C_{60} Self-Assembled Monolayer Using Diamine as a Prelayer

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(Received May 19, 2000; CL-000484)

Diamines ($NH_2(CH_2)_nNH_2$; n = 4, 6, 12) have been employed as a prelayer for immobilizing C_{60} onto ITO electrode. The C_{60}/diamine/ITO system reveals good electrochemical responses for surface-confined C_{60}.

C_{60}-Containing self-assembled monolayers (SAMs) are of great current interest with respect to transferring unique C_{60} properties to various materials by surface tailoring.[1,2] There have been several reports on the C_{60} SAMs immobilized onto the surfaces such as indium-tin-oxide (ITO),[3] gold,[4–6] and silicon dioxide.[7] Nevertheless, the well-behaving electrochemistry of the surface confined C_{60} could not be observed owing to the dispersion of formal potential. In this study, we present a modified approach introducing diamines ($NH_2(CH_2)_nNH_2$; n = 4, 6, 12) as a prelayer for immobilizing C_{60} onto the ITO surface. The C_{60}/diamine/ITO system shows nearly ideal electrochemical behaviors of surface-confined C_{60}. Diamines have been employed as a prelayer because they show pronounced reactivity to both ITO and C_{60}. Relevant studies on the spontaneous adsorption of amine moiety onto gold,[8] superconductor,[9] and indium-tin-oxide (ITO)[10] surfaces have been previously reported.

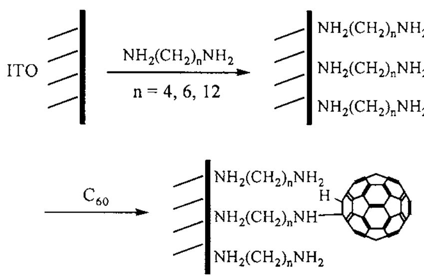

Figure 1. Schematic representation of the modification of ITO surface with diamine and C_{60}.

Figure 1 shows a schematic representation of the formation of C_{60} SAMs using diamine linkages. ITO glass was cleaned with acetone and dried by blowing N_2 stream over the surface. The amine-modified surfaces were formed by 3-day exposure of the ITO to 5 mM diamine in absolute ethanol at room temperature. After rinsing with ethanol, the substrates were dried in vacuum before use. The monolayer formation was confirmed by contact angle measurements. Water contact angle of the prelayers increased as the length of alkyl chains increased (θ = 50°, n = 4; θ = 59°, n = 6; θ = 71°, n = 12), which were comparable to those of the similar amine-terminated monolayer surfaces in other reports.[3,4,11] Surface coverages for these prelayers were measured with the method as previously used.[12] An imine was formed between terminal amine group of the layer and 4-nitrobenzaldehyde. After the hydrolysis of the imine, the amount of reproduced 4-nitrobezaldehyde was quantified with UV-vis absorption spectroscopy. The surface density for diaminododecane (n = 12) layer was ca. 5×10^{-10} mol/cm^2, consistent with that of previous report.[10] For the two shorter diamine (n = 4, 6) layers, the measurements gave the values ca. 2×10^{-10} mol/cm^2, respectively. To immobilize C_{60} onto the prelayer, the diamine/ITO substrates were immersed in a 0.1 M chlorobenzene solution of C_{60} at room temperature for 3 days under Ar atmosphere. The substrates were rinsed and sonicated in pure chlorobenzene to remove physisorbed C_{60}, followed by washing with chlorobenzene and dichloromethane repeatedly. The substrates were dried in vacuum chamber before characterizations. The resulting C_{60} SAMs were characterized by using cyclic voltammetry. Figure 2 shows typical cyclic voltammogram (CV) for the redox reaction of C_{60}, which is on the diaminododecane prelayer. The formal potentials of the two-redox waves were –1.191 and –1.598 V (vs Fc/Fc$^+$) respectively, which were shifted by –0.123 and –0.128 V compared to those for unmodified C_{60} (–1.068 and –1.470 V, inset Figure 2). These cathodic shifts reflect not only the modification of C_{60} but also the presence of the special environment in the C_{60}/diamine/ITO system such as less polar, more alkane-like interface than bulk. Similar anodic shifts for the monolayer of ferrocenylalkanethiol were previously reported.[13] The surface coverage of C_{60} could be calculated as 1.6×10^{-10} mol/cm^2 by integrating the first reductive current in this CV. The real electrode area was 0.38 cm^2, which was determined using electrochemical method based on mass transfer processes.[14] The known coverage for closed packed monolayer of C_{60} is 1.9×10^{-10} mol/cm^2.[15]

The voltammetric responses of the C_{60} SAM at three different scan rates are shown in Figure 3. As expected for the

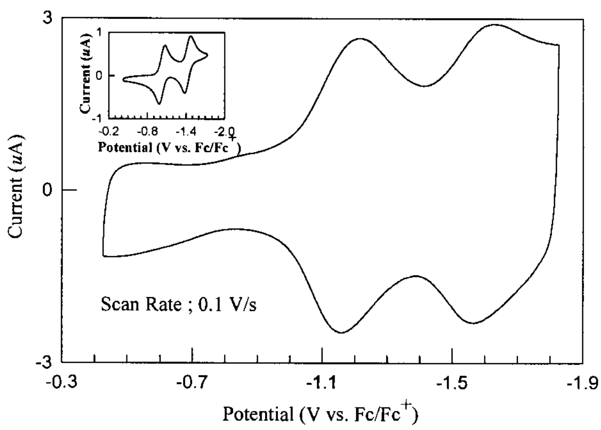

Figure 2. Cyclic voltammogram of C_{60} on $NH_2(CH_2)_{12}NH_2$ modified ITO in CH_2Cl_2/0.1 M Bu_4NPF_6.

