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Graphene Quantum Dots/Graphene Fiber Nanochannels for Osmotic Power Generation

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Experimental Methods

S1. Materials

Potassium chloride (KCl; 99.999%), ammonium hydroxide solution (NH_4OH; 30% NH_3 basis), and potassium permanganate ($KMnO_4$; 99.3%) were purchased from Sigma-Aldrich Co. LLC. Graphite was purchased from Asbury Carbons (grade 2012). hydrogen peroxide (H2O2; 30 wt% in water), sulfuric acid (H_2SO_4; 95%), and hydrochloric acid (HCl; 36 wt% in water) were purchased from Junsei Chemical Co., Ltd. Anhydrous calcium chloride (CaCl2, practical grade) was obtained from Duksan Pure Chemicals Co. Ultrapure deionized (D.I.) water (18.2 MΩ cm) was prepared from a Direct Q3 system (Millipore Inc.). Poly(dimethylsiloxane) (PDMS; Sylgard 184) was purchased from Dow Corning. Ethanol (99.5%) and acetone (99.5%) were purchased from Daejung Chemicals and Metals Co., Ltd.

S2. Synthesis of GO

GO was synthesized following the modified Hummers method.[1] Graphite (10g) and concentrated H_2SO_4 (380 mL) were mixed and stirred together in 5 °C ice bath. $KMnO_4$ (50 g) as oxidizing agent was added to the mixture while keeping temperature below 10 °C. The reaction mixture was stirred for 12 h at 35 °C. Next, D.I. water (500 mL) was added with the temperature maintained below 12 °C. Before acid washing, additional D.I. water (2.5 L) and H_2O_2 (15 mL) were added until the solution became orange-brown color. Then, resulting graphite oxide solution was washed with HCl (1 M solution, 2.5 L) and filtered with cellulose filter paper (maximum degree of fine particle filtration of 2.5 µm, Whatman). After filtration and drying, the resulting cake was further washed and filtered with acetone (2.5 L). The final cake was dispersed in D.I. water to obtain an aqueous solution with a concentration of 0.2 wt% for purification process which involves mild sonication (Powersonic 410, Hwashin Tech. 20 min) and centrifugation. Unexfoliated graphite oxide was removed by centrifuging at 4000 rpm for 1 h using a centrifuge (Gyrozen 1508R, Gyrozen). After discarding the precipitate, the solution was centrifuged one more time at 8000 rpm for 1 h, and the supernatant was dispensed to remove small debris.

S3. Synthesis of GQDs

GQDs were synthesized by solution-phase etching of GO.[2] First, 0.5 mL of NH_4OH and 1 mL of H_2O_2 were added to GO dispersion (10 mL; 0.2 wt%) and the mixture was stirred. The mixture was then heated at 150 °C for 5 h in 50-mL Teflon vessel and sealed in an autoclave. The solution was cooled down and filtered with 0.35-μm and then 0.02-μm syringe filter (whatman) to remove the flocculated aggregates. The filtrate was heated at 100 °C to remove remaining NH_3. GQD powder was obtained by freeze-drying the resulting solution. The GQD powder was re-dispersed in water to hybridize with GO solution.

S4. Wet-spinning of GQD-GO fibers

GQD-GO fibers were prepared at different contents of GQD; 0, 9 and 18 wt%. For example, 18 wt% of GQD-GO fibers were assembled using a GQD-GO mixture solution (0.6 wt%; GQD:GO = 1:5 in w/w). The mixture solution was spun through a diameter (400 μm of diameter, Hamilton) at a fixed injection rate of 10 mL h^{-1} into a 5 wt % $CaCl_2$ coagulation bath. The gel-state GQD-GO fibers in the bath were washed with D.I. water. After drying in 80 °C oven for 30 min, the dry GQD-GO fibers were re-immersed in D.I. water and then a target KCl solution for a day to analyze the ion transporting property. To examine the stability of GQD in GQD-GO hybrid fiber, twenty GQD-GO fibers were dipped in 10 ml of 1M KCl solution. During this procedure, Ca^{2+} in fibers was exchanged with K^+. The photoluminescence (PL) intensities of KCl solution was compared before and after Ca^{2+} exchange process (Fig. S4d). We assume that each fiber contained about 5 μg GQDs so that GQD solution containing 100 μg in 10 mL KCl solution was also prepared for the comparison. As shown in Fig. S4d, after exchange process of GQD-GO fiber, the KCl solution did not show any emission spectra of GQDs.

