Carbon Dots Decorated Hierarchical NiCo$_2$S$_4$/Ni$_3$S$_2$ Composite for Efficient Water Splitting

Xinyu Zhao, Hui Liu, Yuan Rao, Xinlin Li, Jialin Wang, Guangsen Xia, and Mingbo Wu

State Key Laboratory of Heavy Oil Processing, Institute of New Energy, College of Chemical Engineering, China University of Petroleum (East China), Qingdao 266580, People’s Republic of China

ABSTRACT: The decomposition of water into hydrogen and oxygen is an effective method to generate new energy. How to develop highly efficient catalysts with low cost for the hydrolysis of water is a huge challenge. Herein, heterogeneous CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$ nanorods were constructed on nickel foam (CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF) by Co ion exchange on carbon dots (CDs) and sulfur codoped nickel foam (NF). The designed CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF as a self-standing electrocatalyst shows excellent electrocatalytic properties. In the hydrogen evolution reaction process, the current density can reach 10 mA cm$^{-2}$ only with the overpotential of 0.127 V. During the oxygen evolution reaction process, overpotential of 0.116 V is enough to achieve the same current density. Meanwhile, the CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF electrode can serve as both anode and cathode in alkaline electrolyte, and overpotential of 1.50 V can drive the overall water splitting with superior durability. Such excellent properties are mainly due to (1) a large number of exposed active sites provided by carbon dots modified transition metal chalcogenide (NiCo$_2$S$_4$ and Ni$_3$S$_2$), (2) the changed electronic structure caused by the incorporation of carbon dots and Co ions and the synergistic effect between NiCo$_2$S$_4$ and Ni$_3$S$_2$, (3) the accelerated electron transfer and mass transfer processes owing to the hierarchical structure formed by 3D nickel foam and one-dimensional CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF nanorods. This study can facilitate with the production of efficient and non-noble metal catalysts for overall water splitting.

KEYWORDS: Carbon dots, Transition metal chalcogenides, Hydrogen evolution reaction, Oxygen evolution reaction, Water splitting

INTRODUCTION

With the rapid development of our societies, the need for energy is rising sharply. Meanwhile, the limited reservation of conventional fossil energies and the increasingly severe environmental contamination require development of new energy resources that are effective and environmental friendly. As a kind of “green energy” with abundant resources, high effectiveness and no secondary pollution, hydrogen energy is considered as one of the ideal energy sources to solve the energy and environmental crises in the postfossil era. Electrolysis of water is one reliable way to produce hydrogen, during which nonstorable renewable resources (such as solar energy, wind energy, tidal energy, and so on) can be used to generate electricity for electrolyzing water. The electrolyzed water can not only produce hydrogen and oxygen with high purity, but also can store the electric energy into chemical energy for further utilization. However, electrolyzed water is thermodynamically nonspontaneous adverse reaction, requiring a high overpotential for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) to provide a seemingly reaction rate. In order to scale up the hydrogen production, it is necessary to reduce the reaction potential and improve the reaction rate. Thus, the development of efficient and resource-rich catalysts for water electrolysis becomes an urgent issue. Now, platinum group precious metals are commercially used as catalysts for water splitting, but these catalysts are in less reserve and expensive, making them fail to meet the real needs of large-scale production. Therefore, in recent years, many researchers have devoted themselves to the design and development of new catalysts with high efficiency and low cost.

