# Acidified Bamboo-Derived Activated Carbon/Manganese Dioxide Composite as a High-Performance Electrode Material for Capacitive Deionization

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Capacitive deionization (CDI) is an emerging desalination technology which employs high surface area porous electrode materials to eliminate ions from water by electrosorption. Herein, we propose an acidified bamboo-based activated carbon (BAC<sub>a</sub>)/manganese dioxide (MnO<sub>2</sub>) composite synthesize by a simple co-precipitation technique. Bamboo-based activated carbon exhibit high electrical conductivity, hierarchical pore structure, and large specific surface area, due to which it is regarded as a promising candidate for seawater desalination. In this work after acidification, significant amounts of oxygen-containing functional groups are introduced onto the surface of the carbon, which enhanced the hydrophilicity of whole composite, while the MnO<sub>2</sub> nanoparticles with sufficient ion migration channels provide a high adsorption capability and fast reaction kinetics. Consequently, the synthesized BAC<sub>a</sub>/MnO<sub>2</sub> composite achieves a tremendous specific capacitance of 158 F g<sup>-1</sup> at 10 mV s<sup>-1</sup>, excellent electrosorption capacity of 10.3 mg g<sup>-1</sup>, and outstanding recyclability in the application of CDI, which is in comparison better than that of bare bamboo-based activated carbon electrode. The present study endorses the promising application of the low-cost high-performance BAC<sub>a</sub>/MnO<sub>2</sub> in capacitive deionization.

Keywords: biomass, activated carbon, acidification, manganese dioxide, capacitive deionization

## **1. INTRODUCTION**

Recently, water lacking and associated demand of recycling it has put forward a significant amount of limelight on desalination technology [1]. Over the years, capacitive deionization (CDI) emerged as a robust, and famous technique for seawater desalination [2-4]. As compared to traditional approaches such as nuclear distillation [5], electrodialysis (ED) [6], and reverse osmosis (RO) [7], CDI has edge of environmental friendliness, low cost, high energy efficiency, less to none secondary pollution, and high salt adsorption capacity [8, 9]. CDI mechanism is based on the electrochemical double-layer capacitor [10], which includes the charging of electrodes, as a result the anions and cations in the saline are attracted towards the positive and negative electrodes respectively. Moreover, the ions released as long as the potential is removed, enabling the recycling of electrodes, which causes a long lifetime of CDI equipment.

The electrosorption effect of CDI is estimated by the properties of electrode material itself, such as specific surface area, hydrophilicity, and electrical conductivity [11-13]. Carbon materials are the most common electrode materials in CDI cells for instance graphene [14], carbon aerogels [15], carbon nanotubes [16], activated carbon [17, 18], and ordered mesoporous carbon [4, 19]. However, the complexity in preparation process and expensive price of these materials limits the practical application of CDI. To deal with these issues, many reports have been reported with one of them is focused on preparing porous biomass-derived carbon materials, such as tamarind shells [20], sugarcane bagasse [21], coconut shells [22], and banana peels [23]. Their characteristics of high specific surface area, low cost, and environmental friendliness had been validated to meet the requirements of CDI electrodes [24, 25]. Recently, bamboo attained a lot of attention due to its rapid growth so to become harvest-ready in approximately three years, and the cognate of bamboo such as bamboo charcoal is also a promising material in desalination due to its porous structure, abundant raw materials, and environmental friendliness [26-28], but, its poor hydrophilicity and low specific capacitance severely affect the desalination performance. In order to deal with low hydrophilicity, an approach regarding modification of carbon materials by introducing oxygen-containing functional groups was adopted by many researchers [29, 30]. With regards to poor specific capacitance various strategies were researched with one of them is compounding the bamboo charcoal with Transition Metal Oxides (TMO) which is a one universal method to enhance specific capacitance of the carbon materials [31-34]. Among TMO's manganese dioxide (MnO<sub>2</sub>) could be a good choice because of its high theoretical specific capacitance, nature friendliness, and low cost efficiency [35-37]. However, the application of  $MnO_2$  is severely restricted by the poor conductivity [38]. To salvage from this drawback, carbon materials could play a vital role because compositing MnO<sub>2</sub> with carbon materials can drastically improve the conductivity and enhance the electrochemical performance via the combination of pseudo-capacitance and electrochemical double-layer capacitance [39, 40].

