Electronic Supplementary Material (ESI) for Chemical Communications
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Humidity-triggered self-healing films with excellent oxygen barrier performance

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Experimental Section

Reagents and materials. Poly (sodium 4-styrene sulfonate) (PSS) with molecular weight of ~70000 and Poly (dimethyl diallyl ammonium chloride) (PDDA) with molecular weight of ~200000 were purchased from Sigma-Aldrich Company. Polyester (PET) film was purchased from Sinopharm Chemical Reagent Beijing Company. The following analytical grade chemicals were used without further purification: NaOH, $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, KCl, poly(vinyl alcohol) (PVA), $NH_3 \cdot H_2O$, H_2O_2, H_2SO_4. Deionized water was used in all the experimental processes.

Synthesis of MgAl-LDH colloidal suspension. Colloidal LDH suspension was synthesized according to the separate nucleation and aging steps (SNAS) method reported by our group.[1] Typically, 100 ml of solution A ($Mg(NO_3)_2 \cdot 6H_2O$: 0.2 M and

$Al(NO_3)_3 \cdot 9H_2O$: 0.1 M) and 400 ml of solution B (NaOH: 0.15 M) were simultaneously added to a colloid mill with rotor speed of 3000 rpm and mixed for 1 min. The resulting LDH slurry was obtained *via* centrifugation and washed twice with deionized water and then dispersed in 400 ml of deionized water. This aqueous suspension was transferred into a stainless steel autoclave with a teflon lining. After hydrothermal treatment at 110 °C for 24 h, stable homogeneous LDH suspension with narrow size distribution was obtained.

Fabrication of the $(LDH/PSS)_n$ film and $(PDDA/PSS)_n$ film. The $(LDH/PSS)_n$ films were fabricated by layer-by-layer (LBL) assembly technique. Quartz glass, silicon wafer and PET film were used as substrates for various characterizations and tests. Quartz glass substrate was used for UV-vis spectra characterization, and silicon wafer was used for AFM and SEM characterization. All the other measurements are based on the samples on PET substrate. Prior to assembly, quartz glass and silicon wafer were first washed in $NH_3 \cdot H_2O$/30% H_2O_2 (v/v=7:3) and concentrated H_2SO_4 for 30 min each to make the substrates surface hydrophilic and negatively charged. The PET film with thickness of 25 μm was cleaned by sonication in deionized water for 20 min. The substrate was dipped in a colloidal suspension of LDH nanoplatelets (0.2 wt.%) for 10 min followed by washing thoroughly, and then the substrate was immersed into PSS aqueous solution (1.0 g/L) for 10 min. The $(LDH/PSS)_n$ films were fabricated by alternate deposition of LDH nanoplatelets and PSS for n cycles. The resulting $(LDH/PSS)_n$ films were finally rinsed with water and dried at room temperature. As comparison samples, the $(PDDA/PSS)_n$ films were prepared by a similar assembly procedure in a sequence of PDDA (0.2 g/L) and PSS (1.0 g/L) aqueous solution.

Fabrication of the (LDH/PSS)$_n$-PVA film. The permeation of PVA molecules into the (LDH/PSS)$_{20}$ film was performed by dip coating method.[2] The prepared (LDH/PSS)$_{20}$ film on PET substrate was immersed into the PVA solution (0.5 wt.%) by using the Deposition Robots (Riegler & Kirstein GmbH). The film was placed vertically in the solution for 10 min, followed by withdrawing the substrate out of the solution with an ascent velocity of 0.05 cm/min. The resulting film was dried in air for 15 min. The whole process (immersion, withdrawing, drying) was repeated 5 times. In order to enable PVA stick to the (LDH/PSS)$_{20}$ film tightly, the obtained (LDH/PSS)$_{20}$-PVA film was placed in a sealed container purged with N_2, followed by heating at 80 °C for 1 h.

