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CeO₂ nanoparticles decorated on porous Ni–Fe bimetallic phosphide nanosheets for high-efficient overall water splitting

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ABSTRACT

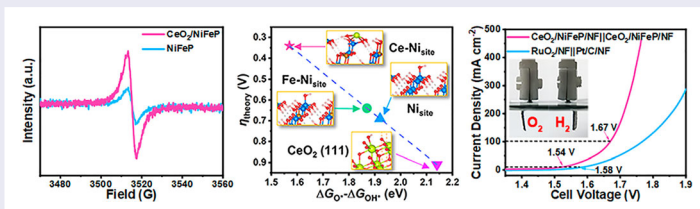
A self-supported electrode was designed and prepared for the first time with CeO₂ nanoparticles decorated on porous Ni–Fe bimetallic phosphide nanosheets, which were grown on high-conductivity Ni foam. Owing to the strong electronic interactions between the heterostructure interfaces and the introduction of oxygen vacancies, such an electrode displays outstanding oxygen evolution reaction performance with an overpotential of 188 mV at 10 mA cm⁻² and the electrolyzer using the electrode as both cathode and anode exhibits a cell voltage of 1.54 V at 10 mA cm⁻².

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KEYWORDS

CeO₂; bimetallic phosphide; oxygen vacancy; water splitting; DFT simulations



IMPACT STATEMENT

The oxygen vacancy engineering strategy was easily achieved by electrodeposition of CeO₂ and it can be extended to the design of other high-efficient and low-cost electrocatalysts.

1. Introduction

The electrocatalytic water splitting has emerged as a hydrogen production technology with advantages of high-purity products and zero carbon emissions, thus attracting much attentions [1–3]. Generally speaking, overall water splitting consists of two half-reactions: the oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode, and a larger operating voltage is required relative to the theoretical limit of 1.23 V [4,5]. At present, noble-metal Pt-based catalysts have been considered to be the most advanced HER catalysts, while RuO₂ and IrO₂ exhibit remarkable performance for OER [6,7]. Nevertheless, high expense, scarcity, and poor durability severely restrict their commercialization. It is thus necessary to explore electrocatalysts, which possess low cost, high activity and

excellent durability, to replace the precious-metal ones. Particularly, bifunctional electrocatalysts with high activity for both reactions are more beneficial for practical applications because of the superiorities of simplifying the equipments and lowering the cost [8]. Therefore, it is extremely important to develop efficient bifunctional electrocatalysts for both HER and OER.

In recent years, transition-metal phosphides (TMPs) are widely reported as effective catalysts for HER owing to their hydrogenase-like catalytic mechanism [9–11]. Meanwhile, recent studies also indicate that TMPs also display excellent catalytic performance for OER, making them potential candidates for high-performance bifunctional electrocatalysts [6,12,13]. More important, it has been reported that doping other metal elements can be an effective method to enhance the catalytic activity of

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TMPs owing to the adjustment of electronic structure and local coordination environment [8,14]. Hence, bimetallic phosphides usually show much superior catalytic activity compared to the monometallic ones [15,16]. However, TMPs generally exhibit disappointing long-term stability during the operation of OER as a result of corrosion and oxidation. Their catalytic activity also needs further improvement.

Recently, some researches have reported that the catalytic performance can be improved by adding co-catalysts [17,18]. Cerium oxide (CeO_2) is a significant rare earth oxide, and it possesses abundant reserves, reversible surface oxygen ion exchange, good electronic or ionic conductivity, and high oxygen-storage capacity [5,19,20]. The flexible transition between Ce^{3+} and Ce^{4+} of CeO_2 , which is conducive to the gain and loss of electrons, not only offers the opportunity to generate strong electronic interactions at the heterointerfaces between CeO_2 and other substances, but also promotes the formation of oxygen vacancies (V_O). Thus, numerous active sites are easy to generate [21–24]. Besides, owing to the remarkable anti-corrosion ability, CeO_2 could be beneficial for distinctly enhancing the stability of electrocatalysts [4,25]. Accordingly, the electrocatalytic performance of TMP-based materials may be improved *via* the efficient strategy of CeO_2 decoration on bimetallic phosphides.

Based on the above considerations, a self-supported electrode was designed and prepared for the first time with CeO_2 nanoparticles decorated on porous Ni-Fe bimetallic phosphide nanosheets, which were grown on high-conductivity Ni foam (denoted as $\text{CeO}_2/\text{NiFeP}/\text{NF}$). Such an electrode combines the following advantages: (i) the decorated CeO_2 nanoparticles can regulate the interface and enrich V_O , promote the strong electronic interactions between NiFeP nanosheets and CeO_2 nanoparticles, and thus improve the catalytic activity; (ii) CeO_2 has the unique property of high oxygen storage capacity, which can immediately assimilate O_2 generated during the reaction, thus promoting the process of OER; and (iii) the high conductivity and porous structure of NiFeP nanosheets greatly facilitate the transfer of electron and mass transport.

