
Electronic Supplementary Information (ESI)

Fabrication of novel graphene/fullerene hybrid lubricating film based on self-assembly for MEMS applications

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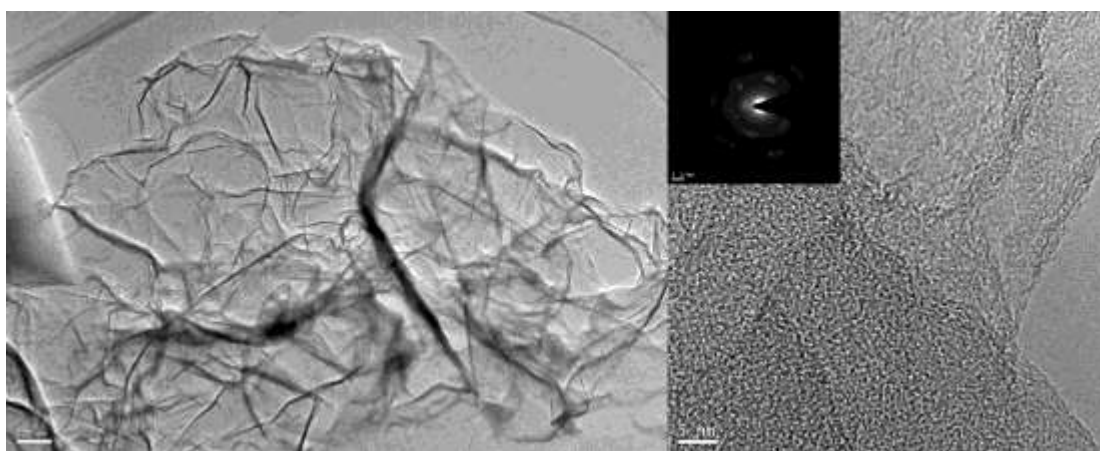
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SI1. Experimental details

Preparation of GO Dispersion.

GO was synthesized from graphite powders according to a modified Hummers' method¹. In detail, the preoxidized graphite powders (1 g) were added to 98% H₂SO₄ (23 mL) in an ice bath. KMnO₄ (3 g) was then added slowly into the mixture with stirring so that the mixture remained below 20 °C. After thorough dispersal, the mixture was stirred at 35 °C for 30 min. Deionized water (46 mL) was then slowly added, and the mixture was kept for 15 min without stirring. The reaction was

terminated by the addition of a large amount of deionized water (140 mL) and 30% H₂O₂ (12.5 mL). The resulting mixture was filtered and subsequently washed with 10% HCl (200 mL) to remove metal ions, and repeatedly washed with deionized water until the pH of the filtrate was neutral. After the dialysis, the products were dried under vacuum at 50 °C for 24 h to obtain a loose graphitic oxide. Finally, the graphitic oxide was redispersed in deionized water under ultrasonic processing for 30 min to yield the desired GO dispersion of 0.4 mg ml⁻¹.



HRTEM image and SAED pattern of GO

The selected-area electron diffraction (SAED) pattern of the graphene showed a clear six-fold pattern, revealing the graphitic crystalline nature of the graphene. The SAED indicated that the characterized graphene nanosheet had four layers, since the four different sets of spots were each attributed to a graphene layer with a distinct orientation.

Fabrication of graphene-C60 hybrid Films.

The silicon wafers were ultrasonicated in acetone followed by ethanol for 10 min, and then were treated in a freshly prepared Piranha solution (a mixture of 7:3 (v/v) 98% H₂SO₄ and 30% H₂O₂) at 90 °C for 30 min. After being rinsed copiously with deionized water and dried in a nitrogen stream, the hydroxylated silicon wafers were then immersed in a freshly prepared 5 mM APTES solution in mixture of acetone and deionized water (a volume ratio of 5:1), and held for 12 h to form APTES monolayer film. The wafers were then taken out and were rinsed copiously with deionized water

