*The 2016 World Congress on*
***Advances in Civil, Environmental, and Materials Research (ACEM16)***
*Jeju Island, Korea, August 28-September 1, 2016*

Keynote Paper

# Solution processing of graphene derivatives for electronic applications

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## ABSTRACT

Owing to their outstanding electrical and mechanical properties, graphene derivatives have attracted immense attention for applications in electronic devices, batteries, and sensors for healthcare. Here, we report the fabrication of three different composites using graphene derivatives via a cost-effective solution-based method. We first fabricated foldable electronic circuits on paper substrates by using the vacuum filtration of graphene nanoplatelets (GNPs) and selective transfer method. The electronic paths of the graphene electronic circuits were maintained even after the repetitive folding and unfolding. We then fabricated flexible, binder-free graphene papers for electrodes in Li ion batteries by using graphene oxide and GNPs. These graphene papers exhibited high electrical conductivity and charge capacity. We also fabricated multi-functional thin film structures of GNPs through a layer-by-layer assembly method. These films showed improved optical transparency and gas barrier properties. Graphene-based strain sensors were also fabricated by coating the surface of these films with stretchable yarns. The graphene strain sensors were used to monitor diverse human motions.

## 1. INTRODUCTION

Graphene derivatives, such as graphene nanoplatelets (GNPs), graphene oxide (GO) and reduced graphene oxides (rGOs), have attracted considerable attention in electronic applications because of their excellent conductivity, gas barrier performance, mechanical properties, and flexibility (Kim 2015, Hyun 2013, Kim 2015, and Park 2015). Many researchers have investigated the properties of graphene prepared by the chemical vapor deposition (CVD) method. The CVD-grown graphene possesses good electrical properties. However, this method is unsuitable for mass-production and industrial use.

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In this work, we fabricated three different applications using graphene derivatives and solution process: foldable graphene electronic circuits, free-standing GNP/GO paper electrodes, and highly stretchable graphene strain sensors. The solution fabrication was carried out by a facile, cost-effective, and scalable method. The foldable graphene circuits on paper substrates were fabricated by the vacuum filtration of a dispersion of GNPs and selective transfer printing method. The free-standing GNP/GO paper electrodes were also obtained by the vacuum filtration of a dispersion of GNP/GO. A strain sensor was fabricated using graphene composite films via the layer-by-layer (LbL) assembly method. These composites containing graphene derivatives showed good performance and potential for diverse electronic applications.

## 2. FABRICATION OF FOLDABLE GRAPHENE ELECTRONIC CIRCUITS ON PAPER SUBSTRATES VIA VACUUM FILTRATION

The foldable graphene circuits were fabricated using a facile solution-based process reported previously (Hyun 2013). We also characterized the obtained foldable graphene circuits. The schematic for the solution-based process used in this work is shown in Figs. 1a–c. The graphene paper was successfully prepared by the vacuum filtration of the dispersion of GNPs with poly(4-styrenesulfonic acid) (PSS). The aromatic rings of amphiphilic surfactants like PSS are easily adsorbed on graphene via the edge-to-face aromatic interactions. (Hyun 2013 and Stankovich 2006) Thus, PSS facilitated the uniform deposition of the GNPs on the paper substrate. Moreover, the sulfonic groups of PSS inhibit the agglomeration of GNPs in a polar solvent (Hyun 2013, Stankovich 2006, and Park 2015). In addition, the hydrophilic sulfonic groups of PSS

