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Article

Facilitating active species by decorating CeO₂ on Ni₃S₂ nanosheets for efficient water oxidation electrocatalysis

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ABSTRACT

In the pursuit of stable, high performance Ni-based oxygen evolution reaction (OER) electrocatalysts, modifying the local chemical compositions or fabricating hybrid nanostructures to generate abundant interfaces for improving the water oxidation activity of electrocatalysts has emerged as an effective strategy. Herein, we report the facile development of a Ni₃S₂-CeO₂ hybrid nanostructure via an electrodeposition method. Benefiting from the strong interfacial interaction between Ni₃S₂ and CeO₂, the electron transfer is notably improved and the water oxidation activity of Ni₃S₂ nanosheets is significantly enhanced. In 1.0 M KOH, the Ni₃S₂-CeO₂ electrocatalyst achieves a current density of 20 mA cm⁻² at a low overpotential of 264 mV, which is 92 mV lower than that of Ni₃S₂. Moreover, Ni₃S₂-CeO₂ exhibits superior electrochemical stability. Density functional theory calculations demonstrate that the enhanced OER electrocatalytic performance of Ni₃S₂-CeO₂ can be ascribed to an increase in the binding strength of the reaction intermediates at the Ni₃S₂-CeO₂ interface.

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1. Introduction

Electrochemical water splitting is an appealing and sustainable technology for producing hydrogen, a promising carbon-free energy carrier [1–5]. However, the oxygen evolution reaction (OER) at the anode involves a four-electron transport process coupled with O–O bond formation and O–H bond cleavage, which is kinetically sluggish and the chief bottleneck for overall water splitting [6–11]. To overcome this kinetic

barrier, identifying efficient electrocatalysts for the OER is a crucial step. Currently, RuO₂ and IrO₂ are considered to be the state-of-the-art catalysts for OER. However, these noble metals are costly and scarce, impeding their large-scale utilization in commercial electrolysis. Therefore, it is highly desirable to develop earth-abundant alternatives for the OER.

Considerable recent efforts have been devoted to developing transition-metal-based electrocatalysts for water oxidation. Metal sulfides have been considered as promising OER electro-

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catalysts owing to their low potential in overall water splitting [12–16]. In particular, Ni_3S_2 has been widely explored for its high conductivity and activity as well as low cost [17–19]. However, the OER performance of Ni_3S_2 still needs further improvement to reduce the energy consumption of the overall water splitting process. Recently, modifying the local chemical composition or fabricating hybrid nanostructures to generate abundant interfaces for achieving high performance of the catalysts has attracted extensive attention [20–23]. In particular, decorating the OER co-catalysts on the anode materials to build rich interfaces has emerged as an effective strategy to address this issue. CeO_2 , with the flexible transition between the Ce^{3+} and Ce^{4+} oxidation states, possesses good electronic/ionic conductivity, reversible surface oxygen ion exchange, and high oxygen storage capacity [24,25]. These unique and intrinsic characteristics enable CeO_2 to serve as a co-catalyst and facilitates the improvement of charge transport and energy conversion efficiency, thus increasing the catalytic activity of the water oxidation catalysts [26–30]. Therefore, CeO_2 decorated on Ni_3S_2 could be a viable route to enhance the performance of Ni_3S_2 electrocatalysts for water oxidation; however, this hypothesis remains unexplored.

Herein, we demonstrate that $\text{Ni}_3\text{S}_2\text{-CeO}_2$ grown on nickel foam ($\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$) is a highly efficient nonprecious metal catalyst for OER in alkaline media. $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ shows excellent OER catalytic performance in a 1.0 M KOH solution and needs a low overpotential of 264 mV to reach 20 mA cm^{-2} , which is 92 mV less than that of $\text{Ni}_3\text{S}_2/\text{NF}$. Notably, it also exhibits superior long-term stability. Density functional theory (DFT) calculations reveal that the $\ast\text{OH}$, $\ast\text{O}$, and $\ast\text{OOH}$ species interact with both Ni and Ce atoms in $\text{Ni}_3\text{S}_2\text{-CeO}_2$, resulting in stronger binding strengths of the reaction intermediates than that in pure Ni_3S_2 or CeO_2 . As a result, $\text{Ni}_3\text{S}_2\text{-CeO}_2$ possesses better OER performance than either pure CeO_2 or Ni_3S_2 .

