Electronic Supplementary Material (ESI) for Nanoscale
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Tuning nanostructure of graphene oxide/polyelectrolyte LbL assemblies by controlling pH of GO suspension to fabricate transparent and super gas barrier films

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1. Experimental set-up

Fig. S1. Homebuilt robotic dipping machine.

2. Chemical compositions of GO

Fig. S2 shows the results of Fourier transform infrared spectroscopy for graphite and graphite oxide. We can see that graphite oxide has many oxygen groups such as hydroxyl (-OH), carboxyl (COOH), epoxy (C-O-C), and caboxylate (COO^-), which provide the negative charge necessary for the layer-by-layer assembly process. Fig.

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S3 indicates that the zeta potentials of GO suspensions are pH-sensitive. GO sheets can form a stable suspension in the pH range of 3-12 because its zeta potential is lower than -30 mV. When the zeta potential values of particles are lower than -30 mV, they are considered to have repulsive forces that are strong enough to maintain a stable solution. From Fig. S3, we can also see that the zeta potential decreases from -25.7 to -51.7 mV in the pH range of 2-8, because the COOH of GO ionizes more to form COO^-. The zeta potential increase (when pH > 8) results from the compression of the double layer at high ionic strengths [1]. The results in Fig. S3 are similar to those in previous reports [1-2]. The typical pKa of COOH groups is around 4.7. According to a previous report [1], the pKa value of the COOH groups of GO is 4.3. The concentration of the ionized group on GO can be roughly estimated to be 0.01-0.04 mol/L in the pH range of 2-12 [1]. X-ray photoelectron spectroscopy gives quantitative data on the chemical compositions of the graphite oxide synthesized by oxidizing graphite. We can discern from Table S1 that the oxygen concentration in the resulting graphite oxide is much higher (30.64 mol%). As listed in Table S2, the concentration of the oxygen groups in graphite oxide is 38.0% (C-O), 9.7% (C=O), and 7.8% (O=C-O).

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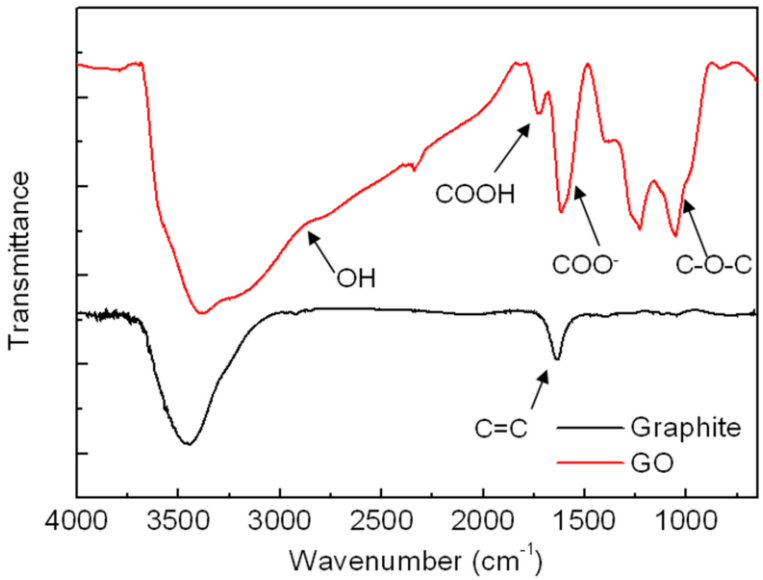

Fig. S2. FTIR spectra for graphite and graphite oxide.

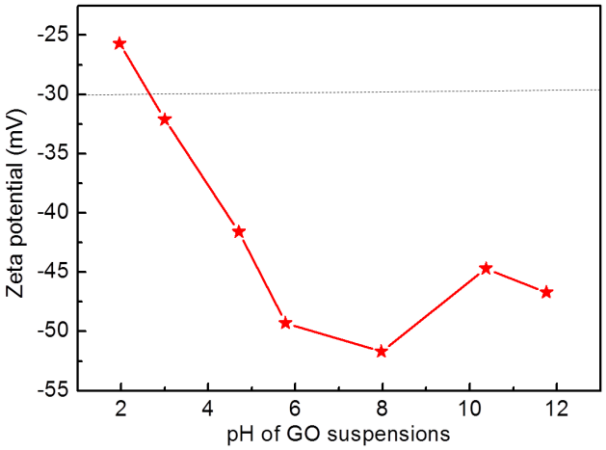

Fig. S3. Zeta potential of GO suspension as a function of its pH.

Table S1 Atomic composition of graphite and graphite oxide.

Material	Atomic composition (%)	
	C	O
Graphite	98.03	1.975
Graphite oxide	69.36	30.64

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Table S2 Composition of the chemical groups of graphite oxide.

