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Electronic Supplementary Information

Metal-organic framework channelled graphene composite membranes for gas separation

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Experimental

Materials

The natural graphite flakes (500 mesh) were supplied by XFnano chemical Co., Ltd., China. $Zn(NO_3)_2\ 6H_2O$, $Cu(NO_3)_2\ 3H_2O$, $FeCl_3\ 6H_2O$, $KMnO_4$, $NaNO_3$ and sodium formate in A.R. grade were supplied by Changzheng Chemical Reagent Co., China. 2-methylimidazole (98%), 1,3,5-benzenetricar-boxylate (98 %) and benzimidazole (98 %) were supplied by Hangzhou Banghua chemical Co., Ltd., China. Methanol, ethanol, isopropanol, tert butyl alcohol, N,N-dimethylformamide, ethanediamine and etc. in A.R. grade were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Pure water was obtained from a self-made RO-EDI system, in which ion concentration was analyzed by IRIS Intrepid ICP and Metrohm 861 Compact IC and controlled to meet the experimental requirement of $\sigma \leq 0.5\ \mu S\ cm^{-1}$. All the regents were used as received.

Synthesis of graphite oxide

Natural graphite flakes (500 mesh) were used to prepare graphite oxide by Hummer's method. 4 g natural graphite flakes and 2 g $NaNO_3$ were gradually added into 92 mL concentrated H_2SO_4 while in an ice bath. 12 g $KMnO_4$ was added extremely slowly to above suspension under stirring to prevent the temperature from exceeding 20 ℃. After keeping the suspension in ice-bath for 2 h, it was heated by oil-bath with temperature of 35 ℃ and maintained for 1 h. Then 184 mL water was poured slowly into the above suspension, and the temperature of oil-bath was increased to 98 ℃. After reaction for 40 min, the suspension was treated by 30 % H_2O_2 solution. Ultimately, the product was washed by dilute HCl solution, collected and dried.

Amination of PVDF hollow fiber

PVDF membrane was soaked in ethanediamine solution (25 %, v/v) in an autoclave. Then the autoclave was heated at the temperature of 150 ℃ for 20 h. After cooling, the aminated membrane was taked out and washed by water for several times to remove unreacted ethanediamine. Ultimately, the aminated PVDF membrane was dried at room temperature for use.

Synthesis of rGO membrane

The graphite oxide was dispersed in water and treated by ultrasound for 2 h to obtain the GO suspension. The GO suspension was centrifuged at 4,000 rpm to remove large particles/aggregates. The obtained GO suspension was transfored into a autoclave. The aminated PVDF membrane was immersed vertically in the GO suspension by using a teflon holder. Then the autoclave was thermal-treated to deposition and reduction of the GO at the 150 ℃ for 12 h. After natural cooling to temperature, the rGO membrane was washed by water and dried.

Synthesis of ZIF-8/rGO membrane

The prepared rGO membrane was immersed in $Zn(NO_3)_2$•$6H_2O$ aqueous solution to make metal ions swarm into the interlayers of the rGO membrane adequately. Nitrogen purging was employed to remove the extra $Zn(NO_3)_2$•$6H_2O$ aqueous solution. The rGO membrane contained Zn^{2+} was dried first and soaked in 2-methylimidazole aqueous solution. For crystallization, the rGO membrane and solution was transferred into autoclave, and heat-treated at 110 ℃ for 5 h. After cooling to temperature, the formed ZIF-8/rGO membrane was taked out and washed by water for several times. Ultimately, the ZIF-8/rGO membrane was dried at 50 ℃ for use.

Synthesis of ZIF-7/rGO membrane

To make metal ions swarm into the interlayers of the rGO membrane adequately, the rGO membrane was soaked in $Zn(NO_3)_2$•$6H_2O$ aqueous solution. After nitrogen purging and drying, the rGO membrane contained Zn^{2+} was immersed in benzimidazole N,N-dimethylformamide solution. Then both the rGO membrane and solution were transferred into autoclave, and heat-treated at 110 ℃. After crystallization, the formed ZIF-7/rGO membrane was taked out and washed by methanol for several times. Ultimately, the ZIF-7/rGO membrane was dried at 50 ℃ for use.

Synthesis of CuBTC/rGO membrane

The rGO membrane was immersed in $Cu(NO_3)_2•3H_2O$ aqueous solution to make metal ions swarm into the interlayers of the rGO membrane adequately. After nitrogen purging and drying, the rGO membrane contained Cu^{2+} was transferred in autoclave which was filled by 1,3,5-benzenetricar-boxylate ethanol solution. The autoclave was heat-treated at 110 ℃ for crystallization. After reaction, the prepared CuBTC/rGO membrane was washed by ethanol for several times and dried at 50 ℃.

