Graphene Oxide Membranes with Tunable Permeability due to Embedded Carbon Dots

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Experimental section

1. Material fabrication

1.1 Synthesis of graphene oxide (GO)

The graphene oxide in this experiment was prepared through modified Hummers-Offeman method.[1] The detailed procedure is as follows:
50 g of H_2SO_4 (98 %) and 2 g of graphite were placed in a reactor cooled to 0 °C using iced water. After mixing the suspension for 30 min, 0.3 g of $KMnO_4$ was added in small portions to keep the temperature in the reactor not more than 10 °C. Thirty minutes later, 6 g of $KMnO_4$ was further added to the suspension gradually. After the $KMnO_4$ feeding was finished, the reactor was heated to about 35 °C and kept at this temperature for an additional 30 min. As the reaction progressed, the suspension became pasty and brownish in colour. At the end of this 30 min period, 90 mL of water was slowly stirred into the paste to prevent violent effervescence, causing an increase in temperature from (90 to 95) °C. The diluted suspension, now brown in colour, was maintained at this temperature for 15 min. The suspension was then further treated with a mixture of 7 mL of hydrogen peroxide 30 %) and 53 mL of water to reduce the residual permanganate and MnO_2 to soluble $MnSO_4$. The suspension was filtered and washed with distilled water three times.

1.2 Synthesis of CDs

The CDs used in this experiment was prepared mainly through our previous reported method.[2] The detail procedure is as follows:
In a typical experiment, 0.5 g of melamine was first dispersed in 18 ml of glycerol. The mixture was heated to 270 °C under nitrogen flow, and 0.5 g of citric acid was quickly added to the hot mixture. The mixture was maintained at 270 °C for 15 min and then cooled to ambient temperature, resulting in a dark brown viscous mixture. The viscous as-prepared CDs were first diluted with 50ml Mill-Q water, followed by filter by sterilized 0.22μm syringe filters. Then 10ml sample was put into the dialysis tubing for purification. The dialysis was repeated 3 times and 2.5 L of Mill-Q water was used each time. CDs penetrated the tubing was collected and concentrated by evaporation for further dialysis with smaller MWCO tubing. The tube with MWCO of 3.5 kDa and 1 kDa are used respectively to get different fractions: > 3.5 kDa, 1 ~ 3.5 kDa and < 1 kDa.

1.3 Fabrication of CDs-GO membrane

The CDs-GO membrane was fabricated by vacuum filtration. A typical procedure was as follows:

15 ml of GO suspension (2.4 mg/ml) was sonicated for 30 min to open the layers of GO. Then the GO solution was mixed with 15 ml CDs solution (50 μg/ml) and stirred for at least 10 min. After mixing, the mixture was kept for 30 min for the attachment of CDs onto GO layers.

The mixture was filtered by a Mixed Cellulose Esters (MCE) filter paper with a pore size of 0.22 μm. The CDs-GO membrane with MCE filter paper was dried in a vacuum oven and peeled after drying.

In this experiment, three fractions of CDs (molecular weight cut off (MWCO) < 1 kDa, 1 ~ 3.5 kDa and > 3.5 kDa, respectively) were used to get membranes with different permeability.

2. Characterization of materials

Morphology:

The morphology of GO layers and CDs were characterized on atomic force microscopy (AFM, Dimension 3000) with tapping mode on a platinum coated mica substrate.

Structure:

FT-IR spectra were collected on Perkin-Elmer Spectrum 100 with resolution of 4 cm^{-1} in transmission mode at room temperature. A baseline correction was applied after the measurement. X-ray photoelectron spectroscopic (XPS) measurements were performed on a Kratos Axis Ultra photoelectron spectrometer which uses Al Kα (1253.6 eV) x-rays. The Raman spectra were collected on Renishaw inVia Raman microscope using 514 nm laser light source.

Membrane porosity:

The membrane porosity was determined by the mass loss of wet membrane after drying.[3] The membrane was mopped with water on the surface and weighed under wet status. Then, the membrane sample was dried until a constant mass. The membrane porosity ε was calculated by eq. 1:

$$\varepsilon = \frac{W_w - W_d}{\rho \cdot v} \cdot 100\% \qquad \text{eq.1}$$

where W_w is the mass of a wet membrane, W_d is the mass of dry state membrane sample, ρ is pure water density, and v is the volume of a membrane in wet state.

