Rational design and fabrication of graphene/carbon nanotubes hybrid sponge for high-performance capacitive deionization†

Xingtao Xu,a Yong Liu,a Ting Lu,a Zhuo Sun,a Daniel H. C. Chua b and Likun Pan*a

Capacitive deionization (CDI) is an emerging technology offering a green and efficient route to obtain clean water. Up to now, the key of CDI technology has been focused on the exploration of electrode materials with a rationally designed structure and excellent performance, because the electrosorption performance of the carbon-based electrodes reported to date cannot meet the demands of practical applications of CDI. Herein, novel graphene/carbon nanotubes (CNTs) hybrid sponge (GNS) structures were designed and fabricated via directly freeze-drying graphene oxide/CNTs mixed solution followed by annealing in nitrogen atmosphere. The morphology, structure and electrochemical performance of GNS were characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, nitrogen adsorption–desorption, cyclic voltammetry and electrochemical impedance spectroscopy. The results show that GNS with 20 wt% CNTs has a maximum specific surface area of 498.2 m$^2$ g$^{-1}$ and a highest specific capacitance of 203.48 F g$^{-1}$ among all the samples. When used as CDI electrode, it exhibits an ultrahigh electrosorption capacity of 18.7 mg g$^{-1}$, and, to our knowledge, this value is superior to those of other carbon electrodes reported recently. GNS should be a promising electrode material for high-performance CDI.

1. Introduction

As water shortage has become a serious global problem, it is generally recognized that desalination of saline water is the most effective solution to increase the supply of freshwater.1 Unlike other desalination techniques, such as distillation, electrodeionisation and reverse osmosis, capacitive deionization (CDI) is conducted at ambient conditions and low voltage (<2 V), and does not require high-pressure pumps, membranes, distillation columns, or thermal heaters.2–8 The principle of CDI is based on imposing an external electrostatic field between electrodes in order to force charged ions to move toward oppositely charged electrodes. The charged ions can be attracted within the electrical double layer (EDL) formed at the interface between a solution and electrode. Therefore, the ion adsorption capacity of an electrode is directly related to the physical properties and internal structure of the electrode materials, such as electrical conductivity, surface area and pore size.9–11

Generally, CDI electrodes are typically made of porous carbon materials with high specific surface area and superior conductivity, including activated carbon (AC),12–14 carbon nanotubes (CNTs),15–18 carbon aerogels (CA),19,20 carbon nanofibers (CNFs),21–24 mesoporous carbon (MC),25,26 carbon nanorods (CNRs)27 and carbon spheres (CS).28,29 Besides these carbon species, graphene with a flexible planar structure (ultrathin layer), high specific surface area (theoretically ~2600 m$^2$ g$^{-1}$) and superior electrical conductivity (~7.2 × 10$^5$ S cm$^{-1}$) has attracted enormous attention for CDI applications.30–36 Up to now, a variety of forms of graphene-based electrode materials have been reported. However, due to the strong π–π interactions between graphene sheets, they tend to restack during preparation processes, which often makes it difficult for ions to gain access to the inner layers of stacked graphene to form EDL, resulting in an unsatisfactory actual electrosorption capacity (0.45–1.85 mg g$^{-1}$).30,31,37

In order to solve this problem, one effective strategy is to combine graphene with some guest materials, such as pyridine,35 MC,35 AC38 and resol,39,40 to fabricate graphene-based composites. Through this way, the electrosorption capacity was enhanced obviously (0.83–3.23 mg g$^{-1}$) compared with graphene. Another strategy is to design a novel structure of graphene, such as three-dimensional (3D) graphene architecture,41 sponge-templated graphene42 and our recently reported graphene sponge (GS).43 These designed graphene architectures usually possess interconnected macro pores that are favorable
for buffering ions to shorten the diffusion distance from an external electrolyte to the interior surface. However, in these graphene electrode solutions, graphene sheets are usually stacked to graphite platelets between macropores,\textsuperscript{44} hampering the electrolyte ions from accessing the inner layers. Therefore, further efforts are still needed to seek an appropriate route to alleviate the inevitable aggregation of graphene sheets in these structures.

