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Layer-by-Layer 적층법을 이용한 중공형
그래핀 캡슐 형성에 관한 연구

Graphene Hollow Capsules Prepared by
the Layer-by-Layer Deposition

2012년 8월

서울대학교 대학원

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지도교수 차 국 헌

이 논문을 공학석사학위논문으로 제출함

2012년 6월

서울대학교 대학원

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Abstract

Graphene Hollow Capsules Prepared by the Layer-by-Layer Deposition

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Since the first successful isolation of graphene in 2004, the field of graphene research has blossomed over the last several years owing to their superior properties such as high electrical and thermal conductivity, strong mechanical strength, flexibility, and so forth. Among many production methods of graphene, the exfoliation of graphite oxide (i.e. graphene oxide (GO)) enables the layer- by-layer (LbL) deposition, which takes advantages of electrostatic attractions between GO sheets.

In the present study, we report graphene hollow capsules, recently reported 3-dimensional graphene structure, made of differently sized GO sheets with aim of accurate control of their mechanical properties. A fabrication of graphene hollow capsule was carried out by electrostatic LbL deposition of oppositely charged GO sheets on silica colloidal templates

followed by template removal with hydrofluoric acid treatment. A dispersion of random-sized GO sheets was separated by modulating their dispersion stability and controlling destruction in grain structure. Dispersion stability of GO sheets was controlled by pH value of solution, directly related to the degree of ionization of their functional groups, and centrifugation. Destruction in grains of GO sheet was simply controlled by ultrasonication. Those size-fractionized GO sheets provide controllability of mechanical properties of capsules, which were confirmed by scanning electron microscopy (SEM) and force spectroscopy by scanning probe microscopy (SPM). Furthermore, the effect of reduction was also investigated via thermal reduction in inert atmosphere.

The present study offers hollow capsules with narrowly size-distributed GO sheets which allow the clear pathway for overcoming intrinsic problem of GO composite system; a heterogeneity in size of GO sheets due to random destruction during exfoliation. This novel graphene hollow capsule system may be appropriate for replacing organic/inorganic capsules widely studied in drug delivery, bio-imaging, and framework for catalysts as graphene provides unique characteristics of biocompatibility, mechanical strength, electrical and thermal conductivity.

Keywords: Graphene Oxide, Hollow Capsule, Layer-by-Layer deposition, Size Fractionation, Force Spectroscopy, Thermal Reduction

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Chapter 1. Introduction

Graphene, atomically thin 2-dimensional layer of carbon honeycomb network connected by sp^2 hybridized bond, is a novel and very prospective carbon nanomaterial. It has been demonstrated that graphene has numerous unique electronic properties, such as ultrafast field-effect mobility¹, massless Dirac fermions², the quantum Hall effect in room temperature³, and superb mechanical strength⁴, thermal conductivity⁵, as well as high transparency of graphene monolayer were also reported⁶.

Based on its fascinating properties, numerous methods including mechanical exfoliation⁷, epitaxial growth⁸, chemical vapor deposition⁹, and chemical exfoliation of oxidized graphite¹⁰ have been developed to produce graphene monolayer sheets. Among those methods, exfoliation of oxidized graphite, also known as graphene oxide (GO), provides stable dispersion of graphene monolayers in aqueous solution and enables preparation of graphene in large quantity¹¹. In addition to advantages in the aspect of production, implantation of chemical functionalities on graphene oxide sheets opens another opportunity toward chemical modification and fabrication of unique structures¹².

Recently, the hollow capsules of reduced graphene oxide was successfully fabricated by incorporating the Layer-by-Layer (LbL) deposition method on sacrificial colloidal templates^{13,14,15}. Combining unique characteristics of graphene such as biocompatibility, electrical conductivity, mechanical property, and flexibility, with advantages of capsule structure,

graphene hollow capsules are expected to be widely adopted into the field of organic/inorganic capsules study¹⁴.

However, the intrinsic drawback of graphene oxide, heterogeneity in size, limits precise control and fabrication of graphene oxide system and still remains as an obstacle in advanced graphene oxide research¹⁶. To overcome this challenge, various approaches such as density gradient ultracentrifugation¹⁷, extended ultrasonication¹⁸, and pH-assisted sedimentation technique¹⁹ have been conducted, although these techniques are restricted in very crude separation or limited processing amount.

Herein, we report the precisely controlled hollow capsules of graphene oxide via electrostatic LbL deposition on colloidal templates as well as size fractionation of graphene oxide by combining pH-assisted sedimentation method and extended ultrasonication. The strategy to tune the mechanical strength of capsules involved the numbers of bilayer, average size of GO sheets that compose capsule wall, and thermal reduction. Prepared hollow capsules of graphene oxide are analyzed via force spectroscopy and visually inspected by scanning electron microscopy.

Chapter 2. Experimental Section

2.1 Materials and characterization

Graphite powder ($<45\mu\text{m}$, $\geq 99.99\%$), potassium persulfate (ACS reagent, 99%), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDC), ethylene diamine (ReagentPlus[®], $\geq 99\%$), potassium permanganate (ACS reagent, $\geq 99\%$) were purchased from Sigma-Aldrich. Sulfuric acid was purchased from PFP chemicals Co., Ltd. and phosphorus pentoxide ($\geq 97\%$) was purchased from Duksan Pure Chemical. All commercially obtained chemicals were used as received without any additional purification. Carboxylated silica colloids were obtained from Microparticles GmbH.

Ultrasonicator (VCX-500, Sonic & Materials) was used to exfoliate graphite oxide. 13 mm solid type probe was used to maximize exfoliation efficiency for 100 mL volume scale. Height profile and lateral size analysis, and force-distance curve were acquired on an atomic force microscopy (AFM, Nanoscope IIIA, Dimension 3100, Digital Instruments) in tapping mode. SEM images were taken on field-effect scanning electron microscopy (FE-SEM) ZEOL JSM-7401F. Zeta potential of colloids was measured by electrophoretic light scattering spectrophotometer (ELS-8000, Ostka). Atomic composition and bond analysis were conducted on a x-ray photoelectron spectroscopy (XPS, AXIS-HSi, KRATOS)

2.2 Synthesis of Graphene Oxide

Graphite oxide was synthesized by the modified Hummers method^{10, 20}. 20 g of graphite powder was added in 30 mL of sulfuric acid (H_2SO_4) and slowly heated to 80 °C. Then 10 g of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) and 10 g of phosphorus pentoxide (P_2O_5) were gradually added for pre-oxidation of graphite powder. The mixture was kept at same temperature for 3.5 h then cooled down to room temperature. Subsequently, the mixture was diluted with deionized water, filtered to remove residual ions and acids. Washing was repeated until pH value of rinse water reaches at 6. The resultant mixture was dried in vacuum oven at 60 °C and used as pre-oxidized graphite powder.