Membrane permeability:

The permeability of CDs-GO membrane was evaluated by water flux rate of membrane. The CDs-GO membrane was fixed on the top of a Whatman™ qualitative filter paper in a syringe filter holder, holding the effective membrane area of 3.14 cm^2. The membrane was initially subjected to deionised water of 0.1 MPa for about 1 h before testing. Then the pure water flux was measured at 0.1 MPa, the volume of water going through the membrane was measured after 10 min. The pure water flux rate can be calculated by the eq. 2:

$$J = \frac{V}{S \cdot \Delta t} \qquad \text{eq.2}$$

where $J\ (L/h \cdot m^2)$ is the water flux rate of membrane, $V\ (L)$ is the volume of permeated water, $\Delta t\ (h)$ is the permeation time.

3. Membrane filtration experiments

The filtration experiments were conducted using three common dyes including methylene blue (MB), methyl orange (MO) and rhodamine B (RhB). 10 ml of each dyes with a concentration of 10 mg/L were applied for filtration. The absorption of MB, MO and RhB in the solution was analysed using UV-Vis spectrophotometer (Agilent 8453 UV-Visible Spectrophotometer) at 663, 464 and 552 nm wavelength, respectively. The Removal Efficiency of dyes was calculated by eq.3:

$$R\% = \frac{A_0 - A}{A_0} \cdot 100\% \qquad \text{eq.3}$$

where $R\%$ is the Removal Efficiency, A_0 is the absorption of dyes before filtration, A is the absorption of filtrate.

4. Supporting Figures and Tables

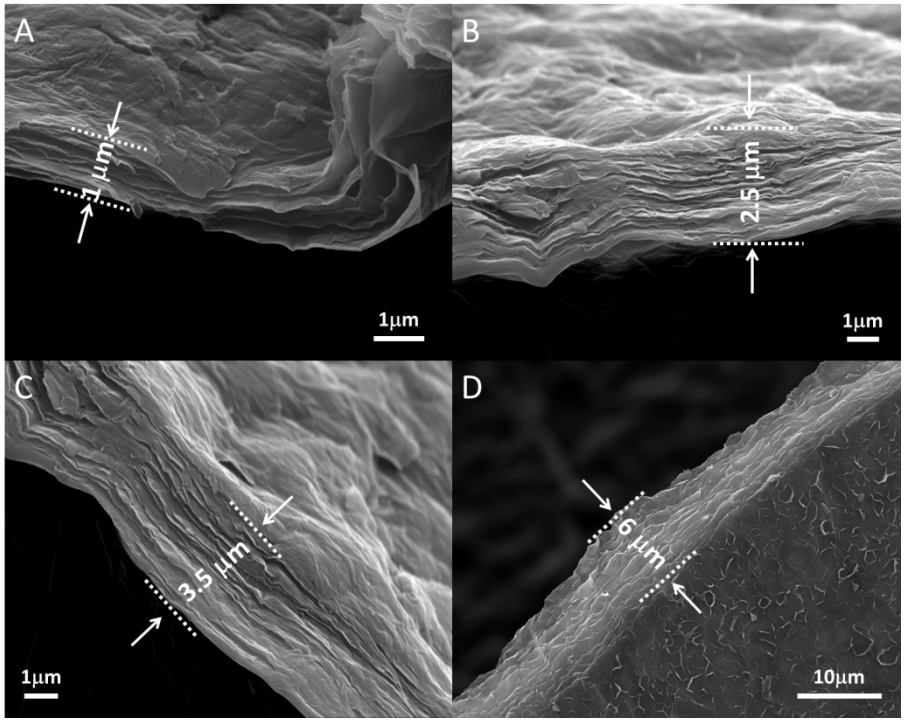

Fig.S1 SEM images of CDs-GO membrane with different amount of GO, A) 10 ml, B) 15 ml, C) 20 ml, D) 30 ml; in all CDs-GO membrane fabrications, 15 ml CDs with MWCO of 1 ~3.5 kDa were used. The thicknesses of membrane were estimated according to the scale bar.

