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Article

Three-dimensional lily-like CoNi_2S_4 as an advanced bifunctional electrocatalyst for hydrogen and oxygen evolution reaction

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ABSTRACT

Designing low-cost, highly efficient, and stable bifunctional electrocatalysts for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is of vital significance for water splitting. Herein, three-dimensional lily-like CoNi_2S_4 supported on nickel foam ($\text{CoNi}_2\text{S}_4/\text{Ni}$) has been fabricated by sulfuration of the Co–Ni precursor. As expected, $\text{CoNi}_2\text{S}_4/\text{Ni}$ possesses such outstanding electrocatalytic properties that it requires an overpotential of only 54 mV at 10 mA cm^{-2} and 328 mV at 100 mA cm^{-2} for HER and OER, respectively. Furthermore, by utilizing the $\text{CoNi}_2\text{S}_4/\text{Ni}$ electrodes as bifunctional electrocatalysts for overall water splitting, a current density of 10 mA cm^{-2} can be obtained at a voltage of only 1.56 V.

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1. Introduction

Electrocatalytic splitting of water via hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is widely considered to be a feasible method of producing high-purity hydrogen fuel from aqueous solutions [1–3]. Nevertheless, both HER and OER require active and durable electrocatalysts to lower their overpotential and overcome sluggish kinetics [4]. To date, Pt has been regarded as the best HER electrocatalyst, while IrO_2 and RuO_2 are the most active electrocatalysts for OER [5]. Unfortunately, the scarcity and extremely high cost of these noble metals severely limit their widespread application. To this end, enormous efforts have been committed to exploring earth-abundant and inexpensive electrocatalysts, especially bifunctional electrocatalysts, for overall water splitting. These include alloys of various three-dimensional (3D) transition metals (Mn, Fe, Co, Ni, etc.) [6] and their oxides/hydroxides

[7–14], sulfides [15–20], selenides [21], phosphides [22], nitrides [23], as well as carbides [17,24,25]. Among these, transition metal sulfides (TMSs), especially CoNi sulfides, have received considerable attention as they exhibit distinctive bifunctional electrocatalytic properties owing to their hydrogenase-like catalytic mechanism [26]. Liu *et al.* [27] proposed a water electrolyzer, which utilized a NiCo_2S_4 nanowire array on carbon cloth (NiCo_2S_4 NA/CC) as a bifunctional electrocatalyst in an alkaline medium, and could obtain 10 mA cm^{-2} at a cell voltage of 1.68 V. Subsequently, Fang *et al.* [28] reported that an alkaline electrolyzer based on $\text{Ni}_{2.3\%}\text{–CoS}_2/\text{CC}$ only needed a cell voltage of 1.66 V to deliver 10 mA cm^{-2} . Although recent years have witnessed remarkable progress in this field of research, developing CoNi sulfides with favorable configurations for extraordinary bifunctional electrocatalytic performance remains a practical challenge.

Notably, 3D materials with unique nanostructures have

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been reported as the most promising electrocatalysts for application in electrochemical reactions due to their large surface area, fast electron transport, and abundance of active sites exposed to the electrolyte [29]. Currently, the majority of TMS-based catalysts are 1D nanowires [19,27,28] and 2D nanosheets [26]. However, these materials tend to aggregate and suffer from low electron transmission capacity, which impedes their electrocatalytic activity. Therefore, one possible solution is to develop TMS-based catalysts with distinct 3D nanostructures to obtain potential electrocatalysts for bifunctional water splitting.

Herein, we report our research on novel 3D lily-like CoNi_2S_4 directly grown on Ni foam ($\text{CoNi}_2\text{S}_4/\text{Ni}$). Benefiting from the active Ni^{6+} and S^{6-} species, large active surface area, mesoporous structure, and enhanced charge transfer capacity, the 3D lily-like $\text{CoNi}_2\text{S}_4/\text{Ni}$ demonstrated excellent catalytic performance and stability toward both HER and OER in basic electrolytes. An alkaline electrolyzer assembled using this versatile $\text{CoNi}_2\text{S}_4/\text{Ni}$ electrode exhibited remarkable activity for overall water splitting with 10 mA cm^{-2} at a cell voltage of only 1.56 V.