2. Experimental

2.1. Preparation of $\text{Ni}_3\text{S}_2/\text{NF}$

A piece of nickel foam (NF; $2 \text{ cm} \times 3 \text{ cm}$) was sequentially treated with HCl, ethanol, and deionized water by sonication for 30 min to make sure that the surface of the NF was cleaned, waiting for use. A total of 0.35 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.25 mmol of thiourea ($\text{CH}_4\text{N}_2\text{S}$) were dissolved in 2 mL of ethylene glycol and 8 mL DI water. After continuously stirring for 30 min, the solution was transferred to a 50 mL Teflon-lined stainless steel autoclave with a piece of NF ($2 \text{ cm} \times 3 \text{ cm}$). Then, the autoclave was sealed and maintained at 160°C for 14 h in an oven. After the autoclave cooled to room temperature, the sample was taken out and thoroughly washed with deionized water and ethanol several times, alternately, and then dried at 60°C .

2.2. Electrodeposition of CeO_2 on $\text{Ni}_3\text{S}_2/\text{NF}$

A piece of $\text{Ni}_3\text{S}_2/\text{NF}$ served as the working electrode for anodic electrodeposition in a three-electrode electrochemical

setup. A platinum plate and a saturated Ag/AgCl electrode were used as the counter and reference electrodes, respectively. CeO_2 layers were coated on the surfaces of $\text{Ni}_3\text{S}_2/\text{NF}$ to form $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ using a solution of 2 mM $\text{Ce}(\text{NO}_3)_3$ and 10 mM NaCl at 0.25 mA cm^{-2} for 10 min at 70°C . Finally, the sample was washed with deionized water and dried at 60°C .

2.3. Electrochemical measurements

Electrochemical measurements were carried out in a conventional three-electrode electrochemical setup with a CHI660E potentiostat (CH Instruments). The as-prepared NF-based electrocatalysts were used directly as working electrodes. A graphite plate and Hg/HgO served as the counter and reference electrodes, respectively. Polarization curves were obtained using linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1} in a 1.0 M KOH electrolyte ($\text{pH} = 14$). Cyclic voltammetry (CV) curves were recorded at different scan rates over a wide potential range to evaluate the double-layer capacitance (C_{dl}) and turnover frequencies (TOFs). The potentials presented in this work were converted to the reversible hydrogen electrode (RHE) according to $E(\text{RHE}) = E(\text{Hg/HgO}) + (0.098 + 0.059 \text{ pH}) \text{ V}$.

2.4. DFT calculations

All calculations were performed using the Vienna ab initio simulation package [31,32]. The ion-electron interactions were described by the projector augmented wave method [33]. The generalized gradient approximation in the Perdew-Burke-Ernzerhof functional [34] and a cut-off energy of 400 eV for the plane-wave basis set were adopted. The convergence threshold was 10^{-5} eV and $0.03 \text{ eV \AA}^{-1}$ for energy and force, respectively. A vacuum space at least $20 \text{ \AA}$ was used to avoid interaction between two periodic units.

The OER follows four elementary steps:

- (1) $\text{H}_2\text{O} + \ast \rightarrow \ast\text{OH} + \text{H}^+ + \text{e}^-$
- (2) $\ast\text{OH} \rightarrow \ast\text{O} + \text{H}^+ + \text{e}^-$
- (3) $\text{H}_2\text{O} + \ast\text{O} \rightarrow \ast\text{OOH} + \text{H}^+ + \text{e}^-$
- (4) $\ast\text{OOH} \rightarrow \text{O}_2 + \text{H}^+ + \text{e}^- + \ast$

The OER activity is evaluated by calculating the reaction free energy of each elementary step, which is calculated by

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S$$

where ΔE is the electronic energy difference, ΔE_{ZPE} and ΔS are the changes in zero-point energies and entropy, respectively, and T is the temperature. E_{ZPE} can be calculated by the following equation:

$$E_{\text{ZPE}} = \frac{1}{2} \sum_i h\nu_i$$

where h and ν are the Planck constant and vibrational frequencies, respectively. The theoretical overpotential, η , is determined by the potential limiting step:

$$\eta = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/\text{e} - 1.23 \text{ [V]}$$

where ΔG_1 , ΔG_2 , ΔG_3 , and ΔG_4 are the reaction free energies of the aforementioned four elementary steps. Moreover, for catalysts with different sites for the adsorption of the reaction intermediates (e.g., $\text{Ni}_3\text{S}_2\text{-CeO}_2$), the most stable site for the ad-

