### **Supplementary Information**

### Novel carbon-based separation membranes composed of integrated

### zero- and one-dimensional nanomaterials

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#### Supporting Note 1: Materials and chemicals.

Chemicals:

Citric acid (ACS reagent,  $\geq$ 99.5%), ammonia (28.0–30.0% NH<sub>3</sub> solution), Sodium sulfate (ACS reagent,  $\geq$ 99.0%), methyl orange (ACS reagent, Dye content 85%), rose bengal (Dye content 95%), brilliant blue R (Dye content ~50%, Technical grade), methylene blue (Dye content,  $\geq$ 82%), and crystal violet (ACS reagent,  $\geq$ 90.0%) were purchased from Sigma-Aldrich and used without further purification. Dopamine hydrochloride (99%), and Trisma base (Primary Standard and Buffer,  $\geq$ 99.9% (titration), crystalline) were purchased from Sigma-Aldrich. Diethylenetriamine (DETA, ReagentPlus®, 99%) was purchased from Sigma-Aldrich.

Single wall carbon nanotube (SWCNT) ((diameter: < 3 nm, length: > 5  $\mu$ m, purity: > 85%) and sodium dodecylbenzenesulfonate (> 95.0%) was purchased from TCI, US, and used as received. Polymeric substrates:

Poly ether sulfone (PES) hollow fiber membrane (pore size: 25 nm; inside diameter: 0.8 mm; outside diameter: 1.2 mm) was purchased from Hydronautics, CA. Poly sulfone (PSf) flat sheet membrane (pore size: 20-30 nm) was purchased from Nanostone Water Co., Oceanside, CA.

#### **Supporting Note 2: Characterizations.**

**Scanning Electron Microscopy.** The membrane surface and cross-sectional morphology were observed by Field Emission Scanning Electron Microscope (Carl Zeiss SUPRA 55 FESEM). For cross-sectional analysis, the sample was cryogenically fractured in liquid nitrogen. All the samples were sputtered for 60 seconds to obtain a thin gold layer before SEM tests.

**X-ray photoelectron spectroscopy.** The material and membrane chemical compositions were analyzed by X-ray photoelectron spectroscopy (Kratos Axis Ultra DLD XPS system). Samples were prepared with the same coating conditions, followed by 4 times thorough wash with DI water on the membrane surfaces, and then soaked in water for another 20 hours to remove residual chemicals.

Attenuated total reflectance-Fourier transform infrared spectroscopy. The material and membrane chemical properties were characterized by Attenuated total reflectance-Fourier transform infrared spectroscopy (PerkinElmer Spectrum 100 FT-IR). Spectra were recorded from 500 to 4000 cm<sup>-1</sup>.

**X-ray diffraction.** Material was investigated by wide-angle X-ray diffraction (Bruker D8-Discover) to measure the *d*-spacing of N-GOQDs. Dry samples were vacuum dried in oven at 40 °C overnight.

Calculation of the *d*-spacing:

The d-spacing can be calculated via Bragg's law:

 $n\lambda = 2d\sin\theta$ 

where *n* is an integer (1,2,3...),  $\lambda$  is the wavelength of the beam,  $\theta$  is the incident angle and *d* is the spacing between diffraction planes.

#### Supporting Note 3: Synthesis of N-GOQDs.

N-GOQD was synthesized by carbonization of citric acid (CA, 99%, Sigma-Aldrich) with ammonia through hydrothermal treatment following our previous work with some modification, which is a facile and economic GOQD synthesis method.<sup>1, 2</sup> In brief, 80 ml of a CA aqueous solution (100 mg/mL) and 20 mL (30%) ammonia aqueous solution were transferred into a Teflon-lined autoclave and were heated at 180 °C for 24 h. After cooling to room temperature, the pH of the light yellow GOQD solution was tuned to 8 by adding NaOH solution (1 mg/mL) dropwise. The dark-yellow N-GOQD solution was dialyzed in dialysis tubing (3000 Da, Spectrum Lab. Inc.) against DI water for 4 h to remove impurities and excess ammonia. After dialysis, an aqueous suspension of N-GOQD was centrifuged at 10,000 rpm to remove any aggregates.



Figure S1. Synthesis of N-GOQD.

#### Supporting Note 4: UV-vis spectrum of N-GOQDs.

Figure S2 shows that the N-GOQD exhibits a sharp peak at 260 nm, which is attributed to the  $\pi$ - $\pi$ \* transitions of aromatic C=C bonds. Note that in N-GOQD, C atoms have a very different chemical environment from large GO flakes, which leads to a significant shift of C=C peak position.



