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. 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 [5,6]. 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, 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 [11]. Therefore, pDop embedded rGO paper can be mechanically strong and electrically conductive without using toxic chemical and/or thermal annealing reduction processes.

2 Experiment and results
2.1 Fabrication of GO
GO was synthesized by the modified Hummers method [12] and its colloidal suspension was prepared in purified water. In this method, graphite powder is pretreated using sulfuric acid (H₂SO₄), potassium persulfate (K₂S₂O₈) and phosphorus pentoxide (P₂O₅). Then, the obtained pretreated graphite is oxidized using potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂) and P₂O₅. After removing Mn catalyst using hydrochloric acid and ethanol, graphene oxide particles are obtained through further rinsing.

Fig. 1. GO solution in water and TEM image
Fig. 1 shows well dispersed brown-color GO solution in water and TEM image of a single later GO which is 10μm size. Fig. 2 shows IR and Raman spectra of manufactured GO. From the IR spectrum, hydroxyl, carboxyl and epoxy functional groups are well identified as well as aromatic sp² carbon bond. From Raman spectrum, graphite’s characteristic 2D peaks disappear in GO and G peak became weak and broad. Also, D peak appears in GO due to the broken sp² network by oxidation.

2.2 Fabrication of GO and pDop/rGO papers

GO and pDop/rGO papers were manufactured using a simple vacuum-assisted filtration method. Since GO has many hydrophilic oxygen functional groups, it can be well dispersed in water. Therefore, GO/water solution is filtrated to obtain pure GO paper. For the pDop/rGO paper, dopamine solution was used instead of distilled water. Here, dopamine hydrochloride is dispersed into pH 8.5 Tris-buffer solution. It is well known that dopamine is easily self-polymerized in alkaline solution as shown in Fig 3. Therefore, simultaneous polymerization and filtration can be achieved in a single-step.
Since the polymerization of dopamine is oxidative, GO can be reduced when pDop is embedded into GO paper’s layers. As shown in Fig. 4, GO paper is semi-transparent while pDop/rGO paper is opaque black. From the SEM image of pDop/rGO paper in Fig. 5, pDop was successfully embedded and infiltrated into individual GO paper’s layers.

2.3 Reduction of GO by pDop

The reduction of GO by pDop was verified using IR spectra for GO, pDop/rGO and NaOH washed pDop/rGO papers. To examine reduction status of GO only, over-remaining pDop was removed using 1M NaOH solution. As seen in Fig. 6, the IR spectrum of pDop/rGO without NaOH treatment shows similar peaks with pure pDop IR peaks such as –OH, aromatic C=C, hydroxyl C=O in catechol group and C-N stretch peak. As for the NaOH treated pDop/rGO paper, 1515 cm⁻¹ characteristic peak of pDop disappeared, which shows that residual pDop was successfully removed. Also, 1718 cm⁻¹ C=O peak in GO disappeared in NaOH treated pDop/rGO, which confirms that GO is reduced by polymerization of dopamine.

2.4 Electrical conductivities

As shown in Fig. 7, pDop/rGO paper showed better electrical conductivity than GO paper. Here, sheet resistance was measured using four-point probe method. At the room temperature, GO paper did not show any electrically conducting behavior while pDop/rGO paper showed 10⁻⁴ S/cm, which can also represent the reduction of GO by pDop. Additionally, low-temperature annealing was also considered. Heat treatment was performed during 1hr at 100, 150 and 200 °C. For each temperature, pDop/rGO paper showed significantly higher electrical conductivity as 320~5,700 times than GO paper.

2.5 Mechanical properties

In order to verify the enhancement of mechanical property by dopamine’s adhesive capability, tensile tests were carried out using Instron 5543 machine. Here, 50N load cell was used and loading rate was 10μm/min. Also, preload was selected as 0.001N. Tensile samples were obtained by cutting papers and sample size was 3mm-width and 15mm-gauge length. Sample thickness was 18 and 20 μm for GO and pDop/rGO papers, respectively. Fig. 8 shows mechanical property result which can be easily seen that pDop/rGO paper has much better strength as 35% improvement. This represents that pDop is effective strengthening materials for the GO papers.
3 Conclusion

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. 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.

References