Graphene/Polyaniline nanocomposite as electrode material for membrane capacitive deionization

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HIGHLIGHTS
• Graphene/Polyaniline nanocomposites were synthesized by chemical polymerization.
• Capacitance of the nanocomposite was higher than that of graphene only.
• Faster and more thorough regenerations of G/PANI electrodes were achieved in CDI.
• This is due to the synergistic interfacial interactions at a layered structure.

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ABSTRACT
Capacitive deionization (CDI) is a novel ion removal technology that uses static electrical force to drive ions to the charged electrode and stores the ions into porous structure of the electrode. Graphene and graphene nanocomposites are considered promising materials for electrodes because of its good conductivity and extraordinarily high specific surface area. Graphene/Polyaniline nanocomposite was chosen that aims to increase the ion-electrosorption capacitance of graphene. In this work, graphene nanosheets were obtained by reducing oxidized graphite flakes. Graphene/Polyaniline (G/PANI) nanocomposites were synthesized by chemical polymerization of aniline in the presence of dispersed graphene sheets. The morphology and electrochemical property of the composite were characterized. The ion removal performance of the composite was determined by using a membrane capacitive deionization (CDI) bench-scale system.

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1. Introduction
Capacitive deionization (CDI) uses an electrical potential of 1–2 V as a driving force to adsorb ions from ion-rich feed flow onto an electrode surface, removing ions from the solution and resulting in deionization/desalination. The electrode materials that hold the adsorbed ions are of critical importance in deciding the ion removal efficiency. The selection and design of electrode materials are the most important factors in the development of CDI technology. The electrode materials should be stable in an aqueous solution with applied electrical potential, and they should be electrically conductive and have a large surface area. Carbon material meets all these requirements. Since the first report of using activated carbon powder as the electrode in 1967 [1], many researchers have followed and used activated carbons in the 1990s, and widespread interests in carbon aerogel led to the first boom in CDI technology [2–7]. During the past decade, the development of novel carbon material with unique nanostructures such as ordered mesoporous carbon (OMC), carbon nanotubes and graphene has provided another opportunity to improve the efficiency of the CDI process.

Zou et al. [8,9] conducted experiments on the synthesis of OMCs and found that compared to activated carbon powder, the larger pore size of OMCs facilitates the adsorption and desorption of ions onto the carbon surface and therefore enhances the efficiency of salt removal. Pan et al. [10–12] did a great deal of work on the application of carbon nanotubes and graphene. Carbon nanotubes exhibited quite efficient regeneration performance due to high electrical conductivity. Graphene showed better deionization performance than activated carbon powder, even with a much lower surface area [13]. Graphene is a two-dimensional material with carbon atoms arranged in a regular hexagonal pattern to form one-atom thick sheets. Carbon atoms are sp2-
bonded in the bond length of 0.144 nm. The electron mobility of graphene can be as high as 200,000 cm²V⁻¹s⁻¹ [14]. This demonstrates that the electrical conductivity of graphene is excellent. More importantly, being a single-atom layer structure, the theoretical surface area of graphene is 2630 m²/g [15]. Most importantly, the interlayered open structure of graphene sheets favors easy ion adsorption and desorption. These properties make graphene an attractive candidate for a CDI electrode.

Wang et al. [16] studied the deionization performance of a type of functionalized graphene nanocomposite and reported that it was a promising electrode material for CDI. The ion-electrosorption capacitance of the nanocomposite is higher than it is with reduced graphite oxides and activated carbons. Lai et al. [17] found a significant increase in capacitance after adding polyaniline to graphene. An improvement in capacitance as high as 8 times was reported. Polyaniline is a conducting polymer that is well known for its easy synthesis, good conductivity and high pseudo-capacitance. Combining polyaniline and carbon as an electrode material for a super capacitor has been widely studied. Polyaniline introduced in the nanocomposite can enhance the capacitance of carbon material, and at the same time the stability of polyaniline can be improved by the carbon contained in the nanocomposite [18]. Composites of single-walled carbon nanotubes (SWCNTs) and PANI have been studied as the electrode material for CDI. The introduction of PANI modified the meso-structure of SWCNTs and facilitated the entrance and exit of ions onto the surface of the electrodes [19]. It was also reported that with graphite and PANI composite as electrode the CDI unit could be regenerated easily [20].