Fabrication of the PVA/PET film: The PVA/PET film was fabricated by spin-coating technique. The PVA solution (4.0 g/L) was spin-coated onto a PET substrate (70 s per cycle, 2100 rpm, 5 cycles). The film was dried at room temperature after each spin-coating process. Finally, the PET substrate coated with PVA film (thickness: ~420 nm) was obtained for control experiment.

The test of self-healing property. The experiment was carried out under the condition of sealed environment with relative humidity of ~85%. We have tested the self-healing property of (LDH/PSS)$_{20}$-PVA/PET film under various humidity conditions. The self-healing process is very slow at low humidity (below 40%), and a higher humidity leads to a faster self-healing process but a slight decrease of barrier behavior. Taking into account the atmospheric humidity range as well as the self-healing rate, we chose the humidity of ~85% as the test condition. Humidity-controlled solutions of saturated KCl was placed in a sealed chamber at 25 °C for 24 h, which achieved constant relative humidity of ~85%.[3] At first,

the $(LDH/PSS)_{20}$-PVA film was cut roughly using a scalpel, which induced a ~2.8 μm wide gap on the film. Subsequently, the damaged film was placed inside the sealed chamber for investigating the self-repairing process. In a control experiment, the $(LDH/PSS)_{20}$ film without PVA was also performed by the same treatment for comparison.

Sample Characterizations. X-ray diffraction (XRD) patterns were recorded by a Rigaku XRD-6000 diffractometer, using Cu Kα radiation (λ = 0.1542 nm) at 40 kV, 30 mA. The UV-vis absorption spectra were collected in the range 200–800 nm on a Shimadzu U-3000 spectrophotometer. The morphology was investigated using a scanning electron microscope (SEM; Zeiss SUPRA 55) with the accelerating voltage of 20 KV, a FEI Cs-corrected Titan 80-300 high resolution transmission electron microscope (HRTEM) operated at 300 kV and a NanoScope IIIa atomic force microscope (AFM) from Veeco Instruments. The Fourier transform infrared (FT-IR) spectra were obtained using a Vector 22 (Bruker) spectrophotometer with 2 cm^{-1} resolution. Oxygen transmission rates (OTRs) were collected using VAC-V2 gas transmission rate testing equipment. All permeability coefficient values were averaged from at least five separate films.

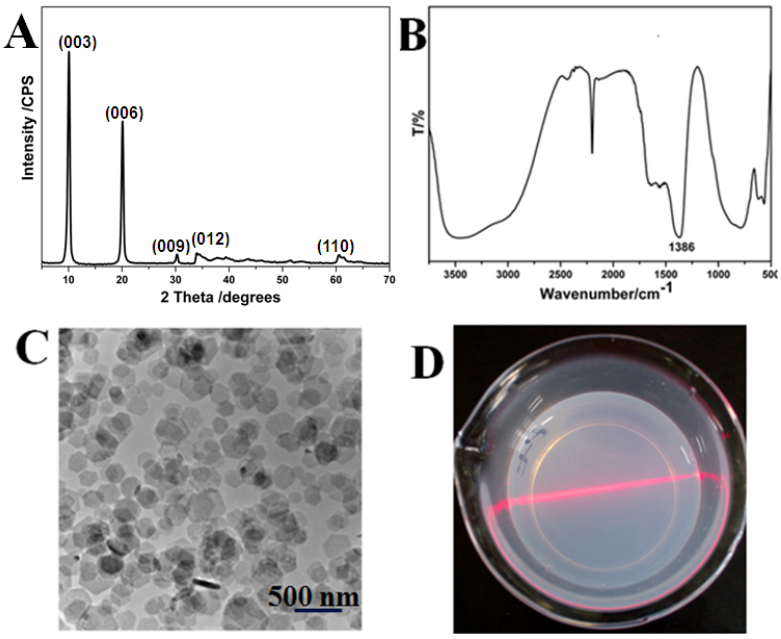

Figure S1. Characterizations of the MgAl-LDH nanoplatelets: (A) XRD pattern; (B) FT-IR spectrum; (C) TEM image and (D) digital photograph of its colloidal suspension.

