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Plasma Engineering of Basal Sulfur Sites on MoS$_2$@Ni$_3$S$_2$ Nanorods for the Alkaline Hydrogen Evolution Reaction

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Inexpensive and efficient catalysts are crucial to industrial adoption of the electrochemical hydrogen evolution reaction (HER) to produce hydrogen. Although two-dimensional (2D) MoS$_2$ materials have large specific surface areas, the catalytic efficiency is normally low. In this work, Ag and other dopants are plasma-implanted into MoS$_2$ to tailor the surface and interface to enhance the HER activity. The HER activity increases initially and then decreases with increasing dopant concentrations and implantation of Ag is observed to produce better results than Ti, Zr, Cr, N, and C. At a current density of 400 mA cm$^{-2}$, the overpotential of Ag500-MoS$_2$@Ni$_3$S$_2$/NF is 150 mV and the Tafel slope is 41.7 mV dec$^{-1}$. First-principles calculation and experimental results reveal that Ag has higher hydrogen adsorption activity than the other dopants and the recovered S sites on the basal plane caused by plasma doping facilitate water splitting. In the two-electrode overall water splitting system with Ag500-MoS$_2$@Ni$_3$S$_2$/NF, a small cell voltage of 1.47 V yields 10 mA cm$^{-2}$ and very little degradation is observed after operation for 70 hours. The results reveal a flexible and controllable strategy to optimize the surface and interface of MoS$_2$ bonding well for hydrogen production by commercial water splitting.

1. Introduction

Development of the modern society demands green energy and sustainable environment[1] and in order to alleviate the shortage of fossil fuel and greenhouse gas emission, hydrogen production by water electrolysis or water splitting is one of the important strategies.[2] In the hydrogen evolution reaction (HER) which is one of the two reactions in water splitting, the best catalysts so far are Pt-based but they suffer from the high price and natural scarcity and therefore, more efficient and economical electrocatalysts are desirable.[3,4] Some transition metal compounds such as Co-based, Ni-based, Fe-based, and Mo-based materials have received attention as catalysts because of the low price, abundant reserve, and special physical properties.[5–10] For example, Mo-based catalysts such as MoSe$_2$ nanosheets, MoP/carbon nanotube hybrids, Ni/MoC heteronanoparticles, MoNi$_{1-x}$/MoO$_3$ nanorod arrays, MoS$_2$-based catalysts, and so on have been proposed.[11–15] Among them, Mo$_2$ materials have great potential as substitutes for Pt-based catalysts in HER due to the unique 2D layer structure and chemical properties.[16] However, it has been shown that the active sites on pure MoS$_2$ are mainly the S sites at the edge, but the S sites on the basal plane are inactive[17] and activation of the S sites on the basal plane of MoS$_2$ is still challenging.[18] The modification strategies of MoS$_2$ follow the following main directions.[19] First, construction of new active sites or activation of S sites on the basal plane can be accomplished by doping MoS$_2$.[20] For example, Tian et al. have reported a MoS$_2$ nanoflake catalyst containing selenium on the surface and cobalt in the inner layer showing good HER activity.[21] Qi et al. have proposed that introducing Pd atoms to the basal plane of defect-rich MoS$_2$
produces Pt-like HER properties such as low onset overpotential, small Tafel slope, and HER durability.[22] Second, heterostructures of MoS₂ can be produced in combination with other suitable materials to activate the S sites on the surface.[23] For instance, Zhao et al. have synthesized 3D graphene aerogel supported layered MoS₂ nanosheets by self-assembly with high catalytic activity and durability in HER.[24] Third, by adjusting the lattice spacing and interface of MoS₂, [25] Wei et al. have demonstrated a technique to activate the monolayer MoS₂ basal plane by introducing domain boundaries.[26] Although modification of the surface of MoS₂ to activate the S sites can indeed improve the activity in HER, there have been few comprehensive studies on the mechanism and effects of the type and amount of dopants to attain the optimal performance.[27] In fact, there has been little work on the use of plasmas to achieve precise control of the active sites on catalysts.[28] Since plasma processes are widely used in the industry, especially microelectronics processing, it is important to study the effects of different dopants and plasma parameters such as fluence on the catalytic activity of HER catalysts.[28,29]

Herein, Ag, Zr, Ti, Cr, C, and N are plasma-implanted into MoS₂@Ni₃S₂ nanorods with different fluences to investigate the effects on the catalytic sites. Our results reveal that Ag ion implantation with the proper fluence leads to the best HER activity. The experimental and theoretical results show that the right amount of implanted Ag in MoS₂ not only maintains the 2D structure with a large surface area, but also introduces a large number of active centers to reduce the hydrogen adsorption energy. The active sites for HER is the S sites on the MoS₂ basal surface directly connected to the doped atoms. The strategy involving structural engineering and plasma processing renders MoS₂@Ni₃S₂ an excellent catalyst for HER, the concept and materials provide insights into the development of high-efficiency water splitting catalysts.

