

A New Self-Assembled Monolayer of Fullerene Derivative and Its Photoelectric Conversion Property

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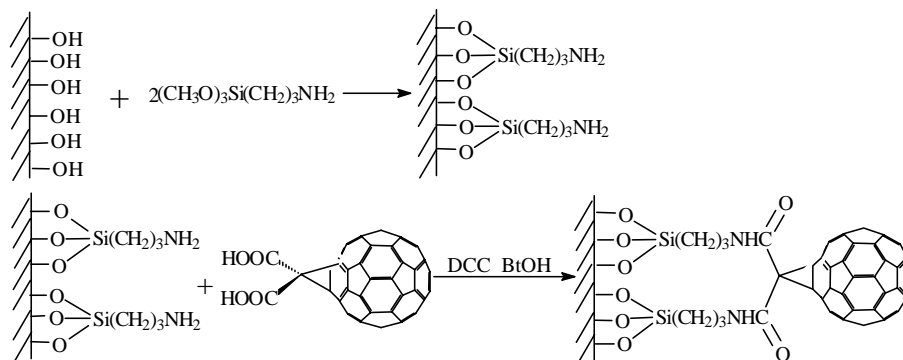
Abstract: A new self-assembled monolayer (SAM) of fullerene derivative has been fabricated and their photoelectric conversion property has been observed. The SAM was fabricated on indium-tin-oxide (ITO) and quartz by amide bonding. It was characterized by contact angle, UV spectrum, and cyclic voltammetry. The mild fabrication conditions and the stability of the SAM provides a way to build three-dimensional structure more easily.

Keywords: Self-assembled monolayer, C₆₀ derivatives, photoelectric conversion.

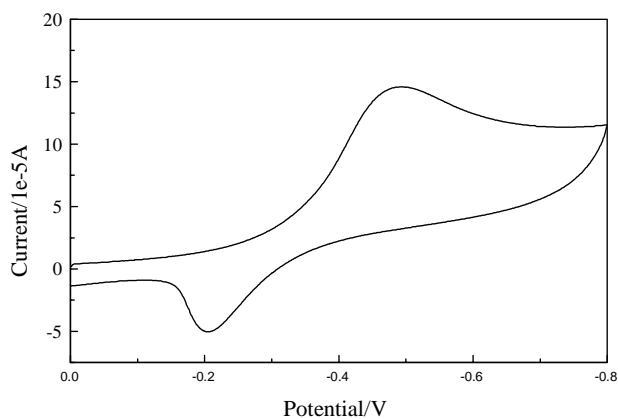
Fullerene has plenty of special optic and electric properties, and has been introduced into films *via* self-assembled monolayer (SAM)^{1,2}. In our SAM fabrication, acylamide bond is chosen as the linking bridge because it can be formed at room temperature and the acylamide derivative of C₆₀ is easy to get. Therefore, it not only provided a new method to get the organized fullerene SAM, but also can be used for multilayer fabrication more easily.

The synthesis of C₆₁(COOH)₂ was carried out following the method of A. Hirsch³. The fabrication of the SAM procedure is shown in **Scheme 1**. The reaction between amino and carboxyl groups can be proved by their characterizations shown below, even though it is very hard to determine whether the carboxyl group on C₆₁(COOH)₂ are all reacted.

The SAM construction began with deposition of the 3-aminopropyl trimethoxysilane on a hydrophilic pretreated indium-tin oxide (ITO) or quartz electrodes according to the method of Haller⁴. Then the aminopropylsilanated ITO or quartz substrates were soaked in a 1mmol/L bromobenzene solution of C₆₁(COOH)₂ which contains 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 C₆₁(COOH)₂. The substrate finally is washed by alcohol or acetone and dried in air. The modified surface is conformed *via* contact angle measurements. The contact angle of the surface of C₆₁(COOH)₂ modified substrate is about 70°, this value is coincident with that reported in reference 1.

Scheme 1 Synthetic scheme for the formation of SAM of $C_{61}(COOH)_2$ **Table 1.** The UV spectrum peaks of $C_{61}(COOH)_2$ in solution and in the SAM

	wavelength (nm)		
$C_{61}(COOH)_2$ in the SAM	206.33	260.53	332.70
$C_{61}(COOH)_2$ in the DMSO	223.00	255.00	327

Figure 1. The cyclic voltammetry of the $C_{61}(COOH)_2$ in the SAM on the ITO. The spectrum was recorded in CH_2Cl_2 which contains 0.1 mol/L Bu_4NClO_4 . A platinum wire is used as the counter electrode and a saturated calomel electrode as the reference electrode.

