Electronic Supplementary Material (ESI) for RSC Advances

Supporting information for

Dispersion of rGO in Polymeric Matrices by Thermodynamically Favorable Self-Assembly of GO at Oil-Water Interfaces

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1. Self-assembly of GO on Toluene-Water interface

As explained, GO layers accumulate at hydrophilic-hydrophobic interfacial area, based on a thermodynamically-driven tendency. Adsorption of the layers replaces the high energy oil-water surface area with low energy particle-oil and particle-water surfaces. So, it is expected that self-assembly of GO particles at oil-water interface leads to remarkable decline in system free energy. The change in free energy, resulted from adsorption of a GO particle is calculated as follows:

$$\Delta\mu = A\,(\gamma_{GO/W} - \gamma_{GO/T} - \gamma_{T/W}) \qquad \text{(S-1)}$$

Where, A is the surface area of a monolayer, and $\gamma_{GO/W}$, $\gamma_{GO/T}$, $\gamma_{T/W}$ are the interfacial tensions of particle-water, particle-toluene and toluene-water, respectively.

The amounts of interfacial tensions were calculated using Wu equation [S1]:

$$\gamma_{a/b} = \gamma_a + \gamma_b - 4 \times [(\gamma_a^{\,d}\,\gamma_b^{\,d}\,(\gamma_a^{\,d} + \gamma_a^{\,d})^{-1}) + (\gamma_a^{\,p}\,\gamma_b^{\,p}\,(\gamma_a^{\,p} + \gamma_a^{\,p})^{-1})] \qquad \text{(S-2)}$$

Where, γ^p and γ^d are the polar and dispersive components of the surface tension (γ) for each phase. Using the available data for water and toluene [S2], $\gamma_{T/W}$ was found to be around 36.4 mN/m. On the other hand, to obtain the corresponding parameter between particle and liquid phases, dispersive and polar elements of GO surface tension are required. In this case, contact angle measurement of 3 different solvents on GO film was employed [S3].

Table 1. Contact angle of different solvents on GO film

Materials	Water	Formamide	glycerol
GO	52.8 (2.6)	24.4 (4.4)	42.1 (3.6)

- Numbers in parentheses are the standard deviation of 3 measurements

Having the amounts of surface tension for each solvent [S4] and measured contact angles, based on Owens-Wendt theory [S3] and by fitting a linear equation, dispersive and polar components of GO surface tension was calculated from slope and interception of fitted line in $\gamma_l^p = 0$ [S3]:

$$[\gamma_l (1 + \cos\theta)] / 2 (\gamma_l^d)^{0.5} = (\gamma_{GO}^p)^{0.5} (\gamma_l^p / \gamma_l^d)^{0.5} + (\gamma_{GO}^d)^{0.5} \quad \text{(S-3)}$$

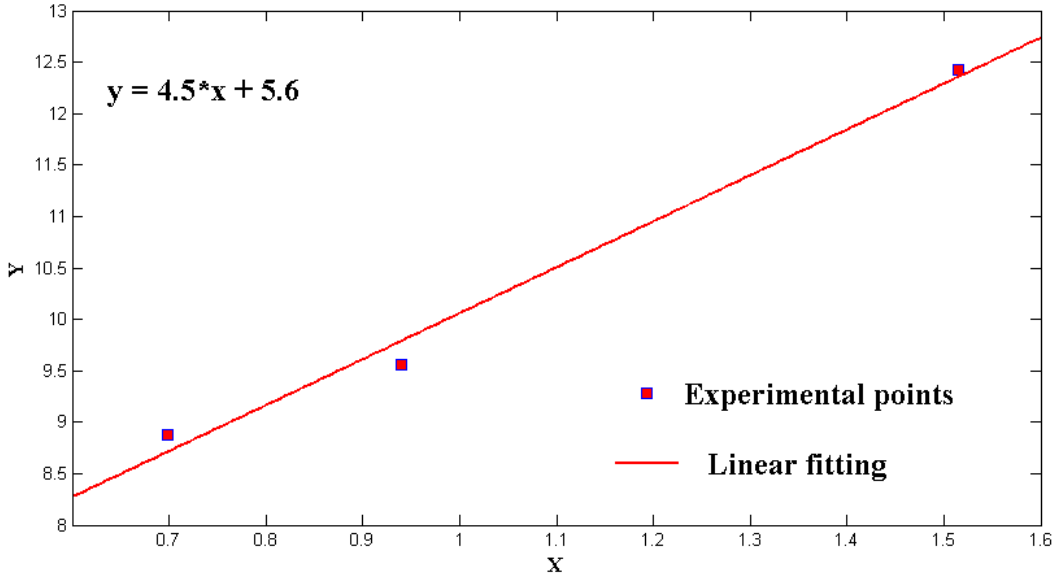


Fig. S1 Plot of $[\gamma_l (1 + \cos\theta)] / 2 (\gamma_l^d)^{0.5}$ versus $(\gamma_l^p / \gamma_l^d)^{0.5}$ for different solvents on GO substrate

Based on Fig. S1, dispersive and polar elements of GO surface tension were found to be 31.36 and 20.25 mN/m, respectively.