Figure S2. UV-vis spectrum for N-GOQD. The inset is a digital picture of N-GOQD under visible light.

#### Supporting Note 5: Photoluminescence spectrum of N-GOQDs.

Photoluminescence (PL) characterization was measured at room temperature in the aqueous solution (Figure S3). The PL spectrum of GOQD showed strong emission peak which is positioned at about 430 nm.



Figure S3. Photoluminescence spectrum for N-GOQD. The inset is a digital picture of N-GOQD under UV-light of 365 nm.

Supporting Note 6: XPS spectrum of N-GOQDs.



Figure S4. XPS full survey of N-GOQDs.

#### Supporting Note 7: XRD of N-GOQDs.

X-ray diffraction pattern of as-produced N-GOQDs was shown in Figure S5 and a broad diffraction peak at 20.3° was observed as the same as graphene or graphene oxide XRD patterns. Compared to graphene film (0.34-0.37 nm), the slightly larger interlayer spacing (0.43 nm) in N-GOQDs revealed that the nano-meter sized graphene flakes are in oxidized state and stacked together exhibiting a completely amorphous state without crystalline phase. On the other hand, the interlayer spacing of N-GOQDs is smaller than that of graphene oxide (0.8-0.9 nm) suggesting that GOQDs are mainly oxidized on the edges due to their small size.



Figure S5. XRD spectrum for N-GOQD.

#### Supporting Note 8: FT-IR of N-GOQDs.

FT-IR spectrum of N-GOQD (Figure S6) exhibited several distinct peaks related to the oxygen functional groups at 3400 cm<sup>-1</sup> (OH stretching vibration), 1726 cm<sup>-1</sup> (C=O stretching vibration), 1621 cm<sup>-1</sup> (O-H bending and aromatic C=C, skeletal ring vibrations from the graphitic domain), 1380 cm<sup>-1</sup> (C-OH stretching vibrations), 1240 cm<sup>-1</sup> (C-O stretching vibrations of epoxy), and 1108 cm<sup>-1</sup> (C–OH stretching vibrations). The peaks at 1587 cm<sup>-1</sup> and 3140 cm<sup>-1</sup> correspond to C-N and N-H bending vibration from typical N-GOQD doped with nitrogen.



Figure S6. FT-IR spectrum for N-GOQD.

#### Supporting Note 9: Synthesis of PD modified SWCNTs.

The synthesis process of PD/SWCNTs has been reported in literatures.<sup>3</sup> Particularly, the SWCNTs was dispersed in 100 mL DI water by adding 10 mg SWCNTs and 100 mg sodium dodecylbenzenesulfonate followed by sonication for 10 hours. The dispersion was then centrifuged at 10,000 rpm for 45 min to remove any undispersed SWCNTs. The concentration of the produced SWCNTs dispersion was 0.02 mg mL<sup>-1</sup>. Then 10 mg dopamine hydrochloride was added followed by stirring for 1 hour at 40 °C, and 10 ml 0.1 M HCl–Tris (pH = 7.5) was added with a further stirring for 36 h at 40 °C. The final solution was centrifuged at 10,000 rpm for 30 min to obtain the PD/SWCNT dispersion. During the SWCNT coating, the bulk dispersion was diluted into 0.005 mg/mL<sup>-1</sup> for membrane deposition.<sup>4</sup>

#### Supporting Note 10: Thickness of SWCNT framework layer.

The SWCNT layer thickness would likely determine the subsequent N-GOQD/SWCNT membrane layer thickness because the SWCNT framework was employed as skeleton for deposition of N-GOQDs. In this work, the thickness of SWCNT framework layer can be controlled by varying the SWCNT seeding time. Two different seeding time (40 and 20 mins) was conducted to prepared SWCNT layer in a thicker and a thinner thickness. As observed from SEM, the thickness for 40 mins seeding samples is around 80-90 nm as shown in Figure S7, while the thickness for 20 mins seeding samples is around 50 nm as shown in Figure 2c.



Figure S7. Cross-sectional SEM images of SWCNT framework with 40 min seeding time. The thickness is observed with 85 nm.

#### Supporting Note 11: XPS spectra of SWCNT framework layer.

The XPS elemental survey was performed on the PD/SWCNT framework membrane. As shown in Table S1 and Figure 2 (f), C 1s peak at 285 eV, N 1s peak at 400 eV and O 1s peak at 532 eV were all observed, while the C1s peak possesses 90.4% over all peak percentage, suggesting the carbon skeleton property of SWCNT support membrane. The nitrogen peak (2.7%) attributes to the PD layer outside the nanotubes. The deconvoluted C1s spectra (Figure S8 (a)) demonstrates the similar result with other publication on PD/SWCNTs film,<sup>3</sup> in which the C-O and C-N peaks were emerged to confirm the PD layer existence. The N1s spectra (Figure S8 (b)) of PD/SWCNT framework showed two nitrogen peaks (N1s) at ~399.6 eV (non-protonated amine groups) and ~401.4 eV (protonated amine groups), further verifying the presence of PD films wrapped on the carbon nanotubes.<sup>5, 6</sup>



Table S1. Full survey of SWCNT layer.

