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Research Paper

CoS_2 nanoneedle array on Ti mesh: A stable and efficient bifunctional electrocatalyst for urea-assisted electrolytic hydrogen production

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ABSTRACT

In this work, we report that uniformly CoS_2 nanoneedle array grown on Ti mesh (CoS_2 NA/Ti) behaves as a stable and efficient bifunctional electrocatalyst for urea-assisted electrolytic hydrogen production via overall urea splitting. As a non-noble metal electrocatalyst, CoS_2 NA/Ti exhibited excellent urea oxidation reaction (UOR) and hydrogen evolution reaction (HER) catalytic activity in 1.0 M KOH with 0.3 M urea solution. Only a cell voltage of 1.59 V is required to achieve a current density of 10 mA cm^{-2} for full urea splitting in 1.0 M KOH with 0.3 M urea.

1. Introduction

Water electrolysis is a consolidated process to produce highly pure hydrogen, which is an ideal choice to replace fossil fuels [1–3]. However, the anodic oxygen evolution reaction (OER) is still the major bottleneck in the overall water splitting process [4,5] and needs much higher activation energy for O-O bond formation [6–8]. Replacing water with other more readily oxidizable species is a promising way for more energy-efficient electrolytic hydrogen production. Urea is an electro-oxidative species with the advantages of cheap, non-toxic and renewable [9–12]. All these advantages make anodic urea oxidation reaction (UOR) an ideal alternative for OER.

Although noble metal-based catalysts such as Pt/C, RuO_2 or IrO_2 can effectively reduce the energy barrier to promote the activity for UOR and hydrogen evolution reaction (HER) of urea electrolysis, however, their scarcity and high cost severely impede the applications [10,13–15]. Thus, there is an urgent call for alternative urea electrolysis catalysts based on the earth-abundant elements. In recent years, transition metal based composites, such as CoP_2 [16], Co-Mo-S [17], $NiCo_2S_4$ [18], $Co(OH)_2$@PANI [19] have been largely explored because of their good catalytic activity and low preparation cost [20,21]. Among these catalysts, cobalt disulfide (CoS_2) outperforms the most transition metal dichalcogenides due to its excellent metallic nature and high catalytic activity, making it a uniquely superior electrocatalyst [22–24]. In addition, long-term stability of CoS_2 was observed in both acidic and alkaline operating environments [23,25]. However, the development of efficient CoS_2 based bifunctional catalysts towards both UOR and HER for an energy-saving electrolytic hydrogen production has not been reported yet.

Herein, we immobilized 1D CoS_2 nanoneedle array on Ti mesh (denoted as CoS_2 NA/Ti) by a facile hydrothermal treatment, followed by a sulfuration process under N_2. The 1D morphology of CoS_2 could expose abundant surface active sites to accelerate the electrolyte transportation [26,27] and facilitate the release of N_2 and CO_2 at anode and H_2 at cathode. The stable interaction between the Ti mesh and CoS_2 nanoneedle array could facilitate the electron transport [28,29] and prevent CoS_2 agglomeration during the urea electrolysis process [20,24,30]. As a result, the electrocatalytic performance of CoS_2 NA/Ti can be achieved at a cell voltage of only 1.59 V to generate a current density of 10 mA cm^{-2} for full urea splitting in 1.0 M KOH with 0.3 M urea.

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2. Experimental

2.1. Materials

Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, AR), sublimed sulfur (S, CP), ammonium fluoride (NH_4F, AR) and urea (H_2NCONH_2, AR) were received from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ti mesh was bought from Hang Xu Company in Hebei province (Hebei, China). Deionized water was utilized for preparation of all solutions. All reagents were analytical grade and utilized without further purification. Pt/C catalyst was purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China).

2.2. Preparation of the cleaned Ti mesh

A piece of Ti mesh ($2 \times 3\,cm^2$) was washed with HCl at 30 °C for 15 min, then rinsed with ethanol and deionized water several times to ensure Ti mesh surface was clean enough for subsequent use.

2.3. Synthesis of CoS_2 NA/Ti mesh

First, the precursor of $Co(OH)_2$ NA/Ti was prepared by one step hydrothermal method. Typically, 1.75 g (6 mmol) of $Co(NO_3)_2{\cdot}6H_2O$, 0.15 g (4 mmol) of NH_4F and 1.20 g (20 mmol) of urea were completely dissolved in 40 mL deionized water, the mixed solution was stirred at room temperature to afford a uniform solution. After that, this solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave. The cleaned Ti mesh ($2 \times 3\,cm^2$) was vertically placed against the wall of Teflon-liner, and maintained at 110 °C for 8 h in a vacuum oven. The $Co(OH)_2$ NA/Ti was rinsed several times by deionized water and ethanol, and dried at 60 °C. Finally, the as-obtained $Co(OH)_2$ NA/Ti precursor was sulfurated by high temperature sulfuration method. A combustion boat loaded with 1.00 g sublimed sulfur powder was placed upstream in a tube furnace, a combustion boat with $Co(OH)_2$ NA/Ti precursor was placed in the downstream of tube furnace. This sample was heated to 400 °C (heating rate: 5 °C min^{-1}) for 2 h under N_2 atmosphere to afford the CoS_2 NA/Ti mesh. And the loading of CoS_2 NA on Ti mesh was 1.48 mg cm^{-2}.

