

# Supporting Information for

## Stitch Graphene Oxide Sheets into Membrane at Liquid/Liquid Interface

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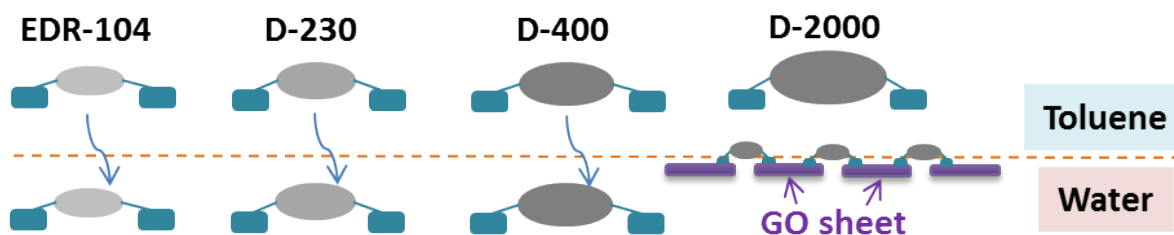
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### S1. Experimental Details

GO was prepared by modified Hummers method, which includes pre-oxidation and oxidation steps. The detailed preparation method refers to our previous publication.<sup>21, 24</sup> The interfacial reaction was performed with bottom aqueous GO solution and top polyetheramine/toluene solution. Four polyetheramines dissolving in toluene top phase (Jeffamine EDR-104, D-230, D-400, D2000, Huntsman Corporation, USA) were used to study the molecular structure effect on GO membrane formation. GO concentration (0.9-2.3 g/L) and D-2000 (0.1-20.0 g/L) concentration were adjusted to study the reactant concentration effect on membrane thickness. The reaction was conducted at different temperatures (20-80 °C) for certain period of time to study the interfacial reaction kinetics.

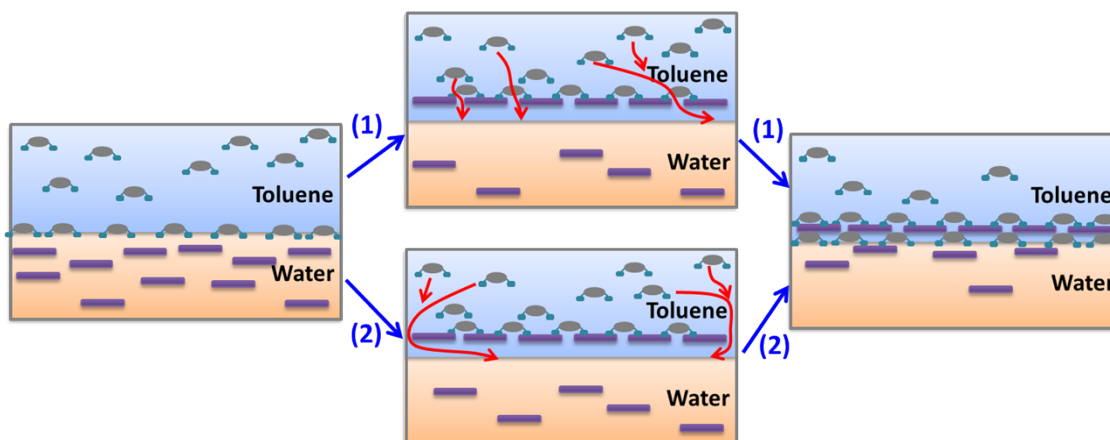
Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific Nicolet 380) was used to identify the interfacial reaction between D-2000 and GO sheet. The GO membrane thickness and surface morphology were characterized by scanning electron microscopy (SEM, JEOL-7401). Surface topography of the membranes was characterized by atomic force microscopy (AFM, NanoScope® IIIa, Digital Instruments). The AFM images were obtained in tapping mode with scanning rate of 0.5 Hz over 20×20 μm area. The transmittance of the GO membrane was measured by UV-Vis spectrophotometer (Shimadzu, UV1601). The experimental photos and videos were taken by a lab camera.

