Plasma Engineering of Basal Sulfur Sites on MoS_2@Ni_3S_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, Mo$_2$S$_3$-based catalysts, and so on have been proposed.$^{[11-15]}$ Among them, Mo$_2$S$_3$ 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. Second, heterostructures of MoS2 can be produced in combination with other suitable materials to activate the S sites on the surface. 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. Third, by adjusting the lattice spacing and interface of MoS2, Wei et al. have demonstrated a technique to activate the monolayer MoS2 basal plane by introducing domain boundaries. 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. In fact, there has been little work on the use of plasmas to achieve precise control of the active sites on catalysts. 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.

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–S5. 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. 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. Therefore, although the specific surface area is similar, Ag500-MoS2@Ni3S2/NF has more micropores suggesting more active sites and perhaps higher catalytic activity.

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). The diffraction peaks marked by squares can be indexed to the (101), (110), (003), (211), and (300) planes of the NiS2 nanorods (PDF#44-1418) 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). The reason for the small diffraction peaks of MoS2 is mainly because the content of MoS2 is very low compared to NiS2, 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 S 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 NiS2 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) Ag$_{250}$-MoS$_2$@Ni$_3$S$_2$/NF, f,g) Ag$_{500}$-MoS$_2$@Ni$_3$S$_2$/NF, and h,i) Ag$_{1000}$-MoS$_2$@Ni$_3$S$_2$/NF; j) EDS spectrum of Ag$_{500}$-MoS$_2$@Ni$_3$S$_2$/NF; k) EDS elemental maps of Ag$_{500}$-MoS$_2$@Ni$_3$S$_2$/NF.

crosscopy (TEM) and high-resolution TEM (HRTEM, Figure 2e–h). Ag$_{500}$-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$_2$.[5,35] 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 Zr$_{500}$-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$_{1/2}$ (873.1 eV) and 2p$_{3/2}$ (855 eV) associated with Ni$^{2+}$ and Ni 2p$_{1/2}$ (878.6 eV) and 2p$_{3/2}$ (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 MoS$_2$ 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 MoS$_2$@Ni$_3$S$_2$/NF are shown in Figures S16–S20, Supporting Information. The two peaks at 184.3 and 182.1 eV are Mo 3d$_{3/2}$ and Zr 3d$_{3/2}$ and Zr 2p peaks become more intense with increasing Zr concentrations.[41] The binding energies of Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ remain at 464.3 and 458.4 eV and those of Cr 2p$_{1/2}$ and Cr 2p$_{3/2}$ 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 MoS$_2$ 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$_2@Ni_3S_2$/NF electrode in 1 M KOH electrolyte. For comparison, the HER characteristics of the pure MoS$_2@Ni_3S_2$/NF, Ag500-MoS$_2@Ni_3S_2$/NF, Cr1000-MoS$_2@Ni_3S_2$/NF, Zr500-MoS$_2@Ni_3S_2$/NF, Ti500-MoS$_2@Ni_3S_2$/NF, C1.0-MoS$_2@Ni_3S_2$/NF, and N1.0-MoS$_2@Ni_3S_2$/NF are also assessed under the same conditions. The iR-corrected polarization curves of the samples are presented in Figure 4b. Ag500-MoS$_2@Ni_3S_2$/NF shows the best activity among the different samples. The overpotential ($\eta$) required for current densities ($j$) of 10 mA cm$^{-2}$ ($\eta_{10}$) and 20 mA cm$^{-2}$ ($\eta_{20}$) are merely 33 and 77 mV, respectively (Figure 4c). In comparison, $\eta_{10}$ and $\eta_{20}$ of MoS$_2@Ni_3S_2$/NF (263 and 306 mV), Cr1000-MoS$_2@Ni_3S_2$/NF (173 and 220 mV), Zr500-MoS$_2@Ni_3S_2$/NF (66 and 112 mV), Ti500-MoS$_2@Ni_3S_2$/NF (43 and 86 mV), C1.0-MoS$_2@Ni_3S_2$/NF (163 and 202 mV), and N1.0-MoS$_2@Ni_3S_2$/NF (153 and 188 mV) are larger than those of Ag500-MoS$_2@Ni_3S_2$/NF. The Tafel plots in Figure 4d confirm the improved HER activity. Compared to MoS$_2@Ni_3S_2$/NF (164.7 mV dec$^{-1}$), Cr1000-MoS$_2@Ni_3S_2$/NF (123.1 mV dec$^{-1}$), Zr500-MoS$_2@Ni_3S_2$/NF (65.3 mV dec$^{-1}$), Ti500-MoS$_2@Ni_3S_2$/NF (52.7 mV dec$^{-1}$), Cr1.0-MoS$_2@Ni_3S_2$/NF (70.4 mV dec$^{-1}$), and N1.0-MoS$_2@Ni_3S_2$/NF (85.7 mV dec$^{-1}$), Ag500-MoS$_2@Ni_3S_2$/NF has smallest Tafel slope (41.7 mV dec$^{-1}$) suggesting better S activation on the MoS$_2$ basal surface and the Volmer–Heyrovsky mechanism. The Volmer–Heyrovsky process is shown in Figure S21, Supporting Information.

