Supplementary Material for Nanoscale

Electronic supplementary information

Functionalized graphene and graphene oxide solution via polyacrylate coating[#]

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1. X-ray Photoelectron Spectroscopy (XPS)

Table S1 summarizes the composition of different samples as estimated from XPS compositional analysis. Figure S1(a-c), shows C-1*s* XPS of powder graphite, polymer coated graphene oxide (GO) and polymer coated graphene (G), respectively. It is important to note that GO and G have polymer coatings and thus it is very difficult to analyze the chemical conversion of GO into G, as contribution from polymer functional groups are also associated in XPS results. We did very details of XPS data analysis and found the signature of polymers as well as the transformation from GO to G, as summarized below. The general features of the spectra shows that the overall spectra are widening from graphite powder to GO to G indicating the graphite powder gradually becoming graphene structure. This is due to incorporation of other species into the sp^2 network of reduced-GO. It is known that, rather than a single symmetry peak with a constant width, the C-1s peak of sp^2 carbon at 284.4 eV becomes asymmetric and broadened towards the high binding energy side as the amount of functional groups increases.[1] The C-1*s* spectra are decomposed into different peaks by curve fitting using Gaussian functions after performing a background correction. These data shows that the graphite powder is mainly composed of graphitic carbon (sp^2) and oxygen/hydrogen bonded carbon, whereas GO and G are composed of graphitic carbon (sp^2), oxygen/hydrogen bonded carbon and small amount of carbon/oxygen bonded nitrogen, sulfur and phosphorous as observed from N-1s, S-2p and P-2p XPS spectra. The binding energy of the C-C and C-

H bonding are assigned at 284.4–285.0 eV and chemical shifts of +1.5 (285.9 -287.0 eV), +2.5 (286.9 – 287.5 eV) and +4.0 eV (288.4 – 289.0 eV) are typically assigned for the C-OH, C=O and O=C-OH functional groups, respectively. [2,3] Most structural models of graphite oxide also include an epoxide group (C-O-C), which should have a C-1s binding energy similar to C-OH.[4] However, in practice, it is very difficult to fix their chemical shift from C-1s peak precisely as mentioned elsewhere.[4] It should be considered that the values of chemical shifts of each functional group from the C-1s peak should have some distributions, e.g. + 1.3 to + 1.7 for C-O, + 2.5 to + 3.0 for C=O and + 4.0 to + 4.5 for COOH.[5,6] Therefore, the peaks in these ranges should be assigned as C-O, C=O and COOH, respectively. On the basis of these peak assignments we have decomposed into different peaks using curve fitting of Gaussian functions as shown in Figure S1(a-c). The different peak position, their identification (probable bonding structure) and full-width at half-maximum (FWHM) for all XPS spectrum are summarized in Table S2. The C-1*s* peak of graphite powder is consisted of four Gaussian peaks (Figure 1a) centered at 284.5 eV (peak I), 286.0 eV (Peak II), 288.8 eV (Peak III) and 291.2 eV (Peak IV). The peak at 284.5 eV indicates that carbon is mostly in the form of graphite and assigned to sp^2 aromatic hydrocarbons.[7,8] The peak at ≈ 286.0 eV can be assigned to C-O[9] and very weak peak at 288.8 eV and 291.2 eV are assigned as the O=C-O groups[9] and CO_2 and/or C-C=O bonds,[10] respectively. The C-1s XPS spectrum of GO indicates a considerable degree of oxidation with four major signatures corresponding to carbon atoms in different functional groups. They are non-oxygenated graphitic sp^2 carbon at ≈ 284.4 eV, C of C-O and/or C-OH bonds with C= N bonds [11,12] at ≈ 285.9 eV, C of C=O bonds at ≈ 287.8 eV and that of C of C-C=O bonds and/or CO_2 at ≈ 292.3 eV.[10] The peak at ≈ 287.8 eV also has the contribution of nitrogen bonded carbon.[13] In addition a peak is observed at ~295.2 eV that attributed as CH_3-CO-OH bonds. In case of G, the spectra shows that the first two peaks are almost identical in position and are assigned as non-oxygenated graphitic sp^2 carbon and C-O / C=N bonds, respectively. But the peak intensity of II-peak is reduced as compared to GO. Assuming that percentage of coating polymer is same for GO and G, this indicates the reduction of GO to G during hydrazine treatment. In addition the peak contributing at 284.4 (±0.1) eV become broader (full width at half maximum - FWHM) and the broad tail towards higher binding energy and reduction of the intensity from graphite powder→GO→G, indicating the contribution of graphene structure. The III-peak of G is shifted to ≈ 288.2 eV, as compared to GO (≈ 287.7 eV), and is assigned as not only C of C=O bonds but also some species of S and P. The peak at ≈ 287.8 eV is observed in GO and G that assigned as the C=O bonds, but Zang et al.[14] mentioned that it is the $\pi \rightarrow \pi^*$ shake-up peak of C_2 that indicates the formation of grapheme structure.[15]

