Nanoarchitectured reduced graphene oxide composite C2N materials as flow electrodes to optimize desalination performance†

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Flow electrode capacitive deionization (FCDI) utilizes flowable electrodes to obtain a continuous and extensible desalination approach, eliminating the discharging step. However, the poor conductivity of flow electrode slurry and high clogging risk during the desalting process can limit desalination performance. Thus, we prepare the C2N@rGO material as a flow electrode to solve the channel blocking problem and improve the salt ion removal performance, maximizing the amount of active particles that can be added to the deionization process by forming a conductive network. The as-synthesized material possesses a large specific surface area, rich micropores, high N-doping, and tunable graphitization structure, which can further enhance the desalination properties of the as-prepared electrode. The results indicate that C2-N@rGO-4% has an optimal porous structure (812.3 m² g⁻¹) and chemical composition (29.5%, N-doping), and the highest specific capacitance (236.6 F g⁻¹). The FCDI results reveal that C2N@rGO-4% has a high salt ion adsorption capacity (180.72 mg g⁻¹), salt ion adsorption rate (0.3043 mg min⁻¹ cm⁻²), salt ion removal efficiency (49.93%), and current efficiency (65.22%) under a 1.81 g L⁻¹ NaCl solution at 1.0 V. Moreover, the results also indicate that the FCDI performance partly relies on the synergistic effect between the porous structure and chemical composition. Therefore, as an electrode material, C2N@rGO has strong potential for application in FCDI systems.

1. Introduction

The problem of water resource shortage and insecurity has become a serious and urgent problem which must be solved.¹ Unusable seawater and non-renewable sewage exacerbate these threats.² The deionization of seawater and sewage is a promising solution to the water shortage problem. One of the most effective technologies for desalting rich-salt water and recycled sewage is capacitive deionization (CDI).³,⁴ However, difficulties in recycling electrode materials limit the ion adsorption capacity and energy efficiency of CDI because the available active material is fixed and requires energy consumption during the electrical discharge process, limiting

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Environmental significance

Our manuscript entitled “Nanoarchitectured Reduced graphene oxide composite C2N materials as flow-Electrodes to optimize desalination performance”, which prepare a new flow-electrode material with a simple way by combining C2N and rGO. rGO was introduced as a conducting agent and basement to form electrically bridge connecting the adjacent C2N particles, improving a removing salt ion property without showing flowing property problem and improving C2N dispersion in flow-electrode slurry. It is greatly improved the salt ion removal performance. Our work can provide a new idea for the practical application of FCDI technology in desalination and provide a guidance for low energy consumption and low-cost desalination technology. Meanwhile, the nano-materials is based on carbon showing an environmentally friendly.
the practical application of CDI in deionization.5 Based on the traditional CDI, flow electrode CDI (FCDI) can improve these problems by using flowable electrodes that can simply realize the replaced electrode.6–8 The FCDI desalination mechanism is a representative of electrodialytical process (Scheme 2). Its utilized electrode slurry flowing through a serpentine channel carved on the current collector. An applied voltage can drive the salt ions present in aqueous solution migrating through ion exchange membrane and entering the flow-electrode. The salt ions will be finally adsorbed on the suspended flow electrode or dissolved in the aqueous phase. According to previous reports, FCDI can continuously carry out desalination in an NaCl solution, reaching \( \sim 35 \text{ g L}^{-1} \) without the need for any discharging processes. Meanwhile, flowable electrodes can ensure the unlimited supply of active materials to obtain a higher salt removal capacity from the saline feed water.9 However, the FCDI method also has some limitations, including poor flow electrode conductivity, which is caused by the suspended mud not being able to form a continuous electrical network.1,10

To maintain the stability of the FCDI operation, the electrode materials loading must be maintained below 10–15 wt%.10 Typically, as the active materials loading in the electrode solution increases, FCDI can obtain a higher electrode conductivity and salt ion removal capacity. The viscosity of the electrode solution is also enhanced, resulting in clogging in the flow channels and electrode outlet.11,13 To overcome these issues, the addition of a surface-modified material and dispersants can enhance the amount of active materials used, up to 35 wt%; the prepared material processes are complex and time consuming, and the coated polymer reduces the pore contents within the materials and further decreases the ion storage space and transfer speed.11 Additionally, the added dispersants increase the material hydration radii and obstruct the contact between the ion in the solution and active material particles, further reducing the deionization performance.12,13