2. Results and Discussion

2.1. Materials and Characterization

Figure 1a illustrates the process in which the MoS₂@Ni₃S₂ nanorods are prepared on nickel foam (NF) hydrothermally and subsequently modified by plasmas. In the first hydrothermal step, uniform and elongated MoS₂@Ni₃S₂ nanorods are produced vertically on the conducting NF framework. The SEM images in Figure 1b,c disclose that the pristine MoS₂@Ni₃S₂ has a nanorod structure with a length of 2 μm and width of 150 nm. During plasma implantation, different elements are implanted into the MoS₂@Ni₃S₂ nanorods with different fluences. As plasma implantation proceeds, the fluence increases and the nanorods are interconnected to form a nanoflower-like or nanonet-like structure. The SEM images of the modified MoS₂@Ni₃S₂ nanorods implanted with different amounts of Ag are depicted in Figure 1d–i. The morphology of the lightly doped MoS₂@Ni₃S₂ is basically unchanged (Figure 1d,e) but for higher fluences, the nanorods aggregate to form a flower-like structure (Figure 1f,g) and finally, the nanorods agglomerate to form a network (Figure 1h,i). This is mainly because the Ag plasma is accelerated by the 25 kV acceleration grid to obtain higher energy and accelerate to the sample surface on the grounded sample stage. Due to its relatively large energy, the morphology of the sample will be greatly changed after a large dose of incorporation to relieve stress. For comparison, the morphology and size of the MoS₂@Ni₃S₂/NF nanorods doped with different elements and concentrations are displayed in Figures S2–S6, Supporting Information. The morphological changes are basically consistent with that observed from the Ag-implanted samples. As shown in Figure 1j,k, Mo, S, Ag, and Ni are distributed uniformly on the surface of Ag500-MoS₂@Ni₃S₂.

The atomic ratios of the metallic elements in the catalysts are determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The Mo/Ni ratios in MoS₂@Ni₃S₂ NF doped with different amounts of Ag are 3–4% and the amounts of MoS₂ in the materials are uniform and stable (Figure 2a). The ratio of Ag to Mo is less than 10% in the near surface as a result of the Gaussian distribution of ion implantation and so the implanted Ag mainly exists as dopants on the MoS₂ surface (Figure 2b). The surface area is one of the important parameters to evaluate the electrocatalytic ability. As shown in Figure 2c, the specific surface areas of the pristine MoS₂@Ni₃S₂/NF, Ag250-MoS₂@Ni₃S₂/NF, Ag500-MoS₂@Ni₃S₂/NF, and Ag1000-MoS₂@Ni₃S₂/NF are 2.57, 2.34, 1.73, and 2.50 m² g⁻¹, respectively. By means of the Barrett–Joyner–Halenda adsorption model, the pore sizes of the samples with different amounts of implanted Ag are 4.44, 2.52, 1.19, and 1.76 nm, indicating that MoS₂@Ni₃S₂/NF and Ag250-MoS₂@Ni₃S₂/NF have mesoporous characteristics and Ag500-MoS₂@Ni₃S₂/NF and Ag1000-MoS₂@Ni₃S₂/NF exhibit microporous characteristics (Figure S7, Supporting Information). Catalysts with more micropores have more surface areas which may lead to a larger number of active sites and better contact between the active sites and substrate.[30] Therefore, although the specific surface area is similar, Ag500-MoS₂@Ni₃S₂/NF has more micropores suggesting more active sites and perhaps higher catalytic activity.[31]

Figure 2d shows the three typical diffraction peaks at 44.5, 52.1, and 76.7° corresponding to the (111), (200), and (220) planes of the Ni substrate (PDF#04-0850).[32] The diffraction peaks marked by squares can be indexed to the (101), (110), (003), (211), and (300) planes of the Ni₃S₂ nanorods (PDF#44-1418)[33] and those at 12.4, 27.8, 38.9, 47.9, 58.8, and 71.4° marked by pentagons are the (002), (004), (103), (105), (008), and (203) planes of the MoS₂ nanosheets (PDF#37-1492).[34] The reason for the small diffraction peaks of MoS₂ is mainly because the content of MoS₂ is very low compared to Ni₃S₂, and the depth of X-ray diffraction (XRD) measurement is also very deep to several microns. Therefore, the diffraction peak of MoS₂ is not clear enough on a strong Ni and Ni₃S₂ substrate. However, the still visible diffraction peaks from MoS₂ shift to smaller angles in general because the atomic radius of Ag is larger than that of Mo thus increasing the interplanar spacing. Moreover, the XRD diffraction peaks of Ni₃S₂ shifts to the high angle direction with the increase of Ag doping, mainly due to the extrusion caused by the high-energy plasma injection process, which makes the lattice spacing smaller. The XRD patterns of the other plasma-doped catalysts in Figure S8, Supporting Information, show that the diffraction peaks from MoS₂ shift to larger angles because the atomic radii of Zr, Ti, Cr, C, and N are smaller than those of Mo and S, so that the unit cell parameters of MoS₂ are slightly reduced.

