Understanding the Role of Nanoscale Heterointerfaces in Core/Shell Structures for Water Splitting: Covalent Bonding Interaction Boosts the Activity of Binary Transition-Metal Sulfides

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ABSTRACT: The appropriate catalyst model with a precisely designed interface is highly desirable for revealing the real active site at the atomic level. Herein, we report a proof-of-concept strategy for creating an exposed and embedding interface model by constructing a unique Co$_9$S$_8$ core with a full WS$_2$ shell (Co$_9$S$_8$/FWS$_2$) and a half WS$_2$ shell (Co$_9$S$_8$/HWS$_2$) to uncover the synergistic effect of heterointerfaces on the catalytic performances. Tailoring the heteroepitaxial growth of WS$_2$ shell, Co$_9$S$_8$/HWS$_2$ with exposed Co–S–W interfaces leads to the exceptional electron density changes on edged-S atoms with large amounts of lone-pair electrons. Meanwhile, the unique Co$_9$S$_8$/HWS$_2$ could accelerate the kinetic adsorption of hydrogen- and oxygen-containing intermediates. Such Co$_9$S$_8$/HWS$_2$ electrocatalysts show extremely low overpotentials of 78 and 290 mV at a current density of 10 mA cm$^{-2}$ for hydrogen evolution reaction (HER) and oxygen evolution reaction, respectively. Using Co$_9$S$_8$/HWS$_2$ as both the cathode and anode, an alkali electrolyzer delivers a current density of 10 mA cm$^{-2}$ at a quite low cell voltage of 1.60 V. The results of both operando Raman spectroscopy and electron spin resonance indicate the presence of S–S terminal and S–S bridging with unsaturated S atoms during the HER process. The present work reveals the synergistic effects of nanoscale interfaces on overall electrocatalytic water splitting.

KEYWORDS: materials chemistry, electrospinning, core/shell structures, heterointerfaces, water splitting

1. INTRODUCTION

Electrocatalytic water splitting has been extensively investigated as a sustainable way of producing H$_2$ and O$_2$ for clean energy applications.$^1$ Advanced electrocatalysts are extremely significant to the half-cell reaction, which includes hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), by lowering the dynamic overpotentials.$^2$–$^4$ Several strategies have been presented for reducing the cost of catalysts, including dilution of Pt alloying and employing earth-abundant transition-metal alloys, dichalcogenides, carbides, phosphides, and nitrides.$^5$–$^6$ However, because of the sluggish electron transfer of HER and OER in alkaline conditions, the kinetic barrier of the elementary steps requires large overpotentials to accomplish the overall reaction.$^7$–$^9$ Therefore, developing novel structures of catalysts to boost both reactions is highly desirable.

Building novel heterostructures by combining the superiorities of HER-active materials with OER-active materials is a promising direction.$^{10}$ Recently, the rational design of the interfacial structure of heterogeneous catalysts is of great importance because it can facilitate chemisorption of reactants on the surface of the electrocatalyst, charge transfer, and reaction kinetic barriers, leading to the enhanced catalytic performance.$^{11}$–$^{13}$ Multicomponent heterostructures can not only comprise abundant interfaces but also assemble distinct building blocks into single entities, thus yielding exceptional electronic structures enabled by the synergistic components.$^{14}$–$^{15}$ However, identifying the real role of interfaces on synergistic effects is much less explored because of the difficulties in the synthesis of controlled interfaces.$^{16}$–$^{19}$ The synergistically designed interfaces in the reported literature studies usually evolve complex interactive contributions from both geometric and electronic effects, which are difficult to distinguish the real contribution of interfaces for enhancements in reaction activity. Therefore, understanding the activity–structure relationship of multicomponent electrocatalysts with nanoscale interfaces is vital for regulating the electrocatalytic activity, thus further facilitating the reasonable structural design of more efficient catalysts.$^{20}$–$^{22}$
Herein, we reported a proof-of-concept strategy for designing nanoscale heterointerfaces through the interfacial engineering in the core/shell structures of binary transition-metal sulﬁdes. The exposed Co−S−W interface in Co₉S₈/HWS₂ and the embedding Co−S−W interface in Co₉S₈/FWS₂ were synthesized by tailoring the heteroepitaxial growth of WS₂ shells on the inner Co₉S₈ cores, oﬀering a direct approach to uncover the synergistic eﬀect of heterointerfaces on the catalytic performances. Co₉S₈/FWS₂ exhibits that the embedding Co−S−W interfaces can only promote the charge transfers from Co to W atoms, suggesting a limited enhancement in the charge density on WS₂ surfaces. Co₉S₈/HWS₂ with exposed Co−S−W interfaces leads to the exceptional electron density changes on edged-S atoms with large amounts of lone-pair electrons, which is capable of providing electron pair to H⁺, thereby enhancing the catalytic performance of HER. Meanwhile, the unique Co₉S₈/HWS₂ makes both the Co₉S₈ and WS₂ phase expose directly to the electrolyte and could favor the kinetic adsorption of hydrogen-and oxygen-containing intermediates. Such Co₉S₈/HWS₂ electrocatalysts show extremely low overpotentials of 78 and 245 mV at 10 mA cm⁻² for HER and OER. Using Co₉S₈/HWS₂ as both the cathode and anode, an alkali electrolyzer can afford a current density of 10 mA cm⁻² at a quite cell voltage of 1.60 V. The results of both operando Raman spectroscopy and electron spin resonance (ESR) indicate the presence of S−S terminal and S−S bridging with unsaturated S atoms during the HER process. The present work reveals the synergistic eﬀects of nanoscale interfaces on overall water splitting through the interfacial engineering in binary transition-metal sulﬁdes.