2 g of pre-oxidized graphite powder was dissolved in 46 mL of cold sulfuric acid in ice bath. Subsequently, 6 g of potassium permanganate (KMnO_4) was gradually added in resultant mixture to prevent the temperature of mixture exceed 20 °C. The mixture was kept for 16 h at 35 °C and 92 mL of deionized water was then added. After 15 min, color of solution changed into yellowish brown, then 280 mL deionized water and 5 mL of hydrogen peroxide (H_2O_2) were added to terminate oxidation reaction. The mixture was filtered and washed with 1:10 hydrochloric acid solution at first, then repeated with warm deionized water until pH value of rinse water became neutral. The washed powder was dried in vacuum oven at 60 °C.

An aqueous graphene oxide solution was prepared by ultrasonication of graphite oxide. 50 mg of graphite oxide was dissolved in 100 mL of deionized water, which provides 0.05 wt% concentration. The solution was then exfoliated for 1 h in ultrasonicator in presence of ice bath. The resultant brown

dispersion was centrifuged at 4000 rpm for 5 min to remove unexfoliated graphite oxide flakes and used as negatively charged graphene oxide (GO-COO⁻) solution.

Positively charged graphene oxide (GO-NH₃⁺) solution was prepared via EDC-mediated amine exchange reaction^{15,21}. 1.25 g of 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide(EDC) and 10 mL of ethylene diamine were added to 100 mL of GO-COO⁻ solution and rapidly stirred for 12 hr. The solution was then dialysis for 4 days in membrane tube to remove any excess chemicals.

2.3 Preparation of Graphene Hollow Capsules

50 μ L of 4 wt% carboxylated silica colloid was diluted with 9.95 mL of deionized water and 1 mL of GO-NH₃⁺ solution (pH 5) was added. After 15 min of vortex mixing, resultant opaque dispersion was centrifuged and washed 3 times at 2000 rpm for 2 min to remove excess GO sheets. Subsequently, GO-COO⁻ solution was added to be coated on GO-NH₃⁺-covered silica colloids under same procedure. This deposition was repeated until 3 bilayers of GO-NH₃⁺/GO-COO⁻ have been coated on colloids.

To obtain hollow capsule structure, GO-NH₃⁺/GO-COO⁻ coated silica colloids were dropped on Si wafer and dried in vacuum oven for 2 h. Dried sample was then dipped into buffered hydrofluoric acid solution for 5 min to selectively remove silica template then gently rinsed in deionized water.

2.4 Size Fractionation of Graphene Oxide Sheets

Size Fractionized Graphene Oxide Sheets (SFGOs) were prepared by separating solution of randomly sized GO sheets in 3 different fractionation conditions. First, 0.05wt% graphite oxide solution was ultrasonicated for 10 h. After sonication, pH value of GO solution was adjusted to 3 and aged for 1 day to stabilize the degree of ionization. GO solution was then centrifuged at 17,000 rpm for 15 min to exclude large-sized GO sheets. Supernatant was collected and purified by dialysis, then used as SFGO1. To prepare SFGO2, 0.05 wt% graphite oxide solution was ultrasonicated for 1 h. Subsequently, pH value of solution was adjusted to 3 then aged for same period. After centrifugation at 17,000 rpm for 5 min, supernatant solution was gathered and purified by dialysis, then used as SFGO2. SFGO3 was separated from 0.05 wt% graphite oxide solution which ultrasonicated for 20 min. After change pH value to 10 and kept for 1 day, solution was centrifuged at 10,000 rpm for 5 min. Precipitation was gathered and re-dispersed in deionized water, and purified by dialysis then used as SFGO3.

2.5 Thermal Reduction of Graphene Oxide Hollow Capsules

Thermal reduction of GO hollow capsules was conducted prior to core removal to prevent any damages to capsule wall caused by emptying inside. Drop-casted $\text{GO-NH}_3^+/\text{GO-COO}^-$ coated silica colloids on Si wafer was thermally reduced in 800 °C furnace for 3 h under nitrogen atmosphere, and

heating rate was 3 °C/min. After reduction, sample was slowly cooled down to room temperature then was treated in the same manner to remove silica core.

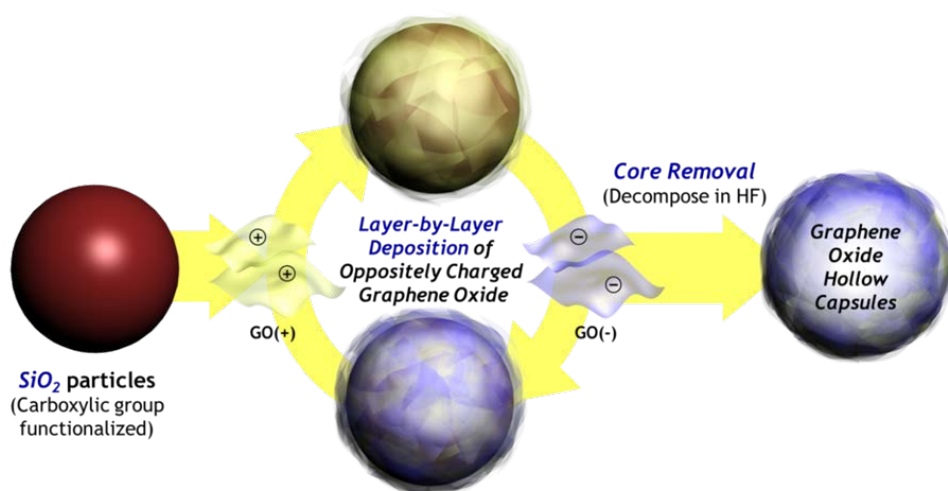
Chapter 3. Results and Discussion

3.1 Layer-by-Layer Deposition of Graphene Oxide

GO was synthesized by the modified Hummers method¹⁰, and subsequent modification by EDC-mediated amine exchange reaction provides positively charged GO sheets¹⁵. Scheme 1 illustrates each step of processing the GO hollow capsules via electrostatic LbL deposition method. The positively charged GO was initially deposited to carboxylated surface of silica colloid by electrostatic attraction and enabled further assembly by providing positively charged surface. To avoid flocculation during LbL deposition, silica particles were mixed to GO away from the stoichiometry, with a large excess amount of GO solution compared to colloidal templates. This imbalanced mixing resulted in a spontaneous and complete coverage of silica particles via electrostatically attracted complexation of the opposite charges. Another important factor of this colloidal templating LbL deposition is a degree of ionization of GO sheets. When a GO solution was mixed to a GO coated silica particles in different pH, i.e. pH 4 GO-NH_3^+ solution and pH 7 colloid, the dispersion experienced a massive and immediate precipitation. Those flocculation resulted from the multisite hydrogen bond generation between deionized amide groups of GO-NH_3^+ and hydroxyl groups of GO-COO^- on surface of particles. Same phenomena occurs in the opposite situation as well, in the case of mixing pH 7 GO-COO^- to pH 4 colloids. In addition, an excess amount of GOs passed from each deposition step that should be removed prior

to the next adsorption was thoroughly removed. Optimum experimental condition was found as a function of GO amount, total volume of process, and charge ratio as discussed above. Successful repetitive depositions of oppositely charged GO were examined by inversions in zeta potential measurements (Figure 1).