The O-1*s* XPS spectrum of graphite powder, polymer coated GO and G are decomposed into two (Figure S2a) or three (Figure S2b and S2c) Gaussian peaks. The peaks at ≈ 532-533 eV are attributed due to C-O, C=O and/or C-OH.[14] The peak at ≈ 532.0 also may be due to the contribution of oxides of nitrogen, sulfur and phosphorus.[14] The peak at ≈ 533.8 eV observed in GO is attributed due to COOH bond.[14] The peak at ≈ 530.6 (±0.3) eV in GO and G is due to the contributions from C=O and O=C-OH groups.[16]

2. Micro-Raman Spectroscopy

In graphene containing structure like CNTs and carbon fibers, Raman spectroscopy can be a sensitive probe for the electronic structure and the presence of defects. Here also significant structural changes occur during the chemical processing from pristine graphite powder to polymer coated graphene oxide (GO), and then to polymer coated graphene (G); as reflected in their Raman spectra (Figure 4). The Raman spectrum of graphite powder, as expected, display a prominent and sharp G-band peak at ~ 1575 cm^{-1} corresponding to the first-order scattering of the E_{2g} mode and comparably weak peak D-band at ~1353 cm^{-1}, generally arise from the presence of defects and disorder, such as the presence of in-plane substitutional hetero-atoms, grain boundaries, aliphatic chain, etc., which serve to lower the symmetry of the quasi-infinite lattice.[17] In polymer coated graphene oxide (GO), the G-band is broadened and shifted to 1597 cm^{-1} and D-band at 1348 cm^{-1} becomes more prominent. This indicates the reduction in size of the in-plane sp^2 domains, possibly due to the extensive oxidation and hence the structural imperfections created by the attachment of hydroxyl and epoxide groups on the carbon basal plane. The Raman spectrum of the polymer coated graphene (G) also contains both G- and D- bands (at 1602 cm^{-1} and 1348 cm^{-1}, respectively); however, with an increased I_D/I_G intensity ratio compared to that of GO (1.12 for graphene oxide (GO) to 1.29 for graphene (G): see Table S1). This change clearly suggests a decrease in the average size of the sp^2 domains upon conversion from graphene oxide (GO) to graphene (G),[18] and can be explained if new graphite domains were created that are smaller in size than ones present in graphene oxide (GO). The intensity of the overtone 2D-band, 2G-band is smaller than the D- and G-bands; hence the I_{2D}/I_G intensity ratio is reduced; further indication of graphitization.[16] In addition a very weak T-band due to the sp^3 vibrational mode[19] and T+D band is observed in graphite powder, but no such peak is seen in graphene oxide (GO)/graphene(G). The overtone 2D-, 2G- and D+G bands are also observed (peak positions are tabulated in Table S1) but their intensity with respect to the D- and G-bands are small. In graphene (G) there is a peak shift for the 2D-band (inset Figure 4) and no obvious shift for the D-band as indicated in Table S1. The shift of the peak positions of 2D-band, indicative of the reduction of graphene oxide (GO) and formation of graphene structure.[16]

3. X-ray diffraction

The XRD pattern shows that the graphite powder have sharp peak at $2\theta = 26^0$, corresponding to a layer to layer distance (*d*-spacing) of about ≈0.333 nm, wheras polymer coated GO and G shows a wide peak at $2\theta = 23^0$ and corresponding layer to layer distance (*d*-spacing) of about ≈0.3867 nm. (Figure S3) The slightly higher value of *d*-spacing in GO and G can be ascribed to the presence of oxygen containg functional groups or other structural defects.