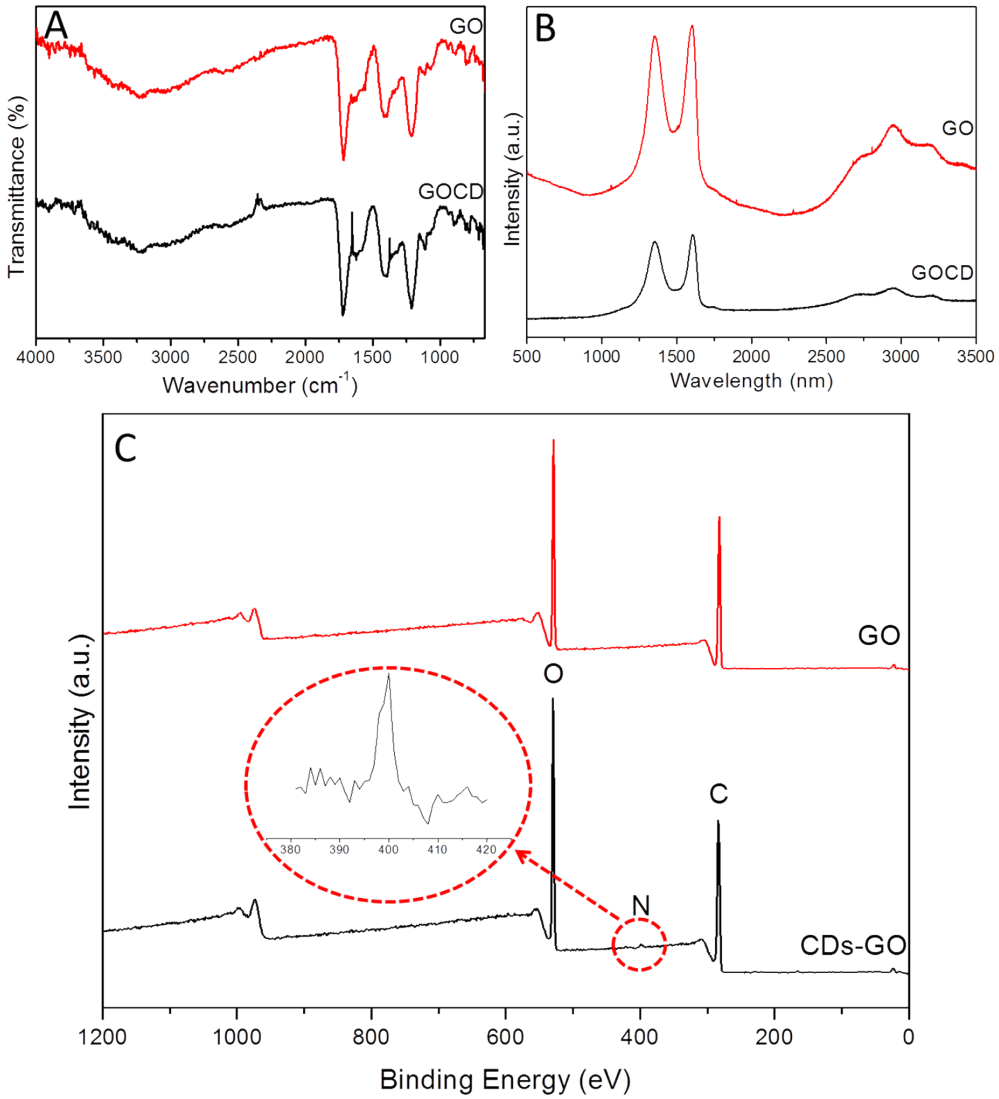

Fig.S2 The FTIR, Raman and XPS spectra of GO and CDs-GO membrane.

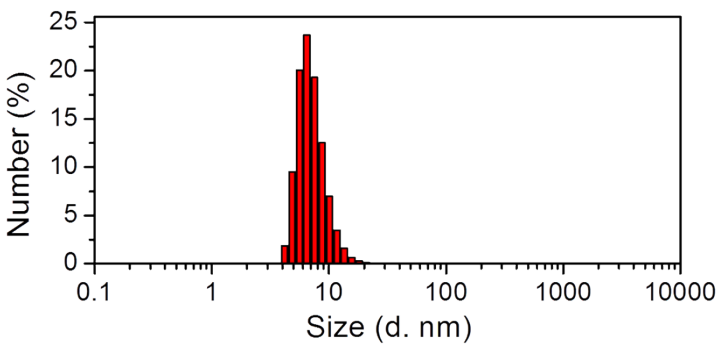

Fig.S3 Monodispersibility of Ag NPs measured by DLS.