Using silica colloids as sacrificial template, subsequent template removal after deposition successfully yield hollow capsule structure, as shown in Figure 2 (b). The buffered hydrofluoric acid solution is essential to selectively and rapidly decompose silica^{22,23}. On the basis of conformal deposition of $\text{GO-NH}_3^+/\text{GO-COO}^-$ on colloidal templates, we have investigated the morphology of hollow capsules with transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Figure 2). Although the aggregation exist in 1 bilayer hollow capsules owing to thin wall thickness of capsules to be stand itself, we found that the GO hollow capsules retain its spherical structure of template as the number of bilayer increased.



Scheme 1. Scheme for LbL deposition of oppositely charged graphene oxide sheets on sacrificial silica template

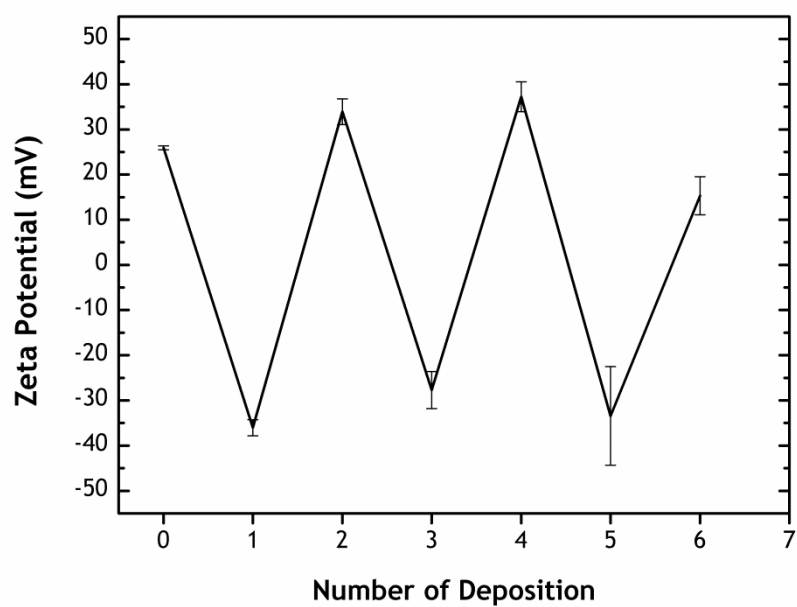


Figure 1. Zeta potentials of GO(+)/GO(-) coated silica particles as a function of deposition number

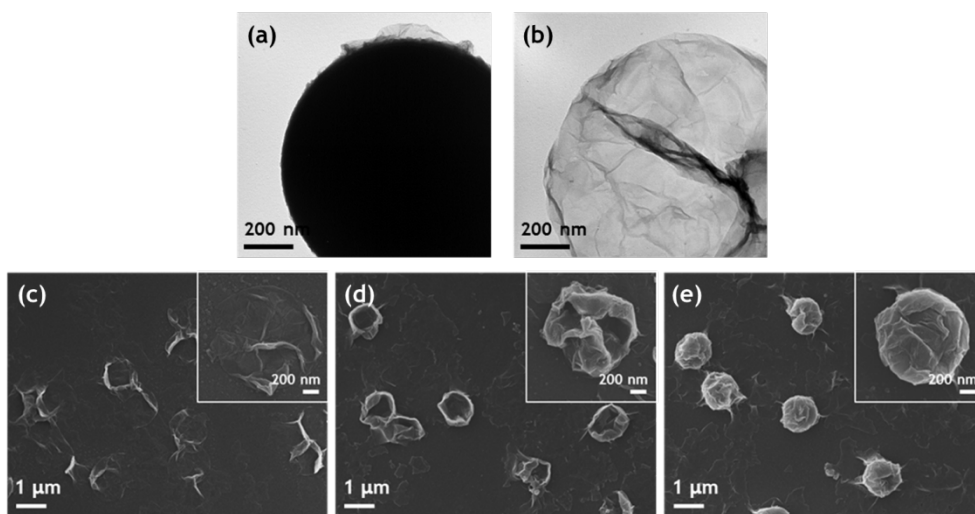


Figure 2. TEM images of (a) GO(+)/GO(-) 3 bilayers coated Silica colloids and (b) GO(+)/GO(-) 3 bilayer hollow capsules; SEM images of (c) 1 bilayer, (d) 2 bilayers, and (e) 3 bilayers hollow capsules. Inlets show magnified images of single hollow capsule

3.2 Hollow Capsules: Size Fractionized Graphene Oxide Sheets

Size fractionation of graphene sheets was first suggested by A. Green et al. by incorporating density gradient ultracentrifugation (DGU) technique in special gradient medium¹⁷. However, the severe centrifugation rate, time, and limitation in process volume and use of specialized medium restricted its capability for production of graphene with desired sizes in large quantity. Recently, X. Wang et al. suggested simple and facile pH-induced sedimentation method to isolate micron-sized GO sheets and nano-sized GO sheets in large quantity by adjusting pH value of GO solution. In this technique, pH value of solution directly affects to the degree of ionization of functional groups on the GO sheets, for example, carboxylic group, which is ionizable so that dominantly contribute to dispersion stability of GO sheets in water¹⁹. Since ionizable carboxylic groups are mostly located at the edges of GO sheets^{24,25}, larger GO sheets that the edge-to-area ratio is smaller lose its dispersion stability easier than smaller GO sheets in low pH and less strengthen in high pH as described in Figure 3.

In addition to pH-induced sedimentation technique, we have extended the sonication time to fractionize lateral size with more narrow size distribution. As increasing ultrasonication time up to 10 h, not only bundles of GO sheets exfoliated into single sheets but also its original grain structure experienced more damages which resulted in smaller pieces of GO sheets. In comparison, the least amount of small GO sheets and preservation of large grain size were yielded via only 10 min of ultrasonication.

Taking advantages of pH-induced sedimentation technique and lateral size-ultrasonication relation, randomly mixed GO solution was successfully separated into 3 different groups (SFGO1, SFGO2, SFGO3). Calculation of average lateral size of GO sheets from AFM images were conducted on 200 different GO sheets in NanoScope Analysis software. As shown in Figure 4, calculated average lateral size of SFGO1 was 59.9 nm with 28.3 nm as standard deviation, SFGO2 was 172 nm with 112.8 nm as standard deviation, and SFGO3 was 485 nm with 194.2 nm as standard deviation.

To investigate the effect of average size of GO sheets that compose capsule wall, GO hollow capsules have been fabricated by SFGOs prepared via same procedure explained previously. SEM images of hollow capsules are shown in Figure 5. According to SEM images and their size distribution, capsule wall composed of smaller size of GO sheets showing less stiffness than others made of larger size. Combined effect of number of bilayers and average size of GO sheets were clearly observed as well. We would discuss about the properties of hollow capsules in the last chapter.