Having surface tension of GO, the amounts of $\gamma_{GO/W}$ and $\gamma_{GO/T}$ were found to be around 16.29 and 18.89 mN/m. Substituting corresponded amounts in equation S-1 and assuming an average surface area of 40 μm^2 for a monolayer (based on average size of sheets from SEM images), reduction of total free energy of the system is confirmed, which supports the possibility of spontaneous self-assembly of GO layers.

2. Additional AFM and SEM images of GO

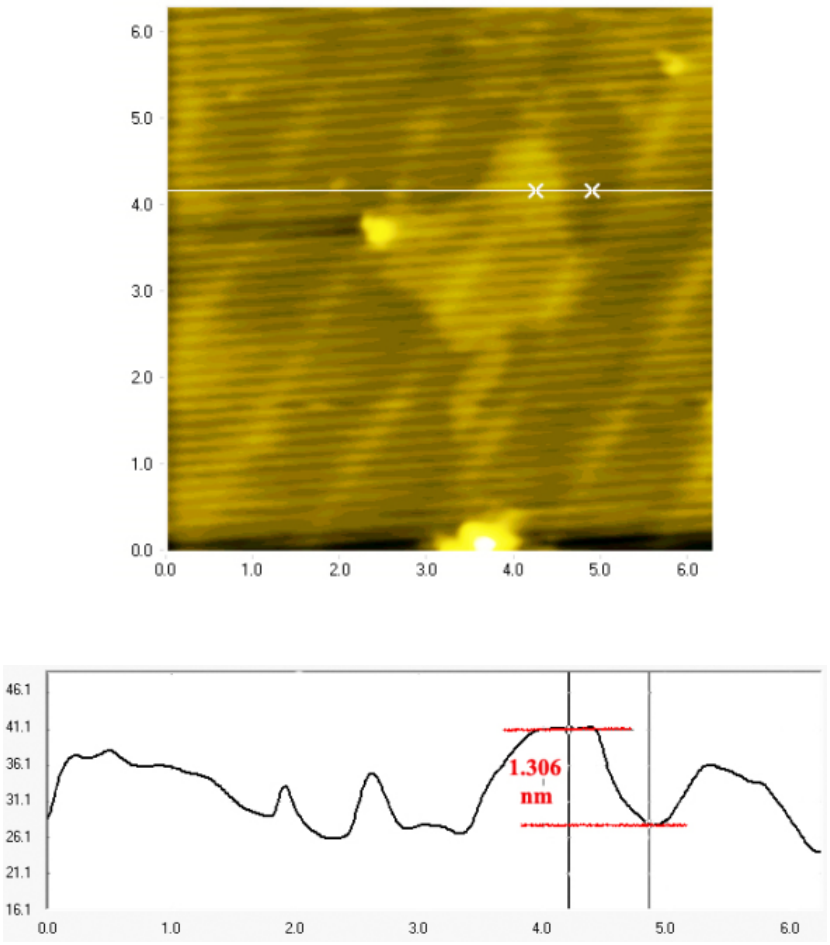


Fig. S2 AFM image of GO sheet and height profile;

