Journal of Colloid and Interface Science 518 (2018) 69–75

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

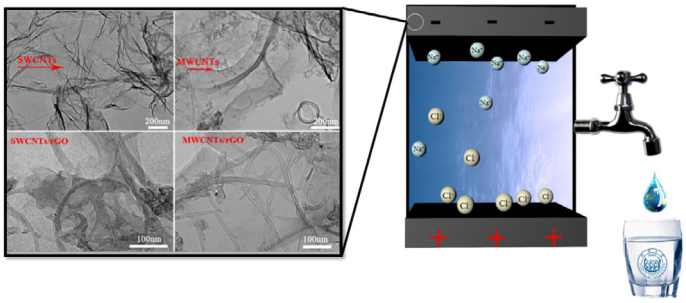
A Comparison of graphene hydrogels modified with single-walled/multi-walled carbon nanotubes as electrode materials for capacitive deionization

Jianglin Cao [a,c], Ying Wang [a], Chunyang Chen [a], Fei Yu [b,*], Jie Ma [a,c,*]

[a] State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, PR China
[b] College of Marine Ecology and Environment, Shanghai Ocean University, Shanghai 201306, PR China
[c] Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, PR China

GRAPHICAL ABSTRACT

Graphene hydrogel modified with SWCNTs or MWCNTs was used as electrode material for capacitive deionization. SWCNTs/rGO hydrogel presented a higher electrosorption capacity (48.73 mg/g) than MWCNTs/rGO, which was attributed to its high specific surface area (308.37 m^2/g) and specific capacity (36.35 F/g).



ARTICLE INFO

Article history:
Received 24 December 2017
Revised 3 February 2018
Accepted 6 February 2018
Available online 7 February 2018

Keywords:
Graphene hydrogel
Carbon nanotube
Electrode material
Capacitive deionization

ABSTRACT

Capacitive deionization (CDI) is a technology used to remove salt from brackish water, and it is an energy-saving, low-cost method compared with other methods, such as reverse osmosis, multi-stage ash distillation and electrodialysis. In this paper, three-dimensional (3D) graphene hydrogels modified with single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) were synthesized by a one-step water bath method to increase the conductivity of materials and reduce the aggregation of the graphene sheets. The CDI performance differences between the two materials were compared and discussed. The results suggested that SWCNTs/rGO had a higher electrosorption capacity (48.73 mg/g) than MWCNTs/rGO, and this was attributed to its high specific surface area (308.37 m^2/g), specific capacity (36.35 F/g), and smaller charge transfer resistance compared with those of the MWCNTs/rGO electrode. The results indicate SWCNTs/rGO is a promising and suitable material for CDI technology and we provide basic guidance for further CNTs/graphene composite research.

* Corresponding authors at: State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, PR China (J. Ma) and College of Marine Ecology and Environment, Shanghai Ocean University, Shanghai 201306, P.R. China (F. Yu).
E-mail addresses: fyu@vip.163.com (F. Yu), jma@tongji.edu.cn (J. Ma).

https://doi.org/10.1016/j.jcis.2018.02.019
0021-9797/

1. Introduction

The shortage of freshwater resources is a worldwide problem that seriously restricts society and economy developments [1,2]. Capacitive deionization (CDI) is an environmentally friendly, low cost, and low energy consumption desalination technology compared with other desalination technologies, such as reverse osmosis, multi-stage ash distillation and electrodialysis [2–4]. CDI is based on the electric double layer (EDL) capacitor theory. The electrode material is an important factor in CDI operation because the electrode material must have a large specific area, good electrical conductivity and good wettability, which are beneficial for the electrosorption capacity [5]. Carbon-based materials have been widely investigated over the past few years, especially two-dimensional (2D) graphene (GR), because of their good conductivity, good strength and flexibility. Li et al. prepared graphene by a modified Hummer's method and obtained an electrosorption capacity of 1.85 mg/g at 2.0 V [6]. However, 2D graphene still has the following shortcomings: (1) Easy aggregation due to strong π-π interactions between the graphene layers, which reduces the conductivity and specific surface area of graphene [7,8]; (2) Complicated electrode preparation methods based on graphene or graphene composite powders; (3) Binder addition results in a performance reduction and complex preparation [9].