References:

1. X. Li, H. Wang, J. T. Robinson, H. Sanchez, G. Diankov and H. Dai, J. Am. Chem. Soc., 2009, **131**, 15939.
2. T.C. Chiang and F. Seitz, Photoemission spectroscopy in Solids, *Ann. Phys.,* 2001, **10**, 61.
3. S. Yumitori, *J. Mater. Sci.*, 2000, **35**, 139.
4. C. Kozlowski and P.M.A. Sherwood, *J. Chem. Soc. Farad T 1 Phys Chem Condensed phases,* 1994, **80**, 2099.
5. K.M. Sundberg, W.H. Smyrl, L.J. Atanasoska and Atanasoski, *J. Electrochem. Soc.,* 1989, **36**, 434.
6. C. Jones, Composites Science and Technology, 1991, **42**, 275.
7. Y. Xia and R. Mokaya, *Adv. Mater. ,* 2004*,* **16***,* 1553.
8. M. A. Baker and P. Hammer, *Surf. Interface Anal.*, 1997, **25**, 629.
9. V.C. Moore, M.S. Strano, E.H. Haroz, R.H. Hauge, R.E. Smalley, J. Schmidt and Y. Talmon, Nano Lett., 2003, **3**, 1379.
10. T. Sato, A. Narazaki, Y. Kawaguchi and H. Niino, *Appl. Phys. A*, 2004*,* **79***,* 1477.
11. Y. Hernandez, V. Nicolosi, M. Lotya, F.M. Blighe, Z. Sun, S. De, I.T. McGovern, B. Holland, M. Byrne, Y. Gun'ko, J.J. Boland, P.Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardac, A.C. Ferrari and J.N. Colemani, *Nat. Nanotechnol.*, 2008, **3**, 563.
12. R.J. Waltman, J. Pacansky and C.W. Bates, Jr., *Chem. Mater.*, 1993, **5**,1799.
13. D. Marton, K.J. Boyd, A.H. Al-Bayati, S.S. Todorov and J.W. Rabalasis, *Phys. Rev. Lett.*, 1994, **73**, 118.
14. G. Zhang, S. Sun, D. Yang, J.P. Dodelet and E. Sacher, *Carbon*, 2008, *46*,196.
15. X. Fan, W. Peng, Y. Li, X. Li, S. Wang, G. Zang and F. Zang, *Adv. Mater.*, 2008, **20**, 4490.
16. D. Yang, A. Velamakanni, G. Bozoklu, S. Park, M. Stoller, R.D. Piner, S. Stankovich, I. Jung, D.A. Field, C.A. Ventrice Jr. and R.S. Ruoff, *Carbon*, 2009, **47**, 145.

17. M. Ramm, M. Ata, T. Gross and W. Unger, *Appl. Phys. A: Mater*, 2000, **70**, 387.

18. F. Tunistra and J. L. Koenig, *J. Chem. Phys.*, 1970, **53**,1126.

19. J. R. Shi, X. Shi, Z. Sun, S. P. Lau, B. K. Tay and H. S. Tan, *Diam. Relat. Mater.*, 2001, **10**, 76.

Table S1: Compositional analysis from and XPS and microstructural analysis from Raman spectra.

Sample	Compositional analysis from XPS					Micro-structural analysis from Raman spectra	
	C	O	N	S	P	Peak positions (cm^{-1})	I_D/I_G ratio
Graphite powder (Aldrich)	97.6	2.4	--	--	--	T-peak 1080 D-peak 1353 G-Peak 1575 T+D-Peak 2446 2D-peak 2702 D+G-peak 2928	0.22
Polymer coated GO	68.0	30.3	0.5	1.0	0.2	T-peak 1128 D-peak 1348 G-Peak 1597 T+D -Peak 2365 2D-peak 2713 2G-peak 3165	1.12
Polymer coated G	77.0	20.0	1.9	0.7	0.4	D-peak 1348 G-Peak 1602 2D-peak 2696 (D+G) peak 2935 2G peak 3183	1.29

Table S2: Bonding and electronic-structural analysis from XPS spectra.

