



Carbon aerogels through organo-inorganic co-assembly and their application in water desalination by capacitive deionization



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ABSTRACT

We report the preparation of a carbon aerogel (CA) material utilizing the simultaneous co-assembly of organic and inorganic precursors, having a high Brunauer–Emmet–Teller surface area of 2600 m²/g, through a one-step sol–gel process. This CA was characterized using different spectroscopic and microscopic techniques. The as-synthesized CA with its tunable porosity, high mechanical strength, transport property and electrical conductivity was found to be a suitable candidate for water desalination via capacitive deionization (CDI). The optimum working potential for CDI was in the range of 1.2–1.4 V. The material was tested for the removal of different ions of varying charges and the experiment was performed for multiple cycles. The result showed high adsorption capacity of 10.54 mg/g for Cl[−] in laboratory batch experiments compared to 3–4 mg/g reported for most of the CDI materials. The materials were also characterized after adsorption/desorption cycles. Adsorption was physical in nature and the ions desorbed completely after reversing the polarity. The result showed that the material can be used for multiple cycles without any change in its spectroscopic and adsorption properties.

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1. Introduction

Shortage of clean drinking water globally, due to rapid increase in population and industrialization; probably the most important problem of the planet, has to be addressed from multiple directions. Environmental contamination and pollution has led to the deterioration of water quality, even in water rich regions [1]. In order to solve the water crisis, we require clean and cost effective methods [2] for decontaminating polluted waters. Desalinating fresh water from rivers or groundwater can generate water suitable for human consumption [3,4]. Reverse osmosis [5], ultra-filtration [6] and electro-dialysis [7] have been traditionally used to generate drinking water from brackish water. However, all these techniques require heavy equipment and more power and therefore, involve high installation and operational costs.

Among all the water desalination processes, capacitive deionization (CDI) is cost effective and easy to operate. CDI removes primarily ions from water by using two oppositely charged carbon electrodes of high porosity, electrical conductivity and a large surface area. The electrodes are separated by a spacer and connected to a direct current (DC) source by a current collector (typically graphite or titanium sheet). On applying a voltage, the surface of the electrodes gets charged and an electrical double layer is formed between the electrode and the solution. These charged electrodes adsorb the counter ions present in the feed water and thereby, desalinate it. The electrodes are regenerated by reversing the polarity discarding the heavily saline stream generated during this step. No additional efforts are required for this process. Capacitive desalination is attractive because it is a non-membrane based approach which requires low voltage (an applied potential between 0.8 and 2.0 V that is below the hydrolysis potential of water at the electrode surface) and requires only low pressure for operation.

The electrode materials that have been used for wastewater treatment using CDI include porous activated carbons [8], carbon cloth [9,10], activated carbon fiber [11], carbide derived carbon (CDC) [12], carbon nanotubes [13], graphene [14], graphene aerogel

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[15,16], carbon–carbon composite [17], conducting polymer carbon composite [18], and carbon metal oxide composites [19]. Among these materials, carbon aerogels (CA) have high surface area (400–1100 m²/g), low resistivity (~400 Ωm/cm), high electrical conductivity and excellent electrochemical stability in aqueous solutions. The main advantage of carbon aerogel is that its micro and meso-porosity can be tuned by using an easy to implement sol–gel technique [20]. The ion adsorption capacity is dependent on tailoring its microstructure [21] either by using an inorganic precursor (like silica) or metal oxides [22,23]. Yang et al. [24] prepared a carbon aerogel on a silica gel template for CDI of NaCl solution. In another study, manganese and iron oxide-doped carbon aerogel electrodes were tested for CDI of saline water [22]. Both the materials showed enhanced capacity than CA alone.

A unique property of a CA is the presence of inter-connected particles, which along with a simple synthesis procedure, is advantageous when used as an electrode in capacitors, fuel cells and Li ion batteries and catalytically active substrates [25]. Previously, resorcinol–formaldehyde (RF) gels have been used to make CAs by combining the two precursors in suitable molar ratios and employing different processing conditions, such as, reactant concentrations, catalyst concentrations, pH, activation temperature and pyrolysis temperature [26,27]. Recently, Wu et al. [21] have synthesized an ordered mesoporous carbon aerogel by incorporating a carbon precursor in a calcium carbonate based hard template network that was subsequently removed selectively to generate mesopores. Surfactant-assisted soft template has also been reported to create a porous carbon structure [25]. However, such techniques are limited by the template size and the pore structure and are therefore, unable to control the pore size distribution and achieve porosity beyond a narrow range.

It is a standard practice to generate carbon aerogels by supercritical drying of wet RF gels and this method requires high pressures (up to 1000 psi) that raises safety issues [28,29], and makes it expensive and difficult to scale-up for industrial use. To reduce the cost, new techniques are needed which will eliminate the supercritical drying step and substitute it with ambient pressure drying at feasible temperatures, while preserving the mechanical strength and maintaining the porosity of the material. Jung et al. [30] have reported RF derived carbon aerogel electrodes for capacitive deionization, prepared by ambient pressure drying.