## S2. Interfacial Reaction and Membrane Transfer



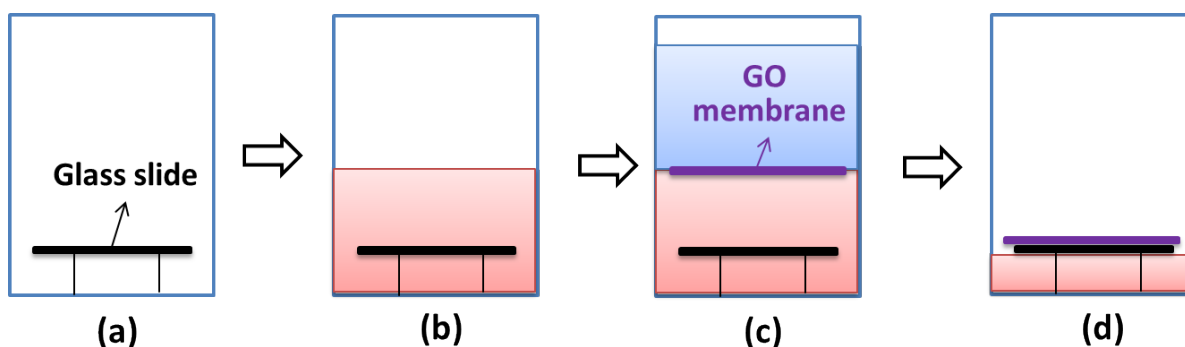
**Scheme S1.** Transport of polyetheramine at toluene/water interface and assembly of GO sheet with D-2000. The circular shaped symbol indicates the hydrophobic ether and the rectangular foot means the hydrophilic amine groups, the drawing is not to scale.

The interfacial behavior of the four polyetheramines is illustrated in Scheme S1. After injecting the polyetheramine/toluene on the top GO solution, the EDR-104, D-230 and D-400 transfer from toluene phase to water phase across the interface due to their hydrophilic nature and react with GO in water phase rather than at interface. While the D-2000 stabilizes at the interface with major hydrophobic portion in toluene phase and hydrophilic amine extends to the water phase. The covalent bonding between amine groups from D-2000 and carboxylic groups from GO sheet stitches the GO sheet together into membrane.



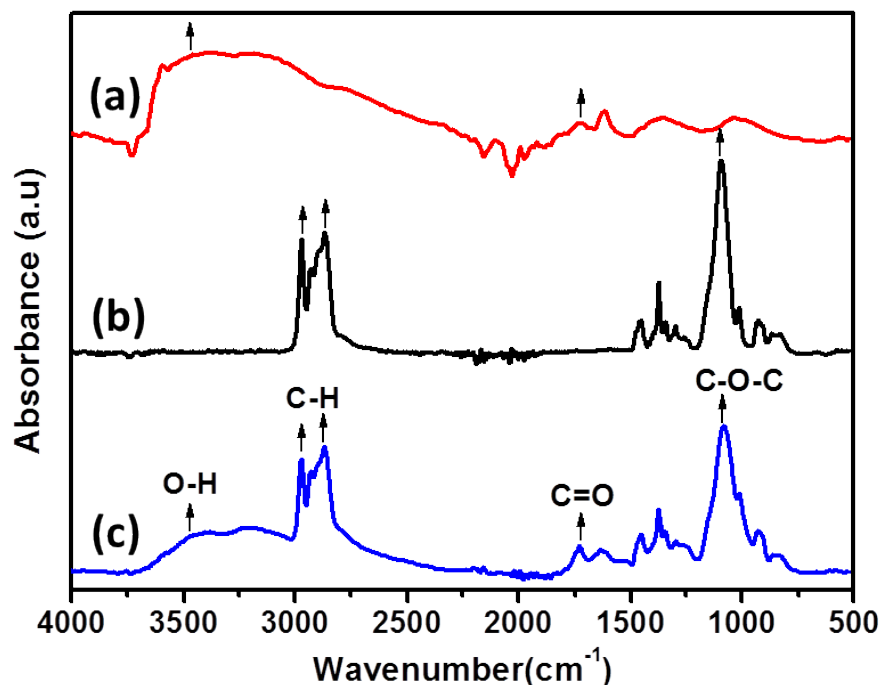
**Scheme S2.** D-2000 transfers from bulk solution to interface along two different paths.

