

## Multilayer Film Fabrication and Photoelectric Conversion Property of Two Pyrrolidinofullerene Carboxylic Acid Derivatives

Tian Xin WEI, Jin ZHAI, Liang Bing GAN, Chun Hui HUANG\*

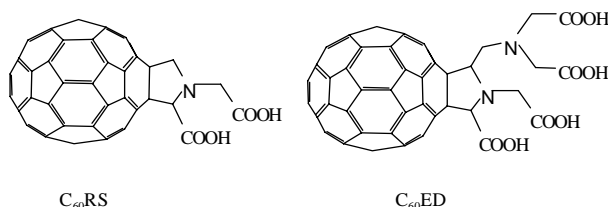
State Key Laboratory of Rare Earth Materials Chemistry and Applications, PKU-HKU Joint Laboratory on Rare Earth Materials and Bioinorganic Chemistry Peking University, Beijing 100871

**Abstract:** Two multilayer films of pyrrolidinofullerene carboxylic acid derivatives, which exhibit photoelectric conversion property, are reported here. The first monolayers were fabricated on hydrophilic indium-tin-oxide (ITO), quartz, and mica by esterification reaction. The multilayers were characterized by contact angle and UV spectrum. The photoelectric conversion properties of both multilayer films were studied.

**Keywords:** Self-assembled multilayer film, fullerene derivative, photoelectric conversion

Fullerene has many special properties<sup>1</sup>, and our group had successfully introduced fullerene into the photoelectric conversion field by Langmuir-Blodgett technology<sup>2</sup>. The only work of fullerene multilayer films that we have seen was done by J. S. Bae<sup>3</sup>. In this paper we tried to introduce fullerene carboxylic acid derivatives into multilayer without organosilicon derivatives and studied their photoelectric conversion properties. A new way of fabricating fullerene multilayer film was reported here. The esterification of carboxyl acid derivatives of fullerene with hydroxyl group on various substrates, such as ITO (Indium-tin-oxide), quartz, and mica were used. The fabrication was easily carried out at room temperature.

**Scheme 1** The structures of experimented fullerene derivatives, C<sub>60</sub>RS, C<sub>60</sub>ED.



### Experimental

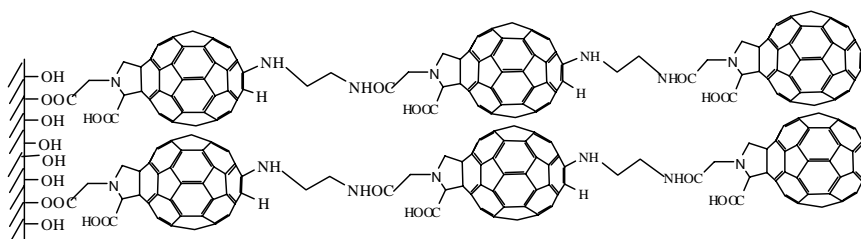
The absorption spectra were measured by a Shimadzu UV-3100 spectrophotometer. The photoelectrochemical studies were performed by using a model 600 voltammetry analyzer (CH Instruments Inc., USA) and a 500 W xenon lamp (USHIO Electric, Japan). An IRA-25S filter was used to avoid the thermoeffect throughout all experiments.

Dicyclohexylcarbodiimide(DCC) and 1H-benzotriazol-1-ol (BtOH) were bought from Aldrich. All other reagents were AR grade and used without further purification.

The structures of experimented fullerene carboxylic acid derivatives were shown in **Scheme 1**. The ester precursors of C<sub>60</sub>RS and C<sub>60</sub>ED were prepared by the photochemical reaction between C<sub>60</sub> and EDTA tetramethyl ester in a binary solvent system containing toluene/methanol, were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and FDMS<sup>4</sup>. C<sub>60</sub>RS and C<sub>60</sub>ED were prepared by the hydrolysis of the esters by a procedure similar to Hirsch's method<sup>5</sup>, and were also characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and FDMS.

Hydrophilic ITO, quartz or mica was soaked in a 1mmol/L bromobenzene solution of C<sub>60</sub>RS or C<sub>60</sub>ED which contained 1mmol/L DCC (dicyclohexylcarbodiimide) and 1mmol/L BtOH(1H-benzotriazol-1-ol), and stirred at room temperature for 1-2 days, then rinsed and sonicated in bromobenzene for 2 minutes to remove residual physisorbed compound. The substrate finally was washed by ethanol or acetone and dried in air. Then the monolayer was obtained. The modified surface is confirmed *via* contact angle measurements. The contact angle of the surface of C<sub>60</sub> modified substrate was about 70° which coincides with that in reference 3. The resulting substrates were then treated in 5 mmol/L ethylenediamine in ethanol solution for 24 hours, rinsed and sonicated in ethanol for 2 minutes, dried in air. Then repeated the steps of formatting monolayer, we got the multilayer films. The process of multilayer film fabrication was similar to that in reference<sup>3</sup>. The possible structure of the multilayer of C<sub>60</sub>RS was shown in **Scheme 2**. The Scheme just shows a possible way, there may also be more than one carboxylic groups of one C<sub>60</sub> derivative molecule, which are bonded with the substrate.