2. Experimental

2.1. Materials

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CH_3CSNH_2 (Thioacetamide, TAA), CON_2H_4 (urea), and NH_4F were purchased from Aladdin. The Ni foam was purchased from Kunshan Electronic Limited Corporation. No additional purification step was performed for all the reagents.

2.2. Synthesis of the CoNi-precursor/Ni

The Ni foam ($3 \text{ cm} \times 3 \text{ cm}$) was immersed in 3 mol L^{-1} HCl solution by sonication and absolute ethanol for 15 min each. Next, 0.175 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.873 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.10 g of urea, and 0.10 g of NH_4F were adequately dissolved in a mixture of 30 mL of deionized water and 20 mL of absolute ethanol under agitated stirring. Next, the homogeneous solution was transferred into a Teflon-lined autoclave (80 mL) with the clean Ni foam in it. The autoclave was sealed and heated at 120°C for 6 h. After it had cooled to ambient temperature, the CoNi-precursor/Ni was taken out and washed with deionized water thoroughly, and then dried at 60°C for 2 h.

2.3. Synthesis of the $\text{CoNi}_2\text{S}_4/\text{Ni}$

The as-prepared CoNi-precursor/Ni was added to 50 mL deionized water with 0.376 g TAA, and the mixture was stirred to form a homogeneous solution. The resulting solution was transferred into an autoclave and heated at 160°C for 4 h. Upon cooling to room temperature spontaneously, the as-made material was washed thrice with deionized water and ethanol to remove impurities on the surface, and then dried at 60°C overnight. The mass loading of $\text{CoNi}_2\text{S}_4/\text{Ni}$ is 3.8 mg cm^{-2} .

2.4. Characterization

The X-ray diffraction (XRD) pattern was obtained from a MSAL-XD2 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM) images were obtained from a Philips SEM-XL30S microscope operated at 15 kV. High-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) coupled with an energy-dispersive X-ray spectroscopy (EDS) analyzer was conducted at an accelerating voltage of 200 kV. Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on PerkinElmer Optima 2000DV. Nitrogen sorption isotherm was tested by a Micromeritics TriStar 3000 analyzer at -196°C . The X-ray photoelectron spectroscopy (XPS) measurements were analyzed by an ESCALab 250.

2.5. Electrochemical measurements

Electrochemical measurements were performed in a standard three-electrode system in which the as-prepared samples, Pt foil, and Hg/HgO electrodes served as the working, counter, and reference electrodes, respectively. The electrolyte was 1.0 mol L^{-1} KOH solution. All potentials were converted *via* the Nernst equation ($E_{\text{RHE}} = E_{\text{Hg/Hg}_2\text{Cl}_2} + (0.059 \text{ pH} + 0.242) \text{ V}$). The polarization curves were obtained by linear sweep voltammetry (LSV) at a scan rate of 1 mV s^{-1} . The overpotentials (η) were computed according to the equation ($\eta = E_{\text{RHE}} - 1.23 \text{ V}$). Electrochemical impedance spectroscopy (EIS) measurements were analyzed in the frequency range of 10 kHz to 10 mHz with an amplitude of 5 mV. Chronoamperometric tests were conducted at given potentials.

