

## Thin Film of Mesoporous MCM-41 Grown on Indium-Tin-Oxide Glass Substrate

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**Abstract:** From a basic solution containing cetyltrimethylammonium cations as the template, thin film of mesoporous MCM-41 has been grown on the surface of a pre-treated indium-tin-oxide conducting glass substrate. The channel axis of the film is oriented parallel with the surface plane of the substrate, and the film is stable after careful removal of template in vacuum.

**Keywords:** mesoporous, MCM-41 film, ITO glass substrate, basic medium, synthesis.

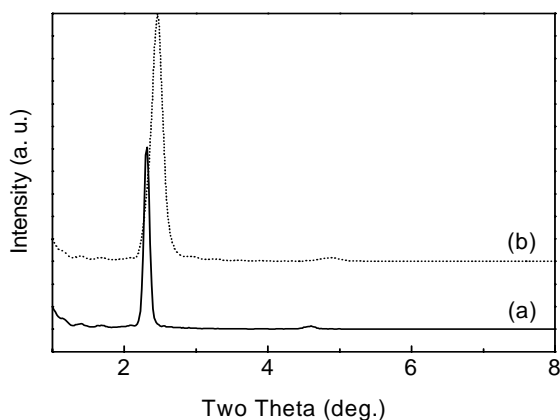
The mesoporous M41S materials have attracted considerable attention since they were first discovered in 1992<sup>1,2</sup>. These materials, among which is the MCM-41 molecular sieve with a hexagonal array of mesopores (diameter 15-100 Å), have enormous potential in applications such as catalysis<sup>3</sup>, host-guest chemistry<sup>4,5</sup> and separation<sup>6</sup>. Uniform thin films based on MCM-41<sup>7-10</sup> have also been prepared at the interfaces of solution/solid and air/solution. However, the previously-reported films were grown invariably from an acidic solution containing surfactant molecules as the structure-directing agent (template), and all the solid substrates employed except for graphite<sup>11</sup> were insulators. Here we present the synthesis of MCM-41 film on the surface of indium-tin-oxide (ITO) glass plate, which is an electrical conductor, from an ammonia solution. X-ray diffraction (XRD) indicated that the arrangement of the mesoporous channels in the film was highly ordered and the structure of the film remains after careful removal of the template in vacuum.

The ITO glass plate (25×15×1.5 mm) was pre-treated by boiling it in a 5 wt% NaOH aqueous solution for 10 minutes, kept in the solution at 50 °C for two hours and washed copiously with distilled water. For the growth of MCM-41 film on the pre-treated ITO glass plate, 200 mL ammonia (26 wt%) aqueous solution was mixed with 280 mL distilled water. To the solution was added 2.0 g cetyltrimethylammonium bromide (CTABr) and the mixture was heated under stirring until the solid was completely dissolved. The pre-treated ITO glass plate was placed in the solution followed by dropwise addition of 13 mL tetraethylorthosilicate (TEOS). The reaction mixture with a pH of about 13 was vigorously stirred at 60 °C

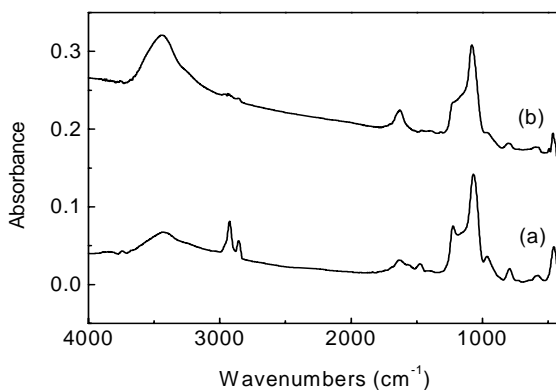
for 2 hours. The ITO glass was recovered from the reaction system and treated ultrasonically to remove the powder particles on its surface. The X-ray diffraction patterns were recorded on a Siemens D5005 diffractometer with Ni-filtered Cu-K $\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ), and the infrared spectra were obtained on a Nicolet Impact 410 FTIR spectrometer for the powder samples collected by scraping the films carefully from the ITO substrate.