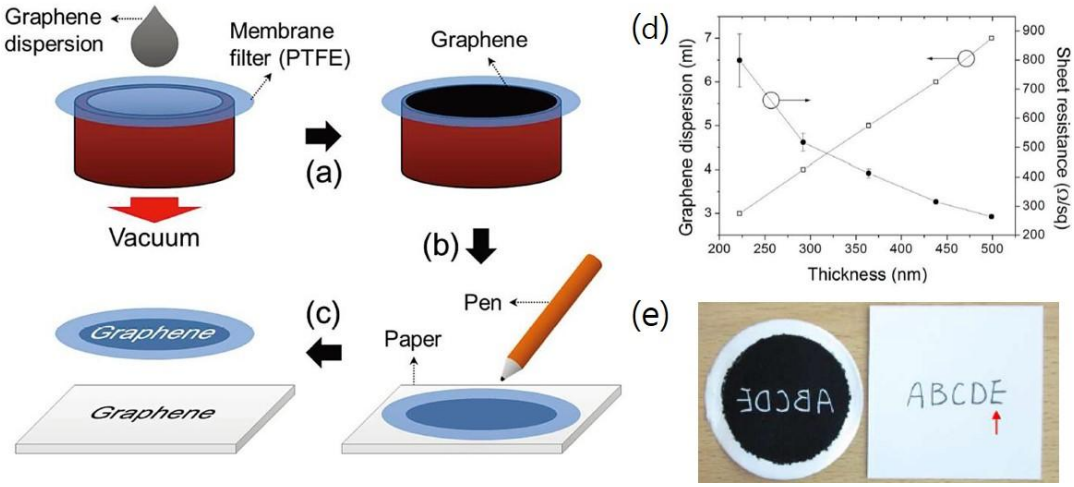


Fig. 1 (a–c) Schematic for the preparation of graphene circuits on paper substrates by using the vacuum filtration and selective transfer methods. (d) The thickness and sheet resistance of the graphene circuits were controlled by varying the amount of the graphene dispersion used (e) Alphabet line patterns could be easily created on the paper substrates without using any specialized mask. [Reproduced with permission from Ref. Hyun 2013, Copyright 2013 Wiley-VCH]

facilitated the separation of the filtered graphene from the hydrophobic surface of the filters. As a result, we could easily fabricate the foldable graphene circuits because of the presence of PSS.

The width and thickness of the electronic circuits could be easily controlled, and the circuit patterns could be obtained without using any specialized mask by the simple selective transfer printing method (Figs. 1d and e). The thickness of these circuits was found to be proportional to the amount of the graphene dispersion used. Hence, the surface resistance of the circuits also showed a gradual decrease with an increase in the amount of graphene deposited on the filter paper (Fig. 1d). In addition, the width could be easily tuned by varying the thickness of the pen tip (Fig. 1c). These results indicate that the dimensions and electrical properties of the circuits could be easily controlled.

To evaluate the folding properties of the graphene circuits, we measured the ratio of conductance (G) to the initial conductance ($G_0$) under negative and positive foldings (Fig. 2a). The relative conductance of the circuits decreased by 4.3 and 6.7% at the foldings of -180 and +180°, respectively, indicating that the conductance of the folded circuits was almost constant with only a slight decrease. Interestingly, as shown in Fig. 2b, the degree of deformation of the circuits was different during the negative and positive angle foldings. This is attributed to the smaller radius of curvature of the circuits under negative folding than that under positive folding. However, the graphene circuits

