Supporting information

# Bio-inspired polyelectrolyte complex/graphene oxide nanocomposite films with enhanced tensile strength and ultra-low gas permeability

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## 1. EXPERIMENTAL SECTION

### *1.1 Materials*

Poly (diallyldimethylammonium chloride) (PDDA, $M_w$: 100 000 ~ 200 000 g/mol, 20 % aqueous solution) and Sodium carboxymethyl cellulose (CMCNa, $M_w$: 90 000) were purchased from Sigma Aldrich. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were analytical reagents. Deionized water with a resistance of 18MΩ cm was used in all experiments. Graphene oxide (GO) nanosheets were prepared via Hummers method.[1] A SEM picture of as prepared GO nanosheets is shown below (Fig. S1).

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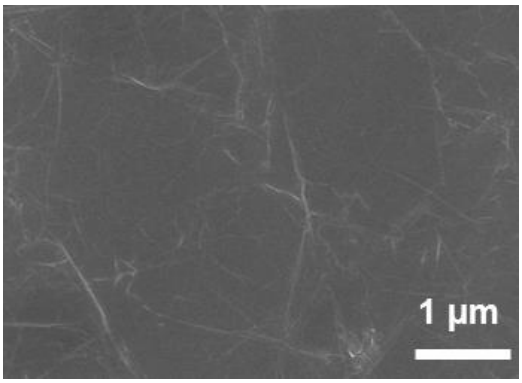


Fig. S1 A SEM characterization of GO nanosheets. Note: wrinkle morphologies that are typical for GO sheets are visualized from the SEM picture.

*1.2 Preparation of PEC@GO nanocomposite and membranes*

300 mL of CMCNa aqueous solution (4.8 g/L) and 200 mL of PDDA aqueous solution (3.2 g/L) were prepared respectively. A designed amount of GO was dispersed in CMCNa solution (CMCNa@GO) under vigorous stir (900 rpm) and ultrasonication (**Fig. S2a**) at a pH of 8. Then, pH of both CMCNa and PDDA solution was tuned to 2.5 using 0.1 M HCl. PDDA solution was quickly poured into CMCNa solution within 3 s under stir (900 rpm) and ultrasonication at 30$^{o}$C. PEC@GO nanocomposites precipitated out quickly upon pouring PDDA solution into CMCNa@GO dispersion (**Fig. S2b**), and were collected by filtration. Afterwards, PEC@GO nanocomposites were washed with deionized water 4 times, and dried at 60 $^{o}$C for 12 h. GO content in the naoncomposite is easily tuned by controlling the GO amount in the CMCNa@GO dispersion. In this study, PEC@GO nanocomposites containing 0.4, 0.8, 1.5, 2.3, and 3.9 v/v% GO were prepared and referred to as PEC0.4, PEC0.8, PEC1.5, and PEC2.3, respectively. Pristine CMCNa-PDDA PEC was prepared in the same way, without the adding of GO in PDDA solution (**Fig. S2c**).

For membrane preparation, 0.45 g PEC@GO nanocomposites was dispersed in 30 mL of 0.04 M NaOH to form 1.5 wt% solution, which was cast onto clean glass slide (25 mm × 75 mm), and dried at 60 $^{o}$C for 24 h to obtain free-standing membranes (**Fig. S2d**) for mechanical tests. Membranes for gas permeation tests were prepared by casting the same solution on a polyacrylonitrile supporting porous matrix membrane, with thickness of top PEC layer being kept ca. 5 μm.