3. Results and discussion

As schematically illustrated in Fig. 1, the 3D lily-like $\text{CoNi}_2\text{S}_4/\text{Ni}$ was synthesized *via* sulfuration of the CoNi-precursor/Ni. Similar to a previous report [15], the XRD patterns of $\text{CoNi}_2\text{S}_4/\text{Ni}$ and CoNi-precursor/Ni were tested using their powders scraped down from the Ni foam. The XRD pattern of the CoNi-precursor in Fig. 2(a) reveals that the peaks at 11.6° , 23.3° , 34.9° , 39.5° , 46.9° , 60.9° , and 62.3° are derived from $(\text{Ni}_{6.10}\text{Co}_{2.90})(\text{OH})_{18.27}(\text{CO}_3)_{1.315} \cdot 6.7\text{H}_2\text{O}$ (JCPDS no. 33-0429), while the other peaks at 17.5° and 36.5° correspond to $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ (JCPDS no. 48-0083). Therefore, we name this mixture precursor as CoNi-C-Co-CHH. After sulfuration, the diffraction peaks of CoNi-C-Co-CHH are not ob-

Fig. 1. Schematic illustration of the fabrication of lily-like $\text{CoNi}_2\text{S}_4/\text{Ni}$.

Fig. 2. (a) XRD patterns of lily-like CoNi₂S₄/Ni (red) and lily-like CoNi-C-Co-CHH/Ni (black); SEM images of lily-like CoNi-C-Co-CHH/Ni (b) and lily-like CoNi₂S₄/Ni (c); (d–f) TEM (d), HRTEM (e), and elemental mapping images (f) of lily-like CoNi₂S₄/Ni.

served. The emerging peaks located at 31.5°, 38.2°, 47.2°, 50.3°, and 55.0° can be clearly attributed to the (311), (400), (422), (511), and (440) planes of cubic CoNi₂S₄ (JCPDS no. 24–0334), respectively. The broad diffraction peaks of CoNi₂S₄ indicate that its crystallinity is not high. Moreover, the ICP analysis reveals that the atomic ratio of Co:Ni is 1.0:2.2 (Table S1).

To observe the morphology of the as-prepared samples, SEM measurements were carried out. It can be seen in Fig. 2(b) that CoNi-C-Co-CHH/Ni exhibits a lily-like morphology with smooth “petals”. Fig. S1(a) reveals that the lily-like CoNi-C-Co-CHH/Ni completely covers the surface of the Ni foam, and the average diameter of the “lily” is about 6.0 μm. After sulfuration, the lily-like morphology of CoNi₂S₄ is well retained (Fig. S1(b)). However, the surface of the “petals” becomes rough (Fig. 2(c)). This might be ascribed to the numerous pores that were formed on the surface of CoNi₂S₄ (Fig. 2(d)). This result can be further probed by the N₂ sorption measurement. As displayed in Fig. S2(a), the pseudo-type IV isotherm with H1 hysteresis loop can be observed, indicating the typical mesoporous feature of lily-like CoNi₂S₄. The pore size of lily-like CoNi₂S₄ is mainly about 28 nm (see inset in Fig. S2(a)). Note that the abundant porous structure will provide more active sites for contact and improve mass diffusion/transport for water splitting [30,31]. The HRTEM image (Fig. 2(e)) displays a well-resolved lattice fringe spacing of 0.17 nm, which is assigned to the (440) plane of CoNi₂S₄. Some amorphous area can also be observed in the HRTEM image, which is consistent with the XRD results. The elemental mapping images illustrate the uniform distribution of Co, Ni, and S in CoNi₂S₄ (Fig. 2(f)).

The XPS spectra of CoNi₂S₄ were also characterized to explore its valence and chemical state. As shown in Fig. S2(b), the Co 2p region was fitted with two spin-orbit doublets. One is at 778.3 and 793.3 eV, and the other is at 781.6 and 798.3 eV. The spin-orbit splitting values of Co 2p_{1/2} and Co 2p_{3/2} for the two spin-orbit doublets are severally 15.0 and 16.7 eV, which cor-