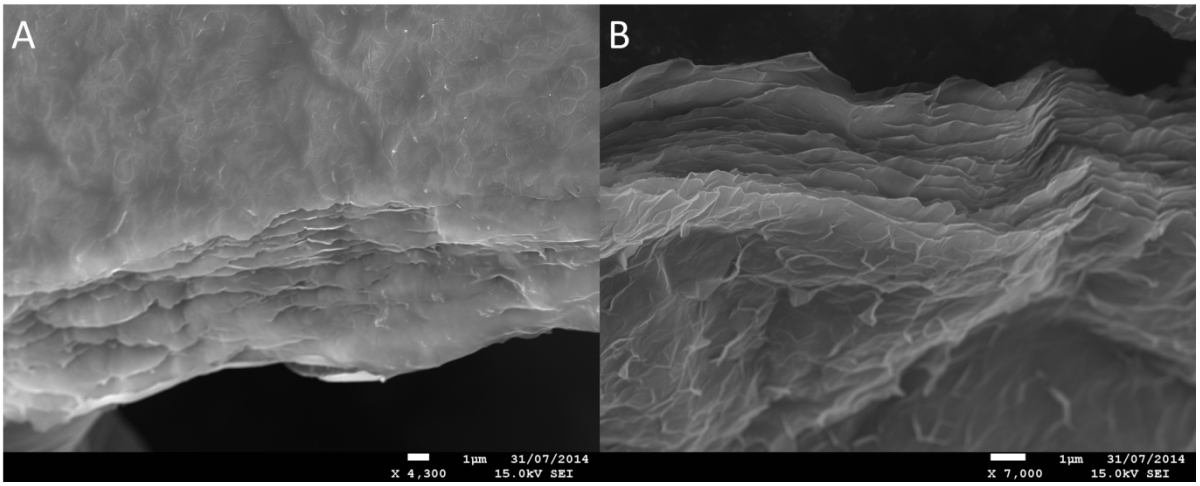

Fig.S4 SEM images of rGO membranes (A) and CDs-rGO membranes (B).

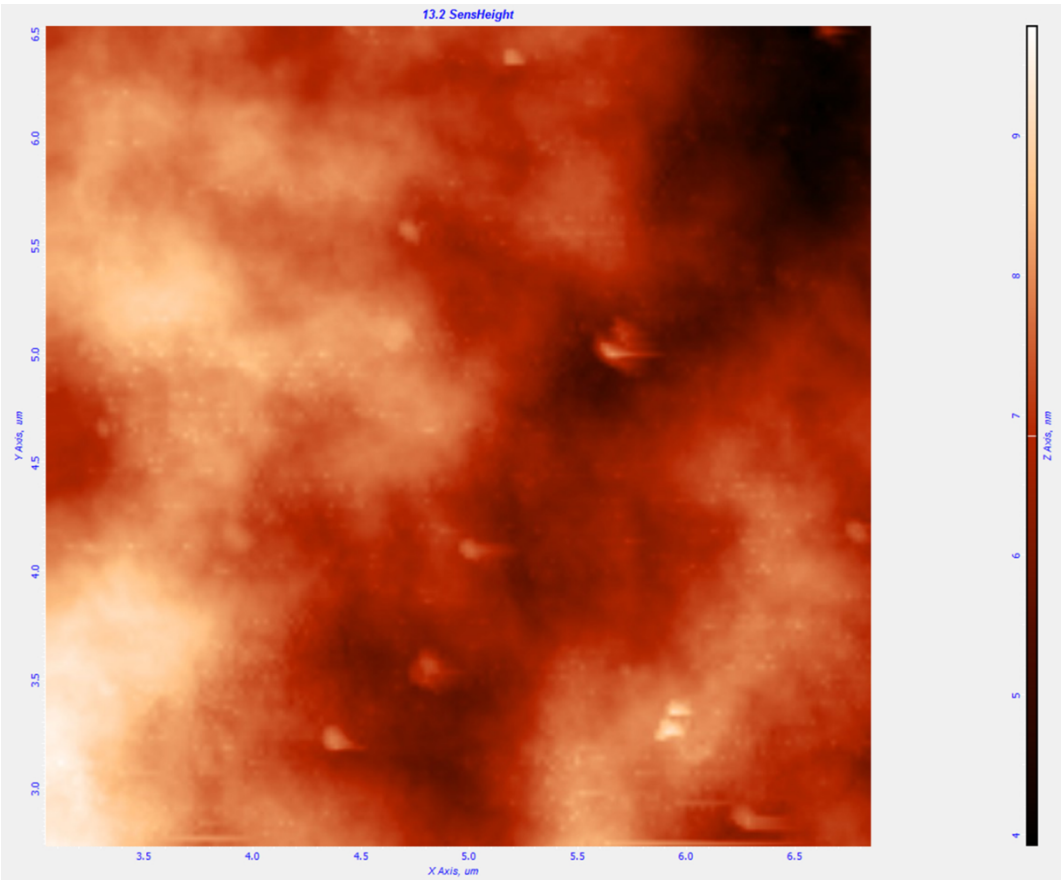

Fig.S5 Surface morphology of CDs-GO membrane collected by AFM.

Table S1 Comparison of water permeability of reported graphene based membranes.

Membrane	Water Flux (L/h·m^2)	Reference
GO	71	4
CHNs-GO	451	4
NSC-GO	695	4
140 ^{o}C-GO	205	5
CCG	250	6
CCG	22	7
GO	53	This Work
CDs-GO (<1 kDa)	138	
CDs-GO (1 ~3.5 kDa)	428	
CDs-GO (>3.5 kDa)	439	

References:

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