Sample	Bonding structure from XPS			
	C-1s XPS		O-1s XPS	
	Peak positions (eV) & their identification	FWHM	Peak positions (eV) & their identification	FWHM
Graphite powder (Aldrich)	284.5 ~ sp^2 C, C-H	0.50	531.7 ~ C-O	2.05
	286.0 ~ C-O/C-OH	1.44		
	288.8 ~ O=C-O / O=C-OH	2.51	533.1 ~ C=O, C-OH	1.87
	291.2 ~ CO_2 and/or C-C=O	2.44		
Polymer coated GO	284.3 ~ sp^2 C, C-H	0.90	530.4 ~ C=O & O=C-OH	
	285.9 ~ C-O/C-OH with C=N & S-O	1.03		1.44
	287.7 ~ C=O & N-O	1.91	532.1 ~ C-O, S-O & P-O	1.29
	292.3 ~ CO_2 and/or C-C=O	1.25		
	295.1 ~ CH_3-CO-OH	0.90	533.8 ~ COOH	3.62
Polymer coated G	284.4 ~ sp^2 C	0.98	530.2 ~ C=O & O=C-OH	
	285.9 ~ C-O/C-OH with C=N & S-O	1.17		1.05
	288.1 ~ C=O & N-O	1.52	531.9 ~ C-O, S-O & P-O	1.53
	292.4 ~ CO_2 and/or C-C=O	1.00		
	295.1 ~ CH_3-CO-OH	0.75	533.2~ C-OH	0.22

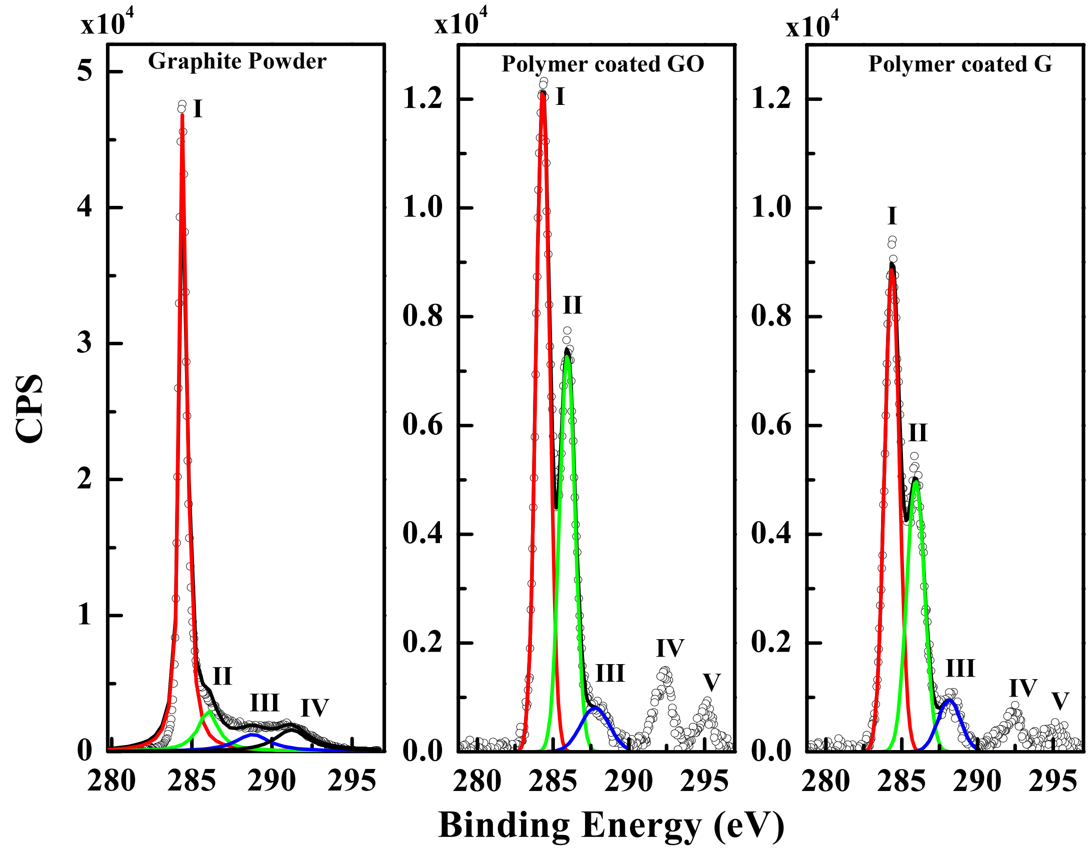

Figure S1: C-1s XPS spectra of (a) graphite powder, (b) polymer coated GO, and (c) polymer coated G.