So far, Fe-, Co-, or Ni-based transition metal chalcogenides (TMCs) materials, for example, Mo$\rightarrow$S$_{16-18}$, Ni$\rightarrow$S$_{19-23}$, Mo$\rightarrow$Se$_{24}$, Co$\rightarrow$Se$_{15}$, and Co$\rightarrow$S$_{26-28}$ have been found can be catalytic activity sites on both HER and OER. As a typical kind of transition metal chalcogenides, Ni$\rightarrow$S materials have different stoichiometric ratios, such as Ni$_3$S$_2$$_{19,21}$$NiS$$_2$$^{21}$ and NiS$_2$$^{23}$ and different morphologies, including nanoparticles$^{24}$, nanosheets$^{19}$ and nanowires$^{19}$. They were reported as effective electrocatalysts. Nevertheless, these catalysts have good performance in single reaction. When they are used as bifunctional catalyst, their catalytic performance is significantly lower than standard electrocatalysts. Fortunately, TMCs compounds have been proved feasible catalysts. For example, Gao et al. prepared MoS$_2$$\rightarrow$Ni$_3$S$_2$
heteronanorods via a hydrothermal method, which show good water splitting performance.\textsuperscript{30} Feng et al. also improved electrocatalytic activity by preparing MoS\textsubscript{2}/Ni\textsubscript{3}S\textsubscript{2} heterostructures.\textsuperscript{31} In addition, Zou et al. prepared Ni\textsubscript{Co}\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2} nanosheets with excellent electrocatalytic performance and stability through the introduction of Co ions.\textsuperscript{32} The electrocatalytic performance can be improved by the synergistic effect among TMCs compound. Nevertheless, it is still difficult to construct efficient electrocatalyst with subtly integrated structure by feasible methods. Cation exchange is versatile and has been used in producing various sulfide nanomaterials.\textsuperscript{33,34}

In order to further improve the performance of the catalyst, different forms of nanocarbon materials were coupled with electrocatalysts to improve the catalytic performance.\textsuperscript{35,36} Carbon dots (CDs) with diameter less than 10 nm are the newest members of carbon material family.\textsuperscript{37} When CDs are employed, there will have large space to improve the catalysis performance of TMCs-carbon materials. This is out of the reason that CDs are 0D nanoparticles with natural merits. On the one hand, compared with those multidimensional carbon materials, CDs are more flexible for forming different structures. On the other hand, when CDs and TMCs assemble together, there will be more active sites exposed. What is more important is that, with the highest specific surface area, CDs can carry more organic groups. This can contribute to the surface wettability. In this way, larger interface area between CDs, TMCs, as well as electrolytes for electrochemical reactions can be formed.\textsuperscript{36} All these merits can ensure a promising future of CDs-TMCs composites in the area of electrocatalyst. Under such inspiration, the preparation of electrocatalyst from CDs modified TMCs via cation exchange was developed to improve catalysis performance. Herein, we designed a new type of material by using a one-step hydrothermal method to grow CDs/Ni\textsubscript{3}S\textsubscript{2} nanorods on nickel foam as precursors, and introducing Co atoms through cation exchange to form a highly efficient CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2} electrode with heteronanorods structure. As it is expected, CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF shows high catalytic activity, outperforming most reported catalysts based on non-noble-metal for water splitting.

**EXPERIMENTAL SECTION**

**Synthesis of CDs/Ni\textsubscript{3}S\textsubscript{2}/NF.** Synthesis of CDs was carried out in accordance with the reported method.\textsuperscript{37} CDs/Ni\textsubscript{3}S\textsubscript{2}/NF nanorods were then synthesized by hydrothermal method. The purchased foam nickel (thickness 1.5 mm) was ultrasonically washed with acetone, hydrogen chloride, ethanol and deionized water for 20 min, respectively. Next, it should be dried at 60 °C for 1 h. Then a piece of foam nickel (1 cm × 4 cm) was immersed into a 50 mL Teflon-lined stainless autoclave containing 4 mol thiourea and 30 mL of 1.0 mg mL\textsuperscript{-1} carbon dots solution. The autoclave was sealed and kept at 180 °C for 3 h in a rotary oven. Then, it was cooled at the room temperature naturally and was washed by deionized water and absolute ethanol for three times repeatedly and was dried in a vacuum oven at 60 °C for 12 h to obtain CDs/Ni\textsubscript{3}S\textsubscript{2}/NF nanorods. In contrast, the synthesis of Ni\textsubscript{3}S\textsubscript{2}/NF requires only the replacement of CDs solution with deionized water under the same conditions.

