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Xuezhu Xu,^{1,*} Jian Zhou,¹ Jacques Jestin,² Veronica Colombo,^{1,3} and Gilles Lubineau^{1,*}

¹King Abdullah University of Science and Technology (KAUST),

Physical Science and Engineering Division, COHMAS Laboratory, Thuwal 23955-6900, Saudi Arabia.

²Laboratoire Léon Brillouin (LLB), CEA Saclay, 91191 Gif-Sur-Yvette, France.

³University of Padua, Chemical and Materials Engineering, Padova, 35122, Italy.

*Correspondence to:

G.L. gilles.lubineau@kaust.edu.sa;

X.X. xuezhu.xu@kaust.edu.sa.

Graphical abstract

Preparation of Water-Soluble Graphene Nanoplatelets and Highly Conductive Films

Xuezhu Xu,^{1,*} Jian Zhou,¹ Jacques Jestin,² Veronica Colombo,^{1,3} and Gilles Lubineau^{1,*}

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

²Laboratoire Léon Brillouin (LLB), CEA Saclay, 91191 Gif-Sur-Yvette, France.

³University of Padua, Chemical and Materials Engineering, Padova, 35122, Italy.

Abstract

This paper tackles the challenge of preparation stable, highly concentrated aqueous graphene dispersions. Despite tremendous recent interest, there has been limited success in developing a method that ensures the total dispersion of non-oxidized, defect-free graphene nanosheets in water. This study successfully demonstrates that few-layer graphene nanoplatelets (GNPs) can form highly concentrated aqueous colloidal solutions after they have been pretreated in a low-concentration inorganic sodium-hypochlorite and sodium-bromide salted aqueous solvent. This method retains the graphitic structure as evidenced by nuclear magnetic resonance spectroscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy. Vacuum-filtrated freestanding films demonstrate an electrical conductivity as high as $3000 \text{ S}\cdot\text{m}^{-1}$. This dispersion technique is believed to be applicable not only for GNPs, but also for dispersing other types of graphitic materials, including fullerenes, single/double/multi-walled carbon nanotubes, graphene nanoribbons and etc.

Keywords

Graphene nanoplatelets, water-soluble, sodium hypochlorite, sodium bromide, colloids, surface and interaction, electrical double layer, DLVO theory, film, conductivity

1. Introduction

The properties of graphene make it an attractive candidate for use in various electrical applications.[1,2] Graphene has a carrier mobility as high as $200,000 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ [3] and a theoretical tensile modulus as high as 1 TPa.[4] It also has a high theoretical specific surface

*Corresponding authors. Tel.: +966 (1)2 808-2983; E-mail: gilles.lubineau@kaust.edu.sa (Gilles Lubineau); Email: xuezhu.xu@kaust.edu.sa (Xuezhu Xu).

area ($2,630 \text{ m}^2\cdot\text{g}^{-1}$),[5] a high thermal conductivity ($\sim 5000 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), and an ultrahigh optical transmittance ($\sim 97.7 \%$).[6] Graphene can be obtained by “peeling off” single defect-free graphene sheets from layered graphite crystals[7] or by growing single graphene sheets directly on metals.[8] Single-sheet production, however, is not viable for mass production, and more scalable routes to graphene production are urgently required. Few-layer graphene nanoplatelets (GNPs), previously called few-layer graphene,[9] graphene nanosheets,[10] and graphene powder that are produced by micromechanical cleavage, are important nanoscale building blocks for various applications. It is surface functionalization-free, typically in the form of few layers (< 3), with an average in-plane dimension of around $10 \mu\text{m}$. Many applications require GNPs to be dispersed in a fluid medium. At this point, the dispersion becomes very critical.[11]

Optimizing dispersion should be done in a non-aggressive and non-destructive way that does not compromise graphene’s sp^2 structure, which affords it its high carrier mobility and ultimately its high electrical conductivity.[3] A few examples of graphene dispersion in liquid media have been reported, and the efficiency of each dispersing fluid can be explained by different mechanisms, e.g., matching in surface free energy, acid protonation, π - π stacking, or Coulomb repulsion. For instance, direct mechanical exfoliation yielding soluble graphene is made possible by the similar surface free energies of graphene and the dispersing liquid medium N-methyl-2-pyrrolidone (NMP),[9,12] and acid protonation by chlorosulphonic acid (HSO_3Cl) has been used to generate repulsive forces between layers, successfully dispersing high concentrations of graphene (up to $2 \text{ mg}\cdot\text{ml}^{-1}$).[13] Moieties and polymers, such as pyrene derivative 1-pyrenebutyrate,[14] dyes,[15] 7,7,8,8-tetracyanoquinodimethane,[16] porphyrin,[17] flavin mononucleotide (FMN),[18–21] and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS),[22,23] have been used to facilitate the dispersion of graphene via π - π stacking. Water alone has proven not to be suitable as a solvent for GNPs because its high surface energy limits the dispersion of graphitic materials, but success has been made by adding a detergent or surfactant, such as bolaamphiphile or sodium dodecyl-benzene sulfonate.[24,25]