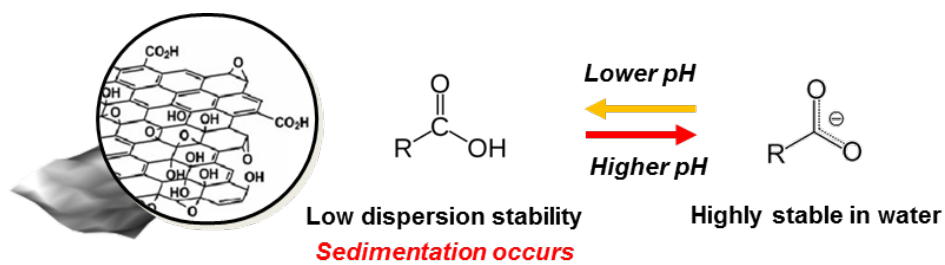


Figure 3. Chemical structure of the GO sheet and structural changes in the degree of ionization of carboxylic group by the pH value of solution

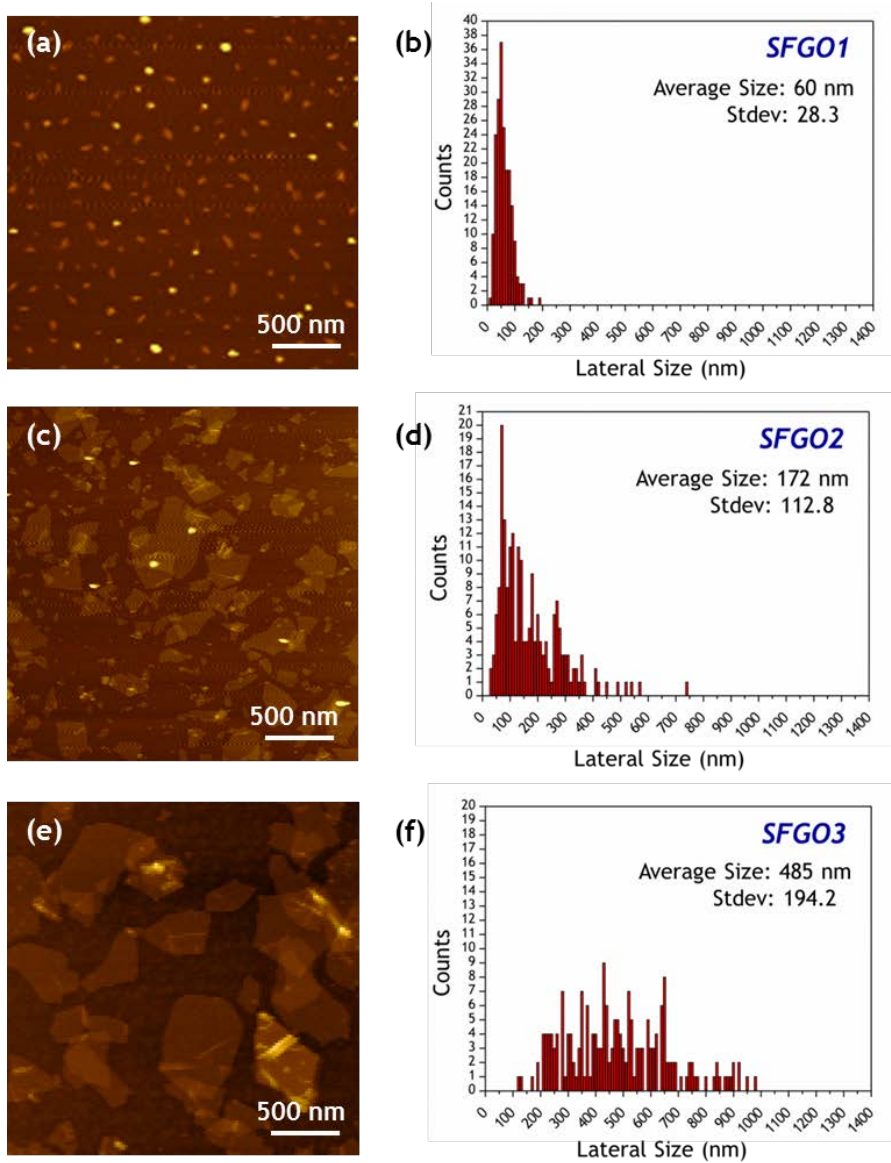


Figure 4. AFM images of (a) SFGO1, (c) SFGO2, (e) SFGO3; size distribution and average lateral size of (b) SFGO1 (d) SFGO2 (f) SFGO3.

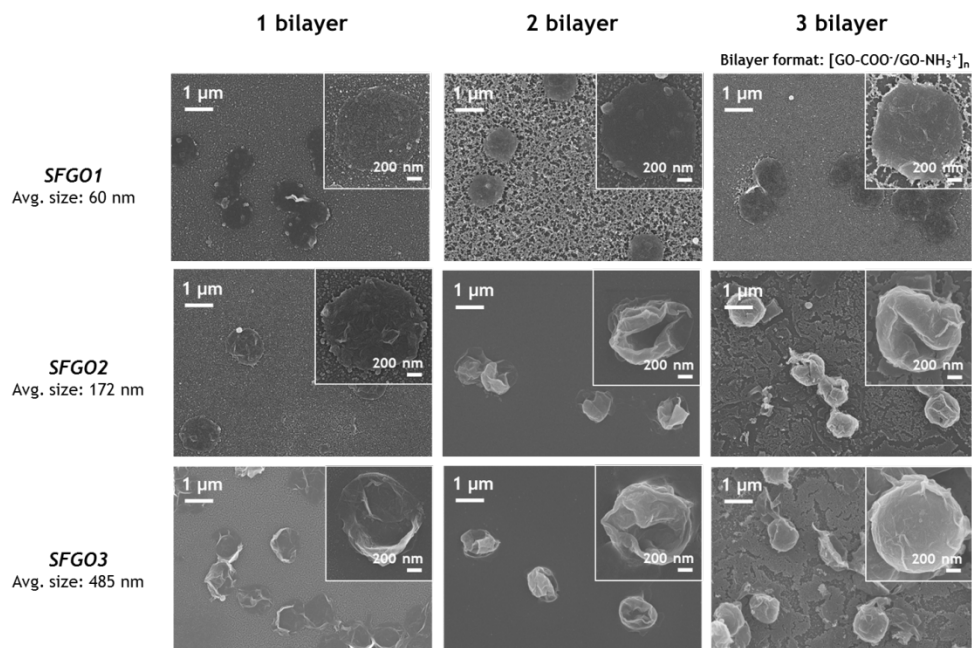


Figure 5. SEM images of hollow capsules composed of (top) SFG01, (middle) SFG02, (bottom) SFG03.