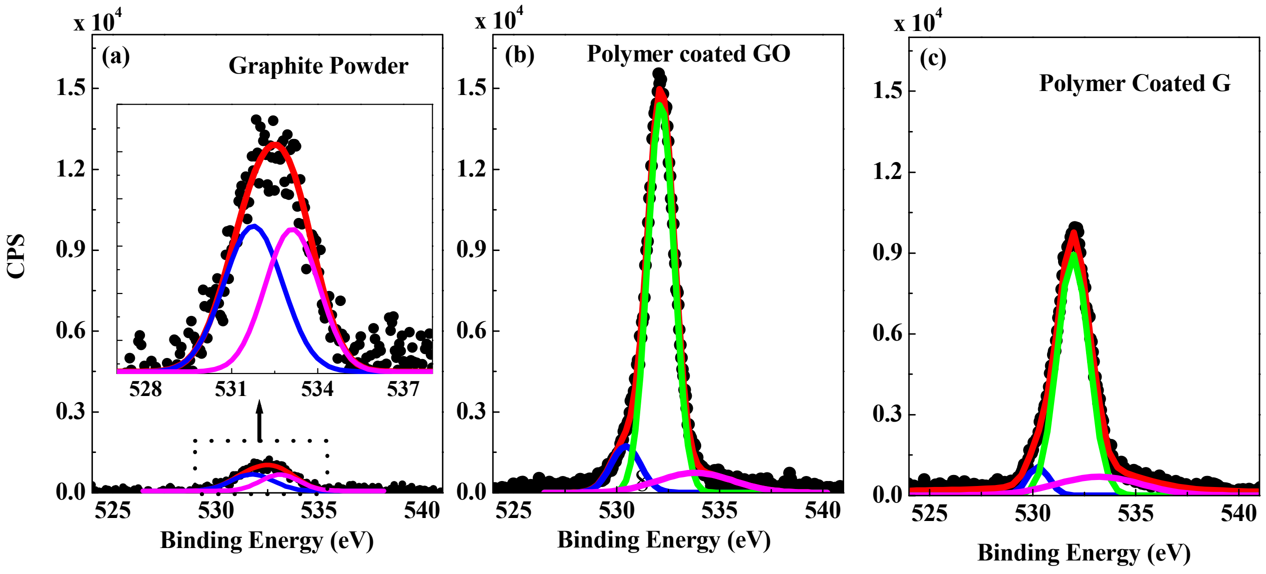

Figure S2: O-1s XPS spectra of (a) graphite powder, (b) polymer coated GO and (c) polymer coated G.