Herein, we successfully prepared acidified bamboo-based activated carbon (BAC<sub>a</sub>)/manganese dioxide (MnO<sub>2</sub>) composite by a simple coprecipitation method and employed it in the CDI cell. The bamboo-derived activated carbon with good electrical conductivity and high specific surface area was obtained by carbonization and activation method. After further acidification treatment, a lot of oxygen-containing functional groups are introduced onto the surface, which effectively improved the hydrophilicity of biomass carbon material and the infiltration of salt solutions while the MnO<sub>2</sub> nanoparticles with large channels anchored on acidified bamboo-based activated carbon improves the overall desalination performance. As a CDI electrode, the BAC<sub>a</sub>/MnO<sub>2</sub> exhibits an excellent electrosorption capacity of 10.3 mg g<sup>-1</sup>, which is 1.16 times higher than that of bamboo-based activated

carbon electrode (8.85 mg g<sup>-1</sup>). This work gives a new insight on the green and sustainable synthesis of carbon/metal oxide composite materials, which have broad application prospects in CDI technology.

#### 2. EXPERIMENTAL SECTION

#### 2.1. Materials

Bamboo was supplied by international center for bamboo and rattan. Potassium hydroxide (KOH), hydrochloric acid (HCl), sodium chloride (NaCl), hydrochloric acid (HNO<sub>3</sub>), potassium permanganate (KMnO<sub>4</sub>), manganese sulfate (MnSO<sub>4</sub>), acetylene black, polyvinylidene fluoride (PVDF), and n-methyl-2-pyrrolidone (NMP) were obtained from Sinopharm Chemical Reagent Co., Ltd. All reagents used in this experiment were of analytical grade without further purification.

#### 2.2. Materials synthesis

#### 2.2.1. Preparation of acidified bamboo-derived activated carbon (BACa)

The bamboo was cleaned by using deionized water and then dried in an oven for 12 h. It was then heated at 900 °C for 2 h in a tubular furnace under a nitrogen atmosphere. The obtained sample was blended homogeneously with KOH powder at a mass ratio of 1: 4. Afterwards the product was transferred into a nickel crucible and annealed at 800 °C for 2 h in the tubular furnace under a nitrogen atmosphere. After reaching to a room temperature, the sample was washed with HCl and then by deionized water until neutrality achieved. The final product obtained was named as bamboo-derived activated carbon (BAC).

2 g BAC and 200 mL HNO<sub>3</sub> (20%) were placed in a three-necked flask, and then the mixture was refluxed for 8 h at 85 °C in a constant temperature water bath. The sample was washed via utilizing deionized water until neutrality is reached and then dried to obtain the acidified bamboo-derived activated carbon (BAC<sub>a</sub>).

# 2.2.2. Preparation of acidified bamboo-derived activated carbon/manganese dioxide composite $(BAC_a/MnO_2)$

The BAC<sub>a</sub>/MnO<sub>2</sub> was prepared by chemical coprecipitated method. 2 g BAC<sub>a</sub> was dispersed in 80 mL H<sub>2</sub>O, 27.6 mL 0.01 M MnSO<sub>4</sub>·H<sub>2</sub>O, and 13.8 mL 0.01 M NaOH solution. After stirring for 3 h, 9.2 mL 0.01 M KMnO<sub>4</sub> was added. The solution was filtered and washed after the completion of reaction. And then the sample was calcined with a muffle furnace at 200 °C for 6 h. The final product obtained was named as acidified bamboo-derived activated carbon/manganese dioxide composite (BAC<sub>a</sub>/MnO<sub>2</sub>). By changing the amounts of MnSO<sub>4</sub>·H<sub>2</sub>O and KMnO<sub>4</sub>, the composites were prepared with different MnO<sub>2</sub> contents (1%, 5%, 10%, and 20%).

