## Accepted Manuscript

Nitrogen-rich microporous carbon materials for high-performance membrane capacitive deionization

Danping Li, Xun-an Ning, Yue Huang, Shengchuan Li

PII: S0013-4686(19)30878-3

DOI: https://doi.org/10.1016/j.electacta.2019.04.172

Reference: EA 34120

To appear in: Electrochimica Acta

Received Date: 25 February 2019

Revised Date: 15 April 2019

Accepted Date: 28 April 2019

Please cite this article as: D. Li, X.-a. Ning, Y. Huang, S. Li, Nitrogen-rich microporous carbon materials for high-performance membrane capacitive deionization, *Electrochimica Acta* (2019), doi: https://doi.org/10.1016/j.electacta.2019.04.172.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



# Nitrogen-Rich Microporous Carbon Materials for high-performance membrane capacitive deionization

Danping Li, Xun-an Ning \*, Yue Huang, Shengchuan Li

Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, School of Environment Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China

\*Corresponding author: Xun-an Ning, E-mail: ningxunan666@126.com, Tel/Fax: (020)3932-2546

## Abstract

Novel two-dimensional carbon nitride hexagonal-like sheets were fabricated from thermal condensation, which uses hexaazatriphenylene-based precursor prepared microporous and oxidation resistant carbons materials (HAT-CN). The results show that the as-prepared HAT-CN is the first electrode utilized in capacitive deionization, due to the rich heteroatom and border-group content, as well as the potential collaborative effect of C and N atoms, displaying the quick ion diffusion and strong charge transfer performance. Additionally, the capacitive deionization performance of HAT-CN is improved by the synergistic contribution of a large accessible surface area, large pore volume, and high graphitization. The electrode of HAT-CN was carbonized at 550 °C which display an excellent specific capacitance of 179.2 F g<sup>-1</sup> in 1-M NaCl solution at a scan rate of 5 mV s<sup>-1</sup>. Subsequently, a high salt adsorption capacity of 24.66 mg g<sup>-1</sup> was attained for an applied voltage of 1.2 V in 500 mg L<sup>-1</sup> NaCl solution, showing good cyclic stability at 30 cycles. Considering those excellent properties of

the prepared HAT-CN, the capacitive deionization electrode should be an ideal candidate for high-performance deionization application.

Keywords: Two-dimensional, Nanoporous Carbon, Capacitive deionization, Desalination

## **1. Introduction**

Shortages in water resources and water security are two of the most important problems threatening and hindering the rapid and sustained development of society, exacerbated by unusable brackish water and the difficulty in regenerating domestic and industrial sewage [1, 2]. Traditional desalination techniques such as membrane distillation, ion-exchange resins, reverse osmosis, and electrodialysis are energy-intensive and costly, including regeneration by environmentally unfriendly means such as the use of an acid or base solution [3-8]. Thus, a novel water desalination technique-capacitive deionization (CDI)-has been rapidly developed because of its excellent performance, which includes high energy efficiency and water recovery and low energy consumption and contamination [9]. CDI refers to the removal of ions using capacitive adsorption. As the voltage is applied, the solution containing the charged substance migrates toward the electrodes and is adsorbed, forming double electric layers (EDLs) on the electrode-liquid interface [10, 11]. Then, the charge is desorbed back into the solution through the cancelation of the electric field or the reversal of the cell voltage. CDI could regenerate and restore during the adsorption and desorption processes [12, 13]. An example is membrane capacitive deionization (MCDI), which integrates commercial ion-exchange membranes onto the CDI devices. It has been demonstrated that the electroadsorption efficiency is improved by greatly reducing the effect of the co-ion [14-16].

A key parameter affecting the desalination efficiency of CDI is the performance of the electrode material, which includes a high surface area and electric conductivity, good wettability, and physicochemical stability [17]. Therefore, carbon materials including activated carbon (AC) [18], carbon aerogel (CA) [20], carbon nanotubes (CNTs) [19, 22], and grapheme [21, 22] have been investigated as the ideal candidates for CDI electrodes, which is benefit by their excellent conductivity, high specific surface area (SSA), and good chemical stability. However, the electrosorption capacity didn't achieve the expected performance due to the available surface area is limited by the van der Waals forces within graphene flakes and unideal wettability of AC and CNTs. [23-24] Also, the high manufacturing cost and complex preparation process is also limited the further application as CDI electrode. [25]

Recently, the 2D crystalline  $C_2N$  network— a structural analog of grapheme, as a novel material, has been synthesized by Mahmood in 2015 [26].  $C_2N$  has regular holes and a large electronic band gap (1.96 eV), which gives it better thermodynamic stability and capacity than that of g- $C_3N_4$ . Researchers are working to synthesize 2D crystals with tuneable structures and properties, using a bottom-up approach [27-30].  $C_2N$  has been found to have broad energy and environmental applications in nanoelectronics sensors, gas storage, and batteries, because of its high surface area, good crystallinity, and fast ion transport [31-33]. This is compared to the original graphene structure, which is surrounded by 6 N atoms, each with a dangling bond in  $C_2N$ . The size of the hole allows the anchoring of a few interacting  $K^+$  or  $CI^-$  atoms. Meanwhile, heteroatom doping can enhance the polarization of the structure and increase specific binding sites, both working together to increase the enthalpies of interaction between the guest and adsorbent species significantly, as compared to carbon materials [34]. Relatively high nitrogen content can enhance hydrophilicity, electric conductivity, and capacity [35, 36]. All these factors indicate that it will be extremely interesting to investigate the feasibility of using  $C_2N$  nanosheet as CDI electrodes. All these highlights show that  $C_2N$  nanosheet has great potential for application in CDI.

In our work, the HAT precursor has been prepared by the simple reaction of hexaketocyclohexane octahydrate and diaminomaleonitrile in hot acetic acid solution, followed by carbonization and simple condensation to remove  $C_2N_2$  species based on  $\pi$ -electrocyclic rearrangements to prepare HAT-CN-X. The template, additional nitrogen sources, and any complicated steps are not required. The electrochemical behavior and MCDI performance of the HAT-CN-X electrode were examined in NaCl aqueous solution. For comparison, an AC electrode was also investigated. As expected, the HAT-CN-X electrode shows better capacitive and desalination performance than AC electrodes. The results indicate that HAT-CN-X is a promising material for MCDI. As far as we know, there have been no reports regarding the use of HAT-CN-X as an electrode in MCDI.