respond to Co³⁺ and Co²⁺, respectively [19]. The atomic ratio of Co³⁺/Co²⁺ is 0.3:1.0, which is obtained by comparing the fitted area [30]. Fig. S2(c) shows the Ni 2p region. The peaks at 856.1 eV for Ni 2p_{3/2} and 874.0 eV for Ni 2p_{1/2} are ascribed to Ni²⁺, while the other two peaks at 858.2 eV for Ni 2p_{3/2} and 876.7 eV for Ni 2p_{1/2} are related to Ni³⁺ [26,27]. The atomic ratio of Ni³⁺/Ni²⁺ is 0.98:1.0. Note that the peak at 853.2 eV is attributed to Ni^{δ+}, which has a positive shift of 1.0 eV with respect to that of metallic Ni (852.2 eV) [32]. Correspondingly, the peak at 162.6 eV is attributed to the negatively charged S^{δ-} (Fig. S2(d)) [33]. The above mentioned positive and negative shifts of Ni^{δ+} and S^{δ-} are mainly ascribed to the partial transfer of the electron density of Ni to S in CoNi₂S₄. The peak at 161.4 eV corresponds to S 2p_{3/2} and is ascribed to S²⁻. Moreover, the peak at 169.4 eV is most likely due to the oxidized species of S with a high oxidation state, which is well in accordance with the literature [26].

The HER performance of CoNi₂S₄/Ni was estimated by LSV characterization in 1.0 mol L⁻¹ KOH solution at a scan rate of 1 mV s⁻¹. For comparison, bare Ni foam, CoNi-C-Co-CHH/Ni, and 50 wt% Pt/C loading on Ni foam (50 wt% Pt/C/Ni [32], loading 3.8 mg cm⁻²) were also tested. Fig. 3(a) displays the polarization curves of these electrocatalysts. The overpotential at a current density of 10 mA cm⁻² (η₁₀) can be employed to evaluate the HER catalytic activity of the electrocatalysts. CoNi-C-Co-CHH/Ni possesses low activity for HER with η₁₀ of 200 mV. As expected, the catalytic performance of CoNi₂S₄/Ni improves sharply at η₁₀ of 54 mV, which is just larger than that (25 mV) of 50 wt% Pt/C/Ni. The η₁₀ of 54 mV of CoNi₂S₄/Ni is also comparable to those of the reported electrocatalysts, as shown in Fig. 3(b), indicating that the as-prepared CoNi₂S₄/Ni electrode is one of the most active electrocatalysts for HER [5,17–19,22,26,34–36].

To elucidate the HER mechanism of the as-synthesized materials, Tafel plots were determined according to the Tafel

Fig. 3. (a) Polarization curves; (b) Comparison of the overpotential of lily-like CoNi₂S₄/Ni with other electrocatalysts, free of noble metals, at 10 mA cm⁻²; (c) The Tafel slopes; (d) The chronoamperometry curves of lily-like CoNi₂S₄/Ni with constant overpotentials.

equation ($\eta = b \log j + a$, where a is a constant, b is the Tafel slope, and j is the current density). It can be seen from Fig. 3(c) that the Tafel slope values of CoNi₂S₄/Ni, CoNi-C-Co-CHH/Ni, 50 wt% Pt/C/Ni, and bare Ni foam are 129.0, 178.3, 29.4, and 229.7 mV dec⁻¹, respectively. The lower Tafel slope value of CoNi₂S₄/Ni with respect to that of CoNi-C-Co-CHH/Ni implies more favorable catalytic kinetics. According to previous reports [19,32], this value of CoNi₂S₄/Ni (129.0 mV dec⁻¹) indicates that it follows the Volmer ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{OH}^-$)-Heyrovsky ($\text{H}_2\text{O} + \text{H}_{\text{ads}} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$) pathway. Moreover, the Ni⁶⁺ and S⁶⁻ species present in CoNi₂S₄/Ni (XPS results in Fig. S2) demonstrate that its HER catalytic mechanism is similar to that of hydrogenases [32,33,37]. Therefore, the high activity of CoNi₂S₄/Ni for HER intrinsically benefits from the Ni⁶⁺ and S⁶⁻ species severally acting as hydride-acceptor and proton-acceptor centers, which can assist in the decomposition of captured H₂O to OH⁻ species and adsorbed H atoms (H_{ads}) in the Volmer step, and then accelerate the detachment of OH⁻ and transformation of H_{ads} to yield H₂ in the Heyrovsky step.