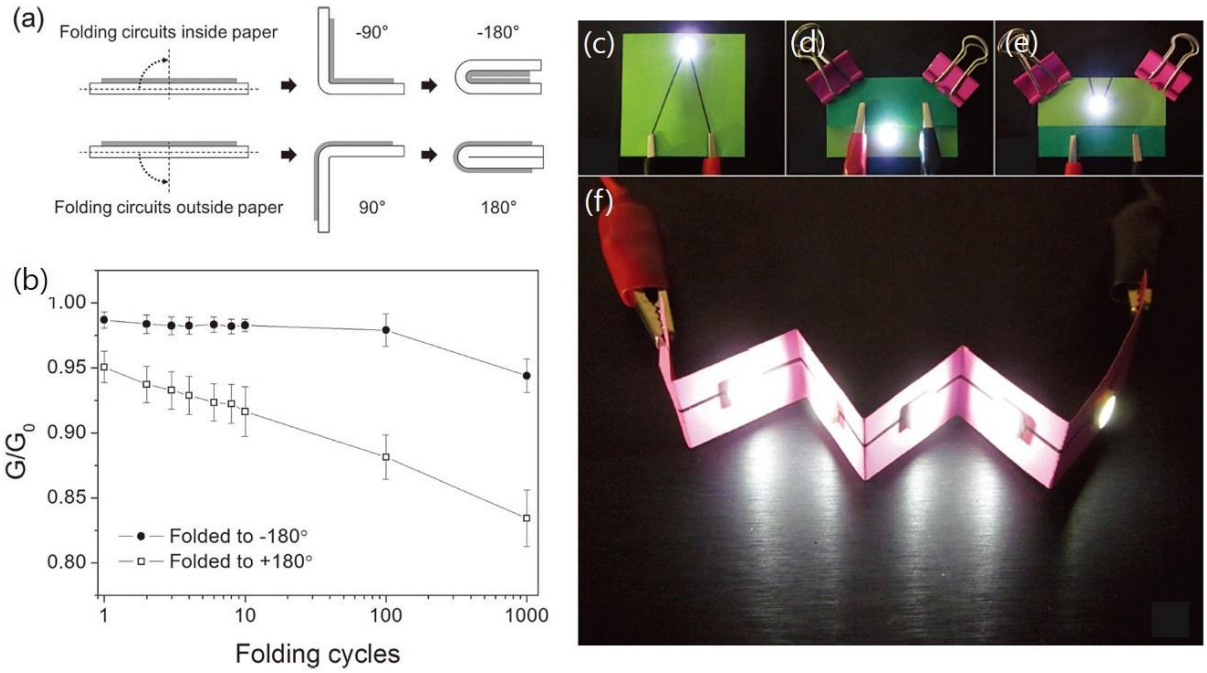


Fig. 2 (a) Schematic for the folding angles of the graphene paper (b) The relative conductance of the graphene circuits after repetitive folding and unfolding tests. (c–e) Photograph showing the operation of an LED chip on the graphene circuits fabricated on paper substrates under the foldings of -180 and +180°, (f) Photograph of an LED chip array on a circuit board under negative and positive angle foldings. [Reproduced with permission from Ref. Hyun 2013, Copyright 2013 Wiley-VCH]

exhibited a better folding stability than the metallic circuits fabricated in a previous study(Siegel 2010). The graphene circuits maintained around 94 and 83% of their conductance under -180 and +180° foldings, respectively after 1000 cycles (Fig. 2b), indicating that these circuits can provide a stable conductance for paper-based electrical applications. To demonstrate their practical applications, we connected light emitting diode (LED) chips to the foldable circuit boards. The LED chips on the circuit boards worked well without getting disconnected under the negative and positive foldings (Figs. 2c–f).

## 3. HIGHLY FLEXIBLE GRAPHENE/GRAPHENE OXIDE PAPERS FOR LITHIUM ION BATTERY ELECTRODES

Flexible, free-standing graphene/graphene oxide papers for electrodes in Li ion batteries (LIBs) were fabricated using a simple solution process via the vacuum filtration method (Figs. 3a and b) (Kim 2015). Since these graphene paper electrodes were formed by using the GNPs with high conductivity, post-annealing treatment was not required to enhance their electrical properties. In addition, the graphene papers fabricated using GNPs had an intrinsic wrinkled structure, leading to the formation of a stacked sheet with high surface area (Figs. 3c and d). This microscopic wrinkled and porous structure is essential for the diffusion channels for the transport of Li ions. More importantly, GO can be used both as a structural stabilizer and Li storage material