**Synthesis of CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF.** The preparation of CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF was conducted through cation exchange reaction between CDs/Ni\textsubscript{3}S\textsubscript{2}/NF and Co ions. CDs/Ni\textsubscript{3}S\textsubscript{2}/NF was immersed into a 50 mL Teflon-lined stainless autoclave that contained ethylene glycol (30 mL) and cobaltous acetate tetrahydrate (2.5 mmol). After that, at 200 °C, it was sealed and placed in a rotating oven for 12 h. The obtained sample was washed with deionized water and anhydrous ethanol repeatedly and dried in a vacuum oven overnight to obtain CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF. For comparison, the TMCs without carbon dots (NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF) was prepared. For NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF, the loading mass was about 4 mg cm\textsuperscript{-2}. This number was obtained by accurate weighing of the analytical balance before and after hydrothermal treatment.

**Materials Characterizations.** The X-ray diffraction patterns (XRD) were recorded on a PANalytical X-ray Diffractometer (Cu K\textalpha) with a 2θ range from 10° to 70°. The Raman spectra were recorded on a Raman spectrometer of Renishaw. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALAB 250XI X-ray spectrometer with Al as a photo source. All XPS curves were fitted and background subtracted. Scanning electron microscopy (SEM) measurements were performed on a ZEISS MERLIN. Transmission electron microscopy (TEM) characterizations were performed on a JEM2100 F scanning transmission electron microscopy. The obtained self-supporting electrode was directly used in electrochemical performance characterization.

**Electrochemical Measurements.** All the electrochemical measurements were performed on a CHI 760E (CHI Instruments, Shanghai) electrochemical analyzer in a standard three-electrode system. The obtained CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF served as working electrode, a carbon rod was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode in 1.0 M KOH solution. In this study, all shown potentials were calibrated to RHE according to the equation: E(RHE) = E(Ag/AgCl) + (0.197 V) + 0.059 pH. The scanning rate of 5 mV/s for linear sweep voltammetry (LSV) measurements was tested from 0 to 0.8 V. There was no activation before the polarization curves had been recorded. After that, the LSV curves did not go through iR correction. Chronoamperometric measurements were used to get the durabilities of obtained materials. As a comparison, we prepared the Pt/C (20 wt %) and RuO\textsubscript{2} drop coating on NF, and they were used as working electrodes. The following is the typical procedure: (1) 10 μL of Nafion (5 wt %) solution and the 4 mg of Pt/C or RuO\textsubscript{2} were dispersed in 800 μL of anhydrous ethanol by sonication for 60 min. (2) 320 μL of this solution was dropped onto NF (1 cm × 0.6 cm) in order to make sure that the compared electrode has the same working area of CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF and the same loading amount of 4 mg cm\textsuperscript{-2}. (3) In order to avoid the covering materials from falling off, 80 μL of Nafion (0.5 wt %) solution dissolved in ethanol was drop-cast on the surface of the electrode. After that, it was dried in an electric heater.