3.3 Hollow Capsules: Thermal Reduction

Thermal reduction is the most common reduction method for GO on the basis of decomposing oxygen-containing bonds in high temperature with absence of oxygen²⁶. Thermal reduction is an important parameter in GO capsules due to the interlayer distance between sheets and recovery of graphitic structure by removal of functional groups^{6,27}

GO-NH₃⁺/GO-COO⁻ coated silica particles were thermally reduced as described in experimental section. Successful reduction of GO was confirmed by XPS analysis. XPS spectrum of carbon 1s (C1s, 284.6 eV) and oxygen 1s (O1s, 532.0 eV) species for GO-COO⁻ are shown in Figure 6 (a) and (b), spectrum of carbon 1s and nitrogen 1s (N1s, 399.6 eV) of GO-NH₃⁺ are shown in Figure 6 (c) and (d). Degradation of oxygen-containing bonds was confirmed by peak decrease in C1s peak, O1s peak, and N1s peak. In C1s spectrum, hydroxyl group at 286.4 eV, ketone group at 287.8 eV, carboxylic group at 288.4 eV were dramatically reduced in thermal annealing at 800°C, and those reduction are well-matched with correlated decrease in O1s peaks such as ketone group at 531.2 eV, carboxylic group at 529.9 eV, and hydroxyl group at 533.0 eV. In the case of GO-NH₃⁺, similar peak decrease after thermal reduction was observed in C1s peak as well as N1s peaks, such as pyridinic N at 398.2 eV, amide group at 399.6 eV, and amine group in 402.5 eV^{28,29,30}.

Figure 7 is morphology of reduced SFGO hollow capsules taken in every bilayer number by SEM. As observed in previous section, hollow capsules shows trends of retaining its spherical shape of template by increasing bilayer number as well as average size of GO sheets. However,

spherical shape is more maintained than GO hollow capsules in even less number of bilayer, and in capsules composed of smaller GO sheets as presented in Figure 8. Though it is not possible to measure the film thickness and roughness of $\text{GO-NH}_3^+/\text{GO-COO}^-$ multilayer capsules in the current experimental set up, a possible explanation for improved stiffness would be the interlayer distance decrease by thermal annealing. In multilayered film of GO sheets, interlayer distance is varies from 0.7 to 1.4 nm which is much larger than that of graphite, 0.34 nm. Large interlayer distance of GO sheets is mainly contributed by the distortion due to sp^3 hybridized bond and steric repulsion of oxygen-containing groups on basal plane of GO sheets. As GO underwent thermal reduction, sp^3 bonds returned to sp^2 planar bond structure and decomposition of oxygen species was occurred. Consequently, decreased interlayer distance resulted in dramatic increase the effect of short distance interaction, van der Waals attraction, while the effect of electrostatic attraction between carboxylic group and amine group became less dominant. Therefore, the force that assembles each GO sheets were shifted from electrostatic interaction at the edge of GO to π - π interaction, resulted in spherical-resemble structures as well as much stretched capsule wall morphology. These explanations will be further discussed in the last chapter.

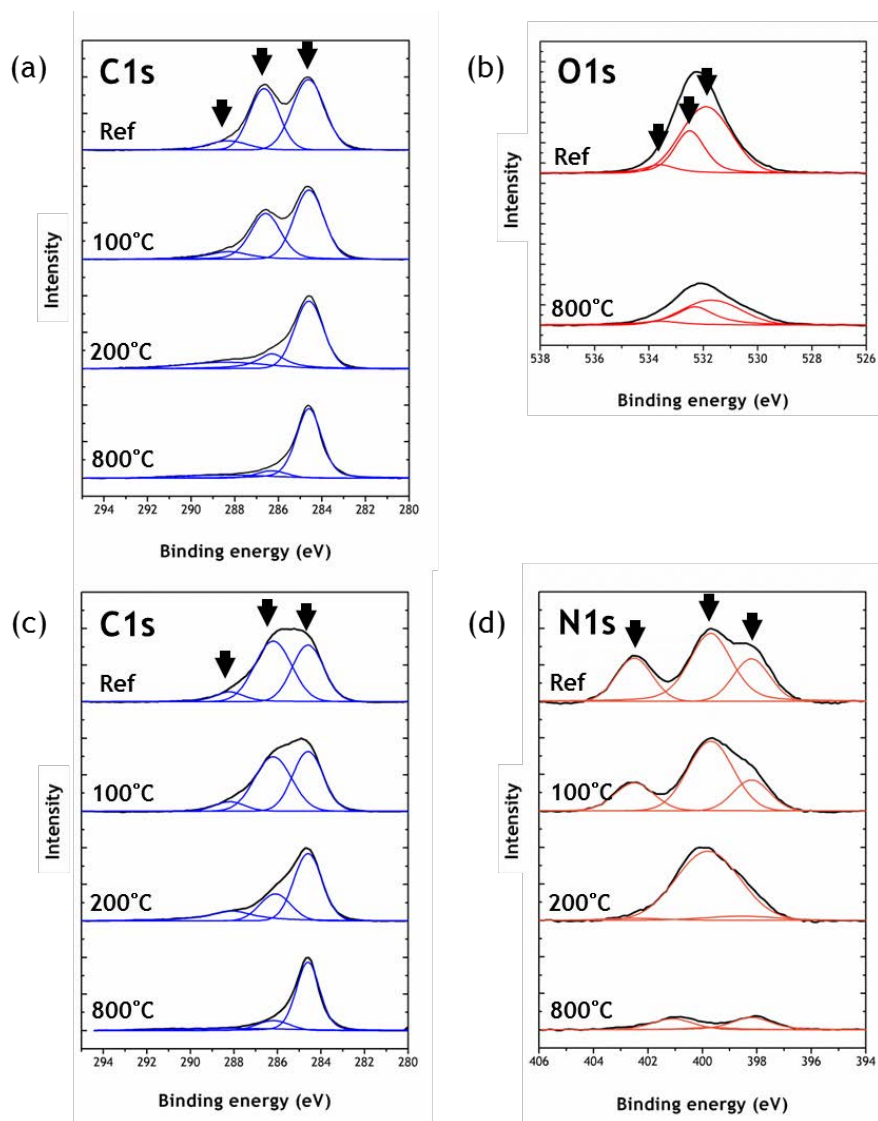


Figure 6. XPS spectrums of GO and reduced GO; (a) C1s peaks (284.6 eV) of GO-COO⁻ (b) O1s peaks (532.0 eV) of GO-COO⁻ (c) C1s peaks of GO-NH₃⁺ (d) N1s peaks (399.6 eV) of GO-NH₃⁺