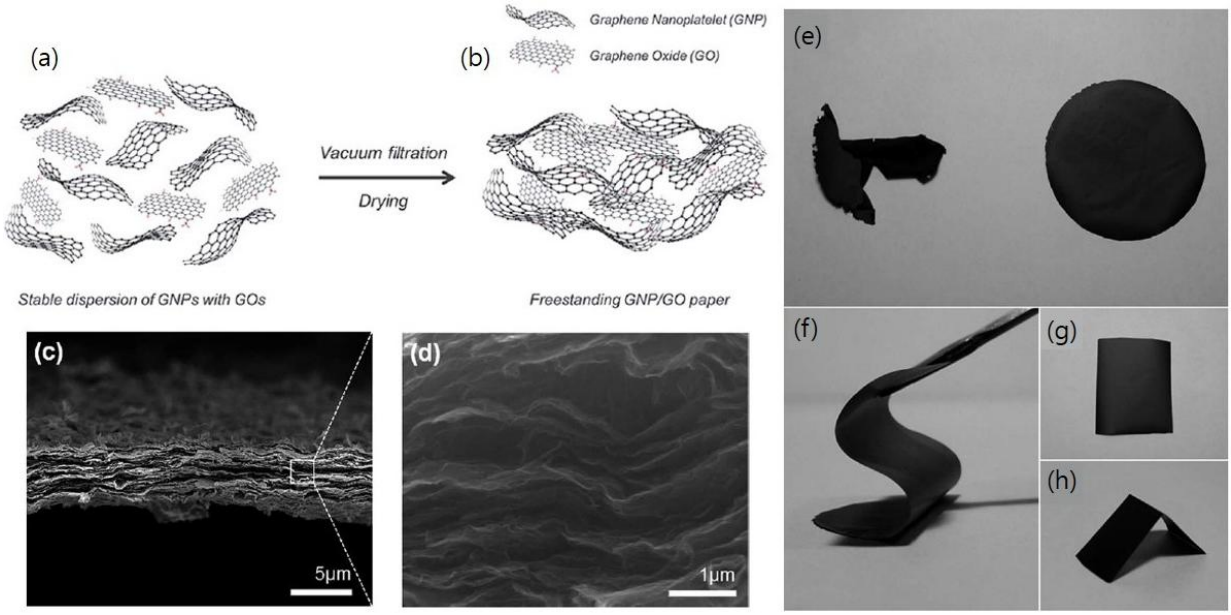


Fig. 3 (a, b) Schematic for the fabrication of GNP/GO papers. (c, d) The cross-sectional SEM images of the GNP/GO paper with wrinkled and open structure. Optical images of the GNP paper (e) without GO (left) and with GO (right), (f–h) GNP/GO papers showing flexible and foldable properties. [Reproduced with permission from Ref. Kim 2015, Copyright 2015 Royal Society of Chemistry]

owing to its amphiphilic surface properties. GO has hydrophobic graphene domains and hydrophilic oxygen functional groups on the basal planes and edges, respectively (Aboutalebi 2011 and Kim 2012). Therefore, in an aqueous solution system, GO acts as an effective two-dimensional surfactant facilitating the fabrication of films having a paper-like structure (Figs. 3e–h).

The GNP/GO papers showed excellent electrical conductivity and desirable structural features without post-annealing treatments. Moreover, the high flexibility of the paper electrodes enabled us to fabricate a fully flexible LIB. As shown in Fig. 4a and b, the bent cell with a bending radius of 15 mm exhibited a stable cycling and capacity retention of 66.7% over 55 cycles. This suggests that GNP/GO papers can be used as potential electrodes in flexible energy storage devices. Furthermore, the pouch-type full LIB cell with a $LiCoO_2$-coated Al foil as the cathode and the GNP/GO paper anode could operate a blue LED under both flat and bent configurations (Figs. 4c and d).

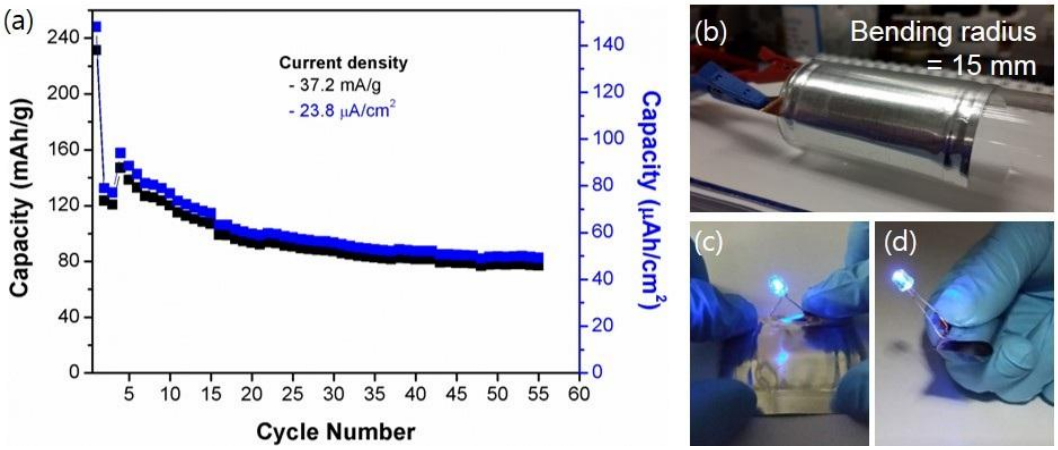


Fig. 4 (a) Specific capacity vs. cycle number for the flexible pouch-type LIB half-cell using a GNP/GO paper electrode at a current density of 37.2 mA $g^{-1}$. (b) Photograph of the flexible cell with a bending radius of 15 mm. (c, d) Photographs of (c) flat and (d) bent LIB full-cell showing that a blue LED worked well in both the cases. [Reproduced with permission from Ref. Kim 2015, Copyright 2015 Royal Society of Chemistry]