#### 2. Experimental

#### 2.1. Fabrication

Hexaketocyclohexane octahydrate, diaminomaleonitrile, acetic acid (AR, 99.5%), nitric acid (AR, 65%), and acetonitrile (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used without further purification. Activated charcoal (AC,  $SSA_{BET} \sim 1000 \text{ m}^2 \text{ g}^{-1}$ ) was purchased from Shanghai Aladdin biochemical technology Co., Ltd., CHN. Cation/anion exchange membranes (LE-HoCM Grion 0011/1201) were supported by Hangzhou Grion Environment Technology Co., Ltd., CHN.

The synthesis of hexaazatriphenylene-hexacarbonitrile (HAT) was carried out according the procedure stated in the literature [37, 38]. Synthesis of HAT: Hexaketocyclohexane octahydrate (8 g, 12.6 mmol) and diaminomaleonitrile (22 g, 100.8 mmol) were refluxed in AcOH (300 mL) for 2 h. The black suspension was filtered off while hot and washed with hot AcOH ( $3 \times 25$  mL), resulting in a black solid. The solid was suspended in 30 % HNO<sub>3</sub> (60 mL) and heated at 100 °C for 3 h. The hot dark brown suspension was poured into ice water (200 mL) and cooled overnight. The suspension was filtered and the solid was refluxed in MeCN (500 mL) for 2 h and was filtered. The filtrate was then evaporated in vacuo to yield an orange solid (4.5 g, yield 50%).

The synthesis of HAT-CN-X was prepared using HAT (1 g) for carbonization in a tubular furnace at different temperatures for 1 h under N<sub>2</sub> gas flow. The heating ramp was set up to be 2 °C min<sup>-1</sup> from 30 to 100 °C, and 5 °C min<sup>-1</sup> from 100 °C to 450,

550, 700 or 800 °C. The described resulting materials are labeled as HAT-CN-X, where CN stands for the element type after carbonization and X refers to the synthesis temperature.

## **2.2.** Characterization

The products were characterized by using a scanning electron microscope (SEM, JEOL JEM-700F, JP) equipped with an energy dispersive X-ray spectrometer (EDS) and a transmission electron microscope (TEM, JEOL, JEM- 200CX, JP). The crystalline structures of the samples were identified by powder X-ray diffraction (PXRD, Bruker, D8, GER) using a Cu-Ka radiation source at 40 kV and 40 mA. Fourier transform infrared (FTIR) spectroscopy was performed with a Perkin-Elmer Spectrum GX at a range of 4000–500 cm<sup>-1</sup>. Raman spectra (HORIBA, LabRam HR Evolution, FR) were recorded at a laser of 532 nm. X-ray photoelectron spectroscopy (XPS) data was recorded on a Thermo Fisher Scientific K-Alpha system equipped with a twin anode Al-Ka (1486.6 eV) X-ray source. C/H/N elemental analysis (EA) was accomplished as combustion analysis using a Vario Micro device. Nitrogen adsorption/desorption isotherms were measured with an ASAP 2460 (Micromeritics, USA) at 77 K. Before the measurements, all samples were degassed 20 h at 493 K under vacuum. The specific surface areas (SSAs) and the pore volumes were calculated using the multi-point Brunauer-Emmett-Teller (BET) model. The pore size distributions were derived from the desorption branches of the isotherms using the nonlocal density functional theory model (NLDFT). The surface wettability of the samples was investigated by a drop-shape analysis system (DingSheng, JY-82B, CN).

Thermogravimetric analysis (TG) was performed on a TG209 (NETZSCH, GER) under nitrogen atmosphere with a 5 °C min<sup>-1</sup> heating rate.

## 2.3 Electrochemical capacitance evaluation

The electrochemical properties were determined by an electrochemical workstation (CHI 660E, Chinstruments, CN). The test uses a three-electrode system in a 1.0-M NaCl solution, which includes a HAT-CN-X electrode, a piece of platinum plate electrode  $(1 \times 1 \text{ cm}^2)$ , and an Ag/AgCl (saturated 1.0-M KCl) electrode, which serves as the working, counter, and reference electrodes, respectively. The working electrode was prepared by mixing the active component, acetylene black, and poly (vinyl alcohol) in a ratio of 8:1:1 wt.% to form homogeneous slurries, then coated onto a titanium mesh and dried at 110 °C in a vacuum oven for 1 h. For comparison, AC and HAT-CN-X electrodes were prepared under the same experimental conditions as the working electrodes.

The electrochemical performance of the electrodes was evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge measurements (GCD) in a potential ranging from 0 to 1.0 V. Electrochemical impedance spectroscopy (EIS) was conducted with an amplitude of 5.0 mV and a frequency range from 100 kHz to 0.01 Hz. The specific capacitances (Cs) were evaluated by the following formula with the CV curves:

$$C_s = \frac{\int I dU}{2m\nu} \tag{1}$$

where  $C_s$  (F g<sup>-1</sup>) is the specific capacitance, I (A) is the response current density, U (V) is the potential window, v (V s<sup>-1</sup>) is the potential scan rate, and m is the mass of the

electrode material.

## 2.4 CDI experiments

The deionization performance of electrodes was investigated in a CDI device apparatus, as shown in Figure S1. The electrode parameters included a mass of about 200 mg, size of  $30 \times 30 \text{ mm}^2$ , and thickness of 0.2 mm. In each experiment, the analytical pure NaCl solution (500, 700, and 1000 mg L<sup>-1</sup>) was continuously pumped from a peristaltic pump into the cell, and the effluent returned to the unit cell with a flow rate of 22 mL min<sup>-1</sup>. The volume of the solution was maintained at 80 mL at 298 K. The voltage was set within a range of 1.2, 1.4, and 1.8 V. The salt adsorption capacity (SAC) was obtained as the following formula:

$$SAC = \frac{C_0 - C_t}{m} \times V$$
(2)

where SAC (mg g<sup>-1</sup>) is the salt electrosorption capacity (mg g<sup>-1</sup>),  $C_o$  and  $C_t$  (mg L<sup>-1</sup>) are the initial and final concentrations of supply water, V (L) is the volume of the solution, and m (mg) is the mass of the electrode material.

## 3. Results and discussion

#### **3.1 Characteristics**

The synthesis process of preparation of HAT and HAT-CN-X is shown in Scheme 1, based on previous studies in which synthesis occurred through the thermal pyrolysis polymerization of hexaketocyclohexane octahydrate and diaminomaleonitrile, and condensation in  $N_2$  atmosphere [34].

