# Efficient 3D Printed Electrodes for Water Desalination – Membrane Capacitive Deionization

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## SUMMARY

There is increasing interests in cost-effective and energy-efficient technologies for the desalination of saltwater. However, the challenge in the scalability of the suitable compositions of electrodes has significantly hindered the development of capacitive deionization (CDI) as a promising technology for the desalination of brackish water. Herein, we introduced a 3D printing technology as a new route to fabricate electrodes with adjustable composition, which exhibited large-scale applications as free-standing, binder-free, and robust electrodes. The 3D printed electrodes were designed with ordered macro-channels that facilitated effective ion diffusion. The high salt removal capacity of 75 mg $g^{-1}$ was achieved for membrane capacitive deionization (MCDI) using 3D printed nitrogen-doped graphene oxide/carbon nanotube electrodes. The improved mechanical stability and strong bonding of the chemical components in the electrodes allowed a long cycle lifetime for the MCDI devices. The adjusted operational mode (current density) enabled a low energy consumption of 0.331 W h $g^{-1}$ and high energy recovery of 27%. Furthermore, the results obtained from the finite element simulations of the ion diffusion behavior quantified the structure–function relationships of the MCDI electrodes.

## KEYWORDS

**Binder-Free, 3D Printing, Capacitive Deionization, Electrodes, Free-Standing.**

## INTRODUCTION

Capacitive deionization (CDI), a promising electrochemical technology, has attracted considerable attention for brackish water desalination. And more recently alternative concepts such as Membrane Capacitive Deionization (MCDI), Flow electrode CDI (FCDI), Flow-through electrode CDI (FtCDI), and Hybrid CDI (HCDI) have been explored to improve the water production as well as salt removal capacities. However, scalability and ease of fabrication of suitable compositions' electrodes has greatly hindered the development of Capacitive deionization (CDI) as a promising technology in desalination of brackish water. Typically, the electrodes are prepared through coating the current collectors by the slurry of the mixture of active materials, conductive additives, and the polymer binders through different coating technologies. Unfortunately, most of the current electrodes' preparation methods are hindered by the major drawbacks of utilizing polymer binder which may block the pathway for ions and increase the internal resistance of the electrodes which later limit the salt removal capacity severely. A radical improvement of electrode performance, however, might be achieved if varieties of free-standing three-dimensional (3D) structures could be developed in alternative ways.

Herein, we demonstrate the experimental process to construct 3D free-standing and binder-free electrodes in MCDI applications. The experiments confirmed that 3D printed electrodes are promising to fabricate the designed macro-architectures which facilitate the effective ions diffusion. The schematic of the preparation of the electrodes is shown in Figure 1.

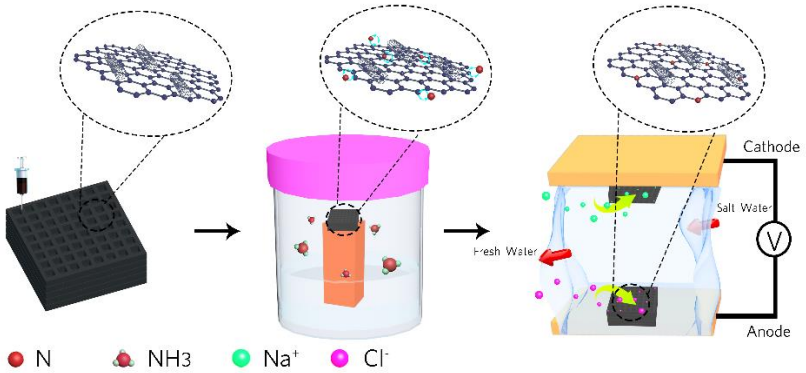


Figure 1, Schematic of the preparation process for the electrodes and the MCDI device

