

pH-Responsive Optical Modulation of Chemically Reduced Graphene through Noncovalent Interaction with Poly(acrylic acid)

Jung Yup Lee and Insik In*

Department of Polymer Science and Engineering, Chungju National University, Chungju 380-702, Korea

(Received October 28, 2011; CL-111055; E-mail: in1@cju.ac.kr)

pH-responsive chemically reduced graphene/poly(acrylic acid) (PAA) assembly is simply formulated through noncovalent interaction. Graphene/PAA assembly shows optical absorbance change depending on pH of the solution. Structural rearrangement of graphene/PAA assembly might contribute this optical modulation at different pH through either “hydrophobic interaction dominating” mode in strongly acidic medium or “charge repulsion dominating” mode in strongly basic medium.

Solubilization of chemically reduced graphene has been extensively attempted through various covalent or noncovalent chemistry since the pioneering work done by Stankovich et al. in 2007 in order to utilize outstanding electrical, thermal, and mechanical properties of graphene through wet chemistry.¹ While significant efforts have been concentrated on the covalent chemistry initially,² various noncovalent chemistries have been rivaling covalent chemistries owing to their simplicity and versatility. Either π - π interaction,³ micellar encapsulation,⁴ or hydrophobic interaction⁵ has been uncovered to be effective for producing stable dispersion of chemically reduced graphene in solvent media in the presence of polymers or small molecules which can interact on graphene plates through corresponding interaction. Exploiting benefits of noncovalent chemistry prompts us to develop certain stimulus-responsive graphene/polymer assemblies. Recently, thermo-responsive graphene/poly(*N*-isopropylacrylamide) (PNIPAM) assembly which shows lower critical solution temperature (LCST) has been designed through hydrophobic interaction in our group.⁶ Prepared graphene/PNIPAM assembly showed solubility switching and absorbance change depending on temperature variation.

Herein, we simply demonstrate pH-responsive graphene/poly(acrylic acid) (PAA) assembly through noncovalent chemistry. PAA has been utilized to enhance direct exfoliation of natural graphite into individual graphene sheets in *N*-methyl-2-pyrrolidone (NMP),⁷ but pH-responsive optical modulation of chemically reduced graphene has not been reported by using PAA through noncovalent interaction. While initial formulation of soluble graphene/PAA assembly (1:100 or 1:50 of graphene oxide (GO) to PAA mass ratio) was not successful, optimization of feeding ratio (here, 1:10) surprisingly produced clear and stable dispersion of chemically reduced graphene/PAA assembly. Probably, “side-by-face” interaction of PAA chains on graphene plates in 1:10 feeding ratio might be more effective to produce solubilized chemically reduced graphene than “end-by-face” interaction in either 1:50 or 1:100 feeding ratio.⁶ In detail, 5 mg of PAA in 5 mL of deionized water was mixed with freshly prepared GO solution (0.5 mg in 5 mL of deionized water with sonication for 30 min). Then, a few drops of hydrazine monohydrate were added to the above bright brown GO/PAA mixture. Reduction of this GO/PAA mixture solution at 80 °C

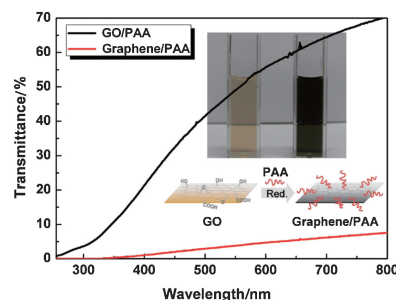


Figure 1. UV-vis spectra of solutions of GO and graphene/PAA (1:10) assembly (the insets are schematic illustration for the preparation of graphene/PAA assembly).

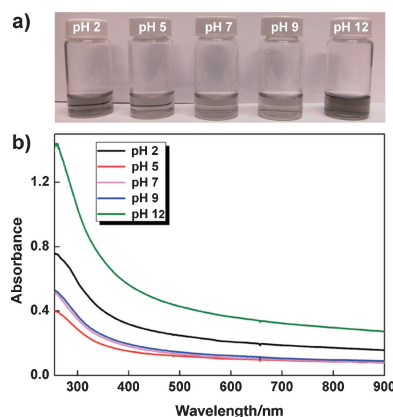


Figure 2. a) Photos and b) UV-vis spectra of solution of graphene/PAA (1:10) assembly at different pH.

for 24 h resulted in dark black-colored chemically reduced graphene oxide/PAA dispersion (Figure 1). Much decreased transmittance of graphene/PAA assembly in the whole wavelength range and stability of prepared graphene/PAA dispersion well support the effective assembly formation between chemically reduced graphene and PAA.

To elucidate the detailed interaction parameter between graphene plates and PAA chains, we modulated pH of graphene/PAA assembly solution between 2 and 12. The concentrations of both graphene and PAA were set to be constant in all cases. Graphene/PAA solution was stable without forming any graphite-like precipitation in every pH (Figure 2a). Next, ultraviolet-visible (UV-vis) spectroscopy of prepared graphene/PAA solution was monitored at different pH (Figure 2b). Interestingly, there was significant change of optical absorbance depending on pH of graphene/PAA solution. The highest absorbance was observed at pH 12. Decreasing of pH to 5 induced decrease of optical absorbance, and then further decreasing of pH to 2

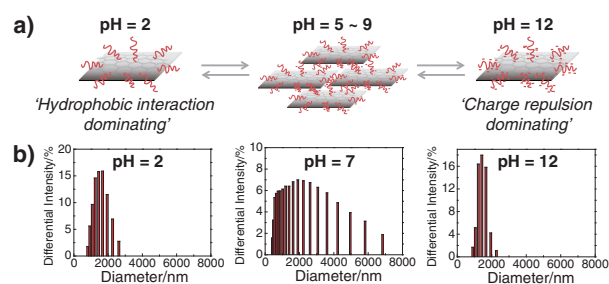


Figure 3. a) Schematic illustration of modulation of interaction parameter of graphene/PAA assembly and b) DLS spectra of graphene/PAA assembly solution (1:10) at different pH.

