Electronic Supporting Information

ESI-1. Experimental details

We synthesized graphene oxide (GO) powder by an improved Hummers' method.[1] Concentrated H_2SO_4 (69 mL) was slowly added into the mixture of graphite flakes (3.0 g) and $NaNO_3$ (1.5 g). The mixture was cooled down to 0 ^{o}C in a ice bath. $KMnO_4$ (9.0 g) was then added into the mixture slowly. The mixture was kept at 35 ^{o}C and stirred for 30 min. Subsequently, 138 mL water was slowly added into the mixture. This produced large amount of heat and raised the reaction temperature up to 98 ^{o}C. The mixture temperature stayed at 98 ^{o}C for 2 h and then slowly cooled down by water bath. Additional 420 mL water and 3 mL of H_2O_2 (30%) were added into the mixture. After cooling down to the room temperature, the product was collected by vacuum filtration. The final GO product was washed with 200 mL water, 200 mL 1 mol/L HCl, and 200 mL ethanol for two times. The as-prepared GO was dried in vacuum oven at 40 ^{o}C first and then made into 2 mg/mL GO dispersion by sonication in DI water for 1 hour. Centrifugation was performed for the GO dispersion at 10,000 rpm for 30 min to remove large agglomerations.

We used a UV lamp (B-100Y, Mineralogical Research Company) to treat the centrifuged GO dispersion with different time, 0, 10, 30, 60 and 90 min. In order to achieve the uniformity of the UV treatment, a magnetic stirrer was applied and kept rotating in the GO dispersion when UV etching was performed. The treated GO dispersions were labeled as 0-GO, 10-GO, 30-GO, 60-GO and 90-GO, where 0-GO means GO dispersion with 0 min UV treatment, and so on.

GO membranes were fabricated by a vacuum filtration method, as described in our previous study.[2] For contact angle measurements, we chose anodic aluminum oxide (AAO, 20-nm pore size, Whatman) as the filtration support. For water/oil separation tests, we selected polyamide (PA, 200-nm cut-off pore size, Whatman) as the filtration support. The membranes were dried

under vacuum for 12 hours at room temperature. We then closed the vacuum and let it release naturally for good membrane quality.

We used atomic force microscope (AFM) to image both individual GO flakes and GO coatings. To prepare samples for individual GO flake imaging, 0.001 mg/mL GO suspensions (with UV treatment time from 0 to 90 min) were first diluted 500 times. A 4 uL drop of diluted suspension was deposited onto freshly cleaved muscovite mica disks (9.9 mm diameter, Grade V1, Structure Probe, Inc.). For continuous GO coatings imaging, 0.0625 mg/mL GO dispersions (with UV treatment time from 0 to 90 min) was first diluted 30 times and then dropped (1 drop) onto clean mica. Both types of samples were dried for 10 min at 40 ^{o}C prior to AFM imaging. The deposited GO flakes or coatings were imaged using a PicoPlus AFM (Agilent) operated in the tapping mode. All images were collected using N-type silicon cantilevers (FORTA-50, Nanoscience Instruments, Inc.) with spring constants of 1.2-6.4 N/m, resonance frequencies of 47-76 kHz, and nominal tip radius of < 10 nm. The height resolution of the AFM scanner is less than 1 A. Thus, with proper calibration, the accuracy of the measured height of surface features is approximately $\pm$0.1 nm. The AFM topography images were analyzed using image analysis software (Scanning Probe Image Processor or SPIP, Image Metrology A/S, Denmark).

Water contact angle in air measurements were taken using VCP optima system (Model: Optima XE). Water droplets (1~2 μL) were dropped carefully onto the surfaces of GO membranes on AAO. Underwater HD contact angle measurements were conducted with a self-designed system including a clear quartz cell serving as the water reservoir and a hooked microsyringe needle. Before the measurements, all samples were first wetted by water and then fixed reversely inside quartz cell which was filled with water.

The surface chemical compositions of the GO were analyzed by XPS (Kratos Axis Ultra DLD instrument equipped with a monochromated Al Ka x-ray source and hemispherical analyzer

capable of an energy resolution of 0.5 eV). To prepare samples for XPS analysis, we deposited 1 drop of 0.0625 mg/mL GO dispersion on to clean silicon wafer and dried at 40 $^{\circ}$C. For C_1s, the signal was fitted by four components: C-C&C=C (284.5 eV), C-O (286.5 eV), C=O (288.0 eV) and O=C-OH (289.0 eV), as shown in Fig. S1 to S5, which are consistent with those have been reported.[3] By integration of each individual peak, the composition for each carbon species could be calculated.