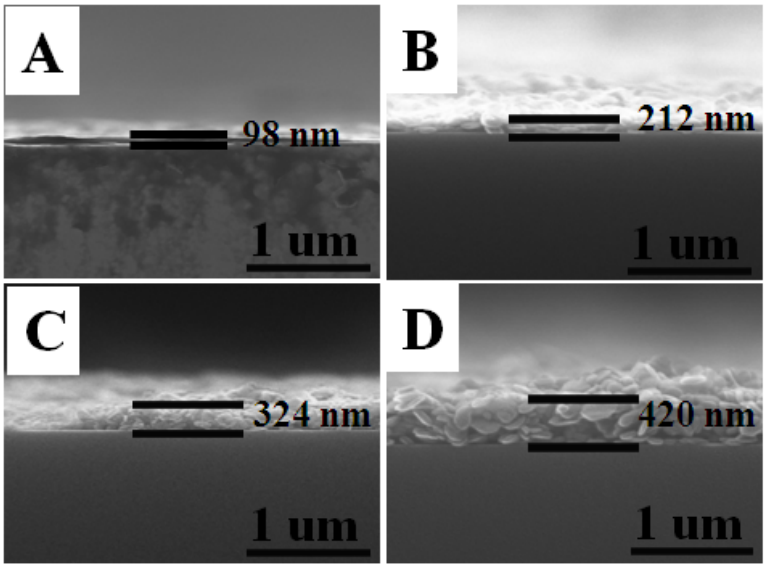

Figure S2. The side-view SEM images of the $(LDH/PSS)_n$ films with n = 5, 10, 15 and 20, respectively (from A to D).

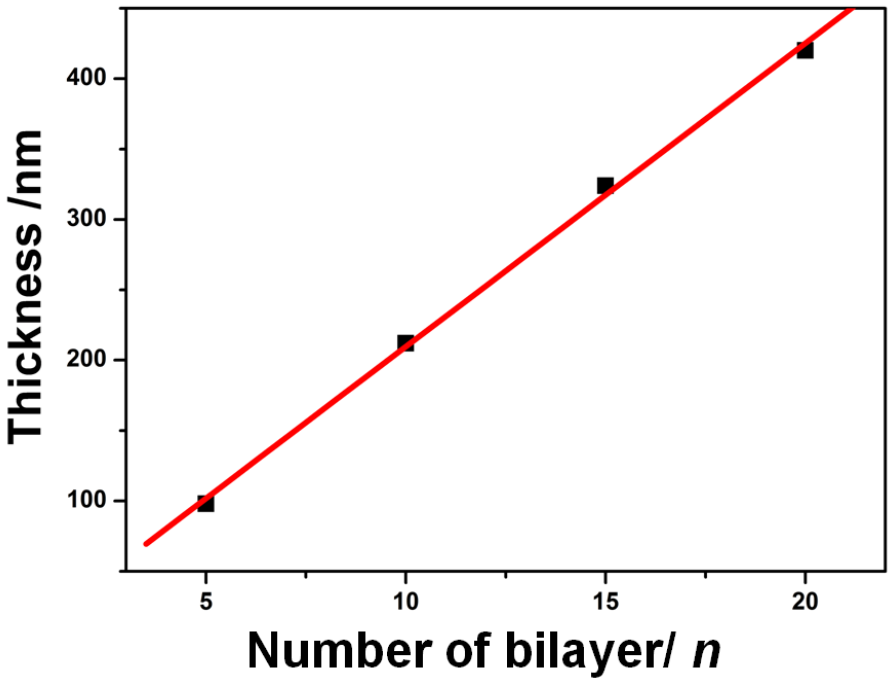

Figure S3. Thickness of the $(LDH/PSS)_n$ films as a function of bilayer number *n*.