The morphology and lattice parameters of Ag500-MoS₂@Ni₃S₂/NF are studied by transmission electron mi-
Figure 1. a) Schematic illustration of the preparation of Ag-doped MoS$_2$@Ni$_3$S$_2$/NF nanorods by plasma doping; SEM images of b,c) MoS$_2$@Ni$_3$S$_2$/NF, d,e) Ag250-MoS$_2$@Ni$_3$S$_2$/NF, f,g) Ag500-MoS$_2$@Ni$_3$S$_2$/NF, and h,i) Ag1000-MoS$_2$@Ni$_3$S$_2$/NF; j) EDS spectrum of Ag500-MoS$_2$@Ni$_3$S$_2$/NF; k) EDS elemental maps of Ag500-MoS$_2$@Ni$_3$S$_2$/NF.

croscopy (TEM) and high-resolution TEM (HRTEM, Figure 2e–h). Ag500-MoS$_2$@Ni$_3$S$_2$/NF has a nanorod structure covered by nanosheets with a diameter of ≈200 nm and length of 2 μm. The HRTEM images in Figure 2g–i show that Ag-MoS$_2$@Ni$_3$S$_2$/NF has lattice spacings of 0.63 and 0.32 nm corresponding to the (002) and (004) planes of MoS$_2$ as well as 0.21 and 0.28 nm corresponding to the (202) and (110) planes of Ni$_3$S$_2$. The interface is formed mainly between the (002) plane of the MoS$_2$ nanosheets and (202) plane of the Ni$_3$S$_2$ nanorods. The TEM and HRTEM images of the other implanted MoS$_2$@Ni$_3$S$_2$/NF samples are depicted in Figures S9–S13, Supporting Information. The diameter of the nanowires is also 150–200 nm and the length is 1–2 μm. The (002) interplanar spacing of Ag-doped MoS$_2$ is slightly larger than that of pristine MoS$_2$, whereas those of the plasma-doped MoS$_2$ is slightly smaller than that of the pristine MoS$_2$. Since Ag has a larger radius, the lattice spacing of MoS$_2$ increases slightly, while the lattice spacings of MoS$_2$ doped with elements with smaller diameters decrease slightly in line with XRD. Besides, the interplanar spacing of Ni$_3$S$_2$ is basically unchanged, which is verified from the side that there is very little Ag plasma implantation into Ni$_3$S$_2$. The selected-area electron diffraction pattern in Figure 2j also discloses a clear lattice composed of diffraction points indicative of excellent crystallinity in the MoS$_2$ nanosheets. Figure 2k shows that Mo, Ag, S, and Ni are distributed evenly throughout the nanorods wrapped by nanosheets and the elemental maps of Zr500-MoS$_2$@Ni$_3$S$_2$/NF (Figure S9, Supporting Information) also disclose uniform distributions of Mo, S, Zr, and Ni. These results corroborate that the 2D structure of MoS$_2$ is not destroyed by plasma implantation and MoS$_2$@Ni$_3$S$_2$/NF is produced successfully.
The XPS survey spectra in Figure 3a–c show the presence of Mo, S, O, C, and Ni together with the dopants. The pure MoS$_2$@Ni$_3$S$_2$/NF in Figure 3d displays two typical Mo 3d peaks at 228.7 and 231.9 eV corresponding to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$.[36] The S 2p spectra in Figure S14, Supporting Information, show two peaks at 162.3 and 163.6 eV consistent with the spin split orbitals of S 2p$_{3/2}$ and S 2p$_{1/2}$, respectively[37] and the Ni 2p spectrum of MoS$_2$@Ni$_3$S$_2$ displays two pairs of peaks for Ni 2p$_{3/2}$ (873.1 eV) and 2p$_{1/2}$ (855 eV) associated with Ni$^{2+}$ and Ni 2p$_{3/2}$ (878.6 eV) and 2p$_{1/2}$ (857.5 eV) stemming from Ni$^{3+}$ (Figure 3e).[38] Figure 3g presents the Mo 3d XPS spectra of Ag250-MoS$_2$@Ni$_3$S$_2$/NF, Ag500-MoS$_2$@Ni$_3$S$_2$/NF, and Ag1000-MoS$_2$@Ni$_3$S$_2$/NF. As the Ag concentration increases, the peaks of Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ shift to lower binding energies[39] but the S 2p peaks shift toward higher binding energies (Figure 3h). The peaks of Ni 2p shifts to the direction of high binding energy with the increase of Ag doping, which demonstrates that the outer electron cloud density of Ni 2p decreases and Ni relatively loses electrons (Figure S15, Supporting Information). As shown in Figure 3i, the peaks of Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ remain at 368.3 and 374.3 eV with increasing Ag concentration[40] and the ratios of Ag to Mo in Ag-doped MoS$_2$ are 14.4%, 25.1%, and
48.9% (Figure 3f) and larger than those determined by ICP, indicating that Ag is mainly concentrated on the surface of MoS₂ and plays a role in the HER activity. The ratios of Ag to Mo obtained by ICP and XPS for increasing Ag concentrations are consistent as shown by a linear relationship. The XPS spectra of the other catalysts including Zr-doped, Cr-doped, Ti-doped, C-doped, and N-doped MoS₂@Ni₃S₂/NF are shown in Figures S16–S20, Supporting Information. The two peaks at 184.3 and 182.1 eV are Zr 3d₃/₂ and Zr 2p peaks become more intense with increasing Zr concentrations.[41] The binding energies of Ti 2p₁/₂ and Ti 2p₃/₂ remain at 464.3 and 458.4 eV and those of Cr 2p₁/₂ and Cr 2p₃/₂ are at 586.5 and 576.4 eV.[42,43] Similarly, with increasing metal dopant concentrations, the XPS peaks become clearer but the structure of MoS₂ is not destroyed. However, the non-metal dopants C and N show different results. The corresponding Mo 3d and S 2p peaks change when the C and N plasma implanta-
2.2. Electrocatalytic Properties in HER

