POLYDOPAMINE EMBEDDED REDUCED GRAPHENE OXIDE PAPER

Wonoh Lee[1*], Jea Uk Lee[1], Jin-Woo Yi[1],
Sang-Bok Lee[1], Joon-Hyung Byun[1*], Byung-Sun Kim[1]

[1]*Composite Materials Center, Korea Institute of Materials Science,*
797 Changwon-daero, Changwon, South Korea, 642-831
** wonohlee@kims.re.kr, bjh1673@kims.re.kr*

Keywords: Dopamine, Graphene Oxide, Graphene Paper, Bio-inspired.

Abstract
In this work, reduced graphene oxide (rGO) paper has been fabricated using bio-inspired adhesive polydopamine (pDop). Dopamine mimics the catechol-amine structure in the mussel's adhesive foot protein, mytilus edulis. Also, dopamine can be utilized as an effective reducing agent due to its oxidative self-polymerization. Therefore, pDop embedded rGO paper can be mechanically strong and electrically conductive without using toxic chemical and/or thermal annealing reduction processes.

1 Introduction
Recently, graphene-based composites have attracted a great deal of scientific and engineering interests because graphene has superior mechanical, electrical, and thermal properties and can produce a dramatic improvement in properties at very low filler content [1-4]. Among many methods to achieve successful reinforcing graphene into the composite materials, the solution-based method is the most promising technique since the homogeneous colloidal suspension can provide high processability and flexibility to the large-scale production [5]. This method produces graphene oxide (GO) through sequential chemical oxidation and exfoliation from graphite powders and then reduced graphene oxide (rGO) is obtained by chemical and/or thermal treatment [6]. Therefore, the rGO derived from graphite by the chemical exfoliation and reduction has been widely adopted in the polymer composites.

Free-standing paper-like nano-materials have been widely utilized as shielding material, chemical filter, conducting barrier and electronic devices owing to their planar structural capability. Especially, carbon-based paper materials are already commercialized such as carbon-nanotube (CNT) bucky paper and graphite foil [7,8]. Recently, graphene-based paper has been rigorously investigated since two-dimensional graphene structure is expected to significantly improve paper's properties than CNT bucky paper and graphite foil [9]. Even though many researches on GO papers reported enhanced mechanical properties, GO papers are electrically insulating. Therefore GO papers require further chemical/thermal reduction process in order to fabricate electrically conducting rGO papers [10]. However, the reduction methods based on chemical and thermal treatment use toxic hydrazine and high temperature annealing step.

In this work, bio-inspired adhesive material, dopamine was utilized to fabricate mechanically strong and electrically conductive rGO papers, since dopamine has both adhesion and reduction properties [11]. To achieve this, GO was manufactured using the modified Hummers method and then pDop/rGO paper was fabricated by a simple filtration. During the filtration, dopamine is self-polymerized within individual layers in GO paper. From the IR spectrum analysis and electrical conductivity measurement, the reduction of GO by pDop was verified. Furthermore, the manufactured pDop/rGO paper showed better mechanical and electrical properties than pure GO paper.

2 Experiments

Here, GO was manufactured from graphite powder by the modified Hummers method in which the pretreatment process is included using weak acid based potassium persulfate and phosphorous pentoxide [12]. In order to characterize the manufactured GO, the Fourier transform infrared (FT-IR) spectroscopy and Raman spectrum analyses were carried out and transmission electron microscopy (TEM) analysis was also conducted to observe the morphology of the GO.

The GO and pDop/rGO papers were manufactured using the simple vacuum filtration process. GO colloidal suspension was prepared with distilled water. As for the pDop/rGO paper, GO solution was prepared in the pH 8.5 tris buffer solution with dopamine hydrochloride. Since the dopamine is self-polymerized under the weak basic condition, both filtration and polymerization occur concurrently. Through the scanning electron microscopy (SEM) observation, the morphological difference of GO and pDop/rGO papers were examined and thermal stability was investigated by the thermogravimetric analysis (TGA). Also, tensile tests were performed for both GO and pDop/rGO papers to verify the improvement of mechanical properties.

