Novel C_{60}-Containing Ultra-thin Film Based on Diazoresin

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A kind of multilayer ultra-thin films was fabricated from diazoresin and water-soluble fullerene derivative $C_{60}(ONa)_n$. Under irradiation of UV light, following the decomposition of -N_2^+ group of diazoresin, the bond nature between the layers of the film will convert from ionic to covalent. As a result the irradiated film possesses high stability towards polar solvents.

Since the third kind of allotrope of carbon–C_{60} was found by Kroto et al. in 1985,[1] the chemistry of C_{60} and its family, known as fullerene, was developed rapidly and has attracted much attention due to their unique chemical and physical properties.[2] The polymer-bound fullerenes are particularly interesting because they combine the polymer's processability and fullerene's unique characteristics. Various kinds of C_{60}-containing polymers have been synthesized and their characteristic such as optical, electrical and soluble properties etc were studied.[3]

A layer-by-layer self-assembly technique, since Decher's pioneering work in 1991,[4,5] was rapidly developed because it is simple in procedure, easy to automate and friendly to environment.[6] However, the coulombic interaction between layers is not strong enough to prevent etching from polar solvents and limits seriously the further development of this technique. Recently, we revealed a very stable utra-thin film based on diazoresin following by UV irradiation.[7] In this article we report first time the fullerene-containing utra-thin film from diazoresin as polycation and $C_{60}(ONa)_n$ as multi-anion via self-assembly technique.

C_{60} was prepared from carbon arc in our laboratory, 99.5%. Diazoresin (DR) was prepared according to the method described elsewhere,[8] M_n~2.1×10^3 g/mol. Fullerols were synthesized according to the reference[9] and described briefly as follows: 2 mL 50% NaOH and 50 mL benzene containing 50 mg C_{60} were added into a 150 mL three necked bottle then 1 mL 10% tetrabutylammonium hydroxide and 5 mL 30% H_2O_2 was added. The mixture was stirred at 25 °C to colorless of the benzene layer then reacted for another 30 min. The water layer was separated from benzene and excessive methanol was added. The $C_{60}(OH)_n$ with brown color was separated by centrifugation. The $C_{60}(OH)_n$ obtained was dissolved in 3 mL water then precipitated with addition of methanol and the purification was repeated three times. From the elementary analysis for the dried sample the "n" of $C_{60}(OH)_n$ can be calculated to be 23 and the weight of dried $C_{60}(OH)_n$ is 60 mg (77%).

The self-assembly multiplayer film was prepared as follows: DR was dissolved in deionized water (1 mg/1 mL) and $C_{60}(OH)_n$ was dissolved in weak alkaline aqueous solution (pH = 8) with the concentration of 0.5 mg/ 1 mL. A quartz wafer (fused silica) as substrate was treated with H_2O_2 (30%) and H_2SO_4 at room temperature before use. The treated substrate was immersed first in $C_{60}(ONa)_n$ solution for 5 min, then rinsing with water thoroughly and drying by flow air, followed by immersion in DR solution for 5 min, rinsing and drying to complete a fabrication cycle. In each cycle, a bilayer of $C_{60}(ONa)_n$ / DR was deposited on both sides of the substrate. The UV–vis spectrum (on Shimadzu 2100) was used to monitor the layer-by-layer deposition. The photoreaction of the films was also determined spectrometrically after UV irradiation.

The ultrathin film with twelve bilayers was fabricated. Figure 1 shows the absorbance at the characteristic absorption of diazonium group of DR in water ($\lambda_{max} = 380$ nm, $\varepsilon > 5 \times 10^4$ mol L^{-1} cm^{-1}), increases uniformly and the inset plot shows the linear relationship of the absorbance and the number of bilayers. Although the direct detection of $C_{60}(ONa)_n$ by UV–vis spectrum is difficult owing to its weak absorption and disturbed badly by the strong absorption of diazoresin, but the film fabricated from $C_{60}(ONa)_n$ and DR layer-by-layer is believable because the absorbance of the film increases linearly with the layer number. The uniform fabrication should not take place without $C_{60}(ONa)_n$.