**RESULTS AND DISCUSSION**

Through the method of cation exchange, we successfully prepared CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF nanorods and the synthesis of CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF is illustrated schematically in Scheme 1. First, CDs/Ni\textsubscript{3}S\textsubscript{2}/NF were hydrothermally prepared by the carbon dots induction method. After that, the obtained CDs/Ni\textsubscript{3}S\textsubscript{2}/NF nanorods precursors and Co ions were subjected to cation exchange reaction at 200 °C, which
produced the CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF nanorods. Here, the synthesis of CDs/Ni\textsubscript{3}S\textsubscript{2} with exposed (021) crystal face is based on our previous work.\textsuperscript{37} The transmission electron microscopy (TEM) images and X-ray diffraction (XRD) pattern of CDs are provided in Figure S1a,b (see Supporting Information). The XRD pattern reveals a much greater diffraction peak centered at 25.7°, which is a characteristic peak of a typical carbon material. In addition, from the TEM image, it can be seen that the distribution of synthesized CDs is relatively homogeneous, and the 0.22 nm lattice spacing shown in the high-resolution TEM (HRTEM) image of CDs also corresponds well to that of graphitic carbon (100) plane. The FT-IR spectra (Figure S1c) demonstrates the existence of various functional groups on CDs. It is obviously different from petroleum coke. Raman spectra (Figure S1d) of petroleum coke and CDs further indicate typical D and G bands of carbon materials. These results clearly indicate the successful formation of CDs. The SEM image (Figure S2) show the growth process of Ni\textsubscript{3}S\textsubscript{2} nanorods with different morphologies. It can be seen that after 1 h reaction at 180 °C, nucleation started on the surface of nickel foam and gradually grew with the continuation of the reaction. The phenomenon of transition growth occurred in after 4 h of the reaction, and nanorods began to gather together. In this experiment, we chose the uniformly distributed CDs/Ni\textsubscript{3}S\textsubscript{2}/NF rod-like structure obtained after 3 h of reaction as a precursor, and then proceeded to the next ion exchange reaction. This reaction can not only maintain the morphology of the precursor well, but also introduce heteroatoms to form heterogeneous surfaces. A comparative experiment was also conducted in the similar condition without adding carbon dots. From the SEM image (Figure S3b), the obvious nanosphere-like structure can be seen, which is obviously different from the rod-like structure formed after carbon dots were added.

Moreover, by the X-ray diffraction (XRD) pattern, it was confirmed that the nanorods belong to NiCo\textsubscript{2}S\textsubscript{4}, Ni\textsubscript{3}S\textsubscript{2} and CDs. As shown in Figure 1a, the diffraction peaks at 31.6, 38.3, 50.5 and 55.3° can be assigned to (311), (400), (511) and (440) planes of the cubic NiCo\textsubscript{2}S\textsubscript{4} phase (JCPDS card No. 20-0782), respectively, and the peaks at 21.8, 31.1, 38.3, 49.7 and 55.1° corresponding to (101), (110), (021), (113) and (122) planes of rhombohedral Ni\textsubscript{3}S\textsubscript{2} (JCPDS card No. 44-1418), respectively.\textsuperscript{19,32} What is more, at 44.5 and 51.8°, the two peaks shown were metallic Ni foam (JCPDS card No. 04-0850). All these showed that successful preparation of CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF after cation exchange reaction between CDs/Ni\textsubscript{3}S\textsubscript{2} and cobalt ions. For comparison, NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF were made by a similar process to that of the preparation of CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF. The XRD patterns show the formation of NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF (Figure S3a). NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF presents nanosphere morphology (Figure S3b) rather than the aligned nanorods architecture of CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF. The typical scanning electron microscopy (SEM) images of CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF demonstrate that the material has a three-dimensional porous structure (Figure 1b). In Figure 1c,d, it can be clearly seen that a uniform layer

**Figure 1.** (a) XRD pattern of CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF. (b, c and d) SEM images of CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF. (e) TEM and (f) high-resolution transmission electron microscopy (HRTEM) images of CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF nanorods. (g) STEM images and the corresponding EDX elemental mapping images of Ni, Co, S and C taken from CDs/NiCo\textsubscript{2}S\textsubscript{4}/Ni\textsubscript{3}S\textsubscript{2}/NF nanorods.
of nanorod structure with length of 50−200 nm covers the surface of the nickel foam skeleton. In order to further prove that the synthesized structure was nanorod, TEM analysis was conducted and the nanorod structure of the material can also be clearly seen in Figure 1e. This indicates that the material can maintain the morphology of the precursor well after the ion exchange reaction. It is worthy of notice that many nanoparticles can be seen in Figure 1e. It is speculated that these nanoparticles may composed with NiCo2S4, Ni3S2 and CDs. Hence, high-resolution TEM (HRTEM) measurement was performed to further confirm the above speculation. As shown in Figure 1f, it can be seen that the material has five different lattice spacings: 0.24, 0.28, 0.23, 0.24 and 0.22 nm, which are corresponding to the (400) lattice plane and (311) lattice plane of cubic NiCo2S4 phase, the (021) lattice plane and (003) lattice plane of the hexagonal Ni3S2, and the (100) lattice plane of the CDs, respectively. In addition, the 90° angle between the lattices corresponds well to the theoretical value of the cubic structure of NiCo2S4, and the 70.7° angle in the Ni3S2 structure corresponds to the theoretical value of (021) lattice plane.32 As it is described, in the CDs/Ni3S2 system, the introduction of Co atoms can form a new NiCo2S4 phase, changing the electronic state of S in the original system. The CDs in the system in turn can affect the electronic state of Co (Figure S7a,b). The interaction between the electrons causes a synergistic effect between the phases of CDs, Ni3S2 and NiCo2S4, so that the performance of the catalyst can be significantly improved.