Due to the amphiphilic nature of D-2000 molecule, it tends to form a well-patterned monolayer at the interface. Once D-2000 reacts with GO sheet, a vacant site will be left at the interface. This vacant site will be immediately filled by two possible ways. One is filled by D-2000 diffusion through GO membrane driving by the concentration difference between bulk solution and interface, path (1) in Scheme R1. The other is filled by neighboring D-2000 molecule until full coverage can be completed by supplying D-2000 around the edge of the membrane, path (2) in Scheme R1. The scheme has been added to the supporting materials.



**Scheme S3.** GO membrane transfer from liquid/liquid interface to glass slide. (a) A glass slide was placed at the bottom of reactor, (b) aqueous GO solution was added to the reactor above the level of glass slide, (c) add oil phase to trigger interfacial reaction and forms GO membrane and (d) remove aqueous phase and allow GO membrane deposit on the glass slide.

### S3. FT-IR Results



**Figure S1.** FT-IR spectrum of (a) GO, (b) D-2000 and (c) GO thin film after interfacial reaction ([D-2000]=5.0 g/L, [GO]=1.4 g/L, Time= 5 hours, temperature=20°C).

FT-IR was used to confirm the interfacial reaction between D-2000 and GO sheet, Figure 2. GO shows typical band 1716  $\text{cm}^{-1}$ , which is attributed to the C=O stretching vibrations from carbonyl and carboxylic groups, Figure S1(a). The band at 1613  $\text{cm}^{-1}$  is arising from the aromatic C=C stretching. In Figure S1(b), the D-2000 shows intense peaks near 3000  $\text{cm}^{-1}$  and 1084  $\text{cm}^{-1}$ , which correspond to the symmetric stretching of C-H bond and vibration of C-O-C, respectively. After reaction, the typical O-H, C=O peaks from GO and C-H, C-O-C peaks from D2000 are well remained in the GO membrane accompanies with the decrease of O-H peak intensity (dehydration reaction consumes -OH from GO) and broaden of C-O-C peak, Figure S1(c). The broadened C-O-C peak is attributed to the overlap of C-O-C and the new formed C-N bond indicating the dehydration reaction between amine and carboxylic groups.

#### S4. X-ray Diffraction

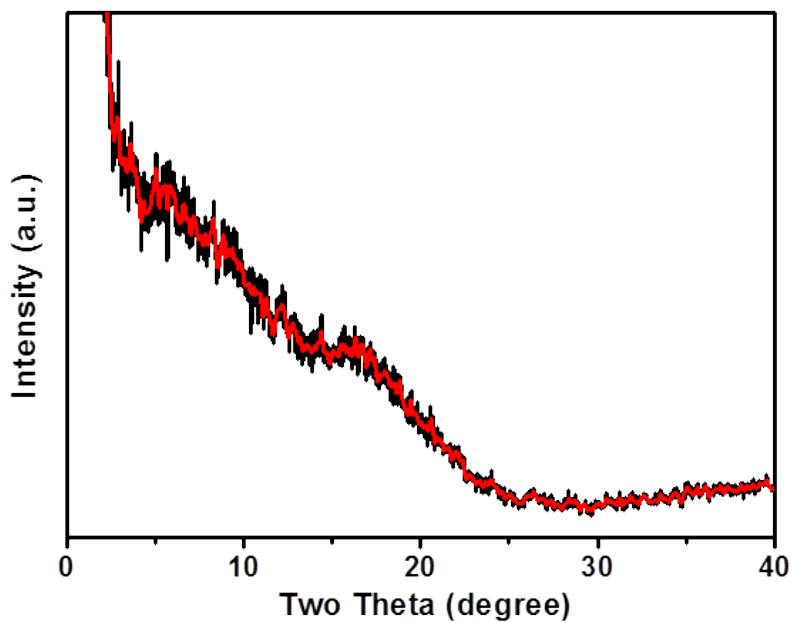


Figure S2. XRD pattern of GO membrane.