In this work, we have used a simple and cost effective sol–gel technique to fabricate a resorcinol–silica composite aerogel monolith with a highly porous structure and high surface area. The interpenetrating network of organic and inorganic phases was self-assembled during the gelation process. After removing the solvent phase present in the monolith, the ambient drying helped to maintain the micro and meso porosity and mechanical integrity of the monolith structure. After carbonization of the prepared monolith, some shrinkage occurred due to the removal of volatile substances generated due to the decomposition of carbonaceous precursors. In further steps, silica was etched from the carbon–silica aerogel to form a carbon aerogel with increased surface area and electrical conductivity. This material was used for water desalination using the CDI technique.

2. Material and methods

2.1. Materials

Resorcinol (R), formaldehyde solution (F), tetraethyl orthosilicate (TEOS), and 3-aminopropyl tri-ethoxysilane (APTES) were purchased from Sigma–Aldrich. Acetone, sodium hydroxide (NaOH), sodium chloride (NaCl), magnesium chloride (MgCl₂), and ferric chloride (FeCl₃) were purchased from LobaChemie. All

reagents were used as-received, without further treatment.

2.2. Synthesis of carbon–silica composite aerogel

Carbon–silica aerogel was prepared by the sol–gel condensation method of resorcinol, formaldehyde and TEOS. Briefly, 0.732 g of resorcinol was mixed in 4.20 mL of acetone, 2.73 mL of TEOS, and 320 μL of APTES, and 240 μL of APTMS was added into the reaction mixture. Finally 1.5 mL of formaldehyde was added and the mixed solution was kept in a polypropylene container. The container was tightly packed to avoid solvent loss. The mixed solution was kept undisturbed at room temperature for 5–6 h for gelation. After gelation was complete, the gel was washed three times with fresh acetone and kept at 60 °C for 10 h in a hot air oven to slowly evaporate the solvents. At this stage, color of the dried gel was reddish brown. Finally, the formed gel was carbonized in a tubular furnace at 900 °C for 1 h in an inert atmosphere using nitrogen gas. The heating rate was maintained at 5 °C/min. The as-synthesized aerogel was the carbon–silica composite aerogel (CSA).

2.3. CDI experimental scheme

CA electrodes of dimension 3 × 3 × 0.5 (l × b × h) cm³ were taken and were separated by a 0.4 mm nylon spacer. Two graphite rods were used as current collectors and were connected to a DC source. This single electrode set-up was immersed in a 100 mL beaker containing 80 mL of NaCl solution of 500 mg/L concentration. Magnetic stirrer was used with a stirring speed of 200 rpm. The electrodes (CA) are connected to the DC source (applied a potential of 1.2 V) such that one of the electrodes becomes positive and the other is negative. When the feed water (NaCl/salt solution) is passed through the electrodes, the cations (Na⁺) and anions (Cl[−]) get adsorbed on the cathode and anode, respectively. This process continues for a certain period of time until the electrodes become saturated enough that it cannot adsorb more ions. At this point, the maximum adsorption capacity of the material is calculated. As the terminals of the DC source are changed, the electrodes also reverse their potential and thereby, desorbing all the adsorbed ions on its surface due to electrostatic repulsion. In this process, the reject comes out as brine and the porous CA material is regenerated to be further used in another adsorption cycle. These steps should continue for multiple times without loss of capacity for ideal CDI electrodes.

2.4. Etching of silica from carbon–silica composite aerogel

Silica was etched from CSA by dipping it in a 2 M NaOH solution at 70–80 °C for 12 h. This step was performed three times for complete removal of silica. After this, the aerogel was washed with water several times to ensure complete removal of NaOH and then dried overnight at 80 °C to remove water. This material was termed as carbon aerogel (CA). The density of the material was found to be 0.13 g/cm³. The ultra low density for this material proves it to be aerogel rather than xerogel as reported elsewhere [31] and was further confirmed by porosity measurements. The total pore volume of the CA was found to be 2.12 cc/g with average pore size of 3.26 nm (data in supporting information (SI), Fig. S1) A schematic of the preparation of CSA and CA by using sol–gel technique is depicted in Fig. 1.

2.5. General characterization

The surface morphology of the prepared samples was characterized by using field emission scanning electron microscopy (FESEM, ZEISS Supra 40VP, Germany). Energy dispersive X-ray

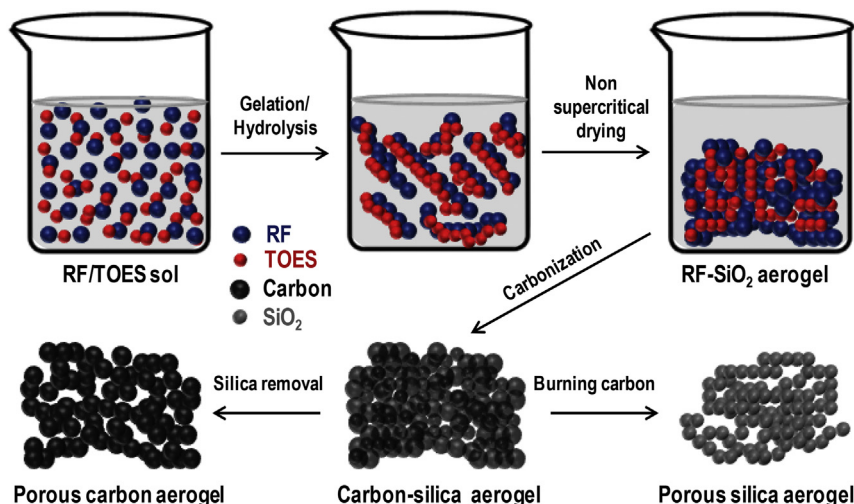


Fig. 1. Schematic of the preparation of carbon aerogel by the sol-gel technique. (A color version of this figure can be viewed online).