Recently, the novel two-dimensional (2D) material C\(_2\)N network was synthesized by Mahmood,14 and used in a CDI electrode for a high electroadsorption capacity (24.66 mg g\(^{-1}\)), because of the rich nitrogen content, large electronic band gap (1.96 eV), regular hexagon, and microporous structure.1 The electrode materials loading must be maintained below 10 wt%.10 However, the non-ideal performance of dispersion in water and weak effect of interconnectivity with electrode particles limited the application as a flow electrode instead of a solid-electrode for the FCDI process.10 In addition, the reduced-graphene oxide (rGO) has a unique geometry, fast electron transportation, and high ion-storing capacity owing to an excellent electron mobility (5106 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) and theoretical large surface area (2630 m\(^2\) g\(^{-1}\)).17–19 However, the available surface area of typically prepared rGO (\(\sim 1000 \text{ m}^2 \text{ g}^{-1}\)) is far below the theoretical surface area because of restacking and superposition, which limits the potential applications of rGO in CDI.

Therefore, we prepared a new flow electrode material in a simple manner by combining C\(_2\)N and rGO, improving the salt ion removal property without exhibiting the flowing property problem. rGO was introduced as a conducting agent and basement to form an electrical bridge connecting adjacent C\(_2\)N particles and to improve C\(_2\)N dispersion in flow electrode slurry. In a previous study, C\(_2\)N particles exhibited an excellent desalination performance in the traditional CDI process, while their deionization performance was enormously increased by the formation of a conductive and ion-transport network because of the rGO. The independent C\(_2\)N particles limited the formation of electrical double layers (EDLs) by low connectivity; that is, vast C\(_2\)N particles remained in the neutral charge form, causing in inadequate utilization of active substances and poor deionization performance.

In this work, C\(_2\)N@rGO has been synthesized by a simple reaction, as shown in Scheme 1, in which a small amount of rGO can easily solve the channel blocking problem and greatly improve the salt ion removal performance, maximizing the amount of C\(_2\)N particles that can be added to the deionization process by forming a conductive network. In addition, the electrochemical behavior of the C\(_2\)N@rGO electrode used in the FCDI system was investigated using electrochemical impedance spectroscopy (EIS) measurements and a cyclic voltammetry (CV) test. The FCDI performance was also investigated in a saline concentration of 1.8 g L\(^{-1}\) at an applied potential of 1.0 V, demonstrating a salt removal rate of 0.3042 mg min\(^{-1}\) cm\(^{-2}\) and a salt ion removal capacity of 180.7 mg g\(^{-1}\). The AC electrode was used as a comparison. As expected, the performances were all higher than those of the AC electrodes. So far, there have been no studies on using C\(_2\)N@rGO material as a flow electrode in the FCDI process.

2. Experimental

2.1. Fabrication

Hexaketocyclohexane octahydrate, diaminomaleonitrile, and activated carbon (BET ~1000 m\(^2\) g\(^{-1}\)) were obtained from Aladdin Industrial Corporation (Shanghai, China). Natural graphite powder (99.95%), acetic acid (99.5%), nitric acid (65%), and analytical-grade acetonitrile were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cation/anion exchange membranes (CEM/AEM, LE-HoCM Grion 0011/1201) were purchased from Hangzhou Grion Environment Technology Co., Ltd., (Hangzhou, China). K\(_2\)MnO\(_4\), H\(_2\)SO\(_4\), and H\(_2\)O\(_2\) (30%) were acquired from the
Tianjin Damao Chemical Reagent Factory (Tianjin, China). All the reagents were used without further purification and ultrapure water was used for the experiments.

C2N was synthesized using a method described in our previous work.1 Hexaketocyclohexane octahydrate (4 g) and diaminomaleonitrile (11 g) were refluxed in AcOH (150 mL) for 2 h. Then, the solid was suspended in 30% HNO3 (60 mL) at 100 °C for 3 h. The suspension was poured into ice water (200 mL) and cooled overnight. The solid was refluxed in MeCN (500 mL) for 2 h. The product was then carbonized in a tubular furnace at 550 °C.

The synthesis of C2N@rGO was carried out according to the one-pot process. GO was prepared based on the method in our previous work.20 The C2N (1 g) was mixed in an HCl solution (60%, 200 mL) by sonication for 0.5 h, then it was continuously stirred for 4 h to protonize its surface. Finally, the functionalized C2N was washed several times with deionized water and alcohol. The C2N (1 g) and GO was added to the deionized water (100 mL) and sonicated for 0.5 h to acquire a uniform suspension. Afterwards, the NaHSO3 (54 mmol) was added to the suspension as a reducing agent, which was stirred at 98 °C for 3 h.21 The as-prepared materials were labeled as C2N@rGO-X, and the X indicates the weight ratios of rGO in the C2N@rGO-X materials, which was set to 2 wt%, 4 wt%, 8 wt%, and 12 wt%.