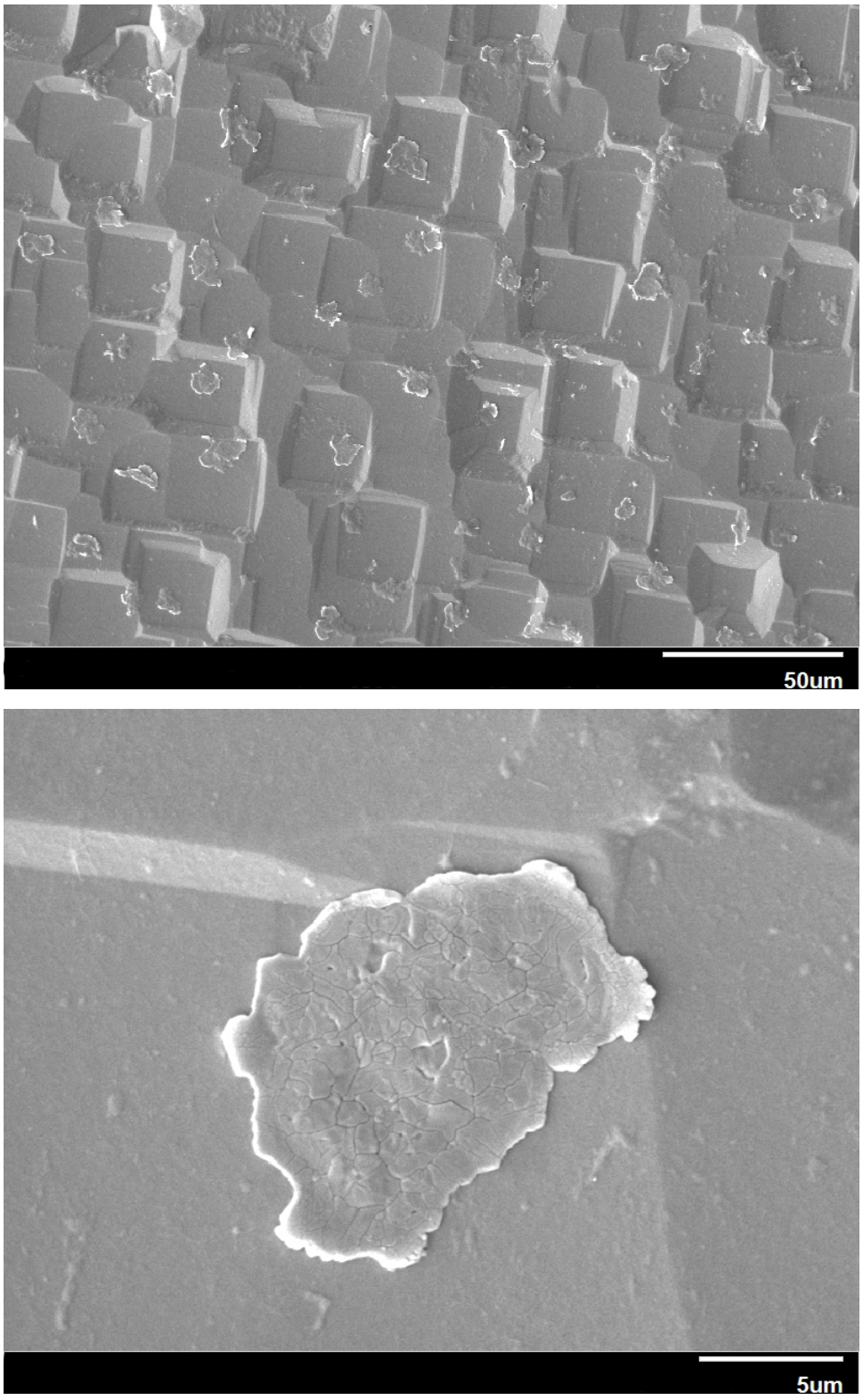


Fig. S3 SEM images of GO sheets coated on silicon wafer substrate; the average surface area of a sheet was found to be around 42.6 μm^2

3. Selection of oily solvent

Here, toluene was employed as the oily phase and the medium for dissolved polymeric chains. However, toluene can be substituted by other alternative solvents, since self-assembly of GO on oily solvents such as xylene is reported. In the case of fabricating composites based on Pickering emulsion method, some specific features are required for a suitable solvent, such as low viscosity to ensure facile formation of oil droplets, high immiscibility with water phase to enhance the possibility of self-assembly of particles (driving force of dispersion) and appropriate solubility of the corresponded polymer in it to prepare a considerable amount of masterbatch.

Table S2 Characteristics of some solvents

Solvent	Interfacial tension with water	Viscosity (cp)	Solubility parameter $(cal.cm^{-3})^{0.5}$
toluene	36.1	0.56	8.9
xylene	37.8	0.6	8.85
benzene	34.1	0.6	9.2
carbon tetrachloride	43.5	0.91	8.6
chloroform	31.6	0.54	9.3
cyclohexane	48.5	1	8.18
carbon disulfide	48	0.36	10

4. Effect of NR concentration on emulsion preparation

As explained, a NR concentration of 20 mg/ml in the toluene phase had been employed to prepare the emulsions. It can be explained that, to obtain satisfactory results there are lower and upper limitations for the concentration of NR. Higher concentrations are more desirable, as it directly determines the amount of dried masterbatch. However, increase in NR concentration can negatively affect the formation of oil droplets [S5]. Based on Fig. S4, fusion and sticking of the droplets are obvious, which is accompanied with non-spherical oil droplets. So, the concentration of polymer can be as high as it doesn't interfere with formation of oil droplets.

