Electrochemistry Communications 49 (2014) 42–46

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Electrocatalytic activity of nitrogen plasma treated vertically aligned carbon nanotube carpets towards oxygen reduction reaction

Palaniappan Subramanian [a], Asaf Cohen [a], Eti Teblum [b], Gilbert D. Nessim [b], Edward Bormasheko [c,d], Alex Schechter [a,*]

[a] Department of Biological Chemistry, Ariel University, Ariel 40700, Israel
[b] Department of Chemistry, Bar-Ilan University, Institute for Advanced Materials and Nanotechnology, Ramat Gan 52900, Israel
[c] Department of Physics, Ariel University, Ariel 40700, Israel
[d] Department of Chemical Engineering and Biotechnology, Ariel University, Ariel 40700, Israel

ARTICLE INFO

Article history:
Received 9 September 2014
Received in revised form 8 October 2014
Accepted 8 October 2014
Available online 12 October 2014

Keywords:
Carbon nanotube carpets
Nitrogen plasma
Oxygen reduction
Chemical vapor deposition
Catalysts

ABSTRACT

We developed a simple and rapid procedure to prepare nitrogen-doped vertically aligned carbon nanotube carpets (VA-NCNTs). The VA-NCNTs were obtained by nitrogen plasma treatment of the vertically aligned multi-walled carbon nanotube carpets (VA-CNTs) directly grown on stainless steel substrates by chemical vapor deposition. This novel electrochemical interface reduces oxygen in lower overpotential under basic condition (onset potential at −0.12 V vs. Ag/AgCl at pH 13) compared to untreated VA-CNTs (onset potential at −0.22 V vs. Ag/AgCl at pH 13). The robustness of these nanostructures and ease of fabrication make VA-NCNTs promising non-platinum oxygen reduction catalysts that could be employed as cathode catalysts in real-time operation of alkaline fuel cell systems.

1. Introduction

Development of oxygen reduction catalysts (ORCs) has attracted increasing attention in recent decades due to the technological importance of oxygen reduction reaction (ORR) in different electrochemical systems including fuel cells, electrolyzers and metal-air batteries [1]. The faster rate of ORR in alkaline medium has driven researchers to develop several noble metal-based ORCs, for application in alkaline fuel cells. Current state of the art Pt-based ORCs are expensive and demonstrate limited long-term stability. In order to overcome the challenges associated with these materials, non-precious metal catalysts (NPMC) were developed [2]. NPMCs are considered as a potential alternative to Pt-based ORCs due to their comparable electrocatalytic activity towards ORR. Many research teams have reported different high performance NPMCs that are claimed to closely match the activity of Pt-based ORCs in alkaline medium [2,3]. However large scale manufacturing of fuel cell stacks is still not viable due to performance loss or durability degradation of the ORCs [4]. The desire for better and cheaper cathode catalysts for ORR in alkaline medium has put nanostructured carbon materials in the forefront of research.

Nitrogen doped carbon nanotubes (NCNTs) have been reported as a promising Pt-free ORCs for alkaline fuel cells [5–8]. Nitrogen-induced charge delocalization of the carbon atoms is believed to change the chemisorption mode of oxygen from usual end-on adsorption (in CNTs) to side-on adsorption (in NCNTs) resulting in the lowering of ORR overpotential [5,9]. Moreover, Yang et al. have recently found that doping-induced charge redistribution could create charged sites favorable for oxygen adsorption, leading to the facilitation of ORR [10,11]. Carbon nanotubes could be doped with nitrogen by the use of nitrogen plasma, which is an ionized gas consisting of ions, electrons, and neutral species, and allows treating the CNTs' exposed surfaces in a relatively short time. Furthermore, this is an economical environmental-friendly process without the need to use any solvent or high temperatures. Although several studies have investigated and reported the synthesis and ORR activity of NCNTs [5,12], to the best of our knowledge there has been no report on the ORR performance of NCNTs prepared by treating dense carpets of vertically aligned carbon nanotubes (VA-CNTs) with nitrogen plasma.

In the present work, we have treated dense carpets of vertically aligned nitrogen-doped carbon nanotubes (VA-NCNTs) on stainless substrates, which we synthesized using chemical vapor deposition (CVD). X-ray photoelectron spectroscopy (XPS), contact angle measurements, infrared and Raman spectroscopy were employed to characterize VA-CNTs and VA-NCNTs. The electro-catalytic activity of the VA-NCNT

* Corresponding author. Fax: +972 9076586.
E-mail address: salex@ariel.ac.il (A. Schechter).