followed by drying in a nitrogen stream, the corresponding films were denoted APTES-SAMs. Subsequently, the APTES-assembled silicon wafers were kept in the aqueous dispersion of GO at 80 °C for 12 h, and then ultrasonicated in deionized water and dried in a nitrogen stream to obtain APTES/GO films. The resultant films were then immersed in 5 mM DA solution in acetone-water (a volume ratio of 10:1), and held for 24h to obtain amine-functionalized graphene (a-G). After that, the sample was gently washed with deionized water several times. Then, the silicon wafers with APS/a-G films were put into a dilute solution of C60 in toluene (1 mM) and kept for 2 days to allow a addition reaction of C60 with the amine-functionalized graphene films, then repeatedly washed with toluene to remove residual physisorbed C60 and dried in a nitrogen stream. Finally, APTES/a-graphene/C60 films were thermally reduced at 200 °C for 2 h at a heating rate of 1 °C min⁻¹ under an argon atmosphere to obtain target graphene-C60 hybrid films. In order to confirm the fact that it is the DA molecules who grafted the C60 molecules on the surface of the graphene, the APTES/GO film was put directly into a dilute solution of C60 in toluene without self-assembly of DA, the resultant film was labeled as APTES/GO/C60. All procedures were carried out in a class-100 clean room at 20 °C and a humidity of 18%.

SI2. Characterization of the films

The GO was characterized using high-resolution transmission electron microscopy (HRTEM, JEM-2010). The static water contact angles of the films were determined using a contact angle meter (DSA100, Krüss, Germany). The water droplet volume used for the measurement was about 5µL. FTIR spectra of the prepared powder samples were recorded with an FTIR spectrometer (IFS 66 V/S, Bruker, Germany). For the film samples, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded with the same spectrometer using a Harrick Scientific horizontal reflection Ge-attenuated total reflection accessory (GATR, incidence angle 65°). In addition, the film samples were characterized by multimode atomic force microscopy (AFM, Nanoscope IIIa, Veeco, tapping mode), X-ray

photoelectron spectroscopy (XPS, PHI-5702, Physical Electronics, with Al K α irradiation) and Raman spectroscopy (Lab JY-HR800, Horiba, with 532 nm laser excitation), while the powder samples were characterized by X-ray diffractometer (XRD, D/Max-2400X, Rigaku Co., Japan, with Cu K α irradiation) with a grazing angle of 5°, and thermogravimetric analyzer (TGA-7, PerkinElmer, USA) in flowing N₂.

The nanofrictions of the lubrication films were measured using a homemade colloidal probe in contact mode under a scan rate of 1 Hz over a 60 μ m scan line. The colloidal probe (normal force constant of 2 N m⁻¹) was prepared by gluing a microsphere with a radius of 28 μ m onto a tipless cantilever. When the microsphere slid at a scan rate of 1 Hz over a 60 μ m scan line, the voltage signals of the lateral torsion of the cantilever were continuously measured as a function of linearly increasing external loads (\sim 270 nN). The nanofriction forces were then further quantified by determining the lateral spring and lateral detector sensitivity according to Vakarelski et al.'s method². The linear relationship of the friction force versus the external load can be described by a modified form of Amonton's law in which the lateral force (F_L) is given by $F_L = \mu F_N + F_0$, where μ is the nanofriction coefficient (NFC), F_N is the normal load, and F_0 is the friction force when the external load is zero. The slope of the curve can be used as the friction coefficient. Each presented curve represents an average of three different measurements. The same colloidal probe was used to obtain the adhesive behaviors of the films. The pull-off force was assumed as the adhesive force, which was given by $F_{\text{adhesion}} = K_c Z_p^3$, where K_c is the normal force constant of the colloidal probe and Z_p is the vertical displacement of the piezotube, that is, the deflection of the colloidal probe. The average of 10 individual measurements was obtained for each sample. Before each test, prescanning of the colloidal probe was carried out on a cleaved mica surface to remove physically adsorbed lubricants. All experiments were carried out at 22 °C with a relative humidity of 30%.

