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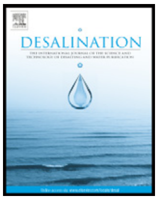

Fabrication of zinc oxide nanorods modified activated carbon cloth electrode for desalination of brackish water using capacitive deionization approach

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ABSTRACT

Capacitive deionization (CDI) is a promising technique for removing dissolved ions from saline water. This method works on electrochemical control to remove ions from aqueous solution upon electrically charging the electrodes (anode and cathode). In this work, highly porous and conducting activated carbon cloth (ACC) material modified with zinc oxide (ZnO) nanorods (ACC:ZnO) was used as base substrate in a flow through capacitor configuration. Simple and low temperature hydrothermal method was used to grow ZnO nanorods on ACC surface in an aqueous media. The desalination process was conducted using 100 ppm sodium chloride (NaCl) solution with the flow rate of 2 ml/min under an applied potential of 1.2 V. Enhancement of salt removal (desalination) and regeneration efficiency of 34% and 24% were achieved respectively.

1. Introduction

Fresh water is an essential resource for life and the necessity to provide water to ever increasing population is leading to water scarcity across the world. Especially in arid countries, accessible drinking or potable water is the major problem due to lack of resources [1]. Altering high salinity water (brackish or sea water) to very low salinity fresh water is practiced using one of the numerous desalination processes currently in use. Forward osmosis (FO), pressure driven reverse osmosis (RO), thermal distillation like multi stage flash (MSF) process and multiple-effect distillation (MED), electrodialysis (ED), ion concentration polarization and capacitive deionization (CDI) [2,3] are a few of the popular technologies in use. Each of these processes has its own advantages and disadvantages; for instance, thermal distillation need high energy [4,5], membrane fouling and complicated maintenances are associated with membrane based desalination [6], secondary pollution occurs in ion exchange desalination systems [2], among others. Single or multi step processes have been developed to circumvent disadvantages of each method. Among them, electrosorption technique or capacitive deionization approach has many advantages being low energy intensive process, relatively inexpensive, simple to regenerate and low fouling of electrodes occurs during the desalination process [7–9].

Capacitive deionization (CDI) method is an electrochemical control technique to remove ions from aqueous solutions by creating an electric double layer on the electrodes when a potential is applied. This method can be operated at low potential ranges of 1.0–1.2 V (slightly below hydrolysis of water ~ 1.23 V) thus avoiding the electrochemical reaction on electrode surfaces. In CDI technology, the electrode surface properties play a vital role in terms of surface area, micro/mesoporous structure, size distribution of pores, functional groups on the electrode surfaces and adsorption or desorption of ions on the surface [10–13]. In 1996, the first capacitive deionization (CDI) device was proposed by Caudle et al. [14] and since then activated carbon [2,15], carbon aerogels [10,16–18], carbon cloth or felt [19–21], carbon sheet [9], carbon nanotube [8,22–24], graphene nano-flakes [25], modified graphite [26] and carbon electrode [27] have been used as electrodes for the removal of ions. Ryo et al. showed that titania incorporated activated carbon and activated carbon cloth enhance the electrosorption efficiency of electrodes [19,28]. Zou et al. also reported that titania nanoparticles impregnated activated carbon electrodes were suitable for brackish water desalination [7]. Recently, Yang et al. used manganese dioxide nanoparticles in nanoporous carbon composite electrodes for capacitive deionization [29]. However, most of these carbon electrode performances need to be further improved for wider application. In this work, activated carbon cloth (ACC) modified with zinc oxide (ZnO) nanorod electrodes were fabricated and the desalination performance using a capacitive deionization (CDI) cell was monitored and reported. ZnO material is naturally hydrophilic due to the presence of hydroxyl group on the surface [30]. Higher surface to

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volume ratio of flat surface can be enhanced by one dimensional nanostructures, for instance nanowires or nanorods, decorated on flat surfaces [31]. Moreover, additional semiconducting material like ZnO on the electrode surface can enhance the electronic property of the surface under applied electric field. Controlled epitaxial growth along the c-axis of ZnO leads to the possibility of enhancing available surface area for adsorption of ions, which is presented in this report.

2. Materials and methods

2.1. Chemicals and substrates

Analytical grade zinc acetate dihydrate ($Zn\ (CH_3COO)_2 \cdot 2H_2O$), sodium hydroxide (NaOH), absolute ethanol (C_2H_5OH), isopropanol (C_3H_7OH), acetone (C_3H_5OH) and hydrochloric acid 34% (HCl) were purchased from MERCK, Germany. Zinc nitrate hexahydrate ($Zn\ (NO_3)_2 \cdot 6H_2O$) was obtained from APS Ajax Finechem, Australia and hexamethylenetetramine ($(CH_2)_6N_4$) was supplied by Aldrich, USA. All the chemicals were used without any further purification. Standard microscope glass slides and activated woven carbon cloth (Zorflex FM-100) were used as substrates for the growth of zinc oxide nanorods forming the composite electrodes.

Microscope glass slides were sonicated in soap water for 20 min and rinsed thoroughly several times with DI water and then sonicated in iso-propanol followed by sonication in acetone for 20 min each time. Finally, cleaned glass slides were stored in an oven at 95 °C until further use. Activated carbon cloth (ACC) of ca. 1.0 mm thickness and specific surface area of about 1043 m^2/g was cleaned with highly concentrated 2 M hydrochloric acid (HCl) heated to 115 °C for 12 h to remove most of the mineral contaminants that are commonly present in ACC. Subsequently, samples were thoroughly rinsed with deionized water and dried in an oven at 100 °C for 24 h and then stored in a desiccator until further use.