Figure S8. XPS spectra of PD/SWCNT support membrane. (a) C1s spectrum; (b) N1s spectrum.

#### Supporting Note 12: ATR-FTIR of SWCNT framework layer.

The SWCNT support layer was also characterized by ATR-FTIR to confirm the successful deposition of the skeleton layer. Figure S9 shows the FTIR spectrum of PD/SWCNT layer, which is very similar to the amino-carbon nanotube polysulfone composite membranes.<sup>7</sup> Peaks at 1147, 1292 and 1321 cm<sup>-1</sup> are corresponded to the stretching vibration of sulfone groups on polysulfone substrate, and 1486 and 1502 cm<sup>-1</sup> are attributed to the aromatic C=C stretching from both SWCNT and polysulfone substrate. The enhanced peaks at 2921 and 2958 cm<sup>-1</sup> suggests the C-H stretching from the PD layer, and new peaks at 1584 and 1235 cm<sup>-1</sup> are possibly due to the N-H bending and C-N stretching from amine group on PD layer, demonstrating the successfully coating of PD/SWCNT framework.



Figure S9. ATR-FTIR spectra of PD/SWCNT support membrane.

## Supporting Note 13: Contact angle and zeta potential measurement of N-GOQD/SWCNT membranes



Figure S10. Contact angle of polymeric substrate, SWCNT mesh, N-GOQD/SWCNT membrane,

and DETA functionalized N-GOQD/SWCNT membrane.

#### Supporting Note 14: N-GOQD flat-sheet membrane fabrication.

The PSf ultrafiltration membranes were employed as substrate for N-GOQD flat-sheet membrane preparation, and the surface morphology of PSf substrates was observed by SEM.



Figure S11. SEM of PSf ultrafiltration membranes. The effective pore size is around 25-30 nm.

The PSf flat sheet membranes were thoroughly washed by DI water first and then soaked in EtOH for 2 hours on a rocking platform shaker. Then the substrates were stored in DI water/EtOH (50/50) mixture for overnight before use. The flat sheet N-GOQD/SWCNT membranes were fabricated on PSf ultrafiltration membranes by two-step vacuum filtration method as shown in Figure S12. Firstly, the PSf substrate was washed with EtOH and then 100 mL DI water was added into the vacuum coating system to thoroughly wash the pores of PSf substrate. Then the vacuum was stopped, and the SWCNT dispersion (0.005 mg/mL) was added for coating. The vacuum was reapplied until all the solution was drained out. The SWCNT was uniformly coated on the PSf substrate surface and a rinsing step was followed with 100 mL DI water under vacuum. A heat-drying step was then conducted at 60 °C in an oven for 2 hours. The second vacuum coating was performed with 100 mL N-GOQD dispersion (0.1 mg/mL) and the filtrate was collected for further

coating purpose. After N-GOQD coating, a heating treatment was conducted at 80 °C, and the membrane was dried in oven at 40 °C for overnight.



Figure S12. Flat-sheet N-GOQD/SWCNT membrane coating process.

#### Supporting Note 15: Nanofiltration and desalination measurement.

Dye molecules	Charge	MW	Molecular size
Methyl Orange	-	327	1.2 nm × 0.7 nm
Rose Bengal	-	1017	1.5 nm × 1.2 nm
Crystal Violet	+	408	1.4 nm × 1.3 nm
Methylene Blue	+	320	$1.4 \text{ nm} \times 0.6 \text{ nm}$

Table S2. The properties of different dyes.<sup>8</sup>

The dye removal experiments were conducted with a 50 mL Millipore Amicon dead-end filtration cell (Millipore-Sigma, US). For each testing membrane, it was cut from the middle of the coated membrane, and then a 0.5 cm<sup>2</sup> filtration area was sealed with silicon tap and aluminum sheet as shown in Figure S13.



Figure S13. Flat-sheet N-GOQD/SWCNT membrane for water treatment test.



Figure S14. Zeta potential measurement of N-GOQD based membranes.

