

Electronic Supporting Information

Na⁺-Functionalized Carbon Quantum Dots: A New Draw Solute in Forward Osmosis for Seawater Desalination

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Experimental Section

Fabrication of Na⁺-functionalized carbon quantum dots (Na_CQDs)

The Na_CQDs were prepared as follows. In a typical reaction, 100 g citric acid solid powder was put into a glass beaker covered with a glass slide and was heated at 180 °C for 150 min under air. After the reaction, yellow powder containing carbon quantum dots (CQDs) was produced. The CQDs were then dispersed in water by stirring for 10 min, followed by neutralization with 5.0 M NaOH solution to pH = 7. The resultant Na_CQDs solution was dialyzed using Slide-A-Lyzer G2 Dialysis Cassettes (2K MWCO) for 12 hours and the dialysis process was repeated until there was no significant change of conductivity of the surrounding distilled water.

Material characterizations

Transmission electron microscopy (TEM) images were recorded on a JEM-2100F electron microscope operating at an accelerating voltage of 200 kV. Corresponding particle size distribution histograms were plotted by counting 200 nanoparticles. Energy Dispersive X-ray (EDX) Spectroscopy spectra were recorded using JEOL JSM 6700F scanning electron microscope with Oxford Instruments INCA detector. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using Bruker FT-IR Research Spectrometers. X-ray photoelectron spectroscopy (XPS)

characterizations were performed on a PHI Quantera x-ray photoelectron spectrometer with a chamber pressure of 5×10^{-9} torr, a spatial resolution of 30 μm and an Al cathode as the X-ray source to determine composition of the nanoparticles. The effect of MgCl_2 , NaCl and KCl on Na_CQDs was checked by measuring the osmolality of the Na_CQDs after mixing with 0.1 wt% solution of each salt for 48 h. Negligible osmolality changes ($<1\%$) were observed, indicating minimum poisoning effect of these salts to Na_CQDs .

Forward osmosis (FO) and membrane distillation (MD) tests

FO test were conducted on a lab-scale setup using a thin film composite embedded support membrane (batch number 842121) provided by Hydration Technologies Inc. (Albany, OR). The dimensions of the membrane are 1 cm \times 2 cm. The feed solution was either distilled (DI) water or seawater. The seawater was taken from the sea near Singapore Sentosa beach. Before FO tests, the seawater was filtrated using 220 nm filter membrane to remove large particulate impurities. The draw solution was Na_CQDs solutions with different concentrations. The feed solution and draw solution flowed concurrently through the two sides of the cell channel at a flow velocity of 25 cm s $^{-1}$. Water fluxes were measured with the selective layer of the membrane in contact with the draw solution. For the regeneration of draw solution via MD, a multi-bore PVDF hollow fiber (MBF) membrane with lotus root-like geometry was used as the MD membrane. The effective MD membrane surface area is 22.4 cm 2 . The diluted draw solution after FO process was circulated through the shell-side of the MD module after heated up to 45 $^{\circ}\text{C}$. DI water as the permeate solution was concurrently circulated through the lumen side of the MD module after cooled to 10 $^{\circ}\text{C}$. The measured weight change of the solutions and the corresponding calculations for FO and MD water fluxes are provided in Fig. S8-10.

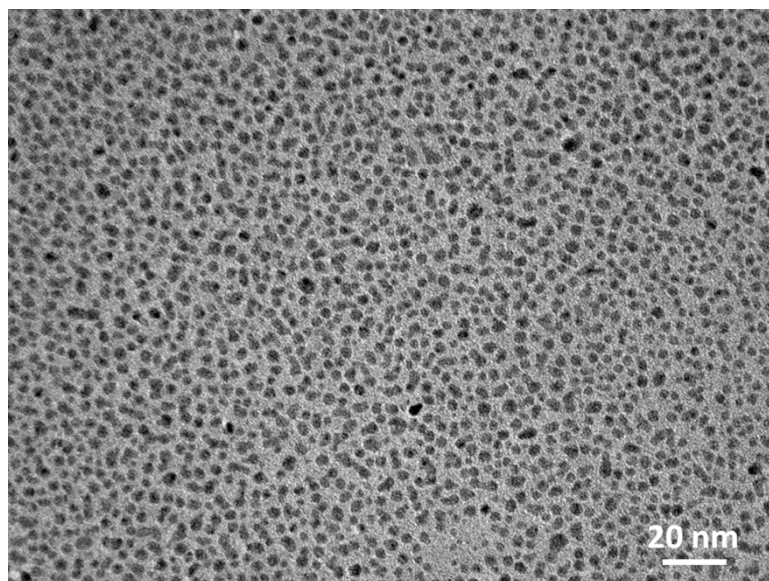


Fig. S1 Low-magnification TEM image of CQDs.

