

Na⁺-functionalized carbon quantum dots: a new draw solute in forward osmosis for seawater desalination†

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A new type of biocompatible draw solute, Na⁺-functionalized carbon quantum dots (Na_CQDs) with ultra-small size and rich ionic species, in forward osmosis (FO) is developed for seawater desalination. The aqueous dispersion of Na_CQDs demonstrates a high osmotic pressure, which allows high FO water flux and negligible reverse solute permeation.

Surface-passivated carbonaceous quantum dots (CQDs) with a size less than 10 nm are a fascinating class of nanostructured carbons discovered recently.^{1–3} CQDs not only inherit the merits of traditional semiconductor-based quantum dots (QDs) such as size-dependent optical properties, but also show advantages like high chemical inertness, biocompatibility and hydrophilicity.^{4–6} They can be produced inexpensively on a large scale by synthetic approaches such as hydrothermal treatment of biomass, oxidation of graphite, and candle burning.^{7–10} To date, CQDs have been explored in a wide range of applications including bioimaging, drug delivery, diagnostics, sensing and energy conversion/storage.^{11–15} Considering their ultra-small size and rich surface chemistry, broader applications are expected for CQDs with further functionalization.

Forward osmosis (FO) is an emerging technology for seawater desalination, wastewater treatment, and green energy.^{16–19} An FO process takes the advantage of the difference in osmotic pressure of two solutions separated by a semi-permeable membrane. Spontaneously, water molecules of the less concentrated solution (feed solution, low osmotic pressure) can be drawn to the solution with higher concentration (draw solution, high osmotic pressure).²⁰ After drawing water, the diluted draw solution can be regenerated for reuse *via* a separation step that concentrates the solution

and produces clean water. Compared to pressure-driven membrane processes such as reverse osmosis (RO) and other water production techniques, FO shows advantages such as high rejection of contaminants, low membrane fouling, and potentially less energy consumption.^{21,22} For a high-performance FO system, the selection of a suitable draw solute is critical.²³ In general, an ideal FO draw solute should have high hydrophilicity to generate high osmotic pressure and hence high water flux, low solute leakage to reduce the replenishing cost, a facile and low-cost regeneration mechanism, and capability for large scale production.²⁴ Two main types of draw solutes, namely inorganic compounds including sodium chloride, magnesium chloride and ammonium bicarbonate, and organic molecules such as sugars, ethanol and polyelectrolytes, have been tested in FO.^{23–25} These draw solutes offer high FO water fluxes, although some challenges, such as high reverse draw solute permeation, energy-consuming regeneration, or damage of the FO membrane, remain unsolved.²⁶ In the past few years, novel draw solutes such as hydrogels, stimuli-responsive materials, and magnetic nanoparticles have also been developed with demonstrated promise.^{16,24} To achieve high water fluxes, the osmotic pressures produced by these draw solutes in aqueous solutions should be improved.

Here we report a new type of FO draw solute based on Na⁺-functionalized carbon quantum dots (Na_CQDs). The fabrication of Na_CQDs is simple and straightforward (Fig. 1). Firstly, citric acid powder is heated in air at a moderate temperature to give CQDs passivated with carboxyl groups. The CQDs are then dispersed in water, followed by adjusting the pH to 7.0 using NaOH.

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† Electronic supplementary information (ESI) available: Details of experimental section, TEM images of CQDs, EDS of citric acid, CQDs and Na_CQDs, XPS spectra, TGA data, biocompatibility test results, photos of aqueous solution of Na_CQDs and the illumination under light, FO and MD water flux measurement and its calculation and the energy-dispersive X-ray spectroscopy spectrum of the dried seawater sample. See DOI: 10.1039/c4cc01603c

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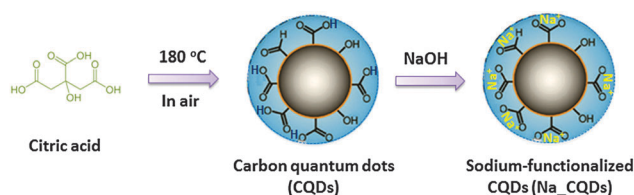


Fig. 1 Schematic illustration for the fabrication of Na⁺-functionalized carbon quantum dots (Na_CQDs).