All the tested membranes were pre-compacted with DI water under 4 bar for 1 hour, then the pure water permeance and salt rejection tests were conducted first before the dye rejection tests. It is noted that between each test, the membrane was washed with DI water under 4 bar for 1 hour to eliminate any fouling effect. Three membranes were used for each experiment to confirm the result. The flux of N-GOQD/SWCNT membrane after 1-hour stabilization for four types of dyes are 11.31 (MO), 9.41 (RB), 9.84 (MB), 6.42 (CV) LMH/bar, respectively.

Solute	Water permeability	Rejection
	(LMH/bar)	
Water	406.63	N/A
water	+00.05	11/2 X
Methyl Orange	168.36	6.1%
Rose Bengal	168.84	55.1%
Crystal Violet	179.98	14.7%
Methylene Blue	152.44	5.6%
Sodium Sulfate	187.96	2.7%

 Table S3. The water permeability and rejection of PSf substrate.

#### Supporting Note 16: Hollow fiber membrane fabrication.

#### 1. Inner surface morphology of PES hollow fiber support.

To prepare a highly permeable membrane and minimize the molecular transport resistance from polymeric hollow fiber substrate, a relatively high base permeance of gases need to be ensured. We selected a commercial poly ether sulfone (PES) ultrafiltration hollow fiber membrane as the base substrate fibers. The base permeances of gases ( $CO_2$  and  $N_2$  in this work) were all higher than 7,000 GPU with negligible selectivity.



Figure S15. SEM of PES hollow fibers. The effective pore size is around 30 nm.

#### 2. Hollow-fiber Coating setups.

Here we proposed a GO seeding and vacuum-assisted coating method with our lab-designed system as demonstrated in Figure S16. The lab-designed coating system involved a syringe to hold coating solutions, a syringe pump (New Era Pump Systems, Inc. US) which can control the flow rate of coating solution, several connecting tubes, a hollow fiber module which fixed a hollow

fiber membrane and two ends of the module are sealed with epoxy, and a vacuum pump connected to a middle hole of the hollow fiber module.



Figure S16. Lab-designed hollow fiber membrane coating system.

#### 3. Hollow fiber membrane module fabrication and sealing.

The hollow fiber substrate was fixed in a Pyrex tube before coating. Three holes were drilled on the two sides respectively as shown in Figure S17.



Figure S17. Photograph of hollow fiber membrane coating module.

To avoid concentration polarization during membrane permeation test, the sweep gas is introduced from one hole at one side and escapes from two holes at the two ends of another side to bring all the permeated  $CO_2$  gas out from the Pyrex tube. Thus, with a continuous and relatively high flow rate sweep gas which is helium, the  $CO_2$  partial pressure at permeate side can be regarded as zero. The sweep gas flowing diagram was shown in Figure S18.



Figure S18. Permeation diagram of sweep gas system.

E-30CL® Hysol<sup>™</sup> Epoxy (Loctite, US) was purchased from Grainger, Inc. Typically, the epoxy was mixed in ratio of 2:1, and loaded into a 10 mL syringe. The epoxy was injected into hollow fiber membrane module after an hour curing, and followed by two hours rolling on an automatic roller to ensure a uniform sealing. The prepared module was then stored at room temperature for 24 hours before it was ready to use.

#### 3. Cleaning of substrates.

The PES hollow fiber membranes were thoroughly washed by DI water first and soaked in DI water for overnight. Then the substrates were dried in oven at 80 °C for 10 hours to further stabilize the membrane structure before coating.

#### 4. Coating processes.

#### N-GOQD hollow fiber membrane fabrication:

Coating solution was prepared by diluting SWCNT suspension and N-GOQD dispersion to specific concentrations (0.005 mg/mL and 0.1 mg/mL respectively in this work) and then sonicated for 10 mins.

Ultrathin N-GOQD/SWCNT membranes were fabricated by seeding and modified vacuumassisted coating method. First, the coating solution (SWCNT or N-GOQD) was pumped into the PES hollow fiber membrane by syringe pump with a constant flow rate of 0.5 mL/min until the solution continuously flow through the coating solution exit channel without any air bubble. Subsequently, the vacuum was applied and the seeding immediately started. Seeding was stopped after a specific vacuum filtration time (20 or 40 mins for SWCNT coating, and 20 mins for N-GOQD coating in this work). To protect the as-seeded SWCNT framework or N-GOQD/SWCNT membrane layers, we simply sealed the two ends of hollow fiber supports with an impulse sealer (PFS-100) and disconnected the coating module from the solution tubes. A vacuum coating and drying step with 30 min was then conducted to pull out all the water from the inside of hollow fiber, and to form a high quality and uniform coating layer. Overall, each layer (SWCNT and N-GOQD layers) was deposited by this two-step vacuum assisted coating method. A heat drying step (60 °C for 2 hours) was only conducted after SWCNT coating and before N-GOQD coating to stabilize the carbon skeleton structure, and a heat treatment at 80 °C was conducted after N-GOQD coating.

