

Supporting Information (SI) for: Graphene-Based Environmental Barriers

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Supporting Text

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References

Graphene oxide synthesis and characterization

Graphene oxide (GO) was prepared by a modified Hummers method with preoxidation treatment [Hummers and Offeman 1958] and purified by a two-step acid-acetone wash for suppressing gelation and removing the salt byproducts [Kim et al. 2010]. The GO was characterized for thickness (layer number) by AFM (Fig. S1), lateral dimension by SEM (Fig. S2), and zeta potential (Fig. S3).

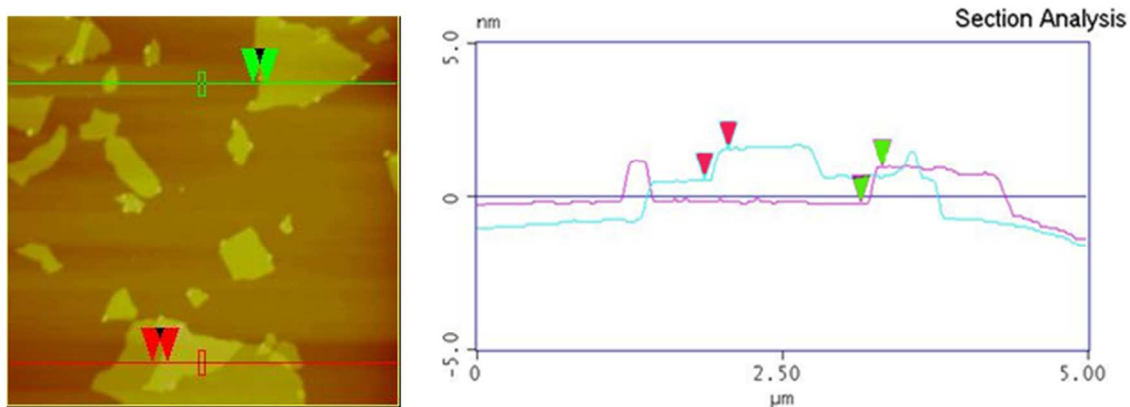


Figure S1. Thickness of GO sheets that are the starting materials for barrier assembly. The graphene oxide sheets were deposited on mica surface, and AFM analysis gives 1.1 nm steps, indicating that the majority of the structures are GO monolayers.

