Supporting Information

[60]-Fullerene and Single-Walled Carbon Nanotube-Based Ultrathin Films Stepwise Grafted onto a Self-Assembled Monolayer on ITO

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Figure S1. FT–IR spectra of pristine SWNT (black curve) and oxidative functionalized SWNT (red curve).

FT–IR of Oxidative Functionalized SWNTs. The functional groups on shortened SWNTs were analyzed using an FT–IR spectrometer (JASCO FT/IR–4100A, Japan) employing the KBr disk method, as shown in Figure S1. The pristine SWNT (black curve) is almost infrared inactive because

of the lack of functional groups.^{1,2} However, for the IR spectrum of oxidative shortened SWNTs (red curve), several intense peaks were observed. The peak occurring at 1730 cm⁻¹ was assigned to the C=O stretching mode of the –COOH groups, and the intense broad peak centered at 3400 cm⁻¹ was assigned to the –OH stretching mode of the –COOH group.^{3–5} These peaks showed that the SWNTs were functionalized by carboxylic acid upon treatment by the acid mixture.

Fourier Transform Infrared–Reflection Absorption Spectroscopy (FTIR–RAS). Infrared absorption spectra of sample surfaces were collected by the reflection–absorption method using an FT–IR spectrometer (JASCO FT/IR–4100, Japan) equipped with a reflector (RAS PRO–410H, JASCO) and an MCT-Mid detector cooled by liquid nitrogen. Spectra were obtained in a chamber purged with dry nitrogen gas for more than 256 scans at 8 cm⁻¹ resolution, using a bare ITO plate as the reference surface.



Figure S2. FTIR-RAS spectra of SAM-ITO, C₆₀-ITO and SWNT-C₆₀-ITO.

The FTIR-RAS spectra of SAM-ITO, C_{60} -ITO and SWNT- C_{60} -ITO ranging from 650 to 4000 cm⁻¹ are shown in Figure S2. From the spectrum of SAM-ITO (black curve), a broad band at around 3500–3000 cm⁻¹ corresponding to the -NH₂ stretch was clearly seen,⁶ which shows the successful

attachment of the (aminopropyl)silanized SAM onto ITO. The peak assigned to the asymmetric stretching and the symmetric stretching of methylene is observed in the band from 2900 to 2800 cm⁻¹.⁷ The broad peak from 1660 to 1480 cm⁻¹ is attributed to amine deformation modes and C-H scissoring vibration.⁶ It is noted that a series of bands between 1290 and 980 cm⁻¹ in the Si–O stretching region probably comes from the alkoxysilane groups, which demonstrates that the grafting APTES molecules were partially hydrolyzed.⁸ However, after further grafting by C_{60} followed by ethylenediamine (blue curve), the attached APTES molecules on ITO performed a thorough hydrolysis assisted by the traces of water in the system, which was confirmed from the single intense absorption of Si–O–Si asymmetric stretch at 1125 cm⁻¹, accompanied by the symmetric stretch at around 800 cm⁻¹. The shoulder peak at around 1210 cm⁻¹ was likely resulted from the silicic acid groups, which protonated the amine units on C₆₀–ITO, as shown in the N 1s XPS feature. In addition, the presence of a shoulder peak at 1390 cm⁻¹ ascribed to the C_{60} skeleton ring vibration,^{9,10} together with the broad peak at 1599 cm^{-1} assigned to N–H stretching modes, showed that C₆₀ was successfully grafted to the ITO surface by means of the amine addition. Encouragingly, the absorption intensity was greatly increased after further grafting by the oxidative functionalized SWNTs. From the spectrum of SWNT- C_{60} -ITO (red curve), the peaks at 1670 cm⁻¹ and 1712 cm⁻¹ are attributed to the amide I vibration mode and the C=O stretch respectively. The peaks at 1452 cm⁻¹ and 1400 cm⁻¹ are characteristic of the carbon skeleton ring vibration of the attached C_{60} . Moreover, the broad intense peak from 3580 cm⁻¹ to 3026 cm⁻¹ resulted from the stretching modes of the N–H bond and the –OH vibration modes of the residual COOH groups on SWNTs. All of these assignments showed that the functionalized SWNTs were grafted to the C₆₀-ITO by use of the amidation coupling, which is consistent with the XPS results.

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