Two ends of the as-coated N-GOQD/SWCNT hollow fiber membrane were cut after drying and the membrane was directly used for permeance tests. Four samples of each type of membrane were prepared and tested for experimental reproducibility.



Figure S19. Photo of the PES blank substrate (top) and as-coated N-GOQD hollow fiber membrane (bottom).

#### Supporting Note 17: Gas permeation measurement.

The measurements of membrane transport properties were conducted by using a gas permeation system (Figure S20). The membrane coating module was loaded in a cylindrical stainless-steel cell with an active membrane area of 0.5024 cm<sup>2</sup> inside an oven (Forced Convention Oven, JeioTech Co., Ltd. US) with accurate temperature control as shown in Figure S21. The feed and the sweep gas flows were designed to be perpendicular in the cell. Feed gas consists of CO<sub>2</sub> (99.999%, Airgas, US) and N<sub>2</sub> (99.999%, Airgas, US) in different concentration by adjusting their flow rate with mass flow controller (MFC). Helium (99.999%, Airgas, US) as sweep gas, carried the permeance gas for composition analysis. Before contacting the as-coated hollow fiber membranes, the feed gas and the sweep gas (He) were saturated with water vapor by bubbling through the humidifiers and then passing an empty bottle with glass beads to remove the condensate water. The relative humidity (RH) at the feed side was detected by a humidity sensor and was >99%. After the membrane separation process, both the retentate and permeate streams leaving the oven were cooled to ambient temperature in their respective water knockout vessels to remove the condensed water before the streams entered an Agilent HP-5890-II gas chromatograph (Agilent Technologies, Palo Alto, CA) for gas composition analyses. Helium was used as the carrier gases for the TCD detector in GC. The gas chromatograph column used was of the RESTEK Rt-U-BOND 19750 (Restek, Bellefonte, PA). Each of the membrane permeation measurement was taken after the membrane had been exposed to the feed and permeate streams under a specific condition (temperature and pressure) until the GC shows constant result for at least 30 mins, which allowed for steady-state permeation. The permeance of CO<sub>2</sub> and N<sub>2</sub> was calculated from the sweep gas flow rate and its composition. The permeate side pressure in the system was maintained at the atmosphere pressure.



Figure S20. Schematic diagram of gas permeation measurement.

The permeation temperature was controlled by the oven, the gas flow rate was calibrated with gas flowmeter (ADM2000, Agilent Tech., DE, US.), and the pressure was adjusted by a back-pressure regulator and measured by a pressure gauge at the exit of feed gas. The feed pressure was set at 1-2 psig to avoid back-flow of sweep gas, and the sweep pressure was set close to atmospheric pressure. Gas flow rates were accurately controlled by flow meters (Brooks Instrument, Hatfield, PA) at 80 cm<sup>3</sup>/min for the feed side and 20 cm<sup>3</sup>/min for the sweep side. Feed and sweep gases directly entered the cell as dry gas or passed through the humidifier as wet gas with >99% humidity (measured by SRH77A Temperature/Humidity Instrument, Cooper-Atkins, CT, US.).



Figure S21. Photographs of lab-designed hollow fiber membrane permeation system. Inside of the oven: (a) is the membrane permeation cell in where the GO-based hollow fiber membrane was installed; (b) is the humidifier to generate saturated feed/sweep gases; (c) is the water trapper to condense the liquid water in the feed/sweep gases before they enter permeation cell. Two high temperature silicone O-rings were used to seal the membrane glass module in the permeation cell.

#### Supporting Note 18: Permeance and selectivity calculations.

Gas permeance of the membranes is customarily expressed in GPU (  $1GPU = 1 \times 10^{-6} cm^3 (STP)/cm^2 \cdot s \cdot cmHg = 3.348 \times 10^{-10} mol/(m^2 \cdot s \cdot Pa))$ , and is calculated by the equation:

$$(P_i/l) = \frac{J_i}{\Delta P_i A}$$

Where  ${P_i/l}$  denotes the gas permeance of "i";  $J_i$  denotes the gas molar flow rate through the membrane (mol/s);  $\Delta P_i$  denotes the gas partial pressure difference between feed and permeate sides (Pa); A denotes the membrane active area (m<sup>2</sup>). The gas selectivity ( $\alpha_{ij}$ ) was calculated by the equation:

$$\alpha_{ij} = (P_i/l)/(P_j/l)$$

The detecting limit of GC is around 0.02% for measured gases in our experiments, and the  $CO_2/N_2$  selectivity reported in this work is based on the highest detectable  $N_2$  permeance during the mixed gas permeation tests; the actual selectivity is expected to be higher than the reported value.