In addition, in HRTEM (Figure S4), the lattice fringe with the spacing of 0.22 nm is the (100) lattice plane of CDs, which fully proves the successfully doping of CDs. Element mapping images (Figure 1g) show that Ni, Co, S, C and other elements were uniformly distributed in the nanorods structure of the material. This also proves that nanorods consist of NiCo2S4, Ni3S2 and CDs. Moreover, from Raman spectra (Figure S5), it further confirmed that CDs/Ni3S2/NF were converted into NiCo2S4/Ni3S2/NF after cation exchange reaction. The illustrated Raman spectra can be divided into two parts: spectra below 400 cm−1 and spectra above 400 cm−1. According to previously published literature, the group with a wavenumber region below 400 cm−1 is the Raman spectral band of Ni3S2, and the group with a wavenumber region above 400 cm−1 is the Raman spectral band of NiCo2S4.39 In addition, the peaks of the CDs were clearly observed at 1375 and 1600 cm−1 (Figure S5b), which are corresponding to the D and G, respectively. These results clearly show that the obtained material contains NiCo2S4 and CDs/Ni3S2. Besides, the Raman bands of NiCo2S4 were not observed in Raman spectra without cation exchange, indicating that the CDs/NiCo2S4/Ni3S2/NF was been successfully synthesized via cation exchange.

The XPS survey spectra of the pristine CDs/NiCo2S4/Ni3S2/NF nanorods indicate the existence of Ni, Co, S, and C, N, O. In the Ni 2p spectrum (Figure S6a), the appreciable fitting peaks at 853.2, 872.6 eV and 856.2, 874.4 eV are ascribed to Ni2+ and Ni3+, respectively. The satellite peaks at 861.2 and 879.2 eV, which are due to shakeup peaks of nickel. Similarly, Figure S6b shows that spin−orbit splitting values of Co 2p1/2 at 15.1 eV and Co 2p3/2 at 16.3 eV are ascribed to Co3+ and Co2+, respectively.40 These results demonstrate the presence of NiCo2S4. In the case of S 2p spectrum (Figure S6c), the strongly fitting peaks centered at 162.0 and 163.2 eV are assigned to S 2p3/2 and S 2p1/2, respectively. In detail, the peak at 163.2 eV is originated from the sulfur−metal bonds and the binding energy at 162.0 eV is attributed to S2− in low coordination at the surface. In addition, S 2p fitting peaks centered at 168.9 eV is attributed to the surface sulfur species at certain higher oxidation states. The XPS spectra of C 1s (Figure S6d), N 1s (Figure S6e) and O 1s (Figure S6f)
confirm the successful introduction of CDs in the CDs/NiCo2S4/Ni3S2/NF system. All the above analytical results suggest that CDs/NiCo2S4/Ni3S2/NF was successfully synthesized.

