



# Enhanced capacitive deionization performance of activated carbon derived from coconut shell electrodes with low content carbon nanotubes–graphene synergistic hybrid additive



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## ABSTRACT

With increasing desalination demand worldwide, electrode materials for capacitive deionization (CDI) have attracted extensive attention recently. To compete with Reverse Osmosis, the performance of CDI electrode still needs to be further enhanced. In this work, graphene (Gr)/carbon nanotubes (CNTs) conducting hybrid was dispersed at as low as 1 wt% in coconut shell derived activated carbon (AC) to fabricate cost effective and high performance electrode for brackish water CDI desalination. The fabricated AC/Gr/CNTs electrodes show an excellent performance with the capacitance of 60 F/g (at 5 mV/s), the salt adsorption capacity of 9.58 mg/g and salt adsorption rate of 1.51 mg/g min at 1.0 V in 200 ppm NaCl solution. It should be highlighted that owing to the synergistic effect, the role of hybrid additive (1 wt%) was demonstrated to be more effective than that of single one, from a technical as well as from an economical viewpoint. To our best knowledge, this is the first study reporting the application of ultra-low content AC/CNTs hybrid in AC based CDI electrodes.

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## 1. Introduction

CDI has been addressed as a promising technology for the desalination process due to its cost efficient and environmentally friendly [1–4]. The CDI characterizations strongly depends upon electrode materials. Having large surface area, high porosity, good conductivity, stability and low-cost, carbon-based materials are considered as ideal for CDI system [5,6]. Derived AC contain functional groups which are beneficial to enhance electrochemical performance [7,8]. Up to now, the development of AC electrode still has had massive technological gaps, including quite low conductivity, a wide range of size distribution and irregular particle forms, all leading to poor electrical contact between AC particles. Therefore,

improving the overall electrochemical performance of AC-based materials still remains a great challenge.

In the context of large-scale production, with focus on balance between cost effectiveness and electrochemical performance, coconut shell, an abundant biomass in Mekong Delta, Viet Nam was chosen to produce CDI electrode matrix, while Gr and CNTs at their low total concentration (1 wt%) serves a hybrid additive. As proved in this study, it is an appropriate approach simultaneously exploiting the abundance of AC, the high surface area and the good electrical conductivity of Gr or/and CNTs [9,10]. Moreover, a remarkable synergetic effect between Gr and CNTs in further enhancement of conductivity, ion diffusion and overall electrochemical performance of CDI electrodes would be also demonstrated.

## 2. Experimental

First, three types of electrodes (AC/Gr, AC/CNTs, AC/Gr/CNTs) were synthesized through multi-step fabrication using AC, Gr,

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CNTs, and polyvinyl alcohol/glutamic anhydride as a binder to the polyester synthetic fiber (PESF) collector, as schematically illustrated in Fig. 1b. Regarding the electrode composition, AC, Gr or/and CNTs act as matrix and conducting agent respectively. Then, the electrodes were characterized using both batch-mode (BM, Fig. 1c) and single pass mode (SPM, Fig. 1d) setup. The salt adsorption capacity (SAC) and average salt adsorption rate (ASAR) are determined in NaCl solution (Supporting Information). The adsorption or desorption were carry out by switching voltages from 1.0 V to 0.0 V accordingly [11].

The morphology of the electrodes was investigated by field emission scanning electron microscopy (FE-SEM, JSM-6510LV, JEOL).

### 3. Results and discussion

The FE-SEM images of AC based electrodes show that the surface has a porous structure with many holes, which provide more active spaces for electrolyte-transport as well as active sites for adsorbed species (Fig. 1d-1). Thus, the morphology of AC/CNTs and AC/Gr/CNTs electrodes clearly demonstrates the homogenous dispersion of Gr, CNTs within AC. Besides, Gr sheets and CNTs in AC/Gr/CNTs electrodes were not only non-agglomerated in the

minor dispersion but their 3D porous structure also is opened and therefore the pore size was redistributed to facilitate ion transportation.