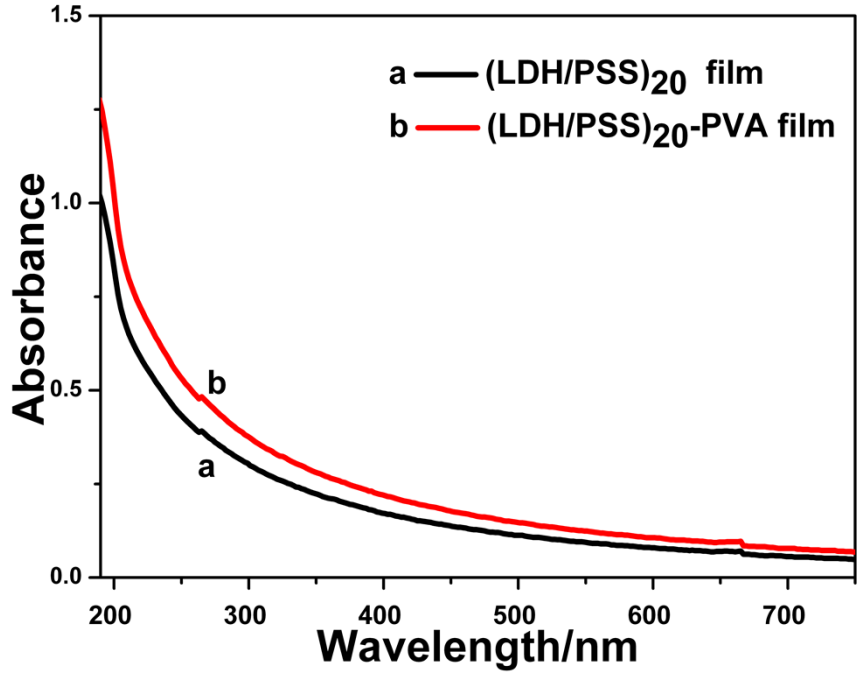

Figure S4. UV-vis spectra of the (a) $(LDH/PSS)_{20}$ and (b) $(LDH/PSS)_{20}$-PVA film, respectively.

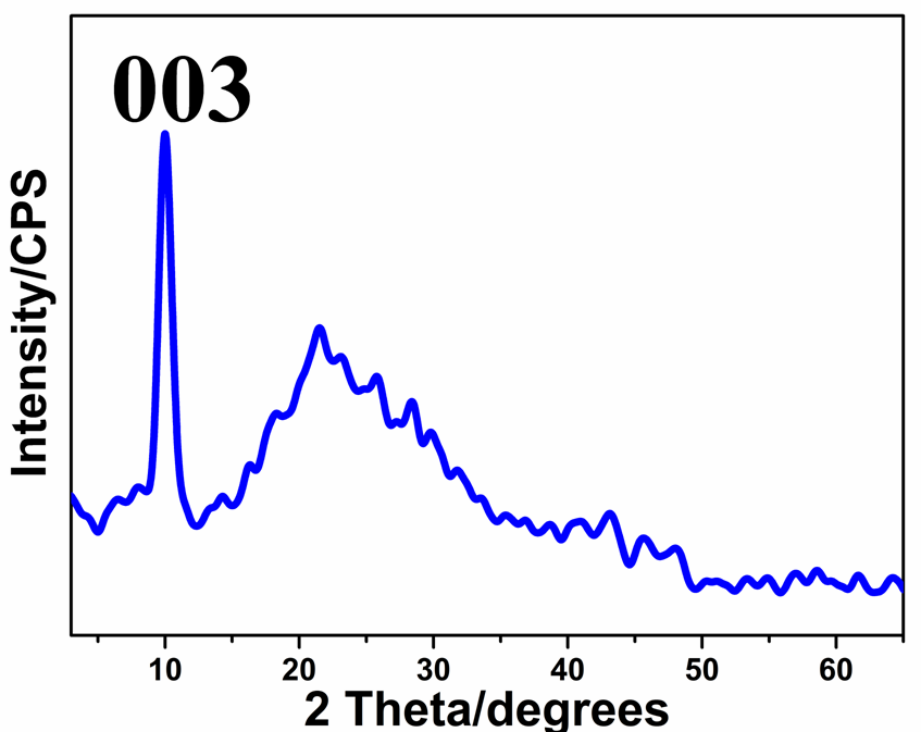

Figure S5. XRD pattern of the as-prepared $(LDH/PSS)_{20}$-PVA film.

