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## Multilayer Assembly of Cationic Fullerene with Interleaved Anionic, Two-Dimensional α-Zirconium Phosphate Single Layer

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The construction of ultrathin multilayer assemblies has been received many attentions for the application in many areas such as integrated optics, vectorial electron transfer, nonlinear optics, sensors and molecular electronics.[1,2] Most of these tasks require for the preparation of well-ordered films composed of molecules with appropriate properties and structures. Several preparation methods have been studied to date: the Langmuir-Blodgett (LB) technique,[3] self-assembly monolayer (SAM) technique[1] based on chemisorption and electrostatic interaction.[2] Recently, Decher *et al.*[4] reported a new and simple technique for fabricating multilayer thin films with controlled thicknesses and layer sequences. This method is based on the spontaneous adsorption of monolayers of organic polyelectrolytes with opposite charges by layer-by-layer deposition. In essence, the electrostatic attraction between opposite charges is the driving force for the multilayer fabrication. The multilayer film prepared in this method showed considerable layer interpenetration,[5] which results in destruction of highly oriented multilayer. This is mainly due to flexibility and linearity of single-chain polymers used as building block. However, the interpenetration of layer could be solved by use of lamellar inorganic solid such as α-zirconium hydrogen phosphate. Mallouk and coworkers[6] reported multilayer films composed of semi-infinite anionic sheets interleaved with polymeric cations. This multilayer assemblies were prepared by sequential adsorption from the suspensions of exfoliated inorganic two-dimensional anion $\alpha\text{-}Zr(OPO_3)_2^{2-}$ (α-ZrP) and solution of polycationic electrolytes.

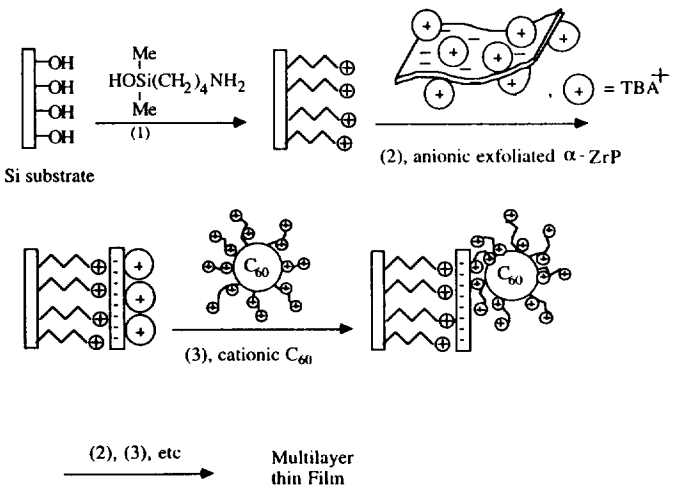


**Figure 1.** Sequential adsorption of singly separated, polyanionic α-ZrP layer prepared by exfoliation of polycrystalline lamellar solid of α-Zirconium hydrogen phosphate with alternate layer of polycationic $C_{60}$. $TBA^+$ = tetra(N-butylammonium) ion.

In this communication, author reports the extention of these last two techniques to fabricate multilayer assembly of fullerene $C_{60}$ and α-ZrP. Fullerene films prepared *via* LB technique,[7] solvent evaporation,[8] resistive evaporation[9] of solid fullerenes and SAM technique[10] have been already reported that they show several interesting mechanical, electrical, superconductive, electrochemical, and optical properties. To my knowledge, this is the first report on the preparation of fullerene multilayer assembly by using electrostatic attraction. The multilayer film prepared in this way would be also expected to show many potential applications based on fullerene properties.

The electron deficient $C_{60}$ undergoes nucleophilic addition reaction with primary and secondary aliphatic amines.[11,12] Treating solid $C_{60}$ with ethylenediamine easily leads to the formation of fullerene-ethylenediamine adduct. This adduct is quite soluble in water due to its basic amine functionalities. Wudl *et al.*[11] reported that $C_{60}$-ethylenediamine adduct has the average stoichiometry of 6 ethylenediamines per adduct molecule from the titration of aqueous solution of the adduct with HCl. The adduct molecule is positively charged in the acidic solution. Positively charged $C_{60}$-ethylenediamine is alternatively interleaved with anionic zirconium phosphate single layer to make multilayer structure.

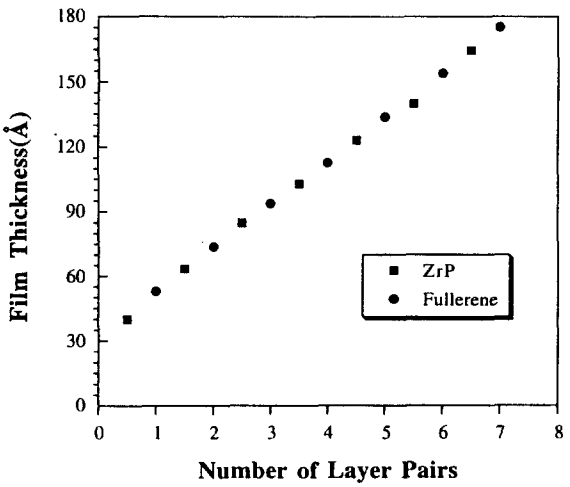


**Figure 2.** Ellipsometric data for α-ZrP/$C_{60}$ multilayer film on Si substrate. Plotted data are total film thickness measured after each adsorption of polyanionic α-ZrP single layer and polycationic $C_{60}$ layer, respectively. The thickness for the zeroth layer pairs is corresponding to the amine anchoring reagent and native silicon oxide layer on the Si substrate.