After finishing the filtration, the obtained papers are dried and pilled-off from the filter paper. Furthermore, in order to investigate the reduction enhancement, thermal annealing was performed at 100, 150, 200, 400, 600 and 800 ^{o}C under N_2 condition. At each annealing temperature, FT-IR and X-ray diffraction (XRD) analysis were carried out for both papers. Also, electrical conductivities were measured using the four-probe method.

3 Results and Discussion

Fig. 1 shows the homogeneous GO solution which has the light brown color and the TEM image of the single GO sheet. The manufactured GO sheets are well dispersed in the distilled water and have about 10 μm size. From the IR spectrum as shown in Fig. 2, aromatic C double bond, hydroxyl, carboxyl and epoxide functional groups are easily observed. Also, D peak is identified as the GO’s fingerprint from the Raman spectrum while 2D peak in the graphite disappear in the GO.

The manufactured GO and pDop/rGO papers were shown in Fig. 3, exhibiting good bendability. The GO paper has the transmittance while the pDop/rGO paper shows complete opaque black color. The SEM images show the paper-like morphology for the through-thickness direction. Note that the pDop/rGO paper shows polydopamine embedded structure in layer-by-layer sequence which may increase the mechanical property.

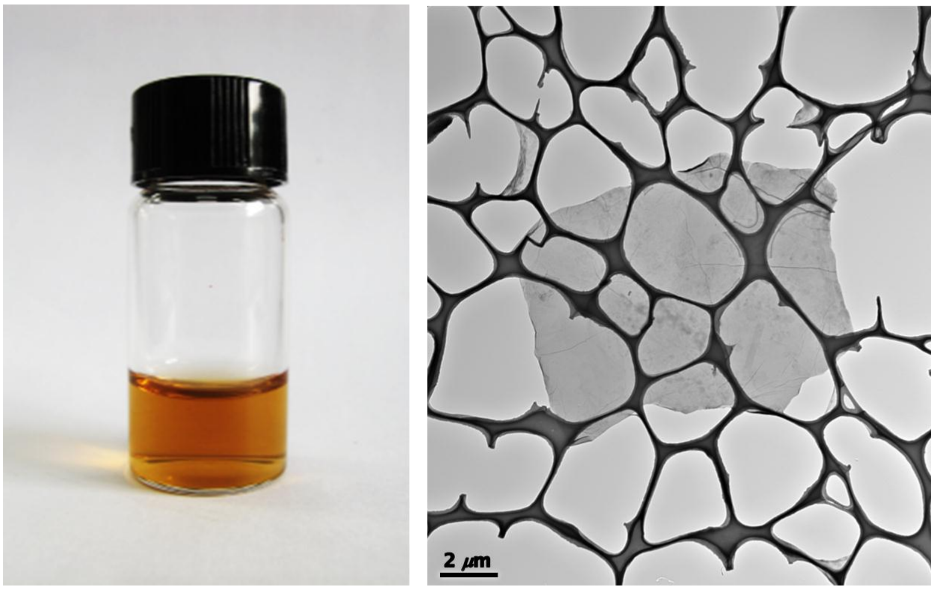

Figure 1. GO colloidal suspension and TEM image of GO single sheet.