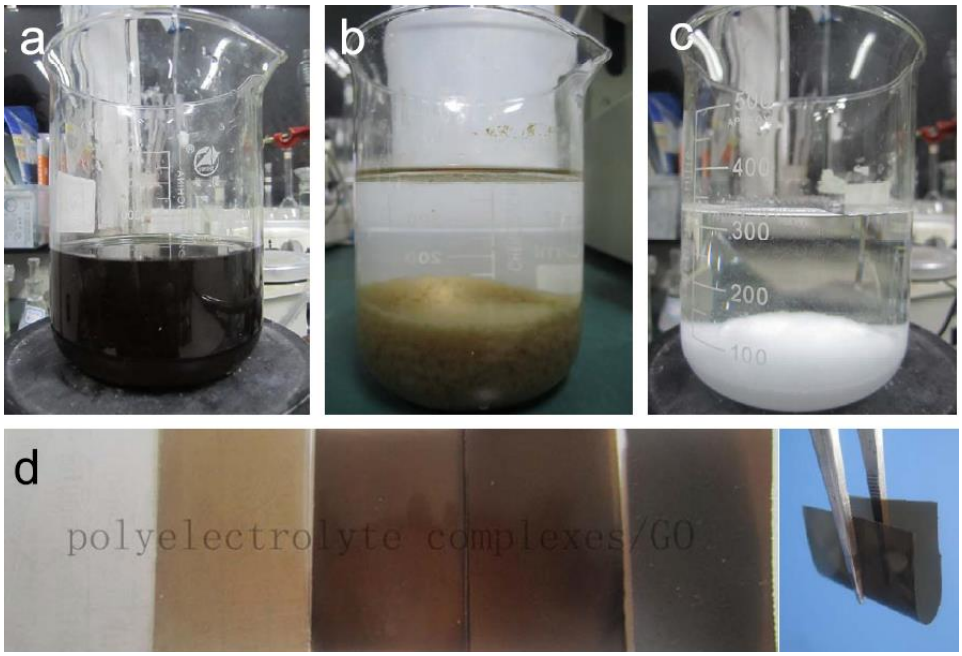


**Fig. S2** Optical photographs of (a) CMCNa@GO solution (pH 2.5), (b,c) CMCNa-PDDA PEC@GO nanocomposite and pristine PEC after the addition of PDDA solution, (d) PEC@GO nanocomposite films contain 0, 0.4, 0.8, 1.5, 2.3 v/v% GO, whereas the underlying word is "polyelectrolyte complex/GO".

*1.3 Instrumentation*

Atomic force microscopy (AFM) (tapping mode) was operated on a Seiko SPI3800N station (Seiko Instruments Inc.), using silicon tips (NSG10, NT-MDT) with a resonance frequency of ca. 330 kHz. Cross-sections of nanocomposite membranes were examined on a field emission scanning electron microscopy (FESEM FEI, SIRION-100, USA). Stretching tests of the PEC@GO nanocomposite membranes were performed on a universal testing machine (SANS CMT4204, Shenzhen, China) at a stretching rate of 1 mm/min (25 $^{o}$C, 20 % humidity. Tensile strength of the nanocomposite membranes was averaged by testing three pieces of PEC@GO hybrid membranes (1 cm × 5 cm).[33] UV-visible absorption spectra (200–500 nm) were measured with a Cary 100BIO UV-vis spectrometer. Zeta potential was measured on a 90 plus particle size analyzer. pH values were measured on a digital pH meter (pHS-25).

## 2. Supplementary data

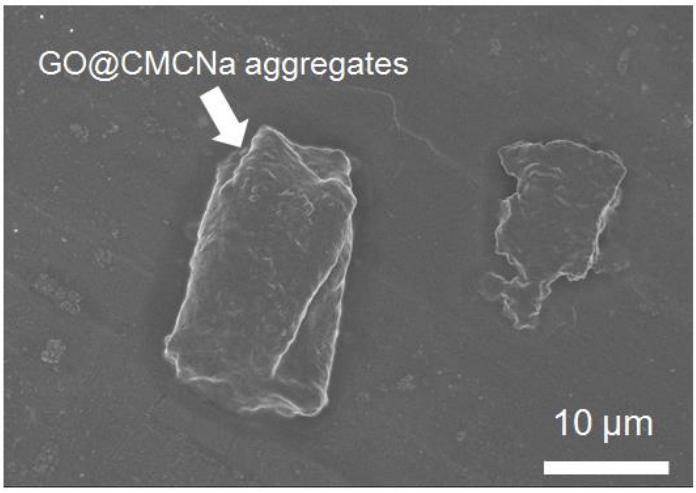


Fig. S3 A SEM micrograph of CMCNa@GO dispersion prepared by dispersing GO into CMCNa solution (pH 2.5) directly.

Table S1 Comparison of mechanical properties of PEC/GO nanocomposite films with state-of-the-art results of other polyelectrolyte nanocomposites.

| Materials | Tensile strength | Yong Modulus | Ref |
|---|---|---|---|
| CMC/PVAM | 60 MPa | N/A | *Ind. Eng. Chem. Res. 2006, 45, 6665* |
| PAA/CS PEC film | 13 MPa | N/A | *J. Membr. Sci. 1997, 135, 161* |
| CMC/gelatin | 40 MPa | N/A | *Polym. J. 2000, 32, 716* |
| PTC/PSA | 32 MPa | 0.56 GPa | *J. Appl. Polym. Sci. 1977, 21,* |
| CS/GO | 89.5 MPa | 2.17 GPa | *ACS Appl. Mater. Interfaces 2010, 2, 1707* |
| CS/GO LbL film | 130 MPa | 20 GPa | *Acs Nano 2010, 4, 4667* |
| CS/MTM film | 99 MPa | 8 GPa | *Angew. Chem. Int. Ed. 2010, 49, 10127* |
| **PEC/GO** | **115 MPa** | **3.7 GPa** | **This work** |

Abbreviations: CMC: Sodiuim carboxyl cellulose, PAA: Poly(acrylic acid), CS: Chitosan, PTC: Poly(vinyl alcohol) acetalized with diethoxyethyltrimethylammonium, PSA: Sulfated poly(vinyl alcohol). PVAM: Polyvinylamine, GO: Graphene oxide, MTM: montmorillonite.

