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# **Electronic Supplementary Information**

Realization of Ultra-High Barrier to Water Vapor by 3D-Interconnection

of Super-hydrophobic Graphene Layers in Polylactide Films

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## Preparation process of PLA microspheres.

To obtain macro-elements of PLA for building superhydrophobic networks, we designed a scheme from emulsion dispersion to get PLA microspheres. Fig. 1A exhibits the specific process: 40 g of PLA was firstly dispersed into 500 ml of CH<sub>2</sub>Cl<sub>2</sub> with vigorous agitation for about 3h at room temperature; similarly, 9g of PVA was simultaneously dispersed into 500 ml of deionized water with vigorous agitation for about 3h at about 60 °C until getting clear solution. Then, pouring PVA solution into PLA solution rapidly with agitation (~270 rpm). After steady agitation for about 2h, we got stable emulsion (oil-in-water) thereinto latex particles of PLA was stabilized by emulsifying agents of PVA. Using visible light to irradiate this emulsion, typical Tyndall effect can be observed (Fig. 1A), which reasonably confirms the formation of PLA emulsion (thereinto PVA was adhered to the surface of latex particle of PLA serving as emulgator). Next, heating the PLA emulsion to 40 °C (the boiling point of  $CH_2Cl_2$ ) to vaporize  $CH_2Cl_2$  out of emulsion for about 1h. Following that, adding 10 g of NaCl into PLA emulsion with rapid agitation (~150 rpm), and the sediments of PLA could be separated out from the solution. Afterward, these sediments of PLA were filtered and washed with deionized water for several times, then dried at 60 °C under vacuum for 48 h to get the white powder of PLA.

## Synthesis of GOgODA.

For the purpose of getting superhydrophobic graphene, we have grafted ODA onto GO by nucleophilic substitution. The synthetic process is illustrated in Fig. 1B. 100 mg of GO was added into 300 ml of deionized water with the aid of vigorous agitation and

ultrasonic treatment for 40 min at room temperature. The resulting stable and uniform suspension was then mixed with the solution of ODA (0.9 g) in 100 ml anhydrous ethanol. The mixture was then sealed in an autoclave with agitation and maintained at 90 °C for 24 h. Afterward, the reaction products were separated by suction filtration, then repeatedly washed with excess ethanol to remove the residual absorbed ODA for about 5 times. Finally, the GOgODA powder was dried in a vacuum at 50 °C for 24 h to remove the residual solvent.

#### **Characterization of GOgODA**

Water contact angle (CA) test. CA test was adopted to characterize the hydrophility of GO and GOgODA. Before testing, dilute solution of GO and GOgODA in water and alcohol with the concentration of 2 mg/ml was coated on PET films. Then volatilizing and drying the coating films at vacuum for 24 h at 45 °C. CA was measured with a deionized water droplet of 5  $\mu$ L on a video optical contact angle system (Krüss, DSA30, Germany) at room temperature.

**Raman spectrum.** Raman spectra were recorded on a Labram HR spectrometer (Horiba, France) using 532 nm laser excitation with a power of 1 mW. The intensity of characteristic bands was obtained by calculating the height of peak.

**X-ray diffraction (XRD).** X-ray diffraction measurements were conducted at the beamline BL15U1 of Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China). The monochromated X-ray beam with a wavelength of 0.124 nm was focused to an area of  $3 \times 2.7 \ \mu\text{m}^2$  (length × width), and the distance from sample to detector was 165 mm. A Mar165 CCD detector (2048 × 2048 pixels with pixel size of 80  $\mu$ m) was

employed to collect diffraction patterns.



**Fig. S1.** (A) Infrared absorption spectrum of GO, ODA and GOgODA. (B) Thermogravimetric analysis curves of GO, ODA and GOgODA.

Fourier-transform infrared (FTIR) spectroscopy. In order to determine the chemical structures of GO and GOgODA, FTIR measurements were performed by using Nicolet 6700 (Thermal Scientific, USA). GO and GOgODA powders were grinded together with KBr powder and cold pressed into a disc with the thickness about 600  $\mu$ m. The scanning range was from 4000 to 400 cm<sup>-1</sup>, and a total of 64 scans were collected at a resolution of 0.5 cm<sup>-1</sup>. Figure S1A shows the infrared absorption spectrum of GO, ODA and GOgODA.

**Thermogravimetric analysis (TGA).** TG 209 F1 instrument (Netzsch, Germany) under a nitrogen atmosphere was used to test the grafting ratio of GOgODA compared with GO. Weight change of the tested specimen in the alumina pan was recorded in a temperature range from 40 to 800°C at a heating rate of 10 °C min<sup>-1</sup>. Figure S1B shows the thermogravimetric analysis curves of GO, ODA and GOgODA.