2. Experimental procedures

The self-supported $\text{CeO}_2/\text{NiFeP}/\text{NF}$ hybrid electrode was fabricated through electrodeposition and the following phosphorization. Firstly, NiFe layered double hydroxide nanosheets were grown on Ni foam (NiFe LDH/NF) by using a potentiostatic electrodeposition method. Next, CeO_2 nanoparticles were deposited on

NiFe LDH/NF ($\text{CeO}_2/\text{NiFe LDH}/\text{NF}$) *via* a galvanostatic electrodeposition route [26]. Finally, $\text{CeO}_2/\text{NiFe LDH}/\text{NF}$ was converted to $\text{CeO}_2/\text{NiFeP}/\text{NF}$ through a thermal phosphorization procedure [27]. Figure 1(a) schematically shows the preparation process. For a comparison, the NiFeP/NF electrode was also fabricated through a similar process without the electrodeposition of CeO_2 . Please see Supporting Information for more details.

3. Results and discussion

The morphology of samples was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (see Figures 1(b,c), and S1–3). In Figure 1(b), a close observation illustrates that $\text{CeO}_2/\text{NiFeP}$ still maintains the morphology of nanosheet (the thickness of ~ 10 nm). These nanosheets are interconnected and stacked, thus generating open porous structure, which is favorable for exposing rich active sites and accelerating the mass transport [28,29]. In Figure 1(c), it can be found that numerous CeO_2 nanoparticles with the average diameter of ~ 5 nm are uniformly distributed on $\text{CeO}_2/\text{NiFeP}$ nanosheets. Figure 1(d) presents the high-resolution TEM (HRTEM) image of $\text{CeO}_2/\text{NiFeP}$. Thereinto, the lattice distances of 0.203 and 0.221 nm are indexed to (201) and (111) planes of NiFeP, as well as 0.191 and 0.271 nm correspond to (220) and (200) planes of CeO_2 , respectively. Figure S4 shows that Ni, Fe, Ce, O, and P elements are uniformly distributed in the whole $\text{CeO}_2/\text{NiFeP}$ nanosheets. The crystal structure of samples was investigated by X-ray diffraction (XRD) (see Figures 1(e), S5, and S6). In Figure 1(e), the XRD pattern shows diffraction peaks of NiFeP, which are nearly identical to those of Ni_2P (JCPDS No. 74-1385) and Fe_2P (JCPDS No. 51-0943). The characteristic peaks of CeO_2 do not appear in the XRD pattern since their intensity is too weak, which may be caused by the small size, low crystallinity, and low content of CeO_2 nanoparticles [18]. After partially enlarging the XRD pattern, the faint peaks of CeO_2 can be observed (see Figure S7). The Fourier transform infrared (FTIR) spectra of the samples show that the peak corresponding to the M–O ($\text{M} = \text{Ni}$ or Fe) bond blue-shifts from 532 to 510 cm^{-1} after the introduction of CeO_2 (see Figure S8). This indicates that the M–O bonds may be partly replaced by the Ce–O bonds at the interface between NiFeP and CeO_2 for the formation of heterostructure [30–33]. The specific surface area and pore size distribution of $\text{CeO}_2/\text{NiFeP}$ can be determined *via* Brunauer-Emmett-Teller (BET) analysis. From the inset of Figure 1(f), the pore size distribution indicates that both mesopores (2–50 nm) and macropores (> 50 nm) exist in $\text{CeO}_2/\text{NiFeP}$. The smaller