spectroscopy (EDS) with elemental mapping (Oxford instruments) was combined with FESEM. The crystal structure of carbon aerogel, before and after desalination, was analyzed by X-ray diffraction (XRD) (PAN Analytic Germany), using a Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) from 5 to 80° at a scanning speed of 2° per min. Raman spectra (Model: Alpha, Make: Witec, Germany) of the CAs were measured in the frequency range of 400–3000 cm^{-1} with a 514 nm laser source. X-ray photoelectron spectroscopy (XPS) was performed with an Omicron ESCA Probe spectrometer employing a polychromatic Mg K α X-ray source ($h\nu = 1253.6 \text{ eV}$). Majority of the spectra were deconvoluted to their component peaks using the software, CasaXPS. The energy resolution of the XPS spectrometer was set at 0.1 eV at a pass energy of 20.0 eV. The binding energy was corrected with respect to C 1s at 284.5 eV.

The surface area and pore volume of CA was measured by the Brunauer–Emmet–Teller (BET) BET-surface area analyzer (Quantachrome) Autosorb iQ. The pore size distribution (PSD) was obtained from the Barrett–Joyner–Halenda (BJH) method. The mechanical strength of the material was measured by Instron 1195 (in compression mode). The electrical conductivity was measured by a four probe point conductivity equipment (SES Instruments, Roorkee). A Keithley current source-voltmeter was attached to the four probe setup for the collection of data. The electrochemical capacitive behavior of CA was determined by cyclic voltammetry (CV). All electrochemical experiments were carried out at room temperature in a three-electrode cell with 1 M NaCl electrolyte solution. CV was performed at various scan rates using a potentiostat/galvanostat (AUTOLAB 302N) in a potential range of -0.8 V to 0.2 V versus Ag/AgCl (3 M KCl). The specific capacitance was calculated from the CV curve based on the following equation:

$$C_m = \left\{ \frac{1}{mR\Delta V} \right\} \int I(V)dV \quad (1)$$

Where, C_m is the specific capacitance, m is the mass of the active material, R is the scan rate, ΔV is the potential window of scanning, which is the integral area under the CV curve.

3. Results and discussion

The carbon aerogel (CA) prepared by our sol-gel method was characterized using different spectroscopic and microscopic techniques. Fig. 2A shows the photograph of the synthesized CA block of 7 cm (length) $\times$ 3 cm (width) $\times$ 1 cm (thick). The material exhibited

high mechanical strength having Young's modulus of 1.12 MPa which was calculated from compressive stress-strain curve (data are shown in supporting information (SI), Fig. S2) and was found to possess high monolithic integrity, such that it can be used as an electrode, without the need of a binder. This would prove to be an advantage as a binder generally decreases the conductivity of an electrode material, and thereby reduces the adsorption capacity. The electrical conductivity of CA was determined to be between 1 and 80 S/m, and its surface area was found to be $\sim 2600 \text{ m}^2/\text{g}$.

The SEM image of carbon silica aerogel (CSA) presented in Fig. 2B clearly illustrates the spherical nature of the carbon nanosphere. The high resolution SEM image (inset in Fig. 2B) of CSA further reveals that the carbon nanosphere has a uniform size of around 200 nm. Fig. 2B also shows the presence of voids in CSA at the nanoscale, which leads to excellent porosity (mesoporosity of 12.5%). The porosity of the material was tuned by using different concentrations of the silica precursor (TEOS). The porosity was very low in the absence of TEOS, but substantially increased upon addition of the SiO $_2$ precursor. However, at an optimum amount of TEOS (2%) the porosity reached a maximum and then decreased with further increase in SiO $_2$ concentration (see Fig. S3) along with a reduction in mechanical strength of CA.

Etching the silica precursor from CSA using 1 M NaOH led to the formation of CA with a increased porosity that enhanced the performance of CDI by 80%. The SEM image of CA is shown in Fig. 2C. Interestingly, while the porosity increased (mesoporosity increased by 15%), the mechanical strength was not adversely affected. XPS was performed to understand the chemical composition of CA. The spectrum displayed in Fig. 2D show that carbon and oxygen are the only two components present in the system. The deconvoluted C 1s spectrum (inset of Fig. 2D) consists of two peaks at 284.5 and 286.7 eV, whose relative intensities suggest that carbon in CA occurs mainly as C=C and partially as C–O. The presence of Si in the parent material (CSA) was confirmed by its XPS spectrum as shown in SI, Fig. S4. The absence of the corresponding peak in Fig. 2D affirms that SiO $_2$ was completely removed by etching.

