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Tuning the layer-dependent doping effect of graphenes by C_{60}

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Supplementary Contents

I. Experimental conditions and Preparations of the hybrids

The graphenes were prepared with the micromechanical cleavage of natural graphite (Alfa Aesar) by using Scotch transparent tape 600 (3M) onto 300 nm SiO_2/Si substrate. The fullerene-functionalization of graphene was operated by vacuum thermal evaporator. Fullerene powder (Alfa Aesar) was put in evaporation boat heating by current. The rate of the deposition, measured by a thickness monitor, was 0.5 Å/s. The vacuum was kept at 10^{-4} Pa. For C_{60}/G hybrid, graphenes are exfoliated upon substrate firstly, followed with the deposition of C_{60}. For G/C_{60} hybrid, C_{60} are firstly deposited on substrate via thermal evaporation, and then graphenes are exfoliated upon C_{60}-Si substrate via micromechanical cleavage.

Layer number of graphenes in the two kinds of hybrids can be preliminarily confirmed by optical microscope technique, which has been widely used in the determination of pristine graphene layer number. Compared with the hybrids with bilayer or trilayer graphenes, hybrids with monolayer graphene have the lowest contrast compared with the substrate, as shown in Fig. S1. The color of the hybrids becomes darker with the increase of graphene layer number.

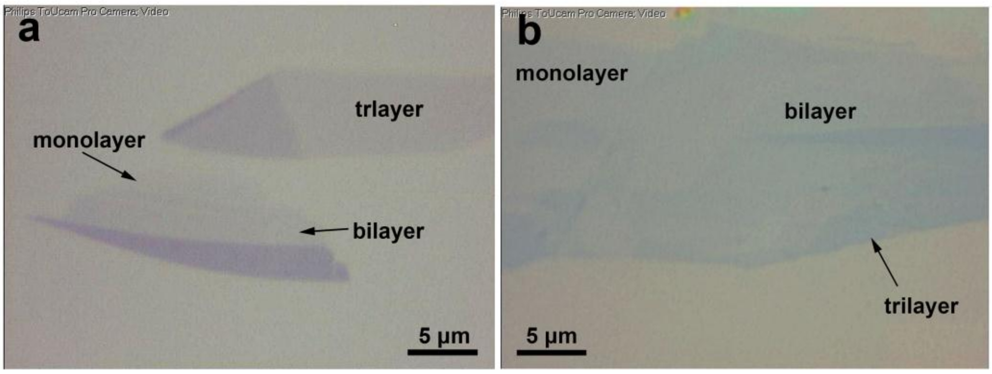

Fig. S1 Optical images of (a) C_{60}/G hybrid and (b) G/C_{60} hybrid.

The micro-Raman spectroscopy (Renishaw in Via Raman Spectroscopy) experiments were performed under ambient conditions with 514.5 nm excitation from an argon ion laser. The laser power on the samples was ~ 0.1 mW to avoid laser induced heating and destroy, and the size of the spot is ~ 1 μm.

A vacuum thermal evaporator was also employed to anneal the samples which were located on the middle of the molybdenum boat heating up by current. The high vacuum was kept for 10 min after the annealing process in order to protect graphene from oxidation.

