Available online at www.sciencedirect.com
SciVerse ScienceDirect
journal homepage: www.elsevier.com/locate/he

Technical Communication

Large-area manganese oxide nanorod arrays as efficient electrocatalyst for oxygen evolution reaction

Shuang Chen [a], Teng Zhai [b], Xi-Hong Lu [b], Man-Zhi Zhang [a], Zhuo-Ying Li [a], Chang-Wei Xu [a,*], Yexiang Tong [b,**]

[a] School of Chemistry and Chemical Engineering, Guangzhou University, No. 230 Waihuanxi Road, Guangzhou 510006, China
[b] MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Institute of Optoelectronic and Functional Composite Materials, Sun Yat-Sen University, Guangzhou 510275, China

ARTICLE INFO

Article history:
Received 14 April 2012
Received in revised form
3 June 2012
Accepted 16 June 2012
Available online 13 July 2012

Keywords:
Oxygen evolution reaction
Manganese oxide
Nanorod arrays

ABSTRACT

Large-area manganese oxide nanorod arrays (MnO_2 NRAs) have been directly grown vertically on Ti foil with a uniform length and diameter by a simple electrochemical method without any templates. The deposition temperature is one of the most important parameters for formation MnO_2 NRAs and at 25 °C no MnO_2 NRAs can be obtained. The results show that MnO_2 has high activity and good stability for oxygen evolution reaction (OER) and the structure of nanorod arrays pronounced enhances MnO_2 activity. The onset potential of MnO_2 NRAs is lower than that of Pt foil and lower 401 mV than that of MnO_2 film, indicating that the structure of MnO_2 NRAs shows an easy OER for water split. The MnO_2 NRAs may be of great potential in electrochemical water split.

1. Introduction

The electrochemical gas evolution during water electrolysis has attracted more and more attention because of the development of sustainable and renewable chemical technologies to produce clean energy sources [1,2]. Alkaline water electrolysis, using electricity generated by renewable sources has been proposed as an environmentally inoffensive route to produce a large volume of hydrogen gas required by a possible hydrogen economy, and the efficiency of water electrolysis is limited by the large anodic overpotential of oxygen evolution reaction (OER) [3,4]. The OER is the anode reaction employed in electrolysis cells and may also serve to balance solar fuel synthesis reactions, e.g. CO_2 reduction to fuel [5]. The rutile-type oxides of RuO_2 and IrO_2 show the lowest OER overpotential, however theses oxides suffer from poor chemical stability in alkaline media [2,6–8]. So other metal oxides such as PbO_2/Co_3O_4, Co_3O_4, Cu–Co oxide, $NiCo_2O_4$, Ni–Li oxides have been developed [9–19]. The manganese oxides have been already demonstrated an activity for the OER [5,20–23]. In this paper, large-area manganese oxide nanorod arrays (MnO_2 NRAs) are directly grown on Ti foil by a simple electrochemical method. The MnO_2 NRAs synthesized on Ti foils and F-doped SnO_2 coated glass substrates by an electrochemical method have been demonstrated to exhibit excellent specific capacitance and good cycling stability for electrochemical

---

* *Corresponding author*. Tel./fax: +86 20 39366908.
** *Corresponding author*.
E-mail addresses: cwxu@gzhu.edu.cn, cwxuneuzsu@126.com (C.-W. Xu), chedhx@mail.sysu.edu.cn (Y. Tong).

http://dx.doi.org/10.1016/j.ijhydene.2012.06.059

supercapacitor [24]. One dimensional (1D) nanoarrays such as nanowire/nanorod arrays are the most attractive materials due to their high interfacial area and fast electrical pathways among the numerous nanostructures [25,26]. Hexagonal WO_3 nanowires show promising electrocatalysts for hydrogen evolution reaction (HER) from water [27].

2. Experimental

All reagents used were of analytical grade purity and purchased from Sigma–Aldrich. Electrodeposition of MnO_2 NRAs was performed in a conventional three-electrode glass cell via an electrochemical approach without any templates. A Ti foil of 1.5 cm × 3 cm (20 mm in thickness, 99.99%) and a graphite rod of about 4.0 cm^2 were used as working electrode and counter electrode, respectively. The reference electrode was saturated calomel electrode (SCE, 0.241 V versus RHE) which was connected to the cell with a double salt bridge. The Ti foil was cleaned ultrasonically in distilled water, ethanol, acetone and then rinsed in distilled water again before being used. The morphologies and microstructures of the prepared products were characterized by field emission scanning electron microscopy (FE-SEM, JSM-6330F), X-ray diffraction (XRD, D8ADVANCE) and transmission electron microscopy (TEM, JEM2010-HR). The chemical state and compositions of products were analyzed using X-ray photoelectron spectroscopy (XPS, ESCALab250). The electrochemical OER of MnO_2 NRAs was carried out in a three-electrode cell using CHI 700C electrochemical workstation (Chenhua, Shanghai) in a temperature-controlled water-bath (Polyscience 9106, U.S.A.). The three-electrode cell configuration was consisted of platinum foil (3.0 cm^2) as counter electrode, SCE as reference electrode, and the products prepared on Ti foil substrate as working electrode at 25 °C. A salt bridge was used between the cell and reference electrode.