2. RESULTS AND DISCUSSION

The mechanism on interfacial synergistic catalysis for core/shell catalysts is very important in water splitting processes. The modulation of interactions at interfaces imposes a substantial inﬂuence on the activity and selectivity of HER and OER, as a result of the geometric/electronic structure of the interfacial sites. In order to reveal the synergistic eﬀect of heterointerfaces on the catalytic performance of water splitting, we designed two diﬀerent nanointerfaces by constructing a unique Co₉S₈ core with a full WS₂ shell (Co₉S₈/FWS₂) and a half WS₂ shell (Co₉S₈/HWS₂). As shown in Figure 1a, Co₉S₈/FWS₂ exhibits embedding Co−S−W interfaces between the core and shell. Through the density functional theory (DFT) models, the embedding Co−S−W interfaces cannot directly contact with the electrolyte. Focusing on the Co₉S₈/HWS₂ model, all of the WS₂, Co₉S₈, and the Co−S−W can directly involve in the reactions. To synthesize the core/shell Co₉S₈/WS₂ structures with diﬀerent interfaces, we ﬁrst used the electrospinning technology to produce the polyacrylonitrile (PAN) nanoﬁbers containing a certain amount of Co and W precursors. Then, after the graphitization process under Ar and S vapor atmosphere at diﬀerent conditions, the former Co/W/PAN nanoﬁbers were converted into Co₉S₈/WS₂/carbon nanoﬁber (CNF) structures. Figures S1 and S2 indicate ﬁeld emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) images of Co₉S₈/FWS₂ and Co₉S₈/HWS₂ nanocrystals. These core/shell nanoparticles were densely and uniformly supported on CNFs, and the CNFs possess abundant porous structure and three-diensional networks, which can facilitate the flow of electrolytes as

Figure 1. (a) Computational model of Co₉S₈/FWS₂ and Co₉S₈/HWS₂ core/shell, and the solvent eﬀect is considered with explicit water molecules. (b) XRD patterns of WS₂/CNFs, Co₉S₈/CNFs, Co₉S₈/FWS₂/CNFs, and Co₉S₈/HWS₂/CNFs. FE-SEM and TEM images of the (c,e) Co₉S₈/FWS₂ and (d,f) Co₉S₈/HWS₂ nanocrystals. (g) HRTEM image of a single Co₉S₈/FWS₂ nanocrystal. The FFT and HRTEM images of the (h,i) WS₂ shell and (j,k) Co₉S₈ core in Co₉S₈/FWS₂. (l) HRTEM image of a single Co₉S₈/HWS₂ nanocrystal. The FFT images of the (m) WS₂ shell and (n) Co₉S₈ core in Co₉S₈/HWS₂. (o,p) HRTEM images of the bent WS₂ shell at the vertex cites.
In Co$_9$S$_8$/HWS$_2$ with a semishell, the (002) cubic phase of Co$_9$S$_8$ in the full core/shell structures (Figure S3 and S4). In Co$_9$S$_8$/HWS$_2$ with a semishell, the (002$^*$) plane peak of WS$_2$ becomes strong and sharp in comparison with that of Co$_9$S$_8$/FWS$_2$. Co$_9$S$_8$ core was hetero-embedded in fullerene-like WS$_2$ shells with several layers, forming the Co$_9$S$_8$-WS$_2$ nanointerfaces. As shown in Figure 1o,p, WS$_2$ nanointerfaces, the well distribution of Co, W, and S elements. Interestingly, the W signals only exist in partial WS$_2$ shells, and the overlap strongly demonstrates that Co$_9$S$_8$ is only coated with a semi-WS$_2$ shell, forming the Co$_9$S$_8$/HWS$_2$ structures. The line scan STEM–EDS images of Co$_9$S$_8$/FWS$_2$ and Co$_9$S$_8$/HWS$_2$ are further investigated and shown in Figure 2f. The W elements in the Co$_9$S$_8$/FWS$_2$ structures are distributed throughout the whole line spectra; however, the Co$_9$S$_8$/HWS$_2$ structures only exhibit a partial distribution of W elements, suggesting that Co$_9$S$_8$ is only coated by a semi-WS$_2$ shell. The density of states (DOS) for Co$_9$S$_8$/FWS$_2$ and Co$_9$S$_8$/HWS$_2$ nanocrystals. (g) DOS of the S 3p of Co$_9$S$_8$/FWS$_2$/CNF and Co$_9$S$_8$/HWS$_2$/CNF model of nanocrystals.

The high-magnification FE-SEM images shown in Figure 1c,e indicate that both the Co$_9$S$_8$/FWS$_2$ and Co$_9$S$_8$/HWS$_2$ nanocrystals exhibit a polyhedral morphology. From Figure 1d, it can be seen that the inner Co$_9$S$_8$ core was completely encapsulated in fullerene-like WS$_2$ shells with several layers, forming the Co$_9$S$_8$/FWS$_2$ core/shell structures. In contrast (Figure 1f), for Co$_9$S$_8$/HWS$_2$, the Co$_9$S$_8$ core was hetero-epitaxially bonded by a partial WS$_2$ shell, exhibiting exposed WS$_2$, Co$_9$S$_8$, and Co–S–W nanointerfaces. As shown in Figure 1g, two different crystal phases were observed at the embedding Co–S–W nanointerfaces, corresponding to the cubic Co$_9$S$_8$ and 2H-WS$_2$ of Co$_9$S$_8$/FWS$_2$. Co$_9$S$_8$ displays a distinguished lattice fringe with a space of 3.0 Å, corresponding to the (311) plane of the cubic Co$_9$S$_8$ phase. The outer WS$_2$ shell exhibits the well-defined lattice fringe with an inter-lamellar spacing of 6.5 Å. The fast Fourier transform (FFT) images of Co$_9$S$_8$/FWS$_2$ exhibit two different diffraction spots, confirming the formation of the 2H phase of WS$_2$ and the cubic phase of Co$_9$S$_8$ in the full core/shell structures (Figure 1h,i). As shown in Figure 1j,k, at the Co–S–W interfaces, the Co$_9$S$_8$ and WS$_2$ shells display well-defined crystal structures without any defects.

For Co$_9$S$_8$/HWS$_2$, as shown in Figure 1l, the Co–S–W nanointerfaces formed through the sulfur atoms bridging Co and W atoms and the WS$_2$ shells exhibit the visible (002) plane with an interlamellar spacing of 6.5 Å. The Co$_9$S$_8$ core was partially exposed as well as the Co–S–W interfaces. Larger amount of unsaturated S atoms were formed throughout the whole exposed Co–S–W nanointerfaces, and these unsaturated S atoms possess abundant lone-pair electrons, leading to the changes of local electronic structures, which benefit the adsorption of protons. The FFT images of Co$_9$S$_8$/HWS$_2$ exhibit two different diffraction spots, confirming the formation of the 2H phase of WS$_2$ and the cubic phase of Co$_9$S$_8$ in the semicore/shell structures (Figure 1m,n). At the side of the exposed WS$_2$ shells, as shown in Figure 1o,p, WS$_2$ displays a curving morphology and an enlarged interlamellar spacing (7.4 Å) of the (002) plane than the bulk WS$_2$, indicating the existence of many defect sites in the semicore/shell structures.