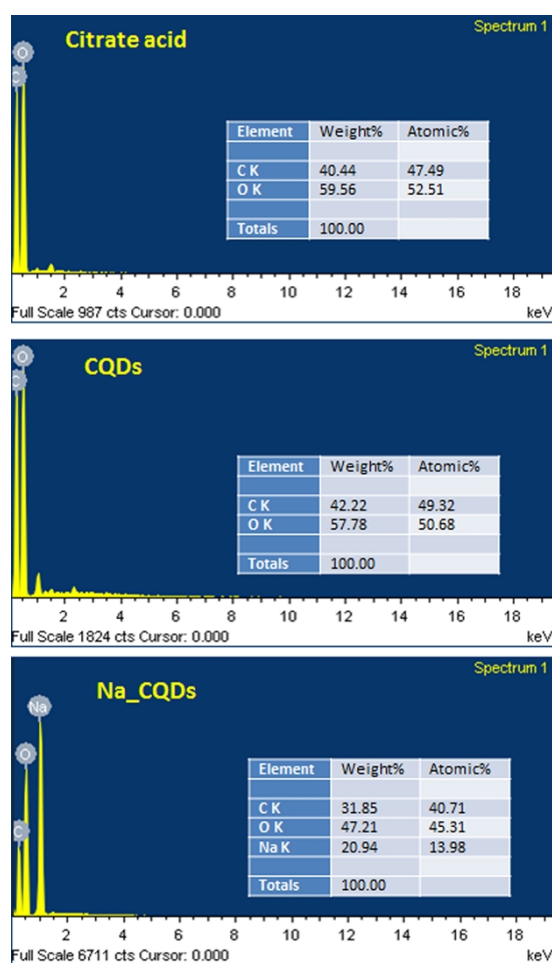


Fig. S2 EDX spectra of citrate acid, CQDs, and Na_CQDs.

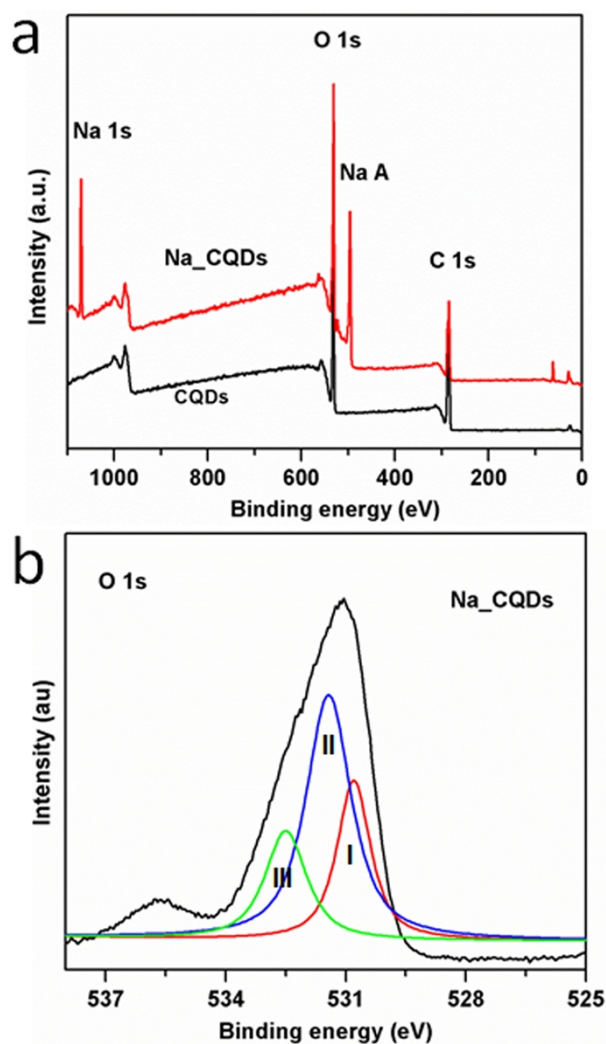


Fig. S3 XPS (a) survey scans of Na_CQDs and CQDs, and (b) high-resolution O 1s spectrum of Na_CQDs.