However, techniques that use highly acidic/organic solvents can have explosive characteristics, be difficult to remove, or introduce components with low conductivity (e.g., PSS in the PEDOT/PSS) into the product. In addition, many of the techniques described above have low scalability, resulting in products with a low concentration of graphene. We report here a very simple and efficient procedure to disperse graphene by means of regular

ultrasonic treatment of GNP powder in water aided by commercially available inorganic salts: sodium hypochlorite and sodium bromide.

2. Experimental section

Few-layered graphene powder (N002-PDR, Angstrommaterials Inc) was used throughout this work. NaClO and NaBr powders were used as the bleaching components (RICCA Chemical Company). NaClO (5 wt.% in water) was used as received. Water used for experimentation was purified by distillation in a Milli-Q (Advantage A10 model) system.

To prepare WSGNPs in aqueous NaClO/NaBr salted colloidal solutions, graphene powder and bleach/water were mixed by a regular bath ultrasonic cleaner (Model: 8510E-MTH, Branson Company). The sonication process worked at the specification of 250 W and 44 KHz at room temperature. Samples were placed randomly in any location within the sonication bath. Sonication time ranged between 10 and 160 min. An Eppendorf 5810 centrifuge was then used to centrifuge the WSGNP/salts/water at 5000 rpm for 5 min to remove the NaClO/NaBr/water mixture. Corning polypropylene (PP) centrifuge tubes (50 mL, outer diameter: 29.1 mm) were used for the centrifugation. Afterward, the resultant WSGNP slurry and ~100 mL of pure water were loaded into a Spectra/Por1 dialysis membrane (64-mm tubing diameter and 6-8-kD pore width) to remove residual chemicals. These dialysis bags were immersed in 5000 mL of deionized water, which was changed every 12 h for 10 d. The concentration of the purified WSGNP/water colloidal solution was adjusted to its original concentration ($1 \text{ mg}\cdot\text{mL}^{-1}$). Vacuum filtration to obtain free-standing WSGNP films was performed using a 47-mm diameter vacuum filter holder assembly (Wheaton Company), which was coupled with a 47-mm diameter, polycarbonate (PC) filter with 0.05- μm pores (Whatman Company). The filtration took ~ 3 h, leaving a wet membrane supported by the PC filter. This “wet-cake” was covered by another piece of PC membrane and was laminated between several layers of tissue papers and then placed between two metal cells (2.4 kg for each, pressure on the film: 0.36 kPa) to ensure that the resultant WSGNP film was compact. The drying process was conducted in a vacuum oven at 100 °C for 12 h.

Both pristine GNP and WSGNP were characterized by thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was scanned by a NETZSCH TG, 208 F1 instrument from 27 to 880 °C at 20 K/min under nitrogen atmosphere protection. DSC was performed on a NETZSCH DSC 204 F1 Phoenix instrument, which was operated from 25 to 400 °C at 25 K/min under nitrogen atmosphere. Figure S1 shows the thermogravimetric

(TG) plot of our GNP material together with that of WSGNP after post-treatment. The figure shows a mass loss ($\sim 10\%$) below $100\text{ }^{\circ}\text{C}$, which we attributed to the removal of adsorbed water and NaClO (boiling point at $101\text{ }^{\circ}\text{C}$). It also shows a slower, steady mass loss ($\sim 12\%$) over the whole temperature range to $377.7\text{ }^{\circ}\text{C}$, which is likely caused by the removal of oxygen functionalities.[20] The final weight fraction of WSGNP is 8.3% , which is believed to be from the attached inorganic salts (NaClO, NaBr) on the WSGNP that were introduced during dispersion. The DSC scan of WSGNP is shown in Figure S2. Compared with the pristine GNP, WSGNP has an additional peak at $\sim 100\text{ }^{\circ}\text{C}$. This peak is very likely introduced by volatile substances, possibly NaClO, given that the DSC of graphite or graphene oxide does not have this peak in the literature.[26] **The expected endothermic peak associated with water removal is hidden by another exothermic process that is not identified at this point.** Conclusively, both TGA and DSC demonstrate how WSGNP differs from graphene oxide, which has a 65% weight loss at $230\text{ }^{\circ}\text{C}$.[27].