The phase morphology of HAT and HAT-CN-X is characterized by SEM and TEM images, as shown in Figure S2 and Figure 1. Clearly, the shape of HAT and HAT-CN-X appear as some accumulation of small regular hexagons and a simply smooth surface in Figure S2 (a–d). Therefore, the macrostructure, caused by the pre-assembly of HAT, can be transferred to HAT-CN-X after carbonization, and the regular shape also showed good mechanical stability. As the carbonization temperature increases, some uniform cracks (5–10 µm in size) begin to form in the plates, which indicates that their structures are made up of small primary slabs, randomly arranged. Furthermore, the evenly porous nanostructures of HAT-CN-450, HAT-CN-550, and HAT-CN-700 are investigated in TEM (Figure 1(e–h)) images. These structures provide more ion-accessible space and significantly increased electrosorption capacitance. However, the structure of HAT-CN-800 appears stacking and interpenetrated with each other in Figure 1(h). There are signs that a structural rearrangement after carbonization changes an inert carbon to a nearly graphitic carbon phase without heteroatoms, following a temperature rise.

The higher nitrogen content was indicated in the as-prepared HAT-CN-X materials at lower carbonization temperatures, characterized by C/H/N EA, with the XPS and EDS mapping spectrometer results shown in Table 1. Clearly, the N elemental content measured by EA (31.5 at.%) is approach by XPS (29.3 at.%) and further demonstrated in the EDS (36.1 at.%) examination. All of the results show that HAT-CN-550 has a nearly perfect C<sub>2</sub>N-type stoichiometry, as previously reported [27, 39]. Moreover, EDS mapping also shows that carbon and nitrogen elements are evenly distributed, as shown in Figure 1(a-d). Therefore, the governed condensation mechanism can guarantee that the stoichiometric composition, calculated for HAT-CN, is transferred to the  $C_2N$ -type products.

XPS was used to identify the composition and functionality characteristics of C and N atoms in the materials, as shown in Figure S3. The N 1s signal (Figure 3) shown exists in cyano (~398 eV), pyrazine (~399 eV), quaternary nitrogen atoms (~400 eV), and oxidized nitrogen (~402 eV) groups after deconvolution. [34] The carbonization temperature can be regulated to control the amount of these groups in the as-prepared products. The increase in temperature is the primary reason for the reduction in N, characterized by the absence of cyano and pyrazine groups, as their content decreased continuously from 10.84 % to 5.00 % and 14.61 % to 9.57 %, respectively. On the contrary, the content of quaternary nitrogen group increases with higher temperature from 4.75 % to 9.83 % because of its higher binding energy. Previous studies have shown that carbon materials with high N-heteroatom content mainly introduced from cyano and pyrazine groups have good wettability and charge transfer ability, and therefore have better capacitive deionization performance. [34, 35]

The C1s spectrum (Figure S4) exists in graphitic C=C carbons (284 eV),  $sp^2$ -hybridized nitrogen atoms (285 eV and 286 eV), oxidized carbon atoms (289–290 eV), and oxidized nitrogen (~402 eV) groups after deconvolution. With the increase in temperature, the single peaks are transferred to lower binding energies, exhibiting a reduction in the positive working potential and less-inert properties of the electrons. Eventually, the inertia is lost again at very high temperatures. However, the content of graphitic C=C is increased at higher temperatures from 6.95 % to 22.12 %. Additionally, the controllable carbon electronic structure and the potential synergistic

effect of C and N atoms would be advantageous to the capacitive and deionization performance.

Figure S5 and Figure 2(a) shows the Raman spectrum of HAT and HAT-CN-X, which is indicated by so-called disordered sp<sup>3</sup> carbon (D-) and crystallized graphitic  $sp^2$  carbon (G-), near 1350 cm<sup>-1</sup> and 1595 cm<sup>-1</sup>, respectively. With the increase in carbonization temperature, the  $I_D/I_G$  ratio increases from 0.96 to 1.21, owing to the opportune adjustability of the carbon structure in six-rings and infrequently replaced N atoms, that is, the continuous formation of the primitive carbon phase. Therefore, material with higher carbon symmetry and electrical conductivity was prepared at higher temperatures.

The FT-IR spectra of the HAT and HAT-CN-450/550/700/800 electrodes are shown in Figure 2(b). All five samples show the appearance of the bands at 1599, 1459, 1333, and 1221 cm<sup>-1</sup>, which indicate stretching vibrations of aromatic CN bonds in condensed N-containing hybridization. The absorption bands at 1333 and 1599 cm<sup>-1</sup> may correspond to the stretching vibrations of the C–N and C=N bonds, respectively. There are less intense peaks of terminal cyano and pyrazine groups at 2242 cm<sup>-1</sup> with increasing synthetic temperature [40]. The results were further confirmed by Raman and XRD spectrum analysis.

X-ray diffraction (XRD) patterns of the as-prepared HAT and HAT-CN-X materials are further investigated. Figure 2(c) revealed that HAT has a crystalline structure by self-assembly because of its strong supramolecular aggregation, making it a hopeful material for the preparation of inert carbons. After condensation, the absence of

#### ACCEPTED MANUSCRIPT

crystalline inorganic impurities led to the formation of an amorphous structure with increasing temperature. The results shown an absence of characteristic peaks of graphitic stacking (20, 26) at high temperature, which may also be the reason for the formation of high specific surface-area carbon. TG analysis of HAT (Figure S6) also confirmed that it decomposes completely below 800 °C. Raman spectra further confirms this result. Nevertheless, the increasing peak intensity (20, 26) indicates that the reemergence of graphitic phase stacking at higher carbonization temperatures is consistent with the TEM results.

Figure 4 shows the contact angle of the as-prepared materials, utilizing water droplets on the surfaces. Their values are summarized in Table 1, showing an excellent surface hydrophilicity for all the as-prepared materials. Meanwhile, all of the values are almost same and both small. The favorable hydrophilicity of HAT-CN-X significantly contributes to its electrosorption performance because of the high nitrogen content and polar groups on its surfaces such as -OH and  $-C \equiv N$ .