#### 2.3. Characterization

The morphologies of the samples were characterized by scanning electron microscopy (SEM, Zeiss Supra55), X-ray diffraction (XRD, Rigaku D/max-2500B2+/PCX system, Cu K  $\alpha$ ,  $\lambda = 1.54056$ Å,  $2\theta = 5-90^{\circ}$ ), Fourier-transform infrared spectroscopy (FT-IR, Nicolet iS50). The BET specific surface area and the BJH pore size distribution were obtained by N<sub>2</sub> adsorption-desorption isothermal (ASAP2020, Micromeritics). Thermal properties of samples were investigated through thermogravimetric (TG) analysis using a NETZSCH-STA449C under an oxygen atmosphere.

#### 2.4. Electrochemical analysis

The electrochemical performance of the above samples was evaluated in a two-electrode system. The working electrode was made by mixing as-synthesized material with PVDF and carbon black with a mass ratio of 8:1:1. The homogeneous paste was evenly coated onto the surface of the nickel foam  $(1.96 \text{ cm}^2)$ . Two electrode plates with similar active material content were selected to form a group, separated by a cellulose separator in the middle, assembled into a button-type CR2032 two-electrode capacitor. Primarily, galvanostatic charge/discharge measurement was operated on CT2001A at different current densities. Cyclic voltammetry (CV) test was performed with a CHI660B electrochemical workstation at scan rates ranging from 10 to 200 mV s<sup>-1</sup>.

#### 2.5. CDI experiment

The performance of the CDI electrode was conducted through a recycling system (Fig. 1), and the photos of related equipment are shown in Fig. S1. The 150 mL of sample solution was circulated through the CDI cell by a peristaltic pump (BQ80S) at 10 mL min<sup>-1</sup>. The CDI cell consisted of electrodes on both sides, which were separated by a spacer at 1 mm for a solution to flow. The self-made plexiglass water tank was cut into different numbers of card slots to increase the amount of brine treatment and to enhance the contacted area between the active material and treatment liquid. The applied voltage operated by the CT2001A is 1.2 V. The change of the solution concentration was recorded by a conductivity meter (FE30). The electrosorption capacity (S, mg g<sup>-1</sup>) was calculated by the following formula:

$$S = \frac{\left(C_0 - C_f\right)V}{M} \quad (1)$$

where M is the mass of the active material (g), V is the volume of solution (L),  $C_0$  and  $C_f$  represent the original and final concentrations of NaCl solution (mg L<sup>-1</sup>), respectively.



Figure 1. Schematic diagram of capacitive deionization system.

#### **3. RESULTS AND DISCUSSION**

The SEM micrograph of the samples are shown in Fig. 2. The longitudinal and transverse section of BAC can be seen from Fig. 2a and its inset respectively, which confirms the retention of natural honeycomb-like structure of bamboo. There are many nano-sized holes in the skeleton of acidified activated carbon, which could be originated by KOH etching during the activation process (Fig. 2b and c). The hierarchical porous structure of BAC promotes the ion migration and the permeability of the electrolyte. As shown in Fig. 2d-f, MnO<sub>2</sub> nanoparticles can be clearly seen on the surface of BAC<sub>a</sub>, which proves that MnO<sub>2</sub> nanoparticles were successfully anchored on the activated carbon due to the chemical coprecipitated method. These  $\alpha$ -MnO<sub>2</sub> nanoparticles with large channels will help in enhancing the overall electrolyte penetration [41], and also provide high specific capacitance which is critical to the energy storage devices.

For the structural analysis, the samples were analyzed by XRD, FT-IR and TG (Fig. 3). As shown in Fig. 3a, BAC and BAC<sub>a</sub> display the broad peaks at around 21° and 43°, indexed to the crystal planes of (002) and (100) [26]. The results indicate the presence of highly amorphous carbon phase in BAC<sub>a</sub>, and also validate the preservation of crystallinity during the acidification treatment. For the BAC<sub>a</sub>/MnO<sub>2</sub> composite, four diffraction peaks are observed at 17°, 25°, 35°, and 42°, which corresponds to the phase of  $\alpha$ -MnO<sub>2</sub> (JCPDS no. 44-0141) [42]. It also confirmed that MnO<sub>2</sub> nanoparticles are uniformly distributed in the BAC<sub>a</sub>, which is highly in accordance with SEM result.



