Highly pore-expanded benzidine-functionalized graphene framework for enhanced capacitive deionization

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GRAPHICAL ABSTRACT
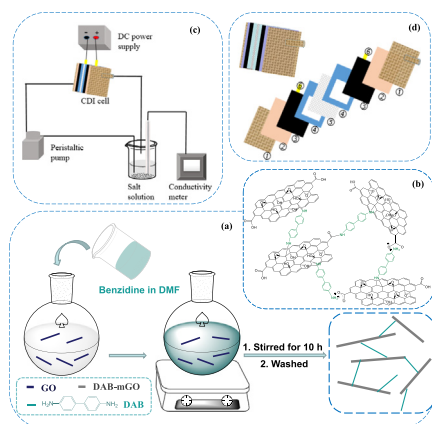
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ABSTRACT

Capacitive deionization (CDI) is a promising technology for water 0. The electrode material plays a vital role in electrosorption capacity. Its porous nanostructure can promote capacitive deionization performance. Here, a "one-pot" synthesis of *p*-phenylenediamine- or benzidine- (DAB) functionalized graphene (DAB-mGO) was achieved using graphene oxide (GO) as a precursor by simultaneous nucleophilic addition, an amide reaction and an electrostatic self-assembly technique. DAB-mGO exhibits a significantly increased conductivity, specific surface area and pore volume compared with GO, which indicates that it can be used as a CDI electrode material for desalination in brackish water. DAB-mGO$_{130}$ that was obtained at 130 °C exhibited electrosorption capacities of 7.88, 8.02 and 13.55 mg/g in Na$^+$, Mg^{2+}, Ca^{2+} solutions, respectively, at 1.4 V. These values are ~1.3–1.5 times higher than commercial activated carbon. These observations indicate that the simple organic functionalization of GO is an effective approach to increase the CDI performance because of the generation of useful

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porous nanostructures. A rational combination of organic molecules and inorganic GO can be used to fabricate environmental and economical CDI electrode for application in CDI and energy storage.

1. Introduction

Because of population growth, industrial and agricultural activities have increased, and insufficient freshwater is available to meet human existence and needs [1]. Fresh water accounts for only 3% of total water, of which < 0.36% is used by humans. [2]. It is critical that economic and effective technologies for freshwater production be established. Several desalination technologies, including reverse osmosis, ion exchange, multi-stage flash desalination, multi-effect distillation, mechanical vapor compression, nanofiltration and electrodeionization have been applied to provide freshwater [3,4]. However, these technologies are limited because of high costs, huge energy consumption and complex equipment [5]. Therefore, it is of interest for scientists and engineers to seek a safe, low-cost, simple and low energy consumption desalination technology [6].

Capacitive deionization (CDI) is an emerging desalination technology that removes charged ions from aqueous solution based on the principle of an electric double-layer (EDL), which has the advantages of low cost, low voltages (< 2 V), no secondary pollution and environmental friendliness. Although CDI technology has some outstanding merits in the terms of cost, energy and environment, it requires further development because it is difficult to screen electrode materials with a better ion-adsorption capacity and reaction rate. The salt-adsorption capacities of CDI electrodes are related closely to their conductivity, hydrophilicity, pore-size distribution, and specific surface area. Over the past decades, various forms of carbon materials have been used to fabricate CDI electrodes because of their easily tunable structural property and good electrical conductivity. These carbon materials include activated carbon (AC) [7], carbon aerogel [8], carbon fiber [9], carbon cloth [10], carbon nanotubes [11,12], mesoporous carbon [13,14], graphene [15] and their composites [16,17].

As a robust two-dimensional material, graphene, a honeycomb crystal lattice that is arranged by one-atom-thick sheets of sp^2-bonded carbon atoms, has many fascinating chemical and physical properties, such as excellent electrical conductivity (~7200 S/m), large specific surface area (theoretical value $2630\,m^2\,g^{-1}$ [18]) and high adsorption capacity [19]. During its preparation process, graphene-based materials tend to reformulate agglomerates and micropores because of the π-π interactions between graphene sheets. This makes it difficult for salt ions to obtain access to the inner layers of stacked graphene to form an EDL or leads to the overlapping of the EDL in micropores [20]. To inhibit the aggregation of graphene, Barakat et al. [21] used TiO_2 nanorods, Yang et al. [22] used Fe_3O_4, Liang et al. [11] used carbon nanotubes, Zou et al. [23] used polyaniline and Zhang et al. [24] used AC and *m*-phenylenediamine to functionalize graphene.