 $N_2$  physisorption isotherms were used to characterize the specific surface area (SSA) and pore size distribution, suggesting type-I isotherms in Figure 2(d). A large amount of  $N_2$  is shown to absorb at  $p/p^0 < 0.1$  with no further adsorption at  $p/p^0 = 0.1-0.9$ , indicating the almost unique microporous properties of HAT-CN. Meanwhile, the inorganic porogen-free, as-prepared samples provide high SSA in the range of 600– 800 m<sup>2</sup> g<sup>-1</sup>, shown in Table 1. The conspicuous micropores have representative geometric shapes and angles of a polycondensed framework, which is condensed from the original nonporous HAT crystals. After condensation, considerable, accessible microporosity is created by a good arrangement of HAT. In addition, the micropore enlarged with increasing synthesis temperature provided an increase in micropore volume. Finally, the adsorption capacity at  $p/p^0 > 0.9$  came from the adsorption on the thin flake surface and within the hierarchical cavity of a wafer. In a previous report, higher SSA of micropores introduced more active sites to adsorb ions [41]. Clearly, HAT-CN-550 exhibits a highly microporous structure, which is essential to its capacitive and deionization property.

## **3.2 Electrosorption experiments**

The electroadsorption behavior of as-prepared samples was analyzed by cyclic voltammetry (CV) measurements. Figure 5(a) shows the CV test for all formulated electrode materials. Clearly, no oxidation/reduction peaks were observed in all the formulations under the selected potential range, indicating that the ions were adsorbed on the electrode surface by forming EDLs due to coulomb interaction rather than electrochemical reaction [41]. Owing to the intrinsic resistance and polarization effect of the electrode little deviation from the standard rectangular structure is evident. However, the CV curve of the as-prepared material also shows an approximately rectangular shape, suggesting that reverse potential scanning can be achieved to rapidly charge the platform, that is, salt ions have an excellent ability to adsorb/desorb from the electrodes quickly.

According to the calculations from the CV curve for a sweep speed of 5 mV s<sup>-1</sup>, the specific capacitance (Cs) is 52.25 F g<sup>-1</sup> for HAT-CN-450, 179.20 F g<sup>-1</sup> for HAT-CN-550, 162.54 F g<sup>-1</sup> for HAT-CN-700, and 99.86 F g<sup>-1</sup> for HAT-CN-800.

13

Clearly, the HAT-CN-550 electrode has the best Cs, as greater graphitization leads to good conductivity and low internal resistance. However, the continuous pore size and relatively integrated structure within flakes supply many more active sites. That is, a more exposed surface can ensure the easier migration of salt ions across the interface between solution and material. [41]

In Figure 5(b), the CV test of HAT-CN-550 was investigated at various scan rates from 1–50 mV s<sup>-1</sup>, showing no oxidation/reduction reaction due to the rectangular nature of the shape of the CV curves. This suggests that the salt ion can move in or out quickly within the electrode, that is, Na<sup>+</sup> and Cl<sup>-</sup> can adsorb/desorb from HAT-CN-550 electrode. Compared to low scan rates (1–10 mV s<sup>-1</sup>), the higher scan rates (50 mV s<sup>-1</sup>) show a CV curve shaped like a piece of leaves, exhibiting a degree of distortion from the rectangle. This indicates the less available SSA in the internal pores of the electrode due to insufficient time for the salt ions to move from solution to materials and accumulate. On the contrary, the ions have sufficient time to diffuse and accumulate in almost all obtainable SSA, producing a preferable capacitive behavior at a slower sweep rate.

For further investigation, the relationship between specific capacitances and sweep rate of HAT-CN-550 electrode is shown in Figure 5(c). Trends of the specific capacitance show an increase, while the sweep rate decreased from 50 mV s<sup>-1</sup> to 1 mV s<sup>-1</sup>, while the specific capacitances for 50, 10, 5, 1 mV s<sup>-1</sup> are 87.76 F g<sup>-1</sup>, 168.43 F g<sup>-1</sup>, 179.20 F g<sup>-1</sup> and 221.28 F g<sup>-1</sup>, respectively.

In Figure 5(d), the influence of ion concentration on the electrical adsorption

property of the HAT-CN-550 electrode was studied with a potential window of 0 to 1.0 V in 0.5-, 1.0-, and 1.5-M NaCl solutions at a scan rate of 5 mV s<sup>-1</sup>. Apparently, the higher concentration of the NaCl solution has larger areas of CV curves, suggesting that salty ion has a better effect of accumulation and adsorption on electrode surface at a higher concentration of NaCl solution, resulting in higher electronic conductivity and more ion contents in EDLs region. Hence, HAT-CN-550 has good electrosorption properties in CDI process, and also has great advantages in seawater desalination.

For further study, the stability and invertibility effect of HAT-CN-550 electrode, the galvanostatic charge-discharge curves (GCD) is tested at a current density of 200 mA  $g^{-1}$  with a potential window of 0 to 1.0 V in 1.0-M NaCl solution, as shown in Figure 6(a). HAT-CN-X electrode is appearance a symmetric triangle feature of ideal capacitor behaviors. It is worth noting that the curves are not an absolute symmetric triangle, which may be the influence of a small pseudo-capacitance emanating from rich-nitrogen content [43]. It also can be found that the HAT-CN-550 electrode has a longer charge/discharge time, that its result is the same as the CV results, suggesting it has higher specific capacitances. In Figure 6(b), it is investigated the GCD curves of HAT-CN-550 electrode at a current density of 100–500 mA  $g^{-1}$ . Clearly, at the beginning of the discharge process appears, the internal resistance drops. A lower gradient means a lower total drag, suggesting HAT-CN-550 electrode has low internal resistance and is suitable for CDI. Furthermore, invertibility and stability are investigated by GCD in 1.0-M NaCl solution at a current density of 200 mA  $g^{-1}$ .

Figure 6(c), it can be found that there is no charge and discharge attenuation after 600 cycles, showing the HAT-CN-550 electrode has the long life for CDI applications due to key features, such as good stability and cyclability performance.

To investigate the electrochemical impedance spectra, it is tested in 1.0-M NaCl solution, as shown in Figure 6(d). The high frequency corresponds to the limiting process of charge transfer and the connection of charge transfer resistance and the EDLs at the contact interface between the electrode and the electrolyte solution. Clearly, a small semicircle at high frequencies can be found, that is, the smaller the charge transfer resistance is due to the smaller semicircle. Meanwhile, it is displayed that higher carbonization temperature will lead to lower charge transfer resistance, which improves the capacitive performance. But all of the as-prepared electrodes have a small interface contact resistance, except of HAT-CN-450 electrode.

#### **3.3 MCDI performance**

The MCDI performance was investigated in a NaCl aqueous solution at a certain voltage and flow rate by batch mode. The MCDI cell fabricated by symmetrical electrodes consist of the as-prepared electrodes, in contrast to the commercially activated carbon (AC) electrodes.