## METHODS

**Fabrication of 3D printed electrodes as the symmetric cathode and anode in MCDI:**
The ink precursor was prepared through dilution and mixing a certain amount of GO: CNT (different ratios of 100:0, 95:5, 90:10, 85:15, 70:30) followed by extended stirring for a few days to ensure a well-dispersed slurry. Subsequently, the mixture was fully dried using the freeze dryer and finally, viscous ink was obtained by redispersion into a small amount of water. The 3D electrodes were printed using a syringe dispenser. Simple cubic-like lattices with controlled layer numbers and area of 16*16 mm on glass slides were printed. The obtained product was freeze-dried followed by subjection to a hydrothermal reaction in a Teflon-lined stainless-steel autoclave at 200 °C for 6 hours to reduce and dope the nitrogen atoms to the 3D printed GO/CNT electrodes and labelled as 3D printed NGO/CNT (See Figure 1).
**3D printed Nitrogen doped GO/CNT electrodes characterization:**
The investigation of the morphology of the 3D printed GO/CNT was done using the Scanning Electron Microscopy (SEM) and shown in Figure 2. From figure 2 (a), the excellent accuracy and integrity of the cubic-like structure are noticeable which are a result of good ink preparation and proper adjustment of the 3D printing process. Moreover, the porous interconnected structure is shown with in Figure 2 (b) and (c). It shows the CNT contents which are distributed along with GO sheets to improve the conductivity and increase the available pore sites.

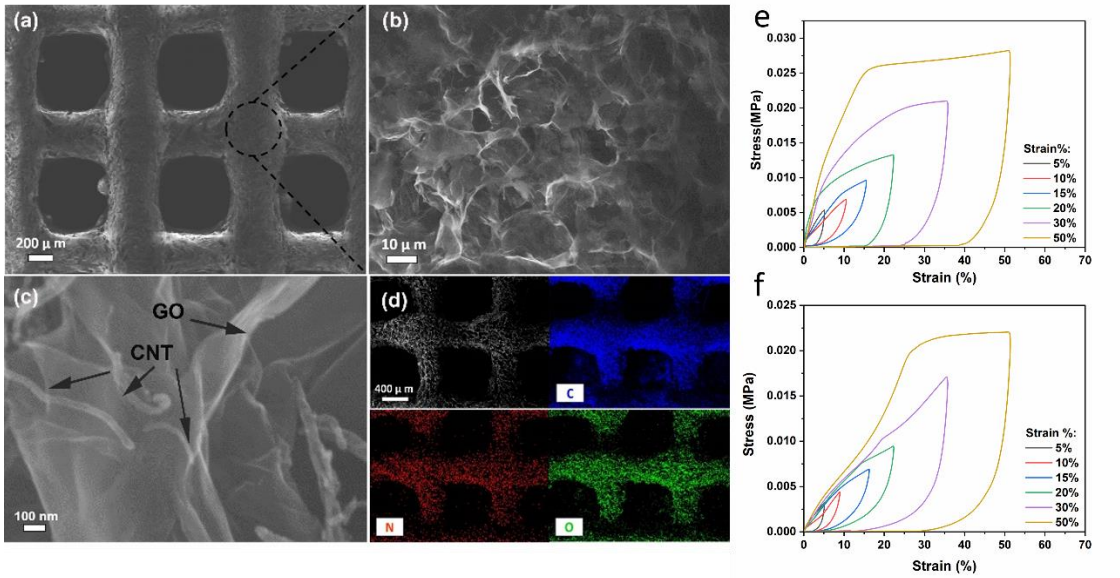


**Figure** 2 (a)–(c) SEM images of 3D printed GO/CNTs at different resolutions; (d) EDS mapping obtained after nitrogen doping. (e) Stress–strain curves of (e) 3D printed GO and (f) GO/CNT.

Furthermore, as illustrated in Fig. 2 (e) and (f), the mechanical robustness of the 3D printed structures was quantified by an in-plane compression test using a dynamic mechanical analyzer (DMA). Both Figures display the compression behavior of the 3D printed macrostructures as a function of the

predefined strain percentage for GO and GO/CNT, respectively. As observed in the Figures, both GO and GO/CNT show reversible non-linear super-elastic compressibility up to strains as high as 50%, indicating good deformation memory effects which makes them suitable as a robust free-standing electrode for MCDI device assembly.