The SEM–EDS of CA illustrated in Fig. 3 shows the presence of carbon and oxygen alone, similar to XPS data in Fig. 2D. The elemental mapping performed on the SEM image in Fig. 3(i) depicted the uniform distribution of carbon (see Fig. 3(ii)) and negligible amount of oxygen (see Fig. 3(iii)) in CA. Fig. 3b shows that the elemental ratio of carbon and oxygen in CA is almost around 19:1, which is in good agreement with the deconvoluted XPS spectrum of C 1s in the inset of Fig. 2D. The SEM–EDS and

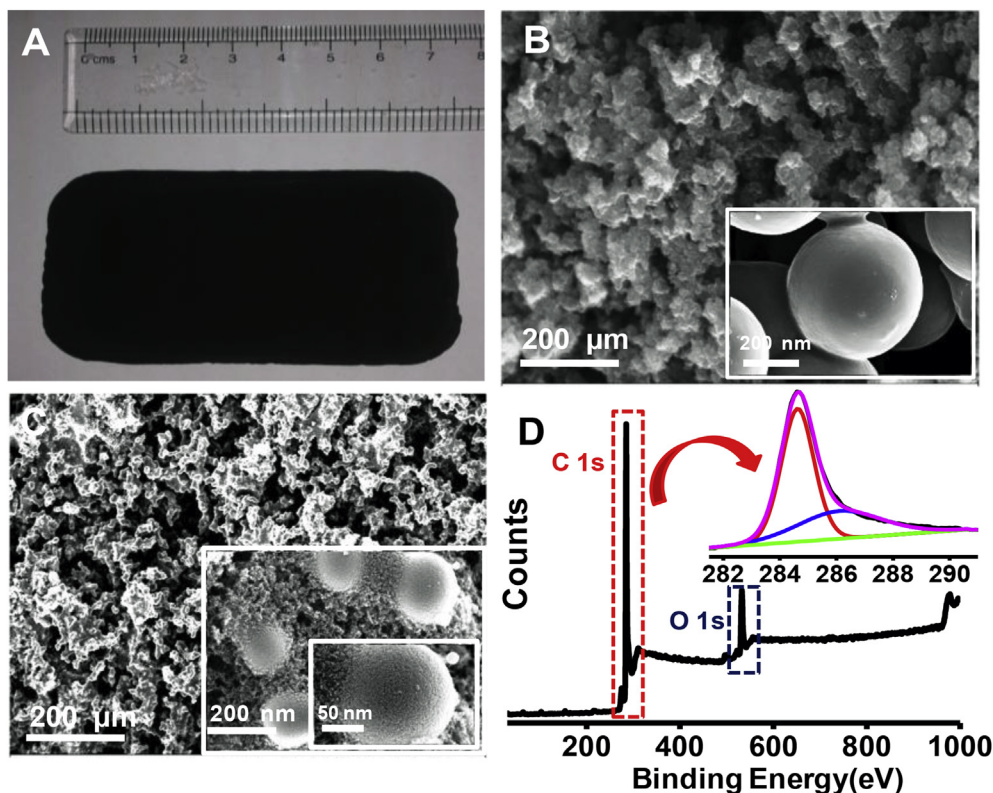


Fig. 2. A) Photograph of carbon aerogel. B & C) FESEM image of Si and Si etched carbon aerogel, the inset in both the figures show higher magnification image and D) XPS spectrum of carbon aerogel, the inset shows the C 1s spectrum. C and O were the only elements noticed. (A color version of this figure can be viewed online).

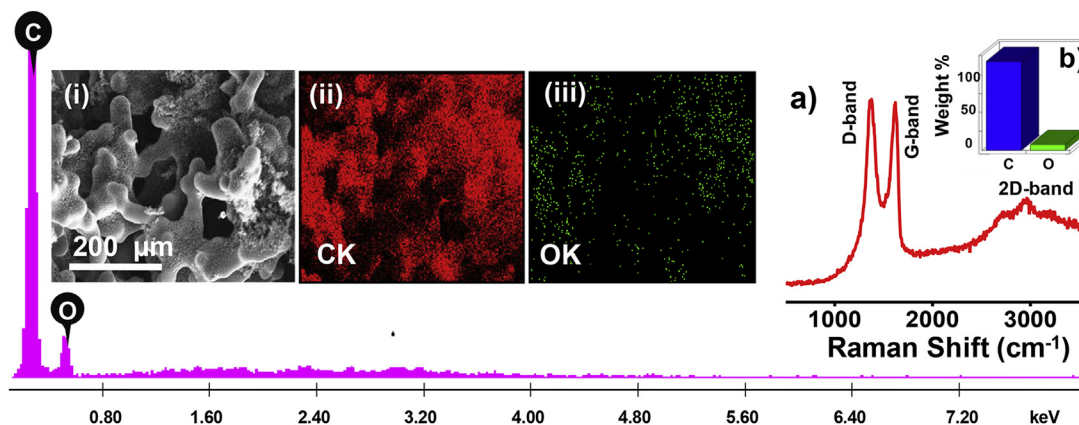


Fig. 3. SEM–EDS of CA showing the presence of carbon and oxygen. The inset displays i) SEM image and EDS mapping of ii) carbon and iii) oxygen, a) shows the Raman spectrum of CA and b) depicts the elemental ratio of carbon:oxygen in ratio 19:1 (SEM–EDS). (A color version of this figure can be viewed online).

elemental mapping results for CSA are provided in SI Fig. S5. The Raman spectrum of CA is shown in Fig. 3a which shows the presence of D, G and 2D bands at 1383, 1601 and 2769 cm^{-1} , respectively. The presence of these bands suggested that the material is graphenic in nature, as expected after a high temperature treatment.

