

Surfactant-free exfoliation of graphite in aqueous solutions

Karen B. Ricardo, Anne Sendeki, and Haitao Liu*

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, U.S.A

1. Materials and Instruments

Lithium chloride, potassium chloride, potassium hydroxide, potassium carbonate, sodium chloride, and sodium carbonate were purchased from Sigma-Aldrich. Sodium hydroxide was purchased from Fisher Scientific. Water was purified by an Easypure water purification system (Thermo Scientific).

The following graphite samples were used in the study: graphite powder from Sigma-Aldrich (SKU # 332461, batch # MKBB2274), graphenium flakes from NGS Naturgraphit, graphite fine powder from Riedel-de Haën (lot # 62910) and graphite powder of different grades (4827, TC307, 4052) from Asbury Graphite Mill Inc. (lot # 20669, 20966, 23184, respectively).

The HOPG substrate used for the AFM imaging was purchased from SPI supplies. The holey carbon mesh grid for the TEM analysis was purchased from Ted Pella Inc. The graphene film prepared for Raman measurements and the determination of the concentration of graphene was made by filtering graphene dispersion through an alumina membrane (Cat. No. 6809-7013) with a pore size of 0.1 μm (Whatman).

For optical characterization, all UV-Vis spectra were taken using a GENESYS 10S UV-Vis with quartz cuvettes. Unless stated otherwise, the absorbance value was measured

at 500 nm. All of the AFM measurements were taken with a Digital Instruments Nanoscope IIIA (Veeco) in tapping mode using silicon tips with a resonance frequency of 320 kHz. Samples for the AFM were prepared using HOPG (SPI-2 grade) as a substrate. Several microliters of the graphene suspension were drop casted and spin-coated at a velocity of 3,000 rpm and gently dried with compressed air. Zeta potential measurements were carried out on a Malvern Zetasizer Nano system with an irradiation from a 633 nm He-Ne laser.

2. Methods

2.1 Typical sample preparation

To prepare a typical sample, 20.0 mL of the NaOH solution was added to a glass vial. Approximately 100 mg of graphite flakes (Sigma-Aldrich) were added to the solution. The solution was then sonicated for the desired time (typically 30 min) using a VWR Ultrasonic Cleaner. After that, centrifugation was performed at a velocity of 2,000 rpm using an Eppendorf Centrifuge 5804. After the centrifugation, the vial was removed and typically 10.0 mL of the upper solution was transferred to a clean vial. Care was taken to transfer only the supernatant and not the large graphite flakes at the bottom of the vial. The resulting suspension was then characterized as described.

2.2 Centrifugation speed effect

To study the effect of the centrifugation speed the sample was prepared as described above with a NaOH solution of pH = 11.0. The sample was sonicated for 30 minutes. The sample was then centrifuged at speeds ranging from 1,000 to 6,000 rpm for 60 min. After centrifugation, 10.0 mL of the resulting suspension was removed using a pipette and stored for characterization.

Loyta et al. showed that centrifugation speed affects the yield of solution exfoliation of graphene.^{1,2} To check if the same effect is observed in the surfactant-free exfoliation method, a similar experiment was performed. The centrifugation velocity was varied from 1,000 to 6,000 rpm. The absorbance value at 500 nm of the dispersion as a function of the centrifugation speed is showed on **Figure S1**.

The general trend demonstrates that at above 2,000 rpm the absorbance value stays almost constant. This result is similar to the graph presented by Loyta et al.¹ The centrifugation speed used in the rest of the experiments was 2,000 rpm, which results in a gray, transparent solution.