XPS survey scans suggest similar compositions of Na_CQDs and CQDs, except for the strong Na signal of Na_CQDs. The O 1s signal of Na_CQDs can be resolved into three peaks centered at 529.8 eV (peak I), 531.8 eV (peak II) and 532.9 eV (peak III), which could be ascribed to O-Na, O=C and O-C, respectively. The O 1s peak further confirms the successful Na⁺ functionalization and the existence of -C=O and -C-O functional groups for Na_CQDs.

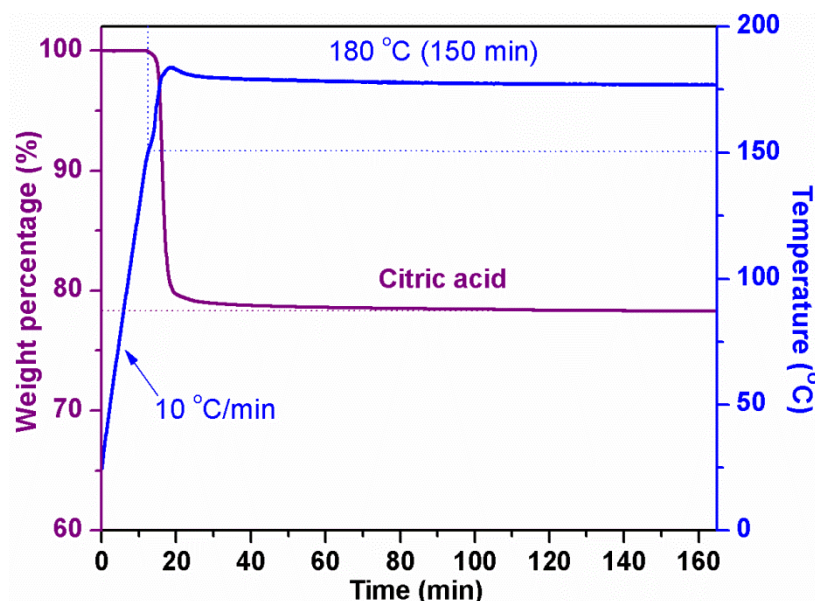


Fig. S4 TGA for citrate acid. The temperature ramping profile (the same as the reaction to synthesize CQDs) is also shown.

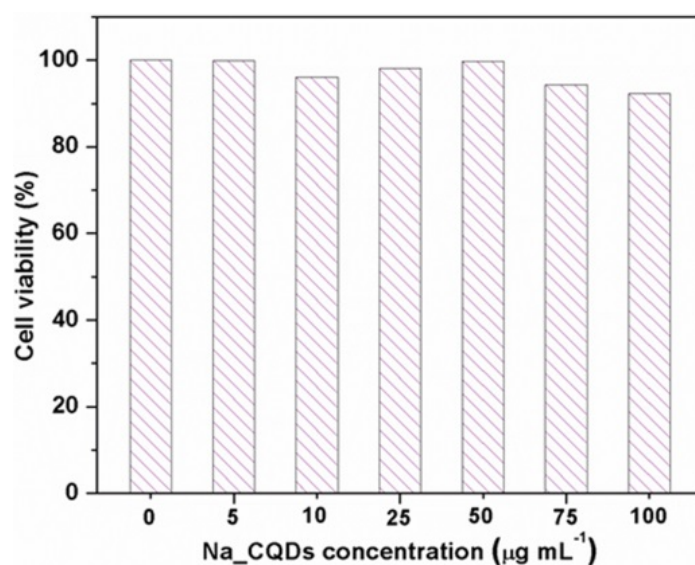


Fig. S5 MTT cytotoxicity assay using MCF7 cells following 24 hour exposure to various concentrations of Na_CQDs. Cell viability value was expressed as percentage of absorbance observed relative to the control wells receiving only culture media.