The plasma-implanted MoS$_2$ shown in Figure 4a swells slightly due to the large number of defects and more catalytic surface area which is likely to adsorb H$_2$O or H atoms in HER. A standard three-electrode system is adopted to evaluate the HER activity of the Ag-doped MoS$_2$@Ni$_3$S$_2$/NF electrode in 1 M KOH electrolyte. For comparison, the HER characteristics of the pure MoS$_2$@Ni$_3$S$_2$/NF, Ag500-MoS$_2$@Ni$_3$S$_2$/NF, Cr1000-MoS$_2$@Ni$_3$S$_2$/NF, Zr500-MoS$_2$@Ni$_3$S$_2$/NF, Ti500-MoS$_2$@Ni$_3$S$_2$/NF, C1.0-MoS$_2$@Ni$_3$S$_2$/NF, and N1.0-MoS$_2$@Ni$_3$S$_2$/NF are also assessed under the same conditions. The Tafel slopes of plasma-doped Ti500-MoS$_2$@Ni$_3$S$_2$/NF are 121.2, 135.3, 151.4, 147.2, and 111.7 mV dec$^{-1}$ and not as good as that of the original MoS$_2$@Ni$_3$S$_2$/NF (164.7 mV dec$^{-1}$). Hence, the proper amount of dopants is crucial to the HER performance. Moreover, the $\eta_{10}$ values of Ti500-MoS$_2$@Ni$_3$S$_2$/NF, Zr500-MoS$_2$@Ni$_3$S$_2$/NF, Cr500-MoS$_2$@Ni$_3$S$_2$/NF, C1.0-MoS$_2$@Ni$_3$S$_2$/NF, and N1.0-MoS$_2$@Ni$_3$S$_2$/NF at 10 mA cm$^{-2}$ are 43, 66, 174, 125, 100 mV, which are 76, 112, 96, 82, and 86 mV lower than those of Ti250-MoS$_2$@Ni$_3$S$_2$/NF (164.7 mV dec$^{-1}$) and Cr250-MoS$_2$@Ni$_3$S$_2$/NF (110.5 mV dec$^{-1}$), and Ag1000-MoS$_2$@Ni$_3$S$_2$/NF (86.4 mV dec$^{-1}$) (Figure 4f and Figure S22, Supporting Information). The small Tafel slope of Ag500-MoS$_2$@Ni$_3$S$_2$/NF suggests a large number of active sites. Ag500-MoS$_2$@Ni$_3$S$_2$/NF requires an overpotential of only 33 mV for a current density of 10 mA cm$^{-2}$, which is 230, 113, and 71 mV less than those of the bare MoS$_2$@Ni$_3$S$_2$/NF, Ag250-MoS$_2$@Ni$_3$S$_2$/NF, and Ag1000-MoS$_2$@Ni$_3$S$_2$/NF (Figure 4f).

