

Electronic Supplementary Information (ESI)

Layer- structured graphene oxide/polyvinyl alcohol nanocomposites: Dramatic enhancement of hydrogen gas barrier property

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Materials:

Graphite and PVA were purchased from Sigma Aldrich, Germany. PET films (Mylar® 500, DuPont, USA) were used as substrates for coating with polymer nanocomposites. Sulfuric acid (H₂SO₄), hydrochloric acid (HCl) and potassium permanganate were purchased from Samchun Pure Chemical Co. Ltd., Korea.

Modification of polyethylene terephthalate (PET) surface:

The surface of PET was modified by plasma treatment.¹ For this purpose; PET films were cut into 6×5 cm sizes. The PET films were first, sonicated with methanol for 30 minutes and then in water for another 30 minutes. After that, the films were dried at room temperature and plasma treatment for 5 minutes was carried out to increase the hydrophilic nature of the PET surface.¹

Synthesis of graphene oxide (GO):

Modified Hummers method² was used to prepare graphene oxide (GO). Typically, 23 ml of concentrated sulfuric was poured in a round bottom (RB) flask and was allowed to stir using a bar magnet. The temperature of the reaction mixture was maintain a 0-5 °C during the reaction period using an ice bath. Then, about 3 gm potassium permanganate was added very slowly during the time span of 10-15 minute into the conical flask with continuously stirring

and the reaction mixture was allowed to stir for another 2 h. After that, the ice bath was removed and the RB was transferred to an oil bath at 35 ± 2 °C and allowed to stir for another 12 h to make a thick paste. Then, 46 mL of ultrapure water was gently poured into the reaction mixture which caused an abrupt rise in reaction mixture temperature to about 90 °C. The reaction mixture was stirred for an additional 30 minutes and 280 mL of water was mixed in with it followed by addition of 1.5 mL (30 %) H₂O₂. After that, a dilute solution of HCl was added to the reaction mixture to remove excess manganese salt. Then, the reaction mixture was repeatedly centrifuged and re-dispersed in water until the pH of the supernatant solution was neutral. Finally, the obtained GO was collected by drying the GO in vacuum at 60 °C for 3 days.

Fabrication of layer-structure graphene oxide and layered structure graphene oxide /polyvinyl alcohol composite nanocomposite-coated PET:

Initially, 100 mg of GO was dispersed in 100 ml water by ultra-sonication for half an hour. Then, this solution was filtered through a 0.2 µm cellulose acetate filter paper using vacuum filtration to reduce the solution volume. After that, this GO solution was transferred into a culture tube. To avoid GO loss, the cellulose acetate membrane was washed with a small amount of water several times and the solution was transferred into the culture tube. Finally, 1 mL of solution was dried at 60 °C and measured weight to determine the concentration of GO (8 mg/ml). A layered structure GO/PVA composite solution was prepared by dissolving the measured amount of PVA (GO: PVA = 8:2) into the layered structure GO solution. Coatings over modified PET substrates were carried at 60 °C by spraying a GO/PVA nanocomposite solution on the PET surface using a spray gun. The samples were dried under air flow. The distance between the spray gun and PET surface remain fixed during the

coating process. The GO coated and PVA coated samples were prepared in a similar manner by taking pure GO and pure PVA solution instead of the GO/PVA solution.

References:

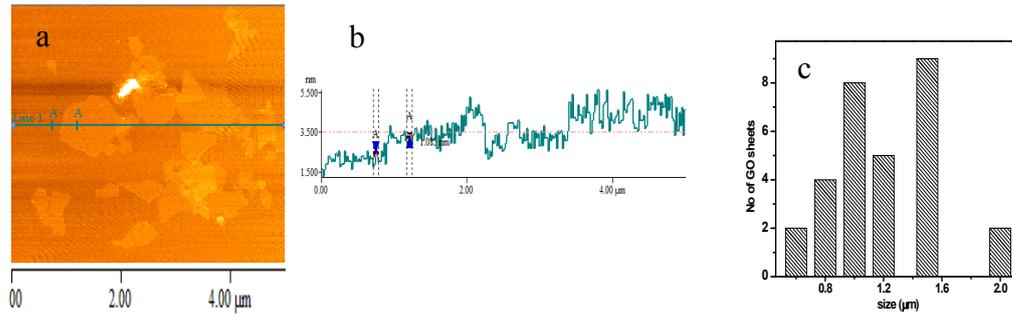
1. Q. T. Le, J. J. Pireaux and J. J. Verbist, *surf. & interface analysis*, 1994, 22, 224.
2. Hummers, W. S., R. E. Jr. Offeman, *J. Am. Chem. Soc.*, 1958, 80, 1339.

