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Controlled synthesis of MnO₂@TiO₂ hybrid nanotube arrays with enhanced oxygen evolution reaction performance

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ABSTRACT

A novel tube-in-tube nanostructure of MnO₂@TiO₂ hybrid arrays has been obtained by a facile and controllable chemical bath deposition method. Scrutiny on the hybrid arrays indicates that the chemical bath deposition method favors the growth of the MnO₂ nanotubes with different diameter which can modulate the oxygen evolution reaction (OER) activity as well as bandgap width of the hybrid. In terms of OER activity, onset potential (E_s) shifts negatively from 0.698 V (vs. Ag/AgCl) of pristine titania nanotube arrays (TNAs) to 0.501 V of the hybrid loaded with 26.6%wt MnO₂, and the current density on the hybrid electrode can be significantly enhanced up to 20.87 mA/cm², almost 97 times higher than that on TNAs electrode (0.214 mA/cm²). Optical absorption measurement suggests that the bandgap width (E_g) can be tuned by loading MnO₂ onto the TNAs implying interaction between the MnO₂ and TNAs. The MnO₂@TiO₂ hybrid nanotube arrays may find promising potential in electrochemical water splitting, photocatalysis, thermocatalysis and other sustainable energy applications.

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Introduction

Due to energy crisis and environmental pollution, the demand for renewable and environmentally friendly energy is steadily increasing. Room temperature electrolysis of water has attracted great interest in developing sustainable energy

because it can produce hydrogen gas for reliable power storage by making full use of some climate- or geography-dependent energy sources such as solar and wind energy [1–3]. In alkaline media, electrochemical water electrolysis involves two half reactions: the cathodic hydrogen evolution reaction (HER)

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and the anodic oxygen evolution reaction (OER)



Of the two half-reactions, the OER requires formation of two oxygen-oxygen bonds in the four-electron redox processes, which makes it more kinetically demanding for water electrolysis [4,5], therefore, development of electrocatalysts with high OER activity is crucial for promoting possible hydrogen economy [6,7]. Noble metals (e.g. Ru, Ir, Pt) and the noble metal oxides (e.g. RuO₂, IrO₂) have been utilized as OER catalysts owing to their high activity, however, these catalysts suffer from poor chemical stability in alkaline media, less abundance and high cost, which hinders their commercialization [8–16].

In terms of non-noble metal based OER catalysts, manganese oxide has attracted special attention owing to its variable crystallographic structures and types distinguished by the different connectivity between basic unit of octahedral [MnO₆] [17], which promises the construction of different manganese oxide nanostructures such as nanoplates [18], nanotubes [19], nanorods [20], urchin-like [21], porous structure [22] and other hierarchical structures [23] with changeable catalytic activities, superior stability and low toxicity [24–28]. As is known, the electrochemical properties of manganese oxide are highly dependent on the underlying support [29]. Recent research has indicated that deposition of manganese oxide on titanium oxide nanostructures can obtain promoted OER activity based on density function theory and experimental results [30].

One-dimensional TiO₂ nanostructures feature high-aspect-ratio with semiconductive nano-object characteristics [31]. By modifying TNAs with MnO₂, both morphological tuning for surface and synergistic effect between the two components are expected to elevate OER activity. Li et al. synthesized manganese oxide/TiO₂ nanorods by hydrothermal method which presented enhanced OER activity due to synergistic effect between the two components [32]; Seong et al. deposited manganese nanoparticles within nanotubular TiO₂ by potential shock method, which demonstrated negatively shifted onset potential and significantly higher current density [30]. In this paper, we report a novel tube-in-tube structure of MnO₂@TiO₂ hybrid nanotube arrays by a facile chemical bath deposition process which features well-controlled size of target materials that follow a “cluster-by-cluster” or “molecule-by-molecule” growth mode [33,34]. The chemical bath deposition method in this study demonstrates well controlled growth of MnO₂ nanotubes with different diameter and the feasibility of low cost processing of an earth abundant material for OER.

To the best of our knowledge, there has no report on the growth of MnO₂@TiO₂ tube-in-tube hybrid nanoarrays by this approach. Compared to other research work in this field, the hybrid nanotube arrays in this work may present following advantages: (1) the tunnel structure of the product can facilitate the diffusion of active species and present high intrinsic activity [35]; (2) The continuous MnO₂ nanotubes can provide a large electrode surface area and good conducting pathways;

(3) The synergistic effect between the two components of the hybrid nanotubes can improve the catalyst OER performances; (4) The metal Ti substrate can act as both a substrate for supporting the nanotube arrays and a superior conductive electrode for electron transport.

Experimental section

Materials and treatment

Titanium (Ti) foils (Sigma-Aldrich, 99.999%, 0.1 mm thick) were cut into 2.5 × 5 cm for growing titania nanotubes by anodization. First, the Ti foils were ultrasonically washed in an acetone solution for 15 min and in an anhydrous ethanol solution for 15 min sequentially, then rinsed with DI water repeatedly to obtain a mirror finish, finally left to dry in air. Ethylene glycol (99%, Sinopharm Chemical Reagent Co., Ltd.), NH₄F (99%, Sigma-Aldrich), potassium manganite (KMnO₄, 99%, Sigma-Aldrich), sulfuric acid (95–98 wt%, Sinopharm Chemical Reagent Co., Ltd.) were utilized for synthesis of MnO₂@TiO₂ hybrid nanotube arrays without further purification. All chemicals used were of analytical reagent grade. Fig. 1 represents the schematic diagram of synthesizing the MnO₂@TiO₂ hybrid nanotube arrays in this work.

Synthesis of TNAs

TNAs were firstly grown by a two-step chemical anodic oxidation. First, TNAs were synthesized on the pretreated Ti foils, by dipping the Ti foils into a solution of ethylene glycol, NH₄F (0.25 mol/L) and DI water (3vt%). The Ti foil was used as an anode, while graphite plate was used as a cathode. A constant voltage of 60 V was applied to the cell for 10 min and, then ultrasonically off a layer of thin film on the surface of the titanium plate in deionized water. By repeating the above process, a constant voltage of 60 V was applied to the cell for 6 h to obtain titania nanotube arrays as shown in Step I of Fig. 1.

Synthesis of MnO₂@TiO₂ hybrid nanotube arrays

Specifically, TNAs template was sonicated in a 0.035 M aqueous KMnO₄ solution for 1hr to absorb MnO₄[−] on the inner wall of the TNAs; then the acidity of the solution was adjusted by adding 3 mM sulfuric acid and the solution was sonicated for 1 h followed by heating the solution to 75 °C to obtain MnO₂ nuclei on the wall of the TNAs as shown in Step II of Fig. 1. After that, MnO₂ nanotubes were gradually formed on the inner surface of the TNAs by modulating the deposition time, and the inner diameter of the MnO₂ nanotubes was tuned by adjusting the deposition time as shown in Step III of Fig. 1.

Characterizations

Phase structure of the products was characterized by Rigaku D/MAX2500V X-ray diffractometer. Composition was determined by a Thermo ESCALAB 250 X-ray Photoelectron Spectrometer (XPS) system. Morphology and microstructure of the

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