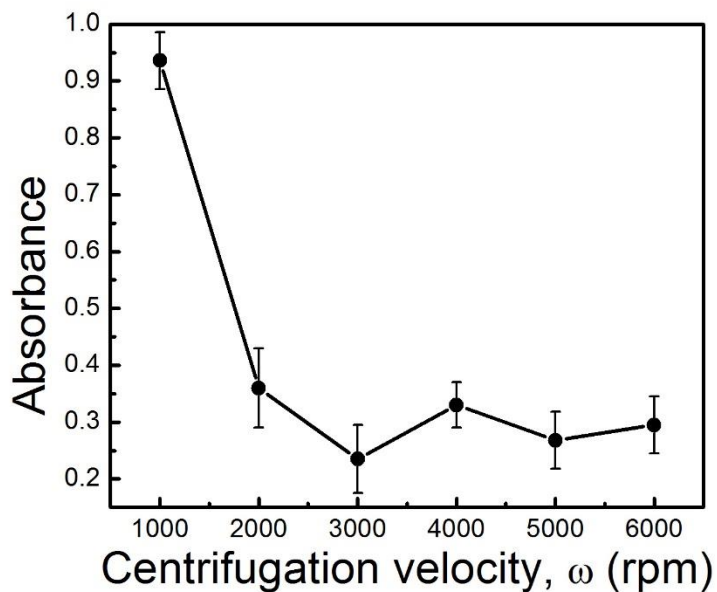


Figure S1. Absorbance value at 500 nm of the exfoliated graphene in NaOH solution as a function of the centrifugation velocity.

2.3 Exfoliation time effect

To study the effect of the sonication time 100 mg of graphite flakes were added to 20.0 mL of a NaOH solution (pH = 11.0). The times for the exfoliation step varied from 5

to 60 minutes. The dispersion was centrifuged at a velocity of 2,000 rpm for 60 min. After centrifugation, 10.0 mL of the resulting suspension was removed using a pipette and stored for characterization.

Among the experiments realized by Li et al. in the exfoliation of graphite in organic solvents, one of them focused on how the exfoliation time affects the absorbance value of the solution with graphene.³ To compare the results between the surfactant-dependent, the exfoliation using organic solvents and surfactant-free graphene dispersions, a similar experiment was carried out. The sonication time varied from 5 to 60 min. Figure S2 shows the absorbance value at 500 nm of the dispersion as a function of the sonication time. After 30 min, the absorbance value at 500 nm does not change in a significant way.

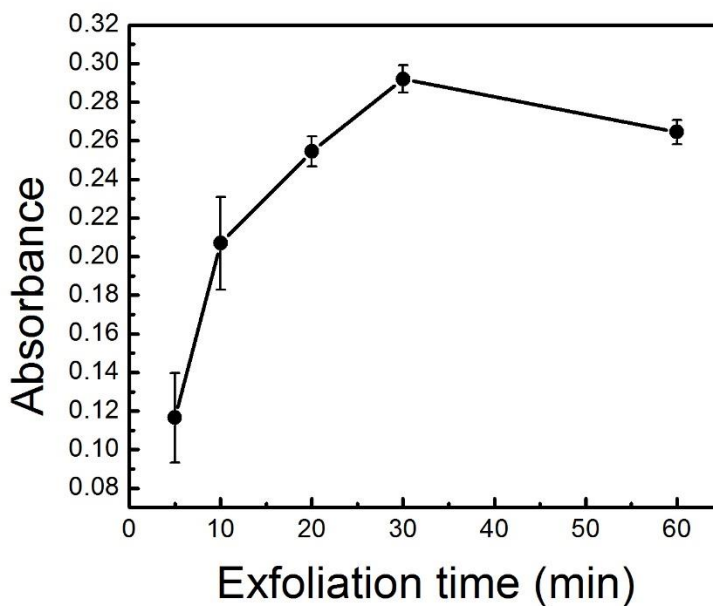


Figure S2. Absorbance value at 500 nm of the exfoliated graphene in NaOH solution (pH = 11) as a function of the exfoliation time. After 30 minutes, the absorbance values are very similar, indicating that there is no need to exfoliate for longer times.

2.4 TEM imaging.

The TEM samples were prepared by diluting a few milliliters of the graphene dispersion onto holey carbon mesh grids. The images were taken using an FEI Morgagni 268 D. Additional TEM images are shown in **Figure S3**.