**CDs/NiCo2S4/Ni3S2/NF toward HER and Mechanism.**

The HER performance test of CDs/NiCo2S4/Ni3S2/NF was conducted in a 1.0 M KOH electrolyte in a three-electrode system. CDs/NiCo2S4/Ni3S2/NF as self-supporting electrodes can be directly used as working electrodes in this system. By contrast, we also tested the performance of bare Ni foam, Pt/C on Ni foam (Pt−C/NF) and CDs/Ni3S2/NF under the same conditions. In Figure 2a, it can be seen that CDs/NiCo2S4/Ni3S2/NF electrode shows excellent HER performance, requiring the overpotential of only 127 mV to achieve the 10 mA cm\(^{-2}\) current density. However, for bare Ni foam and CDs/Ni3S2/NF, it took the overpotentials of 247 and 187 mV to achieve the same current density. CDs/NiCo2S4/Ni3S2/NF have a rather low overpotential compared to the non-noble bifunctional electrocatalytic materials previously reported (Table S1).

The Tafel slopes of CDs/NiCo2S4/Ni3S2/NF, CDs/Ni3S2/NF, bare Ni foam and Pt−C/NF are 148, 155, 164 and 57 mV dec\(^{-1}\), respectively (Figure 2d). This phenomenon indicates that the Volmer reaction is a rate-limiting step in the HER process. The stability of CDs/NiCo2S4/Ni3S2/NF was tested by a 4000 CV cycles polarization test at a voltage of 0 and −0.6 V (Figure 2e). What was interesting was that after 4000 cycles, the performance of HER was even improved. This is because a small amount of high valence Ni and Co can be randomly reduced to metal Ni and Co (Figure S13). In this way, the conductivity and electron transfer rate of CDs/NiCo2S4/Ni3S2/NF can be improved. During stability testing, a 12 h stability test was performed (at a static overpotential of 127 mV). From the stability test, the CDs/NiCo2S4/Ni3S2/NF shows a good stability with almost no large fluctuation in current density. Additionally, the morphology of CDs/NiCo2S4/Ni3S2/NF was basically unchanged after the HER stability test by the characterization of XRD pattern (Figure S8a) and SEM image (Figure. S8b).

It can also be seen in Figure 2a that the hydrogen evolution potential of CDs/NiCo2S4/Ni3S2/NF is second only to the Pt−C/NF electrode. Such good performance may be attributed to the synergistic effect of the Ni and Co metal ions produced by the reduction of CDs/NiCo2S4/Ni3S2/NF nanoclusters. The specific mechanism of HER follows two reactions: \(M + H_2O + e^- \rightarrow M^+ \text{Hads} + OH^-\) (Volmer step) and \(H_2O + M^+ \text{Hads} + e^- \rightarrow H_2 + M + OH^-\) (Heyrovsky step). Through the optimization of these two processes, the catalyst can show highly efficient catalytic performance. According to the related study, it is known that one of the major challenges of using transition metal sulfides in the HER reaction is the formation of strong S−H bonds on the surface of the catalyst, which severely inhibits the reaction rate of HER. Therefore, for the Ni3S2 system introduced in this paper, the adsorption and desorption of H can be balanced by the introduction of Co atoms and CDs (Figure S7d). The electron interaction among Ni3S2, Co and CDs in the CDs/NiCo2S4/Ni3S2/NF can weaken the S−Hads bond formed on the surface of the catalyst, which favors the desorption of H and promotes the Heyrovsky reaction. If only Ni3S2 is used as a catalyst, Hads can be stably and easily adsorbed on the surface of catalyst. However, an excessively stable S−Hads can make the transfer of Hads to H2 difficult, leading to low electrocatalytic activity. This phenomenon can be demonstrated in the analysis of XPS (Figure S7c). It can be seen that after the doping with Co, the peaks of S 2p\(_{1/2}\) and S 2p\(_{3/2}\) of CDs/NiCo2S4/Ni3S2/NF demonstrate negative shifts of 0.24 and 0.21 eV, respectively. In addition, it can also be seen from...
the binding energy of Co atoms had a negative shift of 0.5 eV, indicating that after the Co atoms were incorporated into the system, they were in turn affected by the CDs. This can result in downshift of their d-band center and the optimization of key descriptor for HER performance ($\Delta G_{\text{H}}$), contributing to the catalytic activity for HER. This phenomenon can also be demonstrated in the performance analysis of control experiments (Figure S14a). In addition, the Roman spectra (Figure S7d) can prove that the introduction of Co atoms and carbon dots in the Ni$_3$S$_2$ system can balance the adsorption and desorption of H. When the HER reaction at the potential of $-127$ mV vs RHE for $10$ h were completed, a peak at about $2562$ cm$^{-1}$ was detected for Ni$_3$S$_2$/NF, and a peak about $2500$ cm$^{-1}$ was shown for CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF. These peaks were in line with S–H$_{\text{ads}}$ bonds formed on the catalysts during HER. Compared with that of Ni$_3$S$_2$/NF ($2562$ cm$^{-1}$), Raman shift of S–H$_{\text{ads}}$ for CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF ($2500$ cm$^{-1}$) was about $62$ cm$^{-1}$ red-shifted, which showed that the S–H$_{\text{ads}}$ bonds on CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF were weaker than those on Ni$_3$S$_2$/NF.

**CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF toward OER and Mechanism.**

The OER performance test was conducted in a $1.0$ M KOH electrolyte and a CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF being a self-supporting electrode. Similar measurements for RuO$_2$ modified NF (RuO$_2$/NF), bare nickel foam, and CDs/Ni$_3$S$_2$/NF were also conducted during the controllable experiments. It can be seen from Figure 3a that CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF exhibited the best catalytic activity. Before voltage reached $1.5$ V, its current density was slightly lower than that of CDs/Ni$_3$S$_2$/NF. This is due to the voltage reached $1.5$ V, a large amount of Ni$^{II}$ oxidation of CDs/Ni$_3$S$_2$/NF can be converted into Ni$^{III}$, and there would be a clear oxidation peak, resulting in the sharp rise of current density. However, after the voltage exceeded $1.5$ V, its current density was much higher than that of other materials.

As shown in Figure 3b, CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF only requires the overpotentials of $116$ and $156$ mV for the achievement of the current densities of $10$ and $50$ mA cm$^{-2}$, making it obviously better than other catalysts. It can also be proved in Figures 3c that its catalytic performance is also the best under high current. The performance of this catalyst is much better compared with the most currently reported electrocatalysts (Table S1). The OER kinetics was tested by corresponding Tafel plots ($\eta$ versus log (j)) of these electrodes (Figure. 3d). The Tafel slope of CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF was $99$ mV dec$^{-1}$. This was significantly lower than the Tafel slopes of CDs/Ni$_3$S$_2$/NF ($129$ mV dec$^{-1}$), bare NF ($206$ mV dec$^{-1}$) and RuO$_2$/NF ($135$ mV dec$^{-1}$), showing that CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF had a faster OER rate. The stability of CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF showed no significant change after $4000$ CV cycles polarization tests (Figure. 3e). After a $12$ h galvanostatic test (Figure. 3f), no large attenuation was found, which indicated that this catalyst had a good stability. After the long OER test, the nanorods structure of CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF was only slightly changed by the XRD pattern and SEM characterization (Figure. S9).

**CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF catalyst exhibited such superior OER performance probably because of the synergistic effect of Co, CDs and Ni foam. In general, at the beginning of the OER, OH$^-$ anions were adsorbed and discharged on the surface of catalyst in order to construct the adsorbed OH species. After that, OH$^-$ had reaction with the adsorbed OH species, producing adsorbed atom O as well as H$_2$O and releasing electron. Next, reaction of the adsorbed atom O and OH$^-$ was taken place to form the adsorbed OOH species. After that, the OOH species would react with another OH$^-$ to form adsorbed OOH species.**