**Scheme 2** The possible structure of multilayer film of C<sub>60</sub>RS.



**Table 1** The UV spectrum peaks of C<sub>60</sub>RS and C<sub>60</sub>ED in solution and in the 4-layer film.

		wavelength(nm)		
C <sub>60</sub> RS	in the 4-layer film	208	259	328
	in the DMSO	240	257	330
C <sub>60</sub> ED	in the 4-layer film	208	260	331
	in the DMSO	237	255	326

DMSO is abbreviation of dimethylsulfoxide.

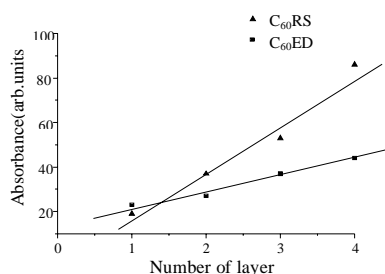
## Result and Discussion

The UV spectrum peaks of C<sub>60</sub>RS and C<sub>60</sub>ED in solution and in the 4-layer films were shown in **Table 1**. Both compounds had three characteristic peaks of C<sub>60</sub>. But different from that in Langmuir-Blodgett (LB) film of C<sub>60</sub><sup>6</sup> or its derivatives<sup>7</sup> that two later peaks

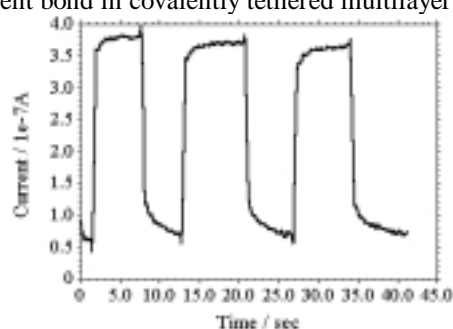
## Multilayer Film Fabrication and Photoelectric Conversion Property of Two Pyrrolidinofullerene Carboxylic Acid Derivatives 163

normally red shifted, two later peaks of both compounds did not shift obviously

**Figure 1** The relationship between the absorption spectra at 259 nm for the multilayer films of C<sub>60</sub>RS and at 260 nm for the multilayer films C<sub>60</sub>ED and the number of multilayer films.



**Figure 2** Photocurrent generation from C<sub>60</sub>RS in covalent tethered multilayer on ITO under irradiation of a white light at 200 mW/cm<sup>2</sup> when the effective irradiation surface area is 1.5 cm<sup>2</sup> without bias potentials. The concentration of the electrolyte solution is 0.1 mol/L KCl.



comparing with that in solution. This difference might come from the strong interaction of C<sub>60</sub> and ITO substrate through the covalent bond in covalently tethered multilayer.

The relationships between the UV absorption values at the absorption peaks of C<sub>60</sub>RS at 259 nm and C<sub>60</sub>ED at 260 nm in multilayer films and the number of layers were shown in **Figure 1**. The good linear relationship of the curves of C<sub>60</sub>RS and C<sub>60</sub>ED with the relation coefficients of 0.984 and 0.988 respectively indicated the formation of the good multilayer.

The photocurrent generation of C<sub>60</sub>RS in the 4-layer films on ITO was shown in **Figure 2**. The Figure shows that when the light is on, the photocurrent immediately increases from about 50 nA to about 350 nA and when the light is off, the photocurrent goes back to about 50 nA at once. This system generated stable cathodic photocurrent of 180 nA/cm<sup>2</sup> while the hydrophilic-pretreated ITO substrate can only generate the anodic photocurrent of about 7 nA/cm<sup>2</sup>. The system of C<sub>60</sub>ED generated stable cathodic photocurrent of 150 nA/cm<sup>2</sup>. The difference of their photocurrent generation might be caused by their different  $\sigma$  bond chain between C<sub>60</sub> and carboxyl groups.

