 represents the XRD patterns of as-prepared FSM-16 and MEH-PPV/FSM-16 composites. Sharp peaks derived from the ordered mesopore were observed for as-prepared FSM-16. For the MEH-PPV/FSM-16 composite, the peaks at the same diffraction angles but with lower intensities were observed. These results indicate that MEH-PPV was adsorbed on the inner surface (pore surface) of FSM-16. Similar results were obtained for the composites prepared using surface-modified FSM-16 and mesoporous organosilica.

Figure 2 represents the  $N_2$  adsorption isotherms of as-prepared FSM-16 and MEH-PPV/FSM-16 composites. The pore volume of the composite was found to decrease with increasing the concentration of the MEH-PPV/CB solution used for the preparation of the composites. It was also found that the relative vapor pressure ( $P/P_0$ ) at which the amount of adsorbed  $N_2$  increased steeply was lowered with increasing the concentration of the MEH-PPV/CB solution. These results clearly show that MEH-PPV was adsorbed on the inner surface (pore surface) of FSM-16. Similar results were obtained for the composites prepared using other mesoporous materials.

According to the TG-DTA measurements, it was shown that the amount of adsorbed MEH-PPV strongly depends on the modification of the surface as follows: The adsorption amounts were 5.36, 1.53 and 0.33 wt% when the adsorbates were non-modified FSM-16 (pore diameter,  $D_p = 2.77$  nm), MPTMS-FSM-16 ( $D_p = 2.27$  nm) and DMPCS-FSM-16 ( $D_p = 2.48$  nm), respectively (the concentration of used MEH-PPV/CB solution was 100 mg/L). In addition, the adsorption amount was 1.61 wt% for the composite prepared using mesoporous organosilica ( $D_p = 2.89$  nm) and MEH-PPV/CB solution (100 mg/L). It is known that the OH groups exist (in the form of Si-O-

H) at the surface of the pore of FSM-16. The organic groups were grafted at the pore surface by the reaction between silane coupling agents and the OH groups, thereby decreasing the number of the OH groups at the surface for the surface-modified FSM-16. Moreover, it is considered that the number of the OH groups in mesoporous organosilica is lower than that of FSM-16 because mesoporous organosilica has organic groups inside the pore wall composed of Si-O network. The OH group at the pore surface is Lewis acid and aromatic ring or ether group in MEH-PPV is Lewis base. Therefore, it is expected that acid-base interaction may play an important role for the adsorption of MEH-PPV on mesoporous materials.

**UV-vis absorption spectrum of the confined MEH-PPV.** The optical absorption edge of a free MEH-PPV was  $\sim 2.0$  eV, which corresponds to the band gap of MEH-PPV. It was shown that the optical absorption edge ( $\sim 2.2$  eV) of the confined MEH-PPV in mesopore is clearly blue-shifted when compared to that of free MEH-PPV. Similar phenomenon was reported for the MEH-PPV adsorbed on nanoporous alumina ( $D_p = \sim 20$  nm) [4]. The observed blue-shift may be attributed to an isolation of the conjugated polymer chains.

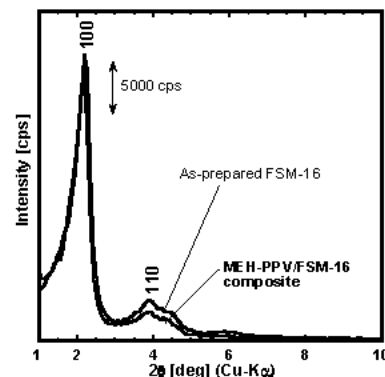


Fig. 1 Powder XRD patterns measured for as-prepared FSM-16 and MEH-PPV/FSM-16 composite prepared using 100mg-MEH-PPV/1L-CB solution.

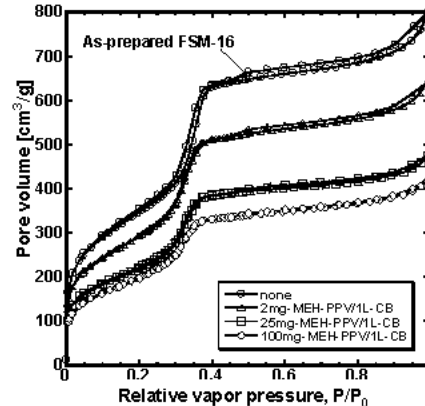


Fig. 2  $N_2$  adsorption isotherms of as-prepared FSM-16 and MEH-PPV/FSM-16 composites: The composites were prepared by using FSM-16 and MEH-PPV/CB solution with given concentrations.

### Conclusions

The amount of the confined MEH-PPV was found to strongly depend on the surface modifications of the mesoporous materials. It is expected that acid-base interaction between pore surface and MEH-PPV may play an important role for the adsorption of MEH-PPV on the mesoporous materials. The optical absorption edge of the confined MEH-PPV was clearly blue-shifted when compared to that of a free MEH-PPV, suggesting the isolation of the conjugated polymer chains.

### References

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