2.2. Characterization
A scanning electron microscope (SEM, JEOL JEM-700F, JP) and transmission electron microscope (TEM, JEOL, JEM-200CX, JP) was used to characterize the microstructures. Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer Spectrum GX, US) was analyzed for the range of 500–4000 cm–1. Raman spectra (HORIBA, LabRam HR Evolution, FR) were used to analyze the in-plane vibrations of the sp2 carbon and disorder-induced mode excited at 532 nm. X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo Fisher Scientific, UK) was carried out on a Kalpa system with Al-Kα (1486.6 eV) radiation. C/H/N elemental analysis (EA) was used a Vario Micro device by combustion analysis. Surface wettability (DingSheng, JY-82 B, CN) was used to investigate the hydrophilicity of the sample surface. ASAP 2460 (Micromeritics, USA) was used to obtain the nitrogen adsorption/desorption isotherms. The Brunauer–Emmett–Teller (BET) and nonlocal density functional theory (NLDFT) models were used to calculate the specific surface areas (SSAs), pore volumes, and pore size distributions.

2.3. Electrochemical characterization
An electrochemical workstation (CHI 660E, CH Instruments, China) was used to characterize the electrochemical performance of the samples. All tests were analyzed using a three-electrode system, consisting of a working electrode, reference electrode (Ag/AgCl, saturated 1 M KCl), and counter electrodes (1 × 1 cm2 Pt slice) in a 1 M NaCl solution. The working electrode was synthesized by active components, CB and PVA (at a ratio of 8:1:1), and coated onto a titanium mesh (1 × 3 cm).

The cyclic voltammetry (CV) measurements were determined by the potential and ranged from 0 V to 1.0 V with a series of scan rates (ν, 1–50 mV s–1). The EIS curves were performed at a certain open circuit voltage, scan frequency (10–2–105 Hz), and oscillation amplitude (5 mV). The specific capacitance (Ce) was computed by eqn (1):

\[ C_s = \frac{\int \Delta V}{2m\Delta V}, \]

where \( m \) is the quality of the active substances in the electrode, \( v \) (V s–1) is the voltage scan rate, \( I \) (A) is the response current, and \( \Delta V \) (V) is the potential difference.

2.4. FCDI experiments

2.4.1. Flow electrode slurry preparation. The flow electrode slurry was synthesized by mixing the as-prepared materials and carbon black (CB) in a deionized water solution where the mass ratio of the as-prepared samples to the CB was 4:1 wt%. Then, the mixture was ultrasonically crushed for 30 min and stirred for 1 h for complete dispersion. The commercial AC powder was used in the control group.

2.4.2. FCDI configuration. In Scheme 2(a), an FCDI device is assembled by two acrylic plate ends, a spacer chamber made of a silicone gasket (thickness of ~1 mm, 90 × 90 mm), two current collector plates, and anion-/cation exchange membranes (CEM/AEM, ~0.5 mm). Therein, the current collector plates consist of the titanium plates that have curved serpentine flow channels (3 mm width, 3 mm depth, and 60 mm length), and the end of the column following a semicircle (inner diameter of 3 mm and outer diameter of 9 mm). There are 11 columns connected together to form an effective contact area of 19.80 cm2.

2.4.3. FCDI operation and performance calculations. In Scheme 2(b), the FCDI test was operated in simulated wastewater (200 mL NaCl solution) with a batch mode that is continuously cycled by a peristaltic pump at 6 rpm. The conductivity of the feed solution was continuously recorded by an online conductivity meter (S470 Seven Excellence, METTLER TOLEDO, Zurich, Switzerland). The curve of relationship between conductivity and ion concentration is exhibited in Fig. S1.† The flow electrode slurries (25 mL, 2.4 wt% each) were continuously cycled between the beaker and FCDI device by a dual-head peristaltic pump (Longer pump, Baoding, China) at 6 rpm in an isolated closed-cycle. During FCDI operation, the electrosorption process was tested at a constant voltage from 0.6 V to 1.2 V by a direct current (DC) power supply (MP3094, Powertech, China), while the electrode regeneration process was carried out by mixing two electrode slurries. Unless otherwise stated, the applied voltage was set to 1.0 V during the electric adsorption process.