As a result, the carboxylic acid groups in CQDs are neutralized to give Na⁺-functionalized CQDs (referred to as Na_CQDs). The detailed procedures can be found in the experimental section (ESI†). Due to the rich ionic species present in Na_CQDs, their aqueous dispersion (0.5 g mL⁻¹) shows osmotic pressure of up to 53.6 atm, much higher than that of seawater (~26 atm). When employed as draw solutes in FO for seawater desalination, Na_CQDs demonstrate high water flux with negligible reverse draw solute permeation.

TEM images in Fig. 2a and b show that the Na_CQDs have an average size of 3.5 nm, similar to that of CQDs before Na⁺-functionalization (Fig. S1, ESI†). The energy dispersive X-ray (EDX) spectrum of the Na_CQDs reveals peaks corresponding to C, O and Na, with atomic percentages of 40.7%, 45.3%, and 14.0%, respectively (Fig. S2, ESI†). On the other hand, CQDs only show signals of C and O (Fig. S2, ESI†). The TEM and EDX results indicate that the Na_CQDs were successfully functionalized with Na⁺ with retained morphology. The presence of Na in Na_CQDs was further confirmed by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 2c, a peak at 1071 eV corresponding to Na 1s is present in the spectrum of Na_CQDs;²⁷ while for CQDs the signal for Na is absent.

FT-IR spectra of CQDs and Na_CQDs show C=O and C-O groups^{13,28} that are inherited from citric acid molecules. In addition, the CQDs exhibit characteristic stretching vibration of C-H at 2950 and below 1350 cm⁻¹, indicating that the CQDs contain incompletely carbonized citric acid. EDX spectra in Fig. S2 (ESI†) demonstrate that the O/C atomic ratio of citric acid is 52.5/47.5, approximately 1.11. In contrast, CQDs show a lower O/C atomic ratio of 1.02, suggesting that a small portion of oxygen groups was lost during the heating process. It is known that citric acid molecules contain abundant -OH groups, which can cause polymerization (carbonization) during the heat treatment at 180 °C, similar to that of glucose to form carbonaceous spheres under hydrothermal treatment.²⁹ The change in weight percentage of citric acid with respect to temperature

was monitored by TGA with results given in Fig. S4 (ESI†). Based on FT-IR and TGA analyses, the formation process of Na_CQDs from citric acid can be summarized as follows. During the moderate heat treatment at 180 °C, citric acid molecules undergo incomplete carbonization by losing some -OH groups, resulting in CQDs with carboxyl groups and an average size of 3.3 nm (Fig. S1, ESI†). Due to the existence of abundant carboxyl groups, CQDs have a relatively acidic nature (pH of around 2.6 at a concentration of 0.4 g mL⁻¹). After adding NaOH, the acidic CQDs were neutralized by converting -COOH groups into -COONa, producing Na_CQDs. The cell viability test demonstrates that the Na_CQDs are highly bio-compatible (Fig. S5, ESI†).

For seawater desalination by FO, high osmolality is critical for the draw solution to offer high osmotic pressure and thus high water flux. The osmolalities of Na_CQDs were measured at various concentrations ranging from 0.2 to 0.5 g mL⁻¹. As shown in Fig. 3a, at 0.2 g mL⁻¹, the osmolality of Na_CQDs is 1410 mOsm kg⁻¹. However, for CQDs at the same concentration, the osmolality is only 360 mOsm kg⁻¹, much lower than that of Na_CQDs. The osmolality of Na_CQDs increases with concentration. At concentrations of 0.4 and 0.5 g mL⁻¹, the osmolalities reach as high as 3140 and 4350 mOsm kg⁻¹, corresponding to osmotic pressures of 30.9 and 53.6 atm, respectively. These osmotic pressures are much higher than that of seawater (~26 atm).²⁴ The high osmotic pressure is clearly attributed to the favorable characteristics of Na_CQDs, namely ultra-small size and rich ionic species. Compared with CQDs, Na_CQDs are Na⁺-functionalized and should be able to dissociate in solution to produce abundant ionic species. The slope of the osmolality vs. concentration curve shown in Fig. 3a slightly decreases at higher concentrations. This is possibly caused by reduced degree of dissociation of the Na_CQDs at higher concentrations. It is worth noting that the Na_CQDs

