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Hybrid architecture of rhodium oxide nanofibers and ruthenium oxide nanowires for electrocatalysts

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ABSTRACT

We report the synthesis and electrochemical performances of the hybrid architecture of rhodium oxide (Rh_2O_3) nanofibers (NF) and highly single crystalline RuO_2 nanowires (NW) by combining the electrospinning process and a simple recrystallization process. The amorphous $Ru(OH)_3 \cdot xH_2O$ precursors at relatively low temperature were efficiently transformed into highly single crystalline RuO_2 nanowires with the tetragonal rutile structure on electrospun Rh_2O_3 nanofibers. Pure Rh_2O_3 NF and hybrid RuO_2 NW–Rh_2O_3 NF exhibited different electroactivities toward H_2O_2 electrochemical reaction: Rh_2O_3 NF facilitates the H_2O_2 oxidation vs. hybrid RuO_2 NW–Rh_2O_3 NF promotes H_2O_2 reduction more favorably. The H_2O_2 reduction free from O_2 reduction interference at RuO_2 NW–Rh_2O_3 NF is advantageous and finds the feasibility for selective H_2O_2 detection in various samples. Furthermore, RuO_2 NW–Rh_2O_3 NF generated a greatly higher current induced by H_2O_2 reduction (i.e., enhanced sensitivity to H_2O_2) than bare Rh_2O_3 NF.

1. Introduction

Hierarchically formed, hetero-structured metal oxide systems have great attentions due to unique catalytic, electrical, and optoelectronic properties under a broad range of compositions [1–9]. Typically, built up from quasi one-dimensional systems, the hetero-structured, branched structures can be easily combined with individual properties from each component without losing their original properties. The engineered, nano-scaled branches can thus provide a large surface area for catalytic reactions and a facile mass transfer platform. Recently, various metal oxides/metal oxides and metal or semiconductor hetero-structured systems were extensively demonstrated via the hydrothermal [8–11] and chemical or physical deposition [12,13] of secondary compositions ("branch structure") on pre-formed nanowire or nanofiber ("core structure"). The electrospinning has been adopted to create the fibrous structures in a relatively large scale with a variety of materials, such as polymers and metal/metal oxide precursors. It can conveniently provide a good, "core" platform to build up the hetero-structured branched systems. However, it seems to be still difficult to control to grow well-defined secondary structures using typical vapor phase depositions or hydrothermal methods with the electrospun core fibrous structures. The vapor-liquid-solid [14,15] (VLS)/vapor-solid [16] (VS) phase growth of the secondary phase has been considered for the controlled deposition and having high coverage density on the first core structure surfaces due to the fast reaction kinetics and relatively small amount of waste production.

Rhodium, typically with its' the oxidized form, are widely used in variety of applications, including catalytic converters for CO oxidation, NO reduction, and N_2O decomposition. Quasi one dimensional structure of rhodium oxide was rarely reported, for

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example, polycrystalline rhodium nanowire formation using electrodeposition through template synthesis [17]. Up to now, the template-free, synthesis of rhodium oxide nanofibers(Rh_2O_3 NF) with a large scale has not been reported. Ruthenium oxide (RuO_2) has excellent chemical and thermal stability so that its nanostructures have been used for many applications such as high energy density capacitors, hydrogenation and the oxidation of CO. In addition, high electrical conductivity of ruthenium oxide often helps to facilitate electrochemical processes when conjunction with platinum and rhodium [18]. Despite the fact that the ruthenium oxide nanowire has excellent properties, very few hierarchical hetero-structure formations with other materials have been demonstrated so far. Recently, we reported ruthenium oxide nanostructure growth on carbon fibers/carbon nanotubes and ruthenium oxide nanowire growth on graphene substrates [19–22].

Herein, we have first prepared rhodium oxide nanofibers by electrospinning and then grown highly crystalline RuO_2 nanowires directly on rhodium oxide nanofibers successfully. Additionally, we examined the electrochemical performances of pure Rh_2O_3 nanofibers (Rh_2O_3 NF) and RuO_2 nanowire–Rh_2O_3 nanofiber hybrid nanostructures exhibited different electroactivities toward H_2O_2 electrochemical reactions.

2. Experimental

2.1. Growth of Rh_2O_3 nanofibers

2.1.1. Synthesis of Rh_2O_3 nanofibers

To prepare the rhodium oxide electrospun fibers, 0.1 g of rhodium chloride hydrate ($RhCl_3 \cdot xH_2O$, Sigma–Aldrich) and 0.2 g of polyvinylpyrrolidone (PVP, Mw $\approx$ 1,300,000, Sigma–Aldrich) were dissolved in 2.2 ml of the mixed solvent including water and ethanol with a volume ratio of 1:1 respectively. After stirring the mixed solution for 24 h, the solution was loaded in a syringe which was attached to the needle tip at the end of the syringe. The flow rate of the solution on the needle tip was operated at 5 μl/min and the distance between the end of needle tip and the surface of a grounded aluminum plate was 7.5 cm via an electrospinning system (NanoNC ESR200R2). The syringe needle was connected to a high voltage power source and applied voltage was 7.0 kV. The stainless steel needle of gauge 25 was used as the syringe needle. The electrospun fibers were dried for 10 min at 60 °C and then the calcination of the $RhCl_3$/polymer nanofibers was performed at 700 °C for 2 h after reaching 700 °C with the ramping speed of 1.6 °C/min.

