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High stability of few layer graphene nanoplatelets in various solvents

X Xu^{1,*}, J Zhou¹ and G Lubineau^{1,*}

¹King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, COHMAS Laboratory, Thuwal 23955-6900, Saudi Arabia

* xuezhu.xu@kaust.edu.sa; gilles.lubineau@kaust.edu.sa

Abstract. Dispersion of few-layer graphene nanoplatelets (GNPs) in liquid media is a crucial step for various applications. Here, we highlight a simple, nondestructive method for preparing stable aqueous colloidal solutions with GNP powder quickly dispersed in 5 wt.% sodium–hypochlorite- (NaClO) and sodium-bromide- (NaBr) salted solvent by bath sonication. This method makes it possible to easily prepare a highly concentrated colloidal solution (1 mg·ml⁻¹) of GNPs that can easily be re-dispersed in water (treated GNPs). The aqueous suspension we prepared remained stable for longer than a few weeks. We made similar tests with various solvents and dispersibility appeared to decrease with decreasing polarity. High-concentration suspensions using our facile dispersion method could be of particular interest to the large community using graphene for a diversity of applications.

1. Introduction

The properties of dispersions are highly dependent upon the nature of the material and the dispersing media interface. All graphitic carbon nanostructures without chemical modification are highly hydrophobic. This hydrophobicity prevents them from forming stable dispersions in aqueous media. Efforts aiming to resolve this limitation are increasing because of the growing interest in applications that require water-based dispersion to promote ecologically friendly processes. Two major methods have been developed to disperse few-layer graphene powder in aqueous media: 1) chemical modification by introducing water-solubilizing functional groups and 2) surfactant wrapping of the graphene sheets to create hydrophilic surfaces. Chemical modification, which includes oxidation or covalent functionalization by introducing sp³-hybridized sites into the graphitic structure, leads to major alterations in the electronic properties of the structure.[1] Surfactants facilitate the quick dispersion of graphene nanoplatelets (GNPs) in water[2] without destroying the graphitic structure; however, an excessively thick layer of surfactant accumulates on the surface of the structure. Thus, the use of surfactants or other methods is not preferred when the purity of GNPs is critical.

2. Materials & methods

Few-layer graphene nanoplatelets (GNPs, N002-PDR), purchased from Angstrommaterials Materials Inc., were used as received. Average lateral dimensions of GNPs were 10 μm and had 95 % carbon content. 5 wt.% Aqueous sodium hypochlorite at 5 wt.% (NaClO) and sodium bromide (NaBr) powders were purchased from RICCA Chemical Company. Methanol, NMP, THF and polymer monomer (1,6-Hexanediol ethoxylate diacrylate) were purchased from Sigma-Aldrich Company. Water was purified by distillation in a Milli-Q (Advantage A10 model) system. UV-vis measurements



of colloidal solutions were recorded from 800 nm – 190 nm at 1-nm intervals using a Cary100 UV-Visible spectrophotometer.

3. Results and discussion

Here, we demonstrate a new method to prepare stable GNP colloidal solutions in aqueous media that does not destroy the sp^2 -hybridization of graphene and does not involve the formation of a thick layer of surfactant on the surface of the structure. As illustrated in Fig. 1, the method involves bath sonication of the GNP powder in a sodium-hypochlorite- (NaClO) and sodium-bromide- (NaBr) salted aqueous solution (NaClO:NaBr 1:1 molar ratio) for 60 min (Step 1). The dispersed GNP product is subsequently washed with water via centrifugation and dialysis for 15 d (Step 2). Once the washed GNPs (treated) are freeze-dried (Step 3), they can easily be re-dispersed in various solvents by mild bath sonication to form a stable GNP colloidal solution (Step 4).

