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# Deposition of Layer-by-layer Inorganic-organic Nano-hybrid Ultrathin Films onto SBA-15

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**Abstract:** Deposition of inorganic-organic nano-hybrid ultrathin films onto mesoporous silicate materials has been proven possible by using layer-by-layer assembly method. In combination with sol-gel method, titania, subsequently dye molecules (or polymer) were successfully fabricated onto the inner wall of SBA-15. Their structures were preliminarily characterized by FTIR and solid-state UV-Vis spectroscopy, thermal analysis, and BET surface area measurements, respectively.

**Keywords:** Mesoporous silicate, titania, dye, polymer, layer-by-layer.

Much effort has been devoted to applying a new kind of mesoporous materials such as MCM-41 or SBA-15, in the development of catalysts, sorbents, sensors, optical applications, optoelectronic devices and molecular recognition materials[1-4], since it has excellent features of uniform channels with controllable nano-order pore diameter and of high surface area. As there are few active sites in their amorphous $SiO_2$ walls, surface functionalization of the $SiO_2$ walls is thus necessary in their potential applications. This motivation has stimulated research in inclusion of metal and semiconductors clusters and wires, oxide and sulfide clusters, metal complexes, and even polymers in these mesoporous materials1. The ability to coat mesoporous materials, with high quality functionalized ultrathin films is a powerful tool.

In last decades, layer-by-layer (LBL) technique based on electrostatic, or other intermolecular interactions presents a new way to form highly ordered ultrathin films with defined and reproducible thickness on a variety of substrates[5]. The combination of charged polyelectrolytes with organic dyes, proteins, viruses, dendrimers, zirconium phosphate, metal nanoparticles, clay minerals, silica, and even metal alkoxides have evidenced the flexibility and promise of this approach[5-10]. Mesoporous silicate materials have plenty of silanol groups in its amorphous $SiO_2$ wall1, which could not only be used as functional groups, but could also be utilized to anchor other active sites. By employing metal alkoxides and organic molecules or polymers with hydroxyl, carboxylic, sulfonic, or phosphatic groups, inorganic-organic hybrid ultrathin films can be grown layer-by-layer, by performing the controlled hydrolysis and condensation

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reactions in separate steps[9, 10]. Thus, based on the LBL technique, it is desirable to fabricate hybrid ultrathin films inside the mesoporous materials. Since composition, thickness, and orientation of each layer in LBL films can be manipulated at the molecular level, it provides a new route for the formation of ordered nano-hybrid structures inside mesoporous materials.

In the present paper, based on LBL technique, we fabricate $TiO_2$ and subsequently organic dye molecules or polymers inside a mesoporous silicate material of SBA-15, and characterize their structures.

## Experimental

The SBA-15 was synthesized according to the literature[11]. After dehydrated in vacuum, 0.5 g calcined SBA-15 was mixed with 50 mL methanol. Then 10 mL 0.005 mol/L tetraethoxy titanium (IV) (TEOT) methanol-toluene solution was added under vigorous stirring. The resulting mixture was stirred at room temperature for 48 h. The solid product was centrifugated, washed with methanol, and dried in vacuum. 0.5 g of titania-modified SBA-15 was mixed with 25 mL of acidic methanol solution, and then 10 mL of 0.01 mol/L dye (or polymer) methanol solution was added under stirring. Rhodamine B, cis-bis(isothiocyanato)-bis(2,2'-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) ($RuL_2(NCS)_2$), and poly(thiophene-3-acetic acid) (PTAA) were used herein. The mixture was further stirred for 24 h at room temperature, following by centrifugation and washing with methanol until un-reacted dye (or polymer) was removed. The solid product was dried at room temperature in vacuum.

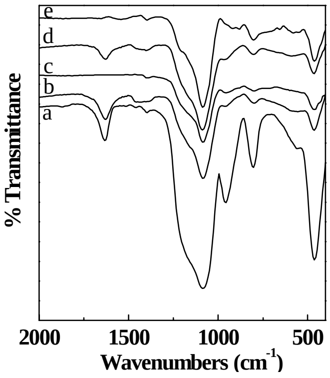
IR spectra were recorded from KBr pellets using a Nicolet Nexus 670 spectrophotometer. Solid-state diffusion-reflectance UV-Vis spectra were measured in a quartz cell on a Jasco solid-state UV-Vis spectrophotometer. TG-DT analysis was carried out from 30 to 600°C by using a Mettler 851e TGA/SDTA analyzer. BET surface areas were measured using nitrogen sorption method on an ASAP 2010 porosimeter. The surface areas were determined by the Brunauer-Emmett-Teller (BET) method.