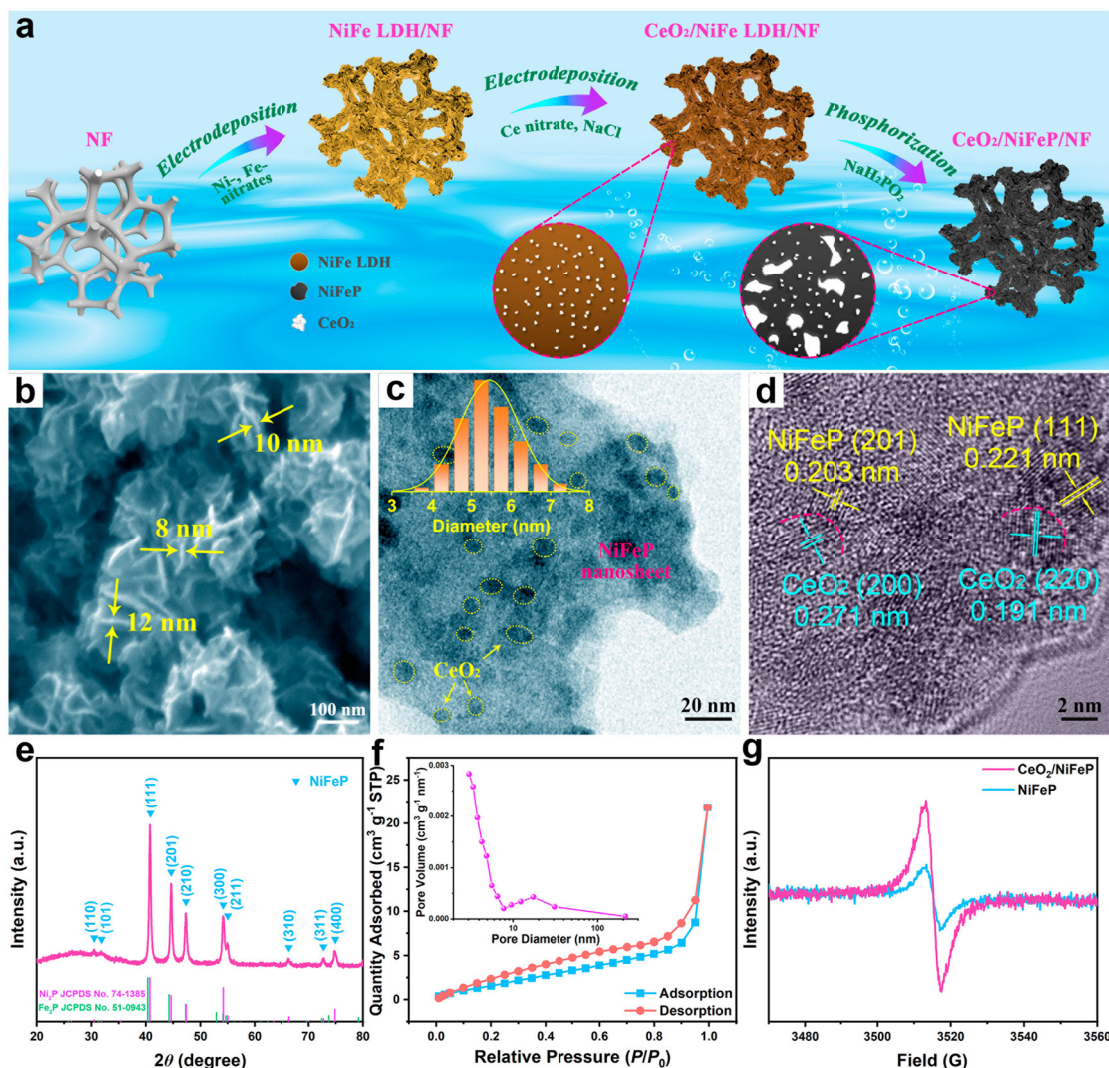


Figure 1. (a) Schematic illustration of the preparation of CeO₂/NiFeP/NF. (b) SEM, (c) TEM, and (d) HRTEM images of CeO₂/NiFeP. The inset of (c) shows a particle size distribution analysis. (e) XRD pattern of CeO₂/NiFeP. (f) N₂ adsorption/desorption isotherms and pore size distribution (the inset) of CeO₂/NiFeP. (g) EPR spectra of CeO₂/NiFeP and NiFeP.

pores mainly account for the shrinkage of the nanosheets during the phosphating process, and simultaneously the generation of the larger pores is caused by the overlapping or cross-linking of nanosheets [34,35]. Such a porosity facilitates gas diffusion and electrolyte permeation during the water splitting, which is beneficial for enhancing the catalytic performance of the CeO₂/NiFeP/NF electrode [36–38]. Particularly, electron paramagnetic resonance (EPR) measurements were used to detect the concentration of V_O. In Figure 1(g), the signal at $g = 2.003$ is caught distinctly in CeO₂/NiFeP, revealing the presence of V_O. These results are attributed to the flexible conversion between Ce³⁺ and Ce⁴⁺, and it is favorable for the gain and loss of electrons, thus promoting the formation of V_O [39].