TEM images were taken using a Tecnai Twin microscope (FEI). TEM samples were prepared from GNP/water and WSGNP/water solutions at $1\text{ mg}\cdot\text{ml}^{-1}$ for 60 min. SAED pattern was obtained from TEM images. SANS for the dispersed samples were measured at rest at the Laboratoire Léon Brillouin (LLB Saclay) on the spectrometer PAXY, by varying the wavelength λ and the sample-to-detector distance D . The three configurations defined by $I = 6\text{ }^{\circ}$ at a sample-to-detector distance of 1.2 m, $I = 6\text{ }^{\circ}$ at a sample-to-detector distance of 6.7m and $I = 15\text{ }^{\circ}$ at a sample-to-detector distance of 6.7 m enable to cover a total q -range from $3\cdot 10^{-3}\text{ }^{\circ}\text{Å}^{-1}$ to $0.4\text{ }^{\circ}\text{Å}^{-1}$. Samples were measured in calibrated quartz cells of 1mm pathway in H_2O as solvent. The 2D patterns were reduced to 1D spectra $I(q)$ versus q after a radial averaging around the center of the scattered beam. Standard corrections by sample thickness, neutron beam transmission, and empty cell signal subtraction, detector efficiency, electronic background and subtraction of incoherent scattering were applied to get the scattered intensities on an absolute scale (cm^{-1}). Data reduction was done using a home-made software "Pasinet". NMR spectroscopy on dried graphene powders were measured at 18 kHz with samples encapsulated in a 3.2-mm rotor with an Ultrashield 400 WB plus (Bruker Corporation). Raman measurements were conducted on a LabRAM ARAMIS using a 473-nm laser source. Zeta potentials of WSGNP dispersions were measured by a zeta-sizer (Malvern Company). The FT-IR spectroscopy measurements were performed on a Nicolet iS10 (Thermoscientific Inc). Dried powders from WSGNP dispersions were produced using a Christ Alpha 1-2 LD plus freeze dryer (Martin Christ Company). We conducted the XPS

studies in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Ka X-ray source ($h\nu = 1486.6$ eV) operating at 150 W with a multi-channel plate with a delay line detector under a vacuum of $\sim 10^{-9}$ mbar. All spectra were recorded using an aperture slot of $300\ \mu\text{m} \times 700\ \mu\text{m}$. Survey spectra were collected using a pass energy of 160 eV and a step size of 1 eV. A pass energy of 20 eV and a step size of 0.1 eV were used for the high-resolution spectra. Samples were mounted in the floating mode to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the sp^2 hybridized (C=C) carbon with the C 1s peak from the carbon nanomaterials set at 284.5 eV. Ion chromatography was measured with an ICS-3000 purchased from Dionex Corporation, and measurements were performed with a 4 x 250-mm analytical tube (IonPac AS15, for anions) from the same company. Ultraviolet-visible (UV-vis) spectroscopy measurements on WSGNP powders in various solvents were recorded from 800 nm to 190 nm at 1-nm intervals by a Cary100 ConC UV-vis spectrophotometer (Agilent Technologies). Sheet resistances were measured using a CMT-SR2000N four-probe system (probe space 1 mm, Materials Development Corporation). Measurements were taken at 10 different locations along each sample and the average value was reported. To ensure accuracy, surface tensions were averaged based on 20 separate measurements using the dynamic surface-tension-ring method at $20.4\ ^\circ\text{C}$ with a Kruss K100 tensiometer (Kruss Company).

3. Results and discussion

First, the GNP powder is dispersed in a specially designed salted solution. Our initial treatment medium comprised water with two salts. We started with 5 wt.% (0.67 M) sodium hypochlorite (NaClO) to which we added sodium bromide (NaBr) at a 1:1 molar ratio with respect to NaClO [22] as illustrated in Fig. 1. The salted solution contained 1.34 M salts (0.67 M of NaClO and 0.67 M of NaBr). After the appropriate dispersal time, all samples were centrifuged at 5000 rpm for 5 min to remove all dispersion medium. Then, we added new water into the obtained treated-GNP slurry, and loaded it into a dialysis bag, which was dialyzed in pure water for 10 d to remove residual ionic chemicals. We name this final product, which can be easily later dispersed in water, water-soluble GNP (WSGNP).