#### Supporting Note 19: Detailed calculation of CO<sub>2</sub> permeance in sweep gas system.

Calculation of gas permeance method is as follows:

Permeance 
$$(mol/(m^2 \cdot s \cdot Pa)) = \frac{Q_{CO_2} \cdot 22.4 \ mol/L}{A \cdot \Delta \pi_{CO_2}}$$

Where  $Q_{CO_2}$  is the volumetric flowrate of CO<sub>2</sub> under the standard condition at the permeate side, in L/s; *A* is the membrane area, in m<sup>2</sup>;  $\Delta \pi_{CO_2}$  is the CO<sub>2</sub> partial pressure difference between feed and permeate sides, in Pa.  $Q_{CO_2}$  can be calculated as follows:

$$Q_{CO_2} = \frac{Vol_{(CO_2)}\%}{1 - Vol_{(CO_2)}\% - Vol_{(N_2)}\%} \cdot Q_{He}$$

Where  $Q_{He}$  is the volumetric flow rate of the carrier gas (helium here) under the standard condition at the permeate side, in L/s;  $Vol_{(i)}$ % is the volume fraction of gas *i* in percentage, %.  $Q_{He}$  is set and controlled by a calibrated mass flow controller,  $\Delta \pi_{CO_2}$  can be calculated from CO<sub>2</sub> feed partial pressure (=total feed pressure× $Vol_{(CO_2)}$ % on the feed side) and permeate partial pressure (= total permeate pressure× $Vol_{(CO_2)}$ % on the permeate side), and  $1 - Vol_{(CO_2)}$ % -  $Vol_{(N_2)}$ % can be analyzed by gas chromatography. Then,  $1GPU = 3.348 \times 10^{-10} mol/(m^2 \cdot s \cdot Pa)$ 

Therefore, we can calculate the gas permeance in GPU with the sweep gas flow rate.

# Supporting Note 20: Gas permeation measurement of SWCNT skeleton layer and base N-GOQD/SWCNT membrane.

Mixed gas (15% CO<sub>2</sub> and 85% N<sub>2</sub>) permeation measurements were conducted with our labdesigned hollow fiber membrane gas permeation system. The feed pressure was maintained at 1-2 psig to avoid any back flow of the sweep gas from the permeate to the feed side. The base gas permeance was firstly investigated for the 50 nm SWCNT coated hollow fibers at room temperature, which exhibited 2,530 GPU for N<sub>2</sub> and 2,045 GPU for CO<sub>2</sub> under dry condition, 2,470 GPU for N<sub>2</sub> and 1,987 GPU for CO<sub>2</sub> under wet condition, respectively. Permeation temperature was then elevated to 75 °C for both dry and wet feed while the permeance maintained almost the same at dry condition (2485 and 2020 GPU for N<sub>2</sub> and CO<sub>2</sub>, respectively) and slightly decreased at wet condition (2315 and 1927 GPU for N<sub>2</sub> and CO<sub>2</sub>, respectively). It indicated that the ultrathin SWCNT mesh layer does not significantly compromise the base permeance for both gases (>7,000 GPU for N<sub>2</sub> and CO<sub>2</sub>). However, the SWCNT "skeleton" exhibited negligible  $CO_2/N_2$  selectivity, apparently resulting from the relatively larger pores of framework layer than the gas molecules.

The coated N-GOQD/SWCNT hollow fiber membranes were then evaluated for  $CO_2$  separation from simulated flue gas. Dry gas test was firstly deployed, and slightly  $CO_2$  selective gas transport was exhibited with  $CO_2$  permeance of 415 GPU and N<sub>2</sub> permeance of 175 GPU with a  $CO_2/N_2$ selectivity of 2.4. Under wet condition, however, the N-GOQD/SWCNT membrane showed a significantly increased selectivity  $CO_2/N_2$  of 29 with a decreased  $CO_2$  permeance of 96 GPU and N<sub>2</sub> permeance of 3.3 GPU. The N-GOQD/SWCNT matrix interstices act as the molecular transport paths, and the selective  $CO_2$  transport is probably due to the highly porous but hydrophilic membrane structure, which could absorb water molecules in the small hydrophilic channels and therefore block most gas molecules. Those water-enriched empty spaces in the hydrated "polyquantum dots" membrane matrix, however, would allow more-soluble  $CO_2$  molecules to pass while block  $N_2$ .