As shown in Figure 7(a), all the as-prepared electrodes cell have a sharp decrease with 10 min at voltage of 1.2 V in initial concentration of 500 mg  $L^{-1}$ , suggesting that the electrodes have an excellent ability to absorb salt ions onto the relatively charged electrodes quickly. With increasing absorption time, conductivity decreases gradually and then is closed to electrosorption equilibrium when the curves flattens out at 60

min. As shown in Figure 7(a), the salt adsorption capacitance (SAC) values of HAT-CN-450, HAT-CN-550, HAT-CN-700, and HAT-CN-800 electrode are 22.79 mg  $g^{-1}$ , 24.66 mg  $g^{-1}$ , 19.13 mg  $g^{-1}$ , and 17.50 mg  $g^{-1}$ , respectively. Compared to the as-prepared sample, the AC electrode has the lowest desalination capacitance (11.14 mg g<sup>-1</sup>). The salt adsorption rate (SAR) is also one of the factors affecting MCDI performance. [44] It can be combined with SAC to form a MCDI Ragone diagram, as shown in Figure 7(b). Clearly, the HAT-CN-550 situated in the upside and right of the CDI Ragone figure indicates the highest SAC, owing to the high micro-porous content and perfect ratio of nitrogen content, including excellent electrical conductivity and a rich vary boundary structure. The AC electrode has the lowest SAC, because of its low micro-porous contributing SSA. Although HAT-CN-700 and HAT-CN-800 electrodes have lower impedance than HAT-CN-550, the impedance of HAT-CN-550 is also small. Moreover, the excellent wettability of HAT-CN-550 contributes to adequate contact between the electrodes and solution, which is one of the key factors for MCDI test. In short, the acquired results explicitly demonstrate the importance of the micro-pore amount and the ratio of nitrogen content in improving the desalination performance of an electro-active material.

To further investigate, the influence of applied voltages ranging from 1.2 to 1.8 V, and concentrations of NaCl solution between 500 mg L<sup>-1</sup> to 1000 mg L<sup>-1</sup> on MCDI performance of the HAT-CN-550 electrode is shown in Figure 7(c). The MCDI behaviors of the HAT-CN-550 electrode were studied at varying test applied voltages from 1.2 to 1.8 V with a flow rate of 22 mL min<sup>-1</sup>. The curves in the figure dropped

sharply within 10 min and reach a stable state within 60 min. Increasing the applied voltage, the SAC is increased from 24.66 to 33.17 mg g<sup>-1</sup>, indicating that the higher potential can produce a stronger electrostatic interaction to bring about a larger removal of NaCl. Meanwhile, MCDI Ragone plots of the HAT-CN-550 electrode performance at applied potentials varying from 1.2 to 1.8 V are exhibited in Figure 7(d). The results reveal that the curves approach more upside and to the right with increase in applied potential, suggesting a higher SAC and SAR increase with the enhancement of the applied potentials. It is noting that no obvious bubbles were found, while the applied potentials were set to 1.8 V, suggesting that no electrolytic reaction of water took place, even at an overvoltage higher than 1.23 V [45] because of the effect on membrane resistance and intrinsic resistance of electrode. [46]

Additionally, the effect of different NaCl concentration on MCDI performance was investigated at the applied potential of 1.2 V. The SAC of HAT-CN-550 electrode in NaCl concentration of 500, 700 and 800 mg L<sup>-1</sup> is 24.66, 26.43, and 30.79 mg g<sup>-1</sup>, respectively. Clearly, the curves increase with increasing NaCl concentration, and the plots show an increase to the right, revealing a higher adsorption mass of NaCl and removal rate due to higher conductivity makes it easy to form EDLs, with a faster transportation speed of the salt ions to the electrode spacing channel when the NaCl concentration in the solution is higher. However, when the increase in ions in the solution is much greater than the adsorption amount, the species of ions in the pore is saturated, leading to a decrease in removal efficiency.

Finally, the effect of the regeneration stability of the HAT-CN-550 electrode was

investigated with a charge voltage of 1.2 V, revealing its ability to absorb, and in a short circuit, to desorb, as shown in Figure 8. The deionization process completes quickly after the charge voltage was applied. Then the short circuit of the cell has a quick desorption performance during the discharge process, suggesting that the HAT-CN-550 electrode has excellent regeneration. Additionally, no apparent decrease in solution conductivity was observed after 30 regeneration cycles, which reveals an excellent regeneration property. Moreover, the electrosorption capacities performance are higher than those for other Nitrogen-doped electrode materials reported in previous work as listed in Table 2. Therefore, the HAT-CN-550 electrode has excellent deionization performance in CDI.

## 4. Conclusions

In conclusion, a novel hexagon-like carbon framework was prepared by condensation of HAT through in situ synthesis and used it as an electrode in capacitive deionization. Results indicate that HAT-CN has a large specific surface area, rich micro-pore structure, and excellent conductivity, which leads to high MCDI performance, contributed by the furnishing of plenty of space and active sites for charge storage. Additionally, HAT-CN has a high nitrogen content, good wettability, and low impedance, which all lead to the fast transport of salt ions. Meanwhile, the HAT-CN electrode, as the heteroatom-based carbon material, reveals favorable regeneration performance. Thus, HAT-CN is a promising electrode material suitable for MCDI application and alkaline treatment.

## Acknowledgements

This work was supported by the Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program [grant number 2017BT01Z032]; the Special Applied Technology Research and Development of Guangdong Province (major project) [grant number 2015B020235013]; the Science and Technology Plan of Guangzhou [grant number 201607010330]; and the Natural Science Foundation of China [Grant No. 21577027].

## References

- [1] Y. H. Teow, A. W. Mohammad, New generation nanomaterials for water desalination: A review, Desalination 451 (2019) 2-17.
- [2] J. Choi, P. Dorji, H. K. Shon, S. K. Hong, Applications of capacitive deionization: Desalination, softening, selective removal, and energy efficiency Desalination 449 (2018) 118-130.
- [3] S. Porada, L. Weinstein, R. Dash, A. V. Wal, M. Bryjak, Y. Gogotsi, P. M. Biesheuvel, Water Desalination Using Capacitive Deionization with Microporous Carbon Electrodes Appl. Mater. Inter. 4 (2012) 1194-1199.
- [4] I. B. Rae, S. Pap, D. Svobodova, S.W. Gibb, Comparison of sustainable biosorbents and ion-exchange resins to remove Sr<sup>2+</sup> from simulant nuclear wastewater: Batch, dynamic and mechanism studies Sci. Total Environ. 650 (2019) 2411-2422.
- [5] D. M. Warsinger, E. W. Tow, L. A. Maswadeh, Inorganic fouling mitigation by salinity cycling in batch reverse osmosis. Water Res. 137 (2018) 384-394.

