Supporting Information for

Self assembly of graphene oxide at the liquid-liquid interface: A new rout to fabrication of graphene based composites

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1- Modeling of nanolayers self-assembly at the interface:

Self-assembly of GO nanosheets at the liquid-liquid interface is driven thermodynamically. Due to the high interfacial tension of two immiscible liquid phases, entrapping the particles, increases the interfacial energy and minimizes the free energy of the system.

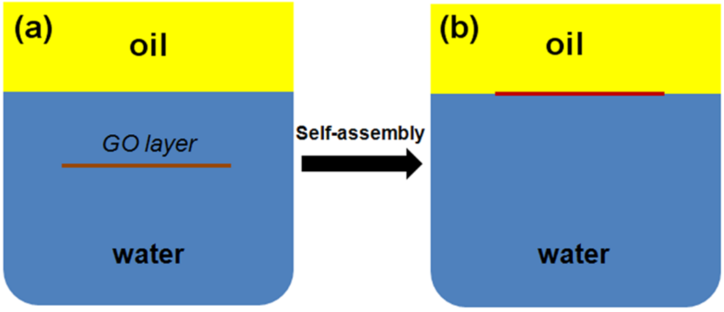

Fig. S1 Two states of nanolayer at (a) water's bulk and (b) oil-water interface.

Initially, GO layer is immersed in aqueous media as shown in Fig. S1 (a). In this state, the surface energy is given as follow:

$$\mu_a = 2A\gamma_{GO/W} \qquad \text{(S-1)}$$

Where A is the surface area of GO sheet and $\gamma_{GO/W}$ is the interfacial tension between water and GO layer.

Inserting GO layer into the interface decreases the interfacial area between oil and water and forms a new interface between oil phase and GO layer. However, due to the atomically thin nature of GO sheet, extend of wetting of GO with oil phase and quantity of new interface of oil-GO is not clearly understood. Let's simply assume a planar interface where one side of GO layer is totally wetted by the oil phase and the other by water (Fig. S1-(b)). The surface energy of the floated GO layer at the interface is given as follow:

$$\mu_b = A\gamma_{GO/W} + A\gamma_{GO/O} - A\gamma_{O/W} \qquad \text{(S-2)}$$

Where $\gamma_{GO/O}$ and $\gamma_{O/W}$ are GO-oil and water-oil interfacial tensions; respectively.

Therefore, change in the surface energy of the system due to the insertion of GO into the water-oil interface is calculated as follows:

$$\Delta\mu = \mu_b - \mu_a = A(\gamma_{GO/W} - \gamma_{GO/O} - \gamma_{O/W}) \qquad \text{(S-3)}$$

Thus, adsorbtion is energetically favorable if:

$$\Delta\mu < 0 \rightarrow \gamma_{GO/w} - \gamma_{GO/O} < \gamma_{O/W} \qquad \text{(S-4)}$$

2-Calculations of interfacial tensions:

Wu equation gives the interfacial interaction among phases as follows[S1]:

$$\gamma_{a/b} = \gamma_a + \gamma_b - 4\times[(\frac{\gamma_a^d \gamma_b^d}{\gamma_a^d + \gamma_b^d}) + (\frac{\gamma_a^p \gamma_b^p}{\gamma_a^p + \gamma_b^p})] \qquad \text{(S-5)}$$

Where γ^d and γ^p are dispersive and polar contribution of surface tension, respectively. Based on available data for water[S2] and MMA[S3] the $\gamma_{O/W}$ is roughly 50.3 mN/m. Polar and dispersive contributions of GO's surface energy are obtained from Wang et al.[S2] as follows:

γ_{GO}^{d} = 19.83 , γ_{GO}^{p} = 29.30 mN/m

Therefore the $\gamma_{GO/w}$ and $\gamma_{GO/O}$ is estimated 6.16 and 16.83mN/m, respectively.

It should be noted $\gamma_{O/W}$ is relatively large for a broad range of immiscible liquids (oils). Therefore, GO is readily adsorbed at the interface of many liquids. In addition, based on the above calculated values for interfacial tension of GO, water and oil and eq. S-3, the energy of adsorbtion for a layer of GO with lateral size of 1μm is approximately $-14.7\times10^{6}k_{b}T$. This indicates very strong affinity of GO layers for adsorbtion and irreversible entrapping at the interface.

3- Additional SEM and TEM images of GO-PMMA particles:

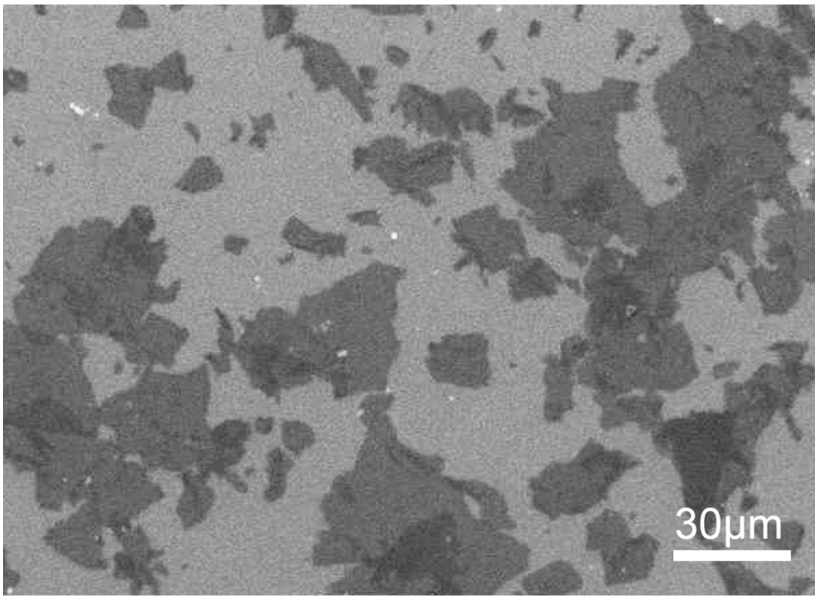

Fig. S2 SEM micrograph of GO sheets (as prepared) coated on Si/SiO2 substrate.