Raman spectroscopy was performed on LabRam HR confocal Raman spectrometer (JY Horiba). The spectrometer is equipped with a liquid-nitrogen cooled, charge-coupled device (CCD) detector, and a He-Ne (632.817 nm) laser for excitation. For sample preparation, 1 drop of 0.0625 mg/mL GO dispersion right after UV treatment was deposited on to a glass slide and dried at 40 $^{\circ}$C for 20 min. The well-known Raman characteristics of carbon materials are the G and D bands (1580 and 1350 cm^{-1}) which are usually assigned to the graphitized structure and local defects/disorders particularly located at the edges of graphene and graphite platelets, respectively.[4, 5] Therefore, a larger I_D/I_G peak intensity ratio can be assigned to higher defects/disorders in the graphitized structure. The UV treated GO dispersions were exposed in air for 12 hours. Afterwards, they were prepared for Raman measurement following the same procedure described above. The results are shown in Fig. S2. It could be noticed that there is no significant change of UV-treated GO after being exposed in air, regarding to the Raman I_D/I_G ratio, indicating this process is irreversible in our case.

Oil rejection was measured using total organic carbon (TOC) analysis method. For each tested membrane or support, we took two filtrate samples during 2 hours emulsion separation tests of each cycle, at 1 hour and 2 hour, respectively. After separation tests, filtrate samples were firstly diluted by 20 times, and then acidified below a pH of 2.0 by adding 10 wt% sulfuric acid to prevent the loss of compounds for dissolved organic carbon analysis. Analysis of organic compounds in these samples was performed using a TOC analyzer (TOC-V$_{CSN}$, Shimadzu

Scientific Instruments, Columbia, MD, USA). Since the total organic carbon in the feed emulsion was known, the organic rejection ratio could therefore be calculated as Oil Rejection = [1 − (TOC$_{filtrate}$/TOC$_{feed}$)] ×100%.

A self-designed stainless steel dead-end module with an effective permeation area of 5.06 cm^2 was used for the water/oil separation experiments. The feed side was connected to a high pressure nitrogen tank, which provided a driving force of 1 bar for pure water permeation and water/oil separation experiments. A magnetic stirring bar was used above the membrane (module placed on a stir table), and kept rotating while permeation/separation tests were performed. An electronic scale (Ohaus, CS Series) was used to measure the filtrate mass. Before oil emulsion separation test, 1-hour pure water permeation was firstly conducted to get the initial pure water flux. The oil-in-water emulsion was then poured into the module with water pre-wetted membranes. Oil emulsion separation test was conducted for 2 h, during which we took 2 samples of the filtrate (1 mL each) at 1 h and 2 h, respectively, for later oil rejection measurements. Afterwards, a simple membrane cleaning process was conducted by carefully flushing the membrane surface with tap water. The pure water permeation, oil emulsion separation, and the cleaning process together were considered as a single membrane performance evaluation cycle. The cycle was repeated 3 times to systematically investigate the membrane fouling behavior and their recovery capability. The filtration process contains three cycles. In each individual cycle, a pure water filtration was performed, followed by an emulsion separation. During the interval between two neighbouring cycles, a simple water flush cleaning process was applied to clean the membrane surface. Fig. S3a shows the performance of a 10-nm 0-GO membrane. For the first cycle, pure water flux through the fresh 0-GO membrane was constant at ~5900 L/(m^2·h·bar) within 1 hour. The initial permeate flux during emulsion separation was 3275 L/(m^2·h·bar), and decreased down to 250 L/(m^2·h·bar) after two hours. For the second cycle, pure water flux could be recovered to about 52% of the one in the first cycle. The initial permeate flux in emulsion

separation was recovered to 1290 L/(m^2·h·bar) and further decreased to 180 L/(m^2·h·bar). Similar

trend was observed for the third cycle. The above results indicate that severe membrane fouling

occurred during the emulsion separation. We then tested the performance of a 10-nm 30-GO

membrane, as shown in Fig. S3b. Compared with 0-GO membrane, 30-GO membrane shows

both higher pure water flux (~7400 L/(m^2·h·bar)) and initial permeate flux (~6360 L/(m^2·h·bar))

during the emulsion separation in the first cycle. Besides, the pure water recovery (89%) in the

second cycle was much higher than that of 0-GO. Similar trend was found in the following cycles.