Fig. 1. The dispersion protocol used in this study. Yellow solution indicates 5 wt.% (1:1 molar ratio) aqueous NaClO) and NaBr salted solution used to disperse different concentrations of GNPs followed by extraction of WSGNPs.

We successfully dispersed concentrations of up to $5 \text{ mg}\cdot\text{ml}^{-1}$ of GNP powder, as demonstrated in Fig. 2 and Movie S1. As a control sample, the same amount of GNP powder was added to 300 mL of pure water. After 10 min (600 s), the GNP powder had completely dispersed in the salted solvent to yield a $5 \text{ mg}\cdot\text{ml}^{-1}$ concentration of colloidal GNP solution. On the contrary, GNPs remained floating on the surface of pure water.

To quantify the improvement in dispersability in aqueous medium after pretreatment, the dispersion status of GNP and WSGNP in water was examined by transmission electron microscopy (TEM) and small-angle neutron scattering (SANS). We initially observed a typical selected-area electron diffraction (SAED) pattern for graphitic crystals, implying that GNPs are crystalline (Fig. 3a). We measured the average size of GNP aggregates to be ca. $12.95 \pm 7.57 \text{ }\mu\text{m}$, as shown in the histogram in Fig. 3a. In comparison, flakes from the WSGNP/water solution were measured to have an average size of $3.86 \pm 1.73 \text{ }\mu\text{m}$ (Fig. 3d). Because the sonication time was the same for both solutions, the smaller size of the WSGNP flakes was likely reflective of the smaller amount of WSGNP that agglomerated due to less interaction between the flakes in the dispersing medium.

Fig. 2. Dispersion process of GNP powders in the salted solvent with a $5 \text{ mg}\cdot\text{ml}^{-1}$ concentration of GNPs.

SANS on GNP/water and WSGNP/water colloidal solutions were collected over a q range of 3×10^{-3} to $0.4 \text{ \AA}^{-1}$. The SANS intensity is proportional to a power law regime according to $I(q) = \varphi V \Delta\rho^2 q^{-D_f}$, where φ and V are the volume fraction and the volume of the objects, $\Delta\rho^2$ is the contrast term relative to the solvent (here water), $q = (4\pi \sin \theta)/\lambda$ is the magnitude of the scattering wave vector and D_f is the fractal exponent of the scattering objects.[28] A fractal exponent of fully dispersed plate-like objects is $D \approx 2$. [29]. Fig. 3b shows that SANS patterns from a GNP/water solution gives an average D value of 2.14, while the patterns of the WSGNP/water solution in Fig. 3e gives an average D value of 2.04. For both cases, the fractal exponent is consistent with the dispersion of 2 dimensional platelets. The absence of plateau at low q indicates that the sizes of the object are larger than the maximum size accessible within the probe q range, typically 200 nm. This is confirmed with the TEM pictures where the size sorting shows micro-size particles. Considering that the particle concentration and the contrast term are similar for both dispersions, one can argue that the larger level of scattering intensity observed for the GNP/water samples is due to the presence of larger volume objects. From the equation of the scattering intensity, the cubic root of the low q intensities between both series - $[250/26]^{1/3} \sim 2.12$ for the 60 min sample – gives directly the ratio between the size of both populations. This value is consistent with the TEM analysis that gives a ratio closer to $2.5 = 7.5/3$ for the maximum of the distribution of the respective sizes.

We modeled the scattering curve (Fig. 3c GNP and Fig. 3f WSGNP for 60 min) using a simple form factor of a 2D planar platelet defined by only two parameters: the diameter of the planar objects D and the layer thickness L . The scattering length density for the graphene has been calculated considering a density of $2.2 \text{ g}\cdot\text{cm}^{-3}$. [30] $\rho_C = 7.33 \times 10^{10} \text{ cm}^{-2}$ and thus gives a contrast term in normal water ($\rho_{\text{water}} = -0.56 \times 10^{10} \text{ cm}^{-2}$) equal to $\Delta\rho = 7.89 \times 10^{10} \text{ cm}^{-2}$. For fitting, the diameters of the planar objects have been fixed to TEM values, respectively equal to $D = 7 \text{ }\mu\text{m}$ for GNP and $D = 3 \text{ }\mu\text{m}$ for WSGNP. As a result, we fitted only the volume fraction of scattered objects and the layer thickness and we found for both samples $\varphi = 0.0225 \text{ }\%$ and $L = 0.5 \text{ nm}$ which are consistent values with sample preparation and monoatomic layer. The main feature of this modeling is that one can observe a very good agreement for the WSGNP sample suggesting a well-defined and well-dispersed organization of the planar objects while the fitting agreement is less for the GNP sample especially at low q suggesting aggregation of the planar objects. From the extrapolation of the intensity when q tends to zero, one can estimated an aggregation number, namely the number of planar object per cluster, which is directly proportional to the ratio between the fitting value and the experimental one: $N_{\text{agg}} = I_{0 \text{ exp}}/I_{0 \text{ calc}} \approx 300/100 = 3$. This aggregation observed for the GNP is consistent with the average slope of 2.14 (Fig. 3b) slightly larger than 2.