II. Raman spectra of C60 powders

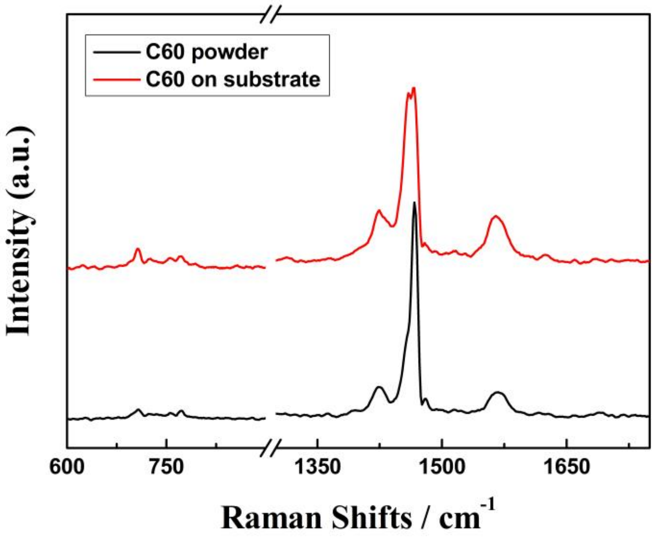

Fig. S2 Raman spectra of fullerene powder and fullerenes deposited on SiO_2/Si substrate

III. Raman spectra of pristine graphenes

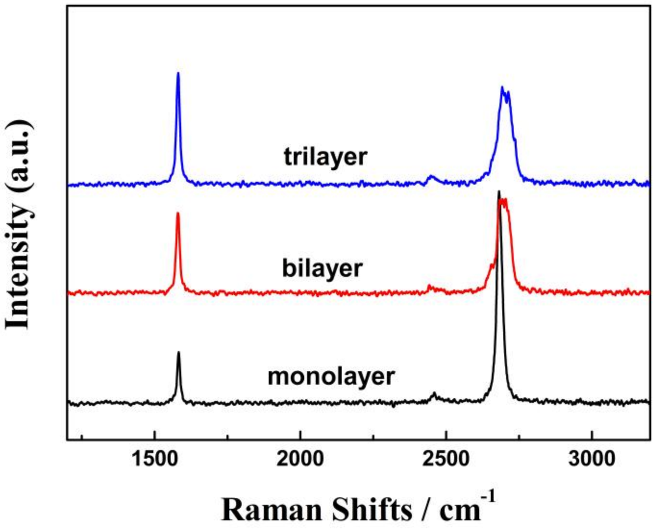

Fig. S3 Raman spectra of pristine *n*-layer graphenes

IV. Analysis of Raman spectra of C_{60}/G hybrid with different thickness of C_{60} film

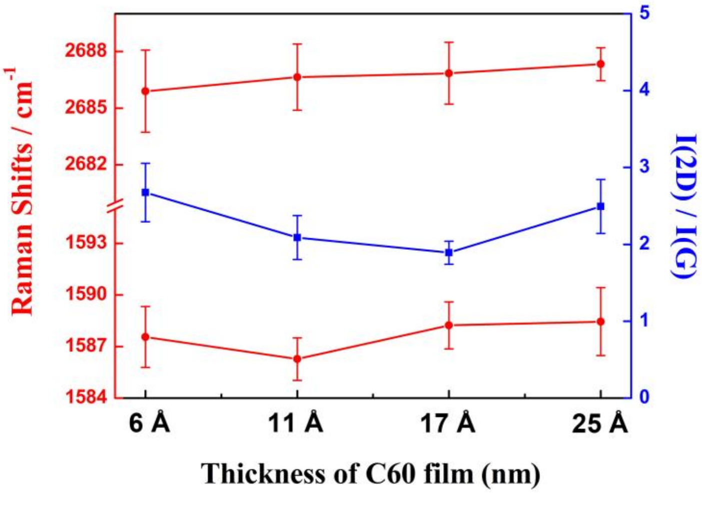

Fig. S4 G, 2D peak positions and peak intensity ratio (I(2D)/I(G)) of C_{60}/G hybrid with different thickness of C_{60} film.