Synthesis of MIL-100/rGO membrane

The rGO membrane was immersed into $FeCl_3$ $6H_2O$ N,N-dimethylformamide solution to make metal ions swarm into the interlayers of the rGO membrane adequately. After nitrogen purging and drying, the rGO membrane contained Fe^{3+} was transferred in autoclave which filled by 1,3,5-benzenetricar-boxylate ethanol solution. The autoclave was heat-treated at 150 ℃ for crystallization. After reaction, the prepared MIL-100/rGO membrane was washed by methanol for several times and dried at 50 ℃.

Synthesis of ZIF-8

ZIF-8 was synthesized following the hydrothermal synthesis. 2-Methylimidazole, sodium formate and zinc chloride were dissolved together in methanol by ultrasonic treatment. The obtained clear solution was pulled into an autoclave. For crystallization, the autoclave was heat-treated at 110 ℃. After reaction, the ZIF-8 particles were isolated by centrifugation. The prepared ZIF-8 was washed by methanol for several times, and then dried at 50 ℃.

Synthesis of rGO and ZIF-8/rGO composite

The GO suspension was centrifuged at 4,000 rpm and transferred into an autoclave. Then it was thermal-treated for reduction of GO at 150 ℃ for 12 h. After natural cooling to room temperature, the rGO sample was washed by water and dried. For preparation of ZIF-8/rGO composite, the rGO sample was fabricated and immersed in $Zn(NO_3)_2•6H_2O$ aqueous solution. Then the rGO sample contained Zn^{2+} was dried first and heated in 2-methylimidazole aqueous solution at 110 ℃ for crystallization. After cooling to room temperature, the formed ZIF-8/rGO composite was washed and dried for XPS characterization.

Permeation measurements

Permeation properties of the prepared membrane were measured as previous study [1]. The diameter of the membrane measured by SEM was used to calculate the effective membrane area for gas separation. The thickness of the membrane was also measured by SEM for calculating the permeability. The membrane was sealed in a membrane module by epoxy glue. The feed gas was used to rinse the module and fed at shell side. The permeate gas were collected and measured at the tube side by a bubble flow-meter. The data was read and recorded until the system running was kept stable. Transmembrane pressure was 1 bar and controlled by the exactitude manometer, with upstream pressure of 2 bar and downstream pressure of 1 bar (atmosphere conditions). Until the system running stably, the volume of the permeate gas was recorded. The gas permeation experiment of H_2 and CO_2 through the ZIF-8/rGO/PVDF membranes was carried out in order of H_2, CO_2, H_2, CO_2, H_2 to CO_2. The gas permeation data were calculated by averaging the measured values of three cycles. This experiment was lasted for 24 h. The selectivity is the ratio value of the two kinds of gas permeation flux. For mixture gas separation, the mixture selectivity of H_2/CO_2 mixture permeation was defined as the quotient of the molar ratios of the components in the permeate, divided by the quotient of the molar ratio of the components in the retentate. The result was calculated from the average of three samples at least.

Characterization

The morphologies of the membranes were observed by a field-emission scanning electron microscope (FESEM) (S-4700, Hitachi, Japan) with accelerating voltage of 15 kV. The element dispersion was characterized by the attached energy-dispersive x-ray spectroscopy (EDS) (GENESIS4000, EDAX, USA). X-ray diffraction (XRD) instrument was employed to investigate the crystalline structure of prepared materials.

The diffraction data were collected by a PNAlytical X' Pert PRO X-ray diffractometer with Cu Kα radiation (λ= 0.154056 nm) at 40 kV and 40 mA. The samples were obtained by grinding the membranes in liquid nitrogen. TEM images were achieved by a JEM-2100 (JEOL Co. Japan) with accelerating voltage of 200 kV. To obtain the sample, the ZIF-8/rGO was scraped from the ZIF-8/rGO/PVDF composite membrane composite membrane. The scrape particles were grinded in liquid nitrogen and treated by ultrasound in water. After ultrasound treatment, the obtained suspension was dropped on an ultrathin carbon film with copper net support and then dried at atmosphere. A RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with an incident radiation of monochromatic Mg Kα X-rays (hν=1253.6 eV) at 250 W was utilized to carry out the X-ray photoelectron spectroscopy (XPS) experiments. RBD 147 interface (RBD Enterprises, USA) was used to collect the spectra of all the elements. A Nicolet 6700 Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR, Thermo Scientific Co.) spectrophotometer with scans of 32 and resolution of 4 cm^{-1} was employed to record infrared spectra. A Micromeritics-Accelerated Surface Area and Porosimetry system (ASAP 2020M+C, Micromeritics Instrument Co., USA) was employed to obtain the N_2 adsorption-desorption isotherms of the prepared membranes. The specific surface area was calculated by Brunauer-Emmett-Teller method. Pore size distributions of membranes were calculated by DFT method. The membranes were grinded in liquid nitrogen to obtain the particle samples. Before the analysis, the samples were degassed in vacuum at150 ℃ for12 h. The thickness of the nanosheets was characterized by using an atomic force microscopy (AFM, Bioscope Catylyst Nanoscope-V, Bruker, USA). The samples were prepared as the TEM, and dropped on a mica plate and then dried at atmosphere.