CNTs, due to their unique pore structure, superior electrical properties, and good mechanical and thermal stability, have been widely utilized in combination with graphene for supercapacitor and CDI applications.\textsuperscript{45–47} Li et al. proposed a reduced graphene/CNTs composite as a CDI electrode, and the inserted CNTs were found to inhibit the aggregation of graphene sheets and increase the conductivity of the electrode.\textsuperscript{48} Despite these progresses, the reported electrosorption capacities of graphene/CNTs composites were still low (0.88–1.41 mg g\textsuperscript{-1}).\textsuperscript{45–47} Therefore, the exploration of novel 3D graphene/CNTs structures for CDI application is necessary due to their expected superior performance. In this work, novel graphene/CNTs hybrid sponge (GNS) structures were fabricated by employing CNTs to intercalate graphene sheets in a GS via directly freeze-drying graphene oxide (GO)/CNTs mixed solution followed by annealing in nitrogen atmosphere. When used as a CDI electrode, GNS exhibits an ultrahigh electrosorption capacity of 18.7 mg g\textsuperscript{-1} in NaCl solution with an initial concentration of $\sim$500 mg L\textsuperscript{-1}.

2. Experimental section

2.1 Preparation of samples

GO was obtained from natural graphite flakes according to the method reported in our previous work.\textsuperscript{38} CNTs purchased from Nanotech Port Co. Ltd (Shenzhen, China) were purified according to the chemical method described in the literature.\textsuperscript{38} In a typical process, CNTs aqueous dispersion ($\sim$4.0 mg mL\textsuperscript{-1}) was added into a 20 mL vial containing GO aqueous dispersion ($\sim$4.0 mg mL\textsuperscript{-1}). In this step, the weight ratio of GO to CNTs was changed by adjusting the volumes of GO solution and CNTs solution. The mixed solution was stirred under magnetic stirring for 2 h, and then the vial was frozen by placing it in a freezer for 2 days. After the mixed solution was completely frozen, the vial was moved to a freeze-dryer and dried at a sublimating temperature of $-53 \degree$C and a pressure $<10$ Pa for 3 days to afford the GO/CNTs hybrid sponge (GONS). Finally, GNS was obtained by annealing GONS in a tubular furnace at 800 $\degree$C under nitrogen flow for 3 h. The as-prepared GNS samples with 10, 20, 30 and 40 wt% CNTs were named as GNS-1, GNS-2, GNS-3, and GNS-4, respectively. For comparison, GS was obtained by a similar procedure according to the method reported in our previous work.\textsuperscript{45}

2.2 Characterization

The surface morphology and structure of the samples were characterized by scanning electron microscopy (SEM, JEOL JSM-LV5610) and transmission electron microscopy (TEM, CM200). The pore size distribution and Brunauer–Emmett–Teller (BET) specific surface area were deduced from the nitrogen physical adsorption measurement data obtained using an ASAP 2010 Accelerated Surface Area and Porosimetry System (Micrometics, Norcross, GA), and the pore size distribution was derived from the adsorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) model. The bulk electric conductivities of the samples were measured using the four-probe method.\textsuperscript{49} X-ray photoelectron spectroscopy (XPS) measurement was performed using an imaging photoelectron spectrometer (Axis Ultra, Kratos Analytical Ltd) with a monochromatic Al K\textsubscript{α} X-ray source. Fourier transform infrared (FT-IR) spectroscopy data were acquired with a Nexus 670 spectrometer. X-ray diffraction (XRD) spectra were acquired using a Holland Panalytical PRO PW3040/60 with Cu K\textsubscript{α} radiation ($V = 30$ kV, $I = 25$ mA). Raman spectra were obtained with a Renishaw inVia microscope. A He–Ne laser (633 nm) was used as the light source for excitation. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out in 1 M NaCl solution by using an Autolab PGSTAT 302N electrochemical workstation in a three-electrode mode, including a standard calomel electrode as reference electrode and a platinum foil as counter electrode. The specific capacitance ($C$, F g\textsuperscript{-1}) can be obtained from CV curves using the following equation:

$$C = \bar{i}(v \times m)$$

where $\bar{i}$ is the average current (A), $v$ is the scan rate (V s\textsuperscript{-1}) and $m$ is the mass of electrodes (g).

2.3 Electrosorption experiments

The electrodes were prepared by mixing 80 wt% of samples, 10 wt% of acetylene black, and 10 wt% of polyvinyl alcohol slurry. The mixtures were pressed onto graphite papers and dried in a vacuum oven at 60 $\degree$C overnight.