- [6] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications. Desalination 264 (2010) 268-288.
- [7] P. Wang, T. S. Chung, Recent advances in membrane distillation processes: Membrane development, configuration design and application exploring. J. Membrane Sci. 474 (2015) 39-56.
- [8] L. H. Chen, A. Huang, Y. R. Chen, Omniphobic membranes for direct contact membrane distillation: Effective deposition of zinc oxide nanoparticles. Desalination 428 (2018) 255-263.
- [9] M. A. Anderson, A. L.Cudero, J. Palma, Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: Will it compete? Electrochim. Acta 55 (2010) 3845-3856.
- [10] Z. Chen, H. T. Zhang, C. X. Wu, L. T. Luo, C. P. Wang, S. B. Huang, H. Xu, A study of the effect of carbon characteristics on capacitive deionization (CDI) performance. Desalination 433 (2018) 68-74.
- [11] C. J. Feng, Y. A. Chen, C. P. Yu, C. H. Hou, Highly porous activated carbon with multichanneled structure derived from loofa sponge as a capacitive electrode material for the deionization of brackish water. Chemosphere 208 (2018) 285-293.
- [12] G. L. Andres, T. Mizugami, Y. Yoshihara, Simulation of an electric behavior of the CDI system. Desalination 419 (2017) 211-218.
- [13] L. Agartan, B.H. Oberst, B.W. Byles, B. Akuzum, E. Pomerantseva, E.C. Kumbur, Influence of operating conditions and cathode parameters on desalination performance of hybrid CDI systems. Desalination 452 (2019) 1-8.

- [14] M. T. Qiao, X. F. Lei, Y. Ma, L. D. Tian, X. W. He, K. H. Su, Q. Y. Zhang, Application of yolk-shell Fe<sub>3</sub>O<sub>4</sub>@N-doped carbon nanochains as highly effective microwave-absorption material. Nano Research. 11 (2018) 1500-1519.
- [15] C. C. Hu, C. F. Hsieh, Y. J. Chen, C. F. Liu, How to achieve the optimal performance of capacitive deionization and inverted-capacitive deionization. Desalination 442 (2018) 89-98.
- [16] C. Y. Li, X. Y. Guo, X. Wang, S. G. Fan, Q. X. Zhou, H. Q. Shao, W. L. Hu, C. H. Li, L. Tong,
  R. R. Kumar, J. H. Huang, Membrane fouling mitigation by coupling applied electric field in membrane system: Configuration, mechanism and performance. Electrochim. Acta 287 (2018) 124-134.
- [17] D. H. Kim, Y. E. Choi, J. S. Park, M. S. Kang, Capacitive deionization employing pore-filled cation-exchange membranes for energy-efficient removal of multivalent cations. Electrochim. Acta 295 (2019) 164-172
- [18] Z. Z. Xie, X. H. Shang, J. B. Yan, T. Hussain, P. F. Nie, J.Y. Liu, Biomass-derived porous carbon anode for high-performance capacitive deionization. Electrochim. Acta 290 (2018)666-675.
- [19] T. Gao, F. Zhou, W. Ma, H.B. Li, Metal-organic-framework derived carbon polyhedron and carbon nanotube hybrids as electrode for electrochemical supercapacitor and capacitive deionization. Electrochim. Acta 263 (2018) 85-93.
- [20] G. Zhu, H.Y. Wang, H.F. Xu, L. Zhang, Enhanced capacitive deionization by nitrogen-doped porous carbon nanofiber aerogel derived from bacterial-cellulose. J. Electroanal. Chem. 822 (2018) 81-88.
- [21] G.M. Luo, Y.Z. Wang, L.X. Gao, D.Q. Zhang, T. Lin, Graphene bonded carbon nanofiber

aerogels with high capacitive deionization capability. Electrochim. Acta 260 (2018) 656-663.

- [22] A. M. Abdelkader, D. J. Fray, Controlled electrochemical doping of graphene-based 3D nanoarchitectures electrodes for supercapacitors and capacitive deionization. Nanoscale 9(2017) 14548-14557.
- [23] B. Mendoza-Sánchez, Y. Gogotsi, Synthesis of Two-Dimen- sional Materials for Capacitive Energy Storage. Adv. Mater. 28(2016) 6104-6135.
- [24] C. Hu, L. Song, Z. Zhang, N. Chen, Z. Feng, L. Qu, Tailored graphene systems for unconventional applications in energy conversion and storage devices. Energy Environ. Sci. 8(2015) 31-54.
- [25] X. Xu, M. Wang, Y. Liu, T. Lu, L. Pan, Metal-organic framework-engaged formation of a hierarchical hybrid with carbon nanotube inserted porous carbon polyhedra for highly efficient capacitive deionization. J. Mater. Chem. A, 4(2016) 5467-5473.
- [26] J. Mahmood, E. K. Lee, M. Jung, D. Shin, I. Y. Jeon, S. M. Jung, H. J. Choi, Seo, J. M. S. Y. Bae, S. D. Sohn, Nitrogenated holey two-dimensional structures. Nat. Commun. 6 (2015) 6486-6493.
- [27]S. Y. Wang, G. Wang, T. T. Wu, Y. Q. Zhang, F. Zhan, Y. W. Wang, J. G. Wang, Y. Fu, J. S. Qiu, BCN nanosheets templated by g-C<sub>3</sub>N<sub>4</sub> for high performance capacitive deionization. J. Mater. Chem. A 6 (2018) 14644-14650.
- [28] D. F. Perepichka, F. Rosei, CHEMISTRY Extending Polymer Conjugation into the Second Dimension. Science 323 (2009) 216–217.
- [29] D. Jariwala, A. Srivastava, P. M. Ajayan, Graphene synthesis and band gap opening. J. Nanosci. Nanotechnol. 11 (2011) 6621–6641.