Characterization:

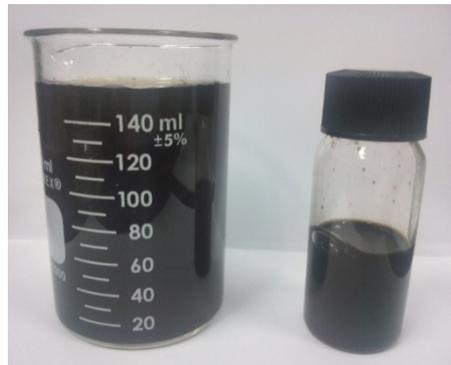
To conduct AFM experiment, the sample was prepared by casting a drop of GO (0.01%, w/v) solution on a mica surface. The sample morphology was observed using AFM (Veeco; model AP 0100) in non-contact mode. For transmission electron microscopy (JEM2200FS Jeol, Japan) of GO, an aqueous solution of layered structure GO (8mg/ml) was diluted to 0.05 % w/v and a drop was allowed to dry at room temperature on a carbon-coated copper grid. The FTIR spectroscopies of PVA, layered GO and layered GO/PVA nanocomposite samples were recorded using an FTIR (Thermo Scientific, USA). A cross-sectional FESEM study of the GO paper, layered structure GO coated PET and layered structure GO/PVA nanocomposite coated PET films was conducted by sputtering osmium prior to examination using a field emission scanning electron microscope (FESEM) (JSM-6701 Jeol, Japan). The surface morphology was also observed by osmium puttering over the specimen surface. Wide angle x-ray scattering (WAXS) of PVA, GO and GO/PVA nanocomposite films were carried out using a D/Max 2500V/PC (Rigaku Corporation, Japan) at room temperature with a scan rate 2 °/min. Hydrogen gas barrier properties of uncoated PET, PVA coated, GO coated and GO/PVA nanocomposite-coated PET samples were measured using a GDP-E (Brugger Feinmechanik GmbH) gas permeability machine. The size of the sample was made 10.17 cm² by using masking film to measure the gas transmittance rate. The measurement temperature was 25 °C and gas supply was carried out at 100 kPa pressure.

Results and discussion:

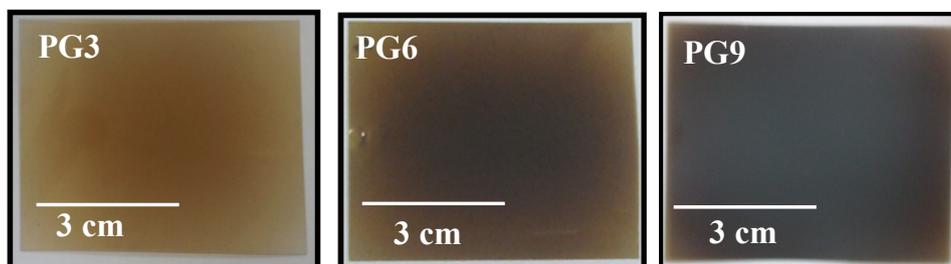
AFM image and the corresponding height profile have presented in SI figure 1a&b. From the figure, it is clear that height of the GO sheet is 1.08 nm. The size distribution of GO sheets has made by measuring the size of GO sheet from ~ 30 objects and has presented in a histogram (SI figure 1c).



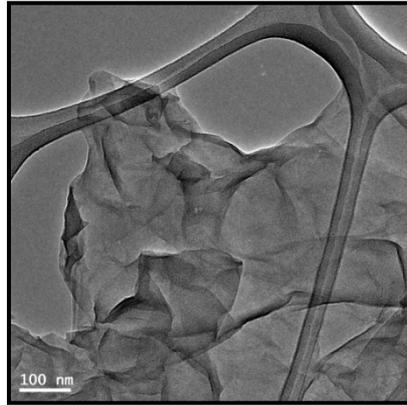
SI Figure 1. (a) AFM image, (b) height profile, and (c) histogram for size distribution of GO sheets from ~ 30 objects



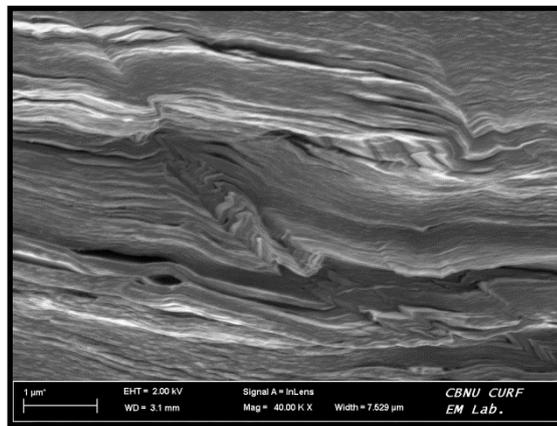
SI Figure 2. Dispersion pictures of GO (1mg/ml) in water before vacuum filtration and (b) layered structure GO (8mg/ml) after reduction of solution volume by vacuum filtration.