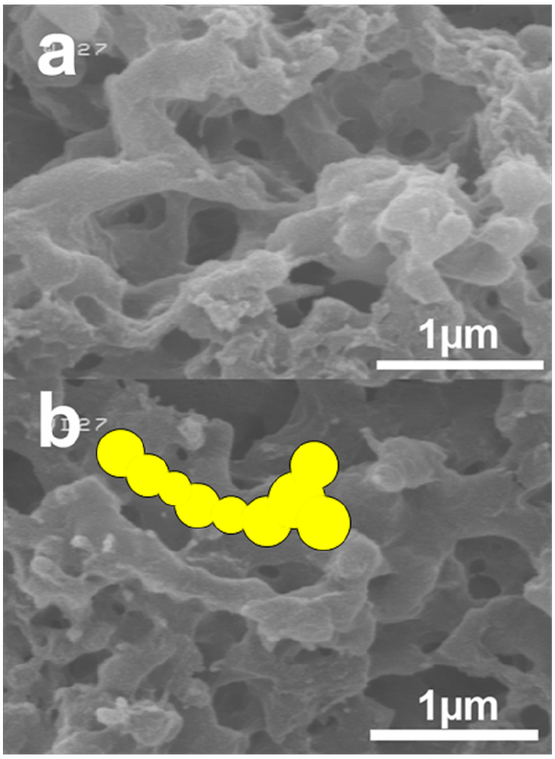

Fig. S3 (a),(b) SEM images of GO-PMMA composites containing 1wt% GO, showing Aggregation of polymer particles.

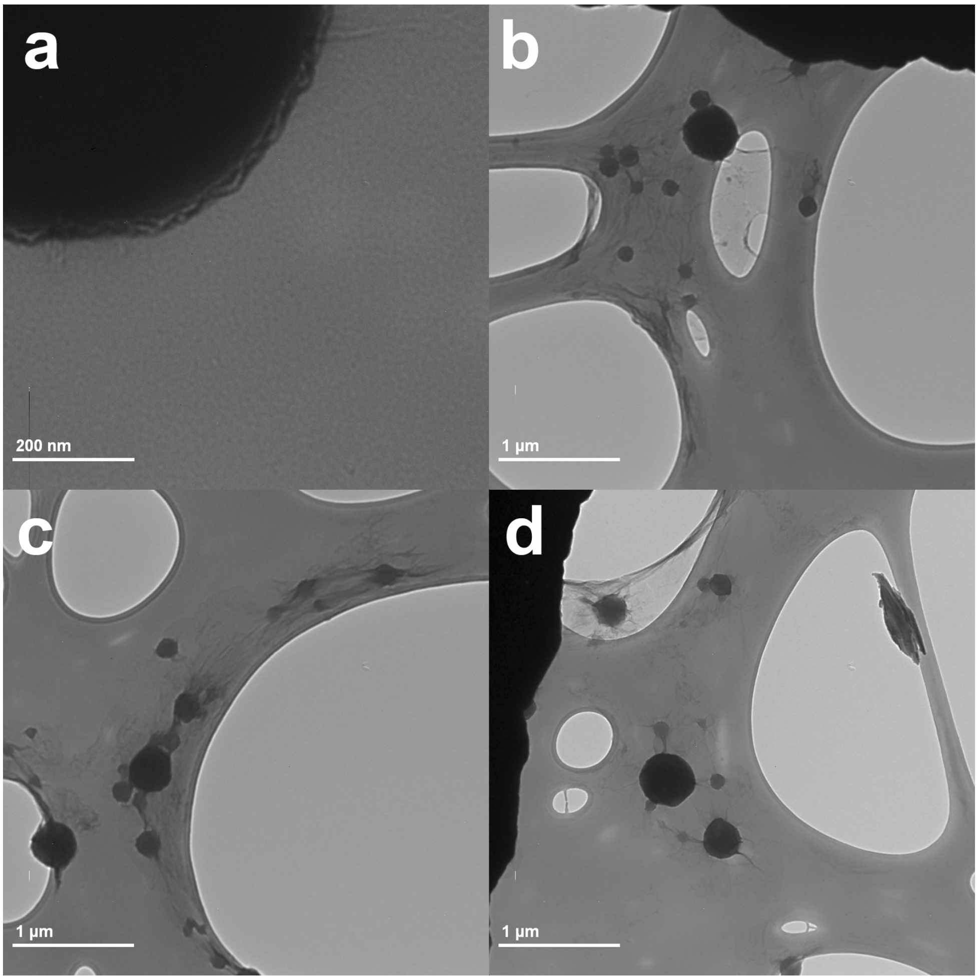

Fig. S4 TEM images of GO-PMMA containing 5wt% of GO, demonstrating polymer particles that are mostly decorated by one nanolayer.

References:

S1 S. Wu, *J. Polym. Sci. Part C: Polym. Sym.*, 1971, **34**, 19.

S2 S. Wang, Y. Zhang, N. Abidi and L. Cabrales, *Langmuir*, 2009, **25**, 11078.

S3 N. R. Raravikar, L. S. Schadler, A. Vijayaraghavan, Y. Zhao, B. Wei and P. M. Ajayan, *Chem. Mater.*, 2005, **17**, 974.