The characteristic parameters of salt ion adsorption capacity (SAC, mg g–1), salt ion removal efficiency (SRE, %), salt ion adsorption rate (SAR, mg min–1 cm–2), and current
efficiency (CE, %) were used to evaluate the FCDI performance and were calculated based on eqn (2)-(5):

\[
\text{SAC (mg g}^{-1}\text{)} = \frac{(C_0 - C_e) \times V}{m},
\]

(2)

where \(C_0\) and \(C_e\) (mg L\(^{-1}\)) are the initial and final ion concentrations of feed solution, respectively, \(V\) (L) is the volume of the feed solution, \(m\) (g) is the mass of the dry flow electrode.

\[
\text{SRE (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100\%,
\]

(3)

where \(t\) (min) is the charging time during the removal process, and \(S\) (19.80 cm\(^2\)) is the effective contact area in the flow electrode plate.

\[
\text{SAR (mg min}^{-1}\text{cm}^{-2}\text{)} = \frac{(C_0 - C_e) \times V}{t \times S}.
\]

(4)

\[
\text{CE (\%)} = \frac{F \times V \times (C_0 - C_e)}{M \times I \times dt},
\]

(5)

where \(F\) (96 485 C mol\(^{-1}\)) is the Faraday constant, \(I\) (A) is the current, and \(M\) (58.5 g mol\(^{-1}\)) is the molar mass.

3. Results and discussion

3.1. Materials characterization

The SEM images of C\(_2\)N and the TEM of the C\(_2\)N and GO samples are shown in Fig. S2† and 1(e and f), respectively. The GO samples are the crumpled thin sheets with high transparency, and the sheet C\(_2\)N material with a regular hexagon was fabricated using the reported method.\(^1,22\) The TEM images of the C\(_2\)N@rGO material are shown in Fig. 1. The C\(_2\)N was successfully immobilized on the rGO surfaces without using any cross-linked molecules. In addition, the introduction of rGO can improve the dispersion performance of C\(_2\)N (Fig. S3†), and the rGO can enhance the interactions between C\(_2\)N sheets. As the mass ratio of rGO is enhanced, the amount of C\(_2\)N accumulating in the rGO is reduced; the even dispersion is further confirmed by the TEM (Fig. 1(a-d)) images. The complex 2D structures can increase the conductivity performance of materials and ion-accessible space, which can significantly enhance the charge transfer speed and electrosorption capacitance. However, the N content decreases with an increase in rGO, that is, the capacitor deionization enhancing effects by doped-heteroatomic may be reduced.

Fig. 2(a) and S4† show the FT-IR spectra of the C\(_2\)N, GO, and C\(_2\)N@rGO-X samples, further demonstrating the successful assembly of C\(_2\)N on the rGO surface. In Fig. 2(a), for the pristine C\(_2\)N samples, the bands ranged from \(~\)1140 to \(~\)1610 cm\(^{-1}\) fit stretching vibrations of aromatic CN bonds. As well, the prominent peaks at \(~\)1340 cm\(^{-1}\) and \(~\)1610 cm\(^{-1}\) were indexed to the stretching vibrations of the C–N and C≡N bonds, and several bands attributed to the terminal cyano and pyrazine groups at approximately \(~\)2240 cm\(^{-1}\).\(^23\) The –NH band (amino group) had a wide peak at approximately \(~\)3440 cm\(^{-1}\). The peak at \(~\)3440 cm\(^{-1}\) clearly weakened with the increase in rGO content, suggesting that the –NH group and –OH group decreases. The hydroxyl groups of GO for the rGO@C\(_2\)N-X composites faded at approximately \(~\)3440 cm\(^{-1}\) the –OH in GO and –NH in C\(_2\)N underwent electrostatic attraction interactions and reduction reaction. The –NH groups translated sp\(^2\) N to produce a \(\pi\)-conjugated interface through a dehydration reaction.\(^24,25\) The peak of 2855 cm\(^{-1}\) indicate the (C–H)\(_\sigma\). In Fig. S4† the peak of 2922 cm\(^{-1}\) and 1398 cm\(^{-1}\) indicate the -CH and C=Cl group. It can be found that the –COOH group (1578 cm\(^{-1}\)) of GO are disappeared and instead by a graphene sheet (1557 cm\(^{-1}\)) of C\(_2\)N@rGO-4%, which is further verified the successful preparation of C\(_2\)N@rGO-X. The results were further confirmed by an XPS spectrum analysis.