S5. Characterization of the nanochannels

Atomic force microscopy (AFM) images of GO sheets were obtained in tapping mode using an AFM system (XE-70, Park Systems). The GQDs were observed with a transmission electron microscope (TEM; JEM-2100F, JEOL) operated at an accelerating voltage of 200 kV. GQDs were deposited on a lacey-carbon TEM grid (Ted Pella, Inc.) by dropping a droplet of a dilute GQD dispersion. Photographs of the fluorescent GQD dispersion are taken with a 356nm UV lamp (ENF-260C/FE, Specroline). PL measurements were carried out using a fluorescence spectrometer (FS-2, Scinco,). Zeta-potential of GO and GQD dispersion with 0.005 wt% of concentration was measured using Zetasizer Nano ZS90 (Malvern Instruments) at various pH range from 1 to 12. X-ray photoelectron spectroscopy (XPS) was performed to estimate the composition of GO and GQDs using a theta-probe based system (Al-Kα radiation; Thermo Fisher Scientific Inc.) equipped with an electron flood gun. The liquid crystalline behavior of GQD-GO dispersion was observed with a polarized optical microscope (Eclipse LV-100N POL, Nikon). X-ray diffraction (XRD) was performed on a MiniFlex benchtop X-ray diffractometer (Rigaku) using a Cu-Kα radiation source (λ=1.5418 Å). Scanning electron microscopy (SEM) images were captured using a Nova NanoSEM 450 microscope (FEI).

S6. Fabrication of measurement stage

A measurement stage of the fiber-based nanochannels was prepared using poly(dimethyl siloxane) (PDMS) elastomer. The pre-polymer was poured in a glass container containing two glass vials (2 cm in diameter) and a sheet of 6-mm-thick glass for forming two reservoirs (25 mL) and a 6-mm-length gap, respectively. The pre-polymer was cured in an oven at 80 °C for 3 h. After the curing process, the stage was washed with water and sonicated with acetone for 5 min to remove residues.

S7. Ion conductance and EIS measurements of GQD-GO fibers

A GQD-GO fiber was immersed in target KCl solution with different concentration ranging from 10 μM to 1M for 24 hours. Then, they were bridged between the source and drain reservoirs containing the target salt solution (Figs. S5a and b). The length and a cross-sectional diameter of fibers are 1 cm and 40 μm, respectively. Then, the membrane stage was sealed in a glass container. Ag/AgCl electrodes were connected between reservoirs and a potentiostat (Ivium-n-stat, Ivium technologies) (Fig. S5c). Ion conductance was measured with linear sweep voltammetry (LSV) in the potential range of −0.4 V to 0.4 V. LSV was performed repeatedly for obtaining reliable results. Electrochemical impedance spectroscopy (EIS) was performed with 1 mM KCl solution at the frequency range of 100 mHz to 1 MHz. From the equivalent circuit model in the Fig. S7, Nyquist plots were fitted. The diameters of the semicircles represent the charge-transfer resistance (R_{ct}) of the fibers. All the measurements were done inside a home-made Faraday cage at ambient temperature and humidity.