2.2. Growth of RuO_2 nanowires on Rh_2O_3 nanofibers

The $Ru(OH)_3 \cdot xH_2O$ precursor were prepared though a chemical reaction by carefully dropping diluted NaOH solution to 5 mM ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$, Sigma–Aldrich, 99.98%) aqueous acidic solution until pH 11.0 at room temperature. During the procedure, the amorphous $Ru(OH)_3 \cdot xH_2O$ precursor was precipitated. To rinse the $Ru(OH)_3 \cdot xH_2O$ precursor, the solution was centrifuged for 20 min 5 times and then 0.1 mg of the precursor was dispersed in 10 mL of water. A few drops of the $Ru(OH)_3 \cdot xH_2O$ precursor solution was directly spread on about 1 mg of the rhodium oxide nanofibers. After drying at 60 °C for 1 h, the sample was placed on the middle of the furnace at 300°C for 4 h. The product was characterized by scanning electron microscopy (SEM), X-ray Diffraction (XRD), micro-Raman spectroscopy and high resolution transmission electron microscopy (HRTEM; FEI Titan TEM/STEM at 300 kV) at room temperature.

2.3. Electrochemical measurements

Hydrogen peroxide (H_2O_2, 35 wt%), potassium nitrate (KNO_3), sodium phosphate monobasic (NaH_2PO_4), sodium phosphate dibasic (Na_2HPO_4), and Nafion (5%) were purchased from Sigma–Aldrich (St. Louis, MO). Oxygen (O_2) and argon (Ar) gases were obtained from Dong-A Gas Co. (Seoul, Korea). As synthesized Rh_2O_3 nanofibers (Rh_2O_3 NF) or RuO_2 nanowires grown on Rh_2O_3 NF (RuO_2 NW–Rh_2O_3 NF) were dispersed in deionized water (2 mg mL^{-1}). 6 μL of the dispersed sample was loaded on a cleaned glassy carbon (GC) disk electrode ($A = 0.071$ cm^2 Bioanalytical Systems Inc.) followed by drying. This sample loading/drying procedure was repeated 5 times, and therefore 30 μL of the sample suspension in total was loaded on a GC electrode. Then, 10 μL of 0.05% Nafion (Sigma–Aldrich, St. Louis, MO) solution was applied on the electrode and dried.

For the following electrochemical experiments, the GC disk electrode loaded with either Rh_2O_3 NF or RuO_2 NW–Rh_2O_3 NF, saturated calomel electrode (SCE, Bioanalytical Systems Inc.), and coiled Pt wire (0.5 mm in diameter) were used as the working, reference, and counter electrodes, respectively. The electroactivities of Rh_2O_3 NF and RuO_2 NW–Rh_2O_3 NF were studied using rotating disk electrode (RDE) voltammetry. RDE voltammetry was carried out with a GC electrode loaded with either Rh_2O_3 NF and RuO_2 NW–Rh_2O_3 NF in 0.05 M phosphate buffer solution (pH 7.4) containing 1 mM H_2O_2. RDE voltammetry of RuO_2 NW–Rh_2O_3 NF was additionally performed in O_2 saturated 0.05 M phosphate buffer solution to study its activity for oxygen reduction reaction. Amperometric responses of Rh_2O_3 NF and RuO_2 NW–Rh_2O_3 NF for H_2O_2 reduction were measured at 0.12 V vs. SCE in 0.05 M phosphate buffer solution (pH 7.4) under stirring into that a standard H_2O_2 solution was added successively to alter the H_2O_2 concentration. To investigate capacitive current behaviors depending on potential scan rate, cyclic voltammetry (CV) was carried out in deaerated 1 M KNO_3 solution (Sigma–Aldrich, St. Louis, MO) solution at different scan rates ranged from 10 to 200 mV s^{-1}.

All aqueous solutions were prepared by using deionized water (18 MΩ cm). RDE-2 rotor/Epsilon electrochemical analyzer (Bioanalytical Systems Inc.) was used for RDE experiments and amperometry and CHI 920C potentiostat was used for amperometry and CV.

3. Results and discussion

3.1. The characterization of electrospun Rh_2O_3 nanofibers and RuO_2 nanowires on Rh_2O_3 electrospun nanofibers

Fig. 1 indicates SEM images of electrospun Rh_2O_3 nanofibers, which was prepared from an ethanol and water solution containing $RhCl_3 \cdot H_2O$ and PVP, before and after thermal annealing process at 700 °C in the air. Fig. 1(a) and (b) indicate that electrospun fibers have the smooth surface and their diameters are mostly in range from 100 to 400 nm. In contrasts, Fig. 1(c) and (d) show that the morphology of these nanofibers were dramatically changed after annealing at 700 °C for 2 h. The surface of electrospun fibers was relatively rough and the diameters of Rh_2O_3 nanofibers were greatly reduced to about 50 nm. It is likely because the removal of the matrix precursor of PVP and the oxidation process of the $RhCl_3 \cdot xH_2O$/PVP composite nanofibers into polycrystalline Rh_2O_3 phase took place during the thermal annealing process. Fig. 2 represents SEM images of hierarchically grown RuO_2 nanowires on electrospun Rh_2O_3 nanofibers by a thermal annealing process from $Ru(OH)_3 \cdot xH_2O$ precursor at low temperature. SEM images of high magnification show that a great density of RuO_2 nanowires were randomly grown by covering the surface normal plane of