Material	Chemical group composition (%)			
	C-C	C-O	C=O	O=C-O
Graphite oxide	44.5	38.0	9.7	7.8

3. Thermal properties of graphite oxide

Based on the thermal gravimetric analysis curves (Fig. S4) of graphite and graphite oxide, measured in nitrogen atmosphere, we can observe only 2-3% wt loss for graphite, indicating that there are few oxygen groups. The graphite oxide indicates two major weight losses, which are attributed to the following: (1) a 10% weight loss below 200 °C, due to the evaporation of the absorbed water in the interlayer spacing of the graphite oxide sheets; and (2) a weight loss between 200 to 300 °C, indicating the decomposition of oxygen-containing groups, the composition of which is about 30 wt%.

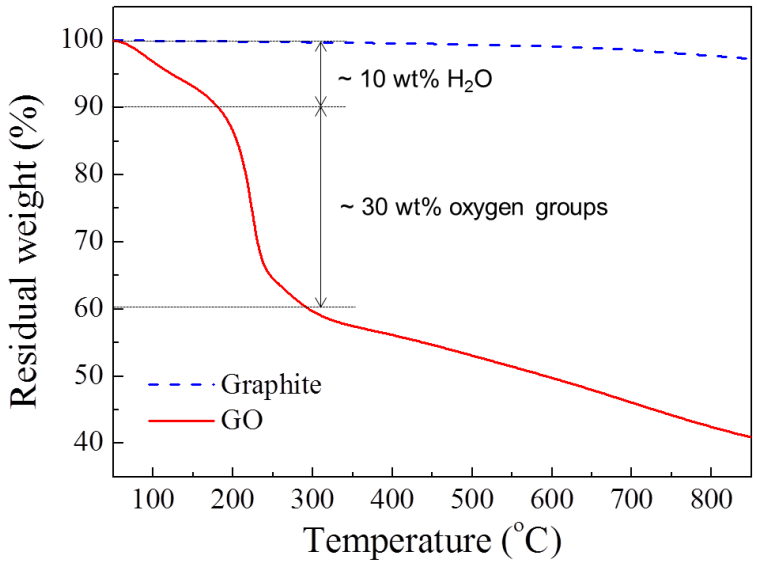

Fig. S4 TGA curves of graphite and graphite oxide.

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4. Barrier performance of assemblies

Table S3 OTR, O_2 permeability, and BIF of PET and GO/BPEI thin-film assemblies.

Assembly	Assembly thickness [a] [nm]	OTR [cm^3 m^{-2} day^{-1} atm^{-1}]	Oxygen permeability [10^{-16} cm^3 cm cm^{-2} s^{-1} Pa^{-1}]		
			Film assembly [b]	Film + substrate	BIF [c] (P_S/P_T)
Pristine PET	-	11.45	-	16.35	1
$(GO/BPEI\text{-}2.5)_5$	12.9	8.77	0.0055	12.53	1.3
$(GO/BPEI\text{-}3.5)_5$	27.1	0.37	0.00012	0.528	30.9
$(GO/BPEI\text{-}3.5)_{10}$	47.2	< 0.05	< 0.000027	< 0.071	> 228.9
$(GO/BPEI\text{-}4.7)_5$	17.4	0.86	0.00018	1.23	13.31
$(GO/BPEI\text{-}6.0)_5$	16.2	5.33	0.00185	7.61	2.15
$(GO/BPEI\text{-}8.0)_5$	16.1	10.29	0.01872	14.69	1.1

[a] The thickness of the film assemblies on Si wafers was measured by ellipsometry.

[b] The permeability of film assemblies was estimated using the calculation method by previous reports. [3-4]

[c] The thin-film barrier performance was judged based on the barrier improvement factor (BIF):

$$BIF = \frac{P_S}{P_T}$$

where P_S = the permeability of the substrate (pristine PET) and P_T = the permeability of film + substrate.

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5. Structure of LbL assemblies