V. Comparison of Raman spectra between pristine graphene and C_{60}/G hybrid

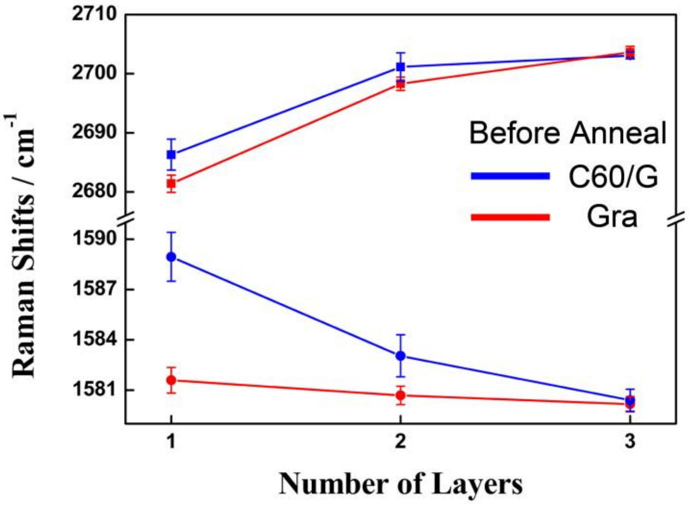

Fig. S5 G and 2D peak positions of pristine *n*-layer graphene and C_{60}/G hybrid with *n*-layer graphene (*n* = 1, 2, 3)

VI. Calculation of doping level for C_{60}/MG, C_{60}/BG and C_{60}/TG hybrids

Based on the previous work about monitoring dopants by Raman scattering,[1, 2] electron density (*n*) and Fermi energy (E_F) shift of *n*-layer graphenes could be estimated from the Raman shifts of G, 2D bonds and intensity ratio of *I*(2D)/*I*(G).

After C_{60} molecules decoration, red Raman shift of G peaks for C_{60}/MG, C_{60}/BG and C_{60}/TG hybrids are ~7.4 cm^{-1}, ~2.4 cm^{-1} and ~0.8 cm^{-1}, respectively. According to the G-peak position varying with electron concentration, Raman shifts of G peak (~7.4 cm^{-1}, ~2.4 cm^{-1} and ~0.8 cm^{-1}) are equivalent to about -6.2×10^{12} cm^{-2}, -4.5×10^{12} cm^{-2} and -2.4×10^{12} cm^{-2} electron concentration, respectively. The minus signs indicate that the dopants for graphene are holes. Moreover, the Fermi energy in graphene changes as $E_F(n)=\hbar|v_F|\sqrt{\pi n}$, where $|v_F|$ is the Fermi velocity.[3, 4] With the value of electron concentration estimated above, the Dirac points move to the valence band about 3.2 meV, 2.7 meV and 0.5 meV for graphene in C_{60}/MG, C_{60}/BG and C_{60}/TG hybrids, respectively.

VII. Comparison of Raman spectra between pristine graphene and C_{60}/G hybrid after anneal

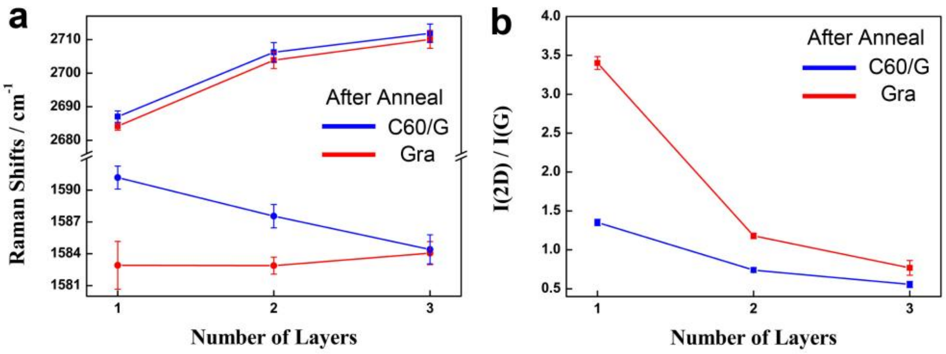

Fig. S6 G, 2D peak positions and peak intensity ratio (*I*(2D)/*I*(G)) of pristine graphene and C_{60}/G hybrid after anneal.

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