Desalination 446 (2018) 51–58

Contents lists available at ScienceDirect

Desalination

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

Facile preparation of graphene coated copper electrodes via centrifugal milling for capacitive deionization applications

Abdul Hai Alami[a,b,*], Kamilia Aokal[b], Abdullah Abu Hawili[c], Rita Hasan[d], Hussain Alawadhi[b,e]

[a] Sustainable and Renewable Energy Engineering Department, University of Sharjah, 27272 Sharjah, United Arab Emirates
[b] Center for Advanced Materials Research, Research Institute of Science and Engineering, University of Sharjah, 27272 Sharjah, United Arab Emirates
[c] Sharjah Research Academy, Sharjah, United Arab Emirates
[d] Mechanical Engineering Department, University of Sharjah, 27272, Sharjah, United Arab Emirates
[e] Applied Physics and Astronomy Department, University of Sharjah, 27272, Sharjah, United Arab Emirates

ARTICLE INFO

Keywords:
One-step synthesis and deposition of graphene
Mechanical synthesis of graphene
Ball milling
Turbostratic graphene
Capacitive deionization

ABSTRACT

This work presents the simple synthesis and simultaneous deposition of graphene nanoplatelets onto pure copper substrates for use as capacitive deionization electrodes. Copper is cheap and abundant material that can easily be fabricated into electrodes but suffers from high reactivity in solution with unpredictable consequences. The deposition of turbostratic graphene layer using the proposed high energy centrifugal milling technique introduces a chemically inert, but electrically conductive surface layer that extends the operational lifetime of the copper working electrode many folds compared to the bare pure copper one. In the trials presented here the operation of the pure copper electrode degraded almost instantly as the electrochemical cell was activated, compared to a smooth 60-minute operation of its graphene-coated counterpart. The graphene electrode was successful in reducing the solution conductance by more than 12% for the test period, which renews the interest in copper as an effective counter electrode for capacitive deionization applications. The quality of graphene deposition is verified via Raman spectroscopy, while the characterization of the copper chloride is done via X-ray Diffraction. The deionization process resulted in the production of $Cu_2Cl(OH)_3$ deposits on the copper electrode, which is mentioned as a viable method of producing it, although it is an unexpected result of this work.

1. Introduction

Graphene is an important two-dimensional material that has prompted many investigations to utilize its attractive thermophysical, electrical and mechanical properties [1–2]. It is used in various applications that include -but are not limited to- electronic devices [3], storage applications such as super capacitors as depicted by Choi et al. [4], and solar cells [5,6]. Huang et al. [8] drew attention to the importance of the graphene-based electrodes in various applications. Moreover, MacHado et al. [9] have investigated the catalyst effects of graphene based materials. The above mentioned properties are usually a function of the number of layers and any intrinsic defects that exist in the structure of the produced graphene. Consequently, the production steps and methods govern the obtained properties [10]. Chang et al. reported on the synthesis of multilayered graphene by mechanical exfoliation [11]. Graphene synthesis and deposition techniques are numerous and vary from chemical vapor deposition (CVD) techniques to electrochemical and plasma-based processes, as well as processes that reduces graphene oxide into the desired graphene material as seen in the work of Guermoune et al. [12], and Li [13]. While such synthesis approaches can produce highly ordered graphene layers, their economic feasibility is still far from attractive, especially that they usually require high temperature and high vacuum conditions. This has imposed an insurmountable limitation on the adoption of a single synthesis pathway, especially that the subsequent transfer of the produced graphene material into its intended host surface is, in its own right, a challenging undertaking. Thus, it is important to investigate facile, fast and cheap alternatives that will streamline both the steps of synthesis and deposition of the graphene material.

Historically, the centrifugal milling process has been used to interdiffuse elemental powders and precursors of different materials to produce nano-sized materials for a multitude of applications [14–16]. The process is straightforward and robust, and while it has many parameters to tune, such as speed, filling ratio, milling time, etc., they are easily being fine-tuned to result in a predictable end product. High energy milling of a graphitic starting material to produce graphene or

* Corresponding author at: Sustainable and Renewable Energy Engineering Department, University of Sharjah, 27272 Sharjah, United Arab Emirates.
E-mail address: aalalami@sharjah.ac.ae (A.H. Alami).

https://doi.org/10.1016/j.desal.2018.09.003
Received 16 August 2018; Received in revised form 3 September 2018; Accepted 3 September 2018

Nomenclature

C	Solution conductance, ms/cm
C_a	Graphene crystallite size, nm
I_G	Intensity of the *G* peak of the Raman spectrum occurring around ~1582 cm^{-1}, A.U.
I_D	Intensity of the D peak of the Raman spectrum occurring around ~1350 cm^{-1}, A.U.
I_{2D}	Intensity of the D peak of the Raman spectrum occurring around ~270 cm^{-1}, A.U.
I	Measured current, A
V	Applied voltage, V
λ	Wavelength of the Raman spectrometer, nm

graphene oxides has been reported, where exfoliation of graphite occurs and results in graphene nano-platelets [17–19].