## 4. HIGHLY MULTI-FUNCTIONAL THIN GRAPHENE FILMS FABRICATED BY USING LAYER-BY-LAYER ASSEMBLY

In this part, we introduce a facile, low-cost, and solution-based nano-fabrication method for the fabrication of thin graphene films, which is based on the alternative adsorption of the materials with secondary interactions and uses an LbL assembly (Kim 2015 and Park 2015). Graphene sheet is the building block of multi-functional films. The LbL-assembled graphene composite films were fabricated by using the secondary interactions including hydrophobic, van der Waals, and hydrogen-bonding interactions between poly(vinyl alcohol) (PVA) and GNP in the presence of PSS (Park 2015, Shim

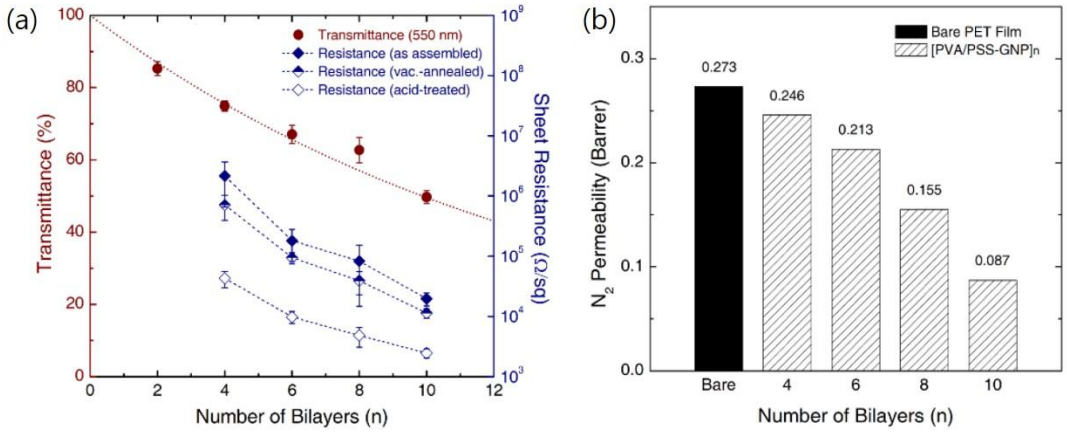


Fig. 5 (a) Transmittance and sheet resistance of thin graphene films as a function of the number of bilayers. (b) Nitrogen gas permeability of the graphene films as a function of the number of bilayers. [Reproduced with permission from ref. Kim 2015. Copyright 2015 IOP Publishing]

