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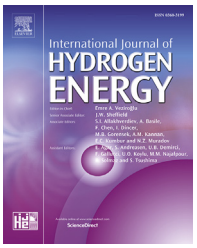

Free-standing carbon nanotubes as non-metal electrocatalyst for oxygen evolution reaction in water splitting

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ABSTRACT

Oxygen evolution reaction (OER) has significant impact on the overall electrochemical water splitting. We introduce, for the first time, a facile approach towards the fabrication of versatile electrode composed of free-standing multiwalled carbon nanotubes (MWCNTs) as electrocatalyst for the water splitting reaction. Directly extracted MWCNTs as sheets from vertically grown arrays transferred over the glass substrate, are used without any post treatment as a working electrode for OER. Onset potential of 1.60 V was achieved for MWCNTs which is significantly reduced as compared to platinum based metal electrode (1.72 V) with excellent current density. No surface modification, metal-free nature, flexibility and low cost with excellent catalytic activity proved this material as a promising candidate for the replacement of metal based electrodes in electrochemical water splitting.

Introduction

Intense climatic changes, rapidly growing global energy demand and waning of the fossil fuels compelled researchers to explore the alternative clean and renewable energy resources [1]. To this end, electrocatalytic/photo-electrocatalytic water splitting to produce O_2 and H_2 gasses has provided abundant resources of renewable energy fuels to empower the sustainable civilization [2–5]. As compared to fossil fuels, hydrogen fuels have splendid advantages with high energy density and minimal environmental hazards [6,7]. In basic medium electro-catalysis of water with oxidation half reaction at anode liberates the oxygen while reduction at cathode produces the hydrogen gas at cathode as given in equations (1) and (2) respectively. However, oxidation half reaction involved in the oxygen evolution reaction is a bottleneck of the overall water splitting process due to the sluggish kinetics in electrochemical process [8] which cause the lowering of the electrode activity with higher overpotential. The efficiency of electrocatalytic system is limited due to these overpotential

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losses associated with OER at the anode in both acidic and basic environments [4,9,10].

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (1)$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (2)$$

Hence, it would be remarkable and significant scientific accomplishment to develop an efficient electro-catalyst for OER with high activity and good durability. To date, different kinds of nanostructures including transition metal based nanomaterials [11–16] and their derivatives [17–22], selenium based nanomaterials [23,24] polymer composites [25–27] and carbon based nanomaterials [28–32] have been utilized for the OER in catalytic water splitting. Carbon nanotubes and graphene widely studied for the electrocatalyst and photo-electrocatalyst in water splitting reaction. It was observed that mostly these materials were surface decorated with some nanoparticles to boost their catalytic activity [27,33–39]. So far, surface modification is a key hindrance to utilize these materials for the scale up production of hydrogen and oxygen via water splitting. Furthermore, to utilize these materials as an active layer, the surface modification of the electrode (Nafion binding and adsorption) is a major hurdle for their practical implementation. Among all above materials for electrochemical water splitting, carbon nanotubes have enormous potentials with sophisticated electrode fabrication and excellent activity towards OER [40]. Along with pristine MWCNTs, their composites are also used as active layer in electrochemical as well as photo-electrochemical water splitting [30,41,42].

Herein we have employed the aligned MWCNTs as sheets over a glass substrate and directly used as working electrode in OER with low overpotential and high current density. Aligned MWCNTs in this study play dual role in OER i.e., electrochemical reaction takes place over the surface of outer wall and charges are transported from the inner walls simultaneously as shown in Fig. 1. Special patterned MWCNTs in the form of sheets used as electrode have many advantages such as easy electrode fabrication, low cost, flexible in nature and excellent electrocatalytic activity. With admirable advantages, these materials could be promising candidates for the replacement of hectic fabrication of surface modified electrodes for the electrochemical water splitting.

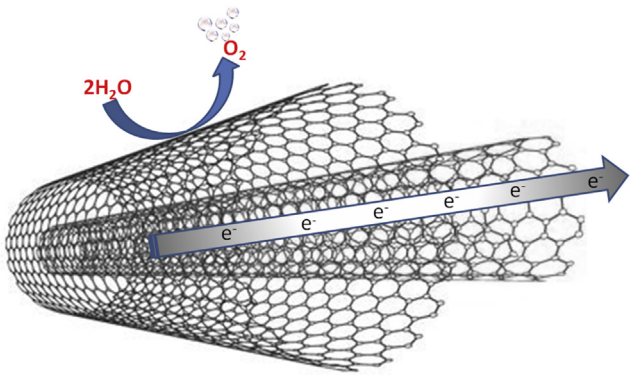

Fig. 1 – Schematic illustration of water splitting for the oxygen evolution reaction using MWCNTs.

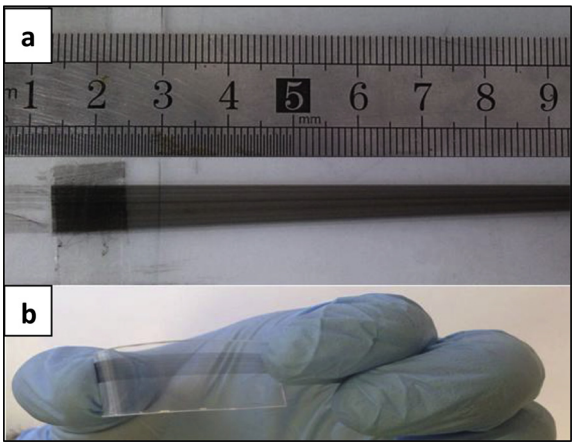

Fig. 2 – (a) Optical image of WMCNTs sheets extracted from vertical arrays and (b) MWCNTs as a sheet over a flexible plastic substrate.

Experimental

Synthesis of MWCNTs arrays

Unique patterned MWCNTs arrays were synthesized by previously reported chemical vapor deposition (CVD) method [43]. Briefly, aluminum oxide (Al_2O_3) thin film (5 nm) was deposited over a silicon substrate and then Fe thin film (1.5 nm) was deposited over the Al_2O_3 layer by electron-beam evaporation method. Aluminum oxide acted as a buffer layer which prevents the penetration of Fe nanoparticles into the silicon substrate. After annealing under argon (Ar), iron thin film is broken down into iron nanoparticles which assist to grow the aligned MWCNTs arrays. A glass tube furnace was used to flow the ethylene as a source gas and hydrogen and argon as carrier gasses with flow rate of 90, 30 and 400 sccm (standard cubic centimeter per minute) respectively. At optimized conditions of temperature ramping and flow rate of gasses, highly aligned MWCNTs arrays were successfully grown as shown in Scanning electron microscopy (SEM) images (Fig. 3). Sharp edge blade was used to pull the sheets from these arrays and was directly transferred to the surface of glass or polyethylene terephthalate (PET) substrate.

Electrochemical measurements

Linear sweep voltammetry (LSV) measurements for OER were carried out at a sweep rate of 10 mVs^{-1} in the potential range between 0.0 and 2.1 V (vs Ag/AgCl) in 3.0 M and 0.1 M NaOH electrolyte. The chronoamperometric (CA) measurements were carried out for the investigation of electrode stability in basic medium (3 M NaOH) for 2000 s under a constant potential of 1.6 V verses reversible hydrogen electrode (RHE).

Physical characterization

SEM images of MWCNTs were taken with Quanta FEG250, Bruker. LSV and CA measurements were carried out using GAMRY Instrument, Reference 1000 Potentiostat/Galvanostat/

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