![Fig. 1 TEM of (a) C\(_2\)N@rGO-2%, (b) C\(_2\)N@rGO-4%, (c) C\(_2\)N@rGO-8%, (d) C\(_2\)N@rGO-12%, (e) GO, and (f) C\(_2\)N electrodes.](image)

![Fig. 2 (a) FT-IR curves of C\(_2\)N@rGO-2/4/8/12%, C\(_2\)N and GO electrodes, (b) Raman spectrum of rGO@C\(_2\)N-2/4/8/12%, (c) Raman spectrum of C\(_2\)N, rGO and rGO@C\(_2\)N-4% and (d) N\(_2\) physisorption isotherms measurement (the inset represents pore size distribution) of rGO@C\(_2\)N-2/4/8/12.](image)
In Table 1, the surface elemental composition and functionality characteristics were characterized by an XPS spectrum analysis, which demonstrated that C, N, and O atoms existed in the samples. In the C1s signal as shown in Fig. 3(a), the peaks at 284 eV and 289 eV fit graphitic C=C carbons and oxidized carbon atoms; the peak of 284 eV for the C2N@rGO-X materials was higher than that for the pristine C2N, illustrating the successful combination of C2N with rGO.\textsuperscript{1,26} The C ratio visibly increased from 55.2% to 71.4% with the added rGO, which was also confirmed by an elemental analysis (EA, Vario MACRO cube, GEM). The graphitic C=C content also increased from 16.0% to 28.5%, improving the conductive ability of the electrode. In Fig. 3(b), the peak of 398–400 eV was ascribed to the cyano and pyrazine groups, ~401 eV and ~402 eV corresponded to quaternary nitrogen atoms and oxidized nitrogen groups, respectively, dividing the N 1s spectrum.\textsuperscript{1} With the increase in rGO proportion, the N element decreased significantly from 35.3% to 23.3%. However, the high N-heteroatom content of the as-prepared materials was mainly derived from the cyano and pyrazine groups; these groups had sufficient wettability and charge transfer ability, which improved deionization performance in a previous report.\textsuperscript{1,27} Therefore, the functional group types and N-heteroatom contents of the as-synthesized material work together to improve deionization performance.

The Raman spectrum was used to analyze the degree of graphitization and defects on the surfaces of the C2N@rGO-X, GO and C2N materials, as shown in Fig. 2(b) and (c). The peaks of ~1350 cm\textsuperscript{-1} and ~1595 cm\textsuperscript{-1} were indexed to disordered sp\textsuperscript{2} carbon in aromatic rings (D-) and crystallized graphitic sp\textsuperscript{2} carbon in rings/chains (G-), respectively. Although the standard explanation of the Raman spectroscopy applies to the primary carbon, and is not strictly suited to N-doping carbon materials owing to the vibrational asymmetry introduced by N-doping, some fascinating information about the composite materials is still available. The D/G value increases from 0.49 to 1.41 when the rGO proportion is increased, that is, the ongoing increases of a phase of pristine carbon content comes from rGO, as observed in Fig. S5.\textsuperscript{†} Thus, materials with higher electrical conductivity and graphitization were synthetized at a higher rGO proportion, the results as the same with XPS. With the enhanced proportion of rGO, the relative intensity of the D2-band shoulder (~2049 cm\textsuperscript{-1}) ascribed to the trans-polyacetylene-chain at the layered edge decreased.\textsuperscript{30,31} Additionally, The contact angle values of the as-prepared materials were nearly the same and small, showing a favorable surface hydrophilicity, which is beneficial for the electrosorption properties because of the high N content and abundant polar groups, as shown in Fig. S6.\textsuperscript{†}

In Fig. 2(d), an N\textsubscript{2} physisorption isotherms analysis was performed to characterize the porous structure of the C2N@rGO-X nanosheets, which shows typical type-I isotherms, suggesting unique microporous properties that are further confirmed by the pore size distribution. The BET analysis results show the high SSA range of 780–820 m\textsuperscript{2} g\textsuperscript{-1} (Fig. 2d and S7).\textsuperscript{†} The higher SSA and micropore contents can provide more active sites to adsorb ions and improve deionization performance.\textsuperscript{24} With an increase in the rGO content, N\textsubscript{2} physisorption isotherms gradually approach VI, and the pore diameter is mildly enlarged (Table 1). Although rGO has its unique structure as one atomic thin layer of carbon that possesses the huge SSA, the restacking of graphene flakes by Van Der Waal’s forces, the ion-accessible surface area of the graphene electrode is much lower than the theoretical value.\textsuperscript{33,34} Moreover, the pore sizes of rGO are not uniform, and their mesopore and micropore contents are similar.\textsuperscript{35,36} Thus, C2N@rGO-4\% possesses the largest microporous structure, which is a prerequisite for high deionization performance.

### 3.2. Electrochemical analysis

Electrochemical measurements were used to inquire into the electrochemical properties of the as-synthetized samples. In Fig. 4(a), the CV curve shape of the C2N@rGO-X electrodes series is similar to a leaf shape, approximately a rectangular shape, indicating that the effects depend on the EDL.