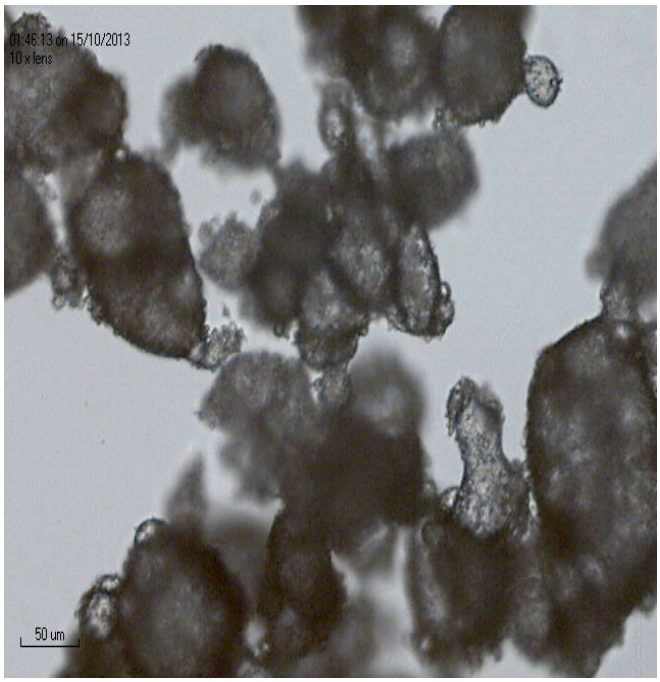
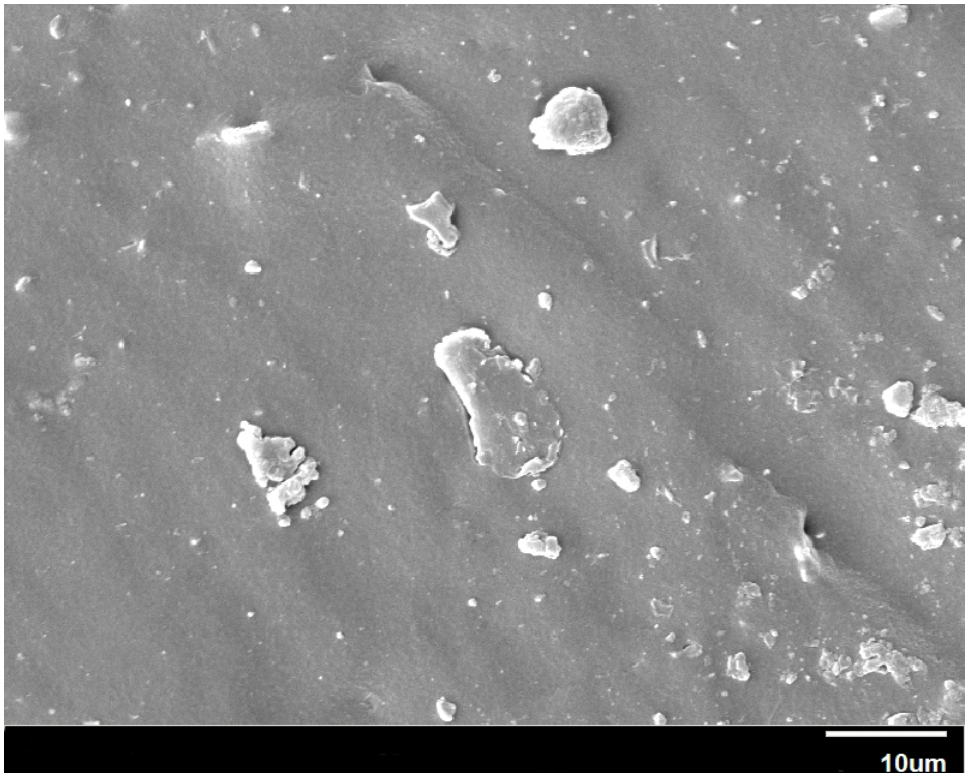


Fig. S4 Optical image of the oil–water system at 35mg/ml concentration of NR (after churning)