The high-angle annular dark-field scanning TEM (HAADF-STEM) and STEM energy-dispersive spectroscopy (EDS) mapping images of Co$_9$S$_8$/FWS$_2$ are shown in Figure 2a,b. The Co, W, and S signals exhibit the octahedral morphologies, and the overlap demonstrates that the Co signals are completely encapsulated in the W and S signals. Focusing on Co$_9$S$_8$/HWS$_2$ (Figure 2c,d), both the HAADF-STEM and the STEM–EDS images confirm the well distribution of Co, W, and S elements. Interestingly, the W signals only exist in partial shells, and the overlap strongly demonstrates that Co$_9$S$_8$ is only coated with a semi-WS$_2$ shell, forming the Co$_9$S$_8$/HWS$_2$ structures. The line scan STEM–EDS spectra of Co$_9$S$_8$/FWS$_2$ and Co$_9$S$_8$/HWS$_2$/HWS$_2$ are further investigated and shown in Figure 2f. The W elements in the Co$_9$S$_8$/FWS$_2$ structures are distributed throughout the whole line spectra; however, the Co$_9$S$_8$/HWS$_2$ structures only exhibit a partial distribution of W elements, suggesting that Co$_9$S$_8$ is only coated by a semi-WS$_2$ shell. The density of states (DOS) for Co$_9$S$_8$/FWS$_2$ and Co$_9$S$_8$/HWS$_2$ is theoretically analyzed by DFT calculations. The semicore/shell structure has distinguished electronic structures as compared with the core/shell structure around...
the Fermi level, indicating different physical–chemical behaviors. Particularly, the significant peaks in the distribution of the DOS for Co9S8/HWS2 confirm that the Co9S8/HWS2 structure is more active than the Co9S8/FWS2 structure (Figure 2g). This is mainly due to the fact that the enhanced electron density at exposed Co–S–W nanointerfaces largely promoted the activity for HER.

Raman spectroscopy is further performed to confirm the varying phases and chemical–physical environment (Figure 3a). Compared with the individual WS2 nanoplates (0.52), Co9S8/FWS2 and Co9S8/FWS2 present higher E2g/A1g values of 1.32 and 1.17, suggesting the few-layer nature of the outer WS2 shell.20 In addition to the intensity variations, the E2g mode peaks exhibit blue shifts of ~6.2 and 3.4 cm−1 for Co9S8/FWS2 and Co9S8/FWS2, respectively, and broaden when compared with pure WS2. This behavior can be attributed to the localized strain and disorder in the core/shell structure with two different lattice constants. Interestingly, a new peak emerges at 127.1 cm−1 in the lower-frequency regions, indicating the presence of a metallic-type WS2 phase because of the formation of Co9S8/HWS2 with distinct electronic structures.21 For all the samples, the D-band related to defects and the G band associated with the vibration of sp2 graphitic crystallites in the CNFs are observed around 1339 and 1593 cm−1, respectively.

To further acquire the element composition and the surface bonding state of Co9S8/FWS2 and Co9S8/HWS2, X-ray photoelectron spectroscopy (XPS) is performed. Pure Co9S8/CNFs and WS2/CNFs are used as control. Figure 3b shows the high-resolution Co 2p XPS region for Co9S8/CNFs, Co9S8/FWS2, and Co9S8/HWS2. The individual Co9S8/CNF exhibits two chemical states of Co3+ and Co2+ ions with binding energies (BEs) of 778.4, 793.6, 781.8, and 798.0 eV, corresponding to Co 2p3/2 and Co 2p1/2, respectively.22 Focusing on Co9S8/FWS2 and Co9S8/HWS2 because of the heteroepitaxial growth of WS2 on Co9S8 surfaces, the BEs for both Co3+ and Co2+ exhibit red shifts ranging from 778.4 to 780.6 eV and from 781.8 to 782.5 eV, respectively, suggesting that the strong electron transfers from Co to W atoms through the construction of Co–S–W nanointerfaces. The peaks at 785.8 and 803.1 eV are the shakeup satellite peaks for all the three samples.

The W 4f and S 2p XPS spectra are shown in Figure 3c,d. Two predominant peaks of W 4f7/2 and W 4f5/2 emerged at 32.7 and 34.8 eV can be observed in the WS2/CNF sample, indicating the 2H phase nature of WS2.23 For Co9S8/FWS2/CNFs, there is a new pair of peaks at 35.8 and 37.8 eV observed besides the doublet peaks for 2H-WS2 located at 32.4 and 34.8 eV. The emerged peaks are attributed to the new chemical states of W incorporated with the Co9S8 at the Co–S–W nanointerfaces. For Co9S8/HWS2/CNFs, both the W 4f peaks for WS2 and Co–S–W display significant blue shifts of about 0.8 and 1.2 eV in comparison with Co9S8/FWS2/CNFs. The relative higher BEs for Co–S–W peaks suggest a strong electronic cloud density because of the unique structure of Co9S8/HWS2 with abundant lone-pair electrons. It demonstrates that the electronic interactions between Co9S8 and WS2 result in the charge redistribution on their interfaces.