Reference:

[1] W. Li, P. Su, G. Zhang, C. Shen and Q. Meng, J. Membr. Sci. 2015, 495, 384-391.

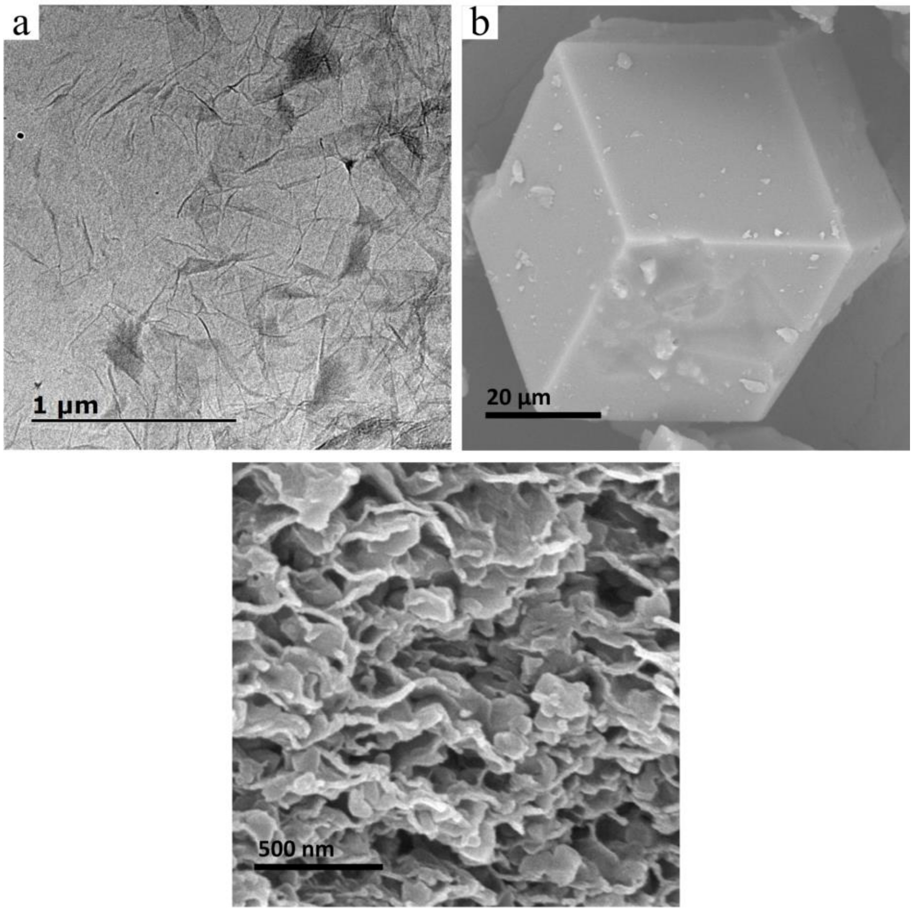

Figure S1. (a) TEM image of GO sheets synthesized by Hummer’s method. (b) SEM image of ZIF-8 synthesized by solvothermal method. (c) SEM image of ZIF-8/rGO composite.