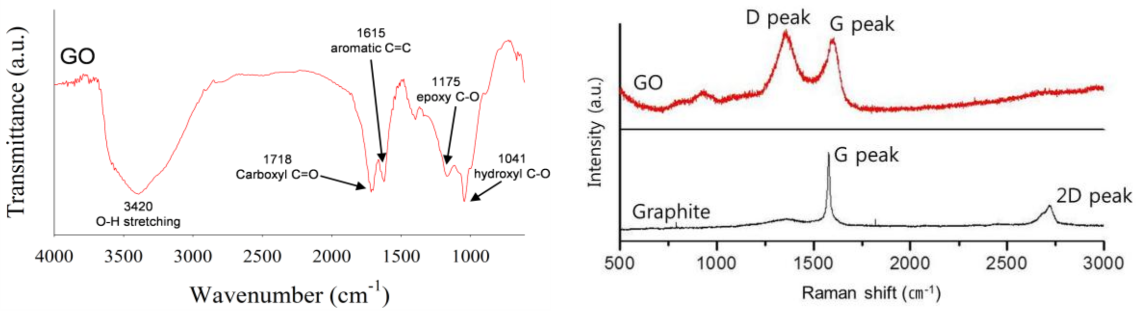

Figure 2. IR and Raman spectra of GO.

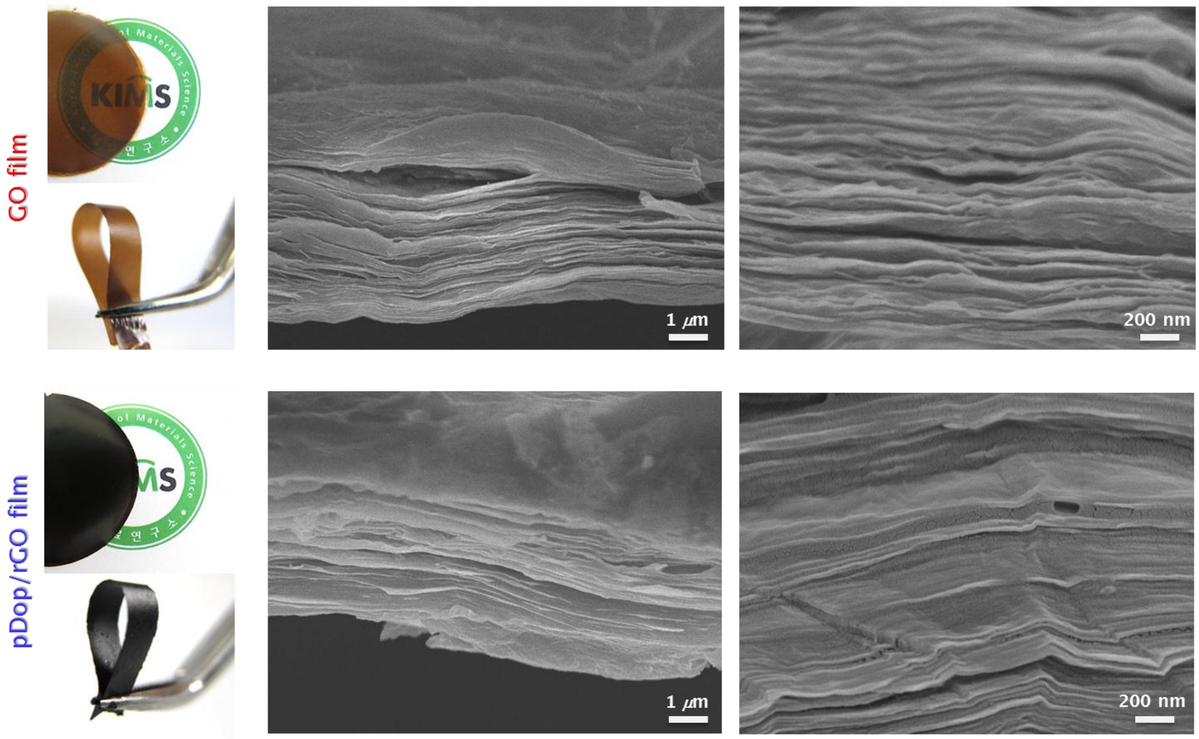

Figure 3. Digital and SEM images of GO and pDop/rGO papers

Fig. 4 shows the result of TGA analysis of polydopamine, GO and pDop/rGO papers. Around 150~200 °C, the stiff weight reduction was observed for both papers which means that large amount of H_2O evaporate. At the 800 °C, GO shows 20% weight residual but pDop/rGO shows better thermal stability owing to the high carbon yield characteristics of polydopamine [13]. This thermally stable and high carbon yield capability may lead to the enhancement of mechanical and electrical properties of the pDop/rGO paper.