**Figure 4.** The OER performance of control experiments (Figure S14b). In general, at the beginning of the OER, OH$^-$ anions were adsorbed and discharged on the surface of catalyst in order to construct the adsorbed OH species. After that, OH$^-$ had reaction with the adsorbed OH species, producing adsorbed atom O as well as H$_2$O and releasing electron. Next, reaction of the adsorbed atom O and OH$^-$ was taken place to form the adsorbed OOH species. After that, the OOH species would react with another OH$^-$ to form adsorbed OOH species. In this way, adsorbed O$_2$ can be formed and another electron can be released. Finally, the adsorbed O$_2$ desorbed from the surface of the catalyst (Figure. S10). In OER, the process in which the adsorbed OOH species were formed was considered as the rate-limiting step. Moreover, the OER activity of transition metal materials depends on the interaction of the adsorbed OOH species with the 3d orbital of transition metals. There are also studies proving that the increase in 3d orbital electron density in Co-based OER catalysts favors the construction of the adsorbed OOH species, which can then help to increase the OER activity. The doping of Co in CDs/Ni$_3$S$_2$/NF catalyst reduced the 2p$_{3/2}$ binding energy of Ni atoms (Figure S7b), reflecting that the doping of Co atoms can reduce the binding energy of Ni atoms and enable Ni atoms. In this way, more electrons can be obtained. In addition, compared with the carbonless system, the binding energy of Co atoms also has a negative shift of $0.5$ eV (Figure S7a), which indicates that there are more electrons in the 3d orbital of Co atoms. This is beneficial to the construction of OOH species. At the same time, this can help to promote the OER. This phenomenon can also be demonstrated in the performance analysis of control experiments (Figure S14b).
and anode was assembled for overall water splitting. The CDs/ NiCo$_2$S$_4$/Ni$_3$S$_2$/NF electrodes showed great stability for the electrolytic reaction for 12 h (Figure 4b). All these show that the catalytic performance of CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF is better than most of the reported bifunctional electrocatalysts for overall water splitting (Table S1).

The reasons why CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF can have such excellent performance for overall water splitting are that (1) NiCo$_2$S$_4$ and Ni$_3$S$_2$ are metal sulfides with good conductivity because they have Ni–Ni bonds. (2) A large number of exposed active sites provided by carbon dots modified transition metal chalcogenide (Ni$_3$S$_2$ and NiCo$_2$S$_4$) and the CDs/Ni$_3$S$_2$/NF precursors have good stability and can fully retain their active sites, which is beneficial to improve the catalytic performance. (3) The strong interfacial interaction at CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF heterojunction interfaces with the strengthened H binding. Therefore, further introduction of a catalytically active phase (NiCo$_2$S$_4$) on the basis of the full play of the advantages of the precursor CDs/Ni$_3$S$_2$/NF can change the electronic structure of S in precursor, balance the absorption and desorption of H in catalytic process, and achieve higher electrochemical active area (Figure S11) and increases the fast charge transfer pathways (Figure S12).

■ CONCLUSIONS

To sum up, a noble-metal-free and self-standing CDs/ NiCo$_2$S$_4$/Ni$_3$S$_2$/NF electrode was constructed successfully by a facile hydrothermal treatment and subsequent ion exchange process. As a catalyst of water splitting, CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF shows excellent electrocatalytic performance compared to reported non-noble metal-free catalysts, and about 1.50 V can drive the overall water splitting with superior durability. The reason why CDs/NiCo$_2$S$_4$/Ni$_3$S$_2$/NF can have such superior electrocatalytic performance is that there are a great number of active sites, the synergy between carbon dots and transition metal sulfides, and the good conductivity of the substrate. In this work, cation exchange for heteroatom doping provides a new reliable method for developing transition metal sulfide electrocatalysts. Hence, the researchers in the fields of electrocatalysis, photocatalysis, energy storage and conversion, etc. also have interest in this work.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b05611.

SEM, TEM and HRTEM; XRD, Raman and XPS; cyclic voltammetry curves and EIS; comparison of water splitting performance (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*M. Wu. E-mail address: wumb@upc.edu.cn.

ORCID

Hui Liu: 0000-0001-7815-4200
Yuan Rao: 0000-0002-6770-6230
Mingbo Wu: 0000-0003-0048-778X

Notes

The authors declare no competing financial interest.

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■ REFERENCES