Microtribological tests were carried out on an UMT-2MT tribometer (CETR, United States) in the ball-on-plate reciprocating mode. Commercially available

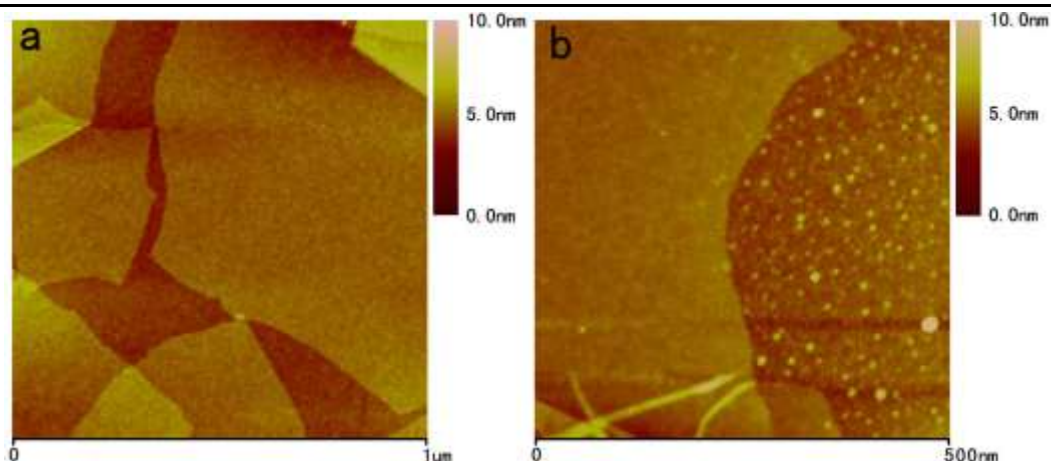
AISI-52100 steel balls with a diameter of 3.18 mm were used as the stationary upper counterparts, while the lower specimens were adhered onto a reciprocating table with a traveling distance of 5 mm. At least three repeated measurements for each test condition were performed. A failure of the film is assumed to occur when the friction coefficient rises sharply to a high and stable value similar to that of a clean silicon oxide (about 0.65), the corresponding sliding time is recorded as the antiwear life of the lubrication film. All tests were conducted at 25 °C and at a relative humidity of 30%.

SI3. Water contact angle (WCA) of the films

Si	APTES-SAM	APTES/GO	APTES/a-GO	APTES/a-graphene/C60
<5°	45°	42°	40°	95°

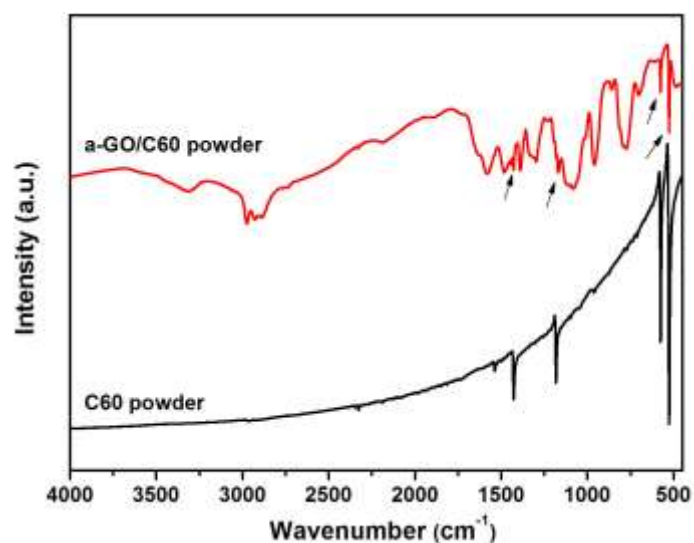
SI3. Water contact angle (WCA) of the films. After a self-assembled monolayer of APTES was covalently anchored onto the silicon wafer, WCA of the Si surface increased from <5° to 45°. The APTES/GO and APTES/a-GO films showed almost the same hydrophilicity, with WCAs of about 42° and 40°. The hydrophilicities were attributed to the outer oxygenous groups on APTES/GO and amine groups of APTES/a-GO. WCA of the APTES/a-graphene/C60 hybrid films increased to 95°. The sharp increase in WCA suggested that surface roughness of APTES/a-graphene/C60 film increased, and most of oxygenous groups had been thermally removed.