Figure 2. SEM images of (a) BAC, (b, c) BAC<sub>a</sub>, and (d-f) BAC<sub>a</sub>/MnO<sub>2</sub>.

The FT-IR spectrum of BAC<sub>a</sub> shows a strong peak at around 3425 cm<sup>-1</sup>, which is indicative of the free hydroxyl groups on the functionalized BAC<sub>a</sub> surface (Fig. 3b). Compared with BAC, the weak diffraction peak at 1637 cm<sup>-1</sup> and another stronger peak at 1706 cm<sup>-1</sup> of BAC<sub>a</sub> corresponding to stretching vibrations of C=C and C=O are due to the reduction of C=C and the formation of more oxygen-containing bonds introduced by acidification [43]. The oxygen-containing bonds provide numerous active sites for chemical sorption and improve the hydrophilicity of the material. In the spectrum of BAC<sub>a</sub>/MnO<sub>2</sub>, the peak at 1050 cm<sup>-1</sup> denoting the presence of the alkoxy C-O became weak significantly, which is probably related to the formation of Mn-O-C. In addition, a new absorption band appeared at 615 cm<sup>-1</sup> that is associated with the stretching vibration of Mn-O [44].



Figure 3. (a) XRD, (b) FT-IR spectra, and (c) TG analysis of the BAC, BAC<sub>a</sub>, BAC<sub>a</sub>/MnO<sub>2</sub>.

To identify the content of  $MnO_2$  in the composite, TG analysis of the samples was carried out (Fig. 3c). The initial weight loss of 4wt% below 350 °C is due to the removal of water. The subsequent

decrease from 350 °C to 500 °C is derived from the oxidation of activated carbon in the air. Eventually, the ratio of MnO<sub>2</sub> in the composite is measured to be ca. 19.3wt%. In addition, compared with BAC and BAC<sub>a</sub>, there is a slightly increase in the thermal stability for BAC<sub>a</sub>/MnO<sub>2</sub> which can be seen from TG analysis. The N<sub>2</sub> sorption isotherm and the BJH pore size distribution of BAC<sub>a</sub> are displayed in Fig. S1. It exhibits a typical type I isotherm behavior and the specific surface area of BAC<sub>a</sub> is 1747 m<sup>2</sup> g<sup>-1</sup> with average pore diameters ranging between 0.5-3 nm. The micropore structure will help to improve the charge transmission at the interface of electrode/electrolyte, promoting the electrochemical performance of the materials.



Figure 4. (a) GCD curves at 0.1 A g<sup>-1</sup>, (b) CV plots at 100 mV s<sup>-1</sup> of the BAC, BAC<sub>a</sub>, and BAC<sub>a</sub>/MnO<sub>2</sub> composite. (c) The BAC<sub>a</sub>/MnO<sub>2</sub> composite at various scan rates in 0.1 M NaCl aqueous solution. (d) Specific capacitances of the electrodes at various scan rates. (e) the cycle performance of the BAC<sub>a</sub>/MnO<sub>2</sub> measured at 0.1 A g<sup>-1</sup>. (f) Constant charge/discharge curves of the BAC<sub>a</sub>/MnO<sub>2</sub> at 0.1 A g<sup>-1</sup>.