http://dx.doi.org/10.1016/j.elecom.2014.10.005
1388-2481/

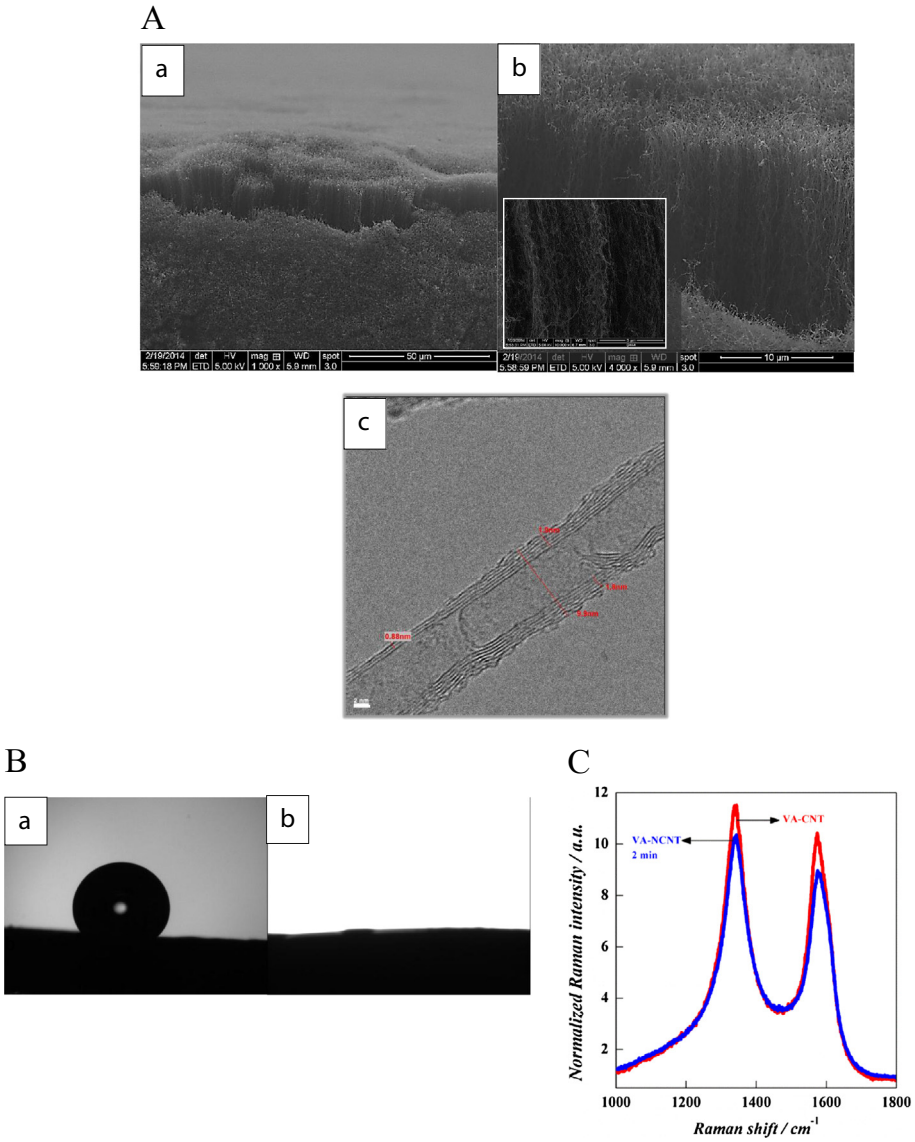

Fig. 1. (A) SEM image of VA-CNTs top-view (a), enlarged view (b), and HRTEM images of VA-CNTs (c); (B) optical image of the water droplet profile deposited onto VA-CNT before (a) and after the 2 min nitrogen plasma treatment (b); (C) Raman spectra of VA-CNTs before (red trace) and after 2 min plasma treatment (blue trace). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

electrode towards oxygen reduction in alkaline medium was studied using cyclic voltammetry.

2. Experimental section

Type 316 grade stainless steel coins (0.5 mm thick, 15.5 mm diameter) were purchased from Tzamal D-Chem laboratories Ltd. and were used as substrates for CNT growth. We performed the CNT synthesis in a three-zone atmospheric-pressure tube furnace (Carbolite model HZS-E), using a single fused-silica tube with an internal diameter of 22 mm [13–15]. The two-first zones of the furnace preheated the precursor gases at 770 °C, decomposing the hydrocarbon gases and forming water vapor from O_2 and H_2 [16].

Nitrogen plasma treatment of the VA-CNTs was performed in a Zepto low pressure plasma system (Diener electronic GmbH, Ebhausen, Germany) equipped with the 40 kHz HF-generator operating between 0 and 100 W. The stainless steel coin with the carpet of VA-CNTs (geometric area of 1.76 cm^2) was introduced into the plasma chamber during a set time; the chamber pressure and plasma power were maintained at 1.2 mbar and 130 W, respectively. The VA-CNTs were characterized using field-emission scanning electron microscopy (FESEM; FEI, Helios 600) operating at 5 keV and high-resolution transmission electron microscopy (HRTEM) using a JEOL-2100 operating at 200 keV. Static contact angles (CA) were measured by the sessile drop technique using 5 μL of deionized water using a remote-computer controlled goniometer system (Rame'-Hart instrument Co, NJ, USA). Raman spectra were recorded with a XploRA ONE™ micro-Raman system (Horiba Scientific, France) using 530 nm laser, power <150 mW.

Fourier transform infrared (FTIR) spectrums were recorded using a Bruker FTIR spectrometer (VERTEX 70) equipped with Opus 7.0 software at 4 cm^{-1}. Dried VA-CNTs and VA-NCNTs separated from the substrate by mild-scratch were mixed with KBr powder (100 mg) in

Fig. 2. (A) FTIR spectra of VA-CNT and VA-NCNT-2 min; (B) XPS survey spectrum of VA-CNT (a), O1s spectrum of VA-CNT (b), survey of VA-NCNT-2 min (c), O1s spectrum of VA-NCNT-2 min (d) and deconvoluted N1s spectrum of VA-NCNT-2 min (e).