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Ion-selective carbon nanotube electrodes in capacitive deionisation

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ABSTRACT

In the capacitive deionisation (CDI) process, counter-ions in the solution are adsorbed on the electrodes, and co-ions are expelled from the electrodes. This so-called co-ion effect hinders desalting performance of the electrodes. To overcome this problem, we directly grafted the carbon nanotubes (CNTs) with sulfonic and amine functional groups, using an aryl diazonium salt solution and 3-aminopropyltriethoxysilane (APTES). These grafted groups can act as ion-selective functional coatings similar to the ion-exchange membranes without adding too much electrical resistance. Also, they can increase the hydrophilicity and wettability of the CNTs' surface. The structure and electrochemical properties of functionalised CNTs are tested for CDI. Four CDI cells were assembled used different combination of the sulfonated and aminated and unmodified CNTs. Improved CDI performance was found when the modified samples were used in aspect of salt-removal capacity and/or electrosorption rate. In summary, the functionalised-CNTs electrodes enhanced the salt-removing performance in the CDI process.

1. Introduction

Fresh water scarcity [1] has prompted significant research interest in the development of new water technologies to meet the demand for an increased fresh water supply. In light of the heightened interest in finding an efficient water desalination/purification process, capacitive deionisation (CDI) technology, which is a novel environmental friendly process for brackish water desalination and water purification, has gained considerable attention from researchers worldwide [2–6]. CDI works as an electrical capacitor: charged ions, such as Na^+, Cl^-, Mg^{2+}, Ca^{2+}, Fe^{3+} and SO_4^{2-}, are electrosorbed on the surface or into the pores of the porous electrodes to form electrical double layers (EDLs) when electrical potential is applied; the ions are released from the electrodes when the charges are removed or reversed. CDI needs a low external power source (lower than 1.23 V to avoid dissociation of water molecule) [7], therefore, consumes little energy. CDI's advantages over other desalination technologies are that it does not need high pressure pumps, high operational maintenance or large amounts of thermal energy [8].

A variety of carbon materials and their composites with metal oxides or polymers were used for CDI [2,6,9–21], and it is claimed that the performance of CDI is largely dependent on the properties of the chosen electrode materials, such as suitable pore structures, excellent electrical conductivity and surface chemical characteristics. Carbon nanotubes (CNTs), as one of the most promising CDI electrode materials, has also wide applications, including advanced polymer composites, Li-ion batteries, fuel cell electrodes and biosensors, due to their unique structure, and outstanding physical and chemical properties [22,23]. In fact, the hydrophobic nature of CNTs hinders their favourable application in electrochemical and water engineering. It is generally acknowledged that surface functionalization of oxygenated groups improves the wettability of carbon surfaces, enhances the access of electrolytes to the surface of carbon electrodes and improves the capacitance value [24–27].

Co-ions effects in the CDI process is described as: counter-ions (opposite charge of electrode) in the solution are adsorbed onto the electrodes and co-ions (same charge of electrode) are expelled. This means that ion adsorption and desorption occur simultaneously in the pore volume of the electrodes, causing a serious reduction in electrosorption efficiency. To solve this problem, firstly, membrane CDI (MCDI) was proposed: a pair of ion-exchange membranes was inserted in front of the cathode and anode electrodes. The ion-exchange membranes only allow counter-ions to permeate through and act as barriers for the co-ions, thus reducing the unregulated movements of the co-ions, especially during the adsorption process [28–31]; secondly, advanced MCDI was tried: coating the carbon electrode with a base polymer, then further sulfonation and amination. The embedded ion exchangers included bromomethylated poly (2, 6-dimethyl-1, 4-phenylene oxide) (BPPO), a mixture of poly (vinyl alcohol) (PVA) and sulfosuccinic acid (SSA) [30,32]. In this paper, alternatively, we proposed a direct and effective way of grafting the ion-selective functional groups on the surface of CNTs, which can act as the ion-exchange membranes, to minimise the co-ions effects problem.

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In this study, we modified the surface of the CNTs by directly attaching sulfonic groups and amine groups using an aryl diazonium salt solution and 3-aminopropyltriethoxysilane (APTES), respectively. The resultant samples were characterised using porosimetry, spectroscopic, dynamic contact angle, conductivity and cyclic voltametric analyses. Originally, sulfonic groups were grafted on graphene to prevent them from aggregating because the charged $–SO_3^-$ groups expelled particles/graphene from restacking [33]. Meanwhile, substrates that were immersed in 3-aminopropyltriethoxysilane (APTES) gained a positive surface charge due to primary $–NH_3^+$ groups [34]. In our research, we found that the surface modifications are beneficial in two ways for CDI: they act as an ion-selective functional coating similar to the ion-exchange membranes; they also increase the hydrophilicity and wettability of the electrode surfaces.

2. Experimental

2.1. Materials

Carbon nanotubes (CNTs) were obtained from Shenzhen Nanotech Port Co. Ltd (Shenzhen, China). The same CNTs showed good capacity when used as Zn^{2+} sorbent [35]. 3-Aminopropyltriethoxysilane (APTES) was purchased from Sigma–Aldrich (Australia). Sulfanilic acid ($4\text{-}(H_2N)C_6H_4SO_3H$), sodium nitrite ($NaNO_2$), chloride acid (HCl) and nitric acid (HNO_3) were obtained from a local supplier. Mili-Q water (Millipore Co. Ltd, Australia) was used for all experiments.