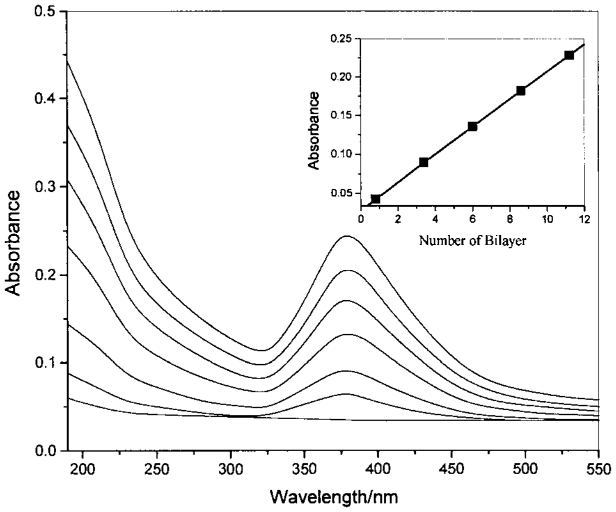


Figure 1. The UV-Vis spectra of $C_{60}(ONa)_n$ / DR multilayer films with different bilayers.
Bilayer number(bottom to top): 0, 2, 4, 6, 8, 10, 12.
Inset plot: the relationship of the absorbance and the number of bilayers.

The photo-decomposition of the multilayer film performed under irradiation of a medium pressure mercury arc (80 W at 10 cm distance). Figure 2 shows the UV–vis spectra of 12 layers film at different irradiated time. The inset plot shows the linear relationship of $\ln(A_0/A_t)$ and t, where A_0 and A_t (corrected by baseline) represent the absorbance of the film before and after irradiation respectively and t is the irradiated time. It indicates the photodecomposition of the film follows the kinetics of the first-order reaction.

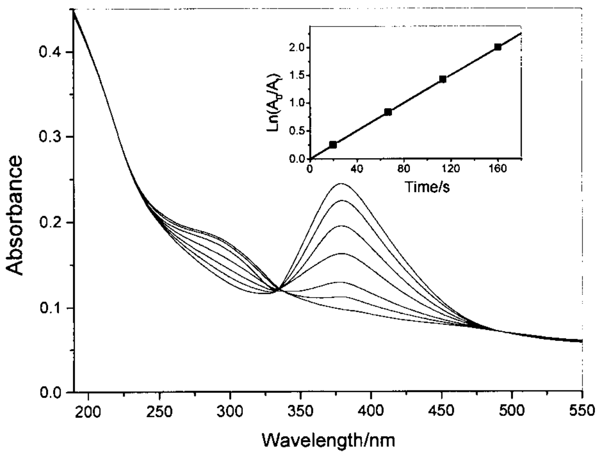
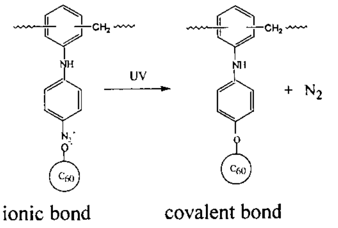
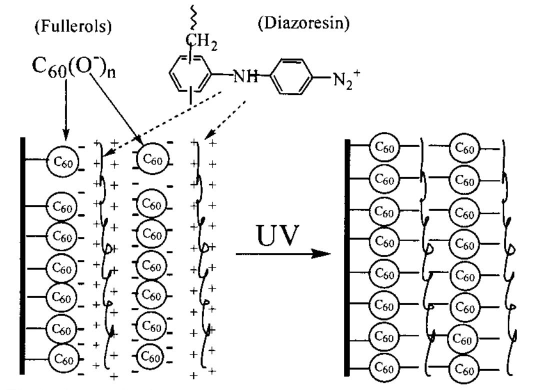


Figure 2. The UV-Vis spectra of C$_{60}$(ONa)$_n$ / DR multilayer film (12 bilayer) irradiated for different time. Irradiation time(s)(from top to bottom): 0, 10, 30, 60, 120, 180, 300. Irradiation intensity: 230μW / cm^2. Inset: the relationship of ln (A$_0$/A$_t$) and time.

It is well known that diazonium group decomposes easily under UV irradiation, usually to produce cationic intermediate. It is reasonable to consider that the phenyl cation formed from DR decomposition should link preferably with the oxygen anion of C$_{60}$(ONa)$_n$ to form covalent linkage as shown in Scheme 1.



Scheme 1. The bond conversion taken place in C$_{60}$(ONa)$_n$ / DR multilayer film under UV irradiation.



The ionic crosslinking between layers before UV irradiation

The covalent crosslinking between layers after UV irradiation

Figure 3. The schematic illustration of the structure change for the C$_{60}$(ONa)$_n$ / DR multilayrs film after UV irradiation.

The stability of the irradiated film towards polar solvents was improved dramatically. The film with 12 bilayers was dissolved out completely as it was immersed for 3 min in *N,N*-dimethylformamide (DMF) but it is no considerable change for the irradiated film after immersion for 12 h in DMF. The high stability of irradiated film should be ascribed to the covalent crosslinking between the layers as schematically illustrated in Figure 3. The crosslinking nature cannot be fully understood because the decomposition of diazonium group is not a single process.

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