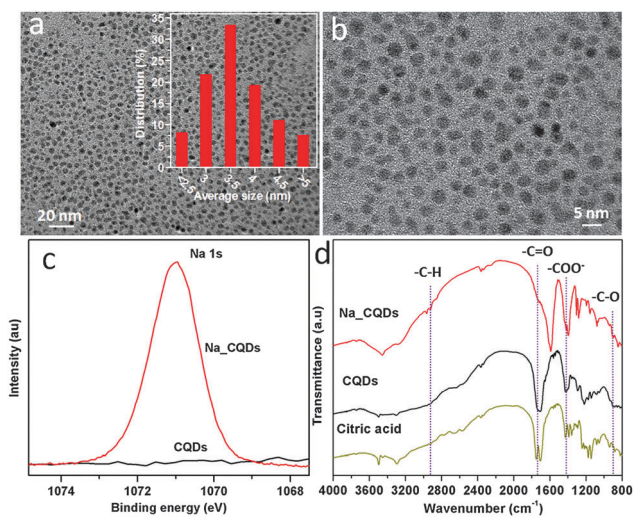


Fig. 2 (a, b) TEM images of Na_CQDs. The size distribution is given in the inset of (a). (c) XPS high-resolution Na 1s spectra of CQDs and Na_CQDs. (d) FT-IR spectra of Na_CQDs, CQDs, and citric acid.

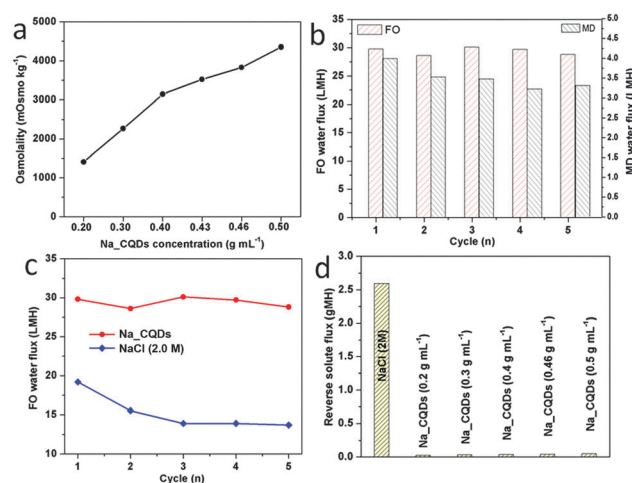


Fig. 3 (a) Osmolalities of Na_CQDs at various concentrations. (b) FO water fluxes with 0.4 g mL⁻¹ Na_CQDs as the draw solution and DI water as the feed solution and MD water fluxes with the diluted Na_CQDs solution as the feed solution. LMH refers to liter per (m² membrane h). (c) Comparison of FO water fluxes between 2.0 M NaCl and 0.4 g mL⁻¹ Na_CQDs draw solutions. (d) Reverse draw solute permeation of 2.0 M NaCl and Na_CQDs at different concentrations. gMH refers to gram solute per (m² membrane h).

exhibited excellent dispersibility in water. Even at a high concentration of 0.5 g mL^{-1} , a stable and uniform aqueous dispersion can be formed (Fig. S6, ESI†).

Na_CQDs solution at 0.4 g mL^{-1} was evaluated as the FO draw solution using DI water as a model feed solution. After each FO test, the diluted Na_CQDs solution was re-concentrated using membrane distillation (MD). For the FO and MD processes, the membranes used are a commercial HTI thin film composite (TFC) embedded support membrane (2 cm^2) and a multi-bore PVDF hollow fiber membrane (28 cm^2), respectively. A detailed experimental setup can be found in the experimental part (ESI†). Based on the weight change of the Na_CQDs solution during FO and MD, as shown in Fig. S8 and S9 (ESI†), the water fluxes were calculated. The FO and MD were repeated five times and the water fluxes are summarized in Fig. 3b. A high FO water flux of 29.8 LMH was achieved for the first cycle with little change in the following cycles. In the 5th cycle, the FO water flux was still maintained at 28.8 LMH . This FO water flux exceeds that of existing draw solutes with typical concentrations such as sugars,³⁰ ethanol,³¹ dendrimers,³² hydroacid complexes,²⁶ polymer hydrogels,³³ polyelectrolytes,³⁴ and polyelectrolyte-functionalized magnetic nanoparticles,^{25,35,36} and it is among the highest water fluxes reported using the same commercial FO membrane.²³ When simulated seawater (0.6 M NaCl) was employed as the feed solution, the FO water flux still reached as high as 7.3 LMH (Fig. S10, ESI†). The reconcentration of Na_CQDs via MD was performed at 45°C . For the 1st cycle, the MD water flux was 4.0 LMH . It slightly dropped in the next few cycles, but still retained 3.4 LMH in the 5th cycle.