Fig. 1. (a) XRD patterns of Ni₃S₂/NF and Ni₃S₂-CeO₂/NF; SEM images of Ni₃S₂/NF (b) and Ni₃S₂-CeO₂/NF (c); (d) TEM image of Ni₃S₂-CeO₂; (e, f) HRTEM images of Ni₃S₂-CeO₂.

sorption of the intermediates is presented in our work.

3. Results and discussion

Ni₃S₂/NF was directly prepared through a hydrothermal reaction, which was then used as a template to fabricate Ni₃S₂-CeO₂/NF via electrodeposition. The X-ray diffraction (XRD) patterns of Ni₃S₂/NF, Ni₃S₂-CeO₂/NF, and CeO₂/NF are presented in Fig. S1(a) and S1 (see electronic supporting information, the same below), respectively. As observed from Fig. 1(a), the XRD peaks of Ni₃S₂-CeO₂ are well matched to those of the typical crystalline structures of Ni₃S₂ (JCPDS No. 44-1418) and CeO₂ (JCPDS No. 78-0694), revealing the coexistence of Ni₃S₂ and CeO₂ in the resultant material. The additional peaks

are attributed to NF (JCPDS No. 04-0850). Scanning electron microscopy (SEM; Fig. 1(b)) confirms that Ni₃S₂ nanosheets with smooth surfaces are uniformly grown on the NF. After electrodeposition, Ni₃S₂-CeO₂ maintains its nanosheet morphology. However, the nanosheet becomes rough. Obviously, the morphology of CeO₂/NF (Fig. S2) is completely different from that of Ni₃S₂-CeO₂/NF. A transmission electron microscopy (TEM) image of Ni₃S₂-CeO₂ (Fig. 1(d)) shows the nanosheet structure. As displayed in Fig. 1(e), high-resolution TEM (HRTEM) images present an apparent interface between the Ni₃S₂ and CeO₂ species. The lattice fringes with the interplanar distances of 0.287 and 0.191 nm (Fig. 1(f)) correspond to the (110) plane of Ni₃S₂ and the (220) plane of CeO₂, respectively. The scanning-transmission electron microscopy energy dispersive spectroscopy (STEM-EDS) element mapping shows Ni and S signals attributable to Ni₃S₂ and Ce and O signals to CeO₂ (Fig. S3).

To probe the strong electronic interaction between Ni₃S₂ and CeO₂, X-ray photoelectron spectroscopy (XPS) was carried out on Ni₃S₂-CeO₂/NF, Ni₃S₂/NF, and CeO₂/NF. The survey XPS spectrum (Fig. S4) confirms the coexistence of Ni, S, Ce, and O. As shown in Fig. 2(a), there are two main peaks at 855.9 and 873.6 eV corresponding to Ni 2p_{3/2} and 2p_{1/2}, respectively, along with two smaller satellite peaks [35–37]. The peak fitted at 852.4 eV is characteristic of Ni⁰ in Ni₃S₂ [36–38]. The two subpeaks at 861.3 and 881.2 eV can be ascribed to the oxidized Ni species, indicating the presence of nickel-oxygen species on the surface of Ni₃S₂, most probably hydrated nickel oxide [36]. The binding energies of Ni 2p_{3/2} and 2p_{1/2} in Ni₃S₂-CeO₂ exhibit a negative shift compared with those in Ni₃S₂, which indicates the existence of strong electronic interaction between Ni₃S₂ and CeO₂. This strong electronic interaction was further examined through the Ce 3d spectra of Ni₃S₂-CeO₂, as shown in Fig. 2(b). For Ce 3d in CeO₂, the peaks located at 920–911 and 903–893 eV correspond to Ce 3d_{3/2} and those located at 877–866 eV correspond to Ce 3d_{5/2}, which demonstrate the coexistence of Ce³⁺ and Ce⁴⁺ in CeO₂ [26,29]. However, the amount of Ce⁴⁺ in Ni₃S₂-CeO₂ hybrid increased compared with that in pure CeO₂, indicating that the valence states of Ce significantly rearranged and gave electrons to Ni in Ni₃S₂-CeO₂ [26,29]. Therefore, the ratio changes of the Ce 3d peaks and peak shifts of Ni 2p in Ni₃S₂-CeO₂ indicate strong electronic interactions between

Fig. 2. XPS spectra in the Ni 2p (a) and Ce 3d (b) regions.