To further understand the efficient catalytic performance of CoNi₂S₄/Ni for HER, the electrochemically active surface area (ECSA) and EIS measurements were obtained. As shown in Figs. S3(a) and (b), the cyclic voltammetry (CV) curves were measured in the region of 0–0.05 V with scan rates in the range 6–14 mV s⁻¹. The values of electrochemical double-layer capac-

itance (C_{dl}) can be computed by using the above CV curves. It is that the linear slope of capacitive currents versus scan rates is equal to $2C_{\text{dl}}$. Moreover, C_{dl} is proportional to ECSA. As shown in Fig. S3(c), the C_{dl} of CoNi₂S₄/Ni (61.0 mF cm⁻²) is about four-fold higher than that (15.6 mF cm⁻²) of CoNi-C-Co-CHH/Ni, revealing that CoNi₂S₄/Ni has exposed more catalytically active sites for HER. Fig. S3(d) shows the Nyquist plots of EIS of CoNi₂S₄/Ni and CoNi-C-Co-CHH/Ni. The smaller charge transfer resistance (R_{ct} , 0.82 Ω) of CoNi₂S₄/Ni with respect to that (4.86 Ω) of CoNi-C-Co-CHH/Ni suggests fast electron transport in the HER catalytic process.

The above experimental results indicate that the efficient catalytic activity of CoNi₂S₄/Ni for HER can be rationally interpreted as follows (1) CoNi₂S₄/Ni has active centers similar to those of effective hydrogenase. The Ni⁶⁺ and S⁶⁻ species in CoNi₂S₄/Ni can be the hydride-acceptors and proton-acceptors to accelerate the HER processes. (2) The rough surface of CoNi₂S₄/Ni possesses a large ECSA to expose more effective active sites. The 3D lily-like morphology and mesoporous characterization of CoNi₂S₄ facilitate contact between the electrolyte and the active sites, thereby improving the utilization efficiency of the active sites. (3) The CoNi₂S₄ directly supported on Ni foam without using the binder endows the electrode with low contact resistance and efficient charge transportation in HER electrolysis.

Stability is another key parameter on the basis of which we can evaluate the performance of electrocatalysts in practical applications. We, therefore, probed the stability of the CoNi₂S₄/Ni electrode using chronoamperometric studies under different overpotential values (Fig. 3(d)). No obvious degradation in the current density was observed, indicating satisfactory durability of CoNi₂S₄/Ni.

Besides the catalytic activity for HER, the catalytic performance of CoNi₂S₄/Ni for OER was assessed. The CoNi-C-Co-CHH/Ni, RuO₂ loading on Ni foam (RuO₂/Ni [23], loading 3.8 mg cm⁻²), and bare Ni foam were also investigated. The overpotential at a current density of 100 mA cm⁻² (η_{100}) was used to evaluate the OER electrocatalytic activity of the as-prepared samples, because of the large oxidation peaks of the CoNi₂S₄/Ni result in an inaccurate analysis of the onset potential. As displayed in Fig. 4(a), the η_{100} of 328 mV for CoNi₂S₄/Ni undoubtedly outperforms that (545 mV) of CoNi-C-Co-CHH/Ni. Surprisingly, the η_{100} of 328 mV for CoNi₂S₄/Ni is also lower than that (376 mV) of RuO₂/Ni and even those of most of the other recently reported OER electrocatalysts (Fig. 4(b)) [18,19,22,27,28,38–42]. Moreover, the lower Tafel slope value of CoNi₂S₄/Ni (124.6 mV dec⁻¹) compared to that of CoNi-C-Co-CHH/Ni (145.2 mV dec⁻¹) demonstrates