2.2. Sulfonation and amination of carbon nanotubes

Prior to use, pristine CNTs were oxidised with concentrated nitric acid at 313 K for 2 h. The created carboxylic and oxygen-containing groups can attached with the hydroxyl groups of the APTES [36] and surface defects would facilitate sulfonation reaction [33]. The sample was denoted as sample C. For sulfonation, the aryl diazonium salt solution was prepared from the reaction of 0.46 g sulfanilic acid and 0.18 g sodium nitrite in 100 g water and 5 g 1 M HCl solution in an ice bath [33]. Then, 0.1 g of the sample C dispersed in 50 ml water was mixed with 2 ml of the aryl diazonium salt solution and kept in an ice bath for 2 h. The resulting sample was denoted as sample C-S. For amination, 0.1 g of sample C was dispersed in 100 ml of acetone under ultra-sonication for 1 h. Then, 0.02 ml APTES was added into the solution under stirring. In the end, the acetone was evaporated [36–38]. The obtained aminated CNTs sample was denoted as sample C-N. The process is illustrated in Fig. 1. The inserted TEM images showed the morphology of CNTs in different treatment stages. Sample C was consisted of CNTs with an average diameter of 10 nm and a length of several micrometers. The main feature was maintained after sulfonation and amination.

2.3. Material characterisations

Nitrogen adsorption–desorption isotherms of the modified CNTs were performed using a BELSORP-mini measuring unit (Particle Test Pty Ltd., Japan) at 77 K. The specific surface areas (S_{BET}) and pore size distribution (PSD) were obtained from the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH)

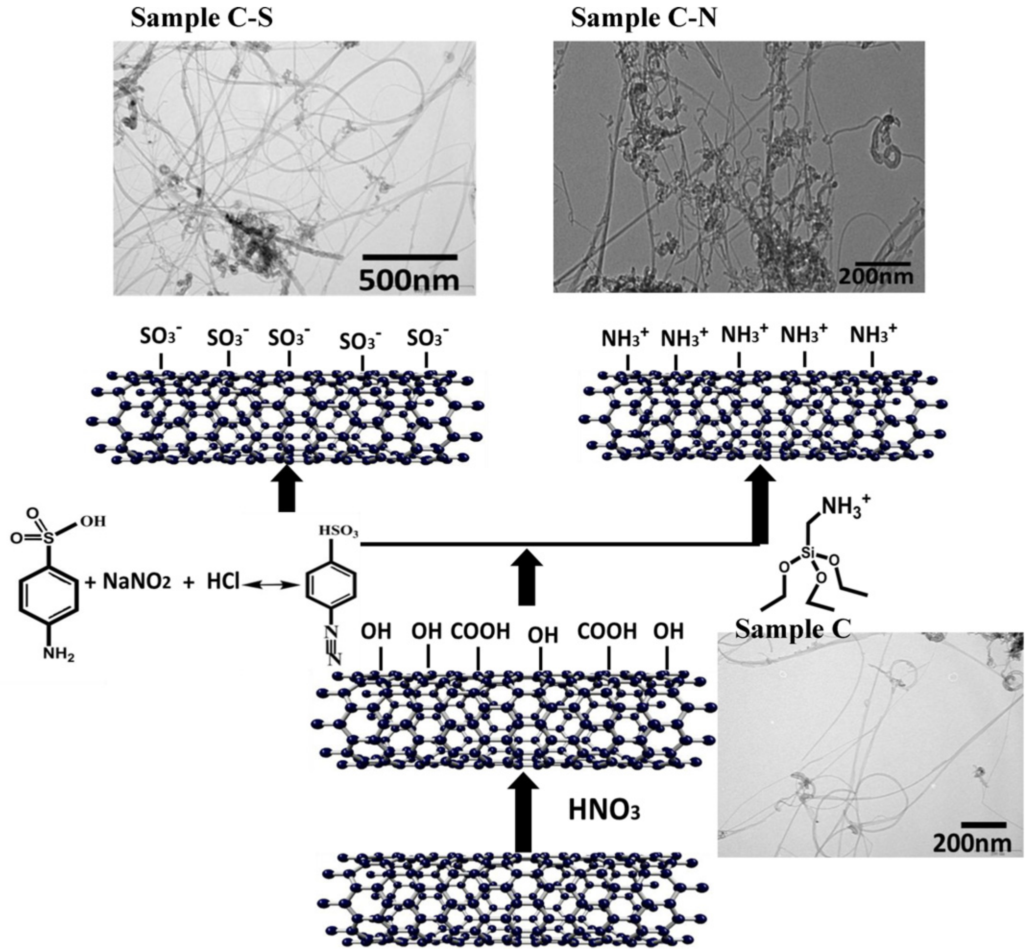

Fig. 1. Schematic representation of sulfonation and amination of CNTs.