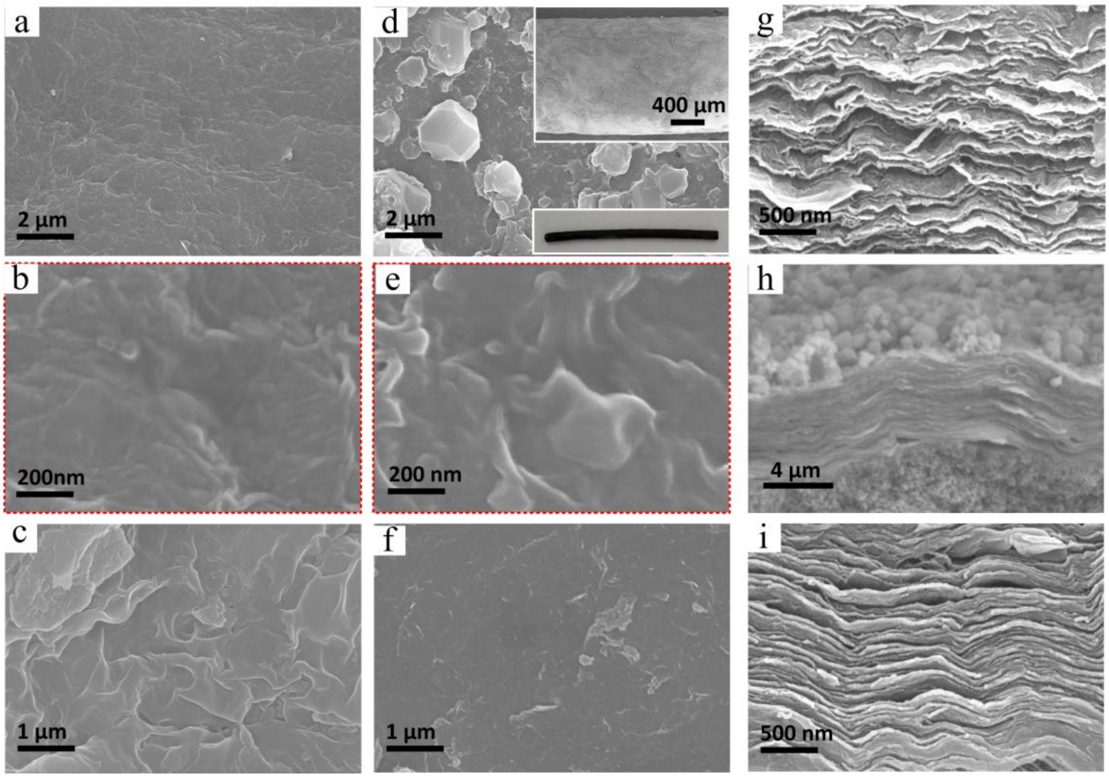

Figure S2. (a,d) Top view SEM images of rGO and ZIF-8/rGO membranes. (b,e) Magnified SEM images of a and d, respectively. (c,f) Inner SEM images of rGO and ZIF-8/rGO membranes. (g-i) Cross-sectional SEM images of rGO and ZIF-8/rGO membranes. SEM images of ZIF-8/rGO reveal that some ZIF-8 crystals exist on the surface of the rGO membrane. Unlike the ZIF-8/rGO composite particle that possesses a porous structure, because the rGO have been assembled on the surface of PVDF hollow fiber, ZIF-8/rGO/PVDF composite membrane shows an excellent layered structure.

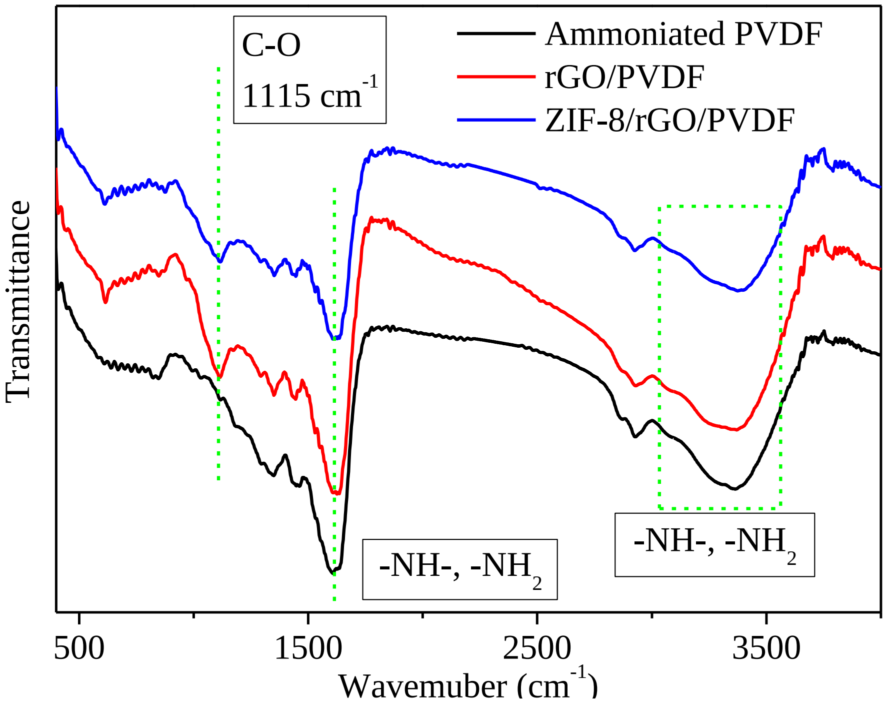

Figure S3. FTIR spectra of aminated PVDF hollow fiber, rGO membrane and ZIF-8/rGO membrane.