The FO water flux of the Na_CQDs solution (0.4 g mL^{-1}) was compared with that of 2.0 M NaCl , which is widely used as a model draw solution in FO. As displayed in Fig. 3c, for the 1st cycle, the FO water flux of 2.0 M NaCl is 19.2 LMH , much lower than that of Na_CQDs. After 5 cycles, the water flux dropped by 29% for 2.0 M NaCl , but only by 3% for Na_CQDs. We also compared the reverse draw solute permeation of 2.0 M NaCl and Na_CQDs at various concentrations (Fig. 3d). For 2.0 M NaCl solution, a reverse draw solute flux of $2.5 \text{ gram per (m}^2 \text{ membrane h) (gMH)}$ was observed. In comparison, negligible reverse solute fluxes ($<0.05 \text{ gMH}$) were found for Na_CQDs. The commercial HTI TFC membrane used in this work has an average pore size of 0.5 nm in the active layer. The Na_CQDs have a size range of 2.5 to 5 nm , much larger than the pore size of the membrane. Therefore, the diffusion of Na_CQDs across the membrane is effectively suppressed, resulting in negligible reverse solute flux.

Combined with the MD process, the Na_CQDs solution (0.4 g mL^{-1}) was further used in FO for seawater desalination. The seawater was taken from the sea near the Singapore coast with a measured osmolality of 880 mOsm kg^{-1} . With a total salt concentration of 27.5 g L^{-1} , the seawater mainly contains Na^+ , Mg^{2+} , K^+ , Cl^- and SO_4^{2-} ions (Fig. S11, ESI†). Minimum poisoning effect of MgCl_2 , NaCl and KCl on the Na_CQDs was observed based on osmolality measurements. Before FO tests, the seawater was filtrated using a 220 nm filter membrane to remove impurities. As shown in Fig. 4, relatively high FO water fluxes of 10.4 and 9.6 LMH were achieved for the 1st and 5th cycles, respectively.

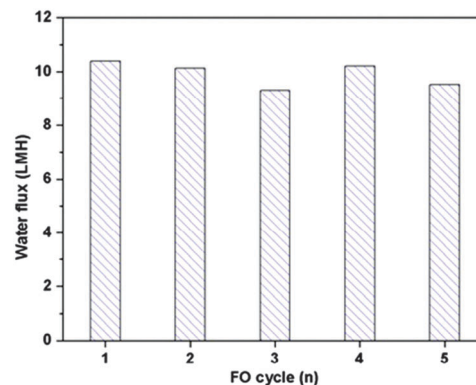


Fig. 4 FO water fluxes with 0.4 g mL^{-1} Na_CQDs aqueous solution as the draw solution and seawater taken from the sea near the Singapore coast as the feed solution. The seawater has an osmolality of 880 mOsm kg^{-1} .

In conclusion, we report a new draw solute, Na^+ -functionalized carbon quantum dots, in forward osmosis for seawater desalination. The unique characteristics of Na_CQDs, including an ultra-small size of 3.5 nm , abundant carboxyl groups, and rich ionic species, favor high osmotic pressure and thus FO water flux. At concentrations of 0.4 and 0.5 g mL^{-1} , the Na_CQDs provide respective osmotic pressures of 30.9 and 53.6 atm , much higher than that of seawater ($\sim 26 \text{ atm}$). In FO tests with DI water as the model feed solution, the Na_CQDs (0.4 g mL^{-1}) showed a water flux of 29.8 LMH , exceeding that of 2.0 M NaCl draw solution by 55%. This FO water flux is among the highest reported. When seawater was used as the feed solution, the Na_CQDs provided a FO water flux of 10.4 LMH with only a slight drop after 5 cycles. In addition, the Na_CQDs showed negligible reverse draw solute permeation. It is worth noting that for practical applications, further investigation is necessary to understand the energy consumption in the FO desalination process using Na_CQDs as draw solutes.

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