Fig. 3. (a) TEM image of GNP aggregates in pure water; inset on the left side shows an SAED image on GNP powder; inset on the right shows histogram of projected GNP flake sizes based on measuring 200 flakes. (b) Variation of the SANS scattering in water as

function of time for GNP. (c) Modeling of the SANS using a form factor of planar object (full black line) for GNP at 60 min. (d) TEM image of the WSGNP/water colloidal solution; inset shows histogram of projected flake sizes. (e) Variation of the SANS scattering in water as function of time for WSGNP. (f) Modeling of the SANS using a form factor of planar object (full black line) for WSGNP at 60 min.

Solid-state ^{13}C NMR and XPS measurements were performed on dried WSGNP powders. The high-resolution spectra of pristine GNP and WSGNP were taken from samples after purification by dialysis. Fig. 4a shows an NMR resonance centered at a chemical shift of 124 ppm, which corresponds to unoxidized sp^2 carbon ($\text{C}=\text{C}$).^[31] Graphene oxide typically presents a disrupted sp^2 -bonded graphitic carbon network.^[11] Because we observed only one peak (at 124 ppm) in our spectrum, we believe that our WSGNPs have a graphitic structure.^[32] The change in the sp^2 carbon structure with respect to dispersion time was further verified by XPS (Fig. 4b). Typically, researchers observe a primary C 1s peak associated with a series of characteristic peaks for C-C (284.8 eV), C-O (286.2 eV), $\text{C}=\text{O}$ (287.8 eV), and $\text{C}(\text{O})\text{O}$ (289.0 eV), identifying the oxidation level of graphitic materials.^[10,33]^[10] Because there was no pronounced peak at 286 eV, we conclude that our WSGNP is either unoxidized or oxidized in very minor proportions with respect to graphene oxide (GO). The O 1s XPS spectra of pristine GNP and WSGNP are shown in Figs. S4 and S5. The peak location of residual oxygen in the pristine GNP is at 532.4 eV, which we assigned to the surface-adsorbed water and other oxygen species.^[34] This peak shifted to 531.2 eV, suggesting that the oxygen types were different. We believe that the new type of oxygen came from NaClO or that there was small amount of oxidation in the graphitic structure. The minor peak we observed at ca. 288.5 eV was similar to that observed in COOH -grafted graphene.^[35] Peaks measured for our WSGNP powders were similar to those measured for the original GNP powder, suggesting that the inorganic salts had a benign effect on the graphitic sp^2 structure.^[10,12] Fig. 4c plots carbon contents (from XPS measurements) against dispersion time, which shows that carbon content decreased from 100 % (pure graphene) to 90 % ($\text{C}:\text{O} = 9:1$). The amount of oxygen induced into WSGNPs was small compared to that induced into GO ($\text{C}:\text{O} = 2.1:1 - 2.9:1$)^[36] derived from graphite via Hummer's, Brodie's, and Staudenmaier's methods (using HNO_3 , KClO_3 , H_2SO_4 , NaNO_3 , KMnO_4 , H_2O_2 , HCl).^[11,37–40] Note that the negligible residual Na^+ content (<1 wt.%) in

dried WSGNPs (Fig. 4d) is expected to have little to no influence on applications that demand good dispersion.