The X-ray diffraction pattern of the as-prepared film on the ITO glass plate is shown in **Figure 1 (a)**. There appear a strong diffraction peak at  $2.32^\circ$  and a weak one at  $4.59^\circ$  ( $2\theta$ ) on the pattern, corresponding to  $d$ -spacings of  $38.02$  and  $19.26 \text{ \AA}$ . These peaks are attributed<sup>11</sup> to the (100) and (200) reflections of the MCM-41 film. The absence of the (110) peak observed for the powder XRD pattern of MCM-41 suggests<sup>7</sup> that the channel axis in the film is oriented parallel with the surface of the substrate plane. When the as-prepared film is subjected to calcination at about  $400^\circ\text{C}$  in vacuum for 4 hours, the intensity of the first peak of the XRD pattern (**Figure 1 (b)**) is enhanced considerably due to the removal of the template molecules present in the as-prepared MCM-41 film. On the other hand, the peak maximum shifts towards higher angles to about  $2.46^\circ$  corresponding to a  $d$ -spacing of  $35.84 \text{ \AA}$ . This peak shift is a reflection of the contraction of the walls around the mesopores in the film. The broadening of the peak after calcination results from slight decrease of the ordering degree of the mesopore arrangement. It is worthwhile to point out that appropriate calcination procedure is very important to retain the mesoporous structure of the film. The temperature increasing rate for the calcination at above  $200^\circ\text{C}$  should be less than  $2^\circ\text{C}/\text{min}$ . Otherwise the MCM-41 structure would collapse after removal of the template molecules. In comparison with those in the powder form of MCM-41, the mesoporous channels in the film are much longer and the decomposed species are more difficult to diffuse out of the channels. The water molecules in the decomposed species attack the walls of the MCM-41 film at elevated temperatures, and as a result, the porous structure of the film deteriorates if the decomposition of the template proceeds rapidly.

**Figure 1.** X-ray diffraction patterns of MCM-41 film on ITO substrate: (a) as-prepared and (b) calcined at  $400^\circ\text{C}$  in vacuum.



**Figure 2.** Infrared spectra of the powder samples collected from the MCM-41 film on ITO substrate: (a) as-prepared and (b) calcined at 400 °C in vacuum.



**Figure 2** shows the IR spectra of the as-prepared film and the film after calcination in vacuum. The spectrum of the as-prepared film exhibits two distinct absorption bands at 2926 and 2856  $\text{cm}^{-1}$  attributable to the asymmetric and symmetric C-H stretching modes of  $-\text{CH}_2$  groups. These two absorptions and the one at 1475  $\text{cm}^{-1}$  due to  $\delta_{\text{C-H}}$  vibration are nearly invisible for the spectrum of the calcined film, indicating that the template molecules are almost completely removed by calcination. The broad absorption at around 3450  $\text{cm}^{-1}$  arises from the presence of water molecules. On the basis of the absorption intensity, it is obvious that the calcined film contains much more water molecules than the as-prepared film. This hydrophilic nature of the calcined MCM-41 film is attributed to the existence of  $-\text{OH}$  groups<sup>12</sup> on the internal surface of the channels of the material. The absorptions at 1220, 1070  $\text{cm}^{-1}$  and those at lower frequencies are assigned to the vibration modes of the  $\text{SiO}_2$  framework of the films, and the spectra within the low frequency region (1300-400  $\text{cm}^{-1}$ ) appear to be similar for the as-prepared and the calcined film samples. Therefore, the calcination process has no significant effect on the structural feature of the walls around the mesoporous channels of the MCM-41 film.

The ITO glass plate remains conductive after the growth of the MCM-41 film on its surface and the calcination process does not affect its conductivity significantly. We also investigated the conducting properties of the films. The preliminary results indicate that the film is a semiconductor and apparent rectifying effect has been observed for the as-prepared MCM-41 film on the ITO substrate. The detail of this intriguing property of the film remains a matter of further investigation.

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