Electrical conductivity determines the charge transfer and internal resistance of a material and its value at room temperature was evaluated for both CSA and CA using the four probe method. It can be seen from Fig. 4A that for achieving the same current, CA requires a much lower potential than CSA. The electrical conductivities of CSA and CA electrodes were calculated to be 2.3 and 71.0 S/m, respectively. The lower conductivity of CSA is due to the

non-conducting nature of silica that is impregnated in the CSA. This interpenetrating network of silica formed between the carbon matrixes reduces electrically conducting pathways.

CV was performed in 1 M NaCl electrolyte solution in a potential window of -0.2 – 0.8 V to determine the potential of CA as a CDI electrode with high electrosorption salt adsorption and specific capacitance. Fig. 4B shows the CV curves of CA obtained at a range of scan rates between 2 and 200 mV/s. It is noticeable that at low scan rates, the CV curve has a rectangular shape, which becomes distorted at high scan rates due to large current and increase resistance. This confirms the picture that at low scan rates, the electrolyte is able to penetrate into the pores of the CA electrode with an unrestricted motion, which does not occur at a high scan

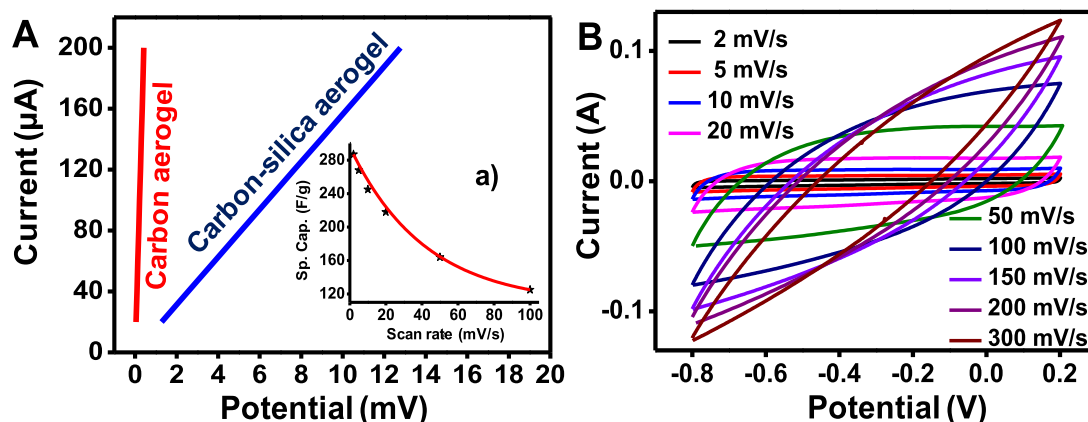


Fig. 4. A) Electrical conductivity of CSA and CA. The inset in the figure shows the variation of specific capacitance with respect to scan rate. B) Cyclic voltammetry of CA using 1 M NaCl as electrolyte. (A color version of this figure can be viewed online).

rate when the ohmic resistance affects the formation of the electrical double layer [32]. The effect of scan rate is also reflected by the specific capacitance which is calculated to be 262 and 86 F/g for CA (inset in Fig. 4A) and 170 and 55 F/g for CSA (from CV curves in SI, Fig. S6) at 2 mV/s and 100 mV/s, respectively calculated from equation (1).

Next, we developed a laboratory batch CDI set-up to examine the desalination performance of CA. The set-up consisted of two CA electrodes (one acting as a positive and the other as a negative electrode) separated by a porous nylon membrane (spacer), and a graphite rod as a current collector. Salt water of known concentration was taken in a glass beaker to function as the electrolyte. The electrodes were dipped into the salt solution along with a conductometer to monitor any change in the conductivity of the solution. Finally, a DC source, which can supply a voltage from 0.0 to 5.0 V, was connected to the graphite rod. The above set-up is illustrated in SI, Fig. S7.

Electrochemical capacity is a measure of the electrosorptive behavior of an electrode material. The electrical double layer formed onto the pores of the electrode material and the electrolyte leads to the adsorption of charged species over the electrode. The thickness of electrical double layer and the size of the charged species, therefore, govern the adsorption capacity. The former parameter in turn depends on the concentration of electrolyte solution and size of the electrolyte ions. Thus, to understand the effect of these key factors on the electrochemical properties of CA, we chose a set of three different salt solutions, namely, NaCl, MgCl_2 and FeCl_3 as electrolytes.