Meanwhile, the S 2p XPS spectra of both Co9S8/FWS2 and Co9S8/HWS2 exhibit coincident BEs of 163.6, 161.3 eV (2p3/2) and 165.3, 162.8 eV (2p1/2) for bridging S2− (Figure 3d), implying the unsaturated S atoms on Co–S and W–S sites.24 The interfacial engineering in Co9S8/HWS2 induces significant blue shifts in S 2p peaks to lower BEs in comparison with Co9S8/FWS2, suggesting a strong charge density on the exposed Co–S–W sites. The two pairs of peaks at 168.2, 169.5 and 166.7, 167.5 eV are associated with the C–S and S=O groups, indicating that the surfaces of CNFs were doped with S atoms during the S vapor process. The DOS, Raman, and XPS results indicate that the formation of Co–S–W could lead to the enhanced electron density on WS2 surfaces. However, the embedding nanointerfaces in Co9S8/FWS2/CNFs only make a small influence on the electron density. For the exposed Co–S–W interfaces with partial WS2 and Co9S8 in Co9S8/HWS2/CNFs, the electron density deeply increases on the exposed interface corresponding to the S–Co covalent bonding.
The side-exposed WS\textsubscript{2} possesses larger amounts of lone-pair electrons at the Co\textsuperscript{−}S\textsuperscript{−}W nanointerfaces, which is capable of providing electron pair to H\textsuperscript{+}. The electrochemical activities of Co\textsubscript{9}S\textsubscript{8}/FWS\textsubscript{2}/CNFs, Co\textsubscript{9}S\textsubscript{8}/HWS\textsubscript{2}/CNFs, and commercial Pt/C are evaluated in both 0.5 M sulfuric acid and 1.0 M potassium hydroxide solution in a traditional three-electrode cell, in which the as-prepared catalyst membranes with dimensions of 0.5 cm \times 0.5 cm were directly used as the working electrode (WE). The individual WS\textsubscript{2}/CNFs and Co\textsubscript{9}S\textsubscript{8}/CNFs were used as control. The linear sweep voltammetry (LSV) curves (Figure 4a) indicate that Co\textsubscript{9}S\textsubscript{8}/HWS\textsubscript{2}/CNFs exhibits a low overpotential of 83 mV (10 mA cm\textsuperscript{−2}) in 0.5 M H\textsubscript{2}SO\textsubscript{4}, which is significantly smaller than the 116 mV of Co\textsubscript{9}S\textsubscript{8}/FWS\textsubscript{2}/CNFs, 163 mV of Co\textsubscript{9}S\textsubscript{8}/CNFs, and 249 mV of WS\textsubscript{2}/CNFs. The commercial Pt/C catalyst shows a smaller overpotential of only 52 mV at 10 mA cm\textsuperscript{−2}. In addition, with the increased current density, the discrepancy between Pt/C and Co\textsubscript{9}S\textsubscript{8}/HWS\textsubscript{2}/CNFs is reduced gradually. Importantly, the current density of Co\textsubscript{9}S\textsubscript{8}/HWS\textsubscript{2}/CNFs reached 100 mA cm\textsuperscript{−2} with an overpotential of only 235 mV, which is much lower than the 376 mV of FCo\textsubscript{9}S\textsubscript{8}/WS\textsubscript{2}/CNFs. The obvious improvement in HER activity was benefited from the designed exposed nanointerfaces and the synergy between WS\textsubscript{2} and Co\textsubscript{9}S\textsubscript{8}.

In an alkaline environment (1 M KOH), the LSV curves (Figure 4b) indicate the overpotentials of 87 and 203 mV (10 mA cm\textsuperscript{−2}) for Co\textsubscript{9}S\textsubscript{8}/HWS\textsubscript{2}/CNFs and Co\textsubscript{9}S\textsubscript{8}/FWS\textsubscript{2}/CNFs, which are slightly lower than that in acidic solution. The Co\textsubscript{9}S\textsubscript{8}/HWS\textsubscript{2}/CNFs exhibited a low overpotential of 87 mV, which is close to that in acidic conditions (83 mV). The perturbations of current density for HER in both acidic and alkaline conditions are attributed to the release of large amounts of formed H\textsubscript{2} bubbles that are produced at higher overpotentials. It should be noted that so far, there have been only a few of electrocatalysts active in both acidic and alkaline medium because of the incompatible activity of the same catalysts that operate in the same pH region.\textsuperscript{10,25,26} The Co\textsubscript{9}S\textsubscript{8}/hWS\textsubscript{2} structures exhibit the abundant unsaturated S atoms at the Co\textsuperscript{−}S\textsuperscript{−}W nanointerfaces and the unsaturated S atoms possess larger amounts of lone-pair electrons, making them capable of providing an electron pair to H\textsuperscript{+}, thereby promoting the absorption energy of H atoms on Co\textsubscript{9}S\textsubscript{8}/HWS\textsubscript{2}.

The OER performance of the as-prepared catalysts is investigated in a 1 M O\textsubscript{2}-saturated KOH electrolyte (Figure 4c). The Co\textsubscript{9}S\textsubscript{8}/HWS\textsubscript{2}/CNFs only requires a low overpotential of 290 mV (10 mA cm\textsuperscript{−2}), which outperformed Co\textsubscript{9}S\textsubscript{8}/FWS\textsubscript{2}/CNFs (342 mV), Co\textsubscript{9}S\textsubscript{8}/CNFs (371 mV), WS\textsubscript{2}/CNFs (502 mV), and commercial IrO\textsubscript{2}/C (320 mV). The overpotentials and corresponding results are summarized in Figure 4d and Figure S7. The OER performance of the as-prepared catalysts is investigated in a 1 M O\textsubscript{2}-saturated KOH electrolyte (Figure 4c). The Co\textsubscript{9}S\textsubscript{8}/HWS\textsubscript{2}/CNFs only requires a low overpotential of 290 mV (10 mA cm\textsuperscript{−2}), which outperformed Co\textsubscript{9}S\textsubscript{8}/FWS\textsubscript{2}/CNFs (342 mV), Co\textsubscript{9}S\textsubscript{8}/CNFs (371 mV), WS\textsubscript{2}/CNFs (502 mV), and commercial IrO\textsubscript{2}/C (320 mV). The overpotentials and corresponding results are summarized in Figure 4d and
Table 1. Comparison of HER Activity Data Among Various Catalysts

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<th>OER $\eta$ [mV] at $j = 10$ mA cm$^{-2}$ (pH = 14)</th>
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Figure 5. (a) LSV curves of Co$_9$S$_8$/HWS$_2$/CNFs and all noble metal IrO$_2$/ClPt/C electrocatalysts in 1 M KOH with a scan rate of 5 mV s$^{-1}$. (b) Chronoamperometric curves of the Co$_9$S$_8$/HWS$_2$/CNFs/Co$_9$S$_8$/HWS$_2$/CNF couple under a static voltage of 1.60 V for 10 h. (c) LSV curves for the Co$_9$S$_8$/HWS$_2$/CNFs/Co$_9$S$_8$/HWS$_2$/CNF couple before and after the 10 h time-dependent testing. The final steps of H$_2$ formations on the surfaces of (d) Co$_9$S$_8$/FWS$_2$/CNFs with one-layer WS$_2$, (e) Co$_9$S$_8$/FWS$_2$/CNFs with two-layer WS$_2$, and (f) Co$_9$S$_8$/HWS$_2$/CNFs with one-layer WS$_2$. (g–i) Electron density differences among the catalysts, where red represents the electron density increase and green represents the electron density depletion. (j) Reaction energy diagrams of the different catalysts during the HER process. (k) S 3p band center of 3-CN and 2-CN S atoms. (l) Electrostatic potential of 3-CN and 2-CN S atoms.

