3D06 C_{60} – SWNT Based Ultrathin Films Stepwise Grafted onto a Self-Assembled Monolayer on ITO

（東邦大複合物性研究センター[1]、東邦大理[1,2]）○ 王 奇観[1], 森山広思[1,2]

A step-by-step method was used to prepare homogeneous ultrathin films composed of [60]-fullerene (C_{60}) and single-walled carbon nanotubes (SWNTs), grafted onto the functional surface of an alkylsilane self-assembled monolayer (SAM) on an ITO substrate with an ITO–C_{60}–SWNT sequence using amine addition across a double bond in C_{60} followed by amidation coupling with acid-functionalized SWNTs. Atomic force microscope and scanning electron microscope images of the resulting composite film showed two-component ball–tube microstructures with high-density coverage, where C_{60} was homogeneously distributed in the SWNT forest. The attachment of SWNTs to the residual amine units in the SAM on the ITO substrate (SAM–ITO) as well as on the C_{60} sphere results in the C_{60} molecules in the aggregated clusters being more separately dispersed, which forms a densely packed composite film as a result of the π–π interaction between the C_{60} buckyballs and the SWNT walls. It was found using ferrocene as an internal redox probe that the oxidative and reductive processes at the film–solution surface were effectively retarded because of obstruction from the densely packed film and the electronic effect of SWNT and C_{60}. In addition, the electrochemical properties of C_{60} on SAM–ITO plates observed by cyclic voltammetry were significantly modified by chemical anchorage using SWNTs. X-ray photoelectron spectroscopy (XPS) analysis also indicated the successful grafting of C_{60} and SWNT. The XPS chemical shift of the binding energy showed the presence of electronic interactions between C_{60}, SWNT, and ITO components. AFM images of these thin films are shown in Fig. 1.

Carbon nanotubes and fullerenes, composed of fascinating cylindrical and spherical graphitic structures respectively, have been studied extensively, with the aim of applying them in many fields as a result of their unique physical and chemical characteristics. Because carbon nanotubes and fullerenes both show photocurrent generation effects, the combination of these two carbon allotropes, which may give rise to novel structures and properties, has been extensively investigated by different methods, such as encapsulation of C_{60} by single-walled carbon nanotubes to fabricate the so-called peapods, covalent linkage of C_{60} clusters to the surfaces of carbon nanotubes, and physical attachment of C_{60} derivatives through π–π interactions with the surfaces of SWNTs. Although there are several examples of combined C_{60}–SWNT ball–tube materials showing photoelectrochemical behaviors, in which the single-walled carbon nanotubes are treated as electron donors or electron-transfer networks, the preparation of their composite films, especially those having stable covalent interactions with substrates, has attracted less attention. It is easy to obtain C_{60} or SWNT films on an optically transparent electrode using electrophoretic deposition; however, for the C_{60}–SWNT two-component film, this technique results in a layer-by-layer structure because of the faster deposition of SWNT than of C_{60}.

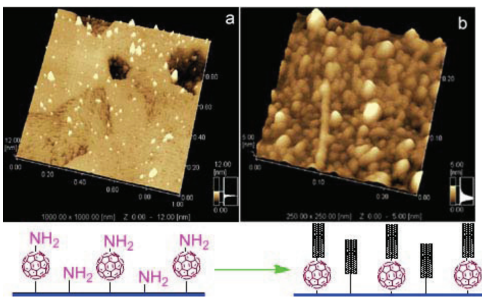
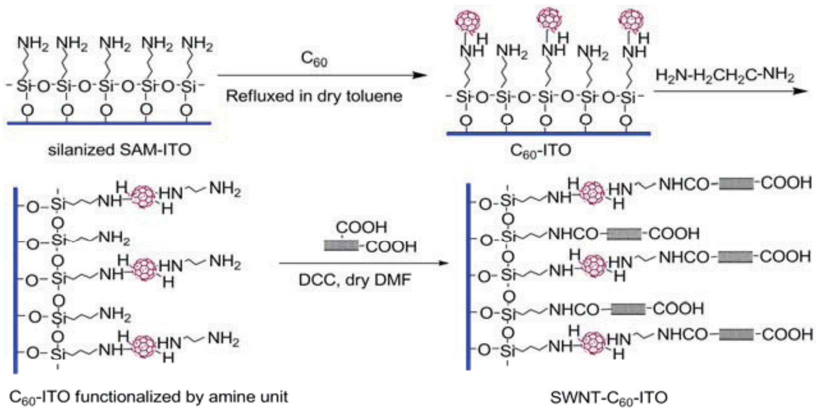