Ni_3S_2 and CeO_2 . For the $\text{S } 2p$ region (Fig. S5(a)), the peaks at 161.6 and 163 eV correspond to $\text{S } 2p_{3/2}$ and $\text{S } 2p_{1/2}$ for the binding energy of Ni-S bonds [35]. Additionally, the peak at 168.9 eV was caused by the surface SO_4^{2-} species due to exposure in air [39]. The binding energies at 529.6 and 531.6 eV for the $\text{O } 1s$ XPS spectrum (Fig. S5(b)) are attributed to O^{2-} derived from CeO_2 and OH^- originating from the adsorbed H_2O on the surface, respectively [30]. These characterization results confirm the synthesis of $\text{Ni}_3\text{S}_2\text{-CeO}_2$.

The electrocatalytic OER performance of $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ (loading: 1.82 mg cm^{-2}) was measured in 1.0 M KOH. For comparison, the water oxidation activity of bare NF, CeO_2/NF , $\text{Ni}_3\text{S}_2/\text{NF}$, and RuO_2/NF were also evaluated. The polarization curves after iR correction were obtained from LSV and all potentials reported in the present work are based on the RHE scale [40–42]. As shown in Fig. 3(a), bare NF displays poor water oxidation activity, whereas RuO_2/NF exhibits the strongest catalytic ability with an overpotential of 200 mV to reach 20 mA cm^{-2} . Compared to bare NF, the electrochemical performance of CeO_2/NF is slightly improved, while that of $\text{Ni}_3\text{S}_2/\text{NF}$ is efficient with an overpotential of 356 mV at 20 mA cm^{-2} . In sharp contrast, $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ exhibits superior OER activity, requiring a much lower overpotential of 264 mV to deliver the same current density. Note that the catalytic activity of $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ is superior to those of other counterparts grown

on NF and some recently reported Ni-based OER electrocatalysts (Table S1). $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ is also efficient under neutral conditions (Fig. S6). The Tafel plots presented in Fig. 3(b) reveal the electrocatalytic kinetics for water oxidation of the samples. $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ possesses a lower Tafel value (146 mV dec^{-1}) than CeO_2/NF (207 mV dec^{-1}) and $\text{Ni}_3\text{S}_2/\text{NF}$ (168 mV dec^{-1}) and only a slightly higher value than the benchmark RuO_2/NF (105 mV dec^{-1}), revealing favorable reaction kinetics for the OER on $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$. The long-term stability is crucial to the practical application of electrocatalysts. The LSV curves are coincident with the initial one after 500 and 1000 cycles of continuous CV scanning (Fig. 3(c)), indicating the high stability of $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$. Furthermore, continuous water oxidation electrocatalysis was performed on $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ at overpotentials of 264 and 307 mV for 24 h (Fig. 3(d)). After oxygen evolution for 24 h, the LSV curve slightly weakened compared with the initial one, further demonstrating the high stability of $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ (Fig. S7). Of note, no obvious loss in current density was observed, further revealing the excellent stability of $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$. The electrochemical stability of $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ for water oxidation was also evaluated by multi-current step tests from 30 to 120 mA cm^{-2} (Fig. S8). The potentials maintain a similar and stable trend in each step, demonstrating good conductivity, mass transportation, and mechanical robustness of $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$. After OER electrolysis

Fig. 3. (a) LSV curves for bare NF, RuO_2/NF , CeO_2/NF , $\text{Ni}_3\text{S}_2/\text{NF}$ and $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ at 5 mV s^{-1} scan rate in 1.0 M KOH; (b) Tafel plots of RuO_2/NF , CeO_2/NF , $\text{Ni}_3\text{S}_2/\text{NF}$ and $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$; (c) LSV curves for $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ before and after 500 and 1000 cycles; (d) Time-dependent current density curves for $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ in 1.0 M KOH.