Table 1. Figures 4e and S8–S10 show the corresponding Tafel slopes of as-prepared catalysts in both acidic and alkaline conditions for HER and OER. The Co$_9$S$_8$/HWS$_2$/CNF exhibits lower Tafel slopes of 56 and 72 mV dec$^{-1}$ in 0.5 M H$_2$SO$_4$ and 1 M KOH, respectively, which is closer to the commercial Pt/C (38 and 45 mV dec$^{-1}$). It is indicated that the HER over Co$_9$S$_8$/HWS$_2$/CNFs followed a Volmer–Heyrovsky mechanism in both acidic and alkaline conditions, and electrochemical desorption is the rate-limiting step. For OER, the Co$_9$S$_8$/HWS$_2$/CNFs also obtained the lowest Tafel slope of 68 mV dec$^{-1}$, which is smaller than that of IrO$_2$ (78 mV dec$^{-1}$). In this work, the excellent HER and OER activity of Co$_9$S$_8$/HWS$_2$/CNFs in both acidic and alkaline medium can be attributed to the increased electron density on the interface between WS$_2$ and Co$_9$S$_8$ corresponding to the S–Co covalent bonding interaction. In comparison with the reported noble-metal-free electrocatalysts, the activity of Co$_9$S$_8$/HWS$_2$/CNFs is better than those of hollow Co$_9$S$_8$@MoS$_2$ heterostructures (210 mV), cobalt-doped Mo$_3$C nanowires (121 mV), hierarchical β-Mo$_3$C nanotubes (172 mV), Ni$_2$P$_4$ nanoparticles (141 mV), and MoS$_2$/Ni$_3$S$_2$ heterostructures (110 mV). The turnover frequency (TOF) is the number of H$_2$ or O$_2$ molecules evolved each second at a specific overpotential, which is utilized to calibrate the intrinsic activity of the electrocatalysts. According to eq S1, the TOFs of different samples are presented against the potentials in Figures S11–S13. Impressively, the TOF values of Co$_9$S$_8$/HWS$_2$/CNFs are larger than those of Co$_9$S$_8$/FWS$_2$/CNFs, Co$_9$S$_8$/CNFs, and WS$_2$/CNFs, revealing that the strong electron transfer via the Co$_9$S$_8$–WS$_2$ nanointerface could indeed improve the HER and OER activity. The Nyquist plots of Co$_9$S$_8$/HWS$_2$/CNFs exhibited the lowest charge-transfer resistance (Figure 4f). The electrochemical surface area (ECSA) is another important factor that affects the activity of electrocatalysts, and it was determined by measuring the double-layer capacitance ($C_{dl}$) at different scan rates. As shown.

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in Figure 4g and Table 1, the CoS$_8$/HWS$_2$/CNFs indicate the highest $C_d$ and ECSA values (123.1 mF cm$^{-2}$, 73.2 cm$^2$) than those of CoS$_8$/CNFs (35.6 mF cm$^{-2}$, 23.7 cm$^2$), WS$_2$/CNFs (17.4 mF cm$^{-2}$, 9.5 cm$^2$), and Co$_9$S$_8$/FWS$_2$/CNFs (82.6 mF cm$^{-2}$, 42.4 cm$^2$).

The stability of the electrocatalyst is an essential parameter for practical operation. The long-term stability of CoS$_8$/HWS$_2$/CNFs for HER and OER in alkaline conditions was investigated by chronopotentiometric curves. As shown in Figure 4h, the CoS$_8$/HWS$_2$/CNFs electrodes indicated a stable current density of around 100 mA cm$^{-2}$ without significant fluctuations for 10 h under overpotentials of 375 and 410 mV in alkaline solutions, respectively. In fact, the CNF hosts could improve the electrochemical stability and resistance against oxidation, while the integrated porous membrane structure (binder-free) and confinement effect help endow CoS$_8$/HWS$_2$ with excellent stability. After continuous OER tests at 100 mA cm$^{-2}$ for 10 h, the postcharacterizations are performed to confirm the unique semicore/shell structure. As shown in Figures S14 and S15, the STEM mapping and XPS of S 2p show that the Co$_9$S$_8$–WS$_2$ core/shell structure and the Co–W–S nanostructure still exist stably. Figure 4i schematically illustrates the feasible HER mechanism on heterostructures of CoS$_8$/HWS$_2$/CNFs. The heterostructures with exposed Co–W–S interfaces and abundant unsaturated S atoms imply a high electron density that is capable of providing electron pair to H$^+$. The unique nanostructures reduce the kinetic energy barrier of the initial water dissociation process (the Volmer step), thereby enhancing HER performance. For OER, the CoS$_8$/HWS$_2$ structures exhibit exposed WS$_2$, Co$_9$S$_8$, and Co–W–S nanointerfaces, providing more directly contact surfaces with the electrolyte. These advantages could adjust the absorption of the OH groups, leading to the reduction in the Gibbs free energies of intermediates and thus further enhancing the OER activity.