The CDI performances were investigated by batch-mode electrosorption experiments with a continuously recycling system, as described in our previous work.\textsuperscript{38} In each experiment, an analytically pure NaCl solution with a volume of 50 mL was employed as the target solution and the flow rate was 27 mL min\textsuperscript{-1}. A direct voltage of 1.2 V was applied on the opposite electrodes. The initial concentration of NaCl solution was $\sim$500 mg L\textsuperscript{-1}, and the solution temperature was kept at 298 K. The relationship between conductivity and concentration was obtained according to a calibration table made prior to the experiment.\textsuperscript{50} The concentration variation was continuously monitored and measured at the outlet of the unit cell by using an ion conductivity meter.

In our experiment, the electrosorption capacity ($I$, mg g\textsuperscript{-1}) was defined as follows:

$$I = \frac{(C_b - C_f) \times V}{m}$$

where $C_b$ and $C_f$ are initial and final NaCl concentrations (mg L\textsuperscript{-1}), $V$ is the volume of NaCl solution (L) and $m$ is the total mass of the electrodes (g).
Charge efficiency ($A$) is a functional tool to gain insight into the double layer formed at the interface between the electrode and solution, as calculated according to the following equation:

$$A = \frac{\Gamma \times F}{\Sigma}$$  (3)

where $F$ is the Faraday constant (96,485 C mol$^{-1}$), $\Gamma$ is the electrosorption capacity (mol g$^{-1}$) and $\Sigma$ (charge, C g$^{-1}$) is obtained by integrating the corresponding current.

3. Results and discussion

Fig. 1 illustrates the method for the fabrication of GNS. As shown, GO solution was first mixed with CNTs to obtain a GO/CNTs mixed solution. After a freeze-drying process, a spongy GONS architecture was obtained, in which the interaction of GO was strong enough so that GO solution could be directly frozen to produce the sponge, and meanwhile CNTs were dispersed between graphene sheets to alleviate the aggregation of graphene sheets. Finally, GONS was reduced by annealing at 800 °C under nitrogen flow to obtain GNS.

Fig. 2 shows the morphology and structure of GNS-2. As shown in Fig. 2a, a spongy GNS with a volume of about 7.5 cm$^3$ has a weight of 19.2 mg, indicating that the as-prepared GNS has an ultralow density of about 2.6 mg cm$^{-3}$, which is comparable to that of the lightest silica aerogels (2–3 mg cm$^{-3}$). The plane view SEM image shows the 3D closely packed and interconnected porous morphology with hierarchical pore

![Fig. 1](image1.png)

Fig. 1 Schematic illustration of the procedure for the preparation of GNS.

![Fig. 2](image2.png)

Fig. 2 Photograph (a), SEM images (b and c) and TEM image (d) of GNS-2.

![Fig. 3](image3.png)

Fig. 3 XPS spectra (a), FT-IR spectra (b) and XRD patterns (c) of GNS.
sizes ranging from nanometers to micrometers (Fig. 2b). Enlarged SEM image and TEM image show that CNTs are dispersed uniformly between graphene sheets (Fig. 2c and d), which can alleviate the inevitable aggregation of graphene sheets, and increase the specific surface area of GNS. These features not only guarantee that the GNS electrode can be wetted quickly by the electrolyte but also release more accessible surface area for ion adsorption during the electrosorption process. The SEM and TEM images of GNS-1, GNS-3 and GNS-4 are shown in Fig. S1.† Clearly, all samples show a morphology with CNTs dispersed uniformly between graphene sheets. However, only small amount of CNTs is found in GNS-1, while in GNS-3 and GNS-4 excessive CNTs tend to aggregate with each other and cover the surface of graphene sheets. Therefore, either low or high CNTs content is not beneficial for forming 3D porous conductive networks.

Fig. 3a–c show XPS spectra, FT-IR spectra and XRD patterns of GNS, respectively. As shown in Fig. 3a, all GNS samples show only the presence of C1s and O1s peaks at about 283 and 533 eV, respectively, and the contents of O element are low (8.1–9.5 at%). In FT-IR spectra, all samples show weak C–O peak at 1110 cm⁻¹ and C=O peak at 1730 cm⁻¹ (Fig. 3b). Both XPS and FT-IR measurements show that during the annealing process, most of the oxygen-containing groups are removed, and therefore the functional groups on the surface of these samples should contribute little to their performance. Furthermore, Fig. 3c displays the XRD patterns of GNS. It can be observed that a diffraction peak appears at 26°, corresponding the (002) plane of graphene and CNTs, and all samples exhibit similar crystallinity.