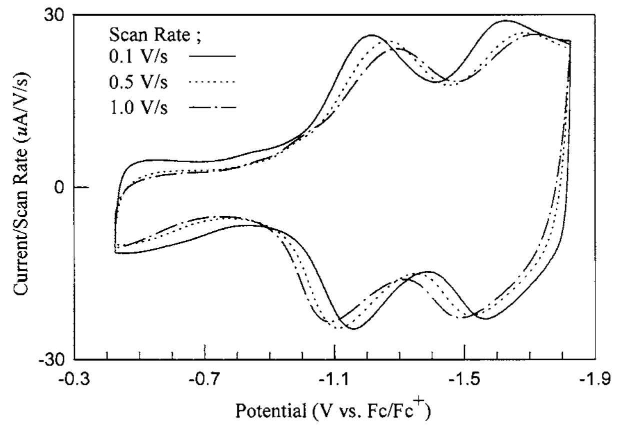

Figure 3. Cyclic voltammograms of $C_{60}/NH_2(CH_2)_{12}NH_2$/ITO in CH_2Cl_2/0.1 M Bu_4NPF_6. Current is normalized with respect to scan rate.

surface bound C_{60} molecules, the first cathodic peak currents showed a linear dependence with respect to the scan rates ($i_c \propto \upsilon$). At 0.1 V/s, peak separations (ΔE_p) of the two redox waves were 50 and 60 mV respectively, and the values were increased with scan rates owing to the kinetic limitations of long-range electron transfer through long alkyl chain between electrode and C_{60}. The full-width at half maximum (fwhm) value is ca. 250 mV, indicating large formal potential dispersion, while the ideal value for the reversible responses is 90.6/n mV. The dispersion may arise from the presence of an ensemble of redox centers, due to the multiple additions of amine to C_{60}. Nevertheless, the peaks of the CVs are well resolved and symmetrical compared to those for previously known C_{60} SAMs.[3,4] It may be attributed to chemical homogeneity of the surface of diamine prelayer for immobilizing C_{60}. Since diamine has one kind of functionality, bound C_{60} is expected to feel unique environment. And it is also inert against unwanted reactions like polymerization. In the case of aminoalkylsiloxane prelayer,[3] the presence of chemical heterogeneity of silanized oxide surfaces could conceivably lead to non-uniform electrochemical behaviors of immobilized molecules.[16] For the two shorter diamines (n = 4, 6) as a result of the low density of the shorter diamine prelayers, however the surface coverages were lower than 1×10^{-10} mol/cm^2, and the waves of CV for C_{60} SAMs exhibit a similar resolution but decreasing ΔE_p. This faster electron transfer kinetics is interpreted as a consequence of decreasing the chain length of diamine and the coverage of C_{60} at the same time. The C_{60}/diamine/ITO system was stable for experimental periods of time. But, when the system was exposed to continuous cycling (> fifty times) over the range of the second reduction potential of C_{60}, the peak currents in CV slightly diminished. This may be resulted from desorption of C_{60}.

In conclusion, we have shown that C_{60} SAMs using diamine prelayer can give well-behaving electrochemical responses. Since diamine can generate chemically homogeneous surface for immobilizing molecules, this diamine system would provide important strategy to study SAMs of C_{60} and its derivatives. The immobilization of metallofullerene onto this diamine/ITO prelayer system is currently in progress.

This work was supported by the Korea Science and Engineering Foundation through both the MICROS center at KAIST and Project No. 1999-1-122-001-5.

References

1 C. A. Mirkin and W. B. Caldwell, *Tetrahedron*, **52**, 5113 (1996).
2 M. Prato, *J. Mater. Chem.*, **7**, 1097 (1997).
3 K. Chen, W. B. Caldwell, and C. A. Mirkin, *J. Am. Chem. Soc.*, **115**, 1193 (1993).
4 W. B. Caldwell, K. Chen, C. A. Mirkin, and S. J. Babinec, *Langmuir*, **9**, 1945 (1993).
5 X. Shi, W. B. Caldwell, K. Chen, and C. A. Mirkin, *J. Am. Chem. Soc.*, **116**, 11598 (1994).
6 H. Imahori, T. Azuma, A. Ajavakom, H. Norieda, H. Yamada, and Y. Sakata, *J. Phys. Chem. B*, **103**, 7233 (1999).
7 V. V. Tsukruk, L. M. Lander, and W. J. Rittain, *Langmuir*, **10**, 996 (1994).
8 O. Domínguez, L. Echegoyen, F. Cunha, and N. Tao, *Langmuir*, **14**, 821 (1998).
9 K. Chen, C. A. Mirkin, R. K. Lo, J. N. Zhao, and J. T. Mcdevitt, *J. Am. Chem. Soc.*, **117**, 6374 (1995).
10 S. Y. Oh, Y. J. Yun, D. Y. Kim, and S. H. Han, *Langmuir*, **15**, 4690 (1999).
11 H. Keller, W. Schrepp, and H. Fuchs, *Thin Solid Films*, **210/211**, 799 (1992).
12 J. H. Moon, J. H. Kim, K. J. Kim, T. H. Kang, B. S. Kim, C. H. Kim, J. H. Hahn, and J. W. Park, *Langmuir*, **13**, 4305 (1997).
13 G. K. Rowe and S. E. Creager, *J. Phys. Chem.*, **98**, 5500 (1994).
14 G. Jarzabek and Z. Borkowska, *Electrochim. Acta*, **42**, 2915 (1997).
15 S. Liu, Y. Lu, M. M. Kappes, and J. A. Ibers, *Science*, **254**, 408 (1991).
16 R. W. Murray, in “Electroanalytical Chemistry,” ed. by A. J. Bard, Marcel Dekker, New York (1984), Vol. 13, p. 228.