Electrochemical impedance spectroscopy (EIS) is an important technique to evaluate the catalytic activity of electrocatalysts. As shown in Figure 4i and Table S2, Supporting Information, Ag500-MoS$_2$@Ni$_3$S$_2$/NF has the smallest charge transfer resistance $R_{\text{ct}}$ ($\Omega$) and $R_\text{f}$ ($\Omega$) implying higher conductivity and more channels for faster ion transfer. For comparison, the EIS data of the other plasma-doped MoS$_2$@Ni$_3$S$_2$/NF samples acquired at -0.1 V versus RHE are shown in Figure S23, Supporting Information. After plasma implantation, MoS$_2$ shows a relatively small impedance and better conductivity, which facilitate transport of electrons and ions in HER. To further investigate the working range and effectiveness of plasma implantation, different amounts of Zr, Ti, Cr, N, and C are implanted into MoS$_2$@Ni$_3$S$_2$/NF. The electrocatalytic activity of Zr-doped MoS$_2$@Ni$_3$S$_2$/NF, Ti-doped MoS$_2$@Ni$_3$S$_2$/NF, N-doped MoS$_2$@Ni$_3$S$_2$/NF, Cr-doped MoS$_2$@Ni$_3$S$_2$/NF, and C-doped MoS$_2$@Ni$_3$S$_2$/NF in HER is assessed under the same conditions. The polarization curves after iR correction in Figures S24–S28, Supporting Information, show that plasma implantation improves the catalytic activity compared to the pristine MoS$_2$@Ni$_3$S$_2$/NF. The activity rises in the beginning and then drops as the dopant concentration increases. The Tafel slopes of plasma-doped Ti500-MoS$_2$@Ni$_3$S$_2$/NF (Figure S24b, Supporting Information), Zr500-MoS$_2$@Ni$_3$S$_2$/NF (Figure S25b, Supporting Information), N1.0-MoS$_2$@Ni$_3$S$_2$/NF (Figure S26b, Supporting Information), Cr500-MoS$_2$@Ni$_3$S$_2$/NF (Figure S27b, Supporting Information), and C1.0-MoS$_2$@Ni$_3$S$_2$/NF (Figure S28b, Supporting Information) are 52.7, 65.3, 116.5, 80.4, and 71.4 mV dec$^{-1}$, suggesting better HER characteristics compared with other samples. However, the Tafel slopes of Ti250-MoS$_2$@Ni$_3$S$_2$/NF, Zr250-MoS$_2$@Ni$_3$S$_2$/NF, Cr250-MoS$_2$@Ni$_3$S$_2$/NF, C2.0-MoS$_2$@Ni$_3$S$_2$/NF, and N4.0-MoS$_2$@Ni$_3$S$_2$/NF are 121.2, 135.3, 151.4, 147.2, and 111.7 mV dec$^{-1}$.
Figure 4. a) Schematic diagram showing the preparation of plasma doped MoS$_2$ and HER characteristics on MoS$_2$@Ni$_3$S$_2$/NF doped with different elements; b) LSV curves; c) overpotentials; d) Tafel plots; HER characteristics of Ag-doped MoS$_2$@Ni$_3$S$_2$/NF; e) LSV curves; f) overpotentials and Tafel plots; g) Capacitive current densities at different scanning rates; h) ECSA of different samples; i) Nyquist plots derived from EIS; j) Stability of Ag-doped MoS$_2$@Ni$_3$S$_2$/NF; k) Comparison of polarization curves.
Ti500-MoS2@Ni3S2/NF, C1.0-MoS2@Ni3S2/NF, and N1.0-MoS2@Ni3S2/NF are 26.8, 23.4, 30.2, 25.4, and 25.7 mF cm⁻², respectively, with the following order: Ag > Ti > Zr > N > Cr. The ECSAs of the Ag-doped samples is larger than those of other dopants (Figure 4h). Again, the catalytic activity increases and then decreases with dopant concentrations consistent with the Tafel slopes and overpotentials.

The electrochemical stability of the catalysts is evaluated by chronopotentiometry and cyclic voltammetry (CV). As shown in Figure 4j, compared to Ag1000-MoS2@Ni3S2/NF and Ag250-MoS2@Ni3S2/NF with too much or too little Ag dopants, the Ag500-MoS2@Ni3S2/NF exhibits not only excellent initial HER activity, but also good electrocatalytic durability. After 50 h, the catalyst retains 97.1% of the activity with basically no decrease in the current density. Moreover, Ag500-MoS2@Ni3S2/NF shows negligible loss in the polarization current density after 5000 cycles and compared with the Tafel slope and EIS data shows negligible loss in the polarization current density after 5000 cycles and compared with the Tafel slope and EIS data.

Zr- and N-doped MoS2 are depicted in Figure 5c,d, respectively, with the following order: Ag > Ti > Zr > N > Cr. The ECSAs of the Ag-doped samples is larger than those of other dopants (Figure 4h). Again, the catalytic activity increases and then decreases with dopant concentrations consistent with the Tafel slopes and overpotentials. 

Structural strain is also an important factor for ΔG*H, because the valence state of the substituted metal atom is lower and the bond with the adjacent S atom is weaker than that of the Mo–S bond.[52,53] As shown in Figure 5g, the Ag–S bond length (2.59 Å) for the pure MoS2 surface is only 80% for instance, Zr250-MoS2@Ni3S2/NF (83.3%), Ti250-MoS2@Ni3S2/NF (78.8%), and Cr250-MoS2@Ni3S2/NF (84.7%). For the non-metallic plasma-doped samples, the samples treated for one hour show a better cycle stability compared to those treated for 0.5, 2, and 4 h. After applying −0.15 V for 30 h, the current densities of C1.0-MoS2@Ni3S2/NF and N1.0-MoS2@Ni3S2/NF are maintained at more than 90% of the initial value, but that of N4.0-MoS2@Ni3S2/NF drops to 78%, indicating that the long-term stability of the carbon or nitrogen-doped samples increases and then decreases with implantation time as well.