Biocompatibility of the Na_CQDs was investigated *in vitro* using MCF7 human breast adenocarcinoma cells. Cell viability was monitored by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay, which is a colorimetric assay used to monitor cell viability by measuring the cleavage of MTT *via* the activity of cellular enzymes in living cells. The cell viability value was expressed as the percentage of absorbance observed relative to the control cells cultured with only culture media. Cell viability of 99.8% was observed for Na_CQDs at a concentration of 0.5 mg mL⁻¹. Even at a higher concentration of 1.0 mg mL⁻¹, cell viability still retains 92.5%. In contrast, for CQDs at the same concentration (1.0 mg mL⁻¹), a

slightly lower viability of 85.6% was observed. This might be due to the acidic nature of CQDs. The cell viability result demonstrates that the Na_CQDs are biocompatible.



Fig. S6 Aqueous solution of Na_CQDs with a concentration of 0.5 g mL⁻¹.



Fig. S7 Aqueous solution of Na_CQDs under 365-nm UV light illumination.

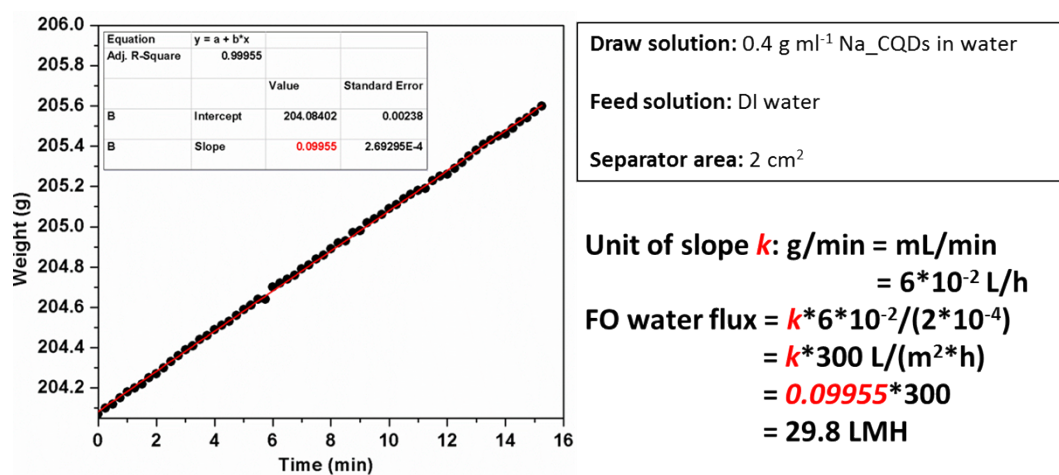


Fig. S8 Weight change of Na_CQDs solution with time during FO and the calculation of FO water flux.

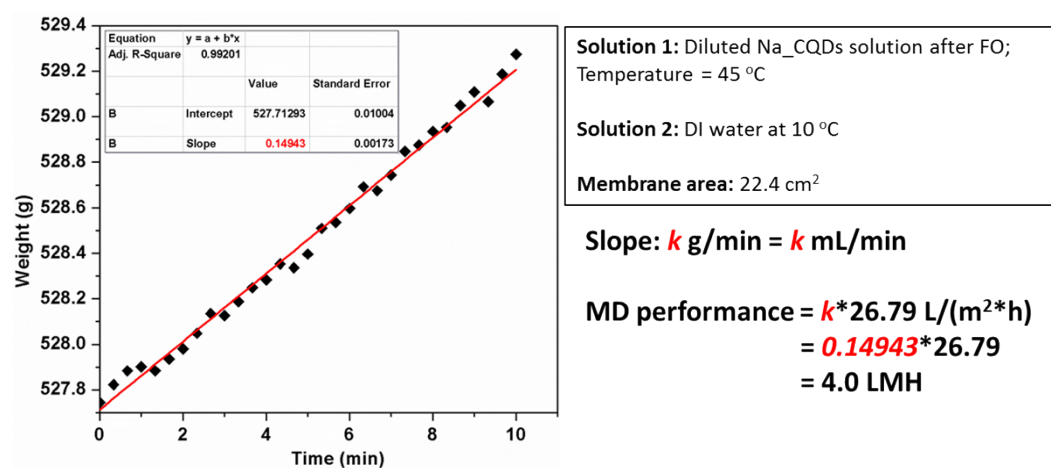


Fig. S9 Weight change of diluted Na_CQDs solution with time during MD and the calculation of MD water flux.