SI4. AFM images of APTES/GO film and APTES/GO/C60 film



In order to confirm further the fact that it is the DA molecules who grafted the C60 molecules on the surface of the graphene, the APTES/GO film (figure a) was put directly into a dilute solution of C60 in toluene without self-assembly of DA, the resultant film was labeled as APTES/GO/C60 (figure b). As shown in figure b, C60 molecules didn't appear on surface of graphene due to absence of amino groups, while were scattered on surface of APTES-assembled SiO₂. Furthermore, because most of amino groups of APTES had been oxidized in the preparation of APTES/GO film, the AFM image showed only very few C60 molecules grafted on unoxidized amino groups of APTES.

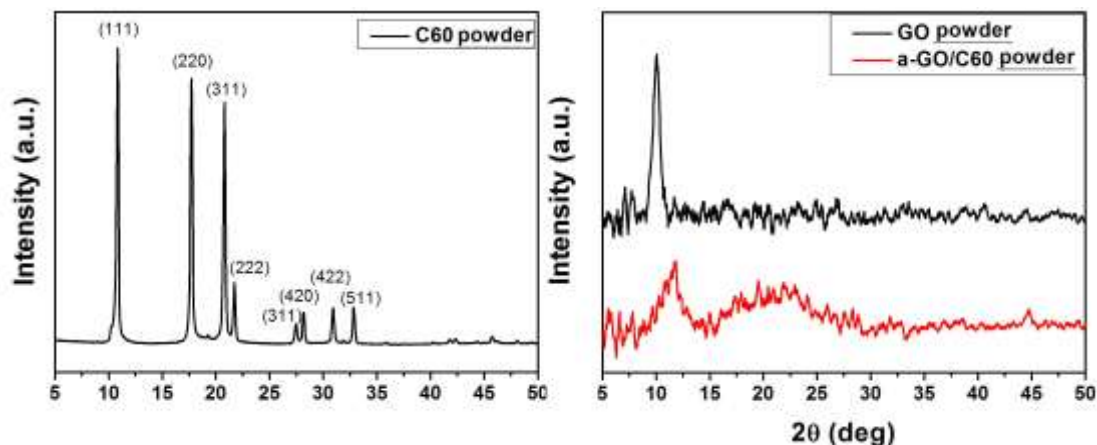
SI5. FTIR of C60 and a-GO/C60 powders



C60 powder exhibited four typical absorption bands at 525 cm⁻¹, 575 cm⁻¹, 1181 cm⁻¹,

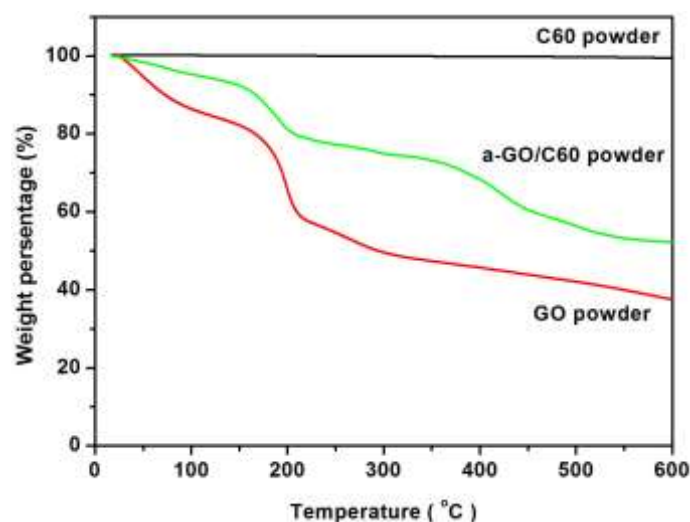
1428 cm^{-1} . These characteristic peaks of C60, although weakened, also appeared in FTIR of the a-GO/C60 powder, which well confirmed that C60 had grafted successfully on surface of graphene.