From the FT-IR result with respect to the thermal annealing as shown in Fig. 5, the carboxyl peak in the pDop/rGO paper at room temperature is similar to the one in the GO paper at the 100 °C. Also, the temperature range where most oxygen functional groups disappear by the thermal treatment is 150~200 °C for GO paper and 100~150 °C for pDop/rGO paper, respectively. Therefore, it can be concluded that the polydopamine increase the reduction performance of GO. Note that the C-N peak in the pDop/rGO paper is from the chemical structure of polydopamine.

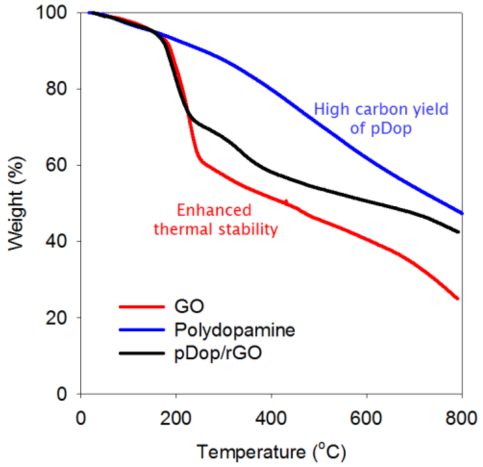

Figure 4. TGA curves of GO, pDop/rGO and polydopamine.

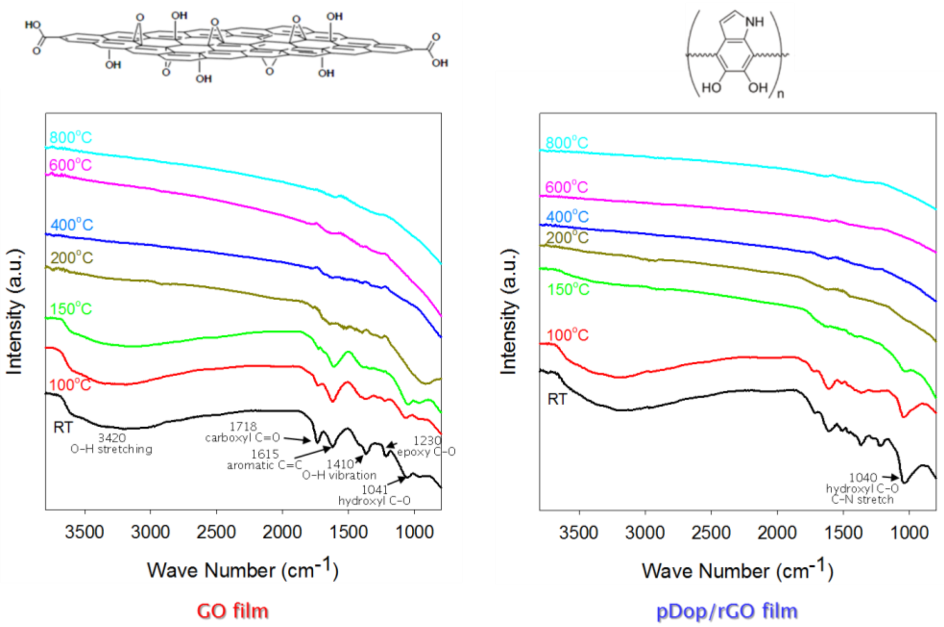

Figure 5. IR spectra of GO and pDop/rGO w.r.t thermal annealing.

Fig. 6 shows the d-spacing values from the XRD analysis. When the temperature increases, the value of d-spacing decreases into the one of graphite, because of the reduction of GO by the removal of oxygen groups. As discussed in Fig. 5, pDop/rGO showed lower sudden reduction temperature and final d-spacing value than GO, which also means that the reduction capability is enhanced by introducing the polydopamine.