The electrodes were scanned at different sweep rates to evaluate the electroadsorption (Fig. 2). The CV curves reveal the quasi-rectangular shapes specified for the capacitive behavior of the electrodes. Accordingly, the ions were migrated on the electrode surface by electrostatic interaction to form the electric double-layer [12,13], the pores act as electrochemically active sites, the specific capacitance ( $C_{sp}$ ) can be considered as a result of the double layer formation. Briefly, the CV characteristics of the hybrid material combines specific features of single individual materials (AC, CNTs, and graphene). Particularly, the CV curve of the hybrid appeared to be more asymmetrical compared to AC. The same behavior can be found in other reports in the literature [14–16]. In our case, when the applied potential was carried out at a low scan rate (<5 mV/s), Gr or/and CNTs led to an enlargement of the voltammogram, resulting in an improvement in charge storage. This is due to the synergistic effect of the formation of the conductive network in the hybrid and the improvement of the surface area provided by AC, CNTs, and graphene components which enhanced the electroadsorption capacity of the hybrid electrodes [15]. Indeed, at a scan rate of 5 mV/s, AC/CNTs and AC/Gr/CNTs electrodes (1 wt%) show

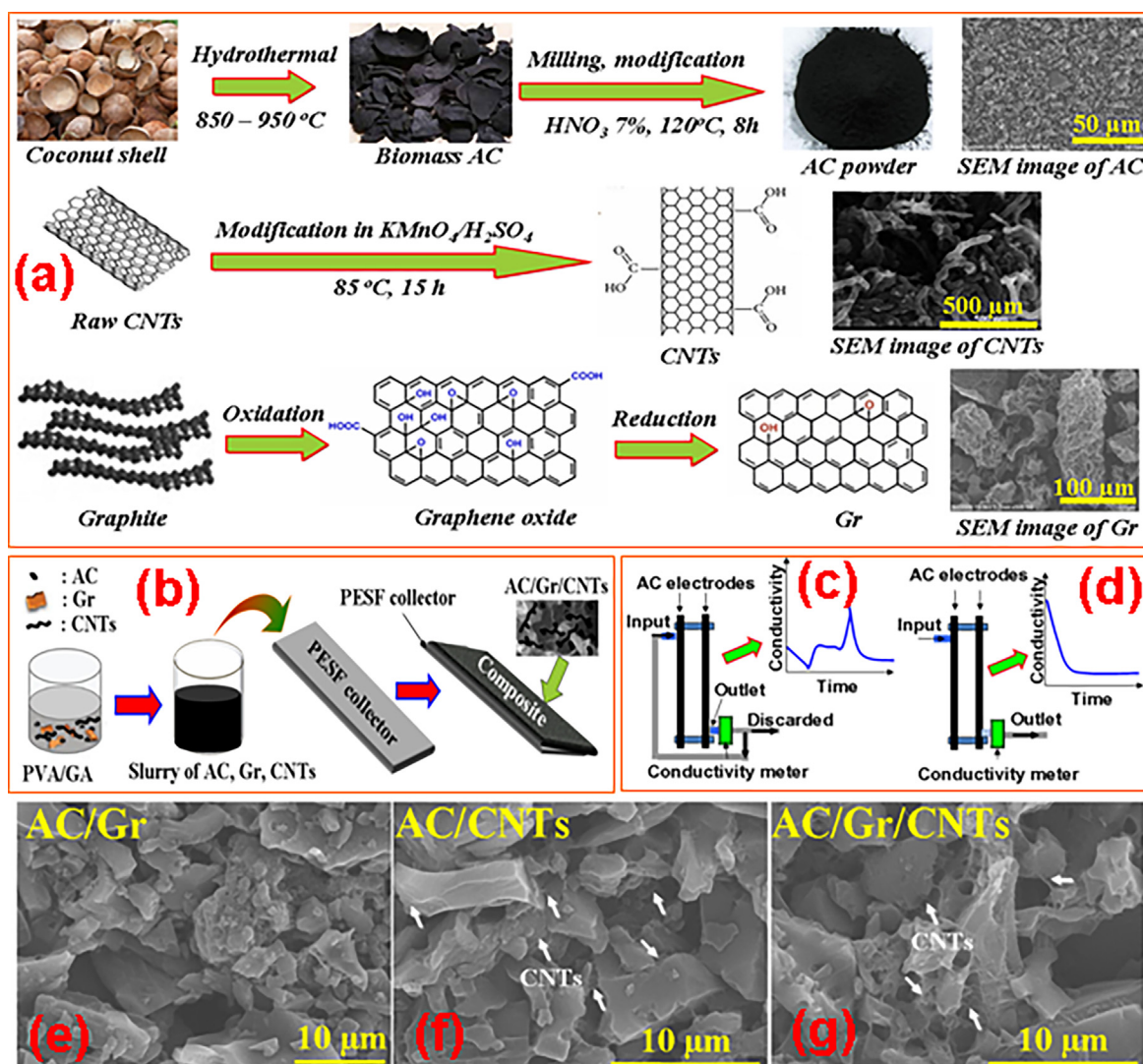


Fig. 1. Pretreatment of AC, CNTs, Gr (a); multi-step electrode fabrication (b); BM setup (c); SPM setup (d); FE-SEM images of AC/Gr (e), AC/CNTs (f); AC/Gr/CNTs (g).

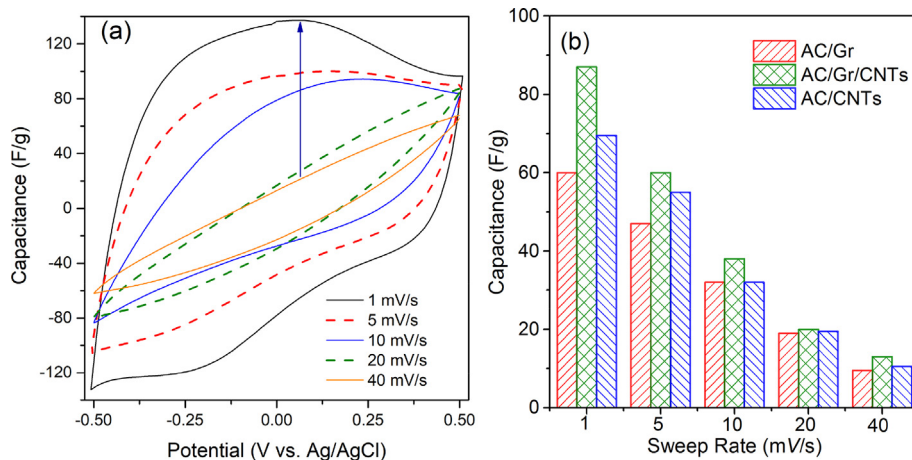


Fig. 2. Voltammograms of AC/Gr/CNTs (a); Capacitance vs. sweep rate (b).

significantly higher capacitance values (55 F/g and 60 F/g, respectively) compared to those of the normalized electrodes with same composition and content of AC and CNTs (with <40 F/g), as reported [17].

The higher specific capacitances of the electrodes at lower scan rates (Fig. 2a) are explained in more details as follows: at lower rates there is enough time for ions to penetrate deeply into pores producing higher charges and higher specific capacitance.

Moreover, the highest  $C_{sp}$  value for AC/Gr/CNTs electrodes can be interpreted taking into account excellent conductivity of individual Gr and CNTs ( $10^4$ ,  $\sim 10^7$  S/m, respectively) as well as synergistic effect of Gr and CNTs when CNTs could effectively prevent Gr from restacking and further enhance their overall conductivity and electrochemical performance. Logically, it can be expected that the AC/Gr/CNTs electrodes should exhibit much better electroadsorption performance compared to pure AC or single AC/Gr, AC/CNTs