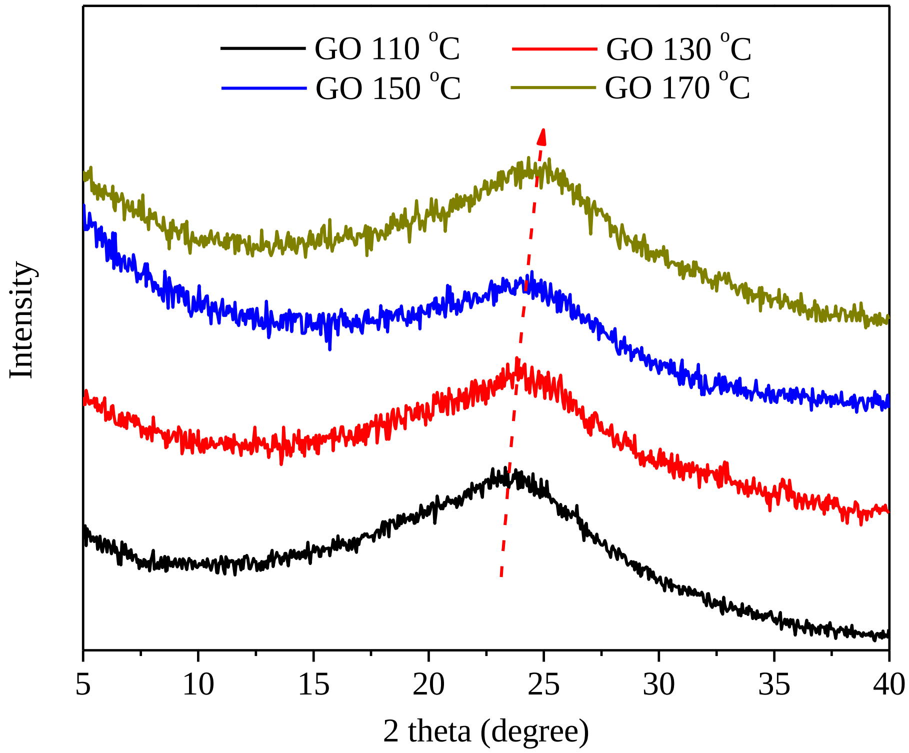

Figure S4. XRD patterns of rGO membranes synthesized at different temperature. With temperature increasing, the 2 theta of the characteristic peak increases, which indicates that the interlayer spacing of the rGO become smaller.

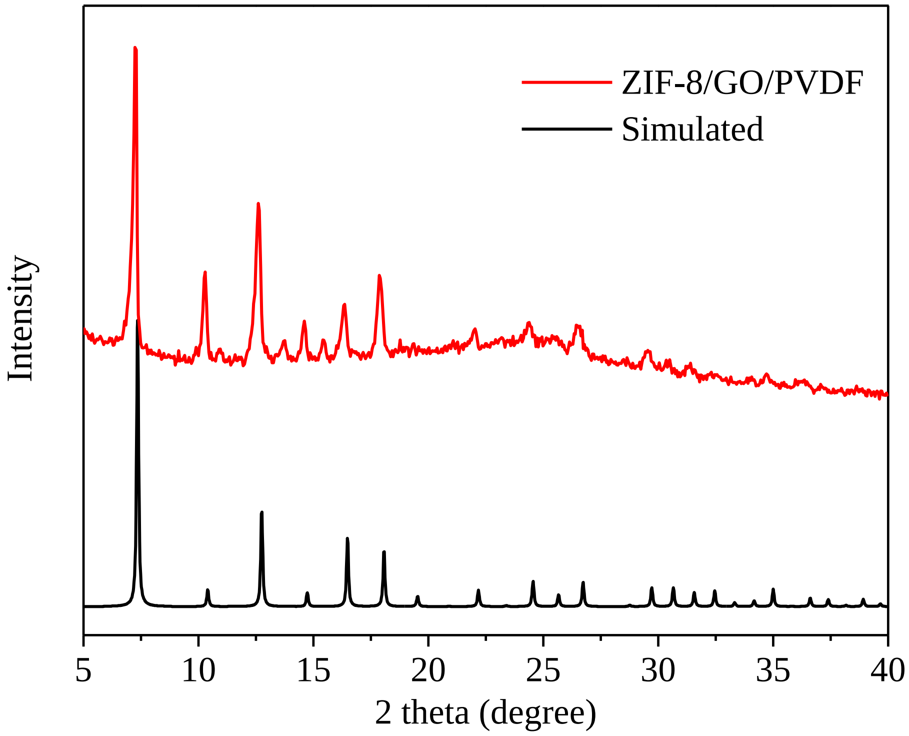

Figure S5. XRD patterns of simulated ZIF-8 and ZIF-8/rGO membranes. The characteristic peaks in XRD pattern demonstrate that the prepared membrane contains the ZIF-8 materials.