The structures of GS and GNS were further investigated by Raman spectra, as shown in Fig. 4. The D-band of graphitic materials is related to disorder and arises due to the breathing mode of k-point phonons of A₁g symmetry, while the G-band is associated with the conjugated structure of sp² carbon domains. The intensity ratio (I_D/I_G) of D-band to G-band is often used as a measure of disorder in graphitic materials. It can be seen that as the CNTs content increases from 10 wt% to 40 wt% in GNS, the I_D/I_G decreases gradually from 0.98 to 0.83. The lower values for GNS than for GS (1.04) show successive increase of graphitization degree with the increase in CNTs content.

Table 1 The specific surface areas, pore volumes, mean pore diameters and bulk electric conductivities of GS and GNS

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_BET (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Mean pore diameter (nm)</th>
<th>Bulk electric conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS</td>
<td>342.9</td>
<td>1.01</td>
<td>11.7</td>
<td>0.91</td>
</tr>
<tr>
<td>GNS-1</td>
<td>419.5</td>
<td>1.29</td>
<td>12.1</td>
<td>1.02</td>
</tr>
<tr>
<td>GNS-2</td>
<td>498.2</td>
<td>1.51</td>
<td>12.4</td>
<td>1.11</td>
</tr>
<tr>
<td>GNS-3</td>
<td>427.0</td>
<td>1.35</td>
<td>12.7</td>
<td>1.19</td>
</tr>
<tr>
<td>GNS-4</td>
<td>368.2</td>
<td>1.21</td>
<td>13.1</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Fig. 4 Raman spectra of GS and GNS.

Fig. 5 (a) Nitrogen sorption isotherms at 77 K and (b) BJH pore size distribution plots of GS and GNS.
Previous work has reported that a high graphitization degree of carbon material always indicates a superior electric conductivity. Therefore, the Raman results demonstrate that GNS should have a superior electric conductivity, which is beneficial for charge transfer during the electrosorption process. Furthermore, the bulk electric conductivities of GS and GNS samples were determined via the four-probe method, as shown in Table 1. It can be seen that the electric conductivities of GNS samples are much higher than that of GS, and the increase in CNTs content facilitates the electron conduction within the GNS, which is consistent with our previous work.

It is well known that the CDI performance is highly sensitive to the specific surface area and pore size distribution of a carbon electrode. A previous report has shown that a large specific surface area together with a suitable pore size distribution containing a large proportion of accessible mesopores is ideal for ion adsorption. The porosity of the as-prepared GS and GNS was studied by nitrogen adsorption–desorption isotherms. As shown in Fig. 5a, all of the isotherms show a typical type IV hysteresis loop as defined by IUPAC, which is characteristic of mesoporous materials. The hysteresis loop which appears at lower relative pressure (0.4–0.8) indicates the presence of mesopores and that at higher relative pressure (0.8–1.0) is attributed to macropores. It is proposed that adsorption occurs on the surface of the graphene sheets and CNTs, which are overlaid with each other and constitute lots of pores contributing to the hysteresis loops. The BJH pore size distribution in Fig. 5b indicates the porosity characteristics of GS and GNS. It can be seen that both GS and GNS show a hierarchical porous structure, and moreover, the introduction of CNTs can increase the percentage of mesopores, which is beneficial to electrosorption. The specific surface areas, pore volumes and mean pore diameters of all samples are shown in Table 1. It can be seen that GNS-2 exhibits the largest surface area (498.2 m² g⁻¹) and pore volume (1.51 cm³ g⁻¹), much higher than those of GS (342.9 m² g⁻¹ and 1.01 cm³ g⁻¹). The reason could be that CNTs are sandwiched between the graphene layers to serve as “spacers” and, as a result, more graphene sheets are separated, which will in turn produce more mesopores and larger specific surface area. It should also be noted that the specific surface area decreases with further increase in CNTs content, which could be caused by the aggregate of CNTs covering the surface of graphene sheets to decrease the exposed surface area.

Fig. 6 (a) CV curves of GS and GNS measured at a scan rate of 10 mV s⁻¹ in 1 M NaCl aqueous solution; (b) specific capacitances of GS and GNS electrodes.