The chemical valence states and surface compositions of CeO₂/NiFeP/NF and NiFeP/NF were investigated by

X-ray photoelectron spectroscopy (XPS). Figures 2 and S9 present the corresponding results. After the introduction of CeO₂, the characteristic peak of Ni²⁺ shifts to a more positive binding energy (~ 0.2 eV) and the peak assigned to Fe^{δ+} also shifts to a higher binding energy (~ 0.3 eV) (see Figure 2(a,b)). These results demonstrate that strong electronic interactions exist between Ni/Fe and Ce atoms, which could promote the electrocatalytic activity [17,40,41]. The Ce 3d spectrum (see Figure 2(c)) discloses the coexistence of Ce³⁺ and Ce⁴⁺ in CeO₂/NiFeP [42], which is due to the unique 4f electronic properties of CeO₂, whose cations can flexibly transform between the Ce³⁺ and Ce⁴⁺ oxidation states. Notably, the amount of Ce³⁺ increases significantly in CeO₂/NiFeP compared with pure CeO₂ nanoparticles, which can introduce abundant V_O [43], further confirmed by the O 1s spectrum (see Figure 2(d)) and Raman

spectrum (see Figure S10). The defective O peak caused by V_O cannot be found in NiFeP, which implies that abundant V_O are generated by depositing CeO_2 . Rich V_O can promote the adsorption of water molecules by the catalytic materials, improve the conductivity of the catalysts, as well as reduce the activation energy of water splitting reaction, further optimizing the electrocatalysis performance [20,23,44,45]. However, excessive V_O may cause the damage of the catalysts structure and the lower valence state of the nearby metal cation, which is not conducive to further improvement of the catalytic performance of transition-metal materials. Therefore, the introduction of an appropriate amount of V_O via the hybridization of NiFeP and CeO_2 species should be a rational strategy to improve the OER activity by the oxygen vacancy engineering. Herein, the concentration of V_O can be regulated by different contents of CeO_2 (see Figure S11).

Electrochemical measurements were performed to test the OER performance with a typical three-electrode system in 1 M KOH electrolyte. To explore the optimal CeO_2 content, different electrodeposition times (300, 600, and 900 s) were used for the galvanostatic electrodeposition of CeO_2 nanoparticles. The obtained samples are denoted as CeO_2 /NiFeP/NF (300 s), CeO_2 /NiFeP/NF, and CeO_2 /NiFeP/NF (900 s), respectively. Table S1 shows the CeO_2 contents of these samples determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). As expected, the CeO_2 /NiFeP/NF electrode owns the highest activity (see Figure S12). Figure 3(a) shows that the CeO_2 /NiFeP/NF electrode displays a smaller overpotential of 188 mV at 10 mA cm^{-2} compared with those of the NiFeP/NF (196 mV), CeO_2 /NiFe LDH/NF (215 mV), NiFe LDH/NF (225 mV), RuO_2 /NF (308 mV), and NF (393 mV) electrodes. These results indicate that both phosphorization and CeO_2 modification play important roles in improving the OER activity. Besides, the catalytic activity of electrocatalysts can also be assessed by Tafel slope. The small Tafel slope generally represents the fast reaction kinetics [46,47]. From Figure 3(b), the CeO_2 /NiFeP/NF electrode shows a lower Tafel slope of only 32 mV dec^{-1} compared with other electrodes (40, 44, 49, and 99 mV dec^{-1} for the NiFeP/NF, CeO_2 /NiFe LDH/NF, NiFe LDH/NF, and NF electrodes, respectively). Moreover, the charge transfer ability of various electrodes was investigated by the electrochemical impedance spectroscopy (EIS) tests (see Figure S13). In order to find out the origin of the advantageous OER activity of the CeO_2 /NiFeP/NF electrode, the electrochemical surface area (ECSA) was derived from the double layer capacitance (C_{dl}) [48,49]. Herein, the C_{dl} values of various electrodes (see Figure 3(c)) are gained via measuring cyclic voltammetry (CV) curves (see Figure

S14) at different scan rates in the nonfaradic region. The results indicate that phosphorization brings a larger ECSA, thereby exposing more abundant active sites to the electrolyte. Furthermore, the specific activity of the CeO_2 /NiFeP/NF electrode is $0.8 \text{ mA cm}_{ECSA}^{-2}$, which is 5.2 times higher than that of the NiFeP/NF electrode at the potential of 1.43 V (see Figure S15). The turnover frequencies (TOFs) of the obtained electrodes were calculated [50,51] and the corresponding results are shown in Figure S16. These demonstrate that CeO_2 decoration can enhance the intrinsic activity of active sites. Figure S17 displays the multi-current step curves of the CeO_2 /NiFeP/NF electrode to study its steady-state activity. Moreover, the potentials of the CeO_2 /NiFeP/NF electrode change a little from 1.47 to 1.49 V after 400 h electrolysis test in Figure 3(d), revealing its superior long-term stability. Owing to the self-supported structure without the introduction of insulative polymer binders, the CeO_2 /NiFeP/NF electrode could withstand violent gas evolution, prevent the agglomeration of active materials, and facilitate fast electron transfer and mass transport [52,53]. The SEM and TEM images show that the nanosheet structure of CeO_2 /NiFeP is still kept after such a long-term stability test. From Figure S18, the theoretical and experimental O_2 generation amounts are almost consistent, which enables the faradaic efficiency of the CeO_2 /NiFeP/NF electrode to be as high as 98%. All these electrochemical measurement results demonstrate that the CeO_2 /NiFeP/NF electrode has outstanding performance towards OER in alkaline electrolyte, superior to most of the reported transition metal-based electrocatalysts (see Figure S19 and Table S2).