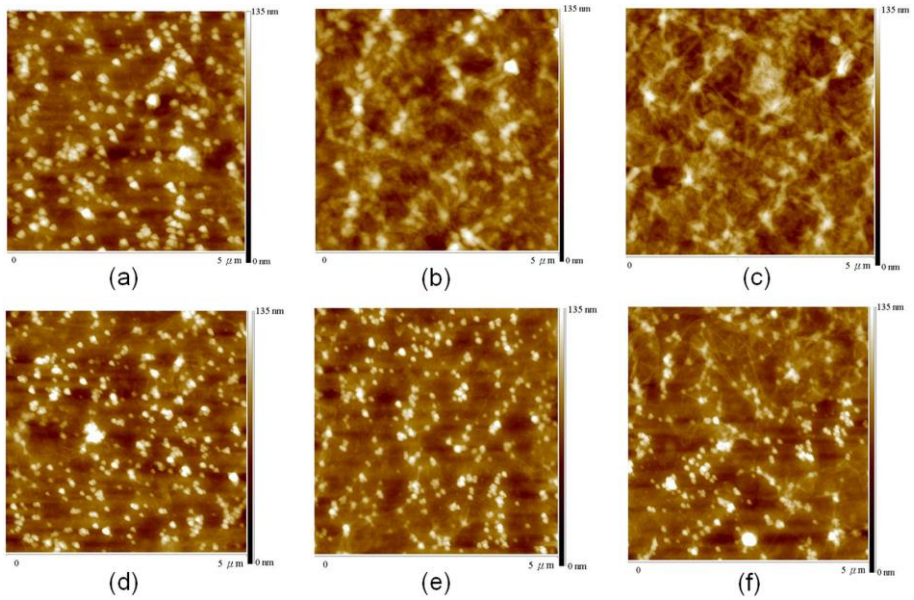

Fig. S5 AFM height-profile images (5 × 5 μm) of the $(GO/BPEI)_5$ films prepared at different pH values of the GO suspension: (a) 2.5, (b) 3.0, (c) 3.5, (d) 4.7, (e) 6.0, and (f) 8.0. (These images were taken in air using the ScanAsyst mode)

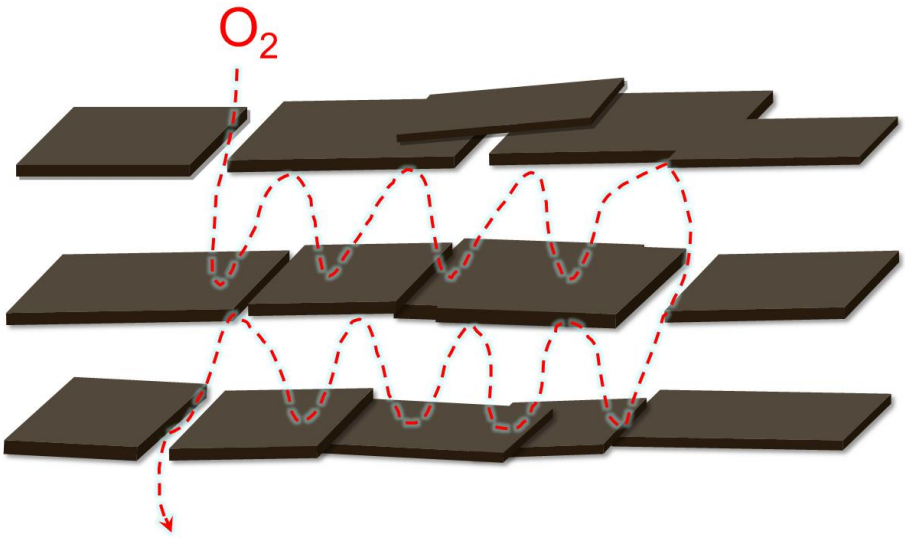

Fig. S6 Route of oxygen passing through the layer-by-layer GO/BPEI film assemblies.

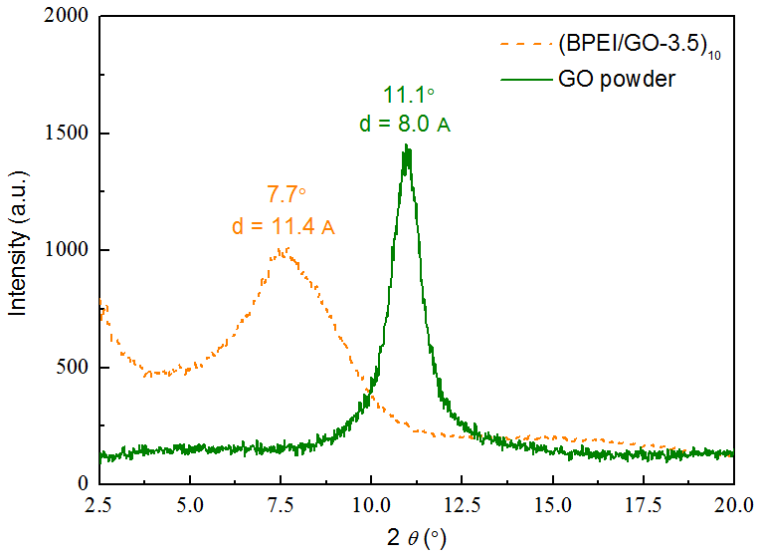

Fig. S7 GIWAXD patterns for $(GO/BPEI\text{-}3.5)_5$ films and XRD patterns for the GO powder.

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