SI6. XRD patterns of C60, GO and a-GO/C60 powders



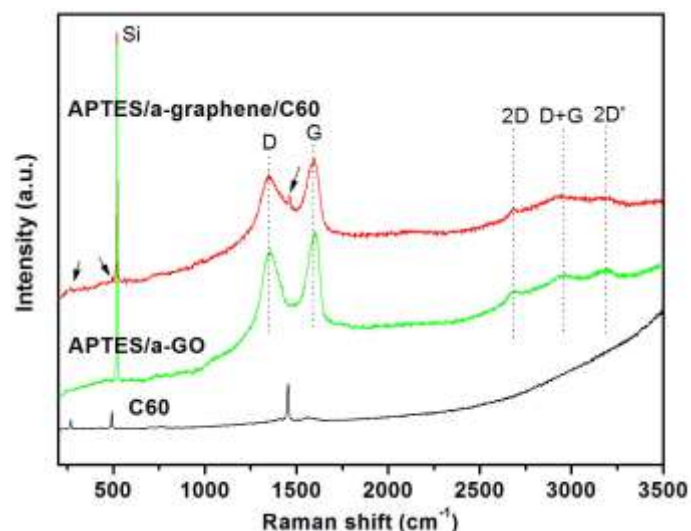
In the XRD pattern of C60 powder with good crystallization, the sharp characteristic peaks were attributed to the (111), (220), (311), (222), (331), (420), (422), and (511) planes, respectively (JCPDS file No.44-0558). The XRD pattern of GO showed a sharp peak which corresponds to an interlayer spacing of ~ 0.8 nm, suggesting the facile exfoliation because of the weakened van der Waals forces between layers of GO. No peak around 26° was found in the pattern, indicating that graphite had been completely oxidized. After reacting with C60, the characteristic peak of GO weakens and broadens due to relatively short domain order of the stacked GO nanosheets. In addition, a new broad diffraction peak in the range of $15\text{--}35^\circ$ appeared in XRD pattern of a-GO/C60 powder. The broad diffraction peak was attributed to C60 grafted on GO nanosheets which was featured by poor crystalline structure.

SI7. TGA of C60, GO and a-GO/C60 powders



TGA analysis were performed on C60, GO and a-GO/C60 powders heated to 600 °C at heating rate 10 °C min⁻¹ under N₂. The C60 hardly decomposed even at 600 °C, while both the GO and the a-GO/C60 showed obvious weight loss below 600 °C. Particularly, weight loss below 100 °C stemmed from the removal of absorbed water. The major mass loss (21 wt%) of the GO which was observed from 160 °C to 210 °C could be assigned to the decomposition of the labile oxygen-containing functional groups, yielding CO, CO₂ and H₂O. Compared with the GO, the weight loss (11 wt%) of the a-GO/C60 at the same temperature range was much lower, indicating that the main oxygen-containing functional groups of GO had been converted or removed after reacting with DA. Thus, a major mass loss for a-GO/C60 from 350 °C to 550 °C was probably caused by the pyrolysis of the silane moieties bonded on graphene surface⁴. The increased remaining weight of a-GO/C60 was due to the grafted C60 which had a higher thermal stability.