According to the previous studies [7,14,54], the TMP-based materials can efficiently catalyze both HER and OER in alkaline media, which could serve to be potential bifunctional catalysts for water splitting and has great promise for further applications in fuel cell. As expected, the CeO_2 /NiFeP/NF electrode displays excellent HER performance in alkaline media (see Figure S20). To evaluate the water splitting catalytic performance of the self-supported CeO_2 /NiFeP/NF electrode, the electrolyzer (denoted as CeO_2 /NiFeP/NF|| CeO_2 /NiFeP/NF) using it as both cathode and anode was measured. In Figure 3(e), the CeO_2 /NiFeP/NF|| CeO_2 /NiFeP/NF electrolyzer displays an excellent activity with cell voltages of 1.54 V to drive 10 mA cm^{-2} and 1.67 V to drive 100 mA cm^{-2} , outperforming those of Pt/C/NF|| RuO_2 /NF (1.58 and 1.77 V) and most of the reported transition metal-based bifunctional catalysts (see Figure S21 and Table S3). Besides, the CeO_2 /NiFeP/NF|| CeO_2 /NiFeP/NF electrolyzer also shows excellent stability (see Figure S22).

To understand the nature behind, CeO_2 /NiFeP/NF after the OER durability test (marked as post-OER) was

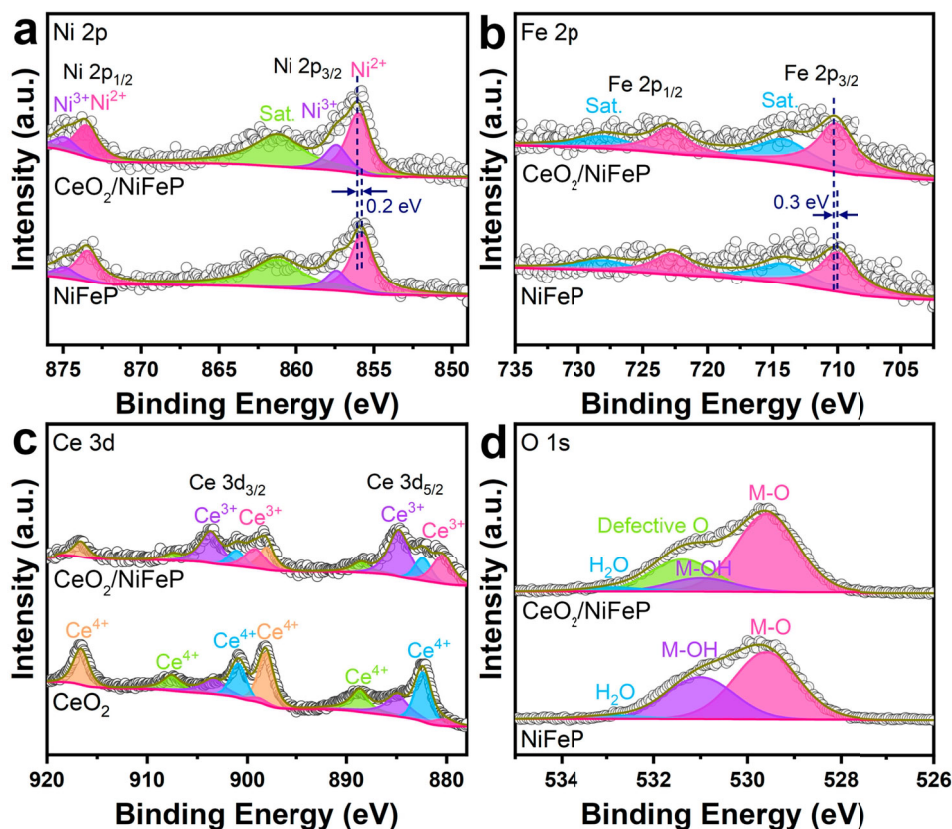


Figure 2. High-resolution XPS spectra of (a) Ni 2p, (b) Fe 2p, (c) Ce 3d, and (d) O 1s for $\text{CeO}_2/\text{NiFeP}/\text{NF}$ and NiFeP/NF .