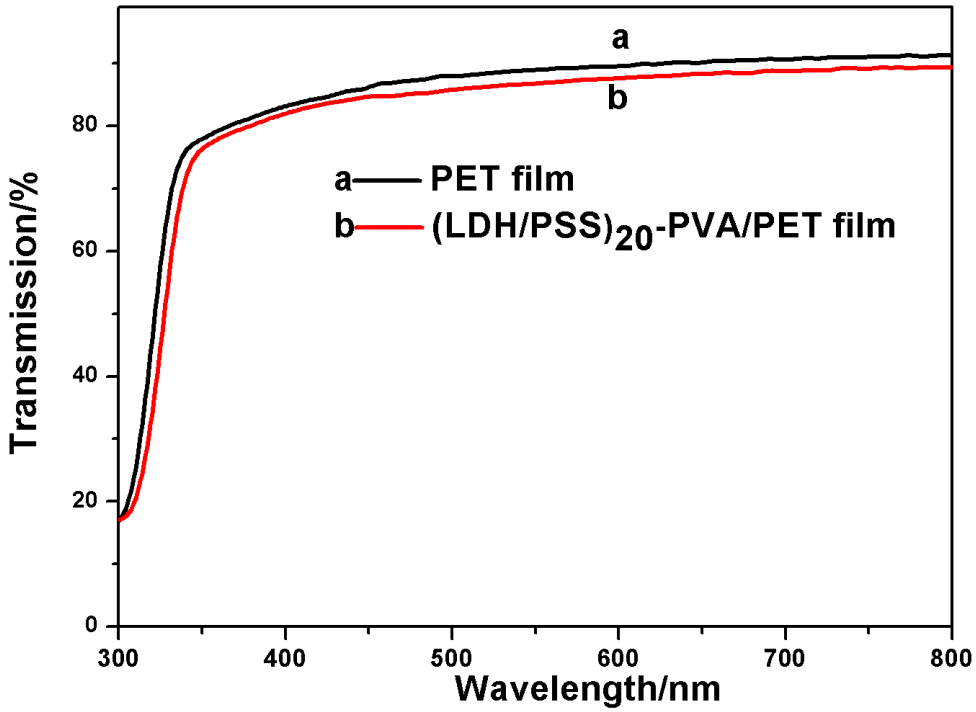

Figure S6. UV-vis transmittance spectra of the (a) pristine PET film and (b) the $(LDH/PSS)_{20}$-PVA/PET film, respectively.