2.4. Synthesis of Pt/C and RuO_2 loaded electrodes

RuO_2 was synthesized as below. 0.01 mol $RuCl_3{\cdot}3H_2O$ was dissolved into 100 mL deionized water and heated at 100 °C for 10 min, 30 mL 1.0 M KOH solution was then added for adjusting the pH value to 11. The resulting mixture was maintained at 100 °C for 45 min under stirring. The precipitate was centrifuged and rinsed several times with deionized water and ethanol to get rid of the

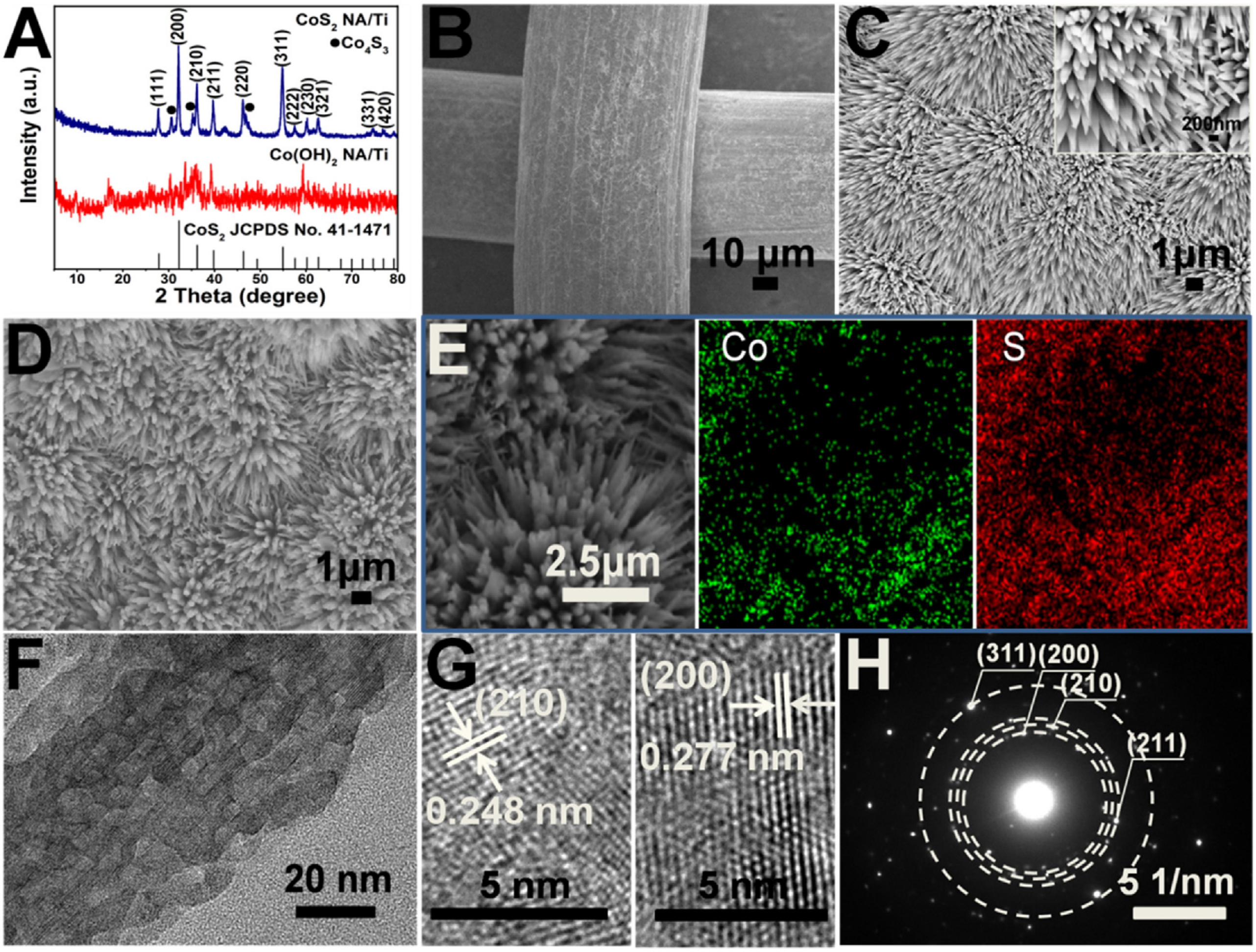

Fig. 1. (A) XRD patterns of $Co(OH)_2$ NA/Ti and CoS_2 NA/Ti. SEM images of (B) bare Ti mesh, (C) $Co(OH)_2$ NA/Ti, and (D) CoS_2 NA/Ti. (E) EDX elemental mapping of Co and S. HRTEM images of CoS_2 NA/Ti (F and G). (H) SAED pattern of CoS_2 NA/Ti. The inset of Fig. 1C represents the magnified SEM image of CoS_2 NA/Ti.