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Fabrication of Layer-by-layer Films of Polyhedral Oligomeric Silsesquioxanes

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Abstract: Layer-by-layer (LBL) self-assembly method was used to fabricate siliceous ultrathin films by using polyhedral oligomeric silsesquioxanes as building blocks. Ammonium salt of octasilsesquioxane acid (OSi_8) and poly(diallyldimethylammonium chloride) (PDDA) were alternately assembled onto CaF_2 slide to form nanocomposite multilayers. Linear build-up of the LBL films was confirmed by UV-Vis spectroscopy. IR spectrum suggests existence of OSi_8 and PDDA in the LBL films. Atomic force microscopic surface topography of the LBL films indicates the OSi_8 covers the entire surface of the topmost layer and shows a granular morphology.

Keywords: Polyhedral oligomeric silsesquioxanes, layer-by-layer, ultrathin films.

In recent years, silsesquioxanes have received great attention due to their special structure and excellent physico-chemical, thermal and mechanical properties[1-8]. The polyhedral oligomeric silsesquioxanes (POSS) has an integral structure with high symmetry and has an average diameter of only 1.5 nm. POSS can be used as building blocks that provide nanometer-scale control to nanostructured materials. Currently a number of applications for these compounds are showing notable results[5-7]. In many cases, POSS has been exploited to form composite ultrathin silica films.

The development of approaches to fabricate ultrathin films has attracted considerable interest. Among all the techniques, layer-by-layer (LBL) self-assembly technique is widely used. It is proved to be the most suitable, versatile and inexpensive means over the past decade. Most importantly, the LBL technique based on electrostatic attraction of oppositely charged species, so the LBL films are stable and can be prepared to tens even hundreds of layers[9,10]. By employing LBL assembly, the composition, thickness, and orientation of POSS in ultrathin films can be manipulated at the nanoscale level.

In this current work, we have prepared a POSS derivative - ammonium salt of octasilsesquioxane acid (OSi_8) and poly(diallyldimethylammonium chloride) (PDDA) nanocomposite multilayers by consecutively adsorbing OSi_8 and PDDA on CaF_2 substrate. The ordered multilayers were characterized by UV-Vis, infrared spectroscopy, and atomic force microscopy.

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Experimental

OSi_8 was synthesized according to the literatures[3,7]. Poly(diallyldimethylammonium chloride) (20 wt% in water, M_w=200,000-350,000) and poly(sodium-4-styrenesulfonate) (PSS) (M_w=350,000) were purchased from Aldrich and used as received.

CaF_2 substrate was cleaned and treated in a mixed solution of $H_2O/NH_3/H_2O_2$ (5:1:1 in volume) for 20 min at 60℃. The treated substrate was dipped into PDDA solution (10 mg/mL, pH=4.9) and PSS solution (10 mg/mL, pH=2) for 10 min alternatively to such alternate deposition can obtain $(PDDA/PSS)_2PDDA$ films. Subsequently the substrate was dipped into OSi_8 solution (0.2 mol/L, pH=11.9) for 1 h, and rinsed with water and dried before being dipped into PDDA solutions. Such alternate deposition was carried out in OSi_8 and PDDA solution to obtain the desired number of OSi_8/PDDA layers. UV-Vis spectra were recorded by using a Unican UV-Vis spectrophotometer. The IR spectrum of the OSi_8/PDDA LBL films was measured in a Nicolet Nexus 670 spectrophotometer in the range of 1000-4000 cm^{-1}. The atomic force microscopy (AFM) was used to investigate the surface morphology of OSi_8 layer.

Results and Discussion

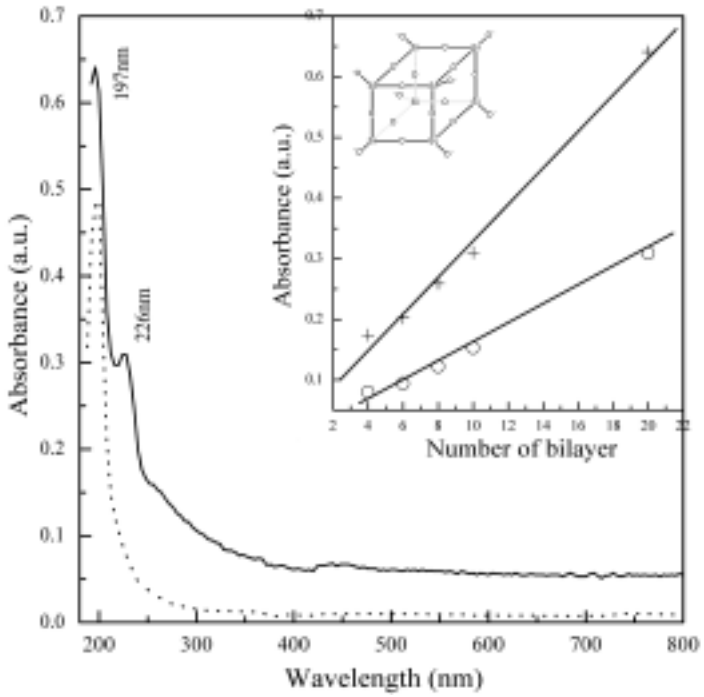
Figure 1 compares UV-Vis absorption spectra of OSi_8/PDDA multilayer film and OSi_8 in aqueous solution. There are two adsorption bands observed at 197 nm and 226 nm in the OSi_8/PDDA LBL films. The peak at 197 nm can be ascribed to the absorbance of OSi_8, while the band at 226 nm is attributed to PDDA, which are almost similar to their solutions. UV-Vis adsorption spectra were also used to follow the growth of OSi_8/PDDA multilayer films up to 20 bilayers. The inset shows that the intensity of the UV-Vis adsorption increases linearly with the deposition layer, indicating that the sequential assembly between OSi_8 and PDDA is regular.

The IR spectrum of a 30-bilayer OSi_8/PDDA LBL film on CaF_2 substrate was measured. The bands at 2921 and 2852 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of CH_2 and the bands at 1410, 1467 and 1596 cm^{-1} are ascribed to vibrations of quaternary ammonium, which confirmed the existence of PDDA. The bands at 1039 and 1114 cm^{-1} are assigned to vibrations of Si-O-Si, which proved that OSi_8 molecules are successfully fabricated. In order to ascertain the stability of the LBL films, the films were put in a desiccator for 17 h. The band of H_2O becomes smaller but the other bands keep unchanged as compared to that without being dried. This fact suggests the LBL film is stable.

The AFM image of the top OSi_8 layer of 6-layer OSi_8/PDDA films on CaF_2 substrate shows that the whole surface has a granular morphology similar to other classes of LBL films [10] and is covered with grains which size is almost 110 nm in diameter. The size is much larger than the isolated molecules, most likely due to the propensity of OSi_8 molecules to aggregate into clusters. It is also indicated that the particles have a relative regular shape, which is essential for preparing well-defined LBL films.

In conclusion, we have demonstrated the fabrication of ordered and well-defined LBL films of OSi_8. The LBL films are uniform and stable in room temperature. Moreover, POSS was described as an effective building block for LBL film formation.

Figure 1 UV-Vis spectra



Dash line: OSi_8 aqueous solution, solid line: 20-bilayer OSi_8/PDDA LBL films on CaF_2 slide. Insert: The change in absorbance of OSi_8/PDDA LBL films with the number of bilayer (PDDA ○, POSS +) and the chemical structure of OSi_8.

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