**MCDI device desalination performance:**

To demonstrate the desalination performance of 3D printed structure within an MCDI assembly, herein, three different samples were printed. The desalination experiments were performed in a NaCl solution with the fixed mass ratio of 1:1 for cathode to anode and the flow rate of 50 mL min $^{-1}$. Herein, the loading mass for each side electrode was kept at around 10 mg, which could be achieved exactly based on the number of printed layers. The voltage window was kept as broad as -1.4 to 1.4 V to increase the removal capacity. The comparison experiments were performed for both 3D printed electrodes and traditionally prepared (non-printed), and the results showed the better performance of 3D printed electrodes due to the higher removal capacity and lower energy consumption (see Figure 3 (a) and (b)).

Moreover, the experimental results were confirmed by Finite Element Simulation, as shown in Figure 3 (c) – (f). In fact, designed macro holes can act as high concentration sources of ions and facilitate the distribution of sodium and chloride ions towards the micro/ mesopores existing in the bulk of the electrodes leading to the higher salt removal via the 3D printed electrodes.

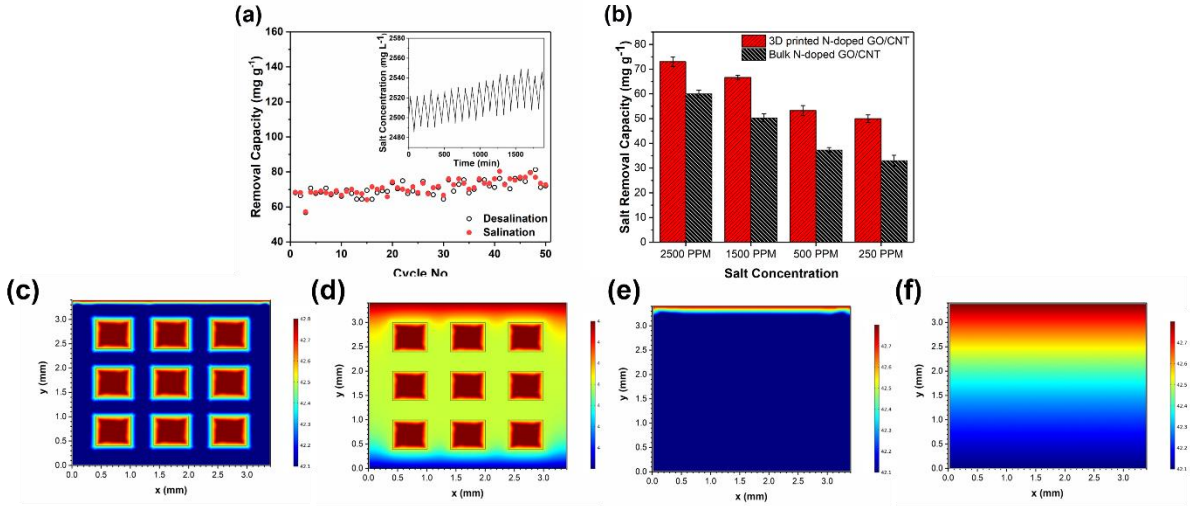


Figure 3, a) The cycling performance of 3D printed N-doped GO/CNT electrodes. (b) The comparison of the salt removal capacity of 3D printed NGO/ CNT and bulk NGO/CNT in solutions. c) Simulation results for the constant concentration gradient between the inlet and outlet (c) and (d) 3D printed NGO/CNT; (e) and (f) bulk NGO/CNT.

## CONCLUSIONS

In summary, this work demonstrates a new and efficient approach to fabricate free-standing and scalable electrodes for MCDI systems. The proposed approach can open a promising way to enhance the possibility of CDI commercialization as a cost-effective and energy-efficient technology to desalinate low to medium saltwater.

## REFERENCES

[1] 3D printed electrodes for efficient membrane capacitive deionization, Sareh Vafakhah et al. Nanoscale Adv., 2019, 1, 4804.