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Research Paper

Facile Synthesis of Nickel Manganese Composite Oxide Nanomesh for Efficient Oxygen Evolution Reaction and Supercapacitors

Yan Zhang, Huijuan Zhang, Ling Fang, Ju Deng, Yu Wang*

The State Key Laboratory of Mechanical Transmissions and School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China

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ABSTRACT

Herein, we introduce a facile two-step means to generate the unique $(NiO)_{0.25}(MnO)_{0.75}$ nanomesh (NiMnO NM) by employing $NiMn_3O_7.H_2O$ nanosheet as precursor. The characteristics of abundant pores, high specific surface area and decreased ion diffusion distance for meshy NiMnO nanomaterial play a major role in both oxygen evolution reaction (OER) and supercapacitors. For OER, the porous NiMnO NM demonstrates enhanced catalytic properties, such as modest onset overpotential of ~270 mV as well as Tafel slope of 41 mV dec^{-1}, large C_{dl} of 22.5 mF cm^{-2}, attractive durability for at least 3000 cycles and improved stability over 80 h at different temperatures in 0.1 M KOH. Meanwhile, the excellent capacitive properties in supercapacitors, including intriguing specific capacitance of 371 F g^{-1} at a high current density of 10 A g^{-1}, admirable rate capability and eminent cycling stability for 5000 cycles at 10 A g^{-1}, are also displayed by NiMnO NM tested in 0.5 M Na_2SO_4. This work gives an example to prepare 2D meshy transition metal composite oxide as highly active electrocatalyst for OER and high-performance electrode material for supercapacitor through a feasible means.

1. Introduction

The severe issue, stern energy crisis, has aroused huge attention owing to ever growing fossil fuel depletion and environmental pollution. In consideration of this, seeking green renewable energy resources as well as exploring efficient energy storage and conversion devices are around the corner [1–3]. Among all the energy carriers, hydrogen (H_2) is treated as a clean alternative to traditional fossil fuels [4,5]. A great many approaches, such as photocatalytic or electrochemical water splitting, can be applied to producing H_2, among which electrochemical water splitting is an effective technology, validly transforming H_2O into H_2 and O_2 via electrolysis [1,6]. The water splitting includes two key half reactions, namely, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The efficiency of H_2 generation is limited by OER [7,8]. To date, a large amount of research has been focused on exploring valuable and high-performance catalysts for OER to accelerate the reaction rate and lower the overpotential [9,10]. At present, the oxides of Ru and Ir are regarded to be the state-of-the-art OER catalysts [7,9]. Nontheless, the widespread application of noble metal-based materials is confined to their limited reserve and expensive cost [7,11]. Given this, non-precious transition metal-based materials, especially transition metal oxides, have been extensively studied as OER catalysts [8,12]. While for energy storage mediums,supercapacitors have aroused tremendous interest on account of their high power density, extra long cycling life, fast charging/discharging rate and excellent cycling stability [13–15]. To our knowledge, supercapacitors can be divided into two classes. One of them is electrostatic double-layer capacitor, utilizing ion adsorption at electron/electrolyte interface to store energy [14]. Another is electrochemical pseudocapacitor, which is characterized with higher capacitance by virtue of reversible redox reaction in the electrode material [13,16]. In General, transition metal oxides, such as ruthenium oxide (RuO_2) [17], manganese oxides (MnO_x) [15], nickel oxide (NiO)[18] and cobalt oxides (CoO_x) [19], are applied as available active materials for redox-type supercapacitors. From the above, it is extremely necessary to exploit abundant, cheap and high-performance transition metal oxides for application in both OER and supercapacitors.

On the basis of the considerable reports, MnO_x with various oxidation states (MnO, MnO_2, Mn_2O_3 and Mn_3O_4) are a sort of

* Corresponding author.
E-mail addresses: wangy@cqu.edu.cn, prospectwy@gmail.com (Y. Wang).

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promising candidate for OER as well as supercapacitors, which exhibit superior electrochemical performance. For example, Gao et al. employed a straightforward *in situ* means to prepare mesoporous MnO_x/S-GC as OER electrocatalysts, demonstrating high catalytic activity [8]. Ying and co-workers designed and synthesized porous MnO/Mn_3O_4 nanocomposites with enhanced capacitance and stability [20]. More valuably, with regard to OER, ion adsorption is a crucial step, and active site takes a major role in OER procedure [21]. Generally, the reaction ($4OH^- \rightarrow 2H_2O + O_2 + 4e^-$) in alkaline condition, which starts with the OH^- anion adsorbed on the surface of catalyst, totally includes the following five steps [22]:

$$A + OH^- \rightarrow A\text{-}OH + e^- \quad (I)$$

$$A\text{-}OH + OH^- \rightarrow A\text{-}O + H_2O + e^- \quad (II)$$

$$A\text{-}O + OH^- \rightarrow A\text{-}OOH + e^- \quad (III)$$

$$A\text{-}OOH + OH^- \rightarrow A\text{-}O_2 + H_2O + e^- \quad (IV)$$

$$A\text{-}O_2 \rightarrow A + O_2 \quad (V)$$

In the equations of (I)–(V), A represents the surface active sites of catalyst. Obviously, O_2 is ultimately released by means of the above-mentioned steps. According to the reaction mechanism, it is significant to attain high-efficiency OER catalysts with numerous active sites by simple and practicable routes. As previously investigated, transition metal composite oxides, e.g. $NiCo_2O_4$ [23], $Mn_xCo_{3-x}O_4$ ($0 \leq x \leq 1$) [24], $Zn_xCo_{3-x}O_4$ and $Cu_xCo_{3-x}O_4$ [25,26], are remarkably more catalytically active than single transition metal oxides for OER because of the improved electrical conductivity and enriched active sites. In the light of these literatures, fabricating Mn-based composite oxides as OER catalysts is a feasible way. Meanwhile, as active materials for supercapacitors, there is a ticklish issue that the low electrical conductivity and poor ion transport rate of MnO_x severely restrict the substantial practical application [27]. To overwhelm this obstacle, constructing Mn-based composite oxides for supercapacitors is a kind of adopted effective measure because higher electrical conductivity and capacitance as well as excellent cycling stability can be achieved [28,29]. In consequence, it is worth to synthesize MnO_x-based composite oxides with special structure for both OER and supercapacitors.

As is known to us all, nanostructured materials, like nanoparticles, nanoplates or nanomeshes, are characterized with high specific surface area, which is not only favorable for increasing active sites and thus enhancing electrocatalytic activity in OER [30,31], but also conductive to improving charge/discharge rate capability in supercapacitors [27]. From the previous literatures [32,33], it is generally acknowledged that nanomesh, unique two-dimensional (2D) porous nanoscale architecture, which perfectly combines the virtues of porous structure and 2D nanosheet, plays a key role in energy storage and conversion. Moreover, the special nanomesh for OER also possesses several advantages. On the one hand, the thin thickness of 2D nanomaterial can reduce ion diffusion path and extend the contact area with electrolyte. On the other hand, the porous structure greatly promotes the diffusion of active species and expedites the surface reaction during the electrocatalytic process [10,21]. Taking these into account, we have

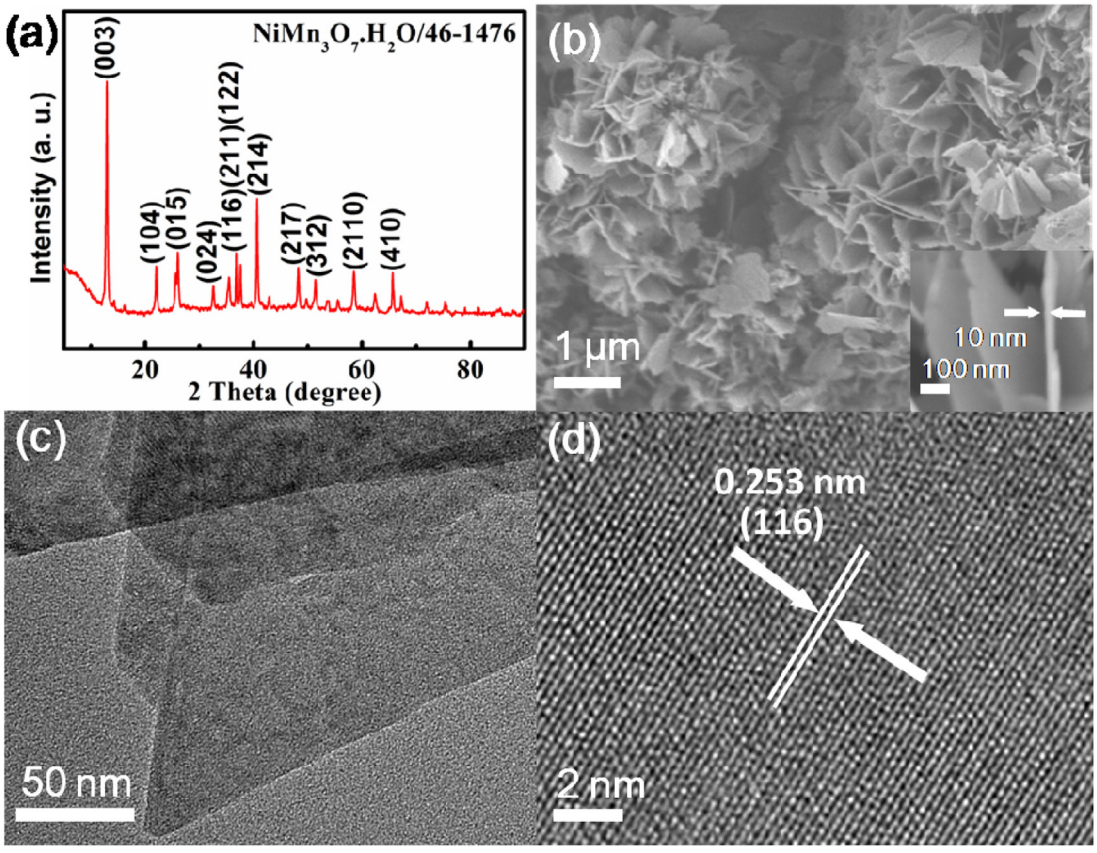

Fig. 1. (a) XRD data, (b) Low-magnification and cross-sectional (inset of b) SEM images, (c) representative TEM and (d) HRTEM images of $NiMn_3O_7.H_2O$ nanosheets.