The surface polydopamine layer of SWCNT offers a large amount of oxygen-containing groups which has strong affinity to the functional groups at the edge of N-GOQDs, and the  $\pi$ - $\pi$  interaction associated with the hydrogen bonding create connection to ensure a solid membrane matrix, allowing smaller molecules to transport through the free volume. Due to the hydrophilic property of the N-GOQD/SWCNT membrane layer, water could be easily trapped inside the gaps to further shrink the channel size and efficiently reject inert gas molecules but favor more water-soluble CO<sub>2</sub> to pass. With the replacement of oxygen groups to amine groups by amine functionalization, a facilitated transport mechanism was endowed to further boost CO<sub>2</sub> transport one order of magnitude higher. On the other hand, the crosslinking agent could potentially fortify the N-GOQD/SWCNT membrane structure by generating crosslinks between PD/SWCNTs and N-GOQDs, and therefore to decrease the free volume size and block almost all the nitrogen molecules, leading to a significant increase of the CO<sub>2</sub>/N<sub>2</sub> selectivity and CO<sub>2</sub> purity in the permeate side.

#### Supporting Note 21: DETA functionalized N-GOQD/SWCNT membrane.

#### 1. Coating solution preparation and XPS of functionalized N-GOQDs.

The DETA functionalized N-GOQD/SWCNT membrane coating solution was prepared by mixing 5 ml of GOQD 0.1mg/ml + DETA (10% wt. %), then was sonicated for 30 min and kept in oven at 80 °C for overnight to form cross-linking between DETA and N-GOQD before the coating on hollow fibers.

The DETA functionalized N-GOQDs was dried in oven and characterized by XPS. The carbon, oxygen, and nitrogen ratios of DETA functionalized N-GOQDs are 70.0%, 17.1% and 13.0% respectively. Compared with the N/C ratio in N-GOQDs (13.9%), the N/C ratio in DETA functionalized N-GOQDs increased to 18.6%, demonstrating the successful grafting of DETA molecules on N-GOQD particles by heat functionalization.



Figure S22. XPS spectrum of DETA functionalized N-GOQDs.

2. Membrane characterizations.



Figure S23. Surface and cross-sectional SEM images of DETA functionalized N-GOQD/SWCNT membranes.



Figure S24. XPS spectrum of DETA functionalized N-GOQD/SWCNT membranes.



Figure S25. ATR-FTIR spectrum of DETA functionalized N-GOQD/SWCNT membranes.

# Supporting Note 22: Gas permeation measurement of DETA functionalized N-GOQD/SWCNT membrane.

Gas permeation measurements of DETA functionalized N-GOQD/SWCNT membrane was were conducted with mixed gas, and very low gas permeance was found for both N<sub>2</sub> (44 GPU) and CO<sub>2</sub> (95 GPU) under dry condition. At room temperature and hydrated state, both N<sub>2</sub> and CO<sub>2</sub> gas permeance on DETA functionalized N-GOQD/SWCNT membrane decreased, mainly due to the further reduced pore size resulted from the amine-crosslinking in membrane interstices. Yet the CO<sub>2</sub>/N<sub>2</sub> selectivity reaches 63, owing to the decreased N<sub>2</sub> permeance from 3.4 GPU on base N-GOQD/SWCNT membrane to 1.3 GPU on DETA functionalized N-GOQD/SWCNT membrane. For CO<sub>2</sub>, however, amine-crosslinking decreases the CO<sub>2</sub> diffusion coefficient but facilitates the CO<sub>2</sub> reaction and sorption rate, and therefore 81 GPU was observed. In another word, the facilitated transport of CO<sub>2</sub> by amine group balanced the decreased CO<sub>2</sub> diffusion rate inside those shrunk transport channels. To achieve activated diffusion process in facilitated transport membrane, temperature was then elevated to 40, 60 and 75 °C.

The influence of feed side absolute pressure on membrane separation performance was investigated and the results are shown in Figure S26. It can be observed that the feed pressure increase causes the CO<sub>2</sub> permeance decrease from 1450 GPU at 114 kPa to 825 GPU at 161 kPa, while the selectivity remains the same as high as ~520. The increased feed total pressure significantly increases the CO<sub>2</sub> partial pressure at feed side. The facilitated transport membrane, however, is saturated rapidly with low CO<sub>2</sub> concentration in the feed side, and further CO<sub>2</sub> concentration increase would not enhance the CO<sub>2</sub> absorption amount inside the facilitated membrane matrix but would increase the CO<sub>2</sub> partial pressure difference ( $\Delta P_{CO2}$ ) which could lead to a low permeance of CO<sub>2</sub>. On the other hand, the N<sub>2</sub> is always very slight permeable in the

membrane, and the  $N_2$  partial pressure difference increase in our testing range would also decrease the  $N_2$  permeance, resulting in the almost stable selectivity.



