



Synthesis of Porous Europium Oxide Particles for Photoelectrochemical Water Splitting



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ABSTRACT

In this paper, we report the facile electrochemical synthesis of porous Eu_2O_3 particles (NPs) and their implementation as photoanode for photoelectrochemical (PEC) water splitting for the first time. These porous Eu_2O_3 NPs exhibit a significant photocurrent density of $40 \mu\text{A cm}^{-2}$ at 0.6 V vs. Ag/AgCl in 1 M KOH electrolyte under white light irradiation (Xe lamp, 100 mW cm^{-2}). Moreover, the as-synthesized Eu_2O_3 NPs have an excellent PEC stability with no obvious decay in its photocurrent after 100 min irradiation.

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1. Introduction

With the increasing demand for clean and renewable energy, numerous efforts have been made to explore various solar harvesting and conversion devices [1]. Photoelectrochemical (PEC) water splitting over semiconductor metal oxides has attracted numerous interests [2–8], because it is a promising and environmentally friendly method to produce hydrogen [9–15]. Among various metal oxides, transition metal oxides, such as TiO_2 [13,16], ZnO [17–19], Fe_2O_3 [20], In_2O_3 [21], have been extensively investigated as photoelectrodes for PEC water splitting, and remarkable progresses have been achieved [22,23]. On the other hand, it is still important to develop new high-efficient photoanodes. In comparison to the transition metal oxides, the PEC properties of rare earth oxides are rarely reported regardless of some rare earth oxides have shown good photoactivity [24,25].

Rare earth oxides have been widely used as high-performance luminescent devices, magnets, catalysts and other functional materials based on the electronic, optical, and chemical characteristics arising from their 4f electrons [26]. Among them, Eu_2O_3 is one of the most interesting rare earth oxides and widely used in up-conversion materials, low voltage cathodoluminescent devices,

high density optical storage devices, lasers, biochemical applications, and catalysts [27–30]. It is well known that the properties of Eu_2O_3 nanomaterials are obviously dependent on the crystallinity, crystallite size, crystallographic orientation, and morphology [28,31]. Therefore, the development of a facile and effective approach to synthesize Eu_2O_3 nanomaterials with controllable size and architecture is very desirable. On the other hand, recent reports have shown that Eu_2O_3 holds great potential as photoactive materials for the photocatalytic degradation of organic pollutants [31–33]. For instance, Yang et al. reported the photocatalytic activity of Ta_2O_5 on degradation of rhodamine B and 4-nitrophenol could be enhanced after mixed appropriate Eu_2O_3 [33]. Nevertheless, to the best of our knowledge, there is no report about the PEC performance of Eu_2O_3 for water splitting so far. Here, we developed a simple and effective method to prepare Eu_2O_3 particle photoanode for the PEC cells. Porous Eu_2O_3 particles (NPs) were synthesized successfully on F-doped SnO_2 (FTO) glass substrates by a simple and facile electrodeposition approach and a subsequent thermal treatment. These porous NPs grown directly on conductive substrates can not only provide a high interfacial area, but also offer a shortened ion diffusion path and fast electrical pathway [1,34]. More importantly, the Eu_2O_3 photoanode exhibited a significant photocurrent density of $40 \mu\text{A cm}^{-2}$ at 0.6 V vs. Ag/AgCl with good photostability. This present work not only provides an alternative approach to prepare Eu_2O_3 on conductive substrates, but also offers the feasibility of Eu_2O_3 as potential photoanode for water splitting.

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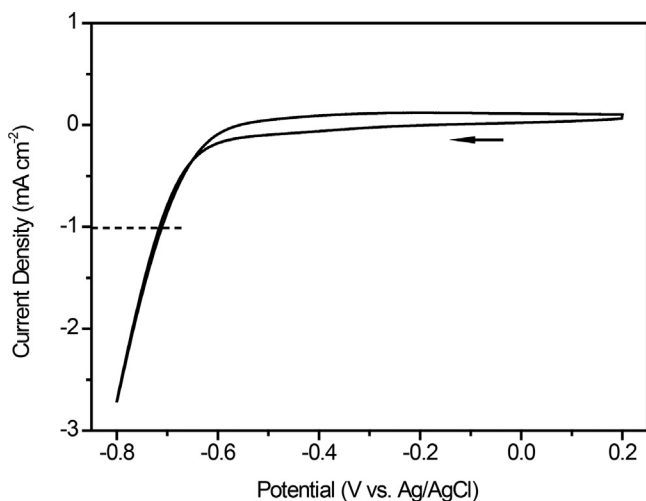


Fig. 1. Cyclic voltammetry of the electrode in the solution of 0.01 M $\text{Eu}(\text{NO}_3)_3$, 0.02 M NH_4Ac and 0.05 M KCl at a scan rate of 50 mV s^{-1} .