Raman spectra in Fig. 4e, present two primary peaks at ~ 1362 and ~ 1587 cm^{-1} , which correspond to D and G bands, respectively.[41] Two additional peaks at 2717 and 2935 cm^{-1} were also observed and associated with the 2D structure (exfoliated single sheet) (Fig. 4f). Fig. 4f-g shows that there is no obvious change in position, full width at half maximum (FWHM) or intensity of Raman peaks on WSGNPs with varying dispersion times. The peak shape and relative broad FWHM of D and G bands in the Raman data presented in this work are consistent with some degree of basal plane defects. The second-order region of the spectrum also shows large FWHM values, consistent with a defective basal plane; however, not to the extent that was observed in GO.[42] Nevertheless, the intensity ratio of D and G bands that qualifies the degree of disorder of various WSGNP powders shows our sample has a ratio similar to that of original GNP, suggesting the salts did not increase the degree of disorder in WSGNPs (Fig. 4h).[41] From the spectrum, the material was clearly defective, but there were no changes to the defect over treatment time. The 2 D/G intensity ratios were GNP = 0.2578; WSGNP (10 min) = 0.2655; (30 min) = 0.1597; (60 min) = 0.2031; (90 min) = 0.1450; (160 min) = 0.2308, which showed that these were many-layered materials. Surface charged fully dried WSGNP films were characterized by Fourier transform infrared (FT-IR) measurements (Fig. 4i). GNPs had a characteristic peak at ~ 2100 cm^{-1} representing its graphitic structure. We are unable to identify the origin for the peak at 2100 cm^{-1} since our FT-IR spectrum was largely different from that of highly oxidized graphene materials.[7][10] The only thing we can say is that this peak is not associated with C-OH, C-H, C=O, which is often common for traditional oxidized graphitic materials. This peak originally came with the pristine GNP. We therefore assume that it would from the impurities or other defects. Absence of functional groups in purified WSGNPs after 100 °C drying implies that sodium hypochlorite and sodium bromide salts have a little covalent effect on the WSGNPs.[43–45] Based on all previous results, we can conclude that the proposed treatment does not significantly interfere with the initial graphitic structure of the GNPs.

Fig. 4. (a) Solid-state ^{13}C NMR spectra of WSGNP powder (dispersion time of 30 min and 160 min). (b) C 1s XPS spectra of pristine GNP and WSGNP. (c) Carbon and sodium content vs. dispersion time in WSGNPs. (d) Raman spectra between $800 - 2000 \text{ cm}^{-1}$ of WSGNP powders. (e) Raman spectra between $2200 - 3500 \text{ cm}^{-1}$ of WSGNP powders. (f) Dependence of Raman peak location of WSGNP at dispersion time; (g) Evolution of FWHM of Raman peaks for WSGNPs against dispersion time. (h) Raman D:G intensity ratio of WSGNP powders. (i) FT-IR spectrum on a piece of WSGNP film.

To better characterize the salted solvent used for treating the GNPs during the first step, we have here a closer look at its ionic content. In a NaClO solution, ionic species (Na^+ , OH^- , and ClO^-) are present when the system is in equilibrium. (Reac. 1):

Chloride ions (Cl^-), hypochlorite (ClO^-), and bromide ions (Br^-) were detected in NaClO/NaBr -salted solution through ion chromatography measurements. We can then

conclude that addition of sodium bromide into sodium hypochlorite generates no new ionic species (Fig. 5).

Fig. 5 Ion chromatography of salts and their compounded mixture at 100 parts per billion (ppb) in water.

In this section, we explain why the GNP powder blended into low-concentration NaClO- and NaBr-salted aqueous solvent so quickly, and how the WSGNP colloidal solutions continued to maintain their high colloidal stability in water. Dispersion of GNP powder was the result of a mixing process that mainly depended on the change in enthalpy of the mixture (ΔH_{mix}) per unit volume, thickness of the flake (T_{flake}), the surface energy (E_G) of graphene and of the solvent ($E_{solvent}$), and graphene's volume fraction (ϕ). We can achieve an estimate with the following relationship:[12,46]

$$\Delta H_{mix} \approx \frac{2}{T_{flake}} (\sqrt{E_G} - \sqrt{E_{solvent}})^2 \phi \quad (\text{eq. 1})$$

Good dispersion requires a minimal energy cost (i.e., $\Delta H_{mix} \approx 0$), which suggests that the surface energy of graphene and solvent should be similar. Because nanotube/graphite has been shown to have a typical surface energy of $\sim 70\text{-}80 \text{ mJ}\cdot\text{m}^{-2}$, [12] the surface energy of the dispersing medium should be in this range. The surface tension (γ) of the solvent can be measured and converted into surface energy ($E_{solvent}$) using eq. 2:[12]