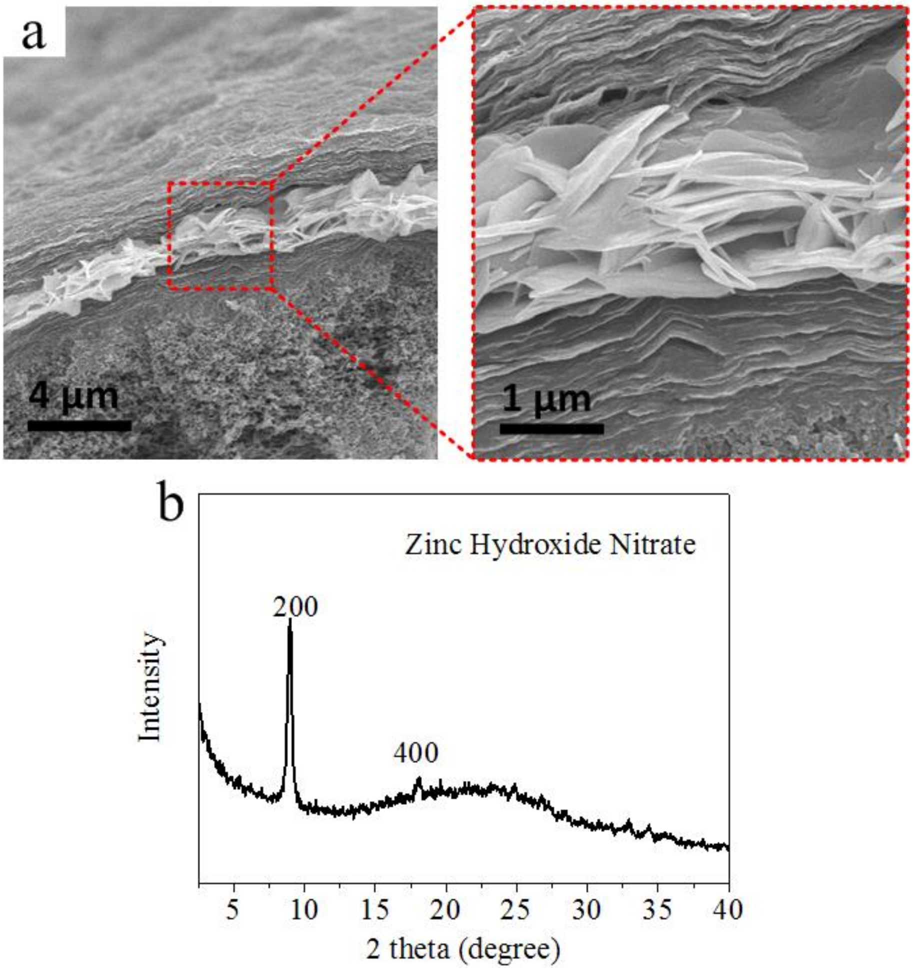

Figure S6. (a) SEM images and (b) XRD pattern of the prepared composite membrane. This composite membrane was synthesized by immersing the rGO membrane in the 2-methylimidazole firstly and then treating it by hydrothermal process in $Zn(NO_3)_2\cdot 6H_2O$ solution. The SEM images and XRD pattern demonstrate that the zinc nitrate hydroxide hydrate has been formed in rGO membrane, rather than ZIF-8 nanosheets. This phenomenon should be attributed to that only a little 2-methylimidazole has been impregnated into the interlayers of rGO membrane.