The action spectrum of the photocurrent generation of the 4-layer film under the irradiation of a white light (200 mW/cm<sup>2</sup>) with different filters was shown in **Figure 3**. The curves in the figure were similar to the curves of their UV spectra, indicating that the fullerene derivatives in the covalently tethered films were responsible for the photocurrent generations.

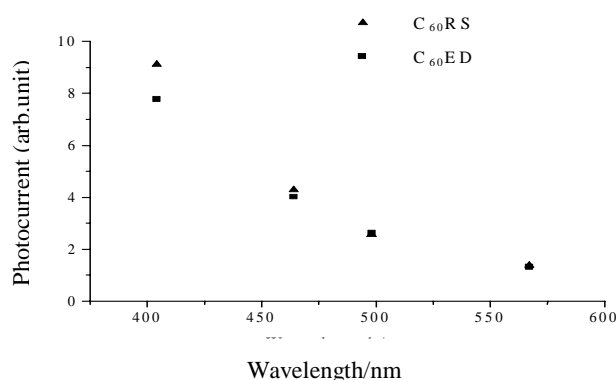
The relationships between the photocurrents and the number of layers were shown in **Figure 4**. Data indicate that the best number of layers for both compounds is 2. These nonlinear relationships might come from that the long  $\sigma$  bond connecting chain of ethylenediamine is poorly conductive and the active molecules of the photocurrent conversion is only those connected closely with ITO electrode.

### Conclusion

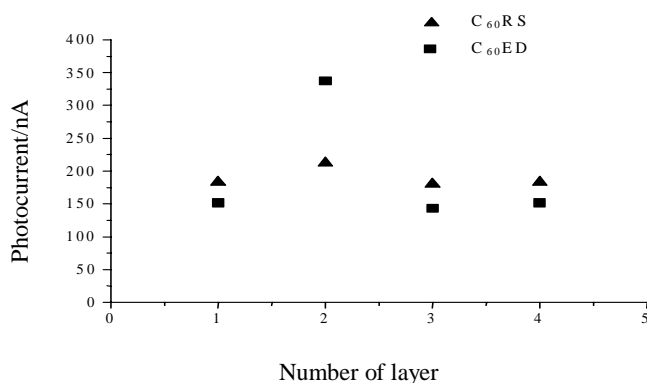
In conclusion, two kinds of multilayer films of C<sub>60</sub> carboxyl acid derivatives that had the photoelectric conversion property were obtained. For both compounds, the optimal number of layers is two. The photocurrent generation of C<sub>60</sub>RS in films is larger than that of C<sub>60</sub>ED. Because this kind of film had good stability and might benefit the

properties related to electricity, the attempt of introducing electron donors and sensitizers into the three dimensional structure of fullerene device by this method is in progress.

**Figure 3** The action spectra of C<sub>60</sub>RS and C<sub>60</sub>ED in covalent tethered multilayer on ITO under irradiation of white light at 200 mW/cm<sup>2</sup> when the effective irradiation surface area is 1.5 cm<sup>2</sup> with bias potential of -100 mV. The concentration of the electrolyte solution is 0.1 mol/L KCl. The intensities of different wavelengths were all normalized.



**Figure 4** The relationship between photocurrents of the multilayer films of C<sub>60</sub>RS and C<sub>60</sub>ED and the number of layers.



### Acknowledgment

The authors thank the State Key Project for Fundamental Research and National Nature Science Foundation of China (29671001) for financial support of this work.

### References

1. P. Maurizio, *J. Mater. Chem.*, **1997**, 7(7), 1097.
2. W. Zhang, L. B. Gan, C. H. Huang, *Synthetic Metals*, **1998**, 96, 223.
3. J. S. Bae, E. R. Kim, H. Lee, *Synthetic Metal*, **1995**, 2063.
4. L. B. Gan, J.F. Jiang, W. Zhang, Y. Su, Y. R. Shi, C. H. Huang, J. Q. Pan, M. J. Lu, Y. Wu, *J. Org. Chem.*, **1998**, 63, 4240.
5. L. Lampartha, A.Hirsch, *J. Chem. Soc., Chem. Commun.*, **1994**, 1727.
6. T. Nakamura, H. Tachibana, M. Yumura, *etc.*, *Langmuir*, **1992**, 8, 4.
7. L. B. Gan, D. J. Zhou, C. P. Luo, C. H. Huang, T. K. li, J. Bai, X. S. Zhao, X. H. Xia, *J. Phys. Chem.*, **1994**, 98, 12459.

**Multilayer Film Fabrication and Photoelectric Conversion Property of 165**  
**Two Pyrrolidinofullerene Carboxylic Acid Derivatives**

Received 23 June 1999  
Revised 6 December 1999