Copper is a commonly used material in energy conversion applications since metrological studies proved that it has attractive thermo physical properties, as well as its low cost [20–21]. On the other hand, the lack of resistance of copper to corrosion has always been a limiting factor to the widespread use in all working environments. For example, the presence of ions such as chloride, sulphate or nitrate copper the external passive oxide film will breakdown, leading the propagation of corrosion rendering the electrode/pipe obsolete. Capacitive deionization (CDI) is an electrosorption technique for the elimination of salt ions from aqueous solutions, and has received extensive attention in recent literature [22–25]. Based on [22], the authors were able to provide efficient working cell voltages of different systems. Coincidentally, carbon materials such as active carbon and mesoporous carbon are proven to enhance the surface catalytic activity of the working electrode surface. However, mesoporous carbon is more efficient than active carbon and its electrosorption capacity is higher than most of carbon materials [26]. Graphene, as a carbonaceous material, is considered a promising CDI electrode material due to the enhancement in conductivity, surface area and stability it introduces to the surface of the electrodes [27]. And since CDI has the operating principal of an electrical capacitor where the adsorption is a function of good electronic conductivity, rapid ion absorption– desorption cycles, electrochemical stability, graphene is believed to have the potential of tuning the reactivity of copper electrodes used for CDI.

This work introduces a novel method to simultaneously produce and deposit turbostratic graphene nano-platelets on copper substrates using dry milling. The starting material for the process is high-purity graphite either in chunks or powder form that is exfoliated under the substantial mechanical forces onto a substrate attached to the inside of a grinding bowl. The energy of the milling process is a function of the rotational speed of the machine, which, for this report, will be varied along with milling time, grinding bowl material, starting graphite material and thickness of the copper substrate. The enhancement achieved to the surface activity by virtue of the added graphene surface layer is investigated for water purification application. Electrodes made of bare copper and others with graphene coated copper are made and tested in 0.1 M NaCl solution. Various characterization techniques and surface morphology observations are employed to examine the produced and deposited materials. Chronoamperometry is used in conjunction with solution conductance measurement to investigate the deionization effectiveness of the produced electrodes.

2. Experimental approach

2.1. Graphene synthesis and deposition

Graphene coatings were synthesized and deposited in 25 ml stainless steel and Teflon crucibles with 2.5 g of graphite powder obtained from a 100 kg 99.95% purity graphite rod of less than 125 μm particle size. A 0.2 mm thick (20 × 100 mm) copper sheet (99.9% from alibaba.com) is used as a deposition substrate. The process is summarized in Fig. 1.

The crucibles were then placed in a Retsch PM100 planetary mill and rotated at different speeds (100, 200, 300, 400, 500 and 600 rpm) for a maximum of 1 h to prevent the production of graphene oxide at extended time intervals. The processes attempted solely relied on centrifugal forces applied on the graphite material after specific operating times, namely 20 or 60 min. The substrates were then collected and sonicated in water/ethanol for further testing and characterization.

2.2. Microstructural methods and spectroscopy

The topography of the deposited graphene on copper electrodes was performed via a scanning electron microscope from VEGA3 TESCAN, operating at 30 kV voltage. Energy-dispersive X-ray spectrometry (EDS) was utilized for elemental analysis in 2D mapping. The Raman spectra were measured with an inVia Raman microscope (Renishaw) with a laser wavelength 514 nm. The inVia Raman microscope also allowed for optical imaging.

2.3. Electrochemical approach for capacitive deionization

The electrochemical trials attempt to investigate the effect of capacitive deionization on a 0.1 M NaCl aqueous solution. The chronoamperometry protocol is conducted at −600 mV against a Hg/HgO reference electrode and a platinum coil acting as a counter electrode. The working electrode will be a graphene coated pure copper substrate chosen from the best trial of high energy milling, and also a pure copper substrate as a reference. The exposed active area of both is 0.5 × 1 cm as the rest of the electrode surface area is sealed with an acrylic adhesive. The setup was connected to a SP-300 Biologic potentiostat, and the solution conductivity is measured every minute using SCT-BENCON-1 conductivity meter. The tests were repeated for three identical electrodes and the test cell is filled each repetition with fresh solution from the same master beaker containing 500 ml of the solution that lasted for the whole trial.

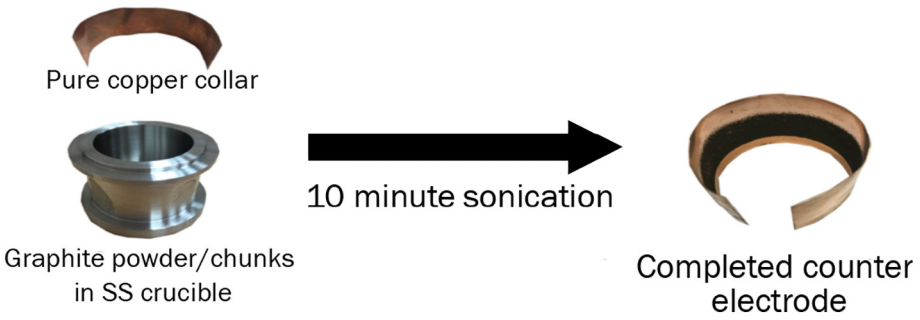

Fig. 1. Solid-state automation process of electrode production.