showed again increase of optical absorbance. This unusual pH-dependent optical modulation of graphene/polymer assembly has been reported recently in graphene/polyacrylamide (PAM) assembly, but the modulation behavior is dissimilar.⁸ The lowest transmittance (the highest absorbance) was observed at pH 7 in the case of graphene/PAM assembly while graphene/PAA assembly showed the highest absorbance at pH 12 together with relatively high absorbance at pH 2. In comparison, both GO and GO/PAA solutions did not show significant change of optical absorbance at different pH. This pH-dependent modulation of optical absorbance in graphene/PAA assembly system might strongly correlate with the modulation of interaction parameter between graphene plates and PAA chains (Figure 3a).

In the first, PAA is the most hydrophobic at pH 2 due to the complete protonation of $-\text{COOH}$ groups. Therefore, hydrophobic interaction between graphene plates and PAA chains is maximized, and relatively well-dispersed graphene/PAA assembly is obtained, resulting in increase of absorbance. It is thought that graphene/PAA assembly switches to “hydrophobic interaction dominating” mode in strongly acidic conditions. In the second, at pH 5–9, hydrophobic interaction of PAA is weakened due to partial deprotonation of $-\text{COOH}$ groups, resulting in partially aggregated graphene/PAA assemblies. Dynamic light scattering (DLS) spectra supports certain aggregation of assembled structures at pH 7, which shows much increased particle size with broader distribution around 7000–9000 nm while graphene/PAA assembly at pH 2 shows much smaller particle size and narrower distribution around 700–2500 nm (Figure 3b). In this aggregated state, it seems that the presence of outer graphene plates might hamper optical absorption of inner graphene plates. In the third, further increasing of pH up to 12 might enhance the reduction of hydrophobic interaction due to complete deprotonation of $-\text{COOH}$ groups but the presence of several negative charges on PAA chains can hinder the aggregation of graphene plates through charge repulsion. Therefore, it is believed that graphene/PAA assembly switches to “charge repulsion dominating” mode in strongly basic conditions. In addition, above optical modulation of graphene/PAA assembly is fully reversible in the variation of pH.

This modulation of interaction parameter between graphene plates and PAA chains is also supported by atomic force microscopy (AFM) analysis of graphene/PAA assembly.⁹ At pH 2, most graphene plates showed plate thickness of around 3.2 nm, which confirms that exfoliation of graphene plates is well maintained through “hydrophobic interaction dominating”

mode in the presence of interacting PAA chains. At pH 12, plate thickness decrease to 1.8 nm. Probably, the presence of several charges on PAA chains in this highly basic condition might induce stretching of PAA chains on graphene plates, resulting in decreased thickness of assembled structure. At pH 7, aggregated structure of thickness more than 11 nm was observed. This result correlates with the formation of bigger aggregation in DLS analysis. Several graphene/PAA assembled structures might stack due to the absence of either strong hydrophobic interaction or charge repulsion.

Filtration of the above graphene/PAA solution produces “graphene only” film without any PAA chains. Interaction between graphene plates and PAA chains might be weakened and finally broken during filtration process. The resulting graphene film was not soluble again in water at any pH. Dispersive Raman spectroscopy of this graphene film shows characteristic increase of D and G band intensity ratio, $I(\text{D})/I(\text{G})$ compared with GO, showing that reduction to graphene is almost completed in the presence of PAA.

In summary, pH-responsive graphene/PAA assembly was simply formulated through noncovalent interaction. Modulation of interaction parameter (“hydrophobic interaction dominating” or “charge repulsion dominating” mode) effectively changes structural arrangement and optical absorbance of graphene/PAA assemblies in the variation of pH, which is useful for the applications of various graphene assemblies in the area of sensing, drug carriers, etc.

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (No. 2010-0004806) and supported by a grant from Human Resource Training Project for Regional Innovation and the Regional Innovation Center (RIC) Program conducted by the Ministry of Knowledge Economy of the Korean Government.

References and Notes

- 1 D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff, *Nature* **2007**, *448*, 457.
- 2 a) N. Mohanty, V. Berry, *Nano Lett.* **2008**, *8*, 4469. b) D. Li, M. B. Müller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat. Nanotechnol.* **2008**, *3*, 101. c) H. J. Salavagione, M. A. Gómez, G. Martínez, *Macromolecules* **2009**, *42*, 6331.
- 3 a) S. Stankovich, R. D. Piner, X. Chen, N. Wu, S. T. Nguyen, R. S. Ruoff, *J. Mater. Chem.* **2006**, *16*, 155. b) Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 5856.
- 4 S.-Z. Zu, B.-H. Han, *J. Phys. Chem. C* **2009**, *113*, 13651.
- 5 a) S. Yoon, I. In, *Chem. Lett.* **2010**, *39*, 1160. b) S. Yoon, I. In, *J. Mater. Sci.* **2011**, *46*, 1316. c) D. Y. Lee, Z. Khatun, J.-H. Lee, Y.-k. Lee, I. In, *Biomacromolecules* **2011**, *12*, 336.
- 6 D. Y. Lee, S. Yoon, Y. J. Oh, S. Y. Park, I. In, *Macromol. Chem. Phys.* **2011**, *212*, 336.
- 7 J. Y. Lee, I. In, *Chem. Lett.* **2011**, *40*, 567.
- 8 L. Ren, T. Liu, J. Guo, S. Guo, X. Wang, W. Wang, *Nanotechnology* **2010**, *21*, 335701.
- 9 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.