Fig. 1 AFM Images of two different thin layer a) and b)

To increase the lifetime of excitons during the photoexcitation, the bundling of SWNT and the clustering of C_{60} should be decreased. Therefore, designing a more uniformly distributed C_{60}–SWNT film on a solid substrate is required for future research. Encouragingly, an increasing number of different techniques have been developed to prepare ultrathin SWNT or fullerene films besides electrophoretic deposition, including drop-drying from solvent, the Langmuir–Blodgett technique, and self-assembled monolayers (SAMs), which pave the way to fabricating SWNT- and fullerene-based composite films for use in different types of devices. Compared with other techniques, the method of chemically SAMs showing high stability is considered an especially promising approach. Recently, SWNT SAMs have been prepared on a Au substrate by a surface condensation reaction, and also, fullerene C_{60} molecules as models have been covalently attached to an amine-terminated SAM on a Si(111) substrate. In the latter case, the experimental XPS data showed the presence of both primary amine groups $–NH_2$ of the SAM on Si(111) and secondary amine groups –NH– during the C_{60} attachment, which indicates the low reaction efficiency of this attachment with a considerable number of amine groups left unreacted, supporting the possibility of introducing other functional molecules. More recently, a stable electroactive SWNT monolayer endcapped by a conductive oligomer was prepared in our group that showed potential application in electrochemical nanoarchitectures.[1)] In view of the intriguing electrochemical properties of C_{60}, introducing C_{60} in the SWNT film may be a good way to modify SWNTs. From the viewpoint of morphology control, here, we report a more homogeneous SWNT–C_{60} film covalently grafted onto an optically transparent SAM–ITO surface using a step-by-step method, by integration of the above preparations of C_{60} SAM and SWNT SAM,[2)] in which the SWNTs were anchored to the unreacted amines of the SAM–ITO as well as to C_{60} aggregates functionalized by amine groups.



Scheme 1.

Schematic illustration of the preparation route to C_{60}–SWNT ultrathin film grafted on ITO step-by-step.

In conclusion, A C_{60} layer was successfully grafted onto a silanized SAM–ITO surface using amine addition across a double bond in C_{60}, which showed a loosely packed spherical morphology with a low coverage because of the low grafting efficiency. To make the C_{60} clusters more separately distributed, a step-by-step strategy was used. After further tethering by a layer of SWNTs functionalized with carboxylic acid, a homogeneous ultrathin film composed of C_{60} and SWNT with a high-density coverage was obtained from the AFM images. (Fig. 1) This uniform ultrathin hybrid film of C_{60} and SWNT may open a route for applications in electrochemical and photoelectronic research.

Acknowledgments. We are grateful to the Sumitomo Corporation for donating the HiPco of the SWNTs from CNI (Texas, USA). We thank Mr. R. Osada, Chiba Institute of Technology, Japan, for measuring the FE–SEM and XPS data, and Mr. A. Kogure, Shimadzu Corporation, Japan, for measuring the AFM. We thank Prof. K. Terada, Faculty of Pharmaceutical Sciences, Toho University, for measuring the NIR, and Mr. M. Fujimoto, JASCO Corporation, Japan, for measuring the FTIR–RAS.

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(2) Wang, Q.; Moriyama, H. *Langmuir* **2009**, in press.