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**Table 1** Summary of characterization results of the C2N@rGO-X materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>C [at %] EA</th>
<th>C [at %] XPS</th>
<th>N [at %] EA</th>
<th>N [at %] XPS</th>
<th>O [at %] EA</th>
<th>O [at %] XPS</th>
<th>SSA/m\textsuperscript{2} g\textsuperscript{-1}</th>
<th>Contact angle/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2N@rGO-2%</td>
<td>68.2</td>
<td>60.9</td>
<td>30.2</td>
<td>27.0</td>
<td>—</td>
<td>9.5</td>
<td>783.5</td>
<td>36.7</td>
</tr>
<tr>
<td>C2N@rGO-4%</td>
<td>69.3</td>
<td>61.3</td>
<td>31.1</td>
<td>29.3</td>
<td>—</td>
<td>9.2</td>
<td>812.3</td>
<td>35.8</td>
</tr>
<tr>
<td>C2N@rGO-8%</td>
<td>70.7</td>
<td>61.9</td>
<td>29.1</td>
<td>24.8</td>
<td>—</td>
<td>14.1</td>
<td>808.9</td>
<td>40.1</td>
</tr>
<tr>
<td>C2N@rGO-12%</td>
<td>71.4</td>
<td>62.2</td>
<td>27.4</td>
<td>23.3</td>
<td>—</td>
<td>14.5</td>
<td>799.3</td>
<td>42.7</td>
</tr>
<tr>
<td>C2N</td>
<td>55.2</td>
<td>62.9</td>
<td>42.9</td>
<td>35.3</td>
<td>—</td>
<td>2.3</td>
<td>771.2</td>
<td>32.8</td>
</tr>
<tr>
<td>GO</td>
<td>95.8</td>
<td>67.3</td>
<td>3.3</td>
<td>2.3</td>
<td>—</td>
<td>30.5</td>
<td>840</td>
<td>51.0</td>
</tr>
</tbody>
</table>
behavior rather than the electrochemical reaction.\(^{32}\) Nevertheless, the phenomenon of slight deviations from the rectangle ascribe to the different functional group contents, SSAs, and applying potentials.\(^{37}\) In the inset of Fig. 4(a), the CV curves of C\(_2\)N exhibit a regular rectangle, but those of the electrodes at 1 M NaCl.

Nevertheless, as the rGO ratio continuously increases to 12%, the low nitrogenous hydrophilicity leads to high hydrophobic property because the more hydrophobic group of C\(_2\)N reacts with rGO materials. Therefore, the electrochemical properties of the electrode are restricted by their chemical composition. Notwithstanding, higher ratio of rGO of C\(_2\)N@rGO-X has large SSA, many pores that cannot be utilized to adsorb ions because of the high surface tension caused by its hydrophobicity, and large Van Der Waal’s forces that come from the rGO itself.\(^{33,35,38}\) The \(C_s\) of C\(_2\)N@rGO-12% decrease because of the negative effects brought on by chemical composition changes that may offset the positive effects gained by the high SSA (pore structure). According to the above results, the excellent electrochemical performance can be acquired by a balance of applicable pore structure and chemical composition, making C\(_2\)N@rGO-4% the best choice.

In Fig. 4(b), the CV curves of the C\(_2\)N@rGO-4% electrode were tested at various scan rates (1–50 mV s\(^{-1}\)). With the enhancement of scan rate, the slope at the negative potential of the CV curves clearly increases, and the CV curve gradually exhibits an irregular rectangle. This suggests that the ions have enough time to move from the electrolyte to the electrode pores at a lower scan rate, which ensures that more SSA is available and pores are accessible, resulting in a better capacitive performance. Additionally, the \(C_s\) values of the C\(_2\)N@rGO-4% electrode at different scan rates is shown in Fig. 4(c). As scan rate increases from 1 mV s\(^{-1}\) to 50 mV s\(^{-1}\), the \(C_s\) values show a decrease from 236.6 F g\(^{-1}\) to 68.4 F g\(^{-1}\). Meanwhile, the C\(_2\)N@rGO-4% electrode shows excellent cycle stability during the 2000th (Fig. 5).

To further investigate, the Nyquist plots analyze the electrical resistance behavior (Fig. 4(d)). The high-frequency region appears as a small semicircle ascribed to the charge SSA to acquire more ion adsorption sites, and a high N-content can help obtain a certain pseudo-capacitance and sufficient hydrophilicity, where the hydrophilicity can ensure that the ions easily move from the electrolyte to electrode. Therefore, improved electrochemical properties of the C\(_2\)N@rGO-4% electrode can be obtained by the positive impacts from the micropore structure and chemical composition coefficients.