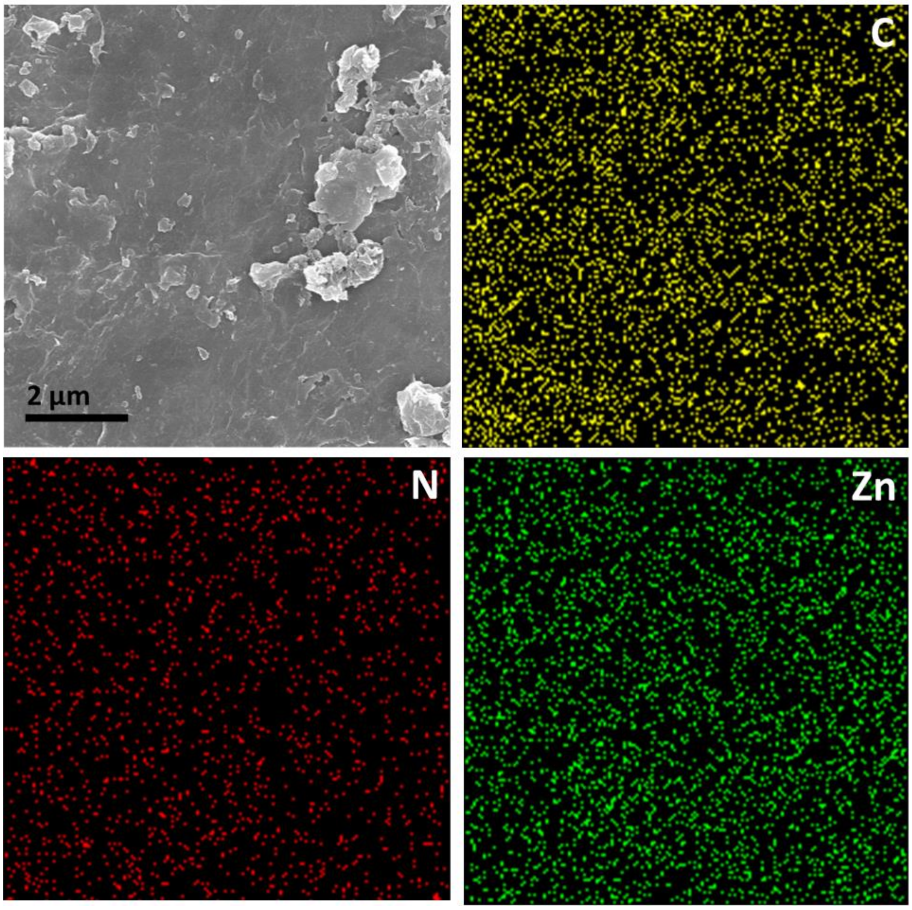

Figure S7. EDS mapping images of inner ZIF-8/rGO membrane. It indicates that ZIF-8 is dispersed in the whole membrane uniformly.

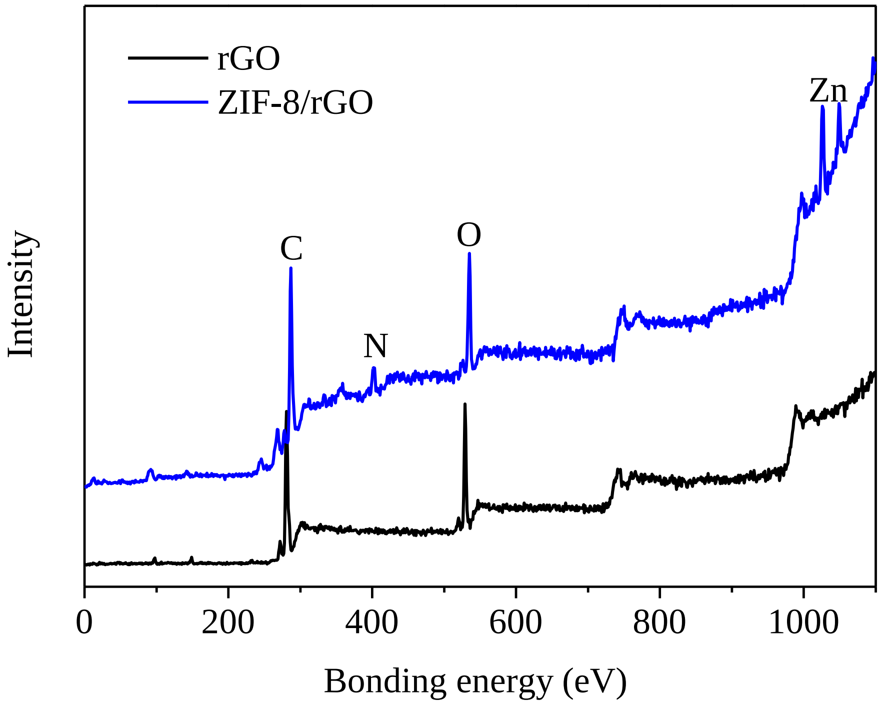

Figure S8. XPS spectra of rGO and ZIF-8/rGO composites. rGO was synthesized by heating GO suspension at the 150 ℃. ZIF-8/rGO composites were prepared by soaking the rGO into $Zn(NO_3)_2$•$6H_2O$ aqueous solution and then heat-treated in 2-methylimidazole aqueous solution at 110 ℃. XPS spectra of rGO displays the characteristic peaks of carbon and oxygen. ZIF-8/rGO possesses zinc and nitrogen besides carbon and oxygen components, which demonstrates that ZIF-8 has been synthesized in ZIF-8/rGO composites.