Fig. 7 (a) Nyquist plots of GS and GNS electrodes in 1 M NaCl aqueous solution. (b) The expanded high-frequency region in (a).
Fig. 8 Concentration and current transients for GNS-2 electrode over 30 minutes in NaCl solution with an initial concentration of ~500 mg L\(^{-1}\) at an applied voltage of 1.2 V.

Fig. 6a shows the CV curves of GS and GNS electrodes at a scan rate of 10 mV s\(^{-1}\) in 1 M NaCl solution with a potential range from −0.2 to 0.8 V. The influence of CNTs content on the electrosorption performance of GNS electrodes was systematically investigated. As clearly seen, no obvious Faradaic reaction is observed from the CV curves, which suggests that the CV behavior results from EDL due to the Coulombic interactions, rather than from electrochemical reduction/oxidation reactions. During the annealing process, most of the oxygen-containing groups are removed, so that no obvious Faradaic activity is detected during the CV measurements. It is noted that the specific capacitances of all GNS electrodes are much higher than that of the GS electrode (Fig. 6b). With an increase in CNTs content, the specific capacitance increases and reaches the highest value for GNS-2. This result is mainly due to the following: the CNTs incorporated into the graphene construct a “plane-to-line” (graphene-to-CNTs) conductive network, which not only improves the accessible surface area, but also acts as conductive channels to decrease the inner resistance of the electrode. However, the specific capacitance decreases with a further increase in CNTs content (GNS-3 and GNS-4), which could be ascribed to the relatively low specific surface area of CNTs. Furthermore, excessive CNTs will cover most of the graphene surface, which makes the transport of the electrolyte ions into the porous structure difficult, resulting in a low specific capacitance.

EIS analysis has been recognized as one of the principal methods to examine the electrical properties of carbon electrodes. The Nyquist profiles of GS and GNS electrodes in 1 M NaCl aqueous solution are presented in Fig. 7. It can be obviously seen that the two plots display similar shapes, consisting of a linear trend at the low-frequency region and a small quasi-semicircle at the high-frequency one. The small quasi-semicircle at the high-frequency region is derived from the double layer capacitance (\(C_{dl}\)) in parallel with the charge transfer resistance (\(R_{ct}\)). The \(R_{ct}\) values for GNS-1, GNS-2, GNS-3 and GNS-4 are around 0.32, 0.20, 0.16 and 0.14 Ω, respectively, which are much lower than that of GS (0.35 Ω), indicating that GNS should have lower charge-transfer resistances.

In an actual case, if the total dissolved solids (TDS, measured in mg L\(^{-1}\)) is higher than 500 mg L\(^{-1}\), water is not suitable for drinking. Therefore, the electrosorption performance of GNS-2 was investigated in NaCl solution with an initial concentration of ~500 mg L\(^{-1}\) at an applied voltage of 1.2 V. The current variations were recorded simultaneously and independently for each experiment (Fig. 8). It can be seen that once the electric field is applied, the concentration decreases sharply. Then, the variation becomes gradually lower until equilibrium is reached. The electrosorption capacity of GNS-2 is 18.7 mg g\(^{-1}\), which is much higher than those of GS (14.9 mg g\(^{-1}\))\(^3\) and graphene/CNTs composites (0.88–1.41 mg g\(^{-1}\))\(^4\). This could be ascribed to the following: (i) the 3D porous structure of GNS-2 with a higher specific surface area provides a short ion diffusion pathway and more available spaces to accommodate ions during the electrosorption; (ii) the CNTs incorporated into the graphene construct a “plane-to-line” (graphene-to-CNTs)