Fig. S2. X-ray photoelectron spectroscopy (XPS) of (A) GO and (B) GOgODA.

**X-ray photoelectron spectroscopy (XPS)**. XPS analysis was performed with Axis Ultra DLD (Kratos, UK) system using focused monochromatized Al (mono)  $K\alpha$  radiation. The most obvious change would be the appearance of nitrogen peak (~400 eV) in Fig. S2B that well demonstrates the success of grafting for octadecylamine to GO. Meanwhile, it can be clearly seen that after grafting reaction, the content of oxygen is decreased obviously (the value of C/O increases from ~0.6 to ~3.5) which results from the partial reduction and nucleophilic substitution. Moreover, the relative amount of carbon increase distinctly, it can be derived from the contribution of carbons from alkane chains (octadecylamine).

Transparency of PLA/GOgODA nanocomposite films.



**Fig. S3.** Digital photograph of PLA/GOgODA composite films with the content of GOgODA, (A) 0.034 vol% and (B) 0.27 vol%.

For comparison, Fig. S3 exhibits digital photograph of PLA/GOgODA composite films with the content of 0.034 vol% and 0.27 vol%, respectively. Obviously, both films maintain commendable transparency, despite there is a little fuzziness in Fig. S3B (0.27 vol%).

## Transparency of PLA/GO nanocomposite films with random dispersion.

In order to compare the transparency between PLA/GO nanocomposite films by random dispersion and PLA/GOgODA nanocomposite with superhydrophobic networks, we provided the results of PLA/GO composite films with random dispersion in our previous works. Solution coagulation was employed to prepare a series of PLA nanocomposite films containing GO. Taking the 0.17 vol% GO/PLA nanocomposite as an example, the detailed preparation procedures were as follows: 25 mg of graphite oxide obtained by the modified "Hummers" method was firstly dispersed into 200 ml of DMF solution with vigorous agitation and ultrasonic treatment for 2 h at room

temperature, forming a stable and uniform GO/DMF suspension. The transparent PLA/DMF solution was obtained by adding 10 g of PLA granules into about 200 ml of DMF solution with the aid of mild stirring for 30 min at 100 °C, and then mixed with the above GO/DMF suspension for 15 min at 100 °C. Upon completion, the resulting homogeneous GO/PLA solution was immediately added into a large amount of vigorously stirred water and the coagulated materials precipitated continuously. Thereafter, the coagulates formed by the GO/PLA nanocomposites were isolated via filtration, washed with water, left in a drying oven at 60 °C to remove bulk solvents, and dried in a vacuum oven overnight at 60 °C to evaporate the any residual solvent. Finally, the composite powders were shaped into a diameter of 100 mm films for barrier measurements by compression molding at 200 °C for 3 min with a pressure of 10 MPa after preheating for 5 min. And then all the films were cooled to room temperature by cold compression molding at a pressure of 10 MPa for 5 min.



**Fig. S4.** (A) Digital image PLA/GO nanocomposite films with increasing GO loading; (B) light transmittance spectra in the range of 250-850 nm for neat PLA and its nanocomposite films with various GO loadings (vol %).<sup>1</sup>

Fig. S4 exhibits the macroscopic digital image and light transmittance spectra in the range of 250-850 nm for neat PLA and its nanocomposite films with various GO loadings (vol %) by random dispersion.<sup>1</sup> Apparently, when the GO loadings is 0.17 vol%, the composite film is basically not transparent, and this transmittance is almost completely under ~6%. However, for the PLA/GOgODA nanocomposite films (0.13 vol%), it is practically transparent and its transmittance is mostly over than ~15%.

# Networks of GOgODA by SEM.



**Fig. S5.** SEM images of fracture surface of PLA/GOgODA composite films with different content. (A) 0.034 vol%, (B) 0.067 vol%, (C) 0.134 vol%, (D) 0.268 vol%.

To get an intuitionistic observation of the network morphology of GOgODA, a field emission scanning electronic microscopy (SEM) (Inspect F, FEI, Finland) with the accelerated voltage of 5 kV was employed. Epoxy resin embedding technology was used to embed the composite films in the epoxy resin. The test specimens were placed in liquid nitrogen for 30 min, then rapidly cryo-fractured by a microtome (Leica RM2235) to obtain smooth surfaces along the depth direction. It should be noted that all the samples were not sputter-coated with gold.

## Characterization of crystalline structure for composite and pure PLA films.

Wide-angle X-ray diffraction (WAXD). In order to determine the detail crystalline morphology of PLA in various composite films, 2D-WAXD measurements were conducted at the beamline BL15U1 of Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China). The monochromated X-ray beam with a wavelength of 0.124 nm was focused to an area of  $3 \times 2.7 \ \mu\text{m}^2$  (length  $\times$  width), and the distance from sample to detector was 165 mm. A Mar165 CCD detector (2048  $\times$  2048 pixels with pixel size of 80  $\mu$ m) was employed to collect diffraction patterns.