#### S5. UV-Vis Transmittance of Membranes

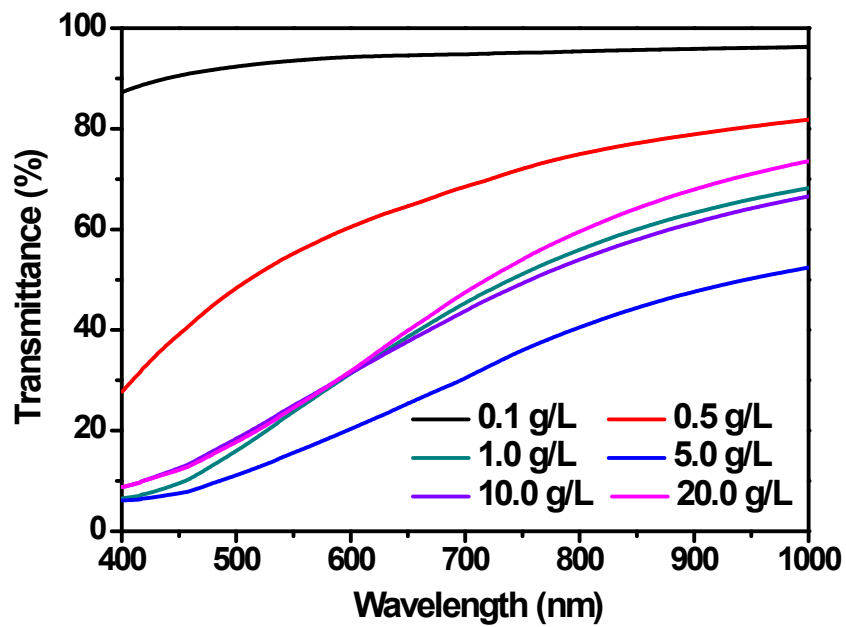
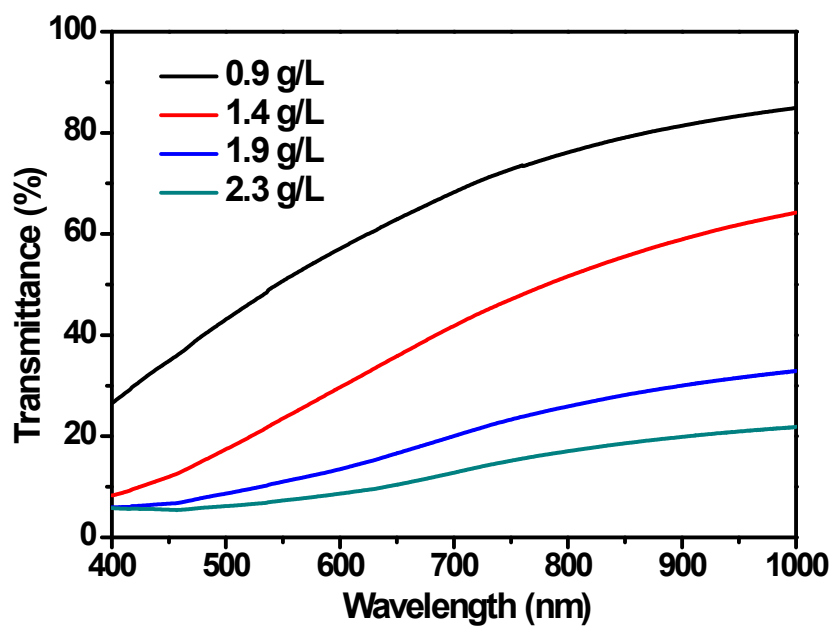
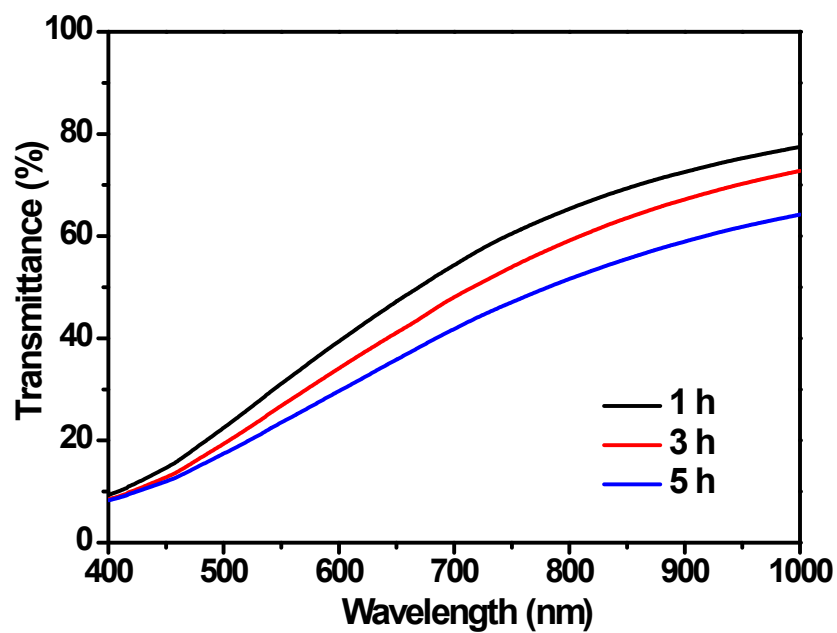