The UV spectrum peaks of $C_{61}(\text{COOH})_2$ in solution and in the SAM film were shown in **Table 1**. There are three peaks under both conditions. The second and third peaks of $C_{61}(\text{COOH})_2$ on the film are 5 nm red shifted compared with those in the dimethylsulfoxide (DMSO) solution. While the first peak is 17 nm blue shifted. This case is similar to that of C_{60} when it was introduced into the LB films⁵

Figure 2. The cyclic voltammetry of the $C_{61}(\text{COOH})_2$ in the solution of DMSO, containing 0.1 mol/L Bu_4NClO_4 . A glass carbon is used as the working electrode, a platinum wire is used as the counter electrode and a Ag/AgCl electrode is used as the reference electrode.

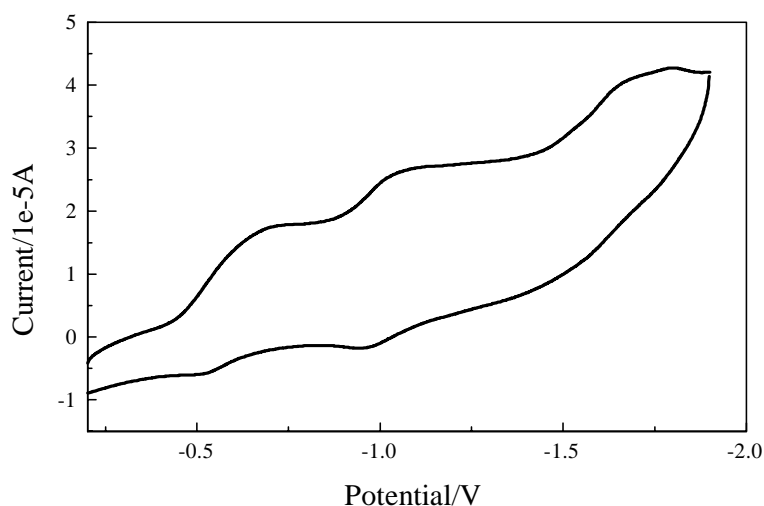
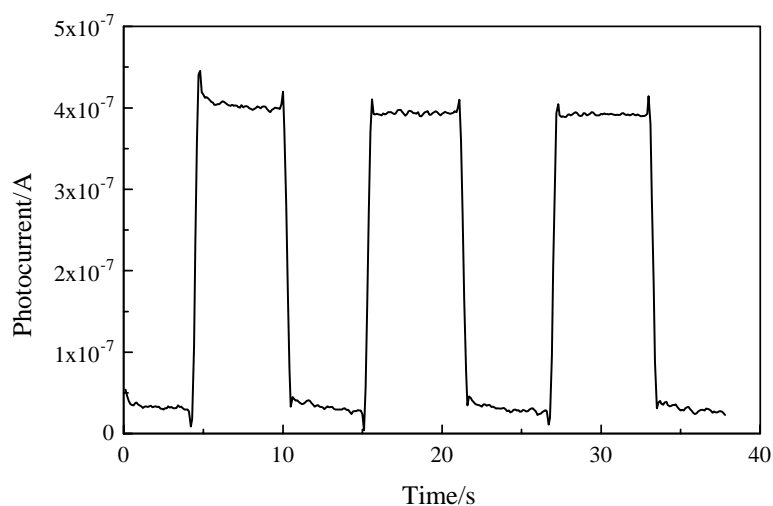


Figure 1 and 2 show the cyclic voltammetry of the $C_{61}(\text{COOH})_2$ in SAM and in the DMSO solution. The curve of $C_{61}(\text{COOH})_2$ in the SAM is different from that in the solution. The redox peaks of $C_{61}(\text{COOH})_2$ -SAM are at -0.5V and -0.2V respectively, while the first redox peaks of $C_{61}(\text{COOH})_2$ in the solution are at -0.7V and -0.5V. This positive shifts of the first redox peaks indicate the formation of the $C_{61}(\text{COOH})_2$ -SAM. The monolayer coverage is about 6.3×10^{-10} mol/cm² calculated from the cyclic voltammetry.

The photocurrent generation of $C_{61}(\text{COOH})_2$ SAM on ITO was shown in **Figure 3**. This system generated steady cathodic photocurrent of 244 nA/cm² while the hydrophilic-pretreated blank ITO can only generate an anodic photocurrent of about 7 nA/cm².

In conclusion, a new method of fabrication of SAM by using acylamidation of $C_{61}(\text{COOH})_2$ with amino group has been obtained and a steady photoelectric generation has been observed. The fabrication is carried out under mild conditions, so it is easy to form multilayer structure. The attempt to get the three dimensional structure based on this method is in progress.

Figure 3. The photocurrent generation from $C_{61}(\text{COOH})_2$ self-assembled monolayer modified ITO electrode upon irradiation of white light at 200 mW/cm^2 when the effective irradiation surface area is 1.5 cm^2 without bias potentials. The concentration of the electrolyte solution is 0.1 mol/L KCl .



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