3. Results and discussions

The MnO_2 NRAs were electrodeposited on the Ti substrate in a solution of 0.01 M $MnAc_2$ + 0.02 M NH_4Ac + 10% dimethyl sulfoxide (DMSO) with a current density of 0.1 mA cm^{-2} for 120 min at 70 °C. Fig. 1a and Fig. 1b are the typical SEM images of MnO_2 NRAs, indicating MnO_2 NRAs were grown vertically on the Ti substrate with a uniform length and diameter. The inset in Fig. 1a shows the cross-section SEM image of MnO_2 NRAs, indicating that the MnO_2 NRAs have a length of 2.5 μm and a diameter of 70–100 nm. There are some smaller manganese oxide wires on the surface of single manganese oxide nanorod, which will enhance active surface of the MnO_2 NRAs. As for the formation process of these branched MnO_2

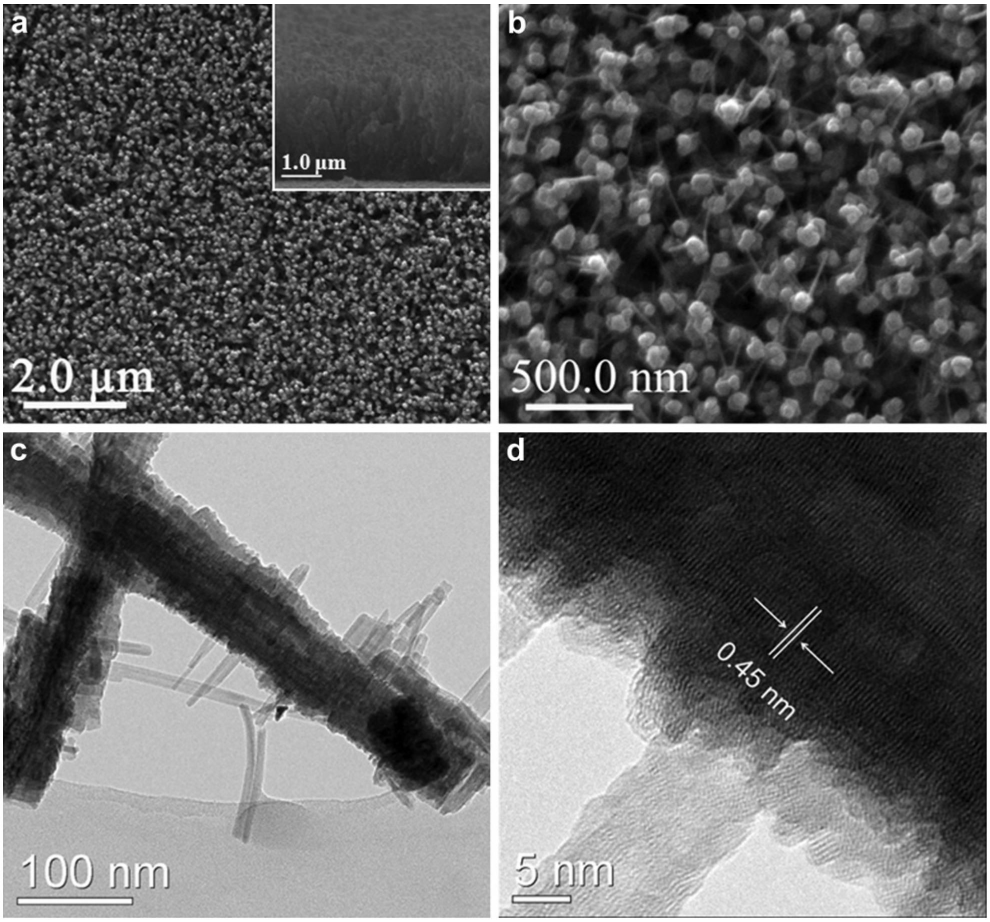

Fig. 1 – a, b) SEM images, c) TEM image and d) HRTEM image of MnO_2 NRAs grown on Ti substrate.