## Results and Discussion

The inorganic-organic hybrid films fabricated inside the SBA-15 were prepared by using layer-by-layer assembly approach, in combination with sol-gel method. The first step is the co-condensation of TEOT with pendant OH groups on the inner wall of the SBA-15. No water is present at this stage in order to prevent hydrolysis of TBOT. The titanium ethoxides covered on the wall of the SBA-15 are then grafted to organic groups in the presence of HCl. In the second step, the interaction between carboxylic group and titanium was confirmed by IR spectroscopy[10].

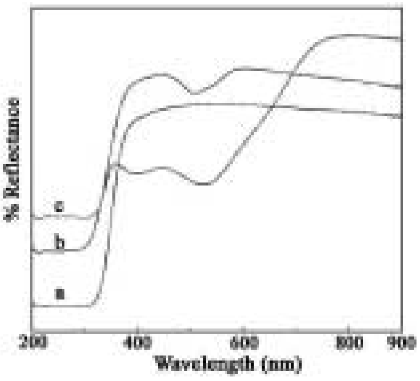
IR spectra were used to monitor the growth of the LBL films inside the SBA-15, as shown in Figure 1. In all the spectra, bands at 1080 and 801 cm-1 are assigned to the asymmetric and symmetric stretching vibrations of framework Si-O-Si, respectively. The Si-O-Ti stretching band appears at 950 $cm^{-1}$ when titanium ethoxides were grafted on the wall of the SBA-1511. There is no significant change in IR spectra, as shown in Figure 1c, d and e, after attaching organic groups on the surface of titania, because the weak bands of organic groups were screened by the strong bands of the SBA-15. However, the interaction between carboxylic groups of dye molecules (or polymer) and titanium was confirmed by our experimental results10. The change of color after grafting also provides evidence for the incorporation of dye molecules (or polymer) into the SBA-15. Further support for the successful surface functionalization inside the SBA-15 is obtained from UV-VIS spectra, TG-DT analysis, and BET surface area measurement.

**Figure 1** FTIR spectra



(a) SBA-15, (b) titania-SBA-15, (c) Rhodamine B-titania-SBA-15, (d) $RuL_2(NCS)_2$-titania-SBA-15, (e) PTAA-titania-SBA-15

**Figure 2** Solid-state UV-Vis spectra



(a) titania-SBA-15, (b) Rhodamine B-titania-SBA-15 and (c) $RuL_2(NCS)_2$-titania-SBA-15

UV-Vis spectra of the titania-modified SBA-15 before and after surface functionalization with organic ligands are shown in **Figure 2**. As there is no any peak in the spectrum of the SBA-15, the band edge of 360 nm observed in **Figure 2a** is from titanium, which is significantly blue shifted as compared to the band edge of 390 nm for the bulk anatase titania, showing the well-known quantum size effect. After bound to dye molecules, the band shifts to 510 nm in the case of Rhodamine B, and to 540 nm in the case of $RuL_2(NCS)_2$. The red shift of the band edge is due to the sensitization effect of the dye molecules.

The DTA-TGA pattern of the $RuL_2(NCS)_2$-titania-SBA-15, shows that there is a weight loss of about 8.6% in the range of 0-123°C, corresponding to desorption of water and ethanol adsorbed in the SBA-15. From 123 to 600°C, there is a broad exothermic peak, corresponding to the loss of organic components inside the SBA-15. The almost identical TGA curves of all the three samples supported very similar coverage.

The difference in BET surface area between SBA-15 (682 m2/g) and titania-modified SBA-15 (468 m2/g) is obvious. This fact indicate that the layer of titania covered on the wall of SBA-15 is not exactly ultrathin, which is much thicker than its counterpart of titania layer in nano-hybrid LBL films on the quartz slide10. After covered with organic groups on the surface of titania layer, the surface area decreases about 25-30% relative to the titania-SBA-15 for all the cases, suggesting that the dye molecules (or polymer) were successfully bound to the titania surface.

In conclusion, titania layer, subsequently the organic ultrathin layer can been fabricated onto the inner wall of the SBA-15 by employing the LBL assembly method, in combination with sol-gel approach. Further effort will be made to optimize the fabrication condition.

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