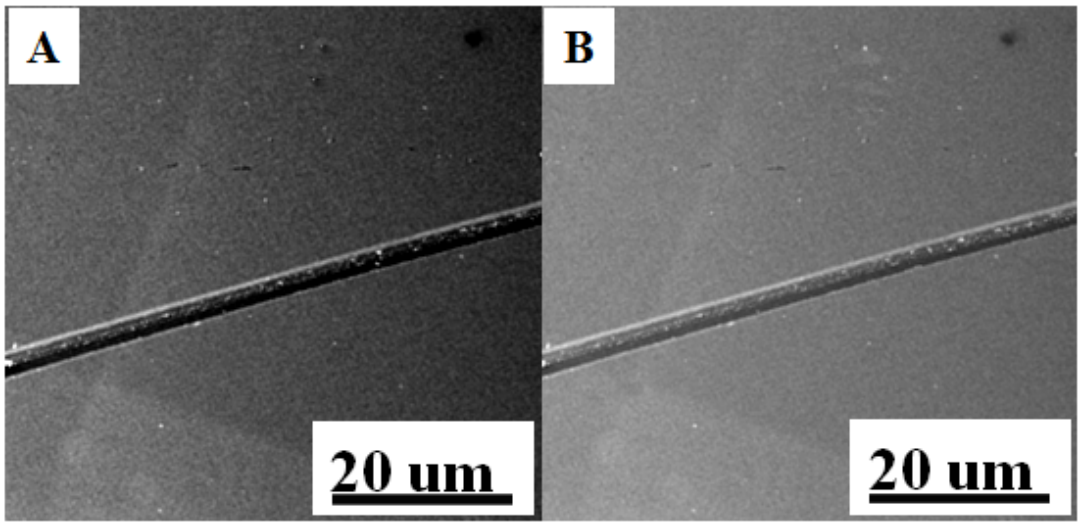

Figure S7. SEM images of the $(LDH/PSS)_{20}$/PET film with a cut of ~2.8 μm (A) before and (B) after being treated at ~85% relative humidity for 75 h, respectively.

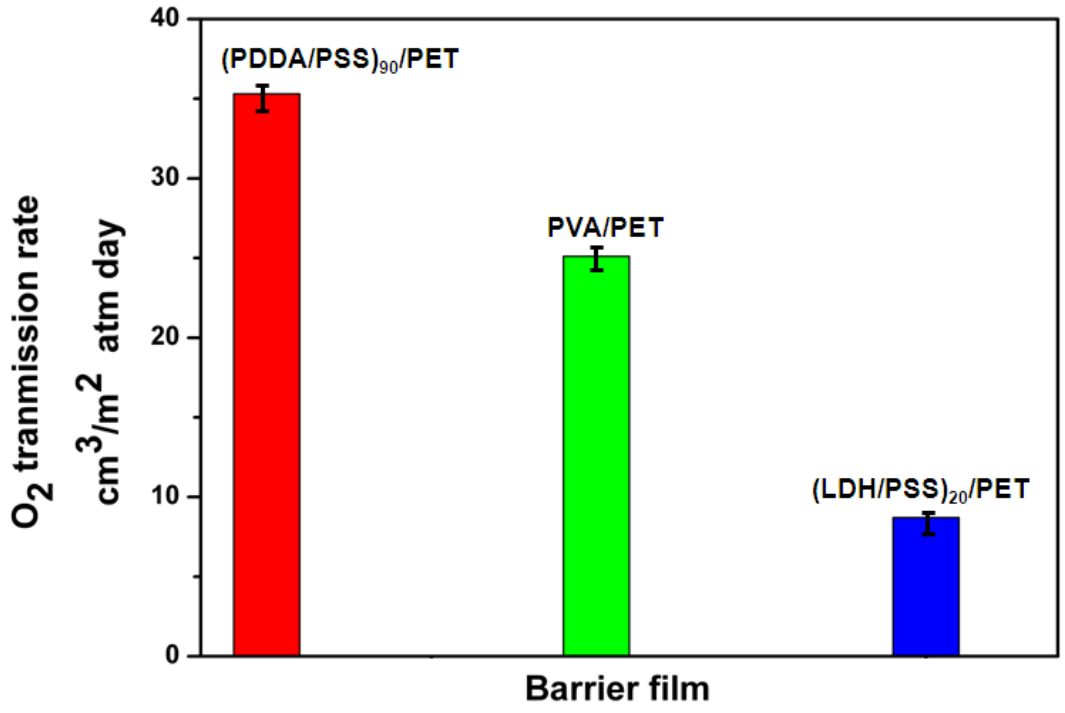

Figure S8. OTR values for $(PDDA/PSS)_{90}$/PET, PVA/PET and $(LDH/PSS)_{20}$/PET film, respectively.