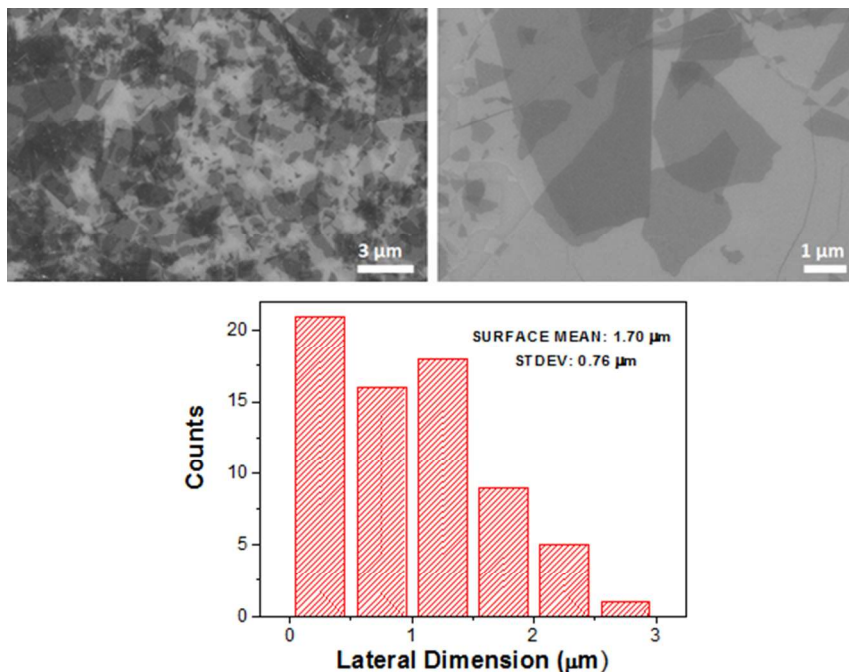


Figure S2. Lateral size of graphene oxide sheets that are the building blocks for barrier assembly in this work. GO sheets were deposited on Si substrate by drop casting a dilute GO suspension. The samples were heated at 700 °C under N₂ for 5 min in order to reduce the GO sheets, and enhance the conductivity which is essential for obtaining clear SEM images. Lateral sizes of GO range from about 0.3 - 3 μm. Counting of 73 GO sheets gives a **surface mean lateral size of 1.7 μm** and a standard deviation of 0.8 μm.

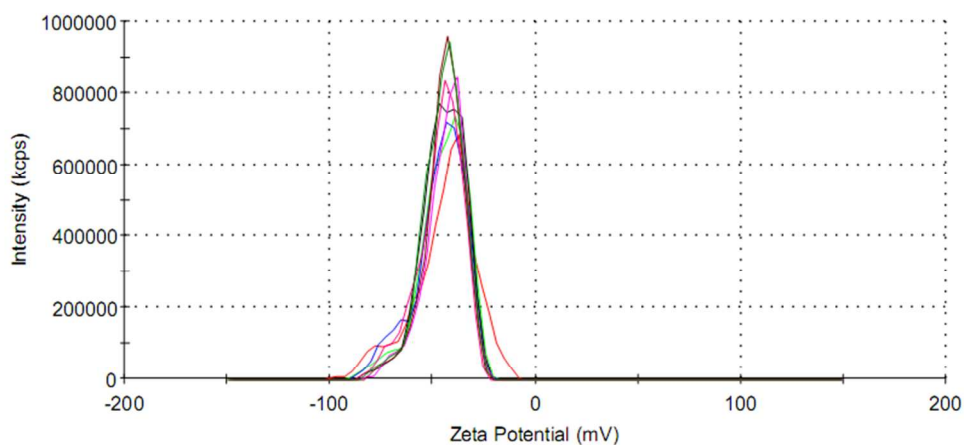


Figure S3. Characterization of GO surface charge in aqueous phase by dynamic light scattering (DLS). The zeta potential of GO sheets in water is approximately -50 mV, which is consistent with their stable dispersion in water.

Equipment and appearance of the raw data

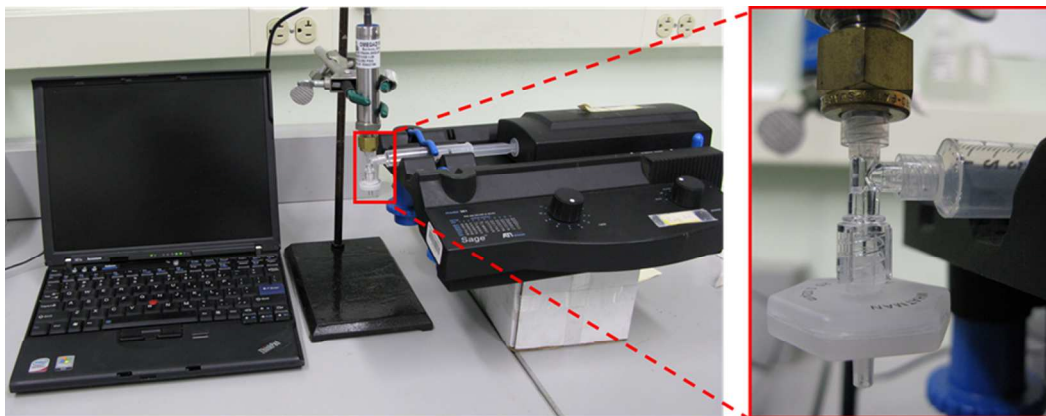


Figure S4. Experimental setup for characterizing GO as a hydraulic sealant. Aqueous suspensions of GO and reference nanomaterials were forced to flow through syringe filters (Anotop 25: filtration area 4.78 cm^2 , pore size 20 nm ; Nylon syringe filters: Cameo 17GN, pore size 220 nm , filtration area 1.0 cm^2) by a syringe pump (Sage 361) at a constant flow rate of 1 mL/min . The hydraulic pressure drop was monitored/recorded by a pressure sensor (USB output PX409, Omega).