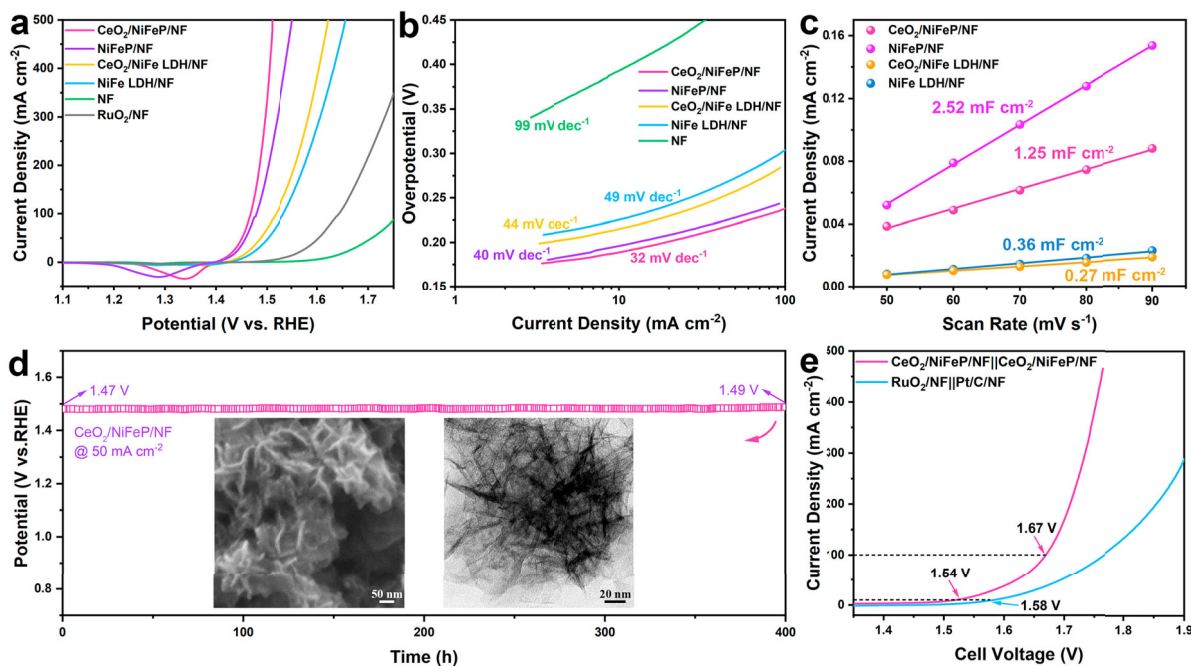


Figure 3. (a) Polarization curves of the $\text{CeO}_2/\text{NiFeP}/\text{NF}$, NiFeP/NF , $\text{CeO}_2/\text{NiFe LDH}/\text{NF}$, $\text{NiFe LDH}/\text{NF}$, RuO_2/NF , and pure NF electrodes. (b) The corresponding Tafel plots. (c) Capacitive current densities at -0.25 V (vs. Hg/HgO) plotted against scan rates. (d) Chronopotentiometric test of the $\text{CeO}_2/\text{NiFeP}/\text{NF}$ electrode at a current density of 50 mA cm^{-2} . The insets of (d) are SEM and TEM images of $\text{CeO}_2/\text{NiFeP}$ after the durability test. (e) Polarization curves of the $\text{CeO}_2/\text{NiFeP}/\text{NF}||\text{CeO}_2/\text{NiFeP}/\text{NF}$ electrolyzer and the $\text{Pt}/\text{C}/\text{NF}||\text{RuO}_2/\text{NF}$ electrolyzer with a scan rate of 1 mV s^{-1} in 1 M KOH .

