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Electrodeposited P–Co nanoparticles in deep eutectic solvents and their performance in water splitting

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ABSTRACT

A facile one-step route has been developed to electrodeposite P–Co nanoparticles on a nickel foam in deep eutectic solvents. The as-prepared catalyst exhibits excellent performance towards both hydrogen evolution reaction and oxygen evolution reaction. Only 62 mV and 320 mV overpotentials were required to reach a current density of 10 mA cm⁻² for hydrogen evolution reaction and oxygen evolution reaction, respectively. That current density is measured at the voltage of 1.59 V for an overall water splitting when used as both anode and cathode. The scanning electron microscopy images indicate a high dispersion of the P–Co sample on the Ni foam. The prepared material possesses a relative high ECSA and a low charge transfer resistance, indicating a large number of active sites for water splitting.

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Introduction

Nowadays, great efforts have been made in search for clean and sustainable energy in order to reduce the use of fossil fuels and relieve pollution problems [1–3]. The water splitting into H₂ and O₂, consists of two half reactions, namely, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). With a theoretical potential of 1.23 V, it is considered as a sustainable and environmentally-friendly method of a fuel production [4,5]. However, the dynamic barrier in HER and OER leads to a much larger overpotential required to carry out this process [6–8]. So far the catalysts

based on noble metals and noble-metal oxides are considered as the best performing ones towards HER and OER [6]. Unfortunately, the large-scale application of these noble-metal-based catalysts is hindered by their reserve scarcity and high price. Therefore, there is an urgent need to develop highly efficient catalysts towards overall water splitting based on earth-abundant materials.

Developing transition-metals-based catalysts, such as Co, Mn, Ni, Cu and Fe attracts much attention for both OER and HER processes [9–12]. Among these materials, Co-based catalysts have been extensively studied for these two half reactions, e.g., CoP, CoO_x for HER and Co₃S₄, Co₃O₄ for OER

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[13–16]. Most of these catalysts have been prepared by a hydrothermal method, and then the discrete catalysts were loaded onto a working electrode with the assistance of polymer binders. However, the use of binders not only changes the catalysts structure, but also hinders the transportation of ions and electrons, which, in turn can result in a decrease of catalytic efficiency [17,18]. Very recently, cobalt phosphide on a nickel foam (CoP@NF), cobalt selenide on a Ti substrate (CoSe@Ti) and cobalt phosphate on a copper substrate (CoP@Cu) were prepared by a simple one-step electrodeposition route in aqueous solutions [12,19,20]. Furthermore, the electrodeposition route has several advantages compared to other routes. They are: 1) the catalyst preparation process is simple and products can be directly electrodeposited onto various substrates at a room temperature; 2) the substrates are generally flexible in terms of sizes, shapes and structures and electrodeposited catalysts on substrates are uniformly distributed [18]; 3) without the presence of polymer binders, the interface between a catalyst and an electrolyte is used efficiently and an unwanted resistance is avoided. Hence, there is an urgent need of the plating solutions that are nontoxic, non-corrosive, and environmentally-friendly, have an excellent conductivity, and a high solubility of metal salts.

Deep eutectic solvent (DES) as a new class of ionic liquid was first discovered by Abbott and coworkers [21,22]. DES exhibits a high solubility of metal salts and high conductivity. It is suitable for the electrodeposition of metals and metal compounds even at a very negative potential. The complex materials based on transition metals addressed as Ni–Mo, Ni–P, Co–Ag, and Ni–Co have been successfully electrodeposited in DES electrolytes [11,23–25]. However, the application of these materials for water splitting has rarely been reported. The objective of this paper is to present a facile potentiostatic electrodeposition method leading to Co_3O_4 and $\text{Co}_2(\text{P}_2\text{O}_7)$ composite (P–Co@NF) with bifunctional catalytic activity for water splitting. By adjusting the ratio of Co and P in DESs, we obtained a series of catalysts, i.e. 1/2P–Co@NF, 1P–Co@NF, 2P–Co@NF, and 3P–Co@NF and explored their performances towards HER and OER. When the ratio of Co and P was 1, the 1P–Co@NF exhibited the best performance. The P–Co nanoparticles were mainly composed of Co_3O_4 and $\text{Co}_2(\text{P}_2\text{O}_7)$ and displayed an outstanding performance for overall water splitting. The 1P–Co@NF nanoparticles electrodeposited from ChCl (choline chloride)-EG (ethylene glycol) system and their performance are discussed below.