2.3. Theoretical Assessment

The HER sites are concentrated on the surface of the catalyst and in this respect, the plasma-modified MoS2 forms the outermost layer on the catalyst. The change of the Gibbs free energy (ΔG*H) between adsorption and desorption of H* on the electrode surface is a key parameter to predict the HER activity and the closer ΔG*H is to zero, the higher is the HER efficiency.[42,47,48] Therefore, ΔG*H for H* adsorbed on the plasma-treated MoS2 surface is first evaluated because H* tends to adsorb onto the sulfur (S) sites.[49,50] The supercell with the 3 x 3 surface unit cells and top-view H* adsorption above the S sites is shown in Figure 5a,b. In the first-principles calculation, H* adsorbed on the S sites of the Cr-, Ti-, Zr-, Ag-, Cu-, and N-doped MoS2 surfaces is derived separately for three dopant concentrations of 11, 22, and 33 mol% according to the XPS data (Figure 3f). The top-views of 11 mol% Zr- and N-doped MoS2 are depicted in Figure 5c,d, respectively.
Figure 5. a) Optimized structure of H\(^*\) adsorption on bare MoS\(_2\)(002); Top views of H\(^*\) adsorption on b) bare MoS\(_2\); c) N–MoS\(_2\), and d) Zr–MoS\(_2\); e) Calculated \(\Delta G_{\text{H*}}\) of MoS\(_2\) doped with different elements; f) DOS of S sites on MoS\(_2\) doped with different elements; g,h) Changes of Ag–S bond lengths before and after H\(^*\) adsorption; i,j) Top-view schematics of different H\(^*\) coverages on 11 mol% Ag-MoS\(_2\); k–n) Top-view schematic of different H\(^*\) coverages on 22 mol% Ag-MoS\(_2\).

As the dopant concentration increases from 11 to 33 mol%, \(\Delta G_{\text{H*}}\) approaches zero initially and then increases, especially Ag, Cu, Ti doped MoS\(_2\), proving that more adjacent S active sites are activated as the dopant concentration goes up consistent with the experimental results. However, if the dopant concentration increases to 33%, \(\Delta G_{\text{H*}}\) of the S active site moves away from the zero point. Therefore, the optimal dopant concentration for activation of adjacent S sites is 22% (Figure S37, Supporting Information). With regard to Ag-doped MoS\(_2\) with concentration of 11% and 22%, the \(\Delta G_{\text{H*}}\) values of one H\(^*\) adsorbed on the active S site is −0.39 and −0.2 eV (monolayer H coverage is 11%), which are below zero suggesting that H\(^*\) can easily adsorb on active S but desorption is relatively difficult. There is thus a certain amount of H atoms adsorbed on the surface of the active site during HER and so calculation of the Gibbs free energy for multiple hydrogen adsorption on the active S site is important. Therefore, \(\Delta G_{\text{H*}}\) for additional H atom adsorption for 11 mol% H coverage and \(\Delta G_{\text{H*}}\) for second H\(^*\) adsorption after one H\(^*\) has already adsorbed to the 3 \times 3 surface...
Figure 6. a) Schematic diagram of the water electrolysis apparatus with two electrodes; b) two-electrode polarization curves obtained at a scanning rate 5 mV s^{-1}; c) Comparison of the experimental and theoretical amount of H2 and O2 produced in overall water splitting; d) Chronoamperometry of overall water splitting at 1.6 V; e) Comparison of the cell voltages to achieve 10 mA cm^{-2} for recently reported electrocatalysts.

unit cell are derived. Here, \( \Delta G_{\text{H*}} \) is defined as follows: 
\[
\Delta G_{\text{H*}} = E_{\text{surf} + \text{H*}} - (E_{\text{surf} + 2 \text{H*}} + 0.5E_{\text{H2}}) + 0.24 \text{eV},
\]
where \( E_{\text{surf} + \text{H*}} \) is the total energy of the supercell with one adsorbed H* and \( E_{\text{surf} + 2 \text{H*}} \) is the total energy of the supercell with two adsorbed H*. The active S site on the surface of 11 mol% Ag-doped MoS2 is occupied by one H* (Figure 5i) and there are still two equivalent activated S atoms that can adsorb the second H*. Figure 5j exhibits the surface structure for second H* adsorption and \( \Delta G_{\text{H*}} \) for second H* adsorption is only \(-0.18\) eV. With increasing H coverage from 11 to 22%, \( \Delta G_{\text{H*}} \) rises from \(-0.39\) to \(-0.18\) eV because adsorption of the first H atom decrease the empty states of the valence orbitals of the other S atom. Hence, adsorption of the second H atom becomes weak. As for the 22 mol% Ag doped MoS2 surface with 11% H coverage in Figure 5k, there are five analogous activated S atoms to adsorb the second H atom. Figure 5l–n exhibit the three typical configurations of two H* adsorbed on the 22% Ag doped MoS2 surface together with the corresponding \( \Delta G_{\text{H*}} \) of the second H*. \( \Delta G_{\text{H*}} \) for adsorption of the second H* atom increases compared to that for the first H*. Remarkably, \( \Delta G_{\text{H*}} \) for the two S active sites connected to the same Ag in Figure 5l is only 0.02 eV and closer to zero, indicating that there are more high active sites on the 22% Ag-doped MoS2 surface. The main reason is that the two H* atoms adsorbed on the two S atoms are connected to the same Ag atom (Figure 5l) and two H* atoms adsorb to two S atoms that connect directly with the Ag atoms at two different positions (Figure 5m,n). As aforementioned, direct adsorption of H* atoms on S atoms bonded to the same Ag atom can release more strain energy in the Ag–S bond. The first H* adsorption releases the main strain energy in the Ag–S bond, whereas the second H* adsorption releases less strain energy and shows a larger \( \Delta G_{\text{H*}} \). The theoretical results are supported by the experimental data acquired from Ag-doped MoS2. All in all, the proper dopant and fluence create more S orbital empty states to promote the HER activity of MoS2.