The capacitance relation with cycle number (the inset represents CV curves after 2000th cycle).
transfer resistance \( (R_{ct}) \), produced by the interface resistances of the electrolyte/electrode.\(^{24}\) It can be seen that \( R_{ct} \) of the C\(_2\)-N@rGO-X electrode ranges from 2–9 Ohm, suggesting a low charge transfer resistance. In addition, the negligible semicircle can be partially ascribed to the sufficient wettability due to the high content of N-doping and rich hydrophilic functional groups.\(^{28}\) The intercept at the \( x \)-axis of the impedance spectra reflects the bulk resistance \( (R_s) \), which corresponds to the contact resistances (between the electrode and current collector) and the intrinsic resistance (between the electrolyte and electrode).\(^{29}\) Although, the C\(_2\)N@rGO-12\% exhibited the smallest \( R_s \) and lowest \( R_{ct} \), showing a better conductivity behavior than other electrodes.

Due to the higher conductivity of rGO, the \( R_{ct} \) and \( R_s \) was increased with the ratio of rGO enhance. But the most perpendicular vertical line appears in the C\(_2\)N@rGO-4\% electrode in the low-frequency region, which represents the better capacitive behavior owing to its faster ion diffusion performance. Only considering the electrode itself, resistance and capacitance performance are affected by the synergistic effects of conductivity, porous structure, and chemical composition.\(^{40}\) The C\(_2\)N@rGO-4\% electrode not only has high conductivity, but it also has large micropores and tuneful \( \pi \)-conjugated structure, which can obtain the rapid ion diffusion channel and short diffusion distance to promote ion diffusion. Additionally, sufficient wettability can provide a smooth porous channel to ensure accessibility to ions within ion diffusion.\(^{41-43}\) Therefore, C\(_2\)N@rGO-4\% should be anticipated to exhibit satisfactory capacitive behavior.

### 3.3. FCDI performance

During the FCDI process, salt ions are separated through the AEM and CEM by applying a certain potential when the salt solution flows through the spacer layer. Then, EDLs are formed at the micro-/mesopores and surfaces of the electrode materials suspended in electrode channels during the electroadsorption process. However, the EDLs are only produced with limited single electrode particles that are in electrical contact with the current collector; that is, the electrode particles make it difficult to obtain EDLs when they are weakly electrically connected or are unable to contact the current collector. Considering the suspended state of the electrode mud, the active substances of the flow electrode slurry is less than 15 wt%. Furthermore, most active substances cannot remove salt ions effectively and maintain a neutral charge state. Therefore, rGO as a base can link with single C\(_2\)N particles, as seen in this work, to adequately use the electrode particles. More C\(_2\)N particles can join to generate EDLs and greatly increase salt ion adsorption capacity, as shown in Scheme 1.

The Fig. 6(a) and S8\(^{\dagger}\) shows the FCDI desalination performance by using the C\(_2\)N@rGO electrode, and by comparing the C\(_2\)N and AC electrodes at the same time, which was tested at an initial conductivity of 1.8 g L\(^{-1}\) at 1.0 V. The electroadsorption performances of the three samples were measured for 30 min. An obvious and rapid adsorption of the salt ions occurred in three samples, while the C\(_2\)-N@rGO electrode exhibited better deionization performance than as-prepared C\(_2\)N and commercial AC electrodes. The conductivity value of the effluent varies in two stages: one is the rapidly decreasing stage within 15 min, and the other is the gradually approaching equilibrium stage, indicating that the absence of discharging processes during the entire

Fig. 6 (a) The conductivity variation with deionization time of C\(_2\)N@rGO-2/4/8/12\% electrode; (b) the SAC, RES and SAR curves of C\(_2\)N@rGO-2/4/8/12\%, C\(_2\)N, GO and AC electrode in an initial concentration of 1.8 g L\(^{-1}\) NaCl solution at 1.0 V; FCDI performance of the C\(_2\)N@rGO-4\% electrode: (c) the variation of applied voltages along with the desalination time and (d) the SAC, RES and SAR curves at different applied voltages; (e) the variation of NaCl concentration along with the desalination time and (f) the SAC, RES and SAR curves at different NaCl concentration.