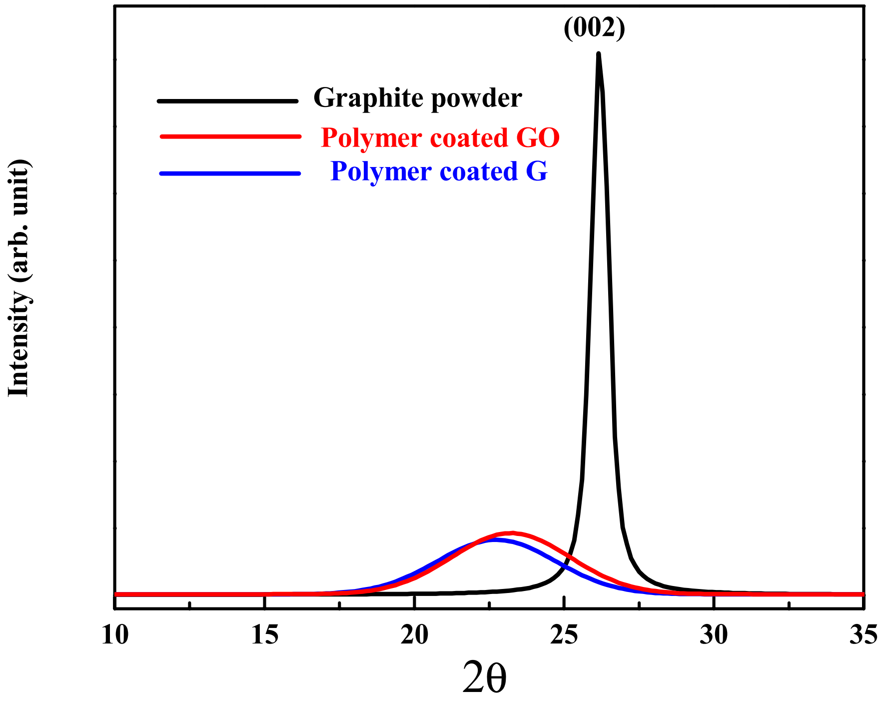

Figure S3: XRD pattern of graphite powder and polymer coated G.

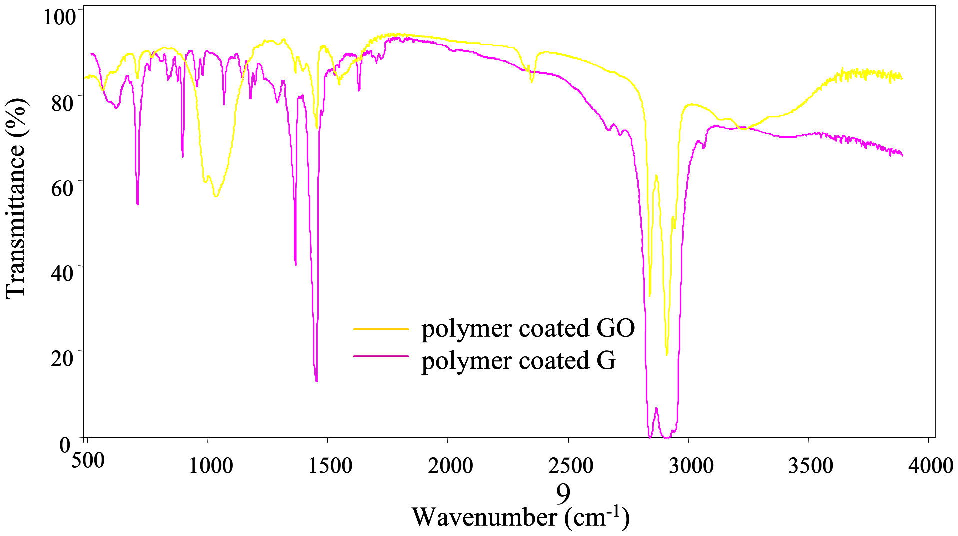

Figure S4. FTIR spectra of polymer coated GO and G showing mainly the signature of polymer functional groups. However, peak intensity at 1200-1500 cm^{-1} for C-O-C, C-OH functional groups decreases in G suggesting the reduction of graphene oxide.