2. Experimental Section

2.1. Preparation of Eu_2O_3 Particles

All other reagents used in this study were of analytical grade and were used directly without any purification. Deionized-water was used throughout the experiments. $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were synthesized by dissolving Eu_2O_3 powders into nitric acid and recrystallization. Firstly, 5 g Eu_2O_3 was dissolved into 100 mL HNO_3 (62.9%, Guagnzhou Chemical Plant) under strong stirring. Then, the clean solution was heated on the hot plate of 200°C for 5 h and then filtered with ethanol for three times. Lastly, the crystal of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ re-dissolved into hot pure water till saturation and then cooled down naturally to get high purity $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (~98.8% calculated from the ICP results). Electrodeposition of $\text{Eu}(\text{OH})_3$ nanostructures were carried out in a conventional three-electrode cell with a graphite rod of about 4.0 cm^2 as the auxiliary electrode. The working electrode was an F-doped SnO_2 coated glass (FTO) with a sheet resistance of $14 \Omega \text{ cm}^2$. A saturated Ag/AgCl electrode was used as the reference electrode, which was connected to the cell with a salt bridge. Before electrodeposition, the FTO glass was cleaned ultrasonically in distilled water, ethanol, and acetone and then rinsed in distilled water again. $\text{Eu}(\text{OH})_3$ particles (NPs) were grown on FTO substrate in a solution containing 0.01 M $\text{Eu}(\text{NO}_3)_3$, 0.02 M ammonium acetate (NH_4Ac) and 0.05 M KCl with a cathodic current density of 1.0 mA cm^{-2} at 70°C for 15 or 30 min. After 15 or 30 min electrodeposition, gray films were obtained, washed by deionized-water and dried in air at room temperature for 6 h. Then, Eu_2O_3 particles could be obtained via a thermal decomposition method by annealing the gray film at 600°C for 4 h in air.

2.2. Materials characterizations

The surface morphology, microstructure and the composition of the samples were analyzed by scanning electron microscope (SEM, Quanta 400), Thermogravimetry (TG 209 F3 Tarsus), X-ray diffraction (XRD, Bruker, D8 ADVANCE) with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), transmission electron microscopy (TEM, JEM2010-HR) and X-ray Photoelectron Spectroscopy (XPS, ESCALab250) and the Raman spectroscopy that tested on a Laser Micro-Raman Spectrometer (Raman, Renishaw inVia) with Ar^+ laser of 633 nm excitation. For the measurement of the TEM, thin film of as-prepared samples were exfoliated from FTO

substrate and ground into powders, then some of the powder was dispersed into ethanol in the ultrasonic bath and the dispersed samples collected with carbon copper grids. The optical properties of the samples were measured with a UV-Vis-NIR Spectrophotometer (UV, Shimadzu UV-3150) and a combined fluorescence lifetime and steady state spectrometer (PL, EDINBURGH).

2.3. Photoelectrochemical characterizations

PEC measurements were carried out in a three-electrode cell with a flat quartz window to facilitate illumination of the photoelectrode surface. The working electrode is the as-annealed film with a light irradiation area of 0.25 cm^2 , while a Pt and an Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. The electrolyte was a 1 M KOH aqueous solution, which was bubbled in Ar for 30 min to remove the dissolved oxygen before PEC measurements. All photoelectrochemical experiments were measured by a CHI 760D electrochemical station under the UV light irradiation that provided by a Xe lamp (Newport 69907, 150 W xenon lamp). The intensity of light is about 100 mW/cm^2 . The incident-photon-to-current-conversion efficiencies (IPCE) were measured with a CHI 760D electrochemical station with a solar simulator (Newport 69911, 300 W xenon lamp) coupled with an aligned monochromator (Oriol Cornerstone 260 1/4 m). All the samples were prepared with a number of three for these electrochemical tests.

3. Results and Discussion

$\text{Eu}(\text{OH})_3$ particles were firstly grown on a FTO substrate via a facile electrodeposition method (Experimental section). Cyclic voltammograms of FTO electrode were used to define the potential region for the deposition of $\text{Eu}(\text{OH})_3$ in the solution containing 0.01 M $\text{Eu}(\text{NO}_3)_3$, 0.02 M ammonium acetate (NH_4Ac) and 0.05 M KCl (Fig. 1). The cathodic reduction wave at about -0.6 V vs. Ag/AgCl corresponds to the reduction of H_2O into H_2 and OH^- , and the later one reacted with the Eu^{3+} to generate $\text{Eu}(\text{OH})_3$:



Scanning electron microscopy (SEM) images in Fig. 2a clearly shows that a large number of nanomaterials with diameters from 80 to 500 nm were obtained. Typical thermogravimetry (TG) curves of $\text{Eu}(\text{OH})_3$ precursor obtained at 30 min electrodeposition is shown in Fig. S1. It can be clearly seen that the total weight loss of $\text{Eu}(\text{OH})_3$ particles is about 23%, which falls in the range of $25\text{--}500^\circ\text{C}$. The mass loss from room temperature to 200°C may be due to the evaporation of adsorptive water on the $\text{Eu}(\text{OH})_3$ surfaces. The other dominant loss in the range of $200\text{--}500^\circ\text{C}$ is 13%, which can be attributed to conversion from $\text{Eu}(\text{OH})_3$ to Eu_2O_3 .

In order to convert $\text{Eu}(\text{OH})_3$ into Eu_2O_3 , the as-prepared $\text{Eu}(\text{OH})_3$ particles were annealed at 600°C in air for 4 h. After annealing, the color of the film changed from grayish brown (inset in Fig. 2a) to white (inset in Fig. 2b). SEM images show the particle size became slightly bigger and more homogeneous after calcination. The change in the Eu_2O_3 particle size after calcination could be the result of annealing, aggregation, and sintering of small particles to form larger, which is in agreement with previous literatures [35,36]. X-ray diffraction (XRD) analysis was used to identify the crystalline phase of these nanomaterials before and after calcination. As shown in Fig. 2c, no obvious diffraction peaks were observed for the as-deposited sample except that of SnO_2 (FTO substrate), revealing that the as-deposited sample may be amorphous. After annealed at

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