2.2. Preparation of ZnO nanoparticles for seeding process

ZnO nanoparticle colloid was prepared by following the procedure reported by Baruah et al. [32–34]. Briefly, a solution of 4 mM sodium hydroxide in absolute ethanol was added drop by drop to 4 mM zinc acetate solution (in absolute ethanol) under continuous stirring. The mixture was then hydrolyzed at 60 °C for 2 h for the precipitation of ZnO nanoparticles. As-synthesized ZnO nanoparticles with a diameter of ca. 6–8 nm in a colloidal solution was transparent and stable at room temperature for a few months.

Clean ACC substrates were then seeded with ZnO nanoparticles by following solution dipping method as described elsewhere [35]. Sample substrates were dipped in the colloidal solution for 30 min and dried in an oven at 95 °C for 30 min. This was repeated twice. The as-seeded samples were then dried in an oven at 95 °C.

For seeding process on microscope glass substrates, 1 mM zinc acetate dihydrate in ethanol was used to grow ZnO crystallites by in-situ precipitation of ZnO nanoparticles [36]. The prepared solution (zinc acetate in ethanol) was deposited drop by drop on glass substrates and dried at 70 °C. In order to obtain uniform layer of ZnO nanocrystallites on the glass substrate, precipitation and drying were repeated for 10 times. Thereafter, seeded glass substrates were annealed at 350 °C for 1 h in the ambient.

2.3. Hydrothermal growth of ZnO nanorods

ZnO nanorods were grown on pre-seeded glass and ACC substrates by a hydrothermal process in an equimolar solution of zinc nitrate hexahydrate and hexamethylenetetramine at 90 °C [36]. The process was carried out with different molar concentrations of precursor solution (10, 15, 20, 25 and 30 mM) for a growth time of 10 h. The precursor solution was replaced every 5 h to ensure adequate supply of zinc ions for the hydrothermal growth [32]. For pH control process, sodium hydroxide solution (pH ~ 12) was used to adjust the initial pH of precursor solution. Following the hydrothermal growth of ZnO nanorods, the substrates were thoroughly rinsed with deionized water (DI) and annealed at 350 °C for 1 h in air.

2.4. Characterization

The surface morphology of ACC: ZnO electrodes was characterized by JEOL JSM-6301F field emission scanning electron microscope (FESEM) working at 20 kV. Image J1.38x (National Institutes of Health, USA) was used to determine the dimensions of ZnO nanorods from the scanning electron micrographs and X-ray Diffraction was performed using a JEOL JDX-3530. Conductivity measurements were carried out using Toshniwal TCM 15 Autoranging conductivity and TDS meter. Cyclic voltammetry measurement was carried out using 0.5 M NaCl solution in electrochemical cell with three-electrode system: platinum wire as counter electrode, Ag/AgCl as reference electrode and ACC:ZnO as working electrode. This system was controlled using a home-made potentiostat equipped with NI USB-6009 driven through in LabView program.

2.5. Capacitive deionization experiments

The desalination/regeneration experiments were conducted using flow through capacitor model. The CDI cell consists of symmetrical electrodes of 8.41 cm^2 (both anode and cathode), a spacer of ca. 650 μm thickness, a reservoir made up of poly-methyl methacrylate (PMMA) (Dow Corning SYLGARD® 184 Silicone elastomer kit), a current collector (glassy carbon electrode) and an acrylic plate (to organize the CDI cell) schematically represented in Fig. 1a. The glassy carbon electrodes (current collector) were used as electrical connection from power supply (DC) to the ACC: ZnO electrodes (anode and cathode). The glassy carbon electrodes were maintained 10 times smaller than the ACC: ZnO electrode surface area. The contact area between ACC: ZnO electrodes and glassy carbon was minimized to avoid the unnecessary leakage current between two glassy carbon electrodes during the process.

To perform the complete cycle of ion removal from the saline solution, two steps were followed (1) desalination: ion-absorption and (2) regeneration: ion-desorption (refreshment of the electrodes in CDI cell was necessary prior to the next step of desalination). This process was implemented using 100 ppm sodium chloride (NaCl) solution with a flow rate of 2 ml/min under an applied potential of 1.2 V (just below the electrolysis potential of water). The saline solution was employed into the CDI cell using gravity flow via infusion drip set. Fig. 1b represents the schematic diagram of the desalination/regeneration performance test bench for CDI cells.

3. Results and discussion

3.1. Optimization of surface area vs. precursor concentration

In order to optimize the maximum available electrode surface by varying the growth of ZnO nanorods on the electrodes, the precursor concentration of the reactants during the hydrothermal growth of the nanorods was varied from 10 to 30 mM for a fixed growth time of 10 h on glass substrates. Depending upon the concentration of starting precursor solution in the hydrothermal bath, varying widths and lengths of ZnO nanorods are obtained [36]. In an earlier work, we have shown that the surface area of ZnO nanorods grown on glass substrates change from 34.27 cm^2 to 47.54 cm^2 when precursor concentration was increased from 0.1 mM to 1 mM [31]. The surface area ratio (total surface area over per unit area) variations or the ZnO nanorods with respect to the ionic concentration of precursor solution are plotted in Fig. 2 (calculation of total surface area over per unit area is provided in