Better antifouling performance of the 30-GO membrane could be attributed to the decreased oil

adhesion on the surface, as indicated by the underwater oil contact angle results. Fig. 4 exhibits

the separation performance of the 60-GO membrane. It is noticed that for the first cycle, both the

pure water flux and initial permeate flux during emulsion separation which was ~8100 and ~6870

L/(m^2·h·bar), respectively, are higher than those of 0-GO and 10-GO membranes, Also, these

values could be maintained for the following two cycles.
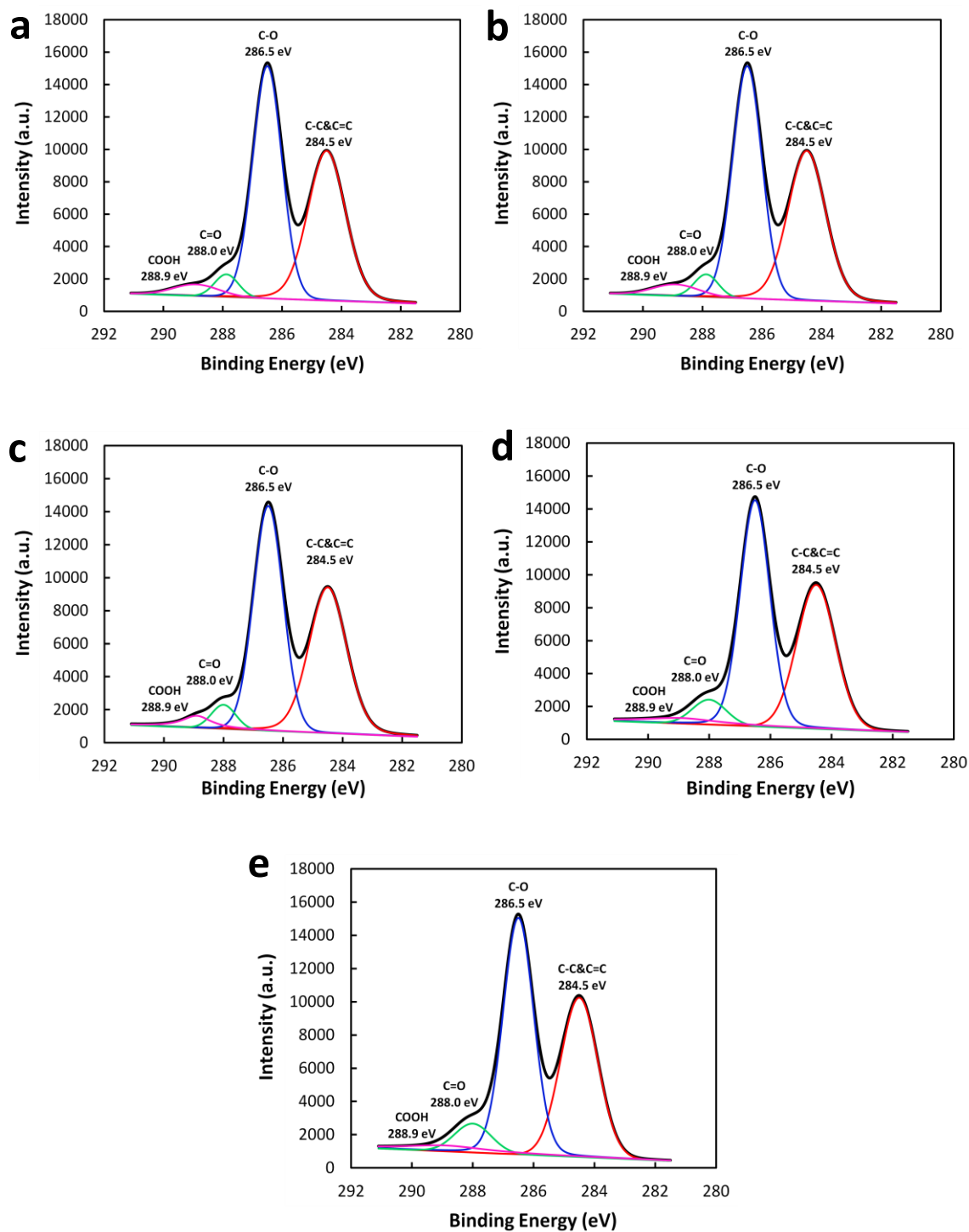