- [30] P. A. Denis, Band gap opening of monolayer and bilayer graphene doped with aluminium, silicon, phosphorus, and sulfur. Chem. Phys. Lett. 492 (2010) 251–257.
- [31] M. Oschatz, L. Borchardt, M. Thommes, K. A. Cychosz, I. Senkovska, N. Klein, R. Frind, M. Leistner, V. Presser, Y. Gogotsi, S. Kaskel, Carbide-Derived Carbon Monoliths with Hierarchical Pore Architectures. Angew. Chem. Int. Ed. 51 (2012) 7577-7580.
- [32] D. S. Su, S. Perathoner, G. Centi, Nanocarbons for the Development of Advanced Catalysts. Chem. Rev. 113 (2013) 5782-5816.
- [33] R. Y. Yan, T. Heil, V. Presser, R. Walczak, M. Antonietti, M. Oschatz, Ordered Mesoporous Carbons with High Micropore Content and Tunable Structure Prepared by Combined Hard and Salt Templating as Electrode Materials in Electric Double-Layer Capacitors. Adv. Sustainable Syst. 2 (2018) 1700128
- [34] W. Ralf, K. Bogdan, S. Aleksandr, H. Tobias, S. Johannes, Q. Qing, A. Markus, O. Martin, Template-, and Metal-free Synthesis of Nitrogen-rich Nanoporous "Noble" Carbon Materials by Direct Pyrolysis of a Preorganized Hexaazatriphenylene Precursor. Angew. Chem. Int. Ed. 57 (2018) 10765 –10770.
- [35] C. Schneidermann, N. Jäckel, S. Oswald, L. Giebeler, V. Presser, L. Borchardt, Solvent-free mechanochemical synthesis of nitrogen-doped nanoporous carbon for electrochemical energy storage. ChemSusChem 10(2017) 2416-2424.
- [35] J. Liang, L. C. Yin, X. N. Tang, H. C. Yang, W. S. Yan, L. Song, H. M. Cheng and F. Li, Kinetically Enhanced Electrochemical Redox of Polysulfides on Polymeric Carbon Nitrides for Improved Lithium-Sulfur Batteries. ACS Appl. Mater. Interfaces, 8 (2016) 25193–25201.
- [36] F. Zheng, Y. Yang and Q. Chen, High lithium anodic performance of highly nitrogen-doped

porous carbon prepared from a metal-organic framework. Nat. Commun. 5 (2014) 5261.

- [37] J. T. Rademacher, K. Kanakarajan, A. W. Czarnik, IMPROVED SYNTHESIS OF 1,4,5,8,9,
  12-HEXAAZATRIPHENYLENEHEXACARBOXYLIC ACID. Synthesis 4 (1994) 378-380.
- [38] B. Kurpil, A. Savateev, V. Papaefthimiou, S. Zafeiratos, T. Heil, S. Özenler, D. Dontsova, M. Antonietti, Hexaazatriphenylene doped carbon nitrides-Biomimetic photocatalyst with superior oxidation power. Applied Catalysis B: Environmental 217 (2017) 622-628.
- [39] N. Fechler, N. P. Zussblatt, R. Rothe, R. Schlogl, M. G. Willinger, B. F. Chmelka, M. Antonietti, Eutectic Syntheses of Graphitic Carbon with High Pyrazinic Nitrogen Content. Adv. Mater. 28 (2016) 1287-1294.
- [40] G. Xin, Y. L. Meng, Pyrolysis Synthesized g-C3N4 for Photocatalytic Degradation of Methylene Blue. J. Chem. 187912 (2013) 1-5.
- [41] Y. Liu, X. Xu, M. Wang, T. Lu, Z. Sun, L. Pan, Metal-organic framework-derived porous carbon polyhedra for highly efficient capacitive deionization. Chem.Commun. 51 (2015) 12020–12023.
- [42] Z. Wang, T. Yan, J. Fang, L. Shi and D. Zhang, Nitrogen-doped porous carbon derived from a bimetallic metal-organic framework as highly efficient electrodes for flow-through deionization capacitors. J. Mater. Chem. A 4 (2016) 10858–10868.
- [43] J. B. Hou, Y. Y. Shao, M. W. Ellis, R. B. Moore and B. L. Yi, Graphene-based electrochemical energy conversion and storage: fuel cells, supercapacitors and lithium ion batteries. Phys. Chem. Chem. Phys. 13 (2011) 15384–15402.
- [44] Z. Wang, T. T. Yan, L. Y. Shi, D. S. Zhang, In Situ Expanding Pores of Dodecahedron-like

Carbon Frameworks Derived from MOFs for Enhanced Capacitive Deionization. ACS Appl. Mater. Interfaces 9(2017) 15068-15078.

- [45] H. Li, L. Zou, L. Pan, Z. Sun, Novel graphene-like electrodes for capacitive deionization. Environ. Sci. Technol. 44 (2010) 8692-8697.
- [46] H. Li, T. Lu, L. Pan, Y. Zhang, Z. Sun, Electrosorption behavior of graphene in NaCl solutions. J. Mater. Chem. 19 (2009) 6773-6779.
- [47] Y. Wimalasiri, M. Mossad, L. Zou, Thermodynamics and kinetics of adsorption of ammonium ions by graphene laminate electrodes in capacitive deionization. Desalination, 357(2015) 178–188.
- [48] Q. Dong, G. Wang, T. Wu, S. Peng, J. Qiu, Enhancing capacitive deionization performance of electrospun activated carbon nanofibers by coupling with carbon nanotubes. J. Colloid Interface Sci., 446(2015) 373–378.
- [49] C. Nie, L. Pan, H. Li, T. Chen, T. Lu and Z. Sun, Electrophoretic deposition of carbon nanotubes film electrodes for capacitive deionization. J. Electroanal. Chem., 666(2012) 85– 88.
- [50] Z. Peng, D. Zhang, L. Shi and T. Yan, High performance ordered mesoporous carbon/carbon nanotube composite electrodes for capacitive deionization. J. Mater. Chem., 22(2012), 6603-6612.
- [51] Y. Q. Li, X. T. Xu, S. J. Hou, J. Q. Ma, T. Lu, J. C. Wang, Y. F. Yao, L. K. Pan, Facile dual doping strategy via carbonization of covalent organic frameworks to prepare hierarchically porous carbon spheres for membrane capacitive deionization. Chem. Commun., 54(2018) 14009-14012.

## Table

Table 1 Summary of characterization results as well as experimental carbon yield of the HAT-CN-X materials.

