INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–6

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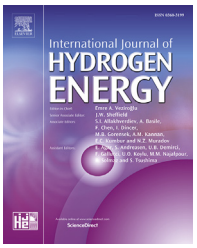

High-temperature-treated multiwall carbon nanotubes for hydrogen evolution reaction

Tri Khoa Nguyen [a,1], *Alexander G. Bannov* [b,1], *Maxim V. Popov* [b], *Jong-Won Yun* [a], *Anh Duc Nguyen* [a], *Yong Soo Kim* [a,*]

[a] *Department of Physics and Energy Harvest Storage Research Center, University of Ulsan, Ulsan 44610, South Korea*
[b] *Department of Chemistry and Chemical Technology, Novosibirsk State Technical University, Novosibirsk, Russia*

ARTICLE INFO

Article history:
Received 20 October 2017
Received in revised form
6 December 2017
Accepted 13 February 2018
Available online xxx

Keywords:
Multi-walled carbon nanotubes
Heat treatment
Hydrogen evolution reaction
Electrocatalysis

ABSTRACT

We investigated the hydrogen evolution reaction (HER) properties of multi-wall carbon nanotubes (MWCNTs) treated at extremely high temperature (2600 °C). The heat treatment not only improves the crystallinity of the MWCNTs, but also reduces the carbon-oxygen (C–O) bonding as it is replaced by the defect-carbon (sp^3 and C–H) bonding. These modifications in the heat treated MWCNT structure lead to the increase of electrochemical charge transfer. The heat treatment of MWCNTs in the composite with Pt (MWCNT-Pt composite) further facilitates electrocatalysis. The MWCNTs-Pt composite shows strong enhancement in the HER performance with an onset of overpotential of −0.04 V vs reversible hydrogen electrode and a Tafel slope of 10.9 mV/decade. This performance is indeed better than that of Pt, which is the best working material for HER.

Introduction

Hydrogen is a green energy carrier to replace fossil fuels. Hydrogen evolution reaction (HER) is a method to produce hydrogen via water electrolysis. Platinum (Pt) is the best catalyst for HER due to its large cathodic current generation at low applied potential. But its high cost is a major disadvantage, preventing its scale-up application [1–6]. Carbon-based materials have been considered a low-cost alternative, as they are earth-abundant for HER commercialization. Pristine carbon materials are inert for electrochemical HER. However, surficial modifications such as doping and hybridization of these materials can be successfully used to improve their HER performance [3,5,7–10]. For example, by using density functional theory (DFT), Zheng et al. found that the Gibbs free-energy of hydrogen adsorption (a major descriptor of HER activity) is −0.08 eV (close to optimal value, 0) for *N* and *P* bi-doped graphene [11]; and Deng et al. indicated that a metal-decorated graphene network may transfer penetrated electrons to the graphene surface, improving HER performance [12]. Recently, homogeneous catalysts derived from carbon nanotubes have been developed for HER. For example, Cui et al. reported that the activated carbon nanotubes via acidic oxidation and subsequent cathodic pretreatment yield excellent HER performance with an overpotential of −100 mV vs reversible hydrogen electrode (RHE) and a Tafel slope of 71.3 mV/decade [13]. Pal et al. synthesized covalently connected carbon nanotubes from inactive pristine and reported its

* *Corresponding author.*
E-mail address: yskim2@ulsan.ac.kr (Y.S. Kim).
[1] These authors contributed equally to this work.
https://doi.org/10.1016/j.ijhydene.2018.02.081

onset potential is −150 mV vs RHE for HER [14]. The heat treatment effect on materials properties have been studied [15–18], however, its effect on HER performance of carbon nanotubes have not been reported yet.

In this report, heat-treated multi-wall carbon tubes (*h*MWCNTs) were prepared at an extremely high temperature of 2600 °C for investigating HER performance. Although intrinsic multi-wall carbon tubes (*i*MWCNTs) are inactive for HER, *h*MWCNTs show the good HER performance arising from an excellent discharge reaction process and a low electrochemical charge transfer resistance. Morphologies, crystallization, and atomic bonding of the *h*MWCNTs were studied for understanding the improved HER mechanism. When the *h*MWCNTs were combined with Pt, the *h*MWCNTs-Pt composite exhibits excellent HER performance with a low value of Tafel slope (10.9 mV/decade), low onset overpotential (−0.04 V vs RHE).

Experiment

Fabrication of hMWCNTs

Commercially available *i*MWCNTs (Shenzhen Nano-Tech Port Co.) were heat treated in a laboratory using Tamman's furnace with a graphite heater [19]. Details of the fabrication process including the scheme of Tamman's furnace and experimental set up are provided in Fig. S1 in SI (supporting information). The samples were put into two graphite crucibles and placed into the heating zone. The space between the crucibles was filled by a carbon filter to prevent the oxidation of the MWCNTs during the heat-treatment process. After the furnace reached the regime parameters, the samples were exposed to a certain temperature at 2600 °C for 30 min.