In this work, G/PANI nanocomposite was used as electrode materials in membrane CDI. Capacitive deionization without membrane is affected by co-ion effects because desorption of co-ion happens at the same time as adsorption of counter-ions. In membrane CDI, cation and anion selective membranes were added to the cathode and anode respectively to prevent co-ion effect and to enhance deionization efficiency [21]. The nanocomposites of graphene and polyaniline were synthesized through in-situ polymerization. The morphology and electrochemical properties of the nanocomposites were studied. The electrosorption property was studied using a bench-scale CDI system.

2. Experimental

2.1. Preparation of graphene dispersion

To prepare graphene dispersion, 1.5 g of graphite flakes was added to a mixture of concentrated nitric and sulfuric acid in the volume ratio of 1:2. The mixture was then put in a water bath at a temperature of 80 °C and stirred for 4.5 h. Following that, the mixture was diluted with 750 ml of deionized water and kept overnight. Then, the mixture was filtered, put into 180 ml of concentrated sulfuric acid and kept in an ice bath. Potassium permanganate was then slowly added to the mixture. After that, the mixture was stirred for 2 h at a temperature of 35 °C in a water bath. Then, the mixture was diluted with 150 ml of deionized water, stirred for another 2 h and diluted again with 375 ml of deionized water. Successively, 30 ml of 30% H₂O₂ was added to the mixture, which then became brilliant yellow with bubbling. The brilliant yellow solution was kept overnight and filtered. Finally, the obtained graphite oxidate (GO) was washed with HCl (1:10 in volume) and deionized water. The GO was then reduced using hydrazine monohydrate to obtain graphene nanosheets.

The graphene nanosheets were ultrasonicated for 1 h in 1 M HCl solution. Then, 69 μl aniline monomer was added to the solution (estimated 4 wt.% of PANI in the composite). The aniline was allowed to adsorb on the graphene sheets for another 1 h in an ultrasonic bath. Ice was then put into the ultrasonic bath and 0.171 g of ammonium persulfate dissolved in 10 ml 1 M HCl was added to the reactant mixture to start polymerization (Fig. 1). After 4 h, the composite was centrifuged and dried.

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Fig. 1. The in-situ polymerization of PANI in the presence of graphene sheets.

Fig. 2. Schematic diagram of the bench-scale CDI system.
2.2. Characterization

The morphology of the graphene only and G/PANI nanocomposite was characterized by transmission electron microscopy (TEM; Philips CM200). To confirm the presence of polyaniline, Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer Spectrum 100) and Raman spectroscopy were used to identify the structure of the graphene and groups of polyaniline (PANI). The FTIR analysis was performed in the attenuated total reflectance (ATR) mode. An MIR-TGS detector was used at the resolution of 4 cm$^{-1}$. Raman spectroscopy was acquired using a Witec alpha300R microscope using a Nd:YAG laser excitation at 532 nm ($E_{\text{las}} = 2.33$ eV). Standalone spectra were collected using integration times of 10 to 20 s for 3 accumulations. Twenty to 30 spectra were collected for each sample in the spectral range 250–2300 cm$^{-1}$ with a nominal resolution of 4 cm$^{-1}$, approximately.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to study the electrochemical properties of the graphene, PANI and the nanocomposite (Autolab PGSTAT128N electrochemical workstation). The three-electrode method was used to evaluate the capacitances of graphene and the G/PANI composite electrodes. A saturated Hg/HgCl$_2$ electrode was used as a reference electrode, a glass carbon electrode was used as a counter-electrode and 1 M NaCl was used as an electrolyte.

2.3. CDI test

The bench-scale CDI system contains an ion adsorption cell, a conductivity meter, a peristaltic pump, a power supply and a feed solution container (see Fig. 2). The cell consists of a pair of electrodes arranged in parallel, and cation and anion selective membranes were added to the counter-electrode as a charge barrier to allow selective passage of ions. Between the two ion exchange membranes, the water-permeable non-conductive spacers were added as an insulator. The feed solution, which contains ions, was pumped through the CDI cell by the peristaltic pump. The power supply provided an electrical potential of 1.2 V between the two electrodes of the CDI cell. Inside the cell, ions were adsorbed onto the electrodes by forming electrical double layers. The conductivity meter was used to monitor the conductivity of the solution, which reflects the amount of ions adsorbed. The feed solution was a NaCl solution with certain concentration. In fabrication of the electrodes, graphite powder (20%) was added as a conductive additive and polytetrafluoroethylene (PTFE) (8%) as a binder. The graphene only, G/PANI composites and graphite powder were grounded together to make a uniform mixture, then PTFE in ethanol solution was added to make the mixture a slurry. The slurry was then casted onto a 70 mm wide × 100 mm long graphite sheet. Finally, the fabricated electrodes were dried overnight before the electrosorption test.