The improved reduction capability is also observed the result of electrical conductivity as shown in Fig. 7. At room temperature, the GO paper is electrically insulating but the pDop/rGO paper exhibit the electrical conductivity even though the value is very small (~10^{-4} S/cm). Also, at every annealing temperature, pDop/rGO paper showed higher electrical conductivity. For the comparison purpose, the electrical conductivity of hydrazine treated reduced graphene oxide (h-rGO) films was also plotted. At the high temperature, the pDop/rGO paper exhibited similar or higher electrical conductivity than h-rGO. This result may come from the high carbon yield of polydopamine

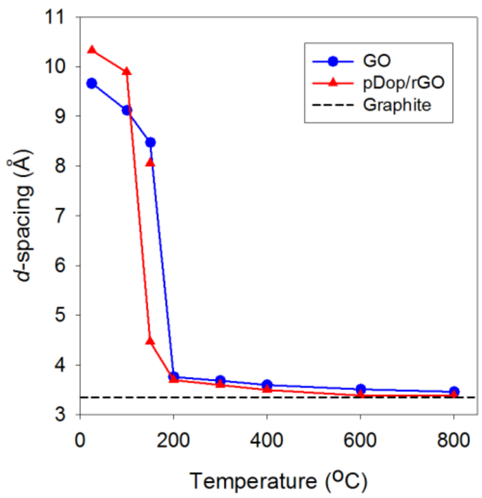

Figure 6. D-spacing plots from XRD analyses of GO and pDop/rGO.

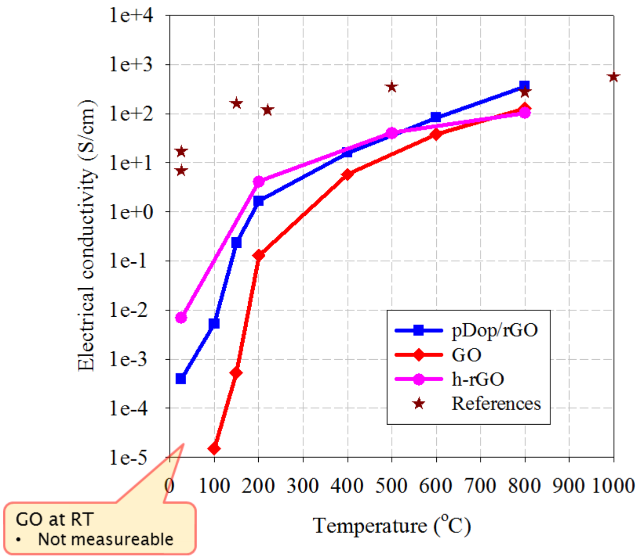

Figure 7. Electrical conductivities of GO, pDop/rGO and h-rGO w.r.t thermal annealing.

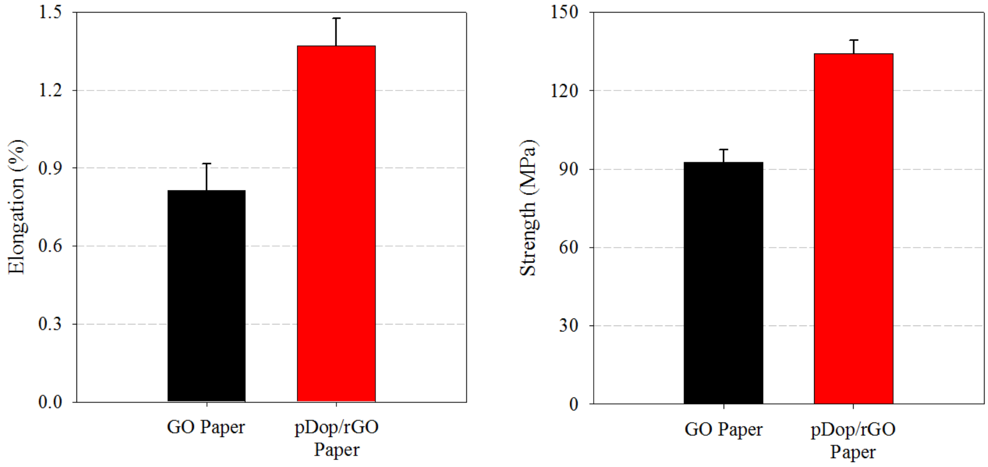

Figure 8. Mechanical properties of GO and pDop/rGO papers.