**Differential scanning calorimeter (DSC).** DSC measurement was performed on a TA Q2000 DSC (TA Instruments, USA). All composite films (~5 mg) were heated from 40 to 190 °C at a heating rate of 10°C/min under nitrogen atmosphere.



**Fig. S6.** (A) 2D-WAXD pattern and (B) 1D-WAXD intensity profiles of amorphous PLA film; (B) DSC heating traces of amorphous PLA films.

An amorphous diffraction halo for and a big amorphous peaks of pure PLA films illustrates it is difficult for PLA to form crystals by traditional compression molding (Fig. S6A). Two distinct transforms including cold crystallization peak (~100 °C) and melting peak (~167 °C) appear in DSC curve of pure PLA (Fig. S6C) likewise proves that it is difficult for PLA to form crystals by traditional compression molding.<sup>2</sup>



**Fig. S7.** (A)-(E) 2D-WAXD patterns of composite films with different loadings. (F) 1D-WAXD intensity profiles of pure PLA film and nanocomposite films. (G) DSC heating traces of pure PLA films and nanocomposite films with different loadings.

The specific structure of polymer matrix especially crystalline textures would likewise exert significant impact on the overall barrier performance of composite films. 2D-WAXD and DSC measurements were used to reveal particular structural information on crystallization of PLA and its nanocomposite films. Fig. S7A-E shows representative 2D-WAXD patterns of pure PLA and its nanocomposite films with various GOgODA loadings. Actually, compared with PLA film by normal compression molding with amorphous structure (Fig. S6), secondary thermal treatment employed in this work can availably promote the growth of crystals of PLA to be more perfect, which is positive for the enhancement of water barrier (Fig. S8). In addition, homogeneous diffraction rings are observed for all samples indicating that a certain amount of crystals were assuredly generated by re-packing of PLA molecular chains into established crystal lattice. Fig. S7F gathers the 1D diffraction intensity profiles by integration from the 2D diffraction patterns. After secondary thermal treatment, representative four distinct diffraction peaks arise up in PLA and composite samples located at q = 10.2(010), 11.4 (200/110), 13.3 (203), and 25.5 (015) of  $\alpha$ -form crystals of PLA, respectively.<sup>3</sup> Meanwhile, the crystallinity in all samples can be calculated to be ~34 %, illustrating that the crystal form of PLA and the course of crystallization cannot be changed by GOgODA networks.

DSC heating trace curves were adopted to elaborate structural transformation by simulating the concrete procedures of initial and secondary compression molding (Fig. S7G). In line with WAXD results, different from PLA film by normal compression molding with two distinct transforms including cold crystallization peak and melting peak (Fig. S6C), there is only one single melting peak confirmed in the samples after thermal treatment. In the process of conventional compression molding, the faster cooling rate from PLA melts to solidified films makes it unable for semi-rigid PLA molecular chains to adjust its conformation to packing into crystals. Secondary thermal treatment (120 °C) can further provide the opportunity to activate PLA molecular chains continuing to form more perfect crystalline entities. But the melting point and

exothermic area under peaks are approximately identical among all the annealed samples. It elucidates that the space of grid within GOgODA networks is sufficient for PLA to form adequate crystals without confinement. The existence of PLA crystallization could be expected for making significantly multiple contributions to the amelioration of water barrier properties (Fig. S8). On the one hand, dense packing of PLA molecular chains in crystals can definitely decrease the free volume preventing the diffusion of water molecules, synchronously, compact PLA lamellae can serve as barrier walls through which the water molecules cannot penetrate. Furthermore, excluding effect of PLA crystallization would compel GOgODA nanosheets out of crystal region, and selective concentration in the interface is further developed for the orientation and even more regular arrangement of GOgODA that is of significant for the enhancement of water barrier property.



Fig. S8. Coefficient of moisture permeability (  $P_{H_2O}$  ) for pure PLA films with the annealing time.

Fig. S8 demonstrates the trend of water vapor permeability ( $P_{H_2O}$ ) for pure PLA films as the annealing time. It can be clearly seen that the quenched PLA film possesses

the largest value of  $P_{H_2O}$  (10.13×10<sup>-14</sup> g·cm/cm<sup>2</sup>·s·Pa); and with the increase of annealing time, the value of  $P_{H_2O}$  is reduced gradually before 15 min (9.30×10<sup>-14</sup> g·cm/cm<sup>2</sup>·s·Pa). This suggests it is enough for PLA to form saturated quantity of crystals (15 min) to barrier water vapor permeation.

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