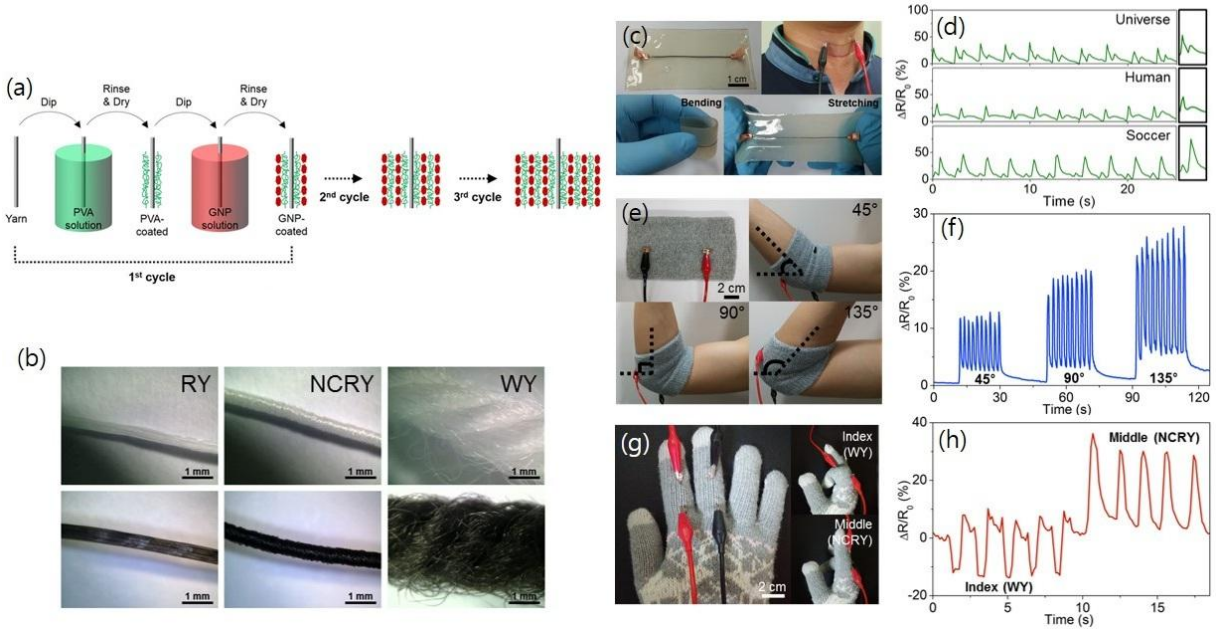


Fig. 6 (a) The LbL assembly method for the fabrication of a graphene-based strain sensor using stretchable yarns. (b) The photographs of the stretchable yarns before and after three cycles of the LbL assembly process. (c) The photographs of the RY strain sensor for the detection of small-scale motions. (c) The relative resistance change signals for different phonations. (e) The photographs of the NCRY strain sensor with an elbow wrap to detect large-scale motions. (j) The change in relative resistance generated by the NCRY sensor as a response to the bending motions. (g) The photographs of the WY and NCRY sensors implanted in a glove to monitor the movements of the index and middle fingers. (h) The relative resistance change signals generated by the WY and NCRY sensors showing distinct signals. [Reproduced with permission from Ref. Park 2015, Copyright 2015 American Chemical Society.]

2007, and Lee 2012). The thin graphene films showed good electrical conductivity, flexibility, optical, and gas barrier properties. As shown in Fig. 5a, the optical transmittance and sheet resistance of the films could be tuned by varying the number of repetitions of LbL steps. In addition, the gas barrier property for nitrogen gas was enhanced with an increase in the number of graphene film layers (Fig. 5b).

Furthermore, we developed stretchable and wearable graphene-based strain sensors using a GNP dispersion solution and stretchable yarns via the LbL technique (Park 2015). Figure 6a shows the schematic for the fabrication of graphene-based strain sensors by using the noncovalent bonding interactions of PVA and GNP in the presence of PSS. The white bare yarns turned black after the LbL assembly processing (three cycles) because of an increase in the number of GNP layers (Fig. 6b). To demonstrate the feasibility of this method, three types of strain sensors were fabricated and the piezoresistive characteristics of these sensors were monitored for different human motions (Figs. 6c–h). The rubber yarn (RY) sensor with high sensitivity is desirable for monitoring small-scale motions (Figs. 6c and d). The nylon covered rubber yarn (NCRY) sensor is suitable for detecting large-scale motions owing to its high stretchability and linear piezoresistivity (Figs. 6e and f). Moreover, since the wool yarn (WY) sensor exhibited a negative sensing response, we could obtain opposite responses for similar bending motions by using the data glove with the WY (Index) and NCRY (Middle) sensors (Figs. 6g and h). These characteristics of the graphene-based sensors enabled us to monitor diverse human motions.

## 5. CONCLUSIONS

In summary, we investigated various solution-based fabrication methods using graphene derivatives for fabricating composites for electronic applications including electronic circuits, battery electrodes, and strain sensors. Foldable electronic circuits were fabricated by the simple vacuum filtration and selective transfer methods. The circuits exhibited a small change in conductance after repetitive folding and unfolding. We also demonstrated a facile solution-based method to fabricate GNP/GO paper electrodes for LIBs. The GNP/GO papers showed increased interlayer spacing and wrinkles resulting in an improved energy storage and good flexibility. Hence, the paper electrodes could be potential candidates for flexible and foldable energy devices. We also fabricated multi-functional thin films of GNPs using the LbL assembly method. The graphene composite films showed optical transparency and improved gas barrier properties. Furthermore, we can fabricate the graphene-based strain sensors using the LbL assembly method to monitor diverse human motions. We believe that these studies provides the practical and meaningful solution-based methods for fabricating graphene-based composites and realizing their electronic applications.

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