The CoS$_8$/HWS$_2$/CNFs heterostructures are used as a bifunctional electrocatalyst for overall water splitting in a two-electrode setup in 1 M KOH solution (Figure S16). As shown in Figure 5a, the CoS$_8$/HWS$_2$/CNFs can reach a current density of 10 mA cm$^{-2}$ at an applied potential of 1.60 V, which is better than that of the IrO$_2$/C and Pt/C electrocatalysts (1.66 mV@10 mA cm$^{-2}$). The combined overpotential is about 360 mV for the electrochemical overall water splitting. The overall water splitting activity of the CoS$_8$/HWS$_2$/CNF heterostructures is much higher than the recently reported electrocatalysts, such as porous NiFe-oxide nanocubes (1.67 V), NiFe-LDH (1.7 V), S–NiFe$_2$O$_4$ (1.65 V), CoP mesoporous nanorods (1.62 V), NiSe nanowires (1.63 V), and Ni$_3$P nanoparticles (1.63 V). Over a 10 h continuous electrolysis at 10 mA cm$^{-2}$, the CoS$_8$/HWS$_2$/CNFs heterostructures show a very stable current density with negligible degradation, indicating the good stability for overall water splitting (Figure 5b). Because of the bubble accumulation and release process of H$_2$ and O$_2$ from the surface of the electrode, the chronoamperometric curve of CoS$_8$/HWS$_2$/CNFs presents serrate-like current density. The bubble release induces the increase in current density, and the recovery suggests the high activity and stability of the CoS$_8$/HWS$_2$/CNFs as bifunctional catalysts for overall water splitting. The LSV curves before and after 10 h of overall water splitting exhibit small differences. The inset in Figure 5c is the photograph of the CoS$_8$/HWS$_2$/CNF electrodes for overall water splitting showing vigorous H$_2$ and O$_2$ production on CoS$_8$/HWS$_2$/CNF electrodes in alkaline solutions.

Seeking for theoretical interpretation and prediction at the atomic level using a quantum-chemical method has become prevailing for better understanding of the science and inherent mechanism of electrocatalysis. We have synthesized two catalyst models with a precisely designed interface and used DFT to reveal the real active site at the atomic level in core/shell structures for water splitting. The Co$_9$S$_8$/FWS$_2$ model (Figure 5d) displays embedding Co–S–W interfaces between the core and shell, which cannot directly access with the electrolyte. Therefore, the embedding Co–S–W interfaces can only promote the charge transfers from Co to W atoms and then slightly improve the charge density of the WS$_2$ surfaces. CoS$_8$/HWS$_2$ with exposed WS$_2$, Co$_9$S$_8$, and Co–S–W interfaces provides more active surface area for the electrolyte. The unique structures not only promote the electron charge transfers from Co to W atoms but also lead to exceptional electron density changes on edged-S atoms with large amounts of lone-pair electrons. For OER, the advantages of CoS$_8$/HWS$_2$ structures with exposed WS$_2$, Co$_9$S$_8$, and Co–W–S nanointerfaces could adjust the absorption of the OH groups, leading to the reduction in the Gibs free energies of intermediates and thus further enhancing the OER activity. The core/shell chemical models of CoS$_8$/FWS$_2$/CNFs with one-layer WS$_2$ (denoted as 1-layer), CoS$_8$/FWS$_2$/CNFs with two-layer WS$_2$ (denoted as 2-layer), and Co$_9$S$_8$/HWS$_2$/CNFs with one-layer WS$_2$ (denoted as edged layer) are shown in Figure 5d–g, in which the final structures of H$_2$ formations are listed. Herein, the AIMD simulation and static computation based on scientific and proper chemical models were carried out for our architectural core/shell electrocatalyst for HER.

The solution environment was constructed and simulated using H$_2$O molecules surrounding the core/shell models of the electrode and further equilibrating at 298 K in 8 ps using the AIMD method. Furthermore, hydronium ions (H$_3$O$^+$) were added to the solution and optimized to construct the electric double layers, thereby the HER mechanism in eqs 1–3 is investigated.

$$\text{H}_2\text{O}^+ + e^- + * = \text{H}_2\text{O} + *\text{H} \quad (1)$$

$$\text{H}_2\text{O}^+ + e^- + *\text{H} = \text{H}_2 \uparrow \quad \text{Volumer–Heyrovsky} \quad (2)$$

$$*\text{H} + *\text{H} = \text{H}_2 \uparrow \quad \text{Volumer–Tafel} \quad (3)$$

The chemical models for engineering the basal plane of WS$_2$ on CoS$_8$ surfaces by introducing the lone-pair electron are illustrated in Figure 5d–f. The electronic structure and charge density are controlled by increasing the amounts of lone-pair electrons at Co–S–W nano interfaces in the semicore/shell structure, making them capable of providing an electron pair to H$^+$, thereby enhancing the HER performance. We first used quantum-chemical computation (see Experimental section) to evaluate the influence of enhanced electron density at Co–S–W nano interfaces on HER activity. The theoretical results indicated that the electron density only significantly increases on the exposed Co–S–W interfaces between WS$_2$ and Co$_9$S$_8$ corresponding to the S–Co coordinate bonding interaction. As shown in Figure 5g,h, for the CoS$_8$/FWS$_2$/core/shell with monolayer and bilayer WS$_2$ shells, no electron density changes and charge polarization on the top surface of WS$_2$ (Figure 5g,h) indicate that the numbers of WS$_2$ layers have little
influence on charge polarization and the charge transfer between the core and high layers (layer number > 3). For Co₉S₈/HWS₂ semicore/shell structures with exposed Co−S−W nanointerfaces, exceptional electron density changes on edged-S atoms with two CNs have been observed (Figure 5i).

From the energy profile (Figure 5j) of HER on all three core/shell structures, we conclude that the HER on 1-layer and 2-layer structures has similar reaction energy paths for reaction barriers except that the former is slightly more exothermic than the latter at the final H₂ formation step. Here, we also determined that the Volmer−Heyrovsky mechanism is more energetically favorable than the Volmer−Tafel one. We further inspected the reaction energy path of HER of the semicore/shell model with an edged layer. Relatively, a significant energy dropping by ~50% implies that the HER performance of Co₉S₈/HWS₂ has been strongly enhanced.

The exposed semicore/shell combines the advantages of enhanced electron density originated from the Co−S−W nanointerfaces and the amounts of lone-pair electrons of exposed S active sites. The p-band center of S atoms in the WS₂ layer for both full and semicore/shell layer models is investigated (Figure S17), and the semicore/shell with exposed interfaces is higher than the full core/shell by 0.32 eV, implying a high electron density on the semicore/shell catalyst (Figure 5k). The DOS of S 3s/p shell computed in Figure S18 with S 3s state in very low energy level is less than −13 eV. We propose that the S 3s state will not take part in the chemical bonding interaction between H and S atoms according to the frontier orbital theory. Therefore, no hybridization orbitals formed between the S 3p and S 3s. Considering a divalent S in the form of S²⁻, the 3-CN S atoms (perfect layer) have no lone-pair electrons, while the 2-CN S atom (edged layer) has a lone-pair electron (Figure 5h), making it capable of providing an electron pair to H⁺, thereby enhancing the HER performance. Meanwhile, the electrostatic potential depicted in Figure 5i shows the difference between edged 2-CN and perfect 3-CN S atoms. The DFT results demonstrate the promising HER catalyst based on a novel heterostructure with lone-pair electrons by an interface engineering strategy.