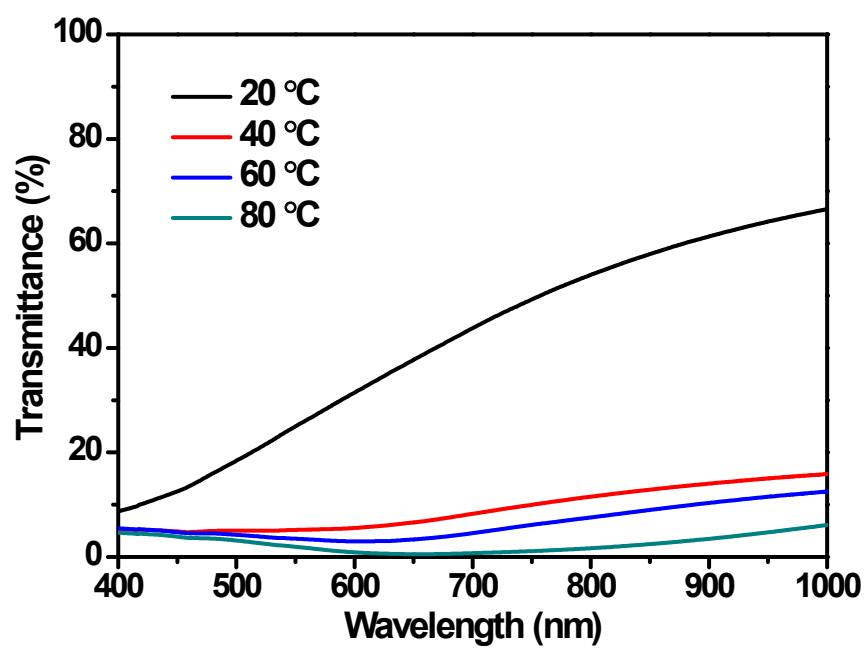
Figure S3. UV-Vis transmittance spectrum of GO membrane as a function of D2000 concentration. [GO]= 1.4 g/L, RT, time=5 hours.



**Figure S4.** UV-Vis transmittance spectrum of GO membrane as a function of GO concentration. [D-2000]=10 g/L, RT, time=5 hours.



**Figure S5.** UV-Vis transmittance spectrum of GO membrane as a function of reaction time. [GO]= 1.4 g/L, [D-2000]=10 g/L, RT.



**Figure S6.** UV-Vis transmittance spectrum of GO membrane as a function of reaction temperature. [GO]= 1.4 g/L, [D-2000]=10 g/L, time=5 hours.