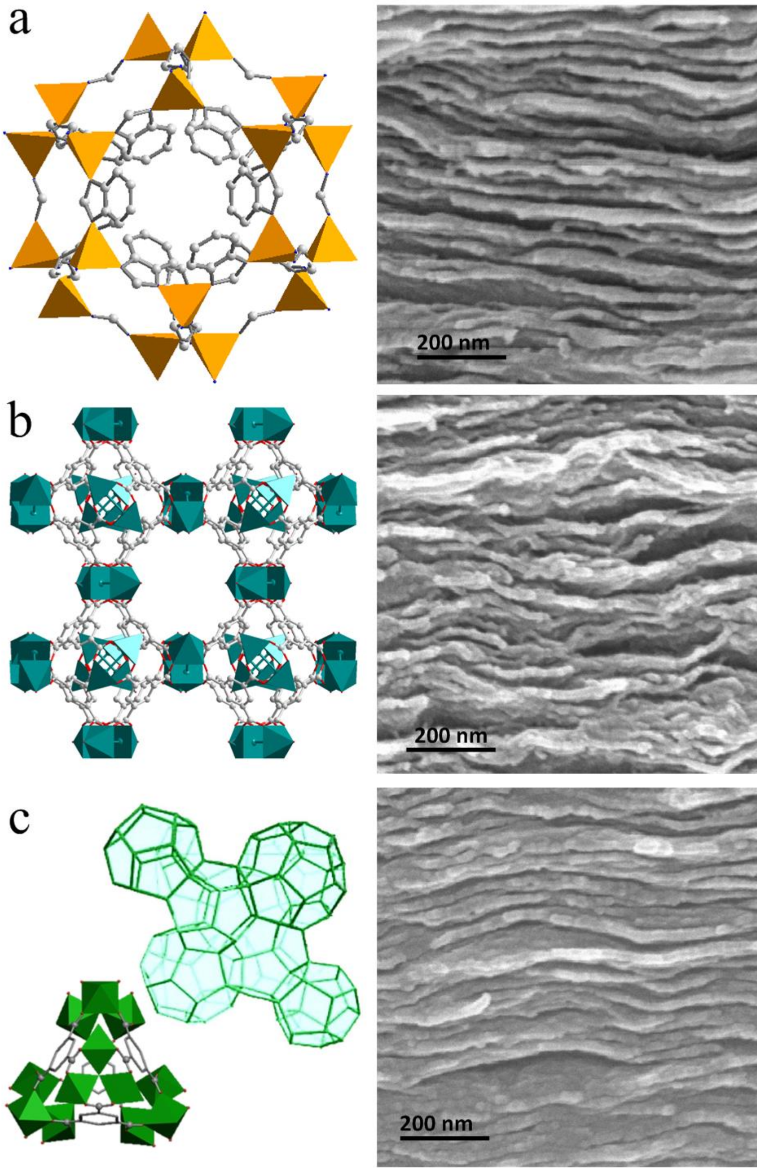

Figure S9. Cross-sectional SEM images and crystalline structure of (a) ZIF-7/rGO, (b) CuBTC/rGO and (c) MIL-100/rGO membranes

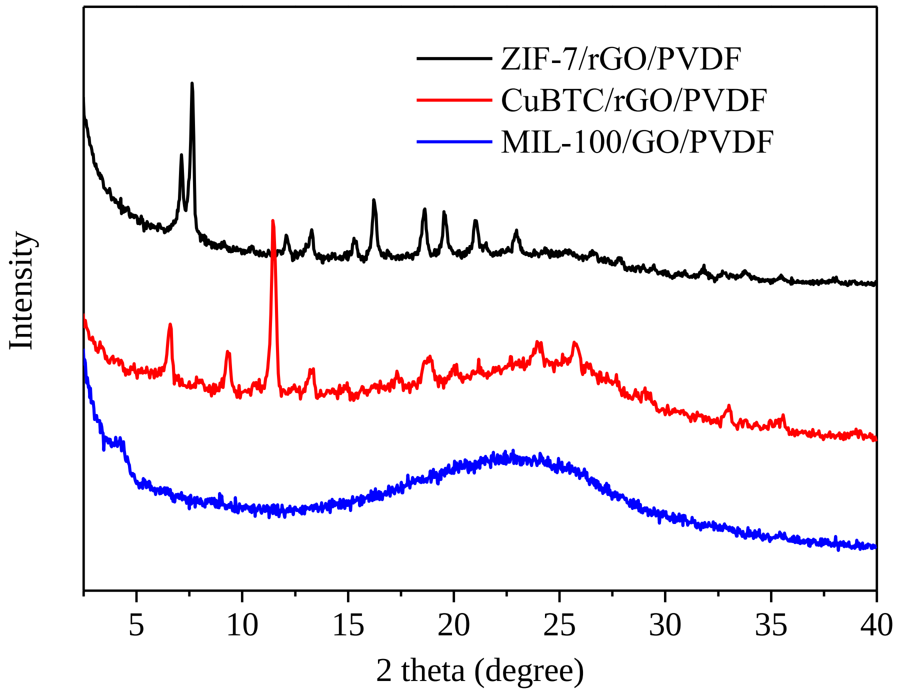

Figure S10. XRD patterns of ZIF-7/rGO, CuBTC/rGO and MIL-100/rGO membranes.