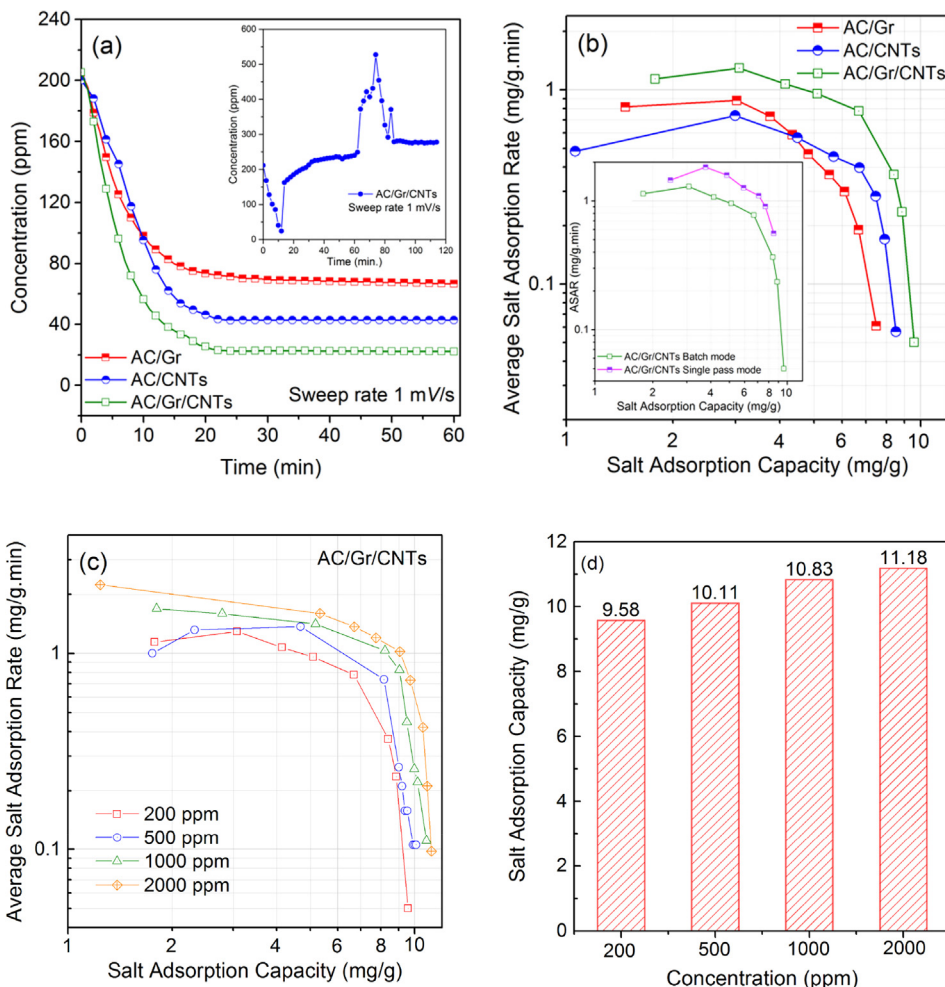


Fig. 3. NaCl concentration change in BM and SPM (inset) setup (a); Ragone plot for AC/Gr, AC/CNTs and AC/Gr/CNTs electrodes in BM setup (inset BM vs SPM) (b); Ragone plot vs. NaCl concentration (c) SAC of AC/Gr/CNTs vs. NaCl concentration (d).

**Table 1**  
SAC comparison among AC based electrodes.

Electrode composition	Salinity (ppm)	Operation voltage (V)	SAC (mg/g) (batch mode)	Ref.
AC	250	1.2	1.98	[20]
AC/PANi	250	1.2	3.15	[20]
ACC	1000	1.6	5.4	[21]
AC/rGO (80/20 wt%)	50	1.2	2.94	[22]
ACF/CNTs (5/95 wt%)	400	1.2	6.4	[23]
Gr/CNTs (1/20 wt%)	780	2.0	26.4	[24]
AC/CNTs (90/10 wt%)	200	1.0	14.1	[11]
AC/Gr (99/1 wt%)	200	1.0	7.49	This work
AC/CNTs (99/1 wt%)	200	1.0	8.51	This work
AC/Gr/CNTs (99/0.5/0.5 wt%)	200	1.0	9.58	This work

PANi: Polyaniline; ACC: Activated carbon cloth; ACF: Activated carbon fiber; rGO: Reduced Graphene oxide.

electrodes, meaning that Gr/CNTs hybrids could serve as a bridge to form a “plane-to-point” (Gr-to-CNTs-to-AC) conducting network, within which ion transfer was greatly improved [7,10,18,19].

