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Short communication

Facile synthesis of large-area CeO_2/ZnO nanotube arrays for enhanced photocatalytic hydrogen evolution

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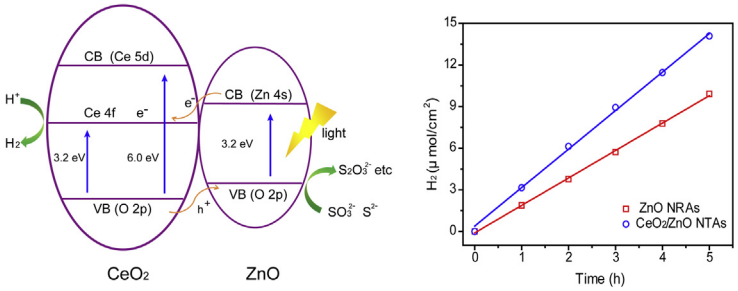
HIGHLIGHTS

- Design of CeO_2/ZnO nanotube array films via a simple two-step electrodeposition process.
- CeO_2/ZnO nanotube arrays exhibit enhanced photocatalytic activity and excellent stability.
- Films on FTO substrates make the collection and recycle of photocatalyst easier.

GRAPHICAL ABSTRACT



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ABSTRACT

CeO_2/ZnO nanotube array films grown on FTO substrates are successfully synthesized by a two-step electrodeposition process. The CeO_2/ZnO nanotube array films exhibit substantially enhanced photocatalytic activity with a hydrogen evolution rate of 2.7 μmol cm^{-2} h^{-1} under white light irradiation and excellent stability. Moreover, the collection and recycle of these immobilized CeO_2/ZnO nanotube array films are much easier compared with the powder photocatalysts.

1. Introduction

As a clean energy carrier without greenhouse gases or other pollutants, hydrogen has gained great interest owing to the increasing demand for energy and environment protection. Searching an effective and low-cost approach to produce hydrogen is very important for hydrogen economy. Photocatalytic hydrogen production is widely recognized as one of the most promising approaches to generate hydrogen, which is produced in a sustainable manner from solar energy without yielding carbon dioxide [1,2]. Recently, nanostructures have received considerable interest for photocatalytic hydrogen production due to their high surface area and rapid charge separation ability. Among various nanostructures, hollow nanotubes are attracting a great deal of attention as photocatalysts because they have higher interfacial area and faster charge transport pathway than nanoparticles and other one-

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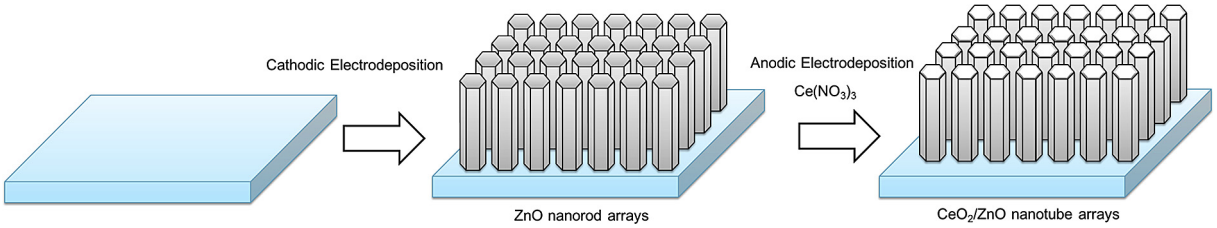

Fig. 1. Schematic diagram of the fabrication process for CeO_2/ZnO nanotube arrays.

dimensional (1D) nanostructures such as nanorods or nanowires [3,4]. Moreover, recent reports have demonstrated that the direct growth of ordered nanotubes on conductive substrates can facilitate the diffusion of active species and transport of electrons, and could further improve photocatalytic performance [5,6]. In recent years, numerous methods including high temperature evaporation, hydrothermal synthesis, anodic oxidation, and template- and surfactant-assisted growth techniques have been developed to prepare nanotubes on conductive substrates [7–11]. Nevertheless, the development of facile, low-cost and effective methods for the large-area synthesis of ordered nanotubes on conductive substrates is highly desirable, but still challenging.