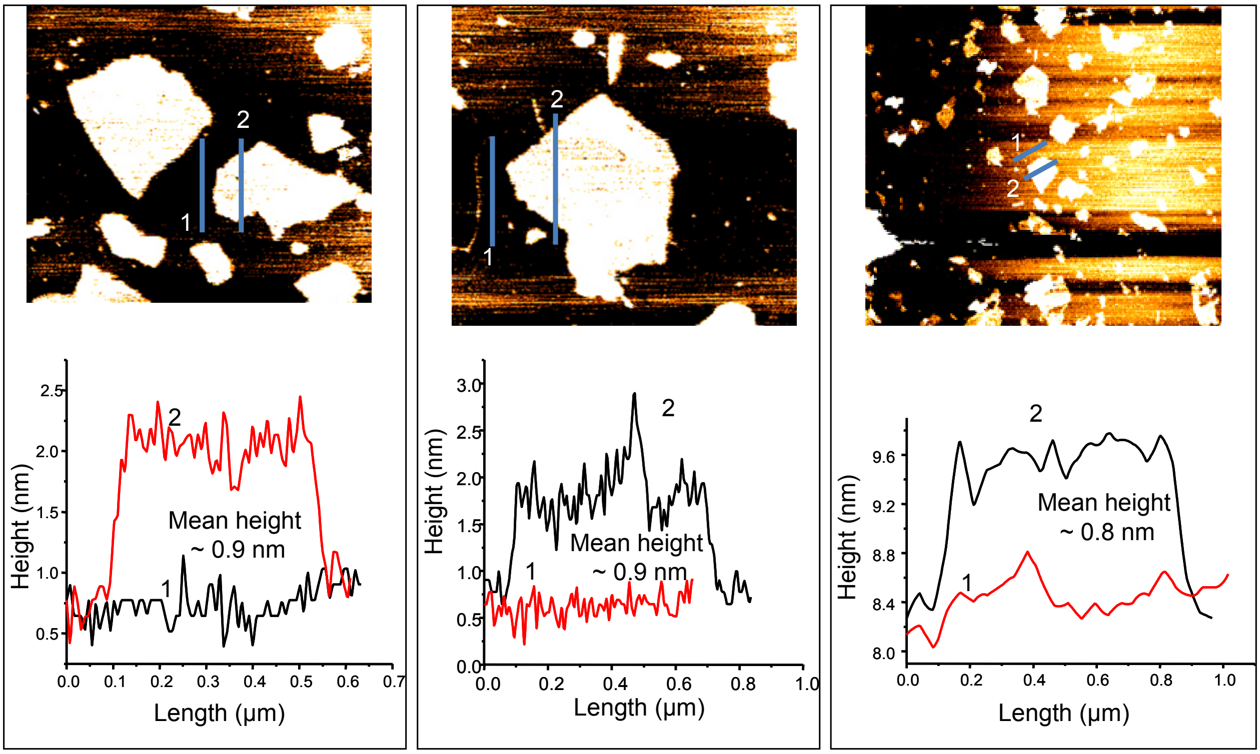

Figure S5. Representative AFM height images of as synthesized GO measured in different areas. Mean height range between 0.8-0.9 nm, suggesting that GO is single layer.

