

Correction to “Role of Solubility Parameters in Understanding the Steric Stabilization of Exfoliated Two-Dimensional Nanosheets by Adsorbed Polymers”

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In this paper, we predicted that the concentration, C , of nanoparticles stabilized by noncovalently attached polymer strands to scale as

$$C \propto \exp \left[- \left(\sqrt{N} \frac{2v_s}{z} \frac{(\delta_s - \delta_p)(\delta_G - \delta_s)}{kT} \right)^2 \right] \quad (1)$$

where N is the number of Kuhn monomers per polymer chain, v_s is the solvent molecular volume, z is the average number of nearest neighbors per solvent molecule, and δ_s , δ_G , and δ_p are the solvent, nanoparticle, and polymer Hildebrand solubility parameters respectively. This equation of course predicts that $\ln C \propto -N$. In the text describing Figure 4B of the paper, we erroneously claimed that the data supported this prediction. However, the data clearly suggests that $C \propto +N$.

When we realized our mistake, we wondered as to the cause of the disagreement between the model prediction and the experimental data. We quickly realized that one source of error related to the sample preparation. The composite dispersions in this part of the study were prepared by sonicating graphite in solutions of polystyrene (PS) in tetrahydrofuran (THF). For each data point the polystyrene molecular weight was varied. We realized that each polymer solution with different molecular weight must also have different viscosity.

This is important because the fluid–solid frictional forces that give rise to sonication-assisted exfoliation of nanomaterials, such as nanotubes or graphene, depend on the viscosity of the dispersing medium.^{1,2} Thus, sonication of a set of samples with increasing molecular weight and so increasing viscosity could result in a systemic error in the dispersed concentration as a function of molecular weight. This might explain the difference between the model prediction and the experimental data.

To counter this, we subsequently used reaggregated, previously exfoliated, graphene as a starting material. Such material is usually prepared by filtering a dispersion of exfoliated graphene in a solvent such as NMP through a porous membrane. After drying, the resultant powder can be redispersed with very little sonication,³ which we hope will minimize the effect of viscosity on dispersed graphene concentration. However, NMP can be very hard to remove completely. As residual NMP could compromise experiments such as these, e.g., by boosting the solubility, we decided to prepare restacked graphene by sonicating in water. To prepare this starting material, graphite (Sigma) was added to 80 mL of deionized water at a concentration of 10 mg/mL. This was sonicated overnight using the same sonic tip as in the paper (7 s on, 10 s off) at 25% of 600 W. The action of sonication tends to break up the graphite into graphene. However, because the solvent is water rather than a stabilizing solvent such as

NMP,^{4–6} the exfoliated graphene will not remain stably dispersed. Rather, the exfoliated graphene will weakly aggregate into restacked graphene. This restacked graphene and any unexfoliated graphite will eventually sediment out of the dispersion. This unstable dispersion was filtered through a porous membrane and placed in an oven at 60 °C for 2 days. This dried powder contains some unexfoliated graphite and reasonable quantities of reaggregated graphene. Preliminary tests show such reaggregated graphene to be very easily redispersed in appropriate liquids without excessive sonication,³ even when prepared with water. However, we note that care must be taken. The powder must be dried exceptionally well. The presence of residual water can destabilize subsequently prepared dispersions. In fact, we find that, to date, polymer stabilized dispersions prepared with water-treated graphene are generally slightly unstable over long times. However, in the present study, this disadvantage outweighs the advantages associated with the ease of dispersion.

This treated powder was added to solutions of polystyrene/THF for PS M_w of 35k, 45k, 100k, 280k, and 600k. The concentration of these samples was 0.3 mg of graphite/3 mg of PC/mL of THF. These samples were then sonicated for 1 h to homogenize and then centrifuged at 1500 rpm for 10 min. The supernatants were collected immediately and UV–vis spectroscopy was performed immediately afterward ($\alpha_{550 \text{ nm}} = 3620 \text{ mL mg}^{-1} \text{ m}^{-1}$) to determine the concentration. This is shown in Figure 1. These data show an initial increase in dispersed graphene concentration as the polymer molecular weight (as represented by N) is increased. This probably represents the

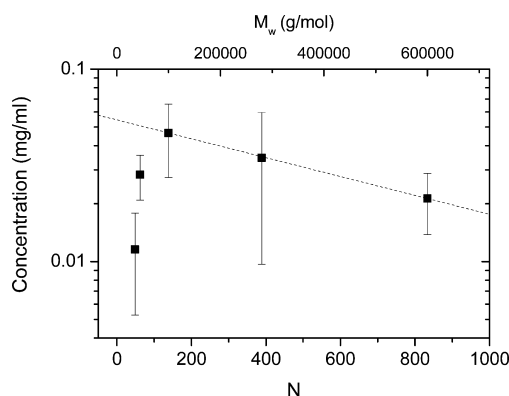


Figure 1. Dispersed concentration of graphene in PS/THF plotted as a function of the number of Kuhn monomers per PS chain, N . The polymer molecular weight is shown on the top axis.

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fact that a minimum molecular weight is required to achieve steric stabilization.

However, for $N \geq 138$, we see a clear exponential decay of concentration with N , as predicted by (1). By fitting this decay, we find $d \ln C/dN = -0.00113$. We can compare this with the value predicted by eq 1 using values of $\delta_G = 21.25 \text{ MPa}^{1/2}$, $v_s = 10 \times 10^{-5} \text{ m}^3/\text{mol}$, and $z = 6$. We find this to be $d \ln C/dN = -0.00032$. That these values are of the same order supports the model derived in our paper.

This work underlines the importance of sample preparation in the area of dispersion chemistry. We note that the effect of varying viscosity may very well have had an effect on the graphene concentrations as a function of polymer solubility parameter presented in Figure 3 of the paper this erratum seeks to correct. However, because we expect no major systematic variation of viscosity with polymer solubility (in the range explored), we expect such an effect to add scatter rather than systematic variations. In addition, we note that in some cases it may be prudent to use reaggregated graphene as a starting material for dispersion studies rather than graphite. However, in such cases it will be extremely important to maximize the removal of residual solvent.

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