Because of the unique heterostructure of Co₉S₈/HWS₂, the exposure of WS₂, Co₉S₈, and Co−S−W nanointerfaces leads to the exceptionally enhanced electron density originated from the Co−S−W nanointerfaces and the amounts of lone-pair electrons of exposed S active sites. We use operando Raman spectroscopy to unravel the structural changes of catalysts during the HER process. The operando Raman spectra of Co₉S₈/HWS₂/CNF catalysts during HER are shown in Figure 6a,b. The Co₉S₈/HWS₂/CNFs exhibit the distinct characteristic Raman peaks at 348 and 414 cm⁻¹, assigned to ν(Mo−S) coupled and ν(Sapical−Mo) vibrations, respectively. The Raman spectra were collected simultaneously, while its CV was measured in 1 M KOH electrolyte. With the changes in the potentials ranged from 0.30 to ~0.25 V, the Raman peaks exhibit blue shifts of ~10 cm⁻¹ for Co₉S₈/HWS₂, suggesting the presence of hydrogen adsorbates on Mo surfaces. The operando Raman spectra of Co₉S₈/HWS₂/CNF electrode
collected at different reaction times during the electrochemical HER at −0.2 V versus RHE in 1 M KOH are shown in Figure 6b. The intensity of Raman peak for $\nu$ (Mo–S)_{ramp} vibrations (330 cm$^{-1}$) becomes stronger than that for the $\nu$ (S_{unalg}–Mo) vibrations (416 cm$^{-1}$) with the increased operation time from 0 to 30 min. The results indicate that more S–S terminal and S–S bridging sites with unsaturated S atoms were generated during the HER process. The ESR spectra in Figure 6c indicates that the Co$_9$S$_8$/HWS$_2$/CNFs display the S vacancy structures, and the S signal is ascribed to the contribution from the Mo–S dangling bonding. The exposed Co–S–W nanostructures are mainly exposed and vacancy sites, which could be active sites for the HER.

The morphology of Co$_9$S$_8$/HWS$_2$/CNFs after the chronocoulometry test for overall water splitting is shown in Figures 6d–f and S19. The high-resolution TEM (HRTEM) image of the Co$_9$S$_8$/HWS$_2$/CNFs (Figure 6d,e) still exhibit the unique semicore/shell structures with distinct exposed WS$_2$ shell, Co$_9$S$_8$ core, and Co–S–W nanointerfaces. The STEM–EDS mapping images (Figure 6f,g) confirm the uniform distribution of Co, S, and W elements, matching well with the semicore/shell structures. The results strongly suggested the good durability and structural robustness. We further obtained the XPS spectra of Co$_9$S$_8$/HWS$_2$/CNFs before and after stability test in acid (Co$_9$S$_8$/HWS$_2$/CNFs-A) and alkaline solution (Co$_9$S$_8$/HWS$_2$/CNFs-B). The XPS spectra are shown in Figure 6h–j. For the Co$_9$S$_8$/HWS$_2$/CNFs, the BEs for main Co$^{3+}$ and Co$^{2+}$ peaks shifted from 780.6, 782.5 to 780.9, 782.7 eV (Co$_9$S$_8$/HWS$_2$/CNFs-A) and 781.8, 783.7 eV (Co$_9$S$_8$/HWS$_2$/CNFs-B). The BEs for the main W 4f peaks of Co$_9$S$_8$/HWS$_2$/CNFs moved from 35.8, 37.7 to 36.3, 38.3 eV (Co$_9$S$_8$/HWS$_2$/CNFs-A) and 35.8, 37.7 eV (Co$_9$S$_8$/HWS$_2$/CNFs-B) (Figure 6h). The shift in the BEs of Co 2p and W 4f XPS spectra for the Co$_9$S$_8$/HWS$_2$/CNFs before and after stability test indicated the strong electron transfers between the Co and W atoms during the continuous electrolysis process (Figure 6i). Focusing on the S 2p XPS spectra, when compared with the SCo$_9$S$_8$/WS$_2$/CNFs, the BEs for bridging S$_{2\text{ff}}$ belong to the unsaturated S atoms on the Co–S and W–S sites, indicating significant shifts from 161.3, 162.8 to 163.2, 165.2 eV (Co$_9$S$_8$/WS$_2$/HCNFs-A) and 163.4, 165.0 eV (Co$_9$S$_8$/WS$_2$/HCNFs-B), suggesting a strong charge density on the exposed Co–S–W sites during the continuous electrolysis (Figure 6j).

Even through the continuous electrolysis at high density, no oxidation states emerged in the Co, W, and S XPS spectra, and the XPS results demonstrated the transition-metal sulfide states. The XPS and DFT results both demonstrated the strong electron transfers among the Co, W, and S atoms during the continuous electrolysis. More importantly, the semicore/shell structures with abundant unsaturated S atoms enhanced the electron density at Co–S–W nanostructures, thus largely promoting the activity of water splitting. The present work creates exposed and embedding interface model to uncover the synergistic effect of heterointerfaces on the catalytic performances of water splitting.

3. CONCLUSIONS

In summary, we have designed two nanointerface models with exposed and embedding Co–S–W interfaces by constructing a unique Co$_9$S$_8$ core with full and half WS$_2$ shells to uncover the interfacial synergistic effects and real active sites at the atomic level. Such Co$_9$S$_8$/HWS$_2$ electrocatalysts show low overpotentials of 78 and 245 mV at 10 mA cm$^{-2}$ for HER and OER. Using Co$_9$S$_8$/HWS$_2$ as both the cathode and anode, an alkaline electrolyzer can afford a current density of 10 mA cm$^{-2}$ at a quite low cell voltage of ca. 1.60 V. According to the DFT calculations, Co$_9$S$_8$/HWS$_2$ with exposed Co–S–W interfaces leads to the exceptional electron density changes on edge-S atoms with large amounts of lone-pair electrons, which is capable of providing electron pair to H$_2$, thereby enhancing the catalytic performance of HER. Meanwhile, the unique Co$_9$S$_8$/HWS$_2$ made the Co$_9$S$_8$ and WS$_2$ phase both exposed directly with the electrolyte and could accelerate the kinetic adsorption of hydrogen and oxygen-containing intermediates. The results of both operando Raman spectroscopy and ESR indicate the presence of S–S terminal and S–S bridging with unsaturated S atoms during the HER process. The heterostructures display enhanced stability revealed by long-term chronopotentiometry tests.