### Table 2 Comparison of electrosorption capacities of various carbon electrodes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Applied voltage (V)</th>
<th>Initial NaCl concentration (mg L(^{-1}))</th>
<th>Electrosorption capacity (mg g(^{-1}))</th>
<th>Specific surface area (m(^2) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC(^{14})</td>
<td>1.2</td>
<td>~500</td>
<td>9.72</td>
<td>1153</td>
</tr>
<tr>
<td>CA(^{20})</td>
<td>1.25</td>
<td>~2900</td>
<td>9.6</td>
<td>~500</td>
</tr>
<tr>
<td>CA(^{36})</td>
<td>1.3</td>
<td>~2000</td>
<td>7.1</td>
<td>113</td>
</tr>
<tr>
<td>CNTs(^{17})</td>
<td>1.2</td>
<td>~3000</td>
<td>1.7</td>
<td>129.4</td>
</tr>
<tr>
<td>CNTs(^{18})</td>
<td>1.2</td>
<td>~3500</td>
<td>9.35</td>
<td>153</td>
</tr>
<tr>
<td>MC(^{26})</td>
<td>1.2</td>
<td>~4600</td>
<td>14.5</td>
<td>488</td>
</tr>
<tr>
<td>GS(^{18})</td>
<td>1.2</td>
<td>~500</td>
<td>5.81</td>
<td>1321</td>
</tr>
<tr>
<td>N-doped CS(^{29})</td>
<td>1.2</td>
<td>~500</td>
<td>14.91</td>
<td>1640</td>
</tr>
<tr>
<td>CNRs(^{37})</td>
<td>1.2</td>
<td>~500</td>
<td>15.12</td>
<td>864.1</td>
</tr>
<tr>
<td>CNTs/graphene(^{45})</td>
<td>1.2</td>
<td>~500</td>
<td>1.4</td>
<td>438.6</td>
</tr>
<tr>
<td>AC/graphene(^{18})</td>
<td>1.2</td>
<td>~500</td>
<td>2.94</td>
<td>779</td>
</tr>
<tr>
<td>Graphene aerogel(^{11})</td>
<td>1.2</td>
<td>~500</td>
<td>9.9</td>
<td>—</td>
</tr>
<tr>
<td>GS(^{33})</td>
<td>1.2</td>
<td>~500</td>
<td>14.9</td>
<td>356.0</td>
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<td>GNS-2 (this work)</td>
<td>1.2</td>
<td>~500</td>
<td>18.7</td>
<td>498.2</td>
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</table>
conducting network, which acts as conductive channels to decrease the inner resistance of the electrode. Furthermore, the charge efficiency of GNS-2 is calculated to be 0.55 according to eqn (3). It should be noticed that the charge efficiency of GNS-2 electrode is less than 1, which is ascribed to the following reasons: (i) during the electrosorption process, the co-ions are simultaneously expelled from the EDL accommodating the adsorbed ions, which has a negative effect on the charge efficiency; (ii) the binder used in the electrode fabrication can decrease the effective surface area and conductivity of the electrode. Fortunately, an effective method has been proposed to solve this problem by introducing charge barrier membrane into CDI.

The electrosorption capacity is an important criterion for the actual application of CDI electrode materials. Therefore, the electrosorption capacity of GNS-2 is also compared to those of other carbon electrode materials reported in the literature (Table 2). Obviously, though GNS-2 has a relatively low specific surface area, it exhibits the highest electrosorption capacity among these carbon electrodes in similar experimental conditions.

As is known, good regeneration is essential for electrode materials. Therefore, electrosorption–desorption behavior of GNS-2 was also investigated by repeating several charging (1.2 V) and discharging processes (0 V) in ~500 mg L\(^{-1}\) NaCl solution, as shown in Fig. 9. It can be seen that GNS-2 electrode can be completely regenerated and reused for over 30 cycles without any decline in performance. Considering its ultrahigh electrosorption capacity and excellent regeneration ability, GNS-2 should be a promising electrode material for high-performance CDI.

4. Conclusions

In this work, GNS structures were designed and fabricated via directly freeze-drying GO/CNTs mixed solution followed by annealing in nitrogen atmosphere. The results show that (i) GNS samples exhibit a 3D closely packed and interconnected porous morphology with CNTs dispersed uniformly between graphene sheets; (ii) GNS-2 shows a maximum specific surface area of 498.2 m\(^2\) g\(^{-1}\) and a highest specific capacitance of 203.48 F g\(^{-1}\) among all the samples; (iii) an ultrahigh electrosorption capacity of 18.7 mg g\(^{-1}\) is achieved for GNS-2 when the initial NaCl concentration is ~500 mg L\(^{-1}\), which is the highest value among carbon electrodes in similar experimental conditions reported in the literature; (iv) the excellent electrosorption performance of GNS-2 is ascribed to its novel 3D structure, large accessible surface area and low charge transfer resistance; (v) GNS-2 should be a promising candidate as electrode material for CDI.

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Notes and references