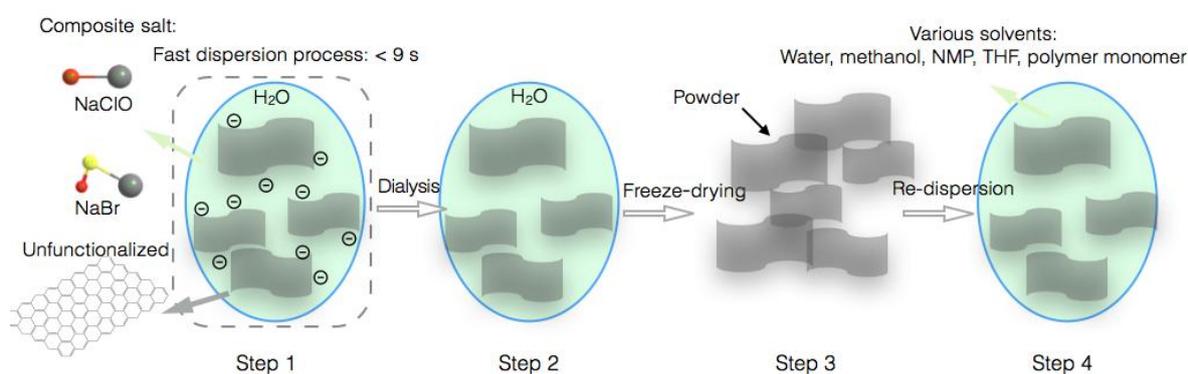


Figure 1. Pristine GNPs are dispersed in aqueous NaClO/NaBr solvent (step 1), purified by dialysis (step 2), freeze-dried (step 3), and re-dispersed in various solvents (step 4).

Figure 2a shows our re-dispersion of treated GNPs in pure water (step 4), which remained as a stable, homogenous colloidal solution ($1 \text{ mg}\cdot\text{ml}^{-1}$) for several weeks. In comparison, Figure 2b shows a pristine GNP (untreated) aqueous colloidal solution of the same concentration, which was not homogenous and features multiple GNP aggregates on the surface of the bottle and agglomerated GNPs. These photos were taken several weeks after preparation of the solutions. Dispersion of GNPs in water is incompatible due to strong van der Waals forces between particles. Although treatment of GNPs left some residual salts, reducing the purity of the solution to some degree, the adsorption of anions (Br^- , ClO^-) by GNPs likely generated electrostatic repulsion between graphitic sheets that eventually stabilized the final aqueous colloidal solution.[5]

During the pre-treatment step (step 1), pristine GNPs have yet to be dispersed correctly in the salted solvent and thus can be efficiently treated. We suspected that the effective dispersion of pristine GNPs in the salted solution could be explained by a close match in surface energies between the GNPs and the NaClO/NaBr-salted solvent. Knowing that graphite has a surface energy of $\sim 70\text{-}80 \text{ mJ}\cdot\text{m}^{-2}$, we measured the surface energy of our NaClO/NaBr-salted solution at $67.85 \text{ mJ}\cdot\text{m}^{-2}$, verifying our prediction. Similarly, N-Methyl-2-pyrrolidone (NMP) was found to be an effective solvent for easily dispersing GNP due to the close match in their surface energies,[3,4] (NMP has a surface energy of $69.50 \text{ mJ}\cdot\text{m}^{-2}$).[4]

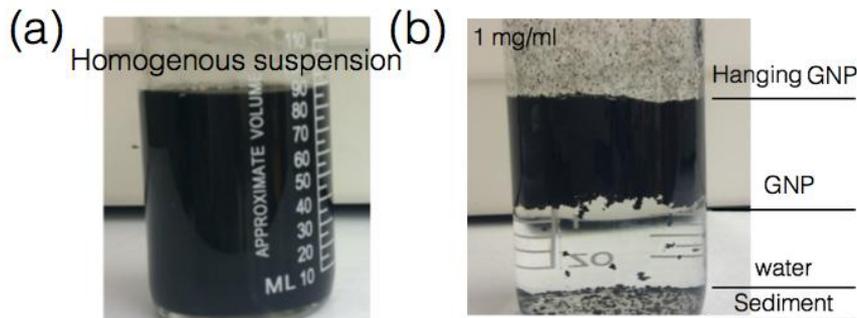


Figure 2. (a) 1-mg·ml⁻¹ treated GNP/water colloidal solution, (b) 1-mg·ml⁻¹ pristine GNP/water colloidal solution. Photos were taken one month after preparation of the solutions.

The treated GNP colloidal solution was freeze-dried to obtain GNP powder and then ~0.8 mg was re-dispersed in ~4.5 ml of water, methanol, NMP, Tetrahydrofuran (THF), or polymer monomer (oil) (0.18 mg·ml⁻¹ concentration of GNP powder) solvents to test their dispersibility (Figure 3a). Solvents had the following polarities: water (1.000) > methanol (0.762) > NMP (0.360) > (THF) (0.207) > polymer monomer (0.001). We found that the treated, freeze-dried GNP powder was extremely compatible with water, spontaneously dispersing within about 193 s. After two rounds of 5 s and one round of 120 s sonications, the powder had totally dispersed in the water with no phase separation overnight. Dispersibility appeared to decrease with decreasing polarity, as evidenced by the large aggregates visible with the naked eye in bottles containing THF and polymer monomer solvents (bottles 4 and 5, respectively). The Beer-Lambert law was used to calculate the molar absorption coefficients, α , of each colloidal solution to evaluate their dispersibility:

$$A = \alpha CD \quad (1)$$

where A is the absorbance, C is the concentration of the solute (g L⁻¹), and D is a 1-cm pathlength. The absorption coefficient α (L g⁻¹ m⁻¹) can be calculated based on the achieved experimental parameters A , C , and D . Figure 3b shows the absorbance of each colloidal solution as calculated by ultraviolet–visible (UV-vis) spectroscopy at 660 nm for 40 h (Figure 3c). Treated GNP dispersed best in NMP and water, and worst in THF and oil. Figure 3d shows the absorption coefficients of treated GNP powders in each solvent. The absorption coefficient of NMP was highest at 1649 L g⁻¹ m⁻¹, followed by water and methanol between 1200 – 1100 L g⁻¹ m⁻¹; the oil and THF had the lowest value at ~ 400 L g⁻¹ m⁻¹. Thus dispersibility of GNP follows NMP > water > methanol > monomer > THF. Over the 40 h stabilization time, the relationship between the absorbance and the calculated concentration of NMP (mg· ml⁻¹) was linear (Figure 3e).

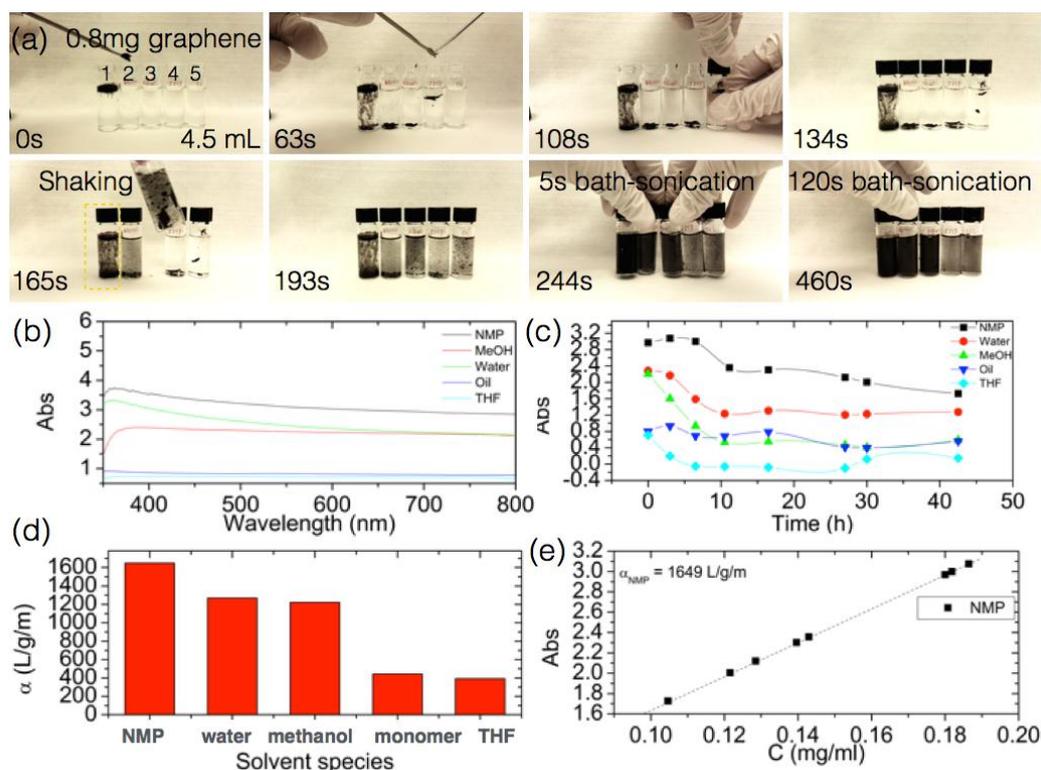


Figure 3. (a) Photos of dispersing treated, freeze-dried GNP in different liquid media. The numbering from 1-5 indicates that the liquid inside the glass bottles is pure water, NMP, methanol, monomer and THF, respectively. (b) UV-vis spectra of as-prepared GNP colloidal solutions as measured instantly. (c) Absorbance changes in UV-vis spectra at 660 nm for treated GNP in NMP, water, methanol, oil and THF suspensions. (d) Calculated absorption coefficients (α) for each solvent. (e) Linear relationship between absorbance and concentration of treated GNP in NMP stabilized for 40 h.

4. Summary

Here, we presented a simple, scalable method of producing a water-soluble few-layer graphene powder by first dispersing the GNPs in a NaClO/NaBr-salted solution. This approach is likely to be of interest to the large body of research/industrial communities.

Acknowledgment

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