Figure 1 schematically shows the sequential adsorption procedure leading to formation of multilayer assembly of fullerene and inorganic α-ZrP on Si substrate. The protonated amine surface after silanization with (4-aminobutyl)dimethylmethoxysilane is immersed in the colloidal solution of singly separated zirconium phosphate layers. Loosely bound, bulky and gleasy tetrabutylammonium ($TBA^+$) ions on one side of anionic α-ZrP single layer are displaced by surface $NH_3^+$, which results in electrostatic binding of α-ZrP layer. Next, the cationic fullerene adduct of ethylenediamine binds to α-ZrP layer by replacing loosely held $TBA^+$ cations on the other side of α-ZrP. Therefore, multilayer film is built up by alternate adsorption of oppositely charged ions. It should be noted that the net, extra charge remained at each adsorption step is prerequisite for continuous multilayer fabrication.

Figure 2 shows that the total film thickness of $C_{60}$-ethylenediamine/α-zirconium phosphate multilayer prepared in alternate adsorption linearly increases as the number of layer pair. Furthermore, the thickness of each individual layer is growing in a regular pattern as the number of layers. This fact indicates that the alternating multilayer films using cationic $C_{60}$-ethylenediamine and anionic zirconium phosphate can be constructed by electrostatic interaction. The transmission UV spectrum of this multilayer film on quartz shows two bands with λmax's at 224, 250 nm. The intensity of absorbance at 224 nm is linearly increased as the number of cationic fullerene layer. This fact also supports multilayer growth in three-dimension. The measured average monolayer thicknesses of $C_{60}$-ethylenediamine and zirconium phosphate are respectively 11.1 (± 1.8) Å and 9.6 (± 2.0) Å. The diameter of buckminsterfullerene ($C_{60}$)[13] is known as 7.1 Å. Ellipsometric thickness of $C_{60}$-ethylenediamine adduct layer is less than the theoretical size (*ca.* 15 Å) of fully extended symetrical adduct molecule by *ca.* 4 Å. However, this difference in size is easily rationalized when considered with small average number (=6) of ethylenediamine attached to fullerene and its unknown packing density. The estimated thickness of anionic α-ZrP single layer in multilayer assembly is in good agreement with crystallograpic data[14] (7.6 Å of layer spacing) of α-zirconium hydrogen phosphate. Currently, the chemical and physical characteristics of fullerene multilayer assembly is being investigated by UV-absorption, X-ray diffraction, elecrochemistry and atomic force microscopy (AFM).

## Experimental

**Materials.** (4-Aminobutyl)dimethylmethoxysilane from United Chemical Technologies was used as received. Fullerene ($C_{60}$, purity 99.95%) was purchased from Fullerenes Enterprise (Bellaire, TX). The exfoliated solution of polycrystalline α-$Zr(HPO_4)_2H_2O$ was prepared by method reported[6] previously. The colloidal solution of zirconium phosphate was finally adjusted to have a constant pH of 8.0 by 0.094 N Tetrabutylammonium hydroxide (TBAH) solution. The water-soluble adduct of $C_{60}$ with ethylenediamine was synthesized as described in literature[11] and identified by IR and FABMS. The IR (KBr) spectrum is similar to that of of fullerene-ethylenediamine adduct reported by Wudl *et al.*[11] FABMS spectrum of the adduct mainly showed clusters of peaks at 780 ($C_{60}(NH_2C_2H_4NH_2)$) and 720 ($C_{60}$) amu. 20 mg of fullerene-ethylenediamine adduct was dissolved in 10 mL of deionized water and its solution was acidified by 0.1 N HCl and adjusted to have pH of 6.0. This yellowish brown solution was used for adsorption of positively charged adduct of $C_{60}$-ethylenediamine on the negatively charged layer of α-zirconium phosphate.

**Preparation of multilayer.** Si(100) substrates were precleaned and silanized as described previously[6]. The aminosilanized substrates (quartz and Si) were immersed in the solution of zirconium phosphate at room temperature for 20 min. After rinsing substrates with deionized water, the substrates were immersed in fullerene-ethylenediamine adduct solution at room temperature. Typical dipping time for this step was *ca.* 30-40 min. Fullerene-ethylenediamine coated substrate was rinsed with deionized water. This substrate adsorbed with positively charged fullerene adduct was consecutively immersed in zirconium phosphate solution.

**Instrumentation.** Ellipsometric measurements were made using a Gaertner model L2W26D ellipsometer with 6328 Å (He-Ne laser) analyzing light and a rotating analyzer. The incident angle was 70°. The refractive index of multilayer film was fixed at 1.54 and the complex refractive index of (Ns=3.875, Ks=−0.018) was used for Si substrate. Film thickness was typically measured and averaged from 8-10 different positions each sample.

Visible absorption spectra were acquired in transmission mode at normal incidence using Hewlett Packard 8452A with diode array detector. The spectral resolution was 2 nm and each spectrum was obtained by 100 times signal integration.

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