Fig. 7 CE with different initial NaCl concentrations at different voltage.
The desalting effect of the C2N@rGO-4% electrode is superior to that of the other electrodes. The C2N@rGO-4% electrode has the highest SAC of 180.72 mg g⁻¹, the largest SEC of 49.93%, and the fastest SAR of 0.3043 mg min⁻¹ cm⁻² compared to the other as-prepared electrodes, as shown in Fig. 6(b). It is further confirmed that the capacitance performance is affected by the synergistic effects of conductivity, porous structure, and chemical composition. Additionally, the potential effects on FCDI cell performance partly rely on the synergistic effects between the porous structure and chemical composition. Therefore, as an electrode material, C2N@rGO has strong potential for application in the FCDI systems.

In conclusion, the C2N@rGO electrode was synthesized by a simple reaction and used as a flow electrode in an FCDI system. The rGO introduced in the C2N-based material can easily solve the channel blocking problem and greatly improve the salt ion removal performance, maximizing the amount of active particles that can be added to the deionization process by forming a conductive network. The material characterization shows that the C2N@rGO material exhibits a large SSA and micropores, high N-doping, and a tunable graphitization structure, the characteristics that lend as-prepared electrode outstanding electrochemical and desalination properties. Additionally, the FCDI results suggest that C2N@rGO-4% has a high SAC (180.72 mg g⁻¹), SAR (0.3043 mg min⁻¹ cm⁻²), and SEC (49.93%). An electrochemical analysis showed that the conductivity of the flow electrode can be increased by introducing rGO, resulting in a conductive network. Moreover, all results indicate that FCDI performance partly relies on the synergistic effects between the porous structure and chemical composition. Therefore, as an electrode material, C2N@rGO has strong potential for application in the FCDI systems.

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Table 2  Comparison with other methods

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Applied voltage/V</th>
<th>NaCl solution</th>
<th>CE/%</th>
<th>SAC/mg g⁻¹</th>
<th>ASAR</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs-MXene</td>
<td>0.8</td>
<td>5–600 mM</td>
<td>~95</td>
<td>15</td>
<td>2.1–5.9 μg cm⁻²</td>
<td>46</td>
</tr>
<tr>
<td>Copper hexacyanoferrate activated carbon</td>
<td>1.2–2.8</td>
<td>10 g L⁻¹</td>
<td>~95</td>
<td>--</td>
<td>0.11 mg min⁻¹ cm⁻²</td>
<td>47</td>
</tr>
<tr>
<td>ZIE-8/ZIF-67</td>
<td>1.4</td>
<td>500 mg L⁻¹</td>
<td>~11.4–12.3</td>
<td>--</td>
<td>1.5–5.5 mM s⁻¹ cm⁻²</td>
<td>48</td>
</tr>
<tr>
<td>Functionalized activated carbon</td>
<td>1.2</td>
<td>55 mS cm⁻¹</td>
<td>~85.6</td>
<td>--</td>
<td>0.7–5.7 mM s⁻¹ cm⁻²</td>
<td>12</td>
</tr>
<tr>
<td>Functionalized carbon nanotubes into activated carbon</td>
<td>1.2</td>
<td>1.1–35.0 g L⁻¹</td>
<td>~96.2</td>
<td>~180.7</td>
<td>0.3–0.9 mg min⁻¹ cm⁻²</td>
<td>10</td>
</tr>
<tr>
<td>C2N@rGO</td>
<td>0.6–1.2</td>
<td>1.8–14.5 g L⁻¹</td>
<td>~95</td>
<td>15</td>
<td>2.1–5.9 μg cm⁻²</td>
<td>Our work</td>
</tr>
</tbody>
</table>

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Conclusions

In conclusion, the C2N@rGO electrode was synthesized by a simple reaction and used as a flow electrode in an FCDI system. The rGO introduced in the C2N-based material can easily solve the channel blocking problem and greatly improve the salt ion removal performance, maximizing the amount of active particles that can be added to the deionization process by forming a conductive network. The material characterization shows that the C2N@rGO material exhibits a large SSA and micropores, high N-doping, and a tunable graphitization structure, the characteristics that lend as-prepared electrode outstanding electrochemical and desalination properties. Additionally, the FCDI results suggest that C2N@rGO-4% has a high SAC (180.72 mg g⁻¹), SAR (0.3043 mg min⁻¹ cm⁻²), and SEC (49.93%). An electrochemical analysis showed that the conductivity of the flow electrode can be increased by introducing rGO, resulting in a conductive network. Moreover, all results indicate that FCDI performance partly relies on the synergistic effects between the porous structure and chemical composition. Therefore, as an electrode material, C2N@rGO has strong potential for application in the FCDI systems.
Conflicts of interest

There are no conflicts to declare.

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Notes and references

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