$$E_{solvent} = \gamma + TS_{solvent} \quad (\text{eq. 2})$$

where T is the temperature ($T = 293.55$ K) and $S_{solvent}$ is solvent's surface entropy (ca. $0.1 \text{ mJ}\cdot\text{K}^{-1}\cdot\text{m}^{-2}$). Surface tensions for water, NaBr/water, NaClO/water, NaBr/NaClO/water were experimentally determined as follows: $\gamma_{water} = 70.37 \pm 0.01$, $\gamma_{NaBr} = 58.74 \pm 0.10$, $\gamma_{NaClO} = 50.71 \pm 0.31$ and $\gamma_{NaClO/NaBr} = 38.50 \pm 0.09 \text{ mN}\cdot\text{m}^{-1}$. These values were then converted to the following respective surface energies ($E_{solvent}$): 99.73, 88.10, 80.06, and 67.85 $\text{mN}\cdot\text{m}^{-1}$, respectively. These surface energies were compared with those of several solvents (NMP, 1,3-dimethyl-2-imidazolidinone, benzyl benzoate, γ -Butyrolactone (GBL) and dimethyl sulfoxide)[12] previously identified to be suitable for graphene dispersions (Fig. 6a). We found that the parameters [γ , E] of NaClO/NaBr [38.5, 67.9 $\text{mJ}\cdot\text{m}^{-2}$] were the closest to those of NMP [40.1, 69.5 $\text{mJ}\cdot\text{m}^{-2}$], which is considered to be an excellent solvent for graphene. Note that the values of surface tension presented here were based on 20 measurements to ensure their accuracy. Obviously, the addition of NaBr salt into NaClO considerably lowers surface tension.

WSGNPs suspended in water was further characterized by zeta-potential (ζ) measurements.[47] Our zeta-potential value (Fig. 6b) was in a range of $|-9.9| \text{ mV}$ to $|-36.2| \text{ mV}$ within 160 min of dispersion time. Based on the negative zeta-potential values, we conclude that all of the ions absorbed on GNPs must be anions carrying “ $-$ ” charges (e.g., Br^- , OH^- , and ClO^-) in our salted solution. This argument is supported by experimental evidence that anions are usually selectively enriched in interfacial layers.[48][49] In particular, behavior of absorbance of ClO^- onto graphitic surfaces is thought to be very similar to the behavior of other ionic species dissociated from acids (PO_2^- , SO_3Cl^-).[13,50] This non-covalent absorbance on graphitic surfaces of anions generates high Columbic repulsion between particles, resulting in a good dispersion effect for graphitic materials. On top of this anion layer, two types of cations, hydronium (H_3O^+ , or called H^+) and sodium (Na^+), are considered to be on top of the negatively charged ionic layer, neutralizing the system (Fig. 6c). The H_3O^+ cations come from the ion dissociation of water:

This type of ionic structure has an intense cancelling effect on the breaking of hydrogen bonds in water (the main reason for high surface tension).[51] This is believed to reduce surface tension of the NaClO/NaBr/water solution.

Fig. 6. (a) Surface energy vs. surface tension of the solvent; values marked with an asterisk were obtained from the literature.[12,46] (b) Zeta-potential of WSGNP colloidal solutions vs. dispersion time. (c) Schematic structure of water/WSGNP interface. (d) Total potential of graphene sheets vs. sheet-sheet distance for WSGNP colloidal solution by DLVO and van der Waals theories. (e) Photos of a freestanding film. (f) Electrical conductivity and sheet resistance (inset) of various WSGNP films with different dispersion times.

The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory[47] is helpful for explaining WSGNP's homogenous status in water and why WSGNPs were easily re-suspended in pure water after we discarded all of the NaClO/NaBr/water solvent.

This theory considers that total potential energy of the particle-particle system is a balance between electrostatic repulsive potential (V_{DLVO}) and van der Waals attractive potential V_{vdW} between sheets (eq. 3-4):

$$V \approx 2V_{DLVO} + V_{vdW} \quad (\text{eq. 3})$$

$$V \approx 4A\epsilon_r\epsilon_0\kappa\zeta^2e^{-\kappa D} - \frac{A\pi\rho^2C}{2D^4} \quad (\text{eq. 4})$$

where A is the area of a single graphene sheet, $\varepsilon_r \varepsilon_0$ is the solvent's permittivity ($\varepsilon_r = 80$, $\varepsilon_0 = 8.85 \times 10^{-12} \text{ C}\cdot\text{V}^{-1}\cdot\text{m}^{-1}$), and the Debye screening length κ^{-1} was calculated to be 14.7 nm according to eq. 5:

$$\kappa^{-1} = \left(\frac{\varepsilon K_B T}{e^2 N_A 2C} \right)^{\frac{1}{2}} \quad (\text{eq. 5})$$