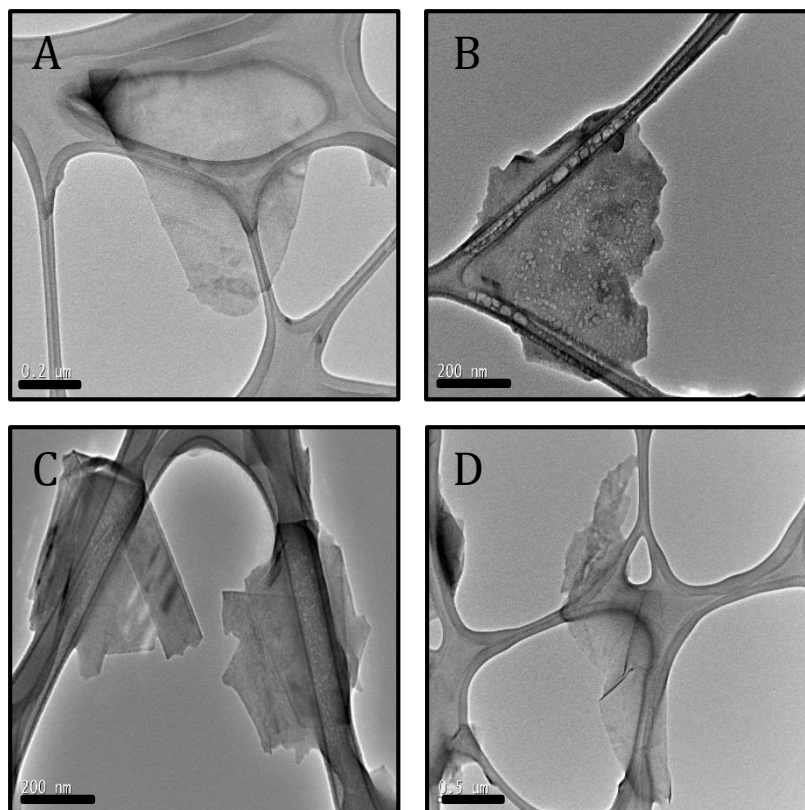


Figure S3. Additional TEM images of the exfoliated graphene flakes.

2.5 pH dependence

To study the effect of the concentration of hydroxide in the solution the samples were prepared with NaOH solution of the following pH values: 7.0, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, and 12. In order to obtain an accurate pH value, all of the solutions prepared were verified with a pH meter. After that, 100 mg of graphite flakes (Sigma-Aldrich) were

added to 20.0 mL of the solution. The sample was then sonicated for 30 minutes and centrifuged for 60 min at a velocity of 2,000 rpm. After centrifugation, 10.0 mL of the resulting suspension was extracted and used for UV-Vis and zeta potential measurements.

2.6 Zeta potential

In order to obtain the zeta potential value, 1.50 mL of the suspended graphene in the NaOH solution was added to a cuvette. All measurements were conducted at 20 °C. The measurements were taken 4 times and the average was reported.

2.7 Determination of the graphene concentration

After a typical sample was prepared, 2.50 mL of the solution was deposited on an alumina filter with a pore size of 100 μm . The solution was filtered 50 μL at a time. After the film was dried for 24 hours the precise mass was obtained.

Another approach used to determine the concentration of graphene in solution was using the Beer-Lambert Law. Using Loyta's absorption coefficient for exfoliated graphene with surfactants at 660 nm of $\alpha = 1390 \text{ mL mg}^{-1} \text{ m}^{-1}$ and a sample prepared using NaOH pH = 11, the concentration was calculated.

2.8 Raman spectroscopy

The film described above was used for the Raman spectrum. The Raman spectrum was measured using home build Raman microscope. A 532 nm laser with a spot size of $\sim 1\mu\text{m}$ through a 40x lens was used. Each Raman spectra was taken with 60 seconds integration time with a low incident laser power of 1.2-1.4 mW to minimize laser induced damage.

2.9 Recycling of graphite

Approximately 100 mg of graphite flakes were added to 20.0 mL of NaOH (pH 11.0) in a glass vial. The solution was then exfoliated for 30 minutes and centrifuged at a velocity of 2,000 rpm for 60 min. After the centrifugation, 17 mL of the solution was transferred to a clean vial and the vial containing the sediment was refilled with more NaOH solution (pH = 11) to obtain a total volume of 20 mL. This solution was then sonicated and centrifuged again. This procedure was repeated 24 times. The dispersion extracted was stored and used for UV-Vis measurements (**Figure S4**).