for 24 h, SEM (Fig. S9(a)) and TEM images (Fig. S9(b)) show that $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ retains its nanosheet morphology after the stability test. As shown in Fig. S10(a), the high resolution XPS spectrum of Ni 2p post-OER reveals decreased intensity of the peaks ascribed to Ni 2p_{3/2} and 2p_{1/2} (855.9 and 873.6 eV) and enhanced intensity at 861.3 and 881.2 eV, which correspond to oxidized Ni species [43]. The S 2p XPS spectrum shows that the signal intensity of S on the surface of $\text{Ni}_3\text{S}_2\text{-CeO}_2$ is significantly reduced after the stability test (Fig. S10(b)) [20]. The reason that no diffraction peaks assignable to Ni (oxy)hydroxide were observed in XRD may be explained by the low content and low crystallinity of Ni (oxy)hydroxide formed in situ (Fig. S11) [20,43]. Similar phenomena have been reported where the transition metal sulfides transform into oxides or (oxy)hydroxides after OER catalysis due to the high oxidation environment, which are believed to be the actual catalytic species for the OER [44].

To further investigate the OER kinetics, electrochemical impedance spectroscopy (EIS) was performed over a frequency range of 1 Hz to 100 kHz. EIS values are usually reflected by the charge transfer resistance (R_{ct}) corresponding to the semicircle in the high frequency region, as displayed in the Nyquist plots (Fig. 4(a)), fitted by the equivalent circuit model (inset of Fig. 4(a)). A lower R_{ct} indicates that a higher charge transfer rate occurs at the catalyst-electrolyte interface [45–48]. $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ gives the minimum R_{ct} (2.456 Ω) in comparison with $\text{Ni}_3\text{S}_2/\text{NF}$ (2.907 Ω) and CeO_2/NF (3.855 Ω), implying a faster electron-transfer rate and more favorable catalytic ki-

netics in the OER process. To evaluate the electrochemical active surface areas (ECSAs) of the electrocatalysts, C_{dl} of as-fabricated samples was measured by the CV method. Fig. S12(a)–(c) presents the CV results of CeO_2/NF , $\text{Ni}_3\text{S}_2/\text{NF}$, and $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ at different scan rates. The calculated C_{dl} values, shown in Fig. 4(b), for CeO_2/NF , $\text{Ni}_3\text{S}_2/\text{NF}$, and $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ are 10.6, 32.1, and 38.3 mF cm^{-2} , respectively, suggesting that $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ possesses more exposed catalytic active sites to catalyze water oxidation than CeO_2/NF and $\text{Ni}_3\text{S}_2/\text{NF}$ [49]. To further investigate the intrinsic activity of the electrocatalysts, TOFs of the samples were also assessed. Toward this end, electrochemistry was employed to estimate the concentration of active sites on the surface of the catalysts; the corresponding calculated details are presented in the ESI. It is assumed that single electron oxidation occurs in the metal centers in $\text{Ni}_3\text{S}_2\text{-CeO}_2$. The surface concentration of active sites can be deduced from the redox peaks in the CV curves (Fig. S13 and 4(c)). The relationship between the potentials and TOFs is displayed in Fig. 4(d). The TOFs of $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ were found to be 0.14 and 0.37 $\text{mol O}_2 \text{ s}^{-1}$ at overpotentials of 400 and 500 mV, respectively, which are significantly higher than those of $\text{Ni}_3\text{S}_2/\text{NF}$ and CeO_2/NF .

First-principles calculations were performed to gain insight into the origin of the excellent performance of $\text{Ni}_3\text{S}_2\text{-CeO}_2$, as shown in Fig. 5. Pure CeO_2 was found to be a poor catalyst for OER with a very high theoretical overpotential of 1.58 V (Fig. 5(a)). For pure Ni_3S_2 , the calculated overpotential is only 0.67 V, which is much lower than that of CeO_2 (Fig. 5(a)). Therefore,

Fig. 4. (a) Nyquist plots of CeO_2/NF , $\text{Ni}_3\text{S}_2/\text{NF}$ and $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ with an equivalent circuit; (b) The calculated C_{dl} ; (c) Oxidation peak current versus scan rate plots; (d) TOF plots for CeO_2/NF , $\text{Ni}_3\text{S}_2/\text{NF}$ and $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$.