2.4. Overall Water Splitting

As the other half-reaction in water splitting, the OER catalytic activity of doped MoS2@Ni3S2/NF is also assessed in the same alkaline electrolyte. Figure S38a, Supporting Information, shows the polarization curves of Ag500-MoS2@Ni3S2/NF, Zr500-MoS2@Ni3S2/NF, N1.0-MoS2@Ni3S2/NF, Ti500-MoS2@Ni3S2/NF, C1.0-MoS2@Ni3S2/NF, bare MoS2@Ni3S2/NF and corresponding Tafel slopes and overpotentials are shown in Figure S38b, Supporting Information. Compared with other electrodes, the Ag500-MoS2@Ni3S2/NF catalytic electrode still has a relatively small OER Tafel slope and overpotential, showing outstanding catalytic activity for OER. Owing to the excellent HER and OER catalytic properties, MoS2@Ni3S2/NF is adopted as both the anode and cathode in a two-electrode system with an alkaline electrolyte (Figure S39, Supporting Information) as illustrated in Figure 6a. As shown in the
polarization of the two electrodes in Figure 6b, Ag500-MoS2@Ni3S2/NF|Ag500-MoS2@Ni3S2/NF only needs 1.47 V to drive a current density of 10 mA cm$^{-2}$, which is far less than that of Ti500-MoS2@Ni3S2/NF|Ti500-MoS2@Ni3S2/NF (1.52 V), Zr500-MoS2@Ni3S2/NF|Zr500-MoS2@Ni3S2/NF (1.5 V), C1.0-MoS2@Ni3S2/NF|C1.0-MoS2@Ni3S2/NF (1.51 V), N1.0-MoS2@Ni3S2/NF|N1.0-MoS2@Ni3S2/NF (1.52 V), Cr500-MoS2@Ni3S2/NF|Cr500-MoS2@Ni3S2/NF (1.55 V), and bare MoS2@Ni3S2/NF|MoS2@Ni3S2/NF (1.6 V). In particular, the driving voltage of the original MoS2@Ni3S2/NF electrode is 1.6 V, which is much larger than those of other electrodes modified by the plasma.

Faraday efficiency is another important parameter to evaluate the efficiency of the electrocatalytic reaction and the gas volume is compared to the theoretical value. Figure 6c shows that the experimental and theoretical values for HER and OER of the Ag500-MoS2@Ni3S2/NF electrode are basically the same approaching 100% and a fairly stable hydrogen/oxygen yield is achieved. The long-term stability of the two electrodes is another important parameter in practice. The overall water splitting apparatus with two electrodes is shown in the inset in Figure 6d and the long-term durability of Ag500-MoS2@Ni3S2/NF, Ti500-MoS2@Ni3S2/NF, and N1.0-MoS2@Ni3S2/NF is assessed by continuous operation at 1.6 V in 1 M KOH. The three plasma-doped electrodes maintain the stability for 70 h without appreciable attenuation (Figure 6d) confirming the important effects of the plasmas. Figure S40. Supporting Information, shows that after the HER stability test, the morphology of the entire electrode is intact and the TEM image shows that the crystal lattice is not damaged. At the same time, Mo, Ni, Ag, and S are still present as shown by EDS. As shown in Figure S41, Supporting Information, the change in the valence state of Ag in the sample is basically negligible, and it mainly plays a role in activating the S site. However, the peak positions of S 2p and Ni 2p have changed a lot, which is attributed to the stability test in an alkaline environment, and part of the S and Ni sites are oxidized. It should be emphasized that the overall water splitting performance of Ag500-MoS2@Ni3S2/NF exceeds that of recently reported Mo-based electrocatalysts (Figure 6f). Our results and analysis reveal that plasma engineering activates MoS2@Ni3S2 leading to enhanced and durable HER activity.

3. Conclusion

MoS2@Ni3S2 is subjected to plasma implantation of metallic and non-metallic elements with different fluorine to modify the surface chemistry and enhance the hydrogen evolution activity. Ag500-MoS2@Ni3S2/NF exhibits the best catalytic activity and durability for HER in an alkaline environment. First-principles calculation reveals that the Gibbs free energy for H atom adsorption on the Ti-, Zr-, Ag-, and Cu-doped MoS2 surfaces are lower than that on the undoped MoS2 surface. The smaller Gibbs free energy stems from empty states in the valence band of MoS2, introduced by these dopants, leading to stronger bonds between S and adsorbed H atoms. $\Delta G_{\text{ads}}$ of 22 mol% Ag-doped MoS2 is only 0.02 eV and close to zero resulting in high HER efficiency. The two-electrode water splitting system with the Ag500-MoS2@Ni3S2/NF anode and cathode needs a battery voltage of 1.47 V to generate a current density of 10 mA cm$^{-2}$. Our results reveal the benefits of plasma engineering and sheds light into the associated mechanisms, which are beneficial to the design and fabrication of transition metal electrocatalysts with high efficiency and robust stability.