S8. Estimation of surface charge density of a single nanochannel

The surface charge density (σ_s) on the nanochannel was determined through single-nanochannel conductance (G_0). Ion conductance can be divided into two regimes of high concentration and low concentration of electrolyte. At low and high concentration regions, the surface charge and the bulk dimensional effect mainly determine the ion conductance, respectively. The equation is given as:[5]

$$G_0 = q\,(\mu_K + \mu_{Cl})CN_A w h_0/l + 2\mu_K\,\sigma_s w/l \tag{1}$$

Here, q is elementary charge, N_A is Avogadro's number, and μ_K and μ_{Cl} are the mobilities of K^+ and Cl^-. In addition, w, l, and h_0 is width, length, and height of a single nanochannel, respectively. To obtain h_0, the thickness of basal plane was subtracted from the height of the nanochannel. G_0 can be obtained by dividing the ion conductance (G) by the number of channels (n) because G is the result of the collective contributions from numerous single channel arrays in the nanochannel. In addition, n can be estimated by dividing the thickness of the fiber by d-spacing of the fiber from the XRD result. In equation (1), the left term is bulk conductance which is dominated by the geometry of channel, and the right term is surface-charge-governed conductance. Therefore, σ_s can be obtained from ion conductance at low KCl concentrations as:

$$\sigma_s \approx G_0 l/2\mu_K w \tag{2}$$

S9. Osmotic power measurement of the nanochannels

For osmotic power measurement, the *cis* and *trans* reservoirs were filled with different concentrations of KCl solution ranging from 1 M to 1 mM to form concentration gradients of 1, 10, and 1000. As shown in Fig. S8b, the voltage (V_{sys}) and current (I_{sys}) of system were obtained by measuring the I-V response. From the equivalent circuit of the system in Fig. S8a, osmotic voltage (V_{os}) is given as: [6]

$$V_{os} = V_{sys} - E_{redox} = E_{diff} - I_{os}\,R_{channel} \tag{3}$$

In Eq. (3), the V_{os} and I_{os} were determined by subtracting the contribution from the redox potential (E_{redox}) of the Ag/AgCl electrodes from the V_{sys} and I_{sys}. The E_{redox} is the voltage drop at the electrode-solution interface and follows the Nernst equation as: [7,8]

$$E_{redox} = \frac{RT}{zF}\ln\frac{\gamma_{C_H} C_H}{\gamma_{C_L} C_L} \tag{4}$$

Here, z, F, R, and T are the charge number, Faraday constant, gas constant, and the temperature, while γ is the mean activity coefficient of KCl solution. The osmotic power (P) generated from the nanochannel is simply calculated as:

$$P = V_{\mathrm{os}} \times I_{\mathrm{os}} \tag{5}$$

As shown in Fig. S8b, P_{max} is calculated when V_{os} is half of the maximum voltage ($V_{\mathrm{os}} = 0.5\, E_{\mathrm{diff}}$). E_{diff} was calculated following Eq. (1) in the main text. Therefore, the maximum osmotic power (P_{max}) is given by:

$$P_{max} = \frac{1\ E_{diff}^{2}}{4R_{channel}} \tag{6}$$

where R_{channel} is the resistance of the nanochannel. Finally, the maximum osmotic power density was obtained by dividing P_{max} by the cross-sectional area of the fibers. The energy conversion efficiency (η) is calculated from t_+ as:[9]

$$\eta = \frac{(2t_{+} - 1)^{2}}{2} \tag{7}$$

References

1 F. Kim, J. Luo, R. Cruz-Silva, L. J. Cote, K. Sohn and J. Huang, *Adv. Funct. Mat.*, 2010, **20**, 2867.

2 H. Park, S. H. Noh, J. H. Lee, W. J. Lee, J. Y. Jaung, S. G. Lee and T. H. Han, *Sci. Rep.*, 2015, **5**, 14163.

3 J. Ji, Q. Kang, Y. Zhou, Y. Feng, X. Chen, J. Yuan, W. Guo, Y. Wei and L. Jiang, *Adv. Funct. Mater.*, 2017, **27**, 1603623.