Here, we studied the amino-modified graphene oxide (GO) as the CDI electrode by a simple one-pot method (Scheme 1a and b). The introduction of $-NH_2$ by the covalent and noncovalent reactions exhibits some advantages: a) it inhibits the aggregation of graphene; b) it increases the hydrophilicity of the CDI electrodes because of the hydrogen bonding between $-NH_2$ and H_2O so that the electrode is in full contact with the salt solution to allow the salt ions to adsorb to the electrode more easily; and c) it allows the salt ions to adsorb more easily on the CDI electrode because of the lone pair of electrons on the $-NH_2$. To explore the desalination performance of the synthesized materials using CDI technology, DAB-functionalized GO at 130 °C (DAB-mGO₁₃₀) as a CDI electrode was used to perform deionization experiments in Na^+, Mg^{2+} and Ca^{2+} solutions.

2. Experimental

2.1. Preparation of PDA-mGO and DAB-mGO

The graphene composites were prepared by a simple one-pot method as CDI electrodes, as shown in Scheme 1a and b. First, graphene oxide (GO) was synthesized from natural graphite by the modified Hummers method [25]. GO was functionalized by *p*-phenylenediamine (PDA) and benzidine (DAB) at different temperatures by using a simultaneously covalent nucleophilic addition reaction and noncovalent electrostatic self-assembly and was termed as PDA-mGO and DAB-mGO, respectively. Briefly, 100 mg GO was dispersed in 50 mL DMF, and 0.5 g PDA was dissolved in another 10 mL DMF solution. The two solutions were mixed, and then stirred for 10 h at different reaction temperature (80, 100, 120 and 130 °C) by a facile one-pot method. After cooled to room temperature, the product were washed for several times with ethanol and dried at 60 °C in vacuum for overnight (Scheme 1a and b). For easy expression, PDA-mGO₈₀ represents the product prepared at 80 °C. Similarly, DAB-mGO nanomaterials obtained at different temperatures (100, 120, 130 and 140 °C) were termed as DAB-mGO₁₀₀, DAB-mGO₁₂₀, DAB-mGO₁₃₀ and DAB-mGO₁₄₀, respectively.

2.2. Electrochemical performance of the synthesized electrodes

All electrochemical performances of the synthesized electrodes were performed on a CHI660E electrochemical workstation (Shanghai, China) at room temperature. The conventional three-electrode mode was employed with a standard calomel electrode (SCE) as the reference electrode, and platinum wire as the auxiliary electrode. The working electrode was made by pressing prepared material (75 wt%), acetylene black (15 wt%) and PTFE (10 wt%) onto a graphite paper (10 × 10 mm). The NaCl solution (1 mol/L) was used as the electrolyte. The potential range of the cyclic voltammetry (CV) measurements was adjusted from −0.4–0.6 V and the effects of the different scan rates were examined by supplying 1, 5, 10, 20, 30, 50 and 100 mV/s.

The specific capacitance C (F/g) was calculated by integrating the area of the CV curve according to the following Eq. (1).

$$C = \frac{\int I dV}{2v\Delta Vm} \tag{1}$$

where C is the specific capacitance (F/g), I is the response current (A), ΔV is the applied potential window (V), v is the potential scan rate (V/s), and m is the mass of active electrode material (g).

Electrochemical impedance spectroscopy (EIS) measurements were performed to evaluate the conductivity of the electrodes and the data was collected. The galvanostatic charge/discharge (GCD) tests were conducted to evaluate the charge-discharge performance.

2.3. CDI experiments

The CDI electrode was made by pressing DAB-mGO₁₃₀ or AC (75 wt %), acetylene black (15 wt%) and PTFE (10 wt%) onto a graphite paper (30 × 30 mm) and each electrode mass was about 0.1 g. Scheme 1c represents the schematic diagram of the electrosorption setup of CDI. The salt solution (volume of 100 mL) with an initial conductivity of ~100 μS/cm was transported into the CDI cell (Scheme 1d) using a peristaltic pump (BT100-2J, Longer pump) and the effluent solution was continuously recycled. DC power supply (RXN-605D) is the source of working voltages of CDI cell and digital conductivity meter (Seven Excellence) was used to measured conductivity change of the solution