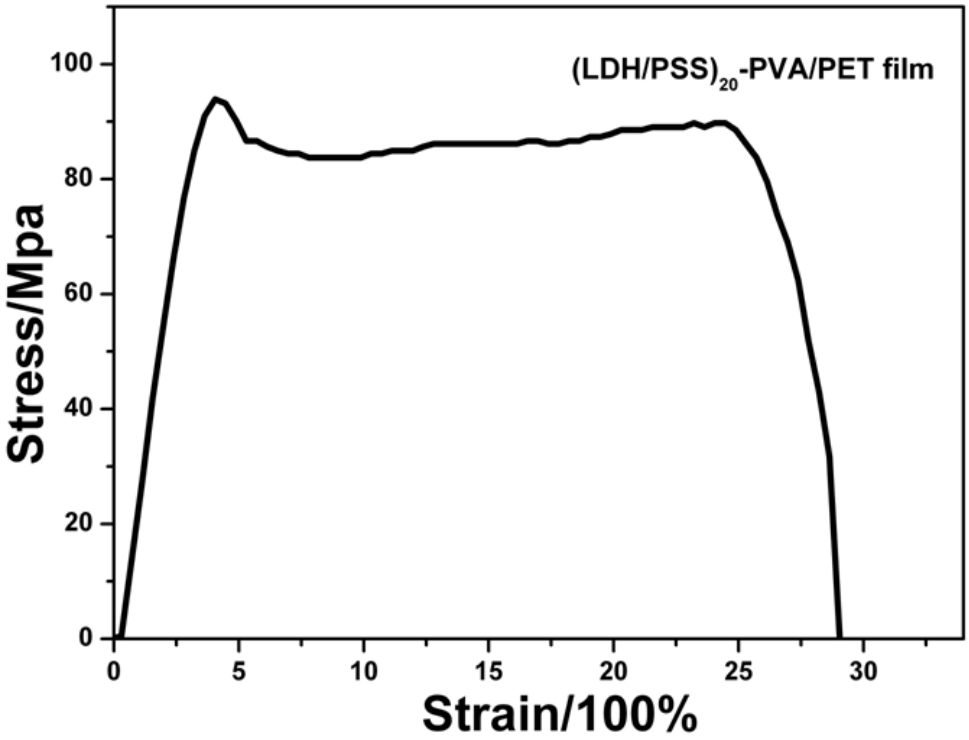

Figure S9. The stress-strain curve of the $(LDH/PSS)_{20}$-PVA/PET film.

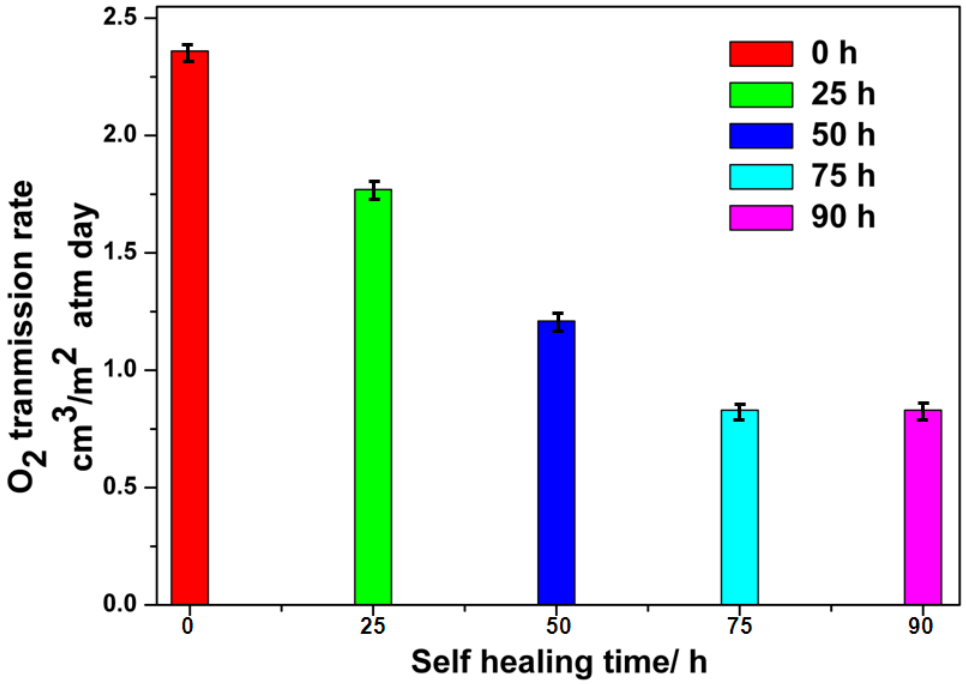

Figure S10. OTR values for the damaged $(LDH/PSS)_{20}$-PVA/PET film at 85% relative humidity in the time range 0–90 h.