4 C. N. Yeh, K. Raidongia, J. Shao, Q. H. Yang and J. Huang, *Nat. Chem.* 2015, **7**, 166.

5 R. B. Schoch and P. Renaud, *Appl. Phys. Lett.*, 2005, **86**, 253111.

6 D. K. Kim, C. Duan, Y. F. Chen and A. Majumdar, *Microfluid. Nanofluidics*, 2010, **9**, 1215.

7 A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, John Wiley & Sons, Inc., Hoboken, 2001.

8 N. Lakshminarayanaiah, *Transport phenomena in membranes*, Academic Press, New York, 1969.

9 J. C. Fair, J. F. Osterle, *J. Chem. Phys.*, 1971, **54**. 3307.

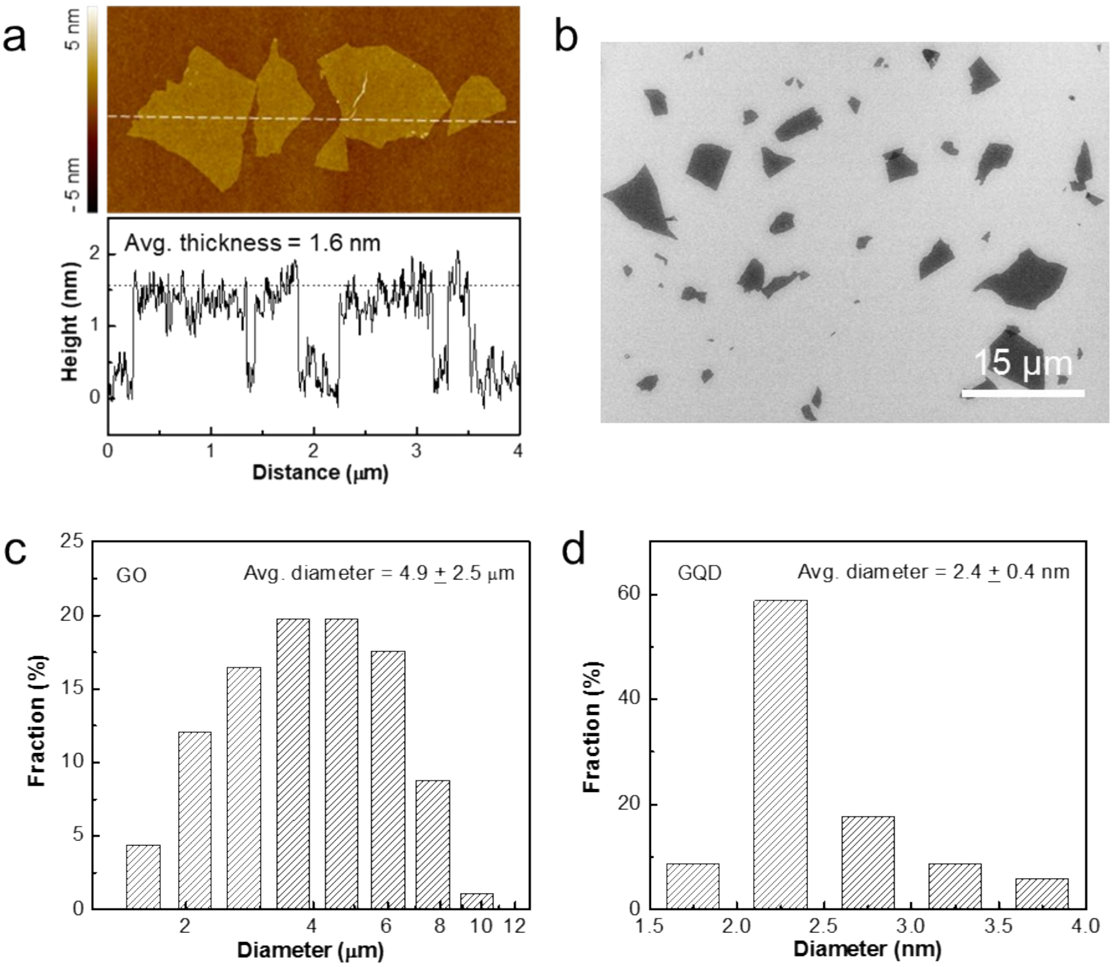

Fig. S1. (a) AFM image of GO sheets (top) and the corresponding height profile (bottom) along the dotted line. (b) Typical SEM image of GO sheets. (c,d) Size distributions of (c) GO sheets and (d) GQDs.