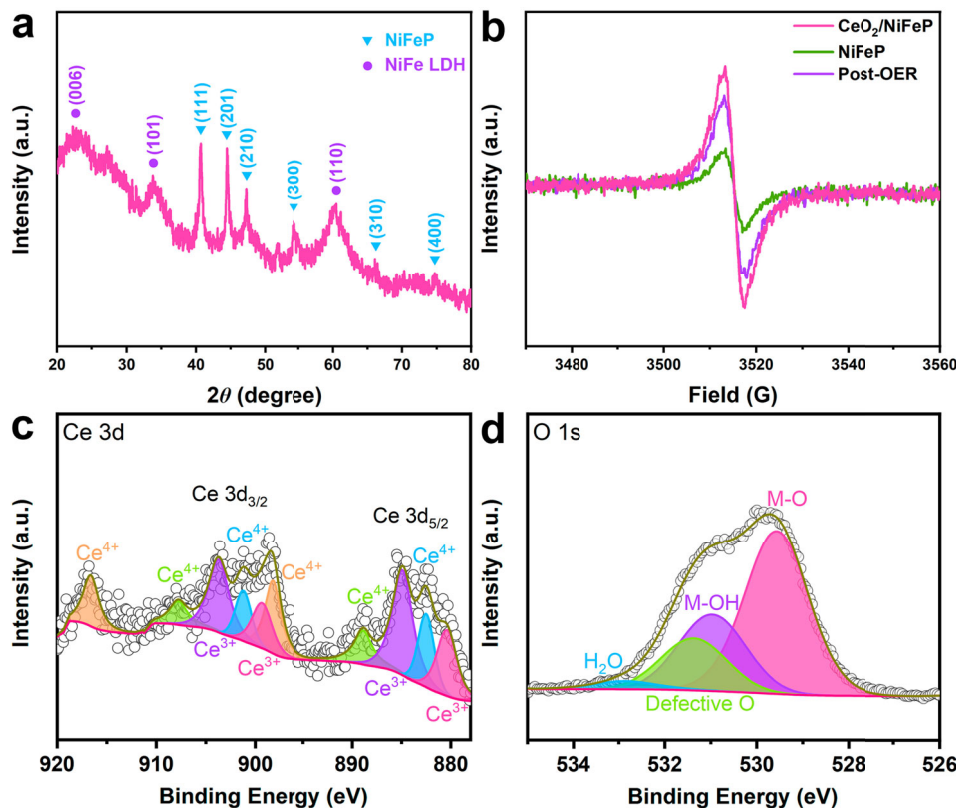


Figure 4. (a) XRD pattern of the post-OER sample. (b) EPR spectra of CeO₂/NiFeP before and after the durability test. High-resolution XPS spectra of (c) Ce 3d, (d) O 1s, for the post-OER sample.

further investigated. Generally, metal phosphides always in situ form insulative oxides/hydroxides on their surface after the OER process, and they are considered to be the true OER active sites [52,55,56]. In Figure 4(a), the XRD pattern of the post-OER sample is compared with that of the original one (marked as initial). Except for the characteristic peaks of NiFeP, the peaks of NiFe LDH are also observed. Moreover, the HRTEM image (see Figure S23), the elemental mapping images (see Figure S24), the ICP-OES results (see Table S4), and the XPS results (see Figure S25) also confirm this point. In Figure 4(b), the signal intensity of V_O becomes a little weaker after 400 h OER test. Even so, there are still a larger number of V_O in the post-OER sample than those in NiFeP, which ensures high activity during the OER process. After the OER test, the Ce 3d spectrum shows that the ratio of Ce⁴⁺:Ce³⁺ obviously increases, indicating that a part of Ce³⁺ was oxidized to Ce⁴⁺ under the OER condition (see Figure 4(c)). In O 1s spectrum (see Figure 4(d)), the intensity of the defective O peak of the post-OER sample relatively decreases compared to the initial sample, which indicates the reduction of V_O.

To disclose the mechanism behind the OER, DFT calculations were implemented by VASP 6.1.0. The most stable configurations of NiOOH and NiFeOOH are shown

in Figure S26. Here, the Ni atoms on the surfaces of NiOOH and NiFeOOH were considered the active sites (donated as Ni_{site} and Fe-Ni_{site}, respectively, see Figure S27). After introducing Fe dopant, Fe-Ni_{site} exhibits better catalytic activity than Ni_{site}, with a lower overpotential (η) of 0.64 V (see Figure S28). Conversely, NiFeP possesses a higher η of 1.32 V, indicating that the oxidized species are the key to enhance the OER performance (see Figure S29). To further clarify the effect of Ce species in CeO₂/NiFeP/NF, the free energies changes on Ce-doped NiFeOOH were calculated (see Figure 5(a,b)). Particularly, one oxygen atom on the surface was removed to simulate the oxygen vacancy. Therefore, this vacancy was considered as the active site (donated as Ce-Ni_{site}, see Figure S27). Furthermore, as a contrast, the catalytic activity of CeO₂ (111) plane was also calculated. It was found that Ce-Ni_{site} owns a much lower η of 0.34 V than that of the CeO₂ (111) plane (η = 0.91 V), which is even better than Fe-Ni_{site} (η = 0.64 V). What is more, the value of $\Delta G_{O^*} - \Delta G_{OH^*}$ is often chosen as the OER descriptor [37]. Figure 5(c) shows that the Ce-Ni_{site} has the lowest value of 1.57 eV, which is close to the optimal value (1.6 eV) [57]. Furthermore, after the addition of Ce, more electrons of the Ni 3d orbitals are observed near the Fermi energy, which means a slightly positive shift of the