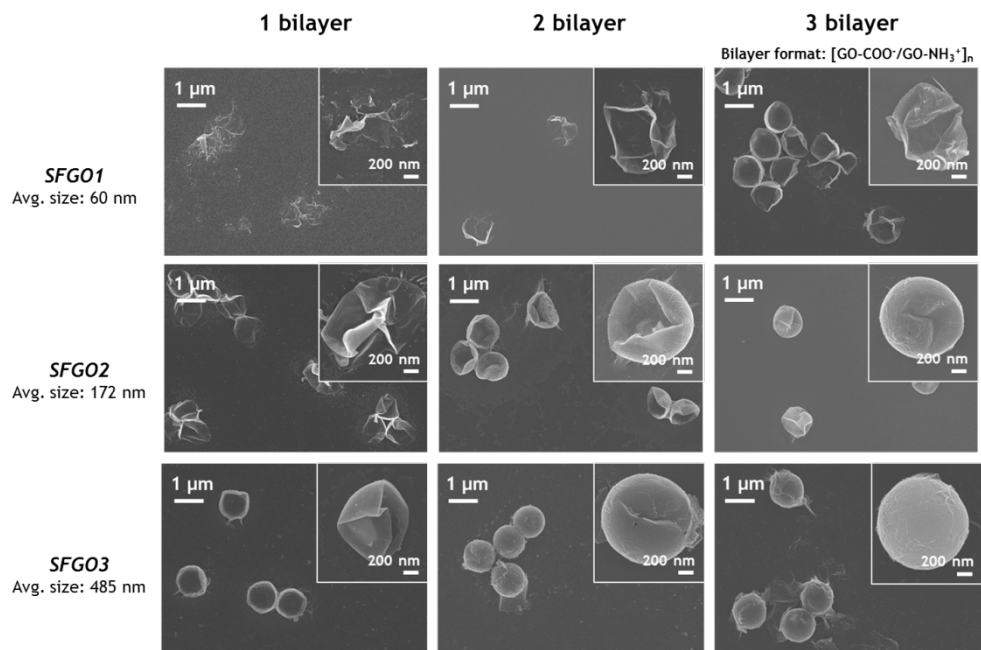


Figure 7. SEM images of reduced GO hollow capsules composed of (top) SFG01, (middle) SFG02, (bottom) SFG03.

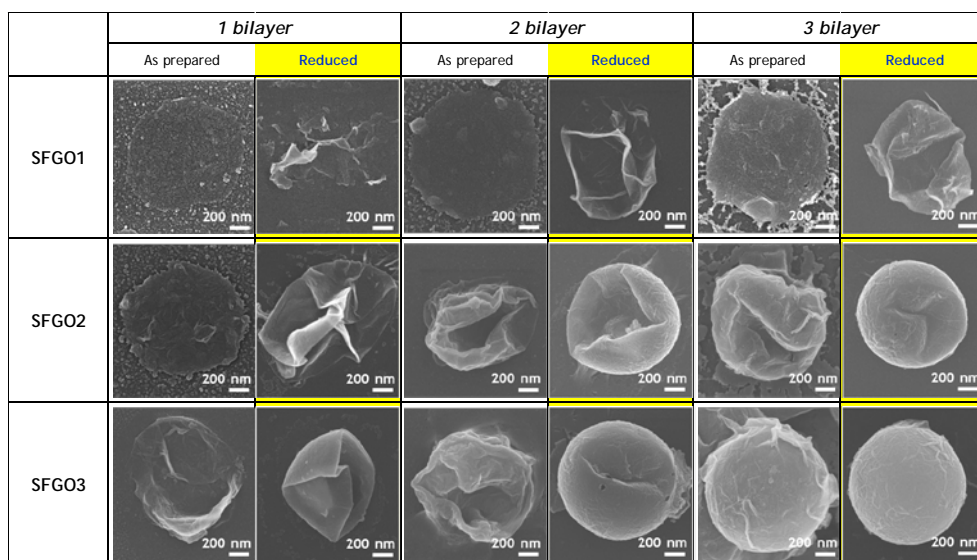


Figure 8. SEM images of GO hollow capsules compared with reduced GO hollow capsules by average GO sheets size and number of bilayers.

3.4 Force Spectroscopy of Graphene Hollow Capsules

Force spectroscopy is a scanning probe microscopy (SPM) based technique to measure the interaction between cantilever and the surface of the sample. In force spectroscopy, the cantilever performs a role of the force sensor that could provide extremely high resolution³¹. To minimize the substrate effect of Si wafer, we used a normal tip usually uses in tapping/contact scans rather than a diamond tip designed for indentation since capsules of low bilayer number showed collapsed morphology so that thickness of capsules often too thin (< 200 nm) to be accurately measured.

In order to measure relative hardness of capsules, the force F between the tip and the sample was calculated from the cantilever's deflection voltage through Hooke's law:

$$F = k \cdot \alpha \cdot V$$

Where k is spring constant of cantilever, α is deflection sensitivity that convert deflection voltage to distance, and V is measured deflection voltage.

Figure 9 (a) is a typical output data of force spectroscopy, called 'force-distance curve (F-D curve)'. As described in Figure 9 (a), once the tip jumps to the sample surface, where distance is zero, the tip starts pushing the surface with some force therefore increase in deflection voltage as well as applied force happen. The measurement of stiffness or compliance of the sample can be obtained by analyzing the slope of this curve, which is referred to relative hardness. Although it was not possible to accurately measure the stiffness of capsule wall in current experimental setup, relative comparison of

hardness of capsules can be provided by contrasting values of relative hardness from series of F-D curves.

Figure 9 is force spectroscopy analysis of 3 bilayer hollow capsules of SFGO1, SFGO2, and SFGO3. According to Figure 9 (d) and Table 1, relative hardness increases from 0.0200 nN/nm to 0.0265 nN/nm by escalating the deposition number, indicates capsule that constructed with larger GO sheets can provide harder mechanical strength. In addition, it also implies the stiffness of GO hollow capsules is tunable as modulate size of GO sheets. These results made good correlation with SEM analysis discussed in chapter 3.2.

The effect of number of bilayer was investigated and summarized in Figure 10 and Table 1. The difference in relative hardness is comparable to the results from the study on average size of GO sheets, however, the actual influence is much greater when we consider the average size of SFGO3 is 8 times larger than SFGO1. Results from Figure 10 are in good agreement with the analysis on SEM images previously discussed in chapter 3.1.

To span our approaches to reduced graphene oxide, we have measured F-D curves of thermally reduced GO hollow capsules by same procedures mentioned above. Since the relative hardness imply the comparative mechanical strength of hollow capsules, the large gap between compared results indicates huge difference of strength exists. As shown in Figure 11 and Table 1, thermal reduction of GO is showing the greatest enhancement in a single treatment. In accordance with previous discussion in chapter 3.2, we have examined the thermally reduced GO hollow capsules exhibit superior

mechanical strength than GO hollow capsules and confirmed that the graphene hollow capsules are able to be designed by modulating GO sheets as well.