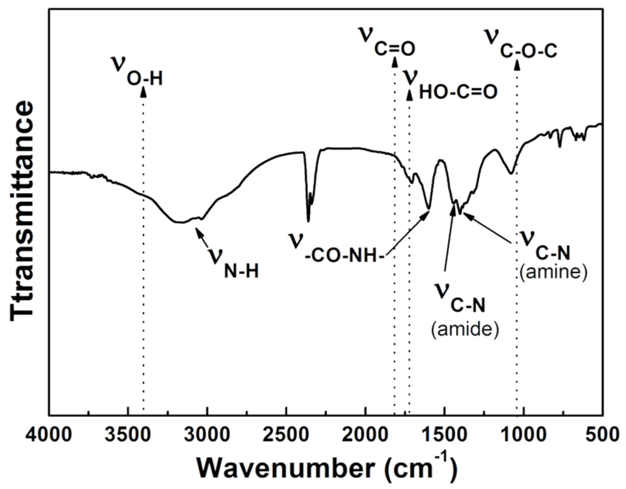

Fig. S2. FT-IR spectrum of GQDs showing the presence of various oxygen-containing functional groups.

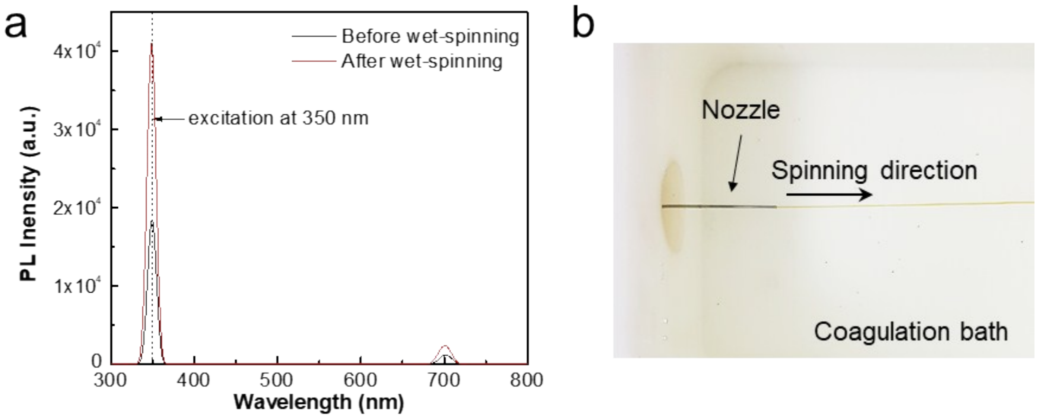

Fig. S3. (a) Photoluminescence spectra of the coagulation solution before and after the wet-spinning of GQD-GO fiber. The solution was excited at 350 nm. (b) Photo-image of the continuous wet-spinning of the GQD-GO fiber.