3. Results and discussion

3.1. Morphology

The morphology of the graphene only and G/PANI nanocomposite was studied by taking TEM images (see Fig. 3a and b). Polyaniline preferably to locate at the edge of graphene sheets with a few dispersed between sheet layers. Aniline was adsorbed onto graphene sheets due to π–π interaction between the benzene rings of graphene and aniline.
prior to polymerization. The growth of polyaniline on the edge was attributed to amide groups that were introduced by reducing GO with hydrazine. The amide group connected graphene and polyaniline intimately and acted as electron bridges to form a large-scale π–π conjugated system, which facilitated the charge transfer between graphene and polyaniline, and resulted in improving the electrochemical stability of the composite \[22\].

The N\textsubscript{2} adsorption desorption isotherm and the pore size distribution of G and G/PANI are shown in Fig. 4. The calculated BET surface area of G and G/PANI was 428 m\textsuperscript{2}/g and 394 m\textsuperscript{2}/g respectively. The pore size of G and G/PANI shows similar pattern in the range of 2–6 nm, while in the G sample there is more pores in the range of 6–10 nm. That is the G/PANI composite has a more homogeneous pore distribution mainly in the range of 2–6 nm because of the introduction of PANI.

### 3.2. FTIR and Raman spectra

Fig. 5a and b shows the FTIR and Raman spectra respectively. The chemical bonding structures of the graphene only, PANI only and G/PANI nanocomposite were characterized by FTIR spectroscopy. PANI peaks in the composite were indicated with green circles. In the spectra of PANI itself, peaks at 1594 and 1493 cm\textsuperscript{-1} were indentified as the vibration of quinonoid and benzene rings. These two peaks shifted to a lower wave number at 1521 cm\textsuperscript{-1} and 1458 cm\textsuperscript{-1} respectively in the composite and partly overlapped by the strong graphene absorption [23]. The read shift in FTIR indicated a higher degree of electron delocalization, which is caused by the interaction between carbon rings of graphene and backbone of polyaniline. The peak located at 1289 cm\textsuperscript{-1} was attributed to C–N vibration in pure PANI, and this peak was found located at 1240 cm\textsuperscript{-1} [24] in the spectra of the G/PANI composite. The presence of polyaniline is also confirmed by the C–H stretch vibration of the benzene ring at 3051 cm\textsuperscript{-1} and the out of plane deformation of C–H in the benzene ring at 816 cm\textsuperscript{-1}.

The results of Raman scattering analysis are complementary to the FTIR spectroscopy and help to identify the presence of PANI in the composite (Fig. 5b). Identical peaks of graphene D band and G band existed in both graphene only and the nanocomposite. For graphene only sample, absorption peak at 1593 cm\textsuperscript{-1}, which is known as G band, is related to the vibration of sp\textsuperscript{2}-hybridized carbon. Another prominent peak at 1349 cm\textsuperscript{-1}, regarded as D band, is ascribed to the conversion of an sp\textsuperscript{2}-hybridized carbon to an sp\textsuperscript{3}-hybridized carbon [25,26]. D band reflects the defects of graphene, which could arise from a partly disordered crystal structure and edge area of the graphene sheets. As the sample was prepared and measured as powder, the smaller size of graphene sheets could also have caused the high intensity of the D band. Compared to the spectra of graphene, the G to D ratio of the two peaks increases slightly for the G/PANI nanocomposite, specifically, the intensity of the D band is decreased while the intensity of the G band is increased, indicating a more ordered structure of the composite. The G band shifts from 1593 cm\textsuperscript{-1} in graphene to 1586 cm\textsuperscript{-1} in the
composite. This shift could be the result of the interaction between the graphene sheets and the polyaniline skeleton, although given the uncertainty on the peak positions is 4 cm\(^{-1}\) this shift can be considered very small and almost negligible. Representative peaks of polyaniline are also found at 776 cm\(^{-1}\), 1161 cm\(^{-1}\) and 1476 cm\(^{-1}\), corresponding to imine deformation, C–H bending of the quinoid ring, and the C=C stretch of the benzene ring respectively\[27\text{–}30\]. These representative peaks can be observed as the spectra of the PANI sample, albeit with a very small shift upwards of only 2 to 4 cm\(^{-1}\) for each peak. Given that the uncertainty on the peak positions is 4 cm\(^{-1}\) this shift can also be considered very small to negligible. Al-Mashat et al.\[31\] used similar Raman measurements and comparisons to verify the formation of graphene/PANI nanocomposites for hydrogen sensing.