The voltage required for CDI was first optimized by measuring the adsorption capacity as a function of the applied voltage (between 0.4 and 2.0 V) using the DC source. It can be seen from Fig. 5A that, when using NaCl as the electrolyte, as the applied voltage was increased the removal capacity of the electrodes also increased. The optimum voltage was found to be 1.2 V, as further increase in voltage over 1.8 V led to electrolysis of water in the presence of NaCl, which was evidenced by the decrease in the volume of water upon prolonged operation. In Fig. 5B the desalination capacity of CA at 1.2 V using different salt solutions (200 ppm) is showcased. It can be seen that higher the valence of the metal ion, higher is the efficiency of salt removal, all other parameters being the same. The maximum adsorption capacity of the material was found to be 7.68 and 10.45 mg/g for CSA and CA, respectively. These values are higher than most of the previously reported adsorption capacities for carbon based CDI electrodes in batch mode [33]. Table 1 shows the comparison of efficiency of different electrode materials

reported in the recent past. The rate of adsorption of the material was evaluated and it was noted that a three step event occurred: a) an initial kinetics where the electro-adsorption was 0.280 mg/min for 12 min (fast kinetics as all the vacant sites are available for adsorption), b) 0.098 mg/min from 12 to 80 min (slow kinetics) and c) 0.002 mg/min from 80 to 120 min (very slow kinetics, where equilibrium is reached and no more adsorption occurred); data are shown in SI Fig. S8a. It was observed that the material reached saturation at 80 min from the initiation of the electro-adsorption process. Lagergren pseudo-first-order [34] and Ho's pseudo-second-order [35] mathematical models were used for describing the kinetic data. Details are given in supporting information Fig. S8. The fitting shows that Lagergren pseudo-first-order matches more with the experimental data as shown in SI Fig. S8b.

To test the potential of CA in real time CDI applications for water treatment, we examined desorption from the electrode material, following an adsorption step, by changing the terminal of the DC source. Multiple such adsorption–desorption cycles were carried out to evaluate the efficiency of the electrodes using 200 ppm of NaCl solution. Fig. 5C and D shows that even after five cycles, there was no loss in the adsorption capacity of both CSA and CA. It can also be deduced that the adsorption efficiency of CA is higher than that of CSA. At the end of each adsorption step, ~60 and 100 ppm of metal ions are adsorbed by CSA and CA, respectively. The effect of varying concentration of the electrolyte was analyzed by performing CDI for CA using NaCl solution at three different concentrations (200, 400 and 800 ppm) (SI, Fig. S9). We found that the adsorption capacity of CA did not change as NaCl concentration was increased and for each case it was ~10 mg/g, this indicates that the material has reached saturation limit at 200 ppm itself. These experiments prove that CA is suitable for CDI applications.

The electrode material (CA) was characterized after one adsorption cycle. For this the adsorption process was continued until the electrodes got saturated using NaCl as the electrolyte. It is seen that the cathode contains only positive ions and the anode contains only negatively charged ions. The SEM-EDS of the cathode and anode in Fig. 6A and B confirm the presence of sodium in the former and chloride in the latter. The elemental mapping shows that these ions are uniformly distributed on the surface of the electrodes. The XRD spectrum of CA before and after a single adsorption step is shown in SI Fig. S10. The XPS spectra of the electrodes after the adsorption step in Fig. 6C and D reaffirm the presence of sodium and chloride ions in the anode and cathode, respectively based on the peaks for sodium and chlorine at 1072.1 eV and 198.5 eV, respectively.

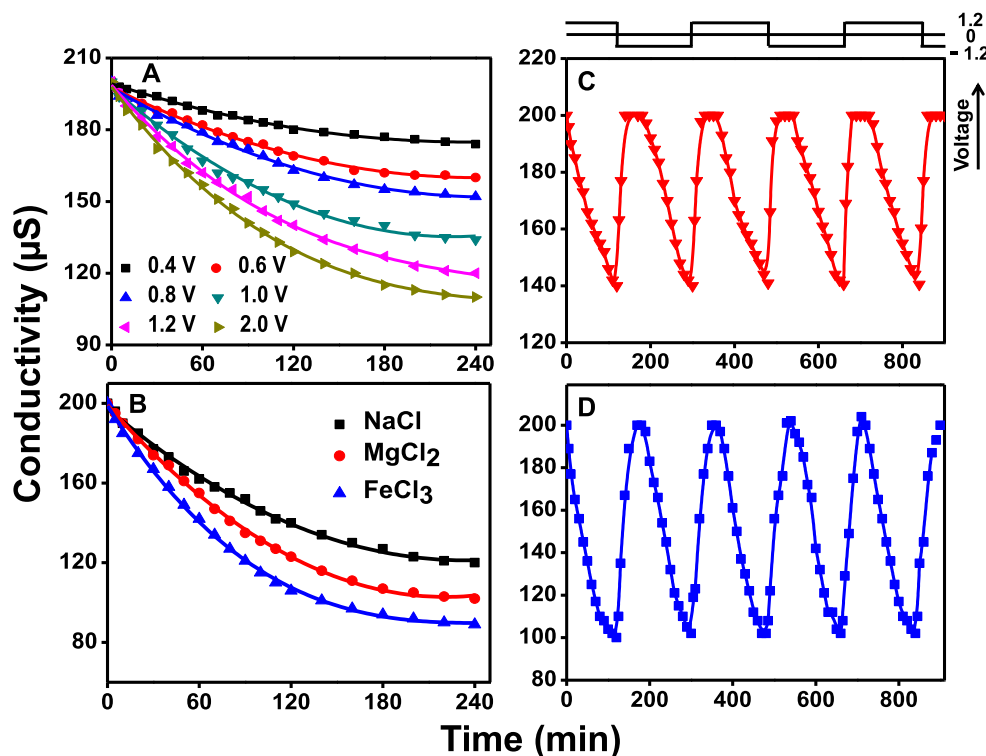


Fig. 5. A) Adsorption capacity of CA (with 1 M NaCl as the electrolyte) as a function of the applied voltage in the range of 0.4–2.0 V and B) CDI performance of CA using different electrolytes at 1.2 V. CDI efficiency of C) CSA and D) CA over five adsorption–desorption cycles. The fit over figure C represents the variation of voltage with respect to time from 1.2 to –1.2 V. (A color version of this figure can be viewed online).