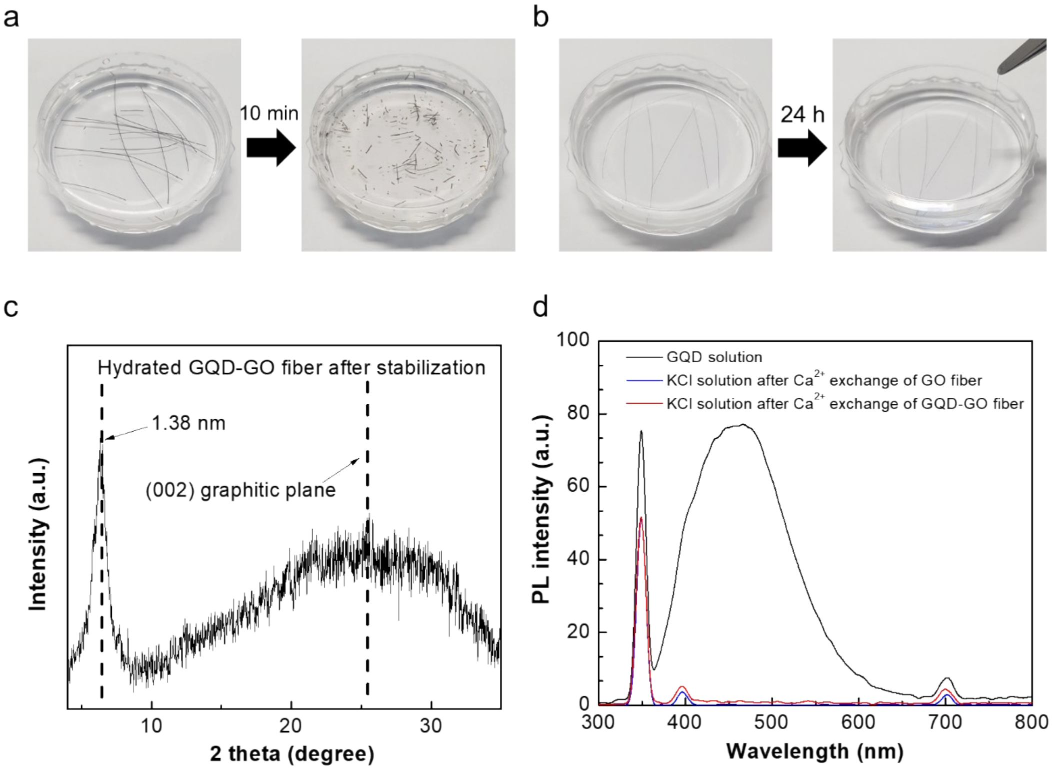

Fig. S4. Water stability of fiber without (a) and with stabilization process (b). (c) XRD pattern of the hydrated fiber after the stabilization process. A peak at about 25° corresponding (002) graphitic plane (d_{002} = 0.335 nm) is distinctly observed. (d) Photoluminescence spectra of the KCl solution after Ca^{2+} exchange of the fibers. The solution was excited at 350 nm. Different from GQD solution, KCl solution after Ca^{2+} exchange of GO and GQD-GO fiber shows no photoluminescence emission spectra under 350 nm excitation.

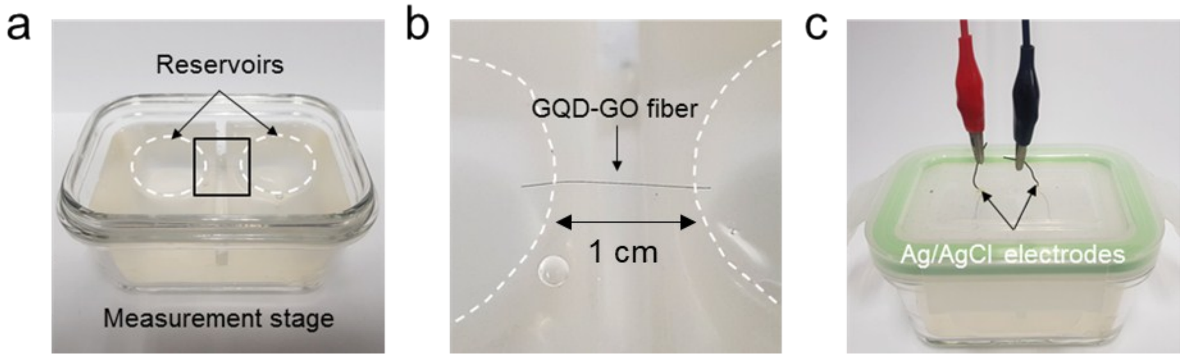

Fig. S5. Experimental set-up for the measurement of the ion conductance and salinity-gradient power generation. (a) Measurement stage with the two reservoirs containing KCl electrolyte. (b) Magnified photo-image of the boxed region in (a) showing a 1cm of GQD-GO fiber bridged between the two reservoirs. (c) The measurement stage was sealed in a glass container and connected to a potentiostat.