HER measurement

To prepare MWCNTs for HER, 0.5 mL of 3 mg/mL MWCNTs in ethanol was mixed with 50 μL of Nafion in an ultrasound for 15 min. To prepare MWCNT-Pt composite for HER, 50 μL of 8 wt % chloroplatinic acid (H_2PtCl_6) was added to the mixture of 0.5 mL of 3 mg/mL MWCNTs in ethanol and 50 μL Nafion, subsequently, treated in the ultrasound for 15 min. To prepare individual Pt for HER, 50 μL of 8 wt% H_2PtCl_6 and 50 μL of Nafion was added to 0.5 mL of ethanol and then ultrasound for 15 min.

For the HER performance measurement, 20 μL of the sample was dropped on 0.07 cm^2 glassy carbon electrode (GCE) and dried at 90 °C for 15 min. The HER measurements including linear sweep, electrochemical impedance spectroscopy (EIS), and the stability study of samples were conducted in an electrochemical workstation (IviumStat, Ivium Tech) with three electrodes including a Pt wire counter electrode, an Ag/AgCl reference electrode, and 0.07 cm^2 GCE. All of the electrodes were dipped in 0.5 M H_2SO_4 electrolyte to evaluate HER properties. The EIS result was fitted using the Ivium Equivalent Circuit Evaluator (Ivium Tech) modeling with 2 constant phase elements (CPE) as shown in Fig. S2 in SI.

Characterizations

The crystalline structure of *h*MWCNTs was investigated by transmission electron microscopy (TEM) using a JEM-2010 (JEOL) microscope with a resolution on the lattice of 0.14 nm at an accelerating voltage of 200 kV. Vibrational features of the samples were determined by Raman spectroscopy using a T64000 system (Horiba Jobin Yvon) with an excitation wavelength of 514 nm. The chemical composition analysis was done by X-ray photoelectron spectroscopy (XPS; Theta Probe AR-XPS System, ThermoFisher Scientific).

Results and discussion

TEM images of MWCNTs before and after heat treatment are shown in Fig. 1. The *i*MWCNTs are not aligned but their outer diameter is rather uniformly distributed from 10 to 20 nm with a narrow inner diameter from 3 to 5 nm (Fig. 1(a)–(c)). There is a certain amount of short fragments in the nanotubes because the as-obtained *i*MWCNTs were subjected to chemical treatment. The crystalline structure of the *i*MWCNTs is found to be disordered with several broken crystals as shown in Fig. 1(c). However, heat treatment of the *i*MWCNTs leads to reordering of the nanotube structures by connecting the broken crystals to form a larger graphite crystallite (Fig. 1(d)–(f)). Therefore, the *h*MWCNTs become more aligned when compared with the *i*MWCNTs. Raman spectroscopy was performed on the samples to further demonstrate the above result, namely, reduction of disordered crystal after heat treatment.

Fig. 2 shows the Raman spectra of the *i*MWCNTs (black) and the *h*MWCNTs (red). The absence of peaks pertinent to the radial breathing mode (RBM) confirms that the samples do not contain any single-walled CNTs [20,21]. Three main bands appearing in the Raman spectra are the D band at 1341 cm^{-1}, the G band at 1566 cm^{-1}, and the G′ band at 2688 cm^{-1}, respectively [22,23]. The D band is associated with the vibration of carbon atoms with a dangling bond in the edge plane of the disordered crystal. The G band is due to the doubly degenerate zone-center mode and corresponds to the vibration of sp^2 bonding. The Raman intensity ratio, $\frac{I_D}{I_G}$, of the *i*MWCNTs and the *h*MWCNTs were found to be 0.96 and 0.36, respectively. According to the Tuinstra-Koenig equation [24], the crystallite size, L_a, determined by $L_a = 2.4 \times 10^{-10}\lambda^4\left(\frac{I_D}{I_G}\right)$ is about 17.4 nm for the *i*MWCNTs and 46.5 nm for the *h*MWCNTs, where the excitation wavelength λ is 514 nm. This result indicates that the crystalline structure of the *i*MWCNTs is more disorder degree than that of the *h*MWCNTs. Together with the TEM results, this clearly demonstrates that heat treatment improves the crystallinity of the MWCNTs, which may be a key factor for reducing charge transfer resistance in the electrochemical process.

Fig. 3 shows the XPS spectra for the C 1*s* and O 1*s* level of the MWCNTs before and after heat treatment. The C 1*s* survey shows the presence of the typical atomic bonding in MWCNTs, which includes C–C (sp^2), defect-C (sp^3 and C–H), C–O, O–C=O, O–(C=O)–O bonding, and π–π^* interaction at 284.55, 285.03, 286.99, 288.65, 290.55, and 291.95 eV, respectively [25]. These atomic bonding are likely stable after heat-treatment with no shift of binding energy and no change in

Please cite this article in press as: Nguyen TK, et al., High-temperature-treated multiwall carbon nanotubes for hydrogen evolution reaction, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.02.081