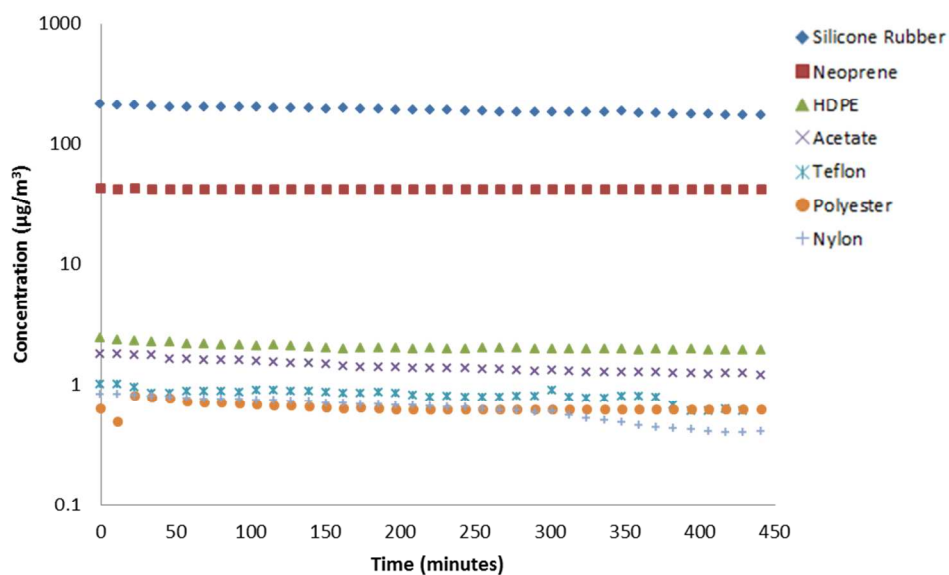


Figure S5. Steady state concentration of mercury vapor above the polymer membranes in the cell. The permeability calculations are based on the final steady state values.

Modeling

Background on the Nielsen model

The Nielsen model is a “detour” model, in which the filler causes the diffusing gas/liquid molecule to follow a more tortuous path [Nielsen 1967; Lu and Mai 2007].

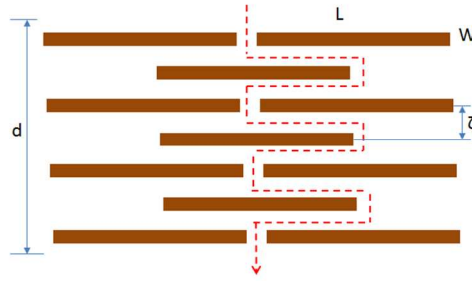


Figure S6. Schematic view for a typical Nielsen diffusion in interlayer spaces to find pathways around individual GO sheets

The tortuosity factor τ (defined as the ratio of the actual distance d' to the thickness d of a specimen)

$$\tau = \frac{\text{distance a molecule must travel to get through film (red dash line)}}{\text{thickness of film}} = \frac{d'}{d} \quad (\text{S1})$$

$$\zeta = \frac{W}{\phi} \quad (\text{S2})$$

$$d' = d + \frac{1}{2} L \frac{d}{\zeta} = d + \frac{1}{2} \frac{L}{W} \phi d \quad (\text{S3})$$

$$\tau = \frac{d'}{d} = 1 + \frac{1}{2} \frac{L}{W} \phi \quad (\text{S4})$$

Thus, the relative permeability can be expressed as:

$$\frac{P}{P_m} = \frac{1-\phi}{\tau} = \frac{1-\phi}{1 + \frac{1}{2} \alpha \phi} \quad (\text{S5})$$

$$\alpha = \frac{L}{W} \quad (S6)$$

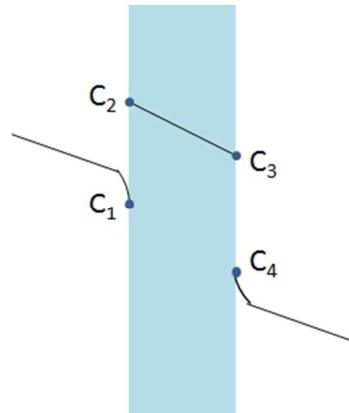
$$1 - \phi \approx 1 \quad (S7)$$

Where ϕ is the volume fraction of filler.

Modification and application of Nielsen model: excluded volume and Hg properties

According to Einstein–Stokes equation (for diffusion of spherical particles through liquid with low Reynolds number), the diffusivity of Hg molecules in water is

$$D = \frac{k_B T}{6\pi\eta r} = \frac{1.38 \times 10^{-16} \text{ g} \cdot \text{cm}^2 / (\text{s}^2 \cdot \text{K}) \times 298 \text{ K}}{6 \times 3.14 \times 8.9 \times 10^{-3} \text{ g} / \text{cm} \cdot \text{s} \times 0.15 \text{ nm} \times 10^{-7} \text{ cm} / \text{nm}} \approx 1.6 \times 10^{-5} \text{ cm}^2 / \text{s} \quad (S8)$$



Hg vapor pressure of 0.3 Pa at 25° C, and solubility of 56 µg/L at 25° C.

$$C_{\text{Hg_water}} = 56 \text{ } \mu\text{g} / \text{lit} \quad (S9)$$

$$C_{\text{Hg_vapor}} = \frac{P}{RT} MW = \frac{0.3 \text{ Pa} \cdot 200.59 \text{ g} / \text{mol}}{0.0831 \frac{\text{lit} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \cdot 298 \text{ K}} \cdot \frac{\text{bar}}{10^5 \text{ Pa}} \cdot \frac{10^6 \text{ } \mu\text{g}}{\text{g}} = 24.3 \text{ } \mu\text{g} / \text{lit} \quad (S10)$$

Then, the partition coefficient is:

$$H = \frac{C_3}{C_4} = \frac{C_{Hg_water}}{C_{Hg_vapor}} = \frac{56 \mu g / lit}{24.3 \mu g / lit} = 2.3 \quad (S11)$$

The permeability of the matrix is:

$$P_m = \frac{D}{d} H \quad (S12)$$

The permeability of the composite (matrix and filler) is:

$$P = P_m \cdot \text{Nielsen-factor} \quad (S13)$$

When the interlayer spaces become small, the excluded volume associated with solvent of size σ becomes significant and the cross-sectional area for lateral diffusion is reduced.

$$\frac{P}{P_m} = \frac{1 - \phi \left(\frac{\sigma + W}{W} \right)}{1 + \frac{1}{2} \alpha \phi} \quad (S14)$$

Where

$$\text{Nielsen-factor} = \frac{P}{P_m} = \frac{1 - \phi \left(\frac{\sigma + W}{W} \right)}{1 + \frac{1}{2} \alpha \phi} \quad (S15)$$

$$\phi = \frac{W}{d_{GO}} \quad (S16)$$

Where d_{GO} is the internuclear spacing between layers in the actual film, which is measurable by diffraction techniques. Then, the permeability in close-packed mixed-matrix-membranes (MMMs) can be expressed as

$$P = DH \frac{d_{GO} - W - \sigma}{nd_{GO} \left(d_{GO} + \frac{1}{2} \alpha W \right)} \quad (S17)$$

Where W is the vdW width of unfunctionalized graphene (0.34 nm), s is the solute diameter (Hg) and n is the total layer number.

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