In contrast, 3D graphene gels have the following advantages over 2D graphene: (1) The 3D, porous structure can provide more ion accumulation sites and accelerate ion transportation, which help increase the adsorption capacity[10–13]; (2) 3D graphene gels have macroscopic features and excellent mechanical properties. Therefore, they can be directly used as electrodes, which alleviates the blocking caused by binders [14,15]. Among 3D graphene materials, graphene hydrogels (GH) and graphene aerogels (GA) are widely used as electrode materials for CDI. They have similar properties, such as preventing the aggregation and restacking of graphene sheets, due to the self-assembly of the graphene sheets. However, the poor supporting capacity, low density, high cost of preparing GA compared with those of GH have limited GA applications. In addition, Chen et al. compared the electrosorption capacity of GH and GA, and the results indicated that GH has a better performance [16]. Ma et al. determined that the specific capacitance of GH (43.61 F/g) is more than two times higher than that of GA (18.65 F/g), and this is due to the water in GH that contributes to its adsorption capacity [17]. Thus, the above studies have proposed that GH is more promising for capacitive deionization due to its remarkable electrosorption capacity and specific capacitance.

Nevertheless, the low conductivity and low adsorption rate of GH limit its electrosorption performance [18]. Composites with carbon nanotubes and graphene have been shown to be a novel method to improve the GH electrosorption capacity because the inserted carbon nanotubes act as conductive networks and inhibit graphene sheet aggregation. For instance, Zhang et al. prepared graphene/carbon nanotube (GR/CNT) composites by a modified exfoliation approach, and the results show that inserting CNTs decreases the inner resistance and improves the conductivity of the electrodes compared with that of GR [19]. However, they prepared GR/CNTs powders with a binder, which blocks the electrodes and complicates the operation. In addition, different CNTs/-graphene composites have not been compared previously.

In this paper, to increase the GH conductivity and to study the performance of different types of CNTs/graphene composites, we used a one-step water bath method to synthesize 3D SWCNTs/rGO and MWCNTs/rGO and compared their different morphologies, electrochemical properties and electrosorption capacities. The results showed that SWCNTs/rGO has a better electrosorption performance of 48.73 mg/g, which is much higher than that of MWCNTs/rGO and other studies [20–22]. According to the results, we attempt to provide basic guidance for further CNTs/graphene composite research.

2. Experimental

2.1. Chemicals

All chemical reagents were of analytical grade and supplied by Sinopharm Chemical Reagent Co., Ltd. (China). These chemicals were used directly without further purification.

2.2. Preparation of the graphene and carbon nanotubes

Graphite oxide was prepared using an improved Hummer's method [23,24]. The graphite oxide was dispersed in deionized water and sonicated in an ultrasound bath for 6 h to obtain a GO aqueous dispersion. Single-walled carbon nanotubes or multi-walled carbon nanotubes were synthesized using floating catalytic chemical vapor deposition [25] and purified using a nondestructive approach [26].

2.3. Synthesis of the SWCNTs/rGO and MWCNTs/rGO

The SWCNTs (34.2 mg; the mass ratio of GO and SWCNTs, 10:1) were dissolved in a 100 mL GO solution (341.6 mg/mL) under ultrasonic conditions for 2 h. To obtain reduced graphene oxide (rGO), ascorbic acid was used as the safe, non-toxic reductant. The ascorbic acid was evenly mixed with the SWCNTs/GO solution at a mass ratio of 1:1 and then heated in water bath at 95 °C for 12 h to obtain the SWCNTs/rGO hydrogel. For the synthesis of the MWCNTs/rGO hydrogel, the same process was used, and the 34.2 mg of the SWCNTs was replaced with the MWCNTs.

2.4. Characterization

The micro-morphologies were observed by transmission electron microscopy (TEM, JEM-2100F) and scanning electron microscopy (SEM, Hitachi 54,800). In addition, a nitrogen-sorption isothermal method was used to examine the surface characteristics with an ASAP2020 instrument. The specific surface areas and pore volumes were determined by the Brunauer-Emmett-Teller (BET) method, and the Barrett-Joyner-Halenda (BJH) method was used to analyze the pore size distribution. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses were carried out with a CHI660D electrochemical workstation in a three-electrode mode, and the platinum (Pt) and Ag/AgCl electrodes were the counter and reference electrodes, respectively. The MWCNTs/rGO hydrogel or SWCNTs/rGO hydrogel was used as the working electrode, and a 1 M NaCl solution was used as the electrolyte. For the EIS test, the amplitude of the alternating current was 10 mA, and the scan frequency ranged from 0.001–1.5×10^6 Hz. For the CV test, the scanning voltage varied from −0.4 V to 0.6 V, and the specific capacitance (C, F/g) is calculated by Eq. (1):

$$C = \frac{\int IdV}{vm\Delta V} \quad (1)$$

where I (A) is the instantaneous current density, V (V) is the voltage, m (g) is the mass of the electrodes, v (V/s) is the potential scan rate, and ΔV (V) is the potential window.