Fig. S1. XPS C_1s spectra for (a) 0-GO, (b) 10-GO, (c) 30-GO, (d) 60-GO and (e) 90-GO.
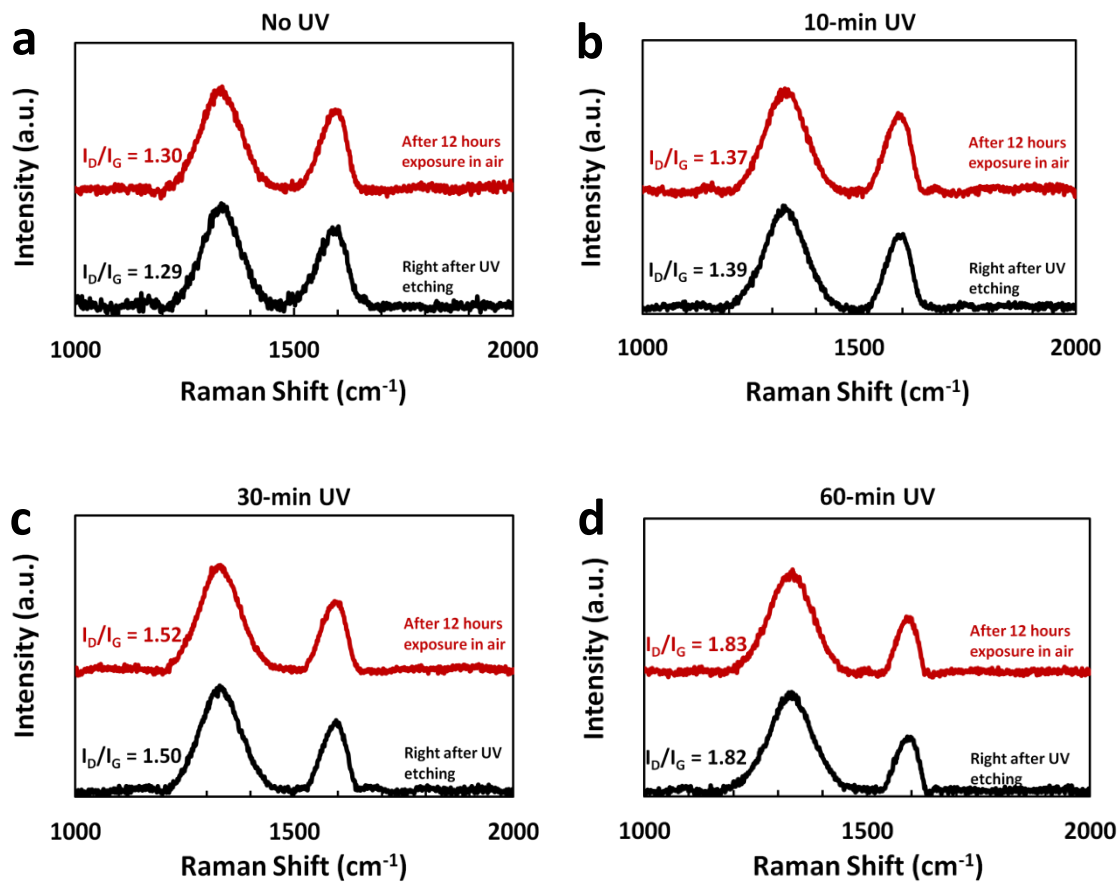
Fig. S2. Raman spectra of (a) 0-GO, (b) 10-GO, (c) 30-GO, and (d) 60-GO dispersions right after UV treatment (black curves) and with 12 hours exposure in air after UV treatment (red curves).
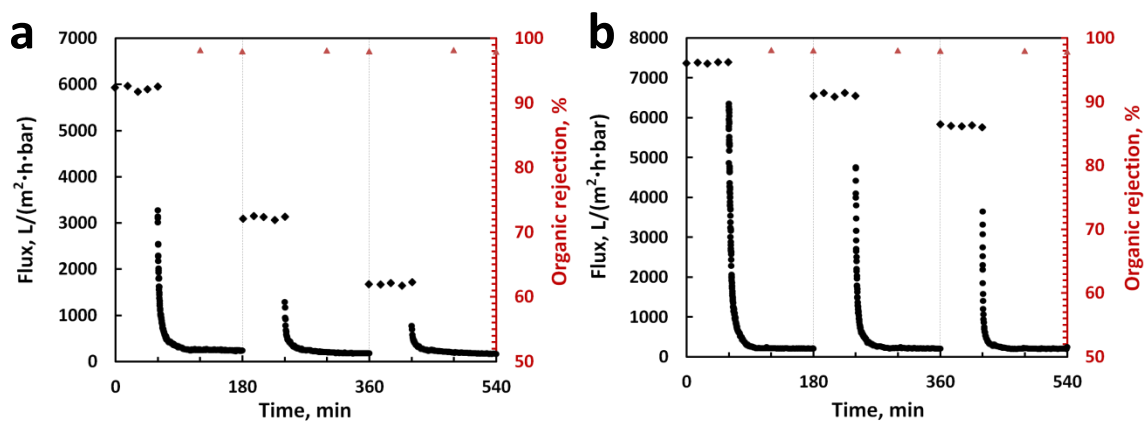
Fig. S3. Cyclic water/oil separation tests for (a) 10-nm 0-GO membrane and (b) 10-nm 30-GO membrane. (●) total flux in oil-in-water emulsion separation. (◆) pure water flux. (▲) total organic rejection.

References for ESI

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