Fig. 5. (a) Calculated free energy diagrams for OER on CeO_2 , Ni_3S_2 and $\text{CeO}_2/\text{Ni}_3\text{S}_2$ surfaces, as presented by red, black and blue lines, respectively. Structures of the reaction intermediates through the OER process on CeO_2 (b), Ni_3S_2 (c) and $\text{CeO}_2/\text{Ni}_3\text{S}_2$ (d) surfaces. Blue, yellow, offwhite, red and white balls represent the Ni, S, Ce, O and H atoms, respectively.

Ni_3S_2 will present better OER performance than CeO_2 . Interestingly, when decorating CeO_2 on Ni_3S_2 to form $\text{Ni}_3\text{S}_2\text{-CeO}_2$, the OER activity can be further improved, and the theoretical overpotential is as low as 0.51 V (Fig. 5(a)). The promotion effect of CeO_2 on the OER performance of Ni_3S_2 can be ascribed to changes in the binding strength of the reaction intermediates [50]. As shown in Fig. 5(b) and 5(c), on both pure CeO_2 and Ni_3S_2 surfaces, the reaction intermediates (*OH, *O, and *OOH) bind with one surface Ce or Ni atom only. Therefore, the binding strengths of the reaction intermediates are relatively weak. For $\text{Ni}_3\text{S}_2\text{-CeO}_2$, the *OH, *O, and *OOH species interact with both Ni and Ce atoms at the interface (Fig. 5(d)), leading to an increase in the binding strength between the catalyst and reaction intermediates. To prove this point, the binding energies of the intermediates on different surfaces are summarized. As shown in Table S2, the binding strengths of all the reaction intermediates (including *OH, *O, and *OOH) on $\text{Ni}_3\text{S}_2\text{-CeO}_2$ are higher than those on the other two surfaces. As a result, $\text{Ni}_3\text{S}_2\text{-CeO}_2$ exhibits better OER performance than both pure CeO_2 and Ni_3S_2 . These computations are in good agreement with the experimental results.

4. Conclusions

In summary, we have successfully developed and demonstrated an effective catalyst for the electrochemical water ox-

idation in alkaline media. CeO_2 as a co-catalyst decorated on Ni_3S_2 considerably enhanced the OER performance of Ni_3S_2 , and $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ needed an overpotential of only 264 mV to achieve 20 mA cm^{-2} , which is much lower than that of $\text{Ni}_3\text{S}_2/\text{NF}$. The enhanced catalytic performance of $\text{Ni}_3\text{S}_2\text{-CeO}_2/\text{NF}$ originates from an increase in the binding strength between the catalyst and reaction intermediates. The current work not only offers a highly active and stable water oxidation electrocatalyst but also provides a new viewpoint for the design and development of transition metal chalcogenides for water splitting.

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Graphical Abstract

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Facilitating active species by decorating CeO₂ on Ni₃S₂ nanosheets for efficient water oxidation electrocatalysis

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Ni₃S₂-CeO₂ is an efficient electrocatalyst for water oxidation in alkaline media, which needs a low overpotential of 264 mV to deliver 20 mA cm⁻², 92 mV lower than that of Ni₃S₂.

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CeO₂修饰Ni₃S₂纳米片用于高效电催化析氧

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摘要: 电化学水分解制氢作为重要的生产氢能的新能源技术, 包括氢气析出反应(HER)和氧气析出反应(OER)。然而, OER进行的是多步电子转移过程, 动力学过程缓慢且过电位高, 严重制约了电解水制氢的发展。因此开发低成本、高效稳定的非贵金属催化剂替代贵金属催化剂(RuO₂, IrO₂)来降低过电位, 减少能源消耗十分必要。Ni₃S₂由于其高导电性、高活性、低成本等优点, 具有作为贵金属催化剂替代品的广阔应用前景, 但其OER性能仍需进一步提高。对已有的有效OER催化剂进