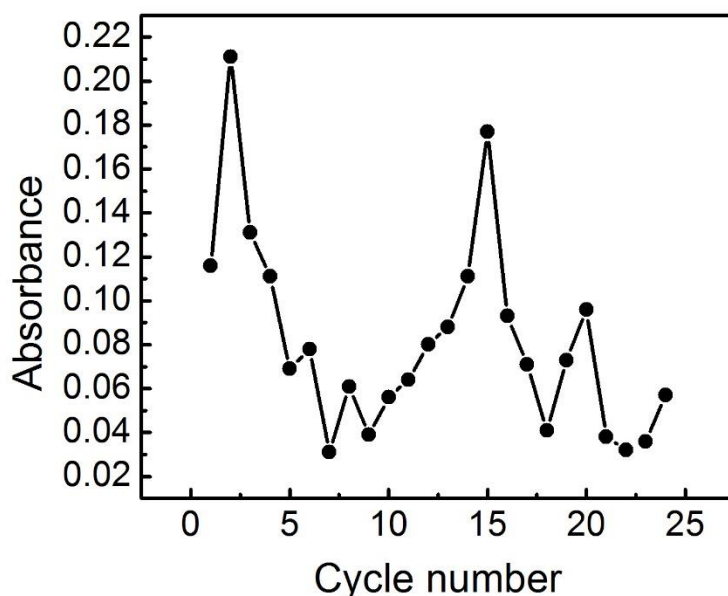


Figure S4. Absorbance value at 500 nm of the exfoliated graphene in NaOH as a function of the cycle number.

2.10 Effect of ions in solution

In a typical experiment, 100 mg of graphite flakes were added to 20.00 mL of a 1.0 mM solution of the desired salt. The salts used to prepare the solutions were NaCl, LiCl, KCl, KOH, K_2CO_3 , and Na_2CO_3 . The samples were exfoliated for 30 minutes and centrifuged at 2,000 rpm for 60 min. After centrifugation, 10.0 mL of the resulting

suspension was extracted and used for UV-Vis measurements.

Li et al. demonstrate that the addition of electrolytes solution lead to immediate aggregation of the suspended graphene sheets.¹ These results served as a basis at analyze the effect of using solutions with different salts to exfoliate the graphene. Neutral (NaCl, LiCl, KCl) and basic (KOH, K₂CO₃, Na₂CO₃) electrolytes were used. The objective of this experiment was to confirm that basic solutions are essential to obtain a high concentration of graphene sheets in a stable, colloidal suspension. **Figure S5** shows the absorbance at 500 nm for the dispersions as a function of the type of salt in the solution.

The graphene exfoliated in neutral salts presents low absorbance values while the ones exfoliated in basic salts presented a high absorbance value. These results confirm that basic salts are needed to obtain a high concentration of graphene flakes.

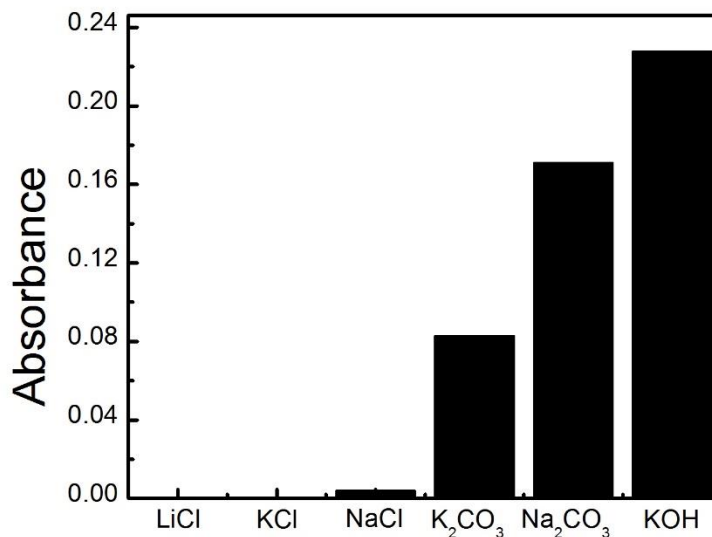


Figure S5. Absorbance value at 500 nm of the exfoliated graphene in different salt solutions. Neutral salts present a low absorbance value, showing that a solution with basic ions is needed to have a high concentration of graphene.

2.11 Exfoliation of different sources of graphite

Six different types of graphite were used in the following experiments. NaOH solution (20 mL, pH = 11) was added to each graphite sample. The samples were exfoliated for 30 min and centrifuged at a velocity of 2,000 rpm for 60 min. After centrifugation, 10.0 mL of the resulting suspension was extracted and used for UV-Vis measurements. Figure S6 shows the absorbance values at 500 nm of the different sources of graphite.