The SAC values in BM setup calculated by Eq. (2) (Supporting Information) were 7.49, 8.51 and 9.58 mg/g, corresponding to the removal efficiencies of 67%, 77% and 87% for AC/Gr, AC/CNTs and AC/Gr/CNTs (in 200 ppm NaCl solution), respectively. Based on the literature data for AC based electrodes, NaCl concentration was usually set between 100 and 2000 ppm, thus, for comparative purposes, solution with 500, 1000 and 2000 ppm of NaCl concentration was selected in our study. It can be seen that SAC and ASAR increase with increasing concentration of NaCl, the highest SAC and ASAR values, obtained for the 2000 ppm NaCl concentration were 11.18 mg/g and 1.74 mg/g min, respectively (Fig. 3d).

The SAC comparison with other AC based electrodes reported in the literature was also listed in Table 1. The following remarks can be drawn: i) the voltage applied in our study is much lower than that of other reported electrodes (typically from 1.2 to 1.6 V or even at 2.0 V) and is fallen into non-Faradaic window (i.e. <1.23 V to avoid water electrolysis); ii) despite comparing SAC values between different electrodes can be problematic due to impossible fixing to the same experimental conditions (electrode composition, salinity, etc...), however, among AC based electrodes, in term of balancing between SAC and additive content, the highest SAC value of 9.58 mg/g was achieved by our AC/Gr/CNTs (99/0.5/0.5 wt%) electrode.

It should be highlighted that both SAC and ASAR values obtained with our AC/Gr/CNTs electrodes are much higher than those of the biomass coconut shell derived AC, surface-area-normalized based electrodes (9.58 mg/g and 1.51 mg/g/min for our electrodes vs. 3.5–4.6 mg/g and 0.5–0.8 mg/g/min for others, as previously reported [23–27]). This finding signifies that added Gr/CNTs hybrid (despite at very low content) synergistically enhance not only the salt adsorption capacity but also the adsorption rate, allowing CDI systems to operate at faster flowrate with less energy consumption.

Except for the BM setup, CDI characteristic parameters could be also determined from SPM experiment. As evidenced in Fig. 3b (inset), Ragone plot of SPM located at upper and right side, showing that SPM is more effective than BM, in term of both SAC and ASAR key parameters.

#### 4. Conclusion

In this study, a particular focus is given to synergistic Gr/CNTs hybrid dispersed at low content into AC for producing high performance (in term of large specific capacitance, high desalination capacity SAC and ASAR) and cost effective (in term of abundant coconut shell derived AC, ultra-low content Gr/CNTs hybrid) CDI composite electrodes. Enhanced electrochemical performance of

AC/Gr/CNTs composite electrodes was clearly demonstrated. In summary, this work provides a simple, low cost, controllable and scalable approach to produce very promising electrode materials for CDI desalination systems.

#### CRediT authorship contribution statement

**Thi Thom Nguyen:** Investigation. **Le Thanh Nguyen Huynh:** Investigation. **Thi Nam Pham:** Methodology. **Thanh Nhut Tran:** Methodology. **Thi Thanh Nguyen Ho:** Data, curation. **Tien Dai Nguyen:** Data curation. **Thi Thu Trang Nguyen:** Project administration, Resources. **Thi Kieu Anh Vo:** Software. **Gia Vu Pham:** Project administration. **Viet Hai Le:** Writing- Original draft preparation, Review. **The Tam Le:** Formal analysis. **Thai Hoang Nguyen:** Visualization. **Hoang Thai:** Supervision. **Trong Lu Le:** Validation. **Dai Lam Tran:** Conceptualization, Funding acquisition, Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2021.129652>.

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