positive OER catalytic kinetics (Fig. 4(c)). The chronoamperometric curve of CoNi₂S₄/Ni in Fig. 4(d) shows an ignorable decline in current density, revealing its good durability. Notably, the first increase in current density in the chronoamperometric curve is ascribed to the oxidation of Ni and Co in the OER catalytic process (Fig. S4). In addition, CoNi₂S₄/Ni exhibits a similar polarization curve between the initial state and after 10 h of OER electrolysis (see the inset of Fig. 4(d)).

Given the excellent electrocatalytic performance of CoNi₂S₄/Ni toward both HER and OER, it may be utilized as a potential anode and cathode for overall water splitting in a two-electrode system. Fig. 5(a) shows that the CoNi₂S₄/Ni couple offers a current density of 10 mA cm⁻² at a cell voltage of only 1.56 V. Although this value is larger than that (1.53 V) of the Ni_xCo_{3-x}S₄/Ni₃S₂/NF couple [34], it is smaller than that of most other bifunctional electrocatalysts reported including Co₉S₈/WS₂ (1.65 V) [5], Co_{6.25}Fe_{18.75}Ni₇₅O_x (1.583 V) [7], Ni/NiTiO₃ (1.63 V) [8], CoNC@MoS₂/CNFs (1.62 V) [17], Ni-Co₂S₄ NW/NF (1.63 V) [19], NiCo₂S₄NA/CC (1.68 V) [27], Ni_{2.3%}-CoS₂/CC (1.66 V) [28], and so on (Fig. 5(b)). Moreover, the CoNi₂S₄/Ni couple also exhibits good stability and retains the current density even after continually operating for 10 h in a basic medium, indicating its efficient water splitting perfor-

Fig. 4. (a) Polarization curves; (b) Comparison of the overpotential of the lily-like CoNi₂S₄/Ni with other noble metal-free electrocatalysts at 100 mA cm⁻² (a the actual overpotentials to reach 100 mA cm⁻² surpass the values shown here); (c) Tafel slopes; (d) Chronoamperometric curve of the lily-like CoNi₂S₄/Ni for OER (inset for polarization curves before and after the stability test).

Fig. 5. (a) Polarization curves of the CoNi₂S₄/Ni couple; the inset is the chronoamperometric curve tested at 1.64 V. (b) Comparison of the required voltage at a current density of 10 mA cm⁻² for the CoNi₂S₄/Ni couple with other transition-metal-based electrolyzers reported in the literature.

mance (see inset in Fig. 5(a)).

4. Conclusions

In summary, 3D lily-like CoNi₂S₄ has been successfully synthesized on Ni foam *via* sulfuration of lily-like Co-Ni-C-Co-CHH/Ni. Notably, lily-like CoNi₂S₄/Ni exhibits excellent catalytic activity and stability for both HER and OER under alkaline conditions. When CoNi₂S₄/Ni is utilized as a bifunctional electrocatalyst for overall water splitting in 1.0 mol L⁻¹ KOH solution, the couple obtained affords a current density of 10 mA cm⁻² at 1.56 V, which is superior to those of most bifunctional electrocatalysts reported in the literature. The remarkable electrocatalytic activity of this 3D lily-like CoNi₂S₄/Ni can be mainly attributed to the charged nature of the metals and sulfur in this material, increased surface roughness along with more exposed active sites, mesoporous structure, and accessible pathways for mass diffusion/transport, thus making this material a promising bifunctional electrocatalyst for water splitting.