The GCD curves at 0.1 A g<sup>-1</sup> and the CV plots at 100 mV s<sup>-1</sup> of the as-prepared samples show ideally isosceles triangular and rectangular shapes (Fig. 4a and b). Compared with BAC and BAC<sub>a</sub>, the BAC<sub>a</sub>/MnO<sub>2</sub> shows longer discharge time and a larger area of the CV curve, which is due to the incorporation of MnO<sub>2</sub> improving the overall specific capacitance of the BAC<sub>a</sub>/MnO<sub>2</sub> composite. Fig. 4c displays the CV plots of BAC<sub>a</sub>/MnO<sub>2</sub> composite at various scan rates in 0.1 M NaCl. The shapes of CV curves (10 mV s<sup>-1</sup>-200 mV s<sup>-1</sup>) deform into a leaf-like shape due to the resistance and polarization of the electrodes. The composite BAC<sub>a</sub>/MnO<sub>2</sub> exhibits specific capacitance of 158, 85, 64, and 50 F g<sup>-1</sup> at 10, 50, 100, and 200 mV s<sup>-1</sup> as represented in Fig. 4d. The specific capacitance decreases as the scan rate increases, which is due to the reason that ions do not have enough time to diffuse into electrode material at high scan rate, and therefore some internal active MnO<sub>2</sub> cannot be fully utilized. The energy storage mechanism of MnO<sub>2</sub> is as follows [45]:

$$(MnO_2)_{surface} + C^+ + e^- \leftrightarrow ([MnO_2]^-C^+)_{surface} \quad (2)$$
  
$$MnO_2 + C^+ + e^- \leftrightarrow ([MnO0]^-C^+)_{intercalation} \quad (3)$$

where C<sup>+</sup> refers to protons (H<sup>+</sup>) or alkaline cations (e.g. Na<sup>+</sup>, Li<sup>+</sup>, and K<sup>+</sup>). These are based on the adsorption/desorption and intercalation/deintercalation of protons and cations on MnO<sub>2</sub>. From the cycling and constant charge/discharge test at 0.1 A g<sup>-1</sup>, it can be observed that the specific capacitance does not seen to be decay even after 500 cycles and all charge-discharge curves show good triangular and symmetrical shapes (Fig. 4e and f). These results reveal that the BAC<sub>a</sub>/MnO<sub>2</sub> has good cycling stability and reversibility. The electrochemical properties of the composites with different MnO<sub>2</sub> content are given in Fig. S2. Among them, the BAC<sub>a</sub>/MnO<sub>2</sub> with 1% MnO<sub>2</sub> shows the best capacitive performance. The trace amount of MnO<sub>2</sub> doping, based on the synergistic effect of double-layer capacitance of BAC<sub>a</sub> and pseudo-capacitance of MnO<sub>2</sub>, greatly improves the electrochemical performance of the BAC<sub>a</sub>/MnO<sub>2</sub> composite.



**Figure 5.** (a) Capacitive deionization performance, and (b) electrosorption capacities of the samples. (c) The desalination-regeneration curve of the BAC<sub>a</sub>/MnO<sub>2</sub> composite electrode.

In order to test the desalination performance of the sample electrode, experiments were performed in 150 mL NaCl aqueous solution. Fig. S3 illustrates the effects of the salt solution flow rate, working voltage, and plate spacing on the desalination performance. The higher the voltage, the better the desalination effect. However, the salt solution becomes pale yellow when the voltage exceeds 1.2 V.

This may be owing to the water decomposition. Therefore, a working voltage of 1.2 V, a plate spacing of 1 mm, and a solution flow rate of 10 mL min<sup>-1</sup> are the optimal operating conditions.

As shown in Fig. 5 (a, b), the electrosorption capacity of BAC<sub>a</sub>/MnO<sub>2</sub> is evaluated to be 10.3 mg  $g^{-1}$ , which is 1.16 times higher than that of BAC. In the initial stage of the curves, the salt solution concentration of all electrodes decreased significantly, which indicates that salt ions were rapidly adsorbed. After that, the concentration prone to be constant that is due to the electrosorption saturation. The higher electrosorption capacity of BAC<sub>a</sub>/MnO<sub>2</sub> is ascribed to the rich porous structure, high adsorption capability, and effective cation intercalation. In addition, there are lots of oxygen-containing functional groups on the surface of the acidified activated carbon, improving the hydrophilicity of composite and with also enhancing the capacitor desalination performance. And MnO<sub>2</sub> can adsorb cations through reversible redox-active reactions. Among the various MnO<sub>2</sub> compositions, the BAC<sub>a</sub>/MnO<sub>2</sub> composite with lower amount (1% mass) of MnO<sub>2</sub> content showed better CDI performance (Fig. S4). Fig. 5c demonstrates the regenerated electrosorptive capacity of the BAC<sub>a</sub>/MnO<sub>2</sub> electrode. It can be seen that the initial salt solution concentration decreases slightly. As compared to other studies (Table 1), the as-prepared BAC<sub>a</sub>/MnO<sub>2</sub> composite exhibit a better electrosorption capacity as CDI electrode. The good electrosorption capacity of BACa/MnO2 composite is due to the salt ions that are concurrently captured by the quasi-capacitive charge storage reaction of MnO<sub>2</sub> and the electric doublelayer of porous biomass activated carbon.