 Table 2 Comparison of electrosorption capacities of Nitrogen-doped electrode materials from this

 study and reported in previous work.

| T[K] | C [at.%] |      |      | N [at.%] |      |      | O [at.%] |     |     | SSA <sub>BET</sub> | Contact  | $I_D/$ | yeild |
|------|----------|------|------|----------|------|------|----------|-----|-----|--------------------|----------|--------|-------|
|      | EA       | EDS  | XPS  | EA       | EDS  | XPS  | EA       | EDS | XPS | $[m^2 g^{-1}]$     | angle[°] | $I_G$  | [%]   |
| 450  | 55.2     | 60.5 | 62.9 | 42.9     | 37.1 | 35.3 | -        | 2.4 | 1.8 | 595.5              | 41.9     | -      | 91.5  |
| 550  | 49.5     | 61.0 | 68.4 | 31.5     | 36.1 | 29.3 | -        | 2.4 | 2.3 | 771.2              | 32.8     | 0.96   | 62.5  |
| 700  | 47.7     | 63.6 | 66.5 | 29.1     | 34.9 | 30.3 | -        | 2.5 | 3.2 | 830.9              | 25.3     | 1.07   | 38.4  |
| 800  | 56.5     | 67.9 | 81.1 | 21.4     | 28.6 | 15.3 | -        | 3.5 | 3.6 | 701.3              | 28.9     | 1.21   | 25.5  |

| Raw materials and preparation procedure   | Applied voltage | Initial concentration/<br>conductivity of salt | Electrosorption capacity | Ref.        |
|---|-----------------|--|--------------------------|-------------|
| Nitrogen-doped graphene sponge fabricated via directly freeze-drying graphene oxide solution followed by annealing in NH <sub>3</sub> atmosphere  | 1.2 V           | 500 mg L <sup>-1</sup><br>NaCl solution        | 21.0 mg g <sup>-1</sup>  | 47          |
| Nitrogen-doped carbon nanorods prepared from<br>naturally based nanocrystalline cellulose through<br>freeze drying with subsequent thermal treatment<br>under an ammonia atmosphere at different<br>temperatures              | 1.2 V           | 500 mg L <sup>-1</sup><br>NaCl solution        | 17.62 mg g <sup>-1</sup> | 48          |
| Nitrogen-doped porous hollow carbon spheres<br>(N-PHCS) prepared by using polystyrene spheres<br>as hard templates and dopamine hydrochloride as<br>carbon and nitrogen sources by carbonization at<br>different temperatures | 1.4 V           | 500 mg L <sup>-1</sup><br>NaCl solution        | 12.95 mg g <sup>-1</sup> | 49          |
| Facile dual doping strategy via carbonization of<br>covalent organic frameworks to prepare<br>hierarchically porous carbon spheres and<br>carbonization at different temperatures   | 1.2 V           | 500 mg L <sup>-1</sup><br>NaCl solution        | 18.5 mg g <sup>-1</sup>  | 50          |
| Two-dimensional boron carbon nitride nanosheets were fabricated using a new approach, which uses $g-C_3N_4$ as both the template and the nitrogen source, boric acid as the boron source and a subsequent pyrolysis process   | 1.4 V           | 500 mg L <sup>-1</sup><br>NaCl solution        | 13.6 mg g <sup>-1</sup>  | 25          |
| Metal-organic-framework (ZIF-67) derived<br>carbon polyhedron and carbon nanotube<br>hybrids(HCN)   | 1.4 V           | 1000 μS cm <sup>-1</sup><br>NaCl solution      | 7.08 mg g <sup>-1</sup>  | 19          |
| Hexaazatriphenylene-based precursor prepared<br>microporous and oxidation resistant carbons<br>materials  | 1.2             | 1200 μS cm <sup>-1</sup><br>NaCl solution      | 24.66 mg g <sup>-1</sup> | our<br>work |

Table 2 Comparison of electrosorption capacities of Nitrogen-doped electrode materials from this study and reported in previous work.

## Figure

Scheme 1 Condensation reaction process

Figure 1 TEM images of (a) HAT-CN-450; (b) HAT-CN-550; (c) HAT-CN-700 and (d) HAT-CN-800.

Figure 2 (a) Raman survey spectra of HAT-CN-450/550/700 /800; (b) FT-IR survey spectra of HAT-CN-450/550/700 /800; (c) PXRD measurements of HAT and HAT-CN-450/550/700 /800; (d)  $N_2$  physisorption isotherms measurement (the inset represents Pore size distribution) of HAT-CN-450/550/700/800.

Figure 3 Fitted N1s XPS line scans of (a) HAT-CN-450; (b) HAT-CN-550; (c) HAT-CN-700 and (d) HAT-CN-800.

Figure 4 Contact Angle measurement of (a) HAT-CN-450, (b) HAT-CN-550, (c) HAT-CN-700, and (d) HAT-CN-800.

Figure 5 (a) CV curves of the electrodes at a potential sweet rate of 5 mV s<sup>-1</sup>; (b) CV curves of the HAT-CN-550 at different scan rates; (c) the specific capacitance of the electrodes at 1-50 mV s<sup>-1</sup>; (d) CV curves of the HAT-CN-550 at different concentration of NaCl.

Figure 6 (a) the GCD curves of the HAT-CN-450/550/700/800 electrodes; (b) the GCD at various current density of HAT-CN-450; (c) continuous GCD curves of theHAT-CN-550 electrodes with a current density of 200 mA  $g^{-1}$ ; (d) the Nyquist plots (the inset represents the details of the Nyquist plots) in 1 M NaCl solution.

Figure 7 (a) the conductivity variation with deionization time (the inset represents the SAC with different material) and (b) CDI Ragone plots of HAT-CN-450/550/700/800 and AC electrodes in a 500 mg  $L^{-1}$  NaCl solution at a cell voltage of 1.2 V with a flow rate of 22 mL min<sup>-1</sup>; CDI

performance of the HAT-CN-550 electrode: (c) the variation of conductivity along with the desalination time (the inset shows the SAC at different applied voltages) and (d) CDI Ragone plots in a 500 mg  $L^{-1}$  NaCl solution at different cell voltages with a flow rate of 22 mL min<sup>-1</sup>; (e) the SAC curves and (f) CDI Ragone plots in different concentrations of NaCl solution at a voltage of 1.2 V with a flow rate of 22 mL min<sup>-1</sup>;

Figure 8 Regeneration performance of the HAT-CN-550 electrode in a 500 mg  $L^{-1}$  NaCl solution at 1.2 V with a flow rate of 22 mL min<sup>-1</sup>.





## Figure 2



Figure 4



Figure 6