Experimental details

Preparation of P–Co@NF catalysts

All reagents were of analytical reagent grade and used as received without any purification. Choline chloride (ChCl, 99%), ethylene glycol (EG, 99%), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 99%) and sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, 99%) were purchased from Fengchuan. Ltd. (Tianjin, China). To remove an oxide layer and organic species, a Ni foam (1 cm × 1 cm) was cleaned by an ultrasonic treatment with HCl (2 M), ethanol and deionized water, respectively. The eutectic solvent was formed by combining ChCl and EG (1:2 M ratio) at

80 °C until a clear homogeneous liquid was obtained. 0.1 M of CoCl_2 was dissolved into the above solvent to get the Co plating bath and by adjusting the concentration of NaH_2PO_2 to 0.05, 0.1, 0.2, and 0.3 M, a series of Co–P plating baths were obtained. The electrodeposition was performed in a conventional three-electrode electrochemical cell using an IM6&ZENNIUM electrochemical workstation. The typical cyclic voltammograms for the ChCl-EG plating bath and the four Co–P plating baths (Figure S1A, S1B), exhibit a reduction peak at the potential of 0.5 V (vs. Ag/AgCl) as a result of the decomposition of DESs [26]. For the CV curve of ChCl-EG bath, no significant current density was recorded in the potential range of –1 V to –2 V (vs. Ag/AgCl) (Figure S1A), indicating that the reaction of impurities in the DES can be ignored in the used potential range [27]. Figure S1B shows a characteristic crossover, which appeared in all CV curves, indicating the presence of a nucleation and growth processes [23]. Potentiostatic experiments were carried out at –1.6 V (vs. Ag/AgCl) with a specific ratio of P to Co at 0.5, 1, 2, and 3 onto the Ni foam. The current-time transients were recorded (Figure S2) and the samples were labeled as 1/2P–Co@NF, 1P–Co@NF, 2P–Co@NF, and 3P–Co@NF, respectively. After the electrodeposition, the as-prepared samples were washed with deionized water and dried at 60 °C for 12 h for further characterization and testing.

Characterization

The morphologies and elemental composition of the samples were determined using a scanning electron microscope (SEM, JSM-6490LV) accompanied with an energy dispersive X-ray spectrometer (EDS). X-ray diffraction (XRD) measurement was performed on a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda = 0.154$ nm) to determine the structure. To further investigate the structure, transmission electron microscopy (TEM), high-resolution TEM (HRTEM), the corresponding selected area electron diffraction (SAED), and electron dispersive spectroscopy (EDS) were conducted on a Jeol JEM 2100F electronic microscope at 200 kV. All the samples for TEM tests were dispersed in ethanol using an ultrasonic method and then dropcasted on the copper grid covered with a carbon film. The X-ray photoluminescence spectra (XPS) was collected using Thermo ESCALAB 250, equipped with an Al-K α X-ray source ($h\nu = 1486.6$ eV).

Electrochemical tests

All electrocatalytic measurements were performed in a typical three-electrode setup using an IM6&ZENNIUM electrochemical workstation in nitrogen-purged KOH (1.0 M) at a room temperature. For the HER test, the as-prepared 1/2P–Co@NF, 1P–Co@NF, 2P–Co@NF, and 3P–Co@NF, a graphite rod and Ag/AgCl electrode were used as working electrodes, a counter electrode and reference electrode, respectively [28]. For the OER test, the as-prepared 1/2P–Co@NF, 1P–Co@NF, 2P–Co@NF, and 3P–Co@NF, Pt wire and Ag/AgCl electrode were used as working electrodes, counter electrode and reference electrode, respectively. For comparison, a Pt wire

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