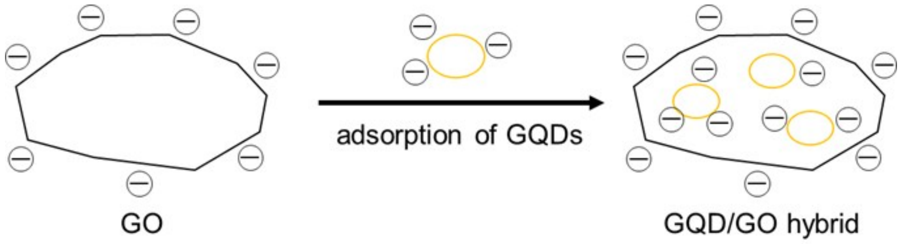

Fig. S6. Schematic model of enhancing charge density by GQD-GO hybridization.

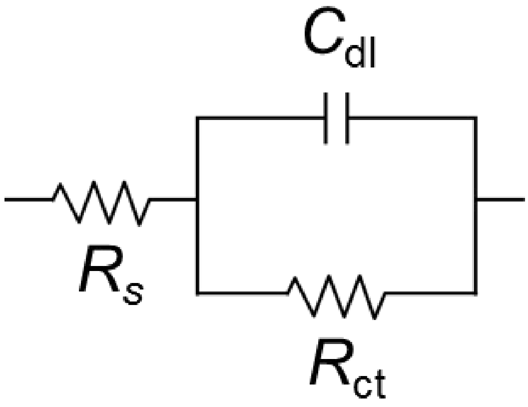

Fig. S7. The equivalent circuit used for the fitting of the EIS curves.

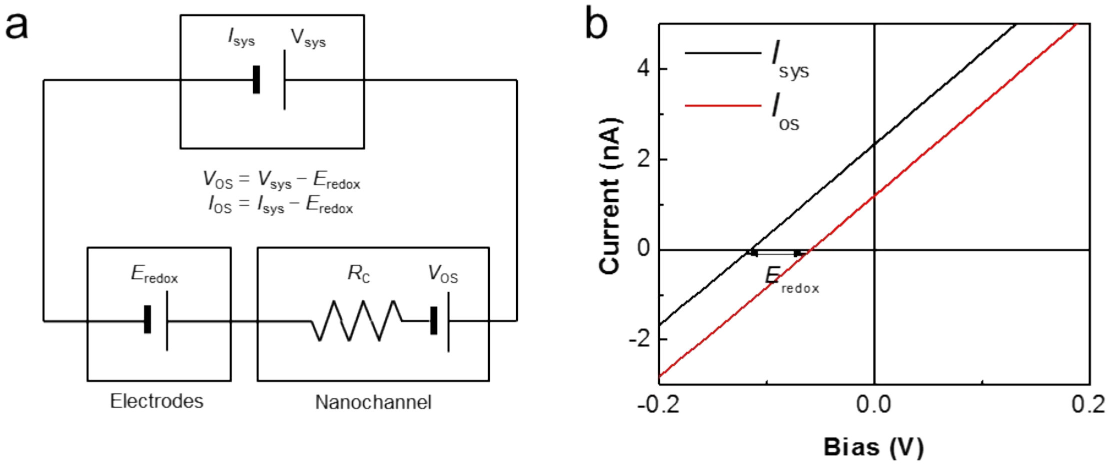

Fig. S8. (a) Equivalent circuit of salinity-gradient power generation system. (b) Typical *I*-*V* curve of the GQD-GO fiber at a concentration gradient of 10. By subtracting redox potential (E_{redox}) from the system voltage (V_{sys}; black line), osmotic current (I_{os}; red line) can be obtained.