Table 1

Comparison of electrode material efficiency in term of salt adsorption capacity in mg/g reported in the recent past.

First author/journal [ref]	Year of publication	Material	Initial salt concentration (mg/L)	Salt adsorption (mg/g)
Joseph C. Farmer/J. Electrochem. Soc. [36]	1996	CA	50	1.40
Kai Dai/Mater. Lett. [37]	2005	CA	500	2.90
Linda Zou/Water Res. [38]	2008	MWCNT's	3000	1.70
Lixia Li/Carbon [39]	2009	Mesoporous carbon	25	0.68
Zheng Peng/J. Mater. Chem. [40]	2012	Mesoporous carbon	50	0.93
Min-Woong Ryoo/Water Res. [41]	2003	Mesoporous carbon–CNTs	46	0.63
Juan Yang/Desalination [42]	2011	TiO AC cloth	5844	4.30
Yu-Jin Kim/Sep. Purif. Technol. [43]	2010	MnO ₂ –AC	25	1.00
X.Z. Wang/Electrochem. Solid-State Lett. [44]	2006	AC	200	3.70
Gang Wang/Electrochim. Acta. [11]	2012	CNT–nanofibers	110	3.30
Haibo Li/J. Electroanal. Chem. [42]	2011	Carbon nanofiber webs	95	4.60
Haibo Li/J. Mater. Chem. [45]	2009	SWCNT's	23	0.75
Zhuo Wang/Desalination [46]	2012	Graphene	25	1.80
Haibo Li/Environ. Sci. Technol. [47]	2010	Functional RGO	65	3.20
Dengsong Zhang/J. Mater. Chem. [48]	2012	Graphene-like nanoflakes	25	1.30
Haibo Li/J. Mater. Chem. [49]	2012	Graphene–CNT	29	1.40
Yue Wang/Desalination [50]	2014	Reduced graphene oxide–AC	50	2.90
Lumeng Chao/J. Mater. Chem. A [51]	2015	CNT–CNT	1000	11.00
Nalenthiran Pugazhenthiran/ACS Appl. Mater. Interfaces. [52]	2015	Polypyrrole/CNT	1000	43.99
Xiaoyu Gu/Electrochem. Acta [53]	2015	Porous carbon materials	40	34.27
Xiaoyu Gu/ACS Sustain. Chem. Eng. [54]	2015	Cellulose derived graphenic fibers	500	13.10
Changming Wang/Desalination [55]	2015	Graphene–Fe ₃ O ₄	300	10.30
		Graphene–chitosan–Mn ₃ O ₄	300	12.70
		AC	100	14.32

The XPS survey spectrum in Fig. 7A represents CA after adsorption–desorption cycles. Fig. 7a represents the XPS spectrum of CA before adsorption (also shown in Fig. 2D). After the first adsorption cycle, the material was characterized (cathode) and it showed sodium at 1072.1 eV along with carbon and oxygen

(Fig. 7b). The same material after desorption (Fig. 7c) shows a similar survey spectrum as that of the initial material (Fig. 7a). Similarly, the same material was characterized by XPS after tenth adsorption–desorption cycle (Fig. 7d and e). Sodium was getting adsorbed on to the electrodes and was desorbed completely after