Materials	Original NaCl concentration $(mg L^{-1})$	Applied voltage (V)	Electrosorption capacity (mg g <sup>-1</sup> )	Ref.
BAC <sub>a</sub> /MnO <sub>2</sub>	~105	1.2	10.3	This
				work
Graphene	50	1.2	4.76	[46]
<b>SWCNTs</b>	500	1.6	5.8	[47]
GE aerogel	1500	1.2	9.9	[48]
MnO <sub>2</sub> /NPC	50	-	0.988	[49]
CNTs	3500	1.2	8.9	[16]
MC	1230	1.2	6.1	[50]
AC-MnO <sub>2</sub>	~25	-	0.99	[51]
GNS-MnO <sub>2</sub>	100	1.2	5.01	[52]
GE/AC	500	1.2	2.9	[53]
MnO <sub>2</sub> @ MWCNTs	~87	1.8	6.65	[54]

Table 1. The comparison of electrosorption capacities of various carbon materials<sup>a</sup>.

<sup>a</sup>Note: NPC for nanoporous carbon, MC for mesoporous carbon, and GNS for graphene nanosheet.

#### 4. CONCLUSION

In summary, we have designed an acidified bamboo-based activated carbon (BAC<sub>a</sub>)/manganese dioxide (MnO<sub>2</sub>) composite by a simple coprecipitation method. Acidified biomass activated carbon

possesses good electrical conductivity, specific surface area, and wettability. Besides  $MnO_2$  nanoparticles are anchored uniformly both on the surface as well as deep within the pores of the acidified biomass activated carbon, which considerably improves the specific capacitance of the BAC<sub>a</sub>/MnO<sub>2</sub> (158 F g<sup>-1</sup> at 10 mV s<sup>-1</sup>). And the composite shows good cycling reversibility after 500 cycles. Furthermore, the electrosorption capacity of BAC<sub>a</sub>/MnO<sub>2</sub> electrode is 10.3 mg g<sup>-1</sup>, which is 1.16 times higher than that of BAC. The remarkable CDI performance of BAC<sub>a</sub>/MnO<sub>2</sub> can be ascribed to the synergistic effect of the fast quasi-capacitive of MnO<sub>2</sub> and the electric double-layer of carbon material. This work provides a general approach to design and fabricate biomass carbon/transition metal oxide composites for capacitive deionization.

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## SUPPORTING INFORMATION



Fig. S1. The photos of (a) CDI circulating system, (b) conductivity meter, (c) CDI cell, and (d) CDI electrodes.



Fig. S2. (a) N<sub>2</sub> adsorption isotherm, and (b) pore size distribution of the BAC<sub>a</sub>.

The mass fraction of  $MnO_2$  was 1%, 5%, 10% and 20%, named as 1%  $MnO_2$ , 5%  $MnO_2$ , 10%  $MnO_2$ , and 20%  $MnO_2$ .



**Fig. S3.** GCD curves of the BAC<sub>a</sub>/MnO<sub>2</sub> with different contents at 0.1 A  $g^{-1}$ .



**Fig. S4.** Capacitive deionization performance (a) at different flow rates, (b) at different potentials, and (c) at different distances between two electrodes.



Fig. S5. Capacitive deionization performance of the BAC<sub>a</sub>/MnO<sub>2</sub> with different contents.

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