4. Experimental Section

Preparation of MoS2@Ni3S2/NF: 0.3 mmol ammonium molybdate and 12 mmol thiourea were added into 50 mL of DI water separately and stirred for 15 min to form a clear solution. The colorless solution and 2 cm × 3 cm clean NF were separately transferred to a hydrothermal reactor maintained at 200 °C for 12 h. After the hydrothermal reaction, the samples were taken out and rinsed with absolute ethanol and DI water for 5 min to remove impurities. Finally, the samples were put in a vacuum oven at 60 °C overnight to dry and prevent surface oxidation.

Plasma Injection MoS2@Ni3S2/NF: A high-energy metal ion plasma system and a multifunctional gas plasma system were used (Supporting Information). The Ag plasma process used to treat MoS2@Ni3S2/NF is described here as an example. The Ag target was polished mechanically. The MoS2@Ni3S2/NF sample and Ag target were transferred to the PI-80A high-energy metal plasma system with a base pressure of 2 × 10$^{-3}$ Pa and Ag plasma ion implantation was performed at an accelerating voltage of 25 kV with a fluence of $5 \times 10^{10}$ ions cm$^{-2}$ on MoS2@Ni3S2/NF (Ag500-MoS2@Ni3S2/NF). In addition, 2.5 $\times 10^{10}$ and 1 $\times 10^{10}$ ions cm$^{-2}$ Ag ions were implanted into MoS2@Ni3S2/NF for comparison (Ag250-MoS2@Ni3S2/NF and Ag1000-MoS2@Ni3S2/NF). The other plasma targets employed to implant MoS2@Ni3S2 included Zr, Ti, Cr, C, and N plasma. The plasma implantation process was similar to that for Ag and three fluences of each element were implanted for comparison. The schematic diagram of the metal plasma and non-metal plasma doping processes is shown in Figure S1, Supporting Information. Compared with the initial NF, the mass loading of the entire Ag500-MoS2@Ni3S2/NF catalytic electrode is 7.13 mg cm$^{-2}$.

Materials Characterization: The surface morphology, size, and elemental composition were characterized by field-emission scanning electron microscopy (Zeiss Gemini 450, Germany) equipped with energy-dispersive X-ray spectrometry (EDS). The phase composition was analyzed by XRD (Rigaku, RINT2100, Japan) with Cu K$\alpha$ radiation ($\lambda = 1.5406$ Å) and TEM and HRTEM were conducted to examine the fine structure and lattice spacing on the JEOL JEM-2010. The elemental maps were acquired by EDS on the SEM and TEM and the elemental concentrations were also determined by ICP-AES (Agilent, USA). The BET specific surface area was determined on the automatic specific surface and pore size distribution analyzer (Quantachrome Instruments, USA) and the surface chemistry was analyzed by X-ray photoelectron spectroscopy (150W, ESCALAB 250) with Al K$\alpha$ radiation. Electrochemical Measurements: The electrocatalytic tests were performed using the three-electrode configuration on the VMP3 (Bio-Logic) in 1 M KOH at room temperature. The sample, saturated calomel electrode, and graphite rod were the working, reference, and counter electrodes, respectively. Linear sweep voltammetry (LSV) was carried out at a scanning rate of 5 mV s$^{-1}$. The potentials in the LSV polarization curves were iR-corrected with respect to the ohmic resistance of the solution and the current densities were based on the geometrical area. The ECSA of the electrode was determined by CV in the non-faradic potential region at different sweeping rates to derive the double layer capacitance ($C_{dl}$) of the catalysts. EIS was conducted at the open circuit and certain potentials in the frequency range from 1 MHz to 0.1 Hz. The overall water splitting experiment was performed in a two-electrode system with two symmetrical electrodes as the anode and cathode.

First-Principles Calculation: In the electrochemical HER, the efficiency depends mainly on the change in the Gibbs free energy ($\Delta G_{\text{ads}}$) between adsorption and desorption of H atoms on the electrode surface. The closer $\Delta G_{\text{ads}}$ is approaching zero, the higher is the HER efficiency[55,56]. To investigate how $\Delta G_{\text{ads}}$ on MoS2 surface varies with the different dopants (C, N, Cr, Ti, Zr, Ag, and Cu), $\Delta G_{\text{ads}}$ and H coverage was derived by first-
principles calculation (Supporting Information). The MoS$_2$ surface was modeled with a supercell with $3 \times 3$ surface unit cell (Figure S34, Supporting Information). If only the last step of the reaction was considered and the desorption state of H$_2$ was regarded as the zero point, the Tafel process and Heyrovsky process show different reaction details, but the Gibbs free energy changes during the process are the same. $\Delta G_{\text{H2}}$ is defined as $\Delta G_{\text{H2}} = E_{\text{surfH2}} - (E_{\text{surfH}} + 0.5E_{\text{H2}}) + 0.24 \text{ eV}$[57,58] where $E_{\text{surf}}$ is the total energy of the supercell with no adsorbed H atom, $E_{\text{surfH2}}$ is the total energy of the supercell with an adsorbed H$_2$ atom, $E_{\text{H2}}$ is the binding energy of a H$_2$ molecule, and 0.24 eV is the change of zero energy and heat of entropy change between adsorption and desorption of a H atom on the electrode surface.[59]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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