5. SEM images of final NR/rGO nanocomposite



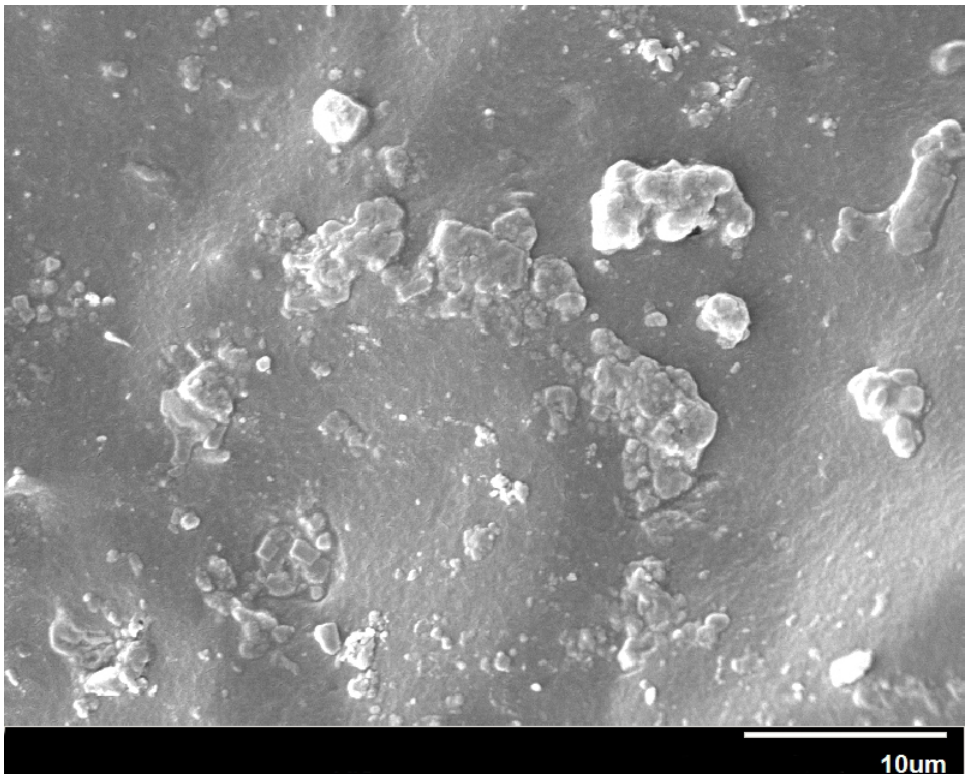


Fig S5 SEM images of the fabricated composite fractured surface (G1.6 sample)

6. DMTA analysis of the NR/rGO composites

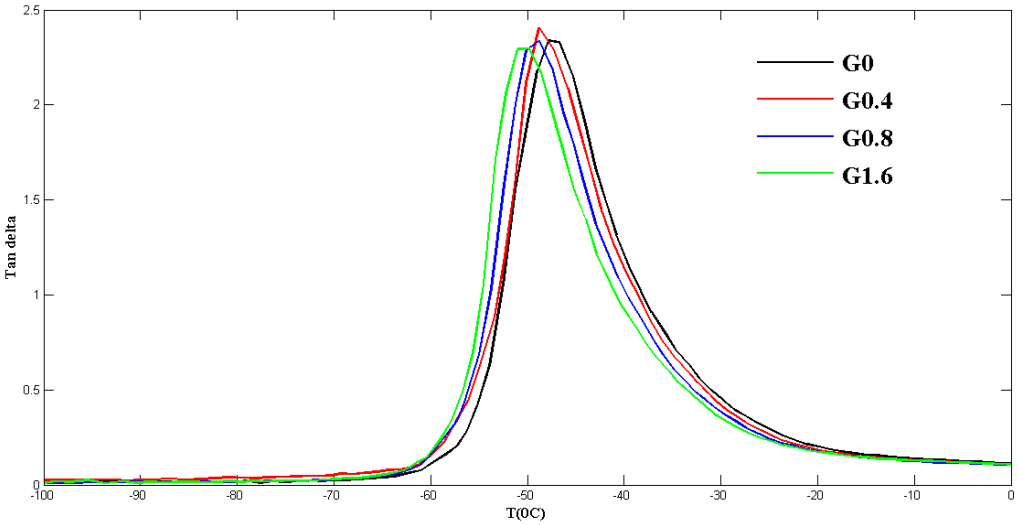


Fig. S6 Tanξ of the NR/rGO composites

References

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