### 3.3. CV

Fig. 6a shows the CV curves of the graphene only, PANI only and G/PANI nanocomposite at the scan rate of 5 mV/s. It shows that the CV of the G/PANI composite exhibits a larger rectangular area, indicating that the nanocomposite has higher double-layer capacitance. The quite rectangular-shaped curves demonstrate ideal double-layer capacitor behavior. The CV of neat PANI shows slight redox peaks and the lowest capacitance among the three in 1 M NaCl solution. Due to the compact contact of the two components as well as the low level of polyaniline in the nanocomposite, the typical redox peaks of polyaniline were not obvious in the composite. Fig. 6b shows the CV curves of the G/PANI nanocomposite at various scan rates. The rectangular shaped curves were well retained at the scan rate of 20 mV/s, showing a stable capacitive behavior at high charge/discharge rate. The graphene sheets acted as a structural support for polyaniline, and the electrochemical property of polyaniline was well retained by the layered structure of graphene nanosheets. The advantage of the integration of both materials was attributed to the good interfacial interactions of the two materials at a layered composite structure. The EIS test was conducted to verify the ion charge transfer resistance (Fig. 7). The PANI only based electrode shows the highest resistance, while the G/PANI composite electrode shows the lowest resistance, confirming a faster interfacial charge transfer rate in the composite.

### 3.4. CDI performance

Ion adsorption tests were conducted at the initial conductivity of 500 μS/cm and 1000 μS/cm in bench-scale CDI cells. The experiments were conducted in a batch operation mode. At 500 μS/cm initial concentration, conductivity removals were 86% for electrodes made of...
graphene, and 94% for those made of the G/PANI nanocomposite. At the higher initial conductivity of 1000 μS/cm, conductivity removals were 52% and 65% respectively for the electrodes made of the graphene only and G/PANI nanocomposite. The maximum amount of salt removal occurred at the highest initial concentration. Curves relating to changes of conductivity during adsorption and desorption processes are shown in Fig. 8. In the adsorption step, conductivity of the solution dropped quickly after the potential of 1.2 V was applied. The decreasing rate slowed down in several minutes and became slower and slower while the capacity of the electrodes was fully reached. The desorption step was achieved by reversing the electrical charge. The release of ions was rapid at the beginning of the electroosorption due to the high ionic density at the surface of the electrodes. The G/PANI composite electrode was regenerated much faster than the graphene only electrode. Specifically, in the regeneration procedure, it took 20 min for the conductivity changing from 344 to 982 μS/cm in the case of G/PANI electrode, while it took 27 min for the conductivity changes from 481 to 979 μS/cm in that of G only electrode. The fast regeneration of G/PANI electrode might be because of the fast charge transfer rate in the composite. PANI acted as conducting chains that connected the graphene sheets. When the electrode field was reversed it took less time for the electrode to respond to the reversing. Fig. 9 shows the conductivity curves of several cycles of charge/discharge operations. It seems that a faster regeneration of the composite electrode was achieved than that of the graphene only electrode.

4. Conclusion

As a promising desalination technology, CDI has been drawing increased attention. Developing more efficient electrode materials is the key to improving salt removal performance. In this work, a novel G/PANI nanocomposite was synthesized and used it as an electrode material in CDI. The results showed that G/PANI was synthesized successfully, with polyaniline dispersed mainly at the edge of the graphene sheets. Cyclic voltammetry analysis indicated that the specific capacitance of the G/PANI nanocomposite electrodes was increased compared to the graphene only electrodes. In addition, faster regenerations of the G/PANI nanocomposite electrodes were achieved. This is attributed to the synergistic interfacial interactions of the two materials, that is, graphene and polyaniline, at a layered nanocomposite structure.

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References