Transition metal oxides such as TiO_2, ZnO and $BiVO_4$ have been extensively investigated as photocatalysts for photocatalytic hydrogen production [12–17]. Little attention has been paid to the rare earth oxides, regardless of their outstanding optical and catalytic properties. In recent years, CeO_2 has attracted increasing interest as a photoactive material because it has strong redox capability, and a relatively small band gap of 3.2 eV that originates from the O 2p to Ce 4f transition [18]. Additionally, CeO_2 nanostructures such as hexagonal nanorods and nanowires have been examined in photocatalytic hydrogen evolution, and they have shown good photocatalytic activity [6,19,20]. However, the large-scale fabrication of CeO_2 nanostructures with good photocatalytic activity, especially for commercial manufacture, is still very challenging. In this paper, we report a facile and cost-effective electrochemical method to synthesize large-area CeO_2/ZnO nanotube arrays (NTAs) on F-doped SnO_2 (FTO) glass substrates and their improved performance in photocatalytic hydrogen production. The CeO_2/ZnO nanotube arrays were grown on FTO substrates via a two-step electrodeposition process, which involves the cathodic electrodeposition of aligned ZnO nanorod arrays (NRAs) as the template and subsequently anodic electrodeposition of CeO_2 on the ZnO nanorods to form CeO_2/ZnO nanotubes. These CeO_2/ZnO nanotube arrays grown directly on FTO substrates can provide a high interfacial area and superior electron transport pathways, which hence improve their photocatalytic performance. The CeO_2/ZnO nanotube arrays exhibited substantially higher photocatalytic activity than ZnO nanorod arrays, with a hydrogen evolution rate of 2.7 μmol cm^{-2} h^{-1} under white light irradiation and good cycling performance.

2. Experimental

2.1. Materials

The analytical grade of commercially $Zn(NO_3)_2$ (Sinopharm Chemical Reagent Co., Ltd., Beijing, China), $Ce(NO_3)_3$ (Sinopharm Chemical Reagent Co., Ltd., Beijing, China), ammonium acetate (NH_4Ac) (Sinopharm Chemical Reagent Co., Ltd., Beijing, China), hexamethylenetetramine (HMT) (Sinopharm Chemical Reagent Co., Ltd., Beijing, China) and dimethyl sulfoxide (Sinopharm Chemical Reagent Co., Ltd., Beijing, China) were used directly without any purification. The F-doped SnO_2-coated glass (FTO, TCO-15) with a sheet resistance of 14 <OMEGA> per square was purchased from Nippon Sheet Glass Co., Ltd., Tokyo, Japan. The FTO glass was cleaned ultrasonically in distilled water, ethanol, and acetone and then rinsed in distilled water again before electrodeposition.

2.2. Photocatalysts preparation

The CeO_2/ZnO nanotube arrays were synthesized by a two-step electrodeposition process, which is summarized schematically in Fig. 1. First, ZnO nanorod arrays were grown on FTO substrates (4 × 4 cm^2) by cathodic electrodeposition in an aqueous solution containing 0.02 M $Zn(NO_3)_2$, 0.01 M NH_4Ac and 0.01 M HMT with a current density of 0.5 mA cm^{-2} at 90 °C. After 60 min cathodic deposition, a white film was obtained on FTO substrate. The ZnO nanorod arrays were then used as templates for further formation of CeO_2/ZnO nanotube arrays. CeO_2/ZnO nanotubes were directly obtained via anodic electrodeposition in a solution of 0.01 M $Ce(NO_3)_3$ + 10% DMSO (10 vol % DMSO:90 vol % H_2O) with a current density of 0.25 mA cm^{-2} at 90 °C.

2.3. Characterizations and measurements

The surface morphologies and microstructures were analyzed by a field-emission scanning electron microscope (FE-SEM, JSM-6330F) and transmission electron microscopy (TEM, JEM-2010F). The structures of the samples were investigated via an X-ray diffractometer (XRD, D8 ADVANCE) using Cu Kα radiation (λ = 0.15418 nm). The chemical state of the films was analyzed directly using X-ray photoelectron spectroscopy (XPS, ESCA-Lab250). The optical properties of the products were measured with a UV–Vis–NIR Spectrophotometer (UV–Vis–NIR, Shimadzu UV-2450).

The photocatalytic hydrogen evolution reactions were examined in a closed gas circulation and evacuation system. Typically, a piece of large-area ZnO or CeO_2/ZnO films (4 × 4 cm^2) was immersed into 100 mL of 0.1 M Na_2S and 0.1 M Na_2SO_3 mixed aqueous solution in a Pyrex reaction cell. The light source was a 300 W Xe lamp (PLS-SXE-300UV, Beijing Trusttech) supplying the full wavelength illumination. The intensity of the white light was determined by an irradiatometer (BNU photoelectric Co., Ltd., FZ-A) and was about 100 mW cm^{-2}. The amount of hydrogen produced was analyzed using on-line gas chromatography (with a thermal conductivity detector and an N_2 carrier).

3. Results and discussion

Fig. 2a is the photo image of CeO_2/ZnO nanotube arrays obtained on FTO substrate, showing that most of the FTO substrate (around 16 cm^2) was uniformly covered by a thin film with good transmittance. Scanning electron microscopy (SEM) images in Fig. 2b and c clearly show that the white film obtained on FTO substrate was covered by dense and ordered ZnO nanorods. These nanorods