Figure S26. Feed absolute pressure influence on CO<sub>2</sub> separation performance. Test was conducted at 75 °C and wet condition.

#### Supporting Note 23: Activation energy of DETA functionalized N-GOQD/SWCNT



#### membrane.

Figure S27. The  $lnP_{CO_2} - 1/T$  plot for CO<sub>2</sub> absorption/diffusion activation energy of DETA functionalized N-GOQD/SWCNT membrane.

The activation energy of CO<sub>2</sub> absorption/desorption in DETA functionalized N-GOQD/SWCNT membranes can be calculated from Arrhenius equation,

$$P_{CO_2}(T) = A_0 \times exp^{(n)}(\frac{-E_a}{RT})$$

where  ${}^{P_{CO_2}}$  is the CO<sub>2</sub> permeance of membranes,  ${}^{A_0}$  is the Arrhenius pre-exponential factor,  ${}^{E_a}$  is a term associated with the activation energy, R is the universal ideal gas constant, and T is the absolute temperature. The plot revealed that the activation energy is 48.42 kJ/mol, indicating the facilitated CO<sub>2</sub> transport stemed from the high absorption/diffusion rate.

# Supporting Note 24. Explanation for the exponential increase of CO<sub>2</sub> permeance on DETA functionalized N-GOQD/SWCNT membranes at high temperature.

Different dependence of CO<sub>2</sub> permeance on temperature for base N-GOQD/SWCNT and DETA functionalized N-GOQD/SWCNT membranes is due to different interactions of CO<sub>2</sub> with these two types of membranes: chemical vs. physical. For DETA functionalized N-GOQD/SWCNT membrane, activated diffusion of CO<sub>2</sub> (with activation energy of 48.42 kJ/mol (Figure S27)) dominates due to chemical bonding/reactions between CO<sub>2</sub> and grafted amines, whereas for base N-GOQD/SWCNT membrane only physical interaction between CO<sub>2</sub> and the membrane exists. As reported from Robeson's paper,<sup>9</sup> the permeability and permeance coefficients are the products of diffusion coefficient and the solubility coefficient:

Permeance of 
$$CO_2 = \frac{D \cdot S}{l}$$

Permeability of 
$$CO_2$$
 = Permeance  $\cdot l = D \cdot S$ 

Where D is the diffusion coefficient, S is the solubility coefficient, and l is the membrane thickness, a constant number.

Diffusion of CO<sub>2</sub> through DETA functionalized N-GOQD/SWCNT membrane is an activated energy process, therefore the relationship for D, S and permeability as a function of temperature can be expressed as:

$$D = D_0 exp^{[n]} \left(\frac{-E_d}{RT}\right)$$
$$S = S_0 exp^{[n]} \left(\frac{-\Delta H_s}{RT}\right)$$

Permeability of  $CO_2 = P_0 exp[n] \left( \frac{-E_p}{RT} \right)$ 

Where  $E_d$  is the activation energy of diffusion,  $\Delta H_s$  is the heat of sorption, and  $E_p = E_d + \Delta H_s$  is the activation energy of permeation. For DETA functionalized N-GOQD/SWCNT membrane, the activation energy of permeation is 48.42 kJ/mol, as shown in Figure S27.

DETA functionalized N-GOQD/SWCNT membrane is expected to reach saturation in the experimental temperature range due to the strong interaction between CO<sub>2</sub> and chemically bonded DETA, and the increased temperature could exponential increase the diffusion rate as illustrated from the relationship equation between diffusion coefficient and temperature, achieving an activated diffusion process. The selectivity in DETA functionalized N-GOQD/SWCNT membrane is also expected to increase drastically because of the significantly increased CO<sub>2</sub> permeance but almost constant N<sub>2</sub> permeance.

Supporting Note 25: Large-area (10 cm<sup>2</sup>) hollow fiber membrane preparation.



Figure S28. Large-area hollow fiber membrane coating system: (a) and (b) Coating solution; (c) hollow fiber membrane module (10 cm<sup>2</sup>); (d) vacuum line; (e) stop watch.



Figure S29. Photograph of the inner surface of the large area N-GOQD/SWCNT based hollow fiber membrane. The uniform gray color suggests the uniformity of coating process.





Figure S30. Large-area (50 cm<sup>2</sup>) DETA functionalized N-GOQD/SWCNT hollow fiber membrane module.

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