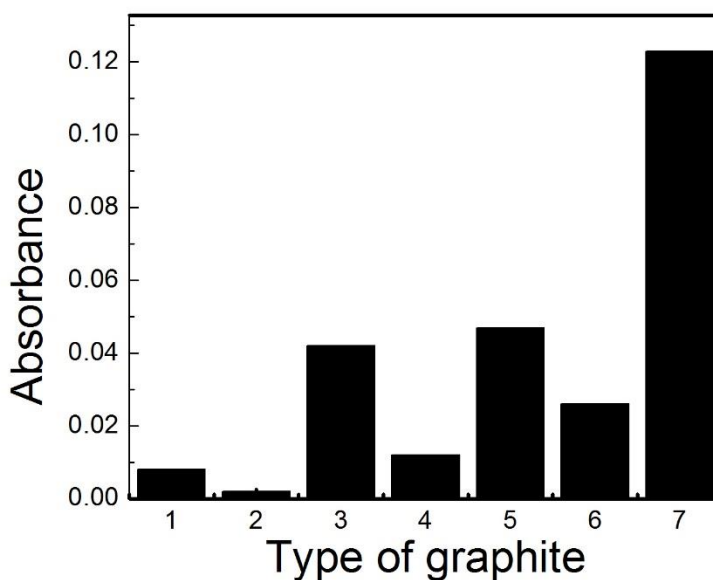


Figure S6. Histogram of the absorbance values at 500 nm of different sources of graphite. 1. HOPG, 2. Graphenium flakes (NGS Naturgraphit), 3. Graphite fine powder from Riedel-de Haën, 4. Asburg Graphite Mills (AGM) light powder [TC307], 5. AGM dense powder [4052], 6. AGM light powder [4827], 7. Sigma-Aldrich graphite flakes used in all other reactions.

2.12 Annealing of graphite

Graphite powder were weighted and placed on a copper foil. This sample was then annealed on a CVD furnace (Linderg Blue M, Thermo Scientific) under an argon flow of

250 sccm at various temperatures, ranging from 50 °C to 600 °C for 1 h. After the sample was cooled down, the graphite was exfoliated as described above.

Figure S7 shows the absorbance value at 500 nm of the graphene dispersion as a function of the temperature of the annealing. A sudden decrease in the absorbance value was observed at 400 °C.

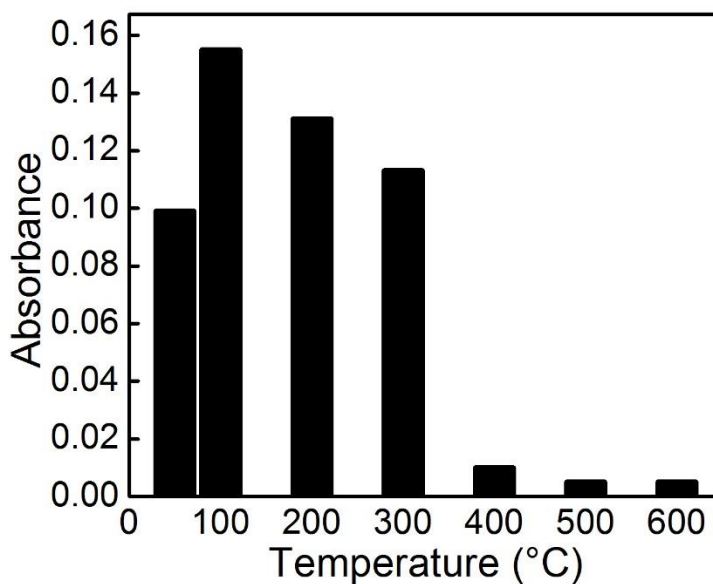


Figure S7. Histogram of the absorbance value at 500 nm of the exfoliated graphene after the graphite was annealed at different temperatures.

2.13 Mass loss of annealing.

Graphite powder (100 mg) were precisely weighted and placed on a copper foil. This sample was folded and annealed at 600 °C for 1 h. After the sample was cooled down, the mass was measured again. For the calculation of the average mass loss, the experiment was repeated 3 times and the average mass loss was found to be 0.06 mg.

REFERENCES

1. Li, D.; Muller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G., Processable aqueous dispersions of graphene nanosheets. *Nat. Nanotechnol.* **2008**, *3* (2), 101-105.
2. Lotya, M.; Hernandez, Y.; King, P. J.; Smith, R. J.; Nicolosi, V.; Karlsson, L. S.; Blighe, F. M.; De, S.; Wang, Z. M.; McGovern, I. T.; Duesberg, G. S.; Coleman, J. N., Liquid Phase Production of Graphene by Exfoliation of Graphite in Surfactant/Water Solutions. *J. Am. Chem. Soc.* **2009**, *131* (10), 3611-3620.