The barrier properties of the damaged $(LDH/PSS)_{20}$-PVA/PET film as a function of self-healing time were studied by OTR measurements. The OTR value decreases gradually along with the increase of self-healing time, indicating the occurrence of self-repairing of the damaged area by humidity. After 75 h, an OTR value of ~0.83 $cm^3m^{-2}day^{-1}atm^{-1}$ was obtained for the film, close to its original one (~0.72 $cm^3m^{-2}day^{-1}atm^{-1}$). Further increase in the treating time (e.g., 90 h) did not show much impact on its self-healing behavior. The results indicate that a self-repairing time of 75 h is necessary at 85% humidity.

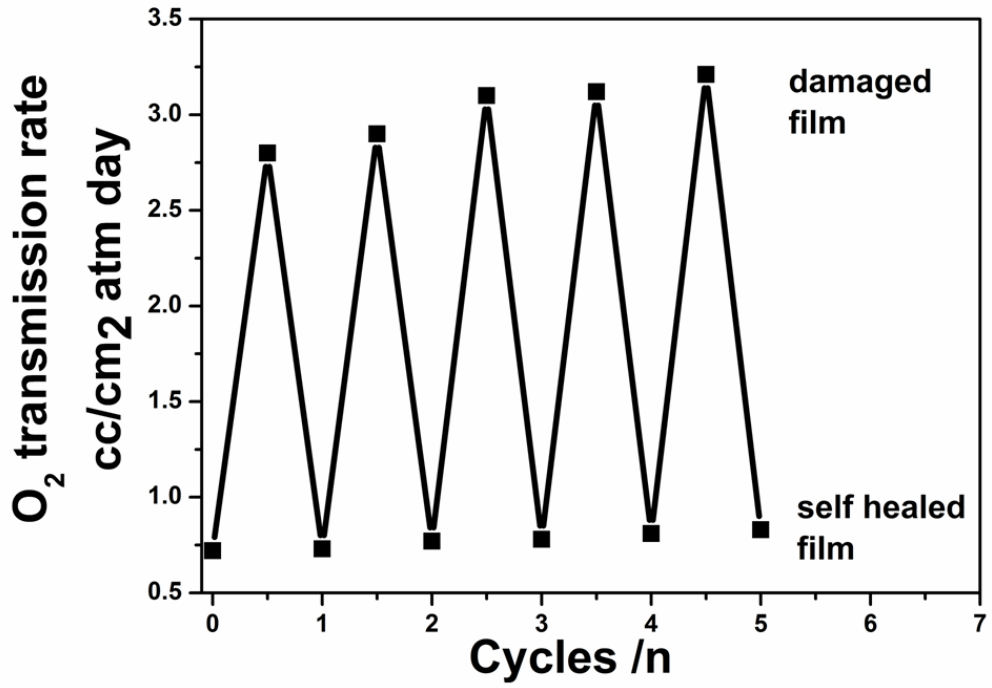

Figure S11. The reversible OTR variation for the $(LDH/PSS)_{20}$-PVA/PET film with alternate damage and self-healing.

References:

[1] J. Han, Y. Dou, M. Wei, D. G. Evans and X. Duan, *Angew. Chem. Int. Ed.*, 2010, **49**, 2171.

[2] Y. Zhao, S. He, M. Wei, D. G. Evans and X. Duan, *Chem. Commun.*, 2010, **46**, 3031.

[3] J. Han, F. Fan, C. Xu, S. Lin, M. Wei, X. Duan and Z. L. Wang, *Nanotechnology*, 2010,

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