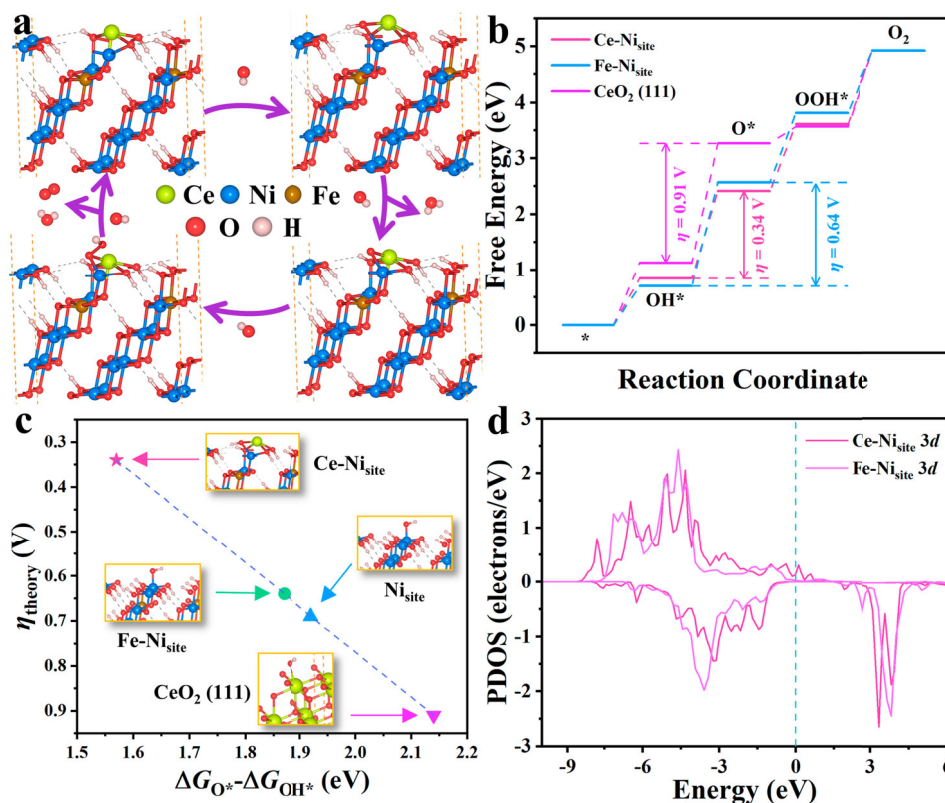


Figure 5. DFT simulation results. (a) Schematic profile of adsorption atomic configuration on the Ce-Ni_{site} during the OER elementary steps. (b) Free energy diagrams along the reaction pathways on Ce-Ni_{site}, Fe-Ni_{site} and CeO₂ (111) plane. (c) Representation of the theoretical overpotential as a function of the difference in O* and OH* adsorption Gibbs energies. (d) PDOS of Ce-Ni_{site} 3d orbitals and Fe-Ni_{site} 3d orbitals. The Fermi energy was set to zero.

d-band center (ϵ_d) (see Figure 5(d)) [53]. This is hopeful to enhance *OH adsorption energy, leading to more favorable OER thermodynamics [58,59].

4. Conclusions

Overall, a self-supported CeO₂/NiFeP/NF electrode was designed and prepared as efficient bifunctional electrocatalyst, which displays outstanding performance towards OER with a low overpotential of 188 mV at 10 mA cm⁻² and Tafel slope of 32 mV dec⁻¹. Besides, the CeO₂/NiFeP/NF||CeO₂/NiFeP/NF electrolyzer requires only a cell voltage of 1.54 V to drive 10 mA cm⁻² for overall water splitting, exceeding the majority of previously reported transition metal-based electrocatalysts. Such superior performance primarily originates from the distinctive properties of CeO₂ nanoparticles, which bring the strong electronic interactions between the interfaces of the heterostructure hybrid, and also introduce rich oxygen vacancies. These could be favorable for the conformation of active sites and the improvement of the intrinsic catalytic activity. Furthermore, DFT simulations indicate that Ce species can efficiently regulate

the energetics for OER intermediates, resulting in more favorable OER thermodynamics.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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