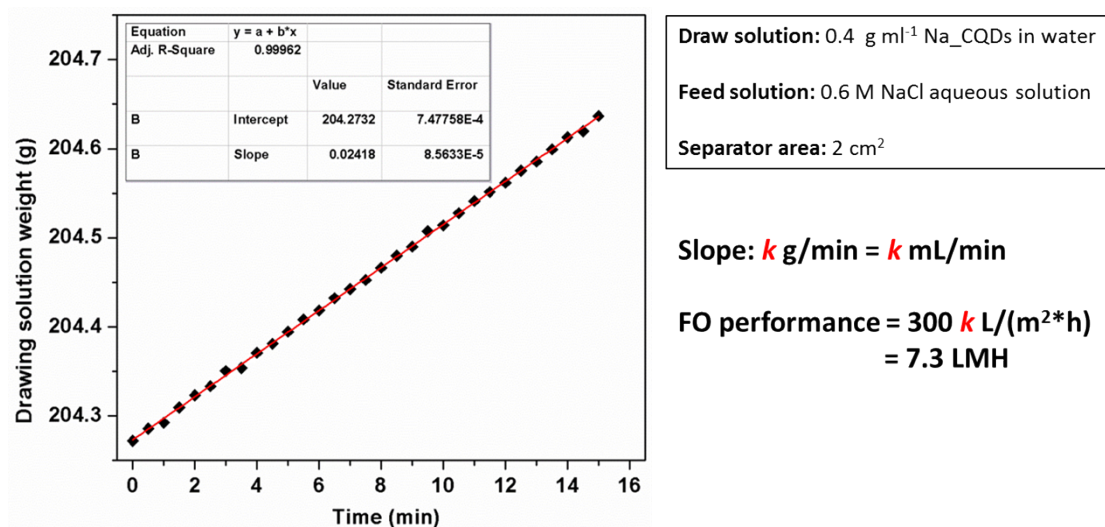


Fig. S10 Weight change of Na_CQDs (0.4 g mL⁻¹) draw solution during FO with 0.6 M NaCl as the feed solution.

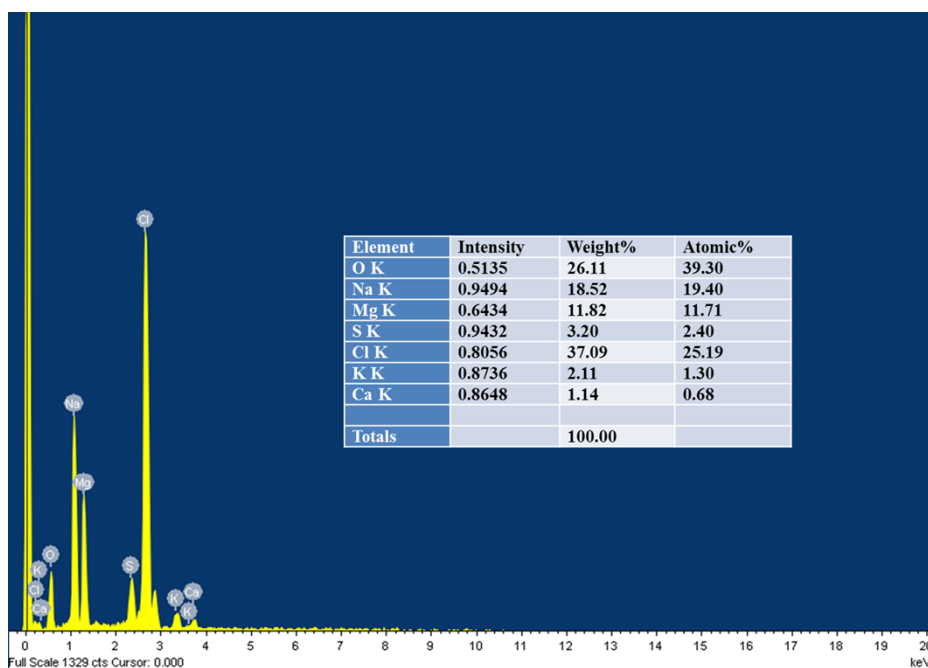


Fig. S11 Composition of the seawater sample taken from the sea near Singapore coast upon evaporation of water measured by Energy-dispersive X-ray spectroscopy (EDS).