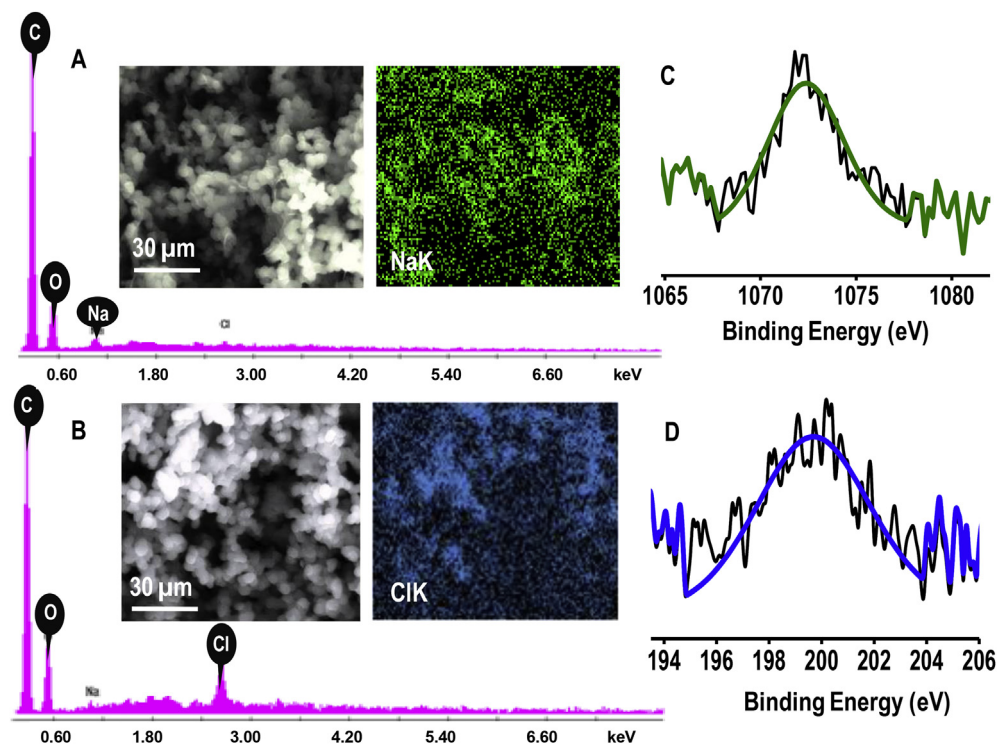


Fig. 6. SEM–EDAX of A) cathode and B) anode and the deconvoluted XPS spectrum of C) sodium in cathode and D) chloride in anode after a single adsorption cycle. (A color version of this figure can be viewed online).

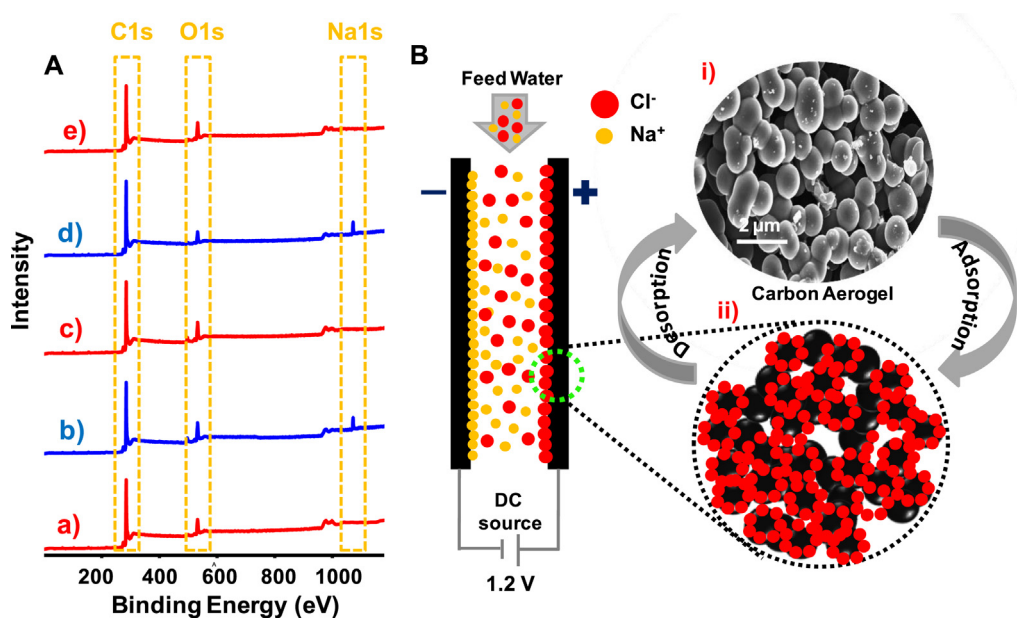


Fig. 7. A) XPS spectrum of carbon aerogel a) before adsorption (pristine CA), b) after adsorption (first cycle), c) after desorption (first cycle), d) after adsorption (tenth cycle) and e) after desorption (tenth cycle). Areas of importance are marked. B) Schematic showing the adsorption of the counter ions on the electrodes. i) FESEM image of carbon aerogel and ii) the schematic of the anode surface showing the presence of anion on its surface after adsorption. (A color version of this figure can be viewed online).

the desorption cycle. The intensity ratio of carbon:oxygen remains the same even after the tenth cycle which confirms that no oxidation is occurring on the electrode surface during the process. The deconvoluted carbon and oxygen spectra of the material (survey spectra are in traces a, d and e of Fig. 7A) show that there is no change in the oxidation state. The data are shown in SI Fig. S11. The data further confirm that the material can be used for multiple

cycles. The schematic in Fig. 7B shows the adsorption–desorption process used in multiple cycles.

4. Conclusion

In this paper we have synthesized a porous carbon aerogel with tunable porosity, high surface area of 2600 m²/g and good

mechanical strength. We employed a simple and cost effective one step sol–gel process, which avoided supercritical and freeze drying processes and did not require any hard or soft template for fabrication. This process to build a carbon inorganic framework can be easily scaled up for industrial applications such as water desalination. The as-synthesized CA was used as a CDI electrode for water desalination to remove salts such as NaCl, MgCl_2 and FeCl_3 . The NaCl removal capacity of CA with and without silica etching was determined to be 10.54 and 7.64 mg/g, respectively at 1.2 V. Multiple adsorption–desorption cycles were performed to test the efficiency of the electrodes and it was illustrated that CA can be scaled up and used in a real time water desalination unit.

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Appendix A. Supporting information

Supporting information related to this article can be found at <http://dx.doi.org/10.1016/j.carbon.2015.12.004>.

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