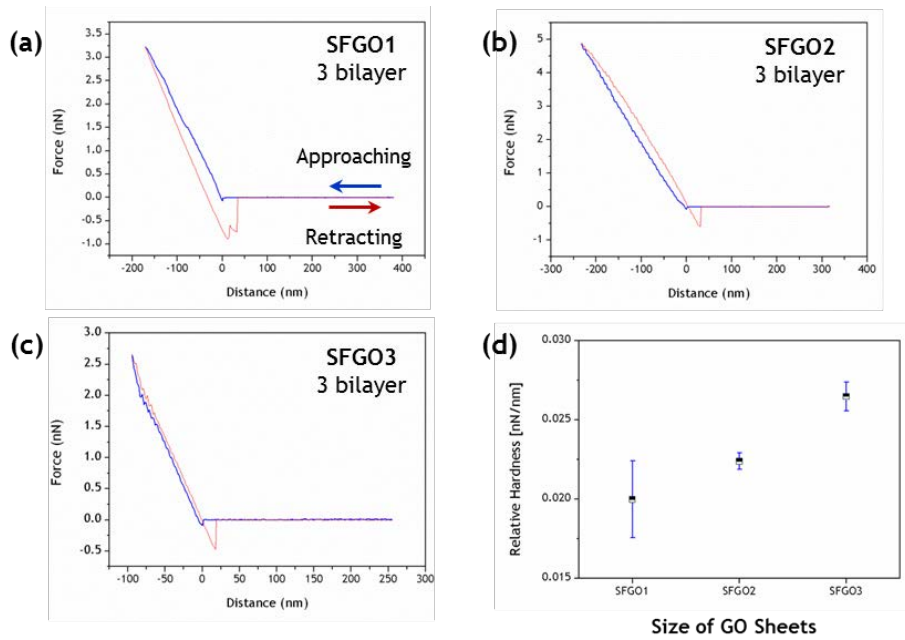


Figure 9. Force-distance curves of (a) 3 bilayers capsule of SFG01 (B) 3 bilayers capsule of SFG02 (c) 3 bilayers capsule of SFG03 (d) average relative hardness of 3 bilayers capsules.

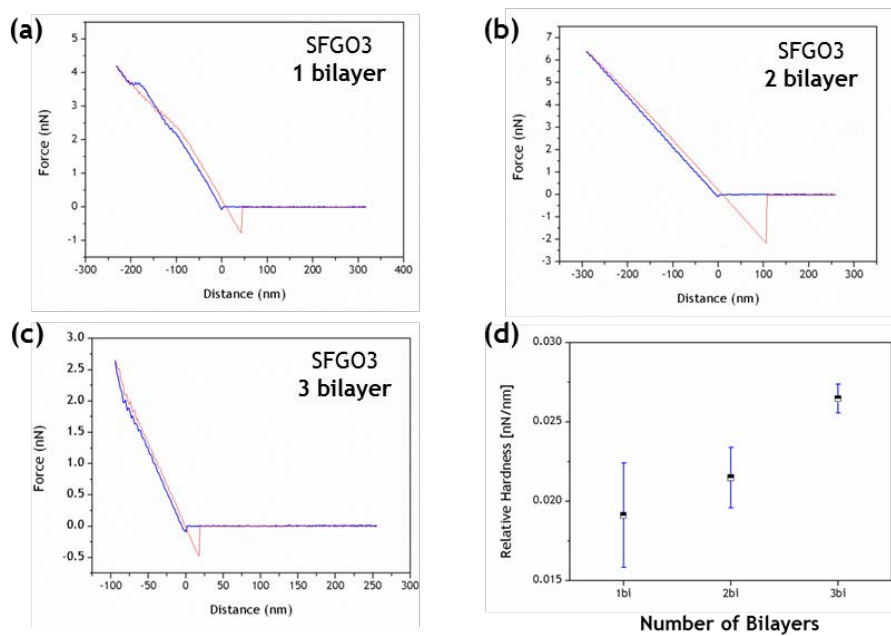


Figure 10. Force-distance curves of (a) 1 bilayer capsule of SFG03 (b) 2 bilayers capsule of SFG03 (c) 3 bilayers capsule of SFG03 (d) average relative hardness of SFG03 capsules.

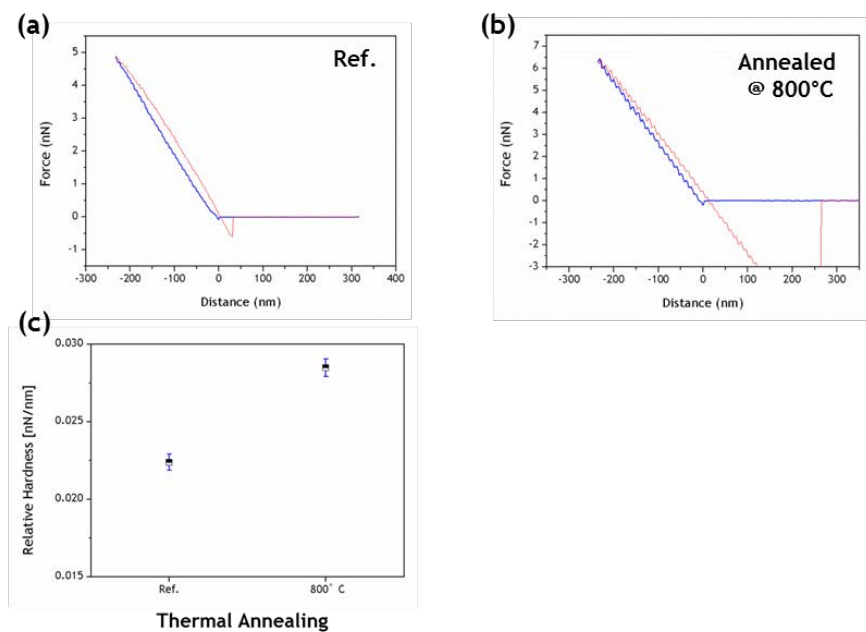


Figure 11. Force-distance curves of (a) 3 bilayers capsule of SFGO2 (b) 3 bilayers capsule of SFGO2 after annealed at 800°C for 3 h (c) average relative hardness of 3 bilayers capsules of SFGO2.

Table 1. Average relative hardness calculated from F-D curves of hollow capsules

	Size of GO Sheets			# of Bilayers			Thermal Annealing	
	SFGO1	SFGO2	SFGO3	1	2	3	N/A	800°C
Relative Hardness [nN/nm]	0.0200	0.0224	0.0265	0.0191	0.0215	0.0265	0.0224	0.0285
St. Dev.	0.0024	0.0005	0.0009	0.0033	0.0019	0.0009	0.0005	0.0006

Chapter 4. Conclusion

Graphene hollow capsule were prepared from LbL deposition of oppositely charged GO sheets followed by removal of silica template for the investigation of relation between various factors and mechanical properties. This system is also anticipated to overcome intrinsic drawback of GO sheets, heterogeneity in size, which limited advanced researches in the field requires accurate fabrication and controllability of properties. Number of bilayer deposition, average size of GO sheets, and thermal reduction affected the structure of hollow capsules, which is able to be examined visually and accurately measured at the same time. To fractionize randomly mixed GO sheets in sizes, combined system of pH-assisted sedimentation and ultrasonication was suggested and statistically examined by AFM. The thermal reduction of GO sheets can reduce its interlayer distance and provide great enhancement in van der Waals attraction. Correlation of morphology of a series of graphene hollow capsules with analysis of mechanical properties was examined by SEM and force spectroscopy by using SPM.