## 3 Oxygen permeability of PEC@GO

### Nielsen model and Cussler model

The permeability for composite membranes with impermeable flakes can be predicted by the Nielsen model Eqs. (2) or Cussler model Eqs. (3).

$$\frac{P}{P_o} = 1 + \alpha\phi \quad (2)$$

where $P_o$ is the permeability of polymer membranes and $P$ is that of nanocomposite membranes, $\alpha$ is the aspect ratio which is defined as half the flake width divided by its thickness(DeRocher et al. / Journal of Membrane Science 254 (2005) 21–30). There are two other limits which depend on the aspect ratio $\alpha$, When $\varphi$<<1 and $\alpha\varphi$ < 1, the equation can be used.

However, when $\varphi$<<1 but $\alpha\varphi$ > 1, the suspension, now termed semidilute, has a relative permeability equal to

$$\frac{P}{P_o} = 1 + \mu\frac{\alpha^2\phi^2}{1-\phi} \quad (3)$$

where $\mu$ is a geometric parameter. The dependence on the square of volume fraction $\varphi$ and aspect ratio $\alpha$ is a consequence of the increased tortuosity and of the reduced area available for diffusion.

The geometric parameter, $\mu$ was set to 1.0 due to GO can be considered as a ribbon-like flake materials.[2] The $\alpha$ was assumed to 30 and 750 for the calculation for Nielsen model and Cussler model, respectively (**Fig. S4**, **ESI†**).

The volume fraction, $\varphi$ for the PECs/GO nanocomposites were calculated by the relationship between mass, volume and density as follow:

$$\phi = \frac{W_1/\rho_1}{W_1/\rho_1 + W_2/\rho_2} \quad (4)$$

where $W_1$ and $W_2$ were the weight of GO and PECs in nanocomposites, respectively. $\rho_1$ and $\rho_2$ were the density of GO (1.80 g/cm$^3$) [3] and PEC (1.37 g/cm$^3$). The density of the membrane was measured by buoyancy technique. A well-dried membrane sample was first weight in air and then immersed in silicone oil at 25 $^o$C and the difference in weight before and after immersion was determined.[4]

$$\rho = \frac{A}{P}\rho_0$$

$\rho_0$– density of silicon oil

*A* – dry weight of samples

*P* – weight difference of dry and wet samples

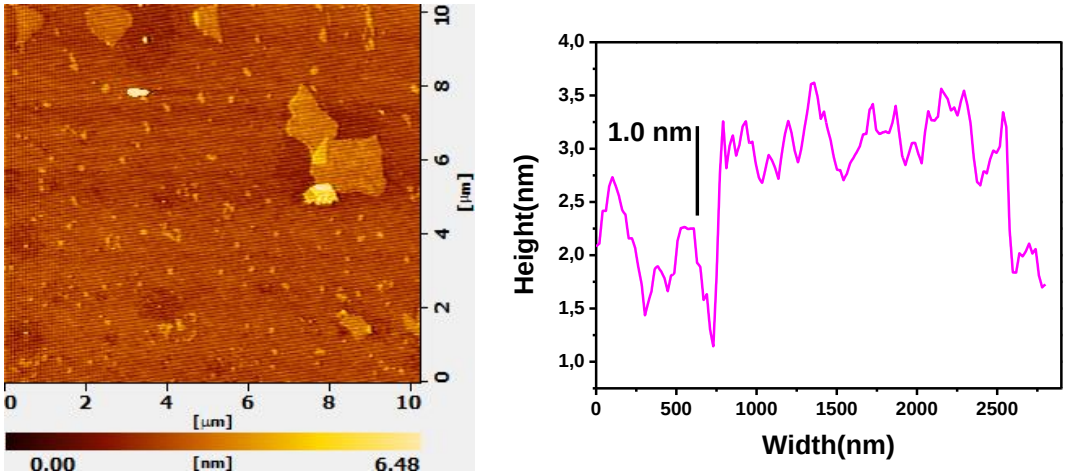


Fig. S4 typical AFM and height profiles of GO nanosheets. Note: in our study, thicknesses of GO nanosheets are all around 1 nm, while their lateral sizes varies from 500 nm to 5 µm.

On basis of our examinations, we choose the average sizes of graphene oxide (GO) as 1.5 µm. Hence, the aspect ratio (half the GO width divided by its thickness) is calculated as 750. This ratio is reasonable compared with GO prepared by others.[5] We also found that the exact value of this aspect ratio does not influence the trend of simulated curve by Cussler and Nielsen model.

## References

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