where $\varepsilon = \varepsilon_r \varepsilon_0$; K_B is the Boltzmann constant; T is the measurement temperature at 300 K; e is the elementary charge; N_A is Avogadro's number; C is the concentration of sodium ions at $4.349 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, which was calculated by taking the sodium content in WSGNP ($\sim 1 \text{ wt.}\%$), the concentration of the WSGNP colloidal solution ($1 \text{ mg}\cdot\text{ml}^{-1}$), and the molar mass of sodium ($22.9898 \text{ g}\cdot\text{mol}^{-1}$); ζ is the zeta potential (we used: -36.9 mV for WSGNP, $\sim 0 \text{ mV}$ for GNP); and D is the distance between sheets. For the surface energy density ($\rho^2 C$) of WSGNP, we used the value for pure graphene that is approximate $6.69 \times 10^{-40} \text{ J}\cdot\text{m}^2$ for calculation. (3) Total potential energy was converted from $\text{J}\cdot\text{m}^{-2}$ to milielectron volt (meV).

Using the parameters, we plotted the interaction energy per surface area V/A ($\text{meV}\cdot\text{nm}^2$) as a function of sheet separation in Fig. 6d; plots of the DLVO and van der Waals components are also included. An upward peak located at D of ca. 20 nm was observed in the curve for $2V_{DLVO} + V_{vdW}$, representing an energy barrier that is believed to result in the stabilization of WSGNP colloids in water.

To demonstrate WSGNP's potential in electrical electronics, dried and flexible freestanding WSGNP films were prepared via vacuum filtration of WSGNP colloidal solutions (Fig. 6e). As plotted in Fig. 6f, electrical conductivity (σ) of obtained films was as high as $2.2 - 3.0 \times 10^3 \text{ S}\cdot\text{m}^{-1}$, and the sheet resistance (R_s) was also low for several $\Omega\cdot\text{sq}^{-1}$ (bulk film thickness ca. 0.039 mm) (Fig. 6f inset). Although the electrical conductivity was not as impressive as graphite-based films, the electrical conductivity was still high compared to previous reports; for example, Si et al. (2008) reported prepared water-soluble graphene without oxygen-containing functional groups with a σ value of $1.25 \times 10^3 \text{ S}\cdot\text{m}^{-1}$. [52] Graphite-exfoliated and ethanol-dissolved graphene film has been measured to have a σ value of $1.13 \times 10^3 \text{ S}\cdot\text{m}^{-1}$. [53] and graphene film bonded non-covalently with water-soluble pyrene ($\text{C}_{16}\text{H}_{10}$) has been measured to have a σ value of $2 \times 10^2 \text{ S}\cdot\text{m}^{-1}$. [14] Preparation of water-soluble graphene films by our salt method is competitive compared with other reported methods. Other solvents, e.g., N-methyl-2-pyrrolidone - NMP, N, N-Dimethylform - DMF, cyclohexanone, o-

dichlorobenzene - DCB, N-Cyclohexyl-2-pyrrolidone - CHP, and dichloroethane (DCE), possess high boiling points (NMP ~200 °C, cyclohexanone ~155 °C, CHP ~154 °C),[54–57] as well as safety concerns leading to challenges in printing and processing. This leads to disadvantages for many integration strategies, especially printing, coating, compositing and exfoliation for which a low boiling point, such as with alcohols and water, is desirable.[58]

4. Conclusion

We reported a new dispersion approach for quickly generating water-soluble GNP colloidal solutions while preserving the graphitic sp^2 structure. Concentrations as high as 5 mg·ml⁻¹ were achieved and maintained for up to several weeks. In addition, the vacuum-filtrated films obtained from WSGNP colloidal solutions demonstrated excellent electrical conductivity. WSGNPs were obtained by pre-treating GNPs in a salted solvent. The salted solvent presented here has the potential for broad interest to the large community using GNPs and other similar types of graphitic materials. We believe our solvation system will also work for high-purity fullerenes, carbon nanotubes (single walled, multi-walled), carbon spheres, graphene nanoribbons, and a variety of other nanomaterials in the carbon family. The only limitation of this dispersion protocol that we foresee is that a small amount of residual ions may not be suitable for some specific applications. Otherwise, this facile, environmentally friendly and potentially scalable preparation for high-concentration graphene colloidal solutions has excellent potential for many applications.

5. ASSOCIATED CONTENT

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7. COMPETING FINANCIAL INTERESTS

The author(s) declare no competing financial interests.

8. SUPPORTING INFORMATION

The Supporting Information, including Movie S1, Figures S1 and S2 description is available on the website.

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