4. EXPERIMENTAL SECTION

4.1. Preparation of the PAN/CowW Nanofiber Membrane. In a typical procedure, Co(NO$_3$)$_2$ and (NH$_4$)$_2$WS$_4$ and PAN were used as the precursor. Certain amounts of Co(NO$_3$)$_2$ and (NH$_4$)$_2$WS$_4$ were dissolved in the PAN/DMF solution (the mass fraction of PAN is about 10 wt%) and then stirred vigorously for 10 h to obtain a homogeneous solution. The electropinning process is carried out as described previously.

4.2. Preparation of Co$_9$S$_8$/FWS$_2$/CNFs and Co$_9$S$_8$/HWS$_2$/CNFs. The Co$_9$S$_8$/WS$_2$/CNF hybrid membrane was prepared in a chemical vapor deposition furnace tube. The CoW/PAN precursor membrane was placed in a ceramic boat. Another ceramic boat with S powder was placed upstream relative to the gas flow direction. By adjusting the mass ratio of Co(NO$_3$)$_2$ and (NH$_4$)$_2$WS$_4$, and the S vapor treatment temperature, Co$_9$S$_8$/FWS$_2$/CNFs and Co$_9$S$_8$/HWS$_2$/CNFs can be obtained. For the preparation of Co$_9$S$_8$/FWS$_2$/CNFs, the CoW/PAN precursor nanofibers with a Co and W mass ratio of 1:2 were heated to 230 °C in air at a heating rate of 5 °C per min and kept at this temperature for 3 h. After the stabilization process, the furnace was continuously heated up. When the temperature heated up to 1000 °C, the S boat was heated to ~200 °C via a heating belt. After 2 h, the S boat furnace was removed and the nanofiber furnace was held constant for 6 h. For the preparation of Co$_9$S$_8$/HWS$_2$/CNFs, the CoW/PAN precursor nanofibers with a Co and W mass ratio of 1:1 were heated to 230 °C in air at a heating rate of 5 °C per minute and kept at this temperature for 3 h. When the temperature reached 400 °C, the S boat reached ~200 °C. After 2 h, the furnace was heated up to 1000 °C at a rate of 5 °C per minute, and the temperature was constant for 6 h.

4.3. Materials Characterizations. FE-SEM, TEM, HAADF-STEM, XRD, XPS, and ESR were performed as described previously.

4.4. Electrochemical Characterization. The HER tests were performed with an Autolab potentiostat/galvanostat (model PGSTAT302N) workstation. The electrochemical experiments were performed in a traditional three-electrode system at 25 °C. A graphite rod acted as a counter electrode (CE). A saturated calomel electrode was utilized as the reference electrode (RE). The Co$_9$S$_8$/FWS$_2$/CNF and Co$_9$S$_8$/HWS$_2$/CNF membranes were tailored into a neat square (0.5 × 0.5 cm) and directly used as the WE in 0.5 M H$_2$SO$_4$ and 1 M KOH, respectively. The polarization curves and stability tests were performed as described previously.

4.5. Operando Electrochemical Raman Test. A round homemade cell was used for the operando Raman test. Ag/AgCl and a Pt wire were used as RE and CE. The WE was sheathed in Teflon. Aqueous 1 M KOH was used as the electrolyte. Electrochemical tests were performed using an Autolab potentiostat/galvanostat (model PGSTAT302N) workstation. Raman spectroscopy was carried out using the apparatus described in ref 40.
4.6. DFT Calculations. All computations were performed using the spin-polarized density functional approximation as implemented in the CP2K package.45 The DFT plus Hubbard U approach was applied to correctly describe electrostatic repulsion interaction and also to localize the electronic configuration Co 3d.46 The Hubbard U–J value is very sensitive to compute the lattice constant of the Co3S4 crystal. Lattice constants optimized with the U–J value at 2 eV are consistent with the experimental result. For considering both 3d electronic localization and lattice constant optimization, a compromised U–J value of 2 eV was adopted in our current theoretical studies. Exchange–correlation energies were computed as described in previous report.45 Solvent effects were included using explicit water solution. The wave function of valent-shell electrons (1s1 for H, 2s22p4 for O, 3s23p4 for S, 3s23p63d74s2 for Co, and 5s25p65d46s2 for W) is computed as previously described.45

The chemical model of the nanocore/shell structure was constructed using an approximate way in which the core acts as a symmetrized and periodic Co3S4 slab and the shell acts as periodic single, double, and edged layers. The stoichiometric periodic slab models of the Co3S4 p(2 × 2) and p(3 × 2) (111) surface constructed with the 25 and 30 Å vacuum layers were adopted. For approaching the real electrochemical environment, three layers of ~40 H2O molecules with addition of H+ cations were introduced inside the vacuum layer to simulate the electrical double layer to study the HER performance. The initial geometric structures were relaxed to a local minimum, and an AIMD simulation was carried out at 298 K to equilibrate waters and interface with a 1 ps time step in a 8 ps timescale. The electrochemical performance of such a core/shell system was explored by means of electronic structure study, static calculation, and molecular dynamic simulation at the same level. The bottom 118 atoms (a half layer of Co3S4-slab) in seven atomic layers were frozen, while the remaining atoms were allowed to relax without constraint. The canonical ensemble (NVT) and Nose–Hoover thermostats were adopted in AIMD simulation.47,48 Transition states were investigated using the climbing image nudged-elastic-band method with a convergence criterion of 0.05 eV Å.49

**ASSOCIATED CONTENT**

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b19382.

FE-SEM and TEM images, XRD patterns, LSV curves, Tafel plots, TOF, HAADF-STEM images and XPS spectra, photograph, and DOS spectra of the as-prepared electrocatalysts (PDF)

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**Notes**

The authors declare no competing financial interest.

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