In Fig. 8, the tensile test results show the enhanced mechanical properties of pDop/rGO paper. The elongation and strength were increased by 70% and 35%, respectively, which means that the adhesive characteristic of polydopamine is effective to increase the mechanical property of graphene paper.

4 Summary

In this work, bio-inspired polydopamine was utilized to enhance mechanical and electrical properties of the graphene paper. Through the simultaneous filtration and polymerization technique of GO and dopamine, polydopamine embedded GO paper was manufactured having the sequentially layer-stacked form. The manufactured pDop/rGO paper showed better thermal stability, reduction performance, electrical conductivity and mechanical properties.

References

[1] Novoselov K.S., Geim A.K., Morozov S.V., Jiang D., Katsnelson M.I., Grigorieva I.V., Dubonos S.V., Firsov A.A., Two-dimensional gas of massless Dirac fermions in graphene, *Nature*, **438**, pp. 197-200 (2005).
[2] Zhang Y.B., Tan Y.W., Stormer H.L., Kim P., Experimental observation of the quantum Hall effect and Berry's phase in graphene, *Nature*, **438**, pp. 201-204 (2005).
[3] Geim A.K., Novoselov K.S., The rise of graphene, *Nature Mater.*, **6**, pp. 183-191 (2007).
[4] Stankovich S., Dikin D.A., Dommett G.H.B., Kohlhaas K.M., Zimney E.J., Stach E.A., Piner R.D., Nguyen S.T., Ruoff R.S., Graphene-based composite materials, *Nature*, **442**, pp. 282-286 (2006).
[5] Stankovich S., Dikin D.A., Piner R.D., Kohlhaas K.A., Kleinhammes A., Jia Y., Wu Y., Nguyen S.T., Ruoff R.S., Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon*, **45**, pp.1558-1565 (2007).
[6] Li D., Muller M.B., Gilje S., Kaner R.B., Wallace G.G., Processable aqueous dispersions of graphene nanosheets, *Nature Nanotechnol.*, **3**, pp.101-105 (2008).
[7] Dowell M.B., Howard R.A., Tensile and compressive properties of flexible graphite foils, *Carbon*, **24**, pp. 311-323 (1986).
[8] Liu J. et al., Fullerene pipes, *Science*, **280**, pp.1253-1256 (1998).
[9] Dikin D.A., Stankovich S., Zimney E.J., Piner R.D., Dommett G.H.B., Evmenenko G., Nguyen S.T., Ruoff R.S., Preparation and characterization of graphene oxide paper, *Nature*, **448**, pp.457-460 (2007).
[10] Chen H., Muller M.B., Gilmore K.J., Wallace G.G., Li D., Mechanically strong, electrically conductive, and biocompatible graphene paper, *Adv. Mater.*, **20**, pp.3557-3561 (2008).

[11] Kang S.M., Park S., Kim D., Park S.Y., Ruoff R.S., Lee H., Simultaneous reduction and surface functionalization of graphene oxide by mussel-inspired chemistry, *Adv. Func. Mater.*, **21**, pp.108-112 (2011).
[12] Marcano D.C. et al., Improved synthesis of graphene oxide, *ACS Nano*, **8**, pp.4806-4814 (2010).
[13] Liu R. et al., Dopamine as a carbon source: the controlled synthesis of hollow carbon spheres and yolk-structured carbon nanocomposites, *Angew. Chem. Int. Edit.*, **50**, pp.6799-6802 (2011).