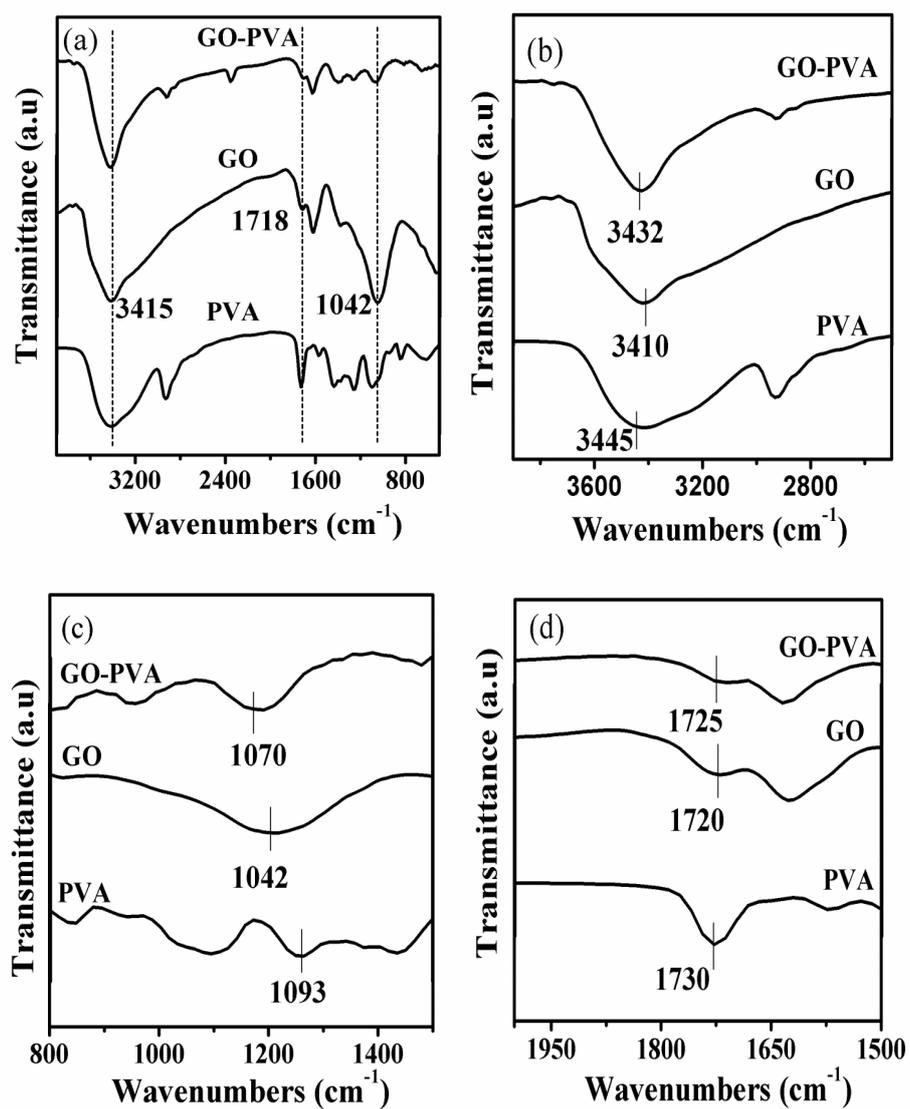
SI Figure 3. Photographs of (a) PG3 (b) PG6 and (c) PG9



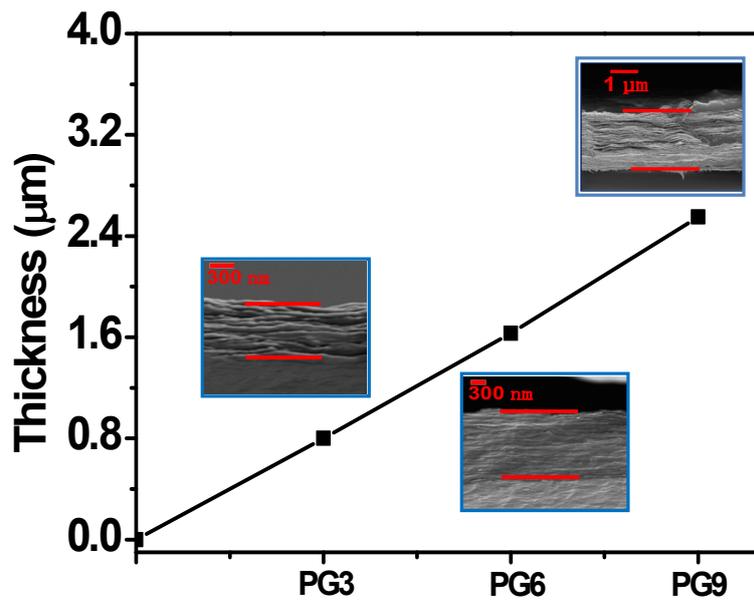
SI Figure 4. TEM image of GO dispersion from aqueous solution.