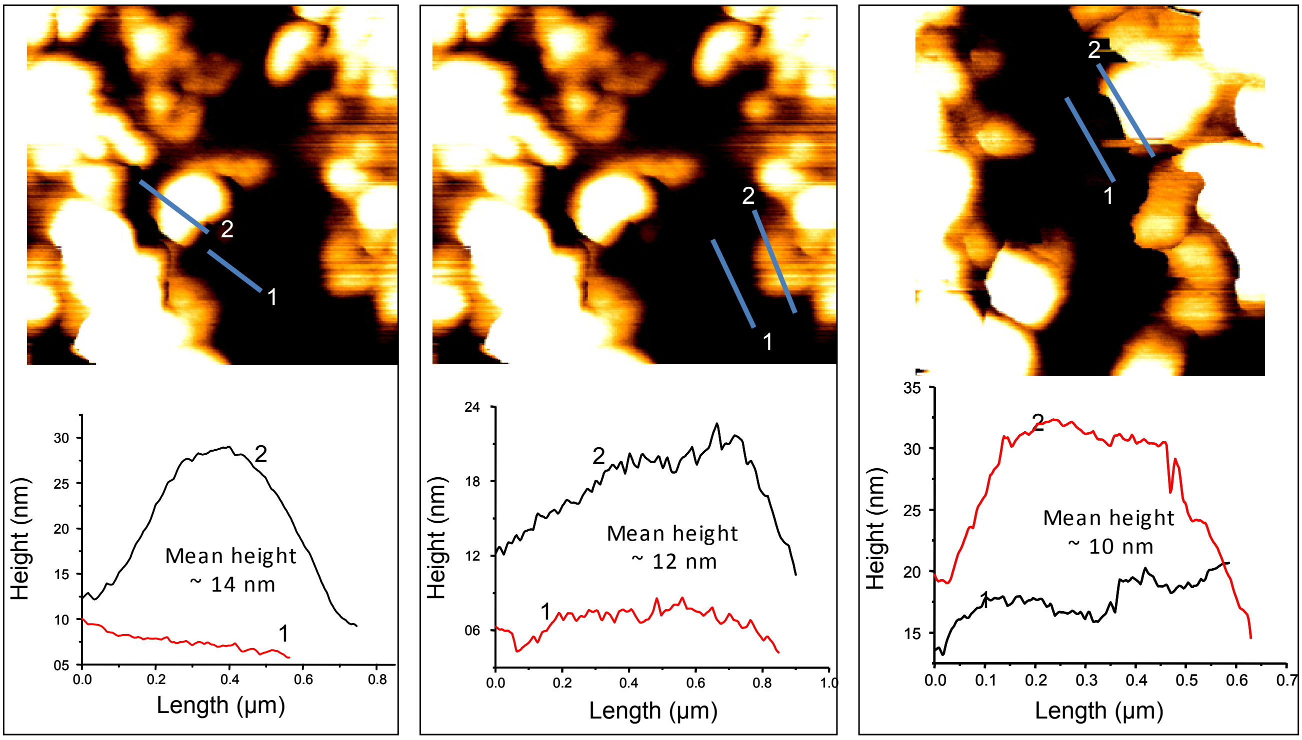

Figure S6. Representative AFM height images of polymer coated G measured in different areas. Mean height ranges between 10-15 nm, suggesting that thickness of coating polymer is about 5-8 nm.

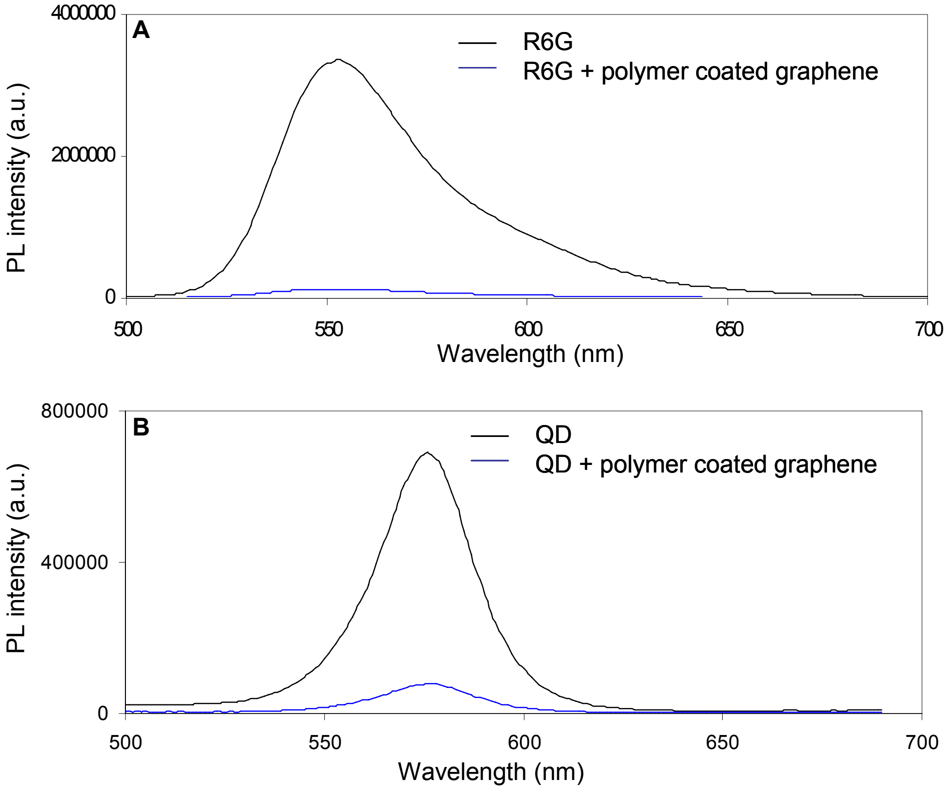

Figure S7. Polymer coated graphene induced fluorescence quenching of rhodamine 6G (R6G) (A) and polyacrylate coated cationic QD (B). Concentration of R6G or QD in the control samples was same as of polymer coated graphene solution. This result shows that polymer coating does not considerably inhibit the access of small molecules and particles close to the graphene surface.