SI8. Raman spectra of C60 powder, APTES/a-GO and APTES/a-graphene/C60 films

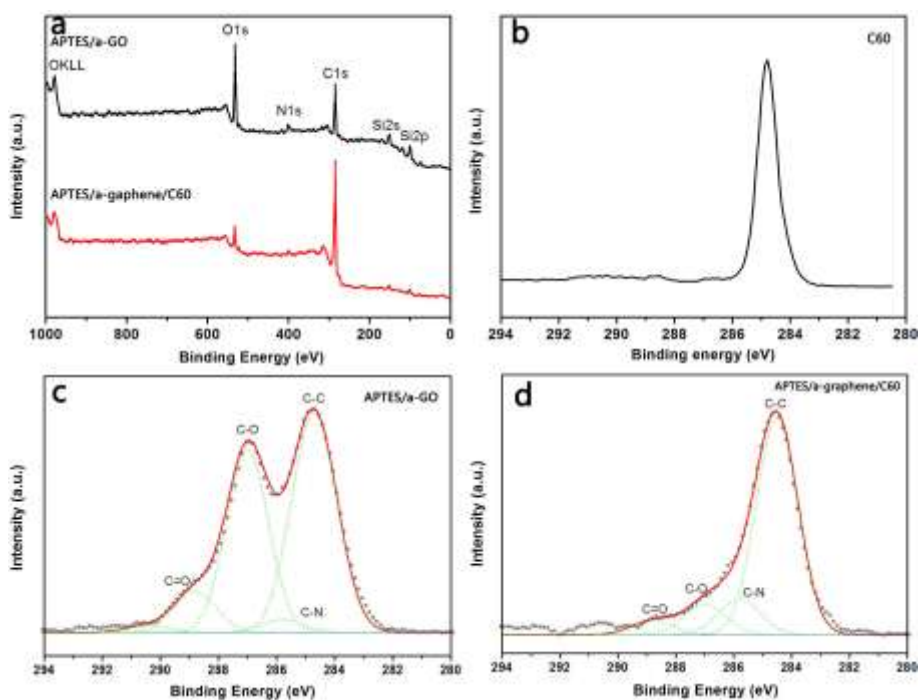


Raman spectrum of the APTES/a-GO film displayed two prominent peaks, namely, the G band at 1600 cm^{-1} corresponding to the in-plane vibration of the sp^2 -hybridized carbon in a hexagonal lattice and the D band at 1355 cm^{-1} , which was associated with the vibration of the disordered sp^3 -hybridized carbon because of in-plane defects. The sharp peak at 520 cm^{-1} arose from silane and Si substrate. In addition of D and G bands of graphene, the peak at 1463 cm^{-1} in Raman spectrum of the APTES/a-graphene/C60 film should be assigned to the pentagonal pinch mode [$A_g(2)$] of C60, which was shifted by 8 cm^{-1} compared with the pure C60 at 1455 cm^{-1} . This observed peak shift sufficiently suggested a strong interaction between the C60 and the graphene nanosheet. Additionally, the G band position for the APTES/a-graphene/C60 film downshifted to 1596 cm^{-1} in comparison with the APTES/a-GO, indicating the charge-transfer from the graphene network to the covalently bound C60⁵. The ratio of the D and G band intensities was widely used as an indication of the disorder or the level of chemical modification in the graphene surface. The grafting of C60 onto graphene and heat reduction caused an increase in the I_D/I_G ratio.

SI9. XPS spectra of C60 powder, APTES/a-GO and APTES/a-graphene/C60 films

XPS analysis was carried out to confirm the effective reactions among a-GO and C60. As shown in following figure, the peak shape of C 1s in the C60 was very narrow and symmetric. The binding energy and the FWHM of the C 1s peak was 284.79 eV and

0.8 eV, respectively. In addition, C 1s spectrum of the C60 showed many carbon π - π^* shake-up peaks around 290.5 eV due to the conjugated bonds in C60 molecule, which were the characteristic features of C60 molecule. C 1s spectrum of APTES/a-GO film exhibited an asymmetrical broadening towards higher binding energy. The peaks centered at 290.5 eV, 288.8 eV, 286.9 eV, 285.8 eV and 284.7 eV were attributed to the characteristic shake-up peak, C=O bonds, C–O bonds, C–N bonds, C–C bonds of the GO and of the silane molecules, respectively. Although the C1s spectrum of APTES/a-graphene/C60 film also exhibited same oxygen functional groups after deoxidization at 200 °C, their peak intensities decreased remarkably, and the major component at a binding energy of 284.7 eV increased significantly. The increasing of the C-C peak intensity along with C-N confirmed that the amino moieties of DA had reacted with C60. In addition, the increasing of the shake-up peak around 290.5 eV confirmed further the presence of C60 molecules on the graphene layers.



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