行表面界面调控是提高催化剂性能的一种有效策略。CeO₂中的Ce³⁺和Ce⁴⁺价态之间可以灵活过渡,使其具有良好的电子/离子导电性、可逆的表面氧离子交换和较高的储氧能力。CeO₂的多价性使其有机会与其它基质产生强烈的电子相互作用,良好的电子/离子导电性和较高的储氧能力是提高催化剂析氧活性的有利因素。因此,用CeO₂对Ni₃S₂进行修饰是提高其析氧活性的有效途径。基于此,本文运用水热和电沉积相结合的方法将CeO₂修饰到Ni₃S₂纳米片上,制备得到生长于泡沫镍上的Ni₃S₂-CeO₂纳米片阵列(Ni₃S₂-CeO₂/NF),并运用X射线粉末衍射(XRD)、扫描电镜(SEM)、透射电镜(TEM)、X射线光电子能谱(XPS)等手段进行了表征,以三电极系统测试了其电催化析氧性能及稳定性,并通过密度泛函理论计算进行了验证。

XRD结果表明,复合材料中确实存在Ni₃S₂和CeO₂。通过SEM发现,泡沫镍基底上均匀分布着Ni₃S₂纳米片阵列;电沉积CeO₂后,Ni₃S₂-CeO₂仍保持其纳米片特性,但表面变得粗糙。Ni₃S₂-CeO₂的TEM结果也证实了纳米片结构的形成,高分辨率TEM图像清晰的显示出Ni₃S₂和CeO₂之间具有明显的界面。XPS结果表明,Ni₃S₂-CeO₂的Ni 2p的结合能与Ni₃S₂相比出现负位移。与纯CeO₂的Ce 3d谱图相比,Ni₃S₂-CeO₂杂化体系中Ce⁴⁺的比例明显增加,表明Ce的价态发生了重排,部分电子转移给了Ni元素。这些结果均说明Ni₃S₂与CeO₂之间存在着较强的电子相互作用。相应的电催化测试结果显示,在1.0 M KOH中,当电流密度达到20 mA cm⁻²时,Ni₃S₂/NF需提供356 mV的过电位,Ni₃S₂-CeO₂/NF只需264 mV的过电位,仅次于RuO₂/NF。而且,Ni₃S₂-CeO₂/NF在中性条件下也显示出了较理想的析氧活性。Ni₃S₂-CeO₂/NF的Tafel斜率明显低于CeO₂/NF和Ni₃S₂/NF,表明其具有良好的OER反应动力学。循环伏安法和计时电位法结果均表明,Ni₃S₂-CeO₂/NF具有良好的电化学稳定性。电化学阻抗谱测试结果表明,与Ni₃S₂/NF和CeO₂/NF相比,Ni₃S₂-CeO₂/NF明显具有更小的半圆直径,说明其电荷转移阻抗更小,进一步表明CeO₂的修饰有助于催化过程中电子的快速转移。在非法拉第区域的循环伏安扫描曲线以及拟合扫描速度对电容电流曲线结果显示,Ni₃S₂-CeO₂/NF的最大电容值大于CeO₂/NF和Ni₃S₂/NF,表明其暴露了更多的活性位点,具有更大的电化学活性表面积;而且,Ni₃S₂-CeO₂/NF在400和500 mV时的电催化析氧转换频率明显高于Ni₃S₂/NF和CeO₂/NF,进一步说明Ni₃S₂-CeO₂/NF具有更高的本征催化活性。密度泛函理论计算表明,由于*OH,*O和*OOH与Ni₃S₂-CeO₂中的Ni和Ce原子相互作用的存在,使得反应中间产物与Ni₃S₂-CeO₂之间的结合强度较纯Ni₃S₂或CeO₂强,使其显示出了更高的OER性能。

在经过24 h连续电解后,SEM和TEM结果均表明,Ni₃S₂-CeO₂/NF材料仍保持了其纳米片形貌。稳定性测试后的XPS结果表明,Ni 2p对应的峰强度降低,而与氧化镍物种对应的峰强度增强;S元素在Ni₃S₂-CeO₂表面的信号强度明显降低。根据文献报道,在强烈的氧化环境下,过渡金属硫化物会部分转化为氧化物或氢氧化物,这通常被认为是OER过程的实际催化物种。

关键词: Ni₃S₂-CeO₂纳米片; 氧析出反应; 碱性条件; 密度泛函理论计算

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