This accurately controlled graphene oxide hollow capsule system would be widely adopted in the application study of graphene oxide as well as hollow capsules such as drug agent, catalyst, and energy storage devices where requires accurately controlled structure and properties. Furthermore, extending of controlled GO system can be done by hybridization with functional objects, modification of functionalities

References

- (1) Bolotin, K. I.; Sikes, K. J.; Jiang, Z.; Klima, M.; Fudenberg, G.; Hone, J.; Kim, P.; Stormer, H. L. *Solid State Communications* **2008**, 146, 351.
- (2) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. *Nature* **2005**, 438, 197.
- (3) Zhang, Y.; Tan, Y.-W.; Stormer, H. L.; Kim, P. *Nature* **2005**, 438, 201.
- (4) Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. *Science* **2008**, 321, 385.
- (5) Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N. *Nano Letters* **2008**, 8, 902.
- (6) Eda, G.; Fanchini, G.; Chhowalla, M. *Nat Nano* **2008**, 3, 270.
- (7) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, 306, 666.
- (8) Berger, C.; Song, Z.; Li, T.; Li, X.; Ogbazghi, A. Y.; Feng, R.; Dai, Z.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; de Heer, W. A. *The Journal of Physical Chemistry B* **2004**, 108, 19912.
- (9) Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J.-H.; Kim, P.; Choi, J.-Y.; Hong, B. H. *Nature* **2009**, 457, 706.
- (10) Kovtyukhova, N. I.; Ollivier, P. J.; Martin, B. R.; Mallouk, T. E.; Chizhik, S. A.; Buzaneva, E. V.; Gorchinskiy, A. D. *Chemistry of Materials* **1999**, 11, 771.
- (11) Park, S.; Ruoff, R. S. *Nat Nano* **2009**, 4, 217.
- (12) Zhu, Y.; Tour, J. M. *Nano Letters* **2010**, 10, 4356.
- (13) Hong, J.; Char, K.; Kim, B.-S. *The Journal of Physical Chemistry Letters*

2010, 1, 3442.

- (14) Caruso, F., Hollow Inorganic Capsules via Colloid-Templated Layer-by-Layer Electrostatic Assembly, Colloid Chemistry II. In Antonietti, M., Ed. Springer Berlin / Heidelberg: **2003**; Vol. 227, pp 145.
- (15) Lee, D. W.; Hong, T.-K.; Kang, D.; Lee, J.; Heo, M.; Kim, J. Y.; Kim, B.-S.; Shin, H. S. *Journal of Materials Chemistry* **2011**, 21, 3438.
- (16) Zhao, J.; Pei, S.; Ren, W.; Gao, L.; Cheng, H.-M. *ACS Nano* **2010**, 4, 5245.
- (17) Green, A. A.; Hersam, M. C. *Nano Letters* **2009**, 9, 4031.
- (18) Khan, U.; O'Neill, A.; Lotya, M.; De, S.; Coleman, J. N. *Small* **2010**, 6, 864.
- (19) Wang, X.; Bai, H.; Shi, G. *Journal of the American Chemical Society* **2011**, 133, 6338.
- (20) Hummers, W. S.; Offeman, R. E. *Journal of the American Chemical Society* **1958**, 80, 1339.
- (21) Hong, T.-K.; Lee, D. W.; Choi, H. J.; Shin, H. S.; Kim, B.-S. *ACS Nano* **2010**, 4, 3861.
- (22) Ababou, Y.; Masut, R. A.; Yelon, A.; Poulin, S. *Applied Physics Letters* **1995**, 66, 3352.
- (23) Wong, L.; Suratwala, T.; Feit, M. D.; Miller, P. E.; Steele, R. *Journal of Non-Crystalline Solids* **2009**, 355, 797.
- (24) He, H.; Klinowski, J.; Forster, M.; Lerf, A. *Chemical Physics Letters* **1998**, 287, 53.
- (25) Lerf, A.; He, H.; Forster, M.; Klinowski, J. *The Journal of Physical*

- Chemistry B* **1998**, 102, 4477.
- (26) Li, X.; Zhang, G.; Bai, X.; Sun, X.; Wang, X.; Wang, E.; Dai, H. *Nat Nano* **2008**, 3, 538.
- (27) Jeong, H.-K.; Lee, Y. P.; Jin, M. H.; Kim, E. S.; Bae, J. J.; Lee, Y. H. *Chemical Physics Letters* **2009**, 470, 255.
- (28) Stankovich, S.; Piner, R. D.; Chen, X.; Wu, N.; Nguyen, S. T.; Ruoff, R. S. *Journal of Materials Chemistry* **2006**, 16, 155.
- (29) Paredes, J. I.; Villar-Rodil, S.; Martínez-Alonso, A.; Tascón, J. M. D. *Langmuir* **2008**, 24, 10560.
- (30) Tsuchiya, S.; Seno, M. *The Journal of Organic Chemistry* **1979**, 44, 2850.
- (31) Han, W., Force Spectroscopy with the Atomic Force Microscope, Agilent Technologies: **2008**.

초 록

본 연구는 Layer-by-Layer 적층법을 이용하여 중공형 그래핀 캡슐을 형성하고 이를 구성하는 산화 그래핀이 캡슐의 기계적 특성에 미치는 영향에 대한 연구로서, 산화 그래핀의 적층 횟수에 따른 두께, 크기, 그리고 열적 환원에 의한 캡슐의 구조적 변화를 다각적으로 관찰하였다. 중공형 캡슐 구조를 구현하기 위해 표면을 카르복실기로 치환시킨 실리카 구형 입자를 템플레이트로 사용하여 불화수소산(hydrofluoric acid)으로 선택적으로 제거하였으며, 산화 그래핀의 크기를 조절하기 위해 용매의 pH 값과 초음파처리 시간을 변경하여 다양한 크기 (59 ~ 485 nm)의 산화 그래핀 용액을 형성하였다. 이와 같은 방법으로 준비된 캡슐은 적층 횟수가 많거나 산화 그래핀의 크기가 클수록 본래 템플레이트의 구형 구조를 유지하는 경향을 보였으며, 특히 열적 환원을 가할 경우 그 변화가 가장 분명하게 관찰되었다. 이러한 경향은 힘 분광기 (force spectroscopy)를 통한 각 캡슐의 상대적 경도분석에서도 동일하게 확인되었다.

주요어: 산화 그래핀, 중공형 캡슐, Layer-by-Layer 적층법, 크기 분화, 힘 분광기, 열적 환원

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