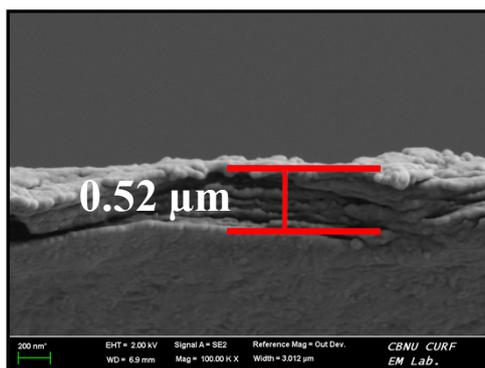
SI Figure 5. FESEM image of GO paper prepared by vacuum filtration.



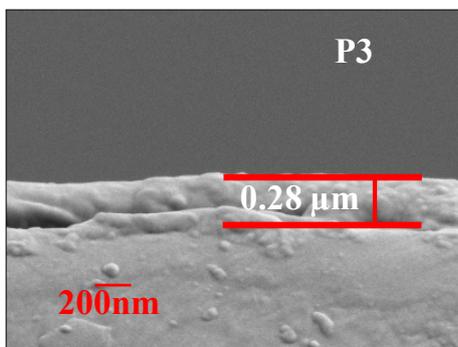
SI Figure 6. FTIR spectra of (a) PVA, layered structure GO and layered structure GO/PVA nanocomposite and their enlarged images showing (b) the -OH stretching band, (c) the -C=O stretching band and (d) the epoxy stretching band.



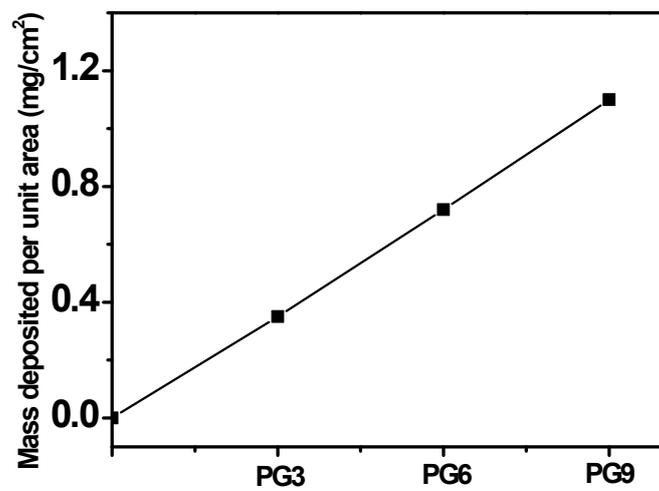
SI Figure 7. Thickness of different GO/PVA nanocomposite-coated samples



SI Figure 8. Cross sectional FESEM image of G3.



SI Figure 9. Cross-sectional FESEM image of P3



SI Figure 10. Mass deposition per unit area of different GO/PVA nanocomposite-coated samples

SI Table-1. Hydrogen barrier parameters of uncoated PET and different GO/PVA nanocomposite coated PET samples.

| Sample | Coating thickness (μm) | Total film thickness (μm) | Hydrogen transmittance rate ($\text{cc m}^{-2} \text{atm}^{-1} \text{day}^{-1}$) | Permeability coefficient ($\text{cc mm m}^{-2} \text{atm}^{-1} \text{day}^{-1}$) |
|--------|-------------------------------------|--|--|--|
| PET | - | 110 | 122 | 13.42 |
| PG3 | 0.82 | 110.82 | 21 | 2.32 |
| PG6 | 1.56 | 111.56 | 14 | 1.56 |
| PG9 | 2.56 | 112.56 | 5 | 0.56 |
| G3 | 0.52 | 110.52 | 69 | 7.62 |
| P3 | 0.280 | 110.28 | 110 | 12.40 |

SI Table-2. Oxygen barrier parameters of uncoated PET and PG3 samples.

| Sample | Coating thickness (μm) | Total film thickness (μm) | Oxygen transmittance rate ($\text{cc m}^{-2} \text{atm}^{-1} \text{day}^{-1}$) | Permeability coefficient ($\text{cc mm m}^{-2} \text{atm}^{-1} \text{day}^{-1}$) |
|--------|-------------------------------------|--|--|--|
| PET | - | 110 | 21.2 | 2.23 |
| PG3 | 0.82 | 110.82 | 0.78 | 0.086 |