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Graphical Abstract

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Three-dimensional lily-like CoNi₂S₄ as an advanced bifunctional electrocatalyst for hydrogen and oxygen evolution reaction

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Three-dimensional lily-like CoNi₂S₄ has been successfully synthesized on Ni foam. Lily-like CoNi₂S₄/Ni can be an efficient and stable bifunctional electrocatalyst. It possesses excellent characteristics for both hydrogen evolution reaction and oxygen evolution reaction, and its performance is comparable to that of most of the electrocatalysts reported in the literature.

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三维百合花状的 CoNi_2S_4 作为先进的双功能电催化剂用于氢析出和氧析出反应

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摘要: 为简化电解水催化剂的合成过程和优化电解水操作系统, 双功能电解水催化剂的研究, 特别是在碱性条件下同时具有优异催化氢析出和氧析出反应性能的双功能电催化剂的研究尤为重要。其中, 过渡金属硫化物, 特别是 CoNi 硫化物, 被报道有与氢化酶类似的催化活性中心, 从而具有优异的催化氢析出和催化氧析出反应性能。虽然有关对过渡金属硫化物的研究很多, 但主要集中在具有一维纳米线和二维纳米片形貌结构的过渡金属硫化物。不幸的是, 这些形貌结构的过渡金属硫化物在电催化过程中容易聚集和受限于电荷传输能力。三维纳米结构的材料具有较大的比表面积以分布更多的活性位点和拥有良好的电子传输能力, 所以, 开发三维纳米结构的过渡金属硫化物材料可能是改进其催化电解水性能的一个好途径。本文采用简单的两步水热法, 通过硫化合成的 CoNi 前体得到了长于泡沫镍上的三维百合花状的 CoNi_2S_4 ($\text{Co-Ni}_2\text{S}_4/\text{Ni}$)。它只需要 54 mV 的过电位即可获得 10 mA cm^{-2} 的催化氢析出反应电流, 是最好的碱性催化氢析出反应电极材料之一。它在驱动 100 mA cm^{-2} 的催化氧析出反应电流时也只需要 328 mV 的过电位。另外, 把 $\text{CoNi}_2\text{S}_4/\text{Ni}$ 分别作为阴极和阳极组装成双电极碱性水电解槽时, 它只需要 1.56 V 的电压即可获取 10 mA cm^{-2} 的催化全电解水电流并具有良好的催化全电解水稳定性。

扫描电子显微镜、透射电子显微镜和 N_2 吸脱附曲线测试结果表明, 该三维百合花状的 $\text{CoNi}_2\text{S}_4/\text{Ni}$ 的表面粗糙度高和拥有多孔特性。多孔结构的 $\text{CoNi}_2\text{S}_4/\text{Ni}$ 可提供更多可接触的催化活性位点, 也有利于催化过程中的电解质和生成的气体的扩散与传递。交流阻抗图谱测试结果表明, $\text{CoNi}_2\text{S}_4/\text{Ni}$ 具有良好的电子传输能力。另外, 不同于前期对尖晶石结构的硫化物 AB_2S_4 的研究结果, XPS 结果表明, $\text{CoNi}_2\text{S}_4/\text{Ni}$ 中含有 Ni^{2+} 和 S^{2-} 活性物种, 表明 CoNi_2S_4 具有与活性氢化酶类似的活

性中心. $\text{Ni}^{\delta+}$ 和 $\text{S}^{\delta-}$ 可分别作为氢氧根和质子的接收体, 协助促进吸附的水分子的分离, 从而提高材料的催化性能. 所以, $\text{Ni}^{\delta+}$ 和 $\text{S}^{\delta-}$ 活性物种的出现, 大比表面积的三维百合花状多孔结构和良好的电荷传输能力等特性集合于 $\text{CoNi}_2\text{S}_4/\text{Ni}$ 上使得 $\text{CoNi}_2\text{S}_4/\text{Ni}$ 具有优异的催化氢析出和催化氧析出反应性能.

关键词: 双功能电催化剂; 氢析出反应; 氧析出反应; 百合花状的 CoNi_2S_4 ; 全电解水

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