The concentration is important to the catalytic effects of the MoS$_2$ nanosheets and Ni$_3S_2$ nanorods. Therefore, three samples implanted with different Ag concentrations, namely Ag250-MoS$_2@Ni_3S_2$/NF, Ag500-MoS$_2@Ni_3S_2$/NF, and Ag1000-MoS$_2@Ni_3S_2$/NF, are studied and the corresponding polarization curves are shown in Figure 4e. As the Ag concentration increases, the catalytic activity goes up initially and then decreases and Ag500-MoS$_2@Ni_3S_2$/NF exhibits the best HER activity. Moreover, Ag500-MoS$_2@Ni_3S_2$/NF shows a Tafel slope of 41.7 mV dec$^{-1}$ which is less than those of MoS$_2@Ni_3S_2$/NF (164.7 mV dec$^{-1}$), Ag$_{250}$-MoS$_2@Ni_3S_2$/NF (110.5 mV dec$^{-1}$), and Ag$_{1000}$-MoS$_2@Ni_3S_2$/NF (86.4 mV dec$^{-1}$) (Figure 4f and Figure S22, Supporting Information). The small Tafel slope of Ag500-MoS$_2@Ni_3S_2$/NF suggests a large number of active sites. Ag$_{500}$-MoS$_2@Ni_3S_2$/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$_2@Ni_3S_2$/NF, Ag$_{250}$-MoS$_2@Ni_3S_2$/NF, and Ag$_{1000}$-MoS$_2@Ni_3S_2$/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, Ag$_{500}$-MoS$_2@Ni_3S_2$/NF has the smallest charge transfer resistance $R_{ct}$ ($\Omega$) and $R_s$ ($\Omega$) implying higher conductivity and more channels for faster ion transfer. For comparison, the EIS data of the other plasma-doped MoS$_2@Ni_3S_2$/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$_2@Ni_3S_2$/NF. The electrocatalytic activity of Zr-doped MoS$_2@Ni_3S_2$/NF, Ti-doped MoS$_2@Ni_3S_2$/NF, N-doped MoS$_2@Ni_3S_2$/NF, Cr-doped MoS$_2@Ni_3S_2$/NF, and C-doped MoS$_2@Ni_3S_2$/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$_2@Ni_3S_2$/NF. The activity rises in the beginning and then drops as the dopant concentration increases. The Tafel slopes of plasma-doped Ti500-MoS$_2@Ni_3S_2$/NF (Figure S24b, Supporting Information), Zr500-MoS$_2@Ni_3S_2$/NF (Figure S25b, Supporting Information), N1.0-MoS$_2@Ni_3S_2$/NF (Figure S26b, Supporting Information), Cr$_{500}$-MoS$_2@Ni_3S_2$/NF (Figure S27b, Supporting Information), and C$_{1.0}$-MoS$_2@Ni_3S_2$/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 Ti$_{250}$-MoS$_2@Ni_3S_2$/NF, Zr$_{250}$-MoS$_2@Ni_3S_2$/NF, Cr$_{250}$-MoS$_2@Ni_3S_2$/NF, C$_{2.0}$-MoS$_2@Ni_3S_2$/NF, and N$_{4.0}$-MoS$_2@Ni_3S_2$/NF are 121.2, 135.3, 151.4, 147.2, and 117.7 mV dec$^{-1}$ and not as good as that of the original MoS$_2@Ni_3S_2$/NF (164.7 mV dec$^{-1}$). Hence, the proper amount of dopants is crucial to the HER performance. Moreover, the $\eta_{10}$ values of Ti$_{500}$-MoS$_2@Ni_3S_2$/NF, Zr$_{500}$-MoS$_2@Ni_3S_2$/NF, Cr$_{500}$-MoS$_2@Ni_3S_2$/NF, C$_{1.0}$-MoS$_2@Ni_3S_2$/NF, and N$_{1.0}$-MoS$_2@Ni_3S_2$/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 Ti$_{250}$-MoS$_2@Ni_3S_2$/NF (Figure S24c, Supporting Information), Zr$_{250}$-MoS$_2@Ni_3S_2$/NF (Figure S25c, Supporting Information), N$_{4.0}$-MoS$_2@Ni_3S_2$/NF (Figure S26c, Supporting Information), Cr$_{500}$-MoS$_2@Ni_3S_2$/NF (Figure S27c, Supporting Information), and C$_{0.5}$-MoS$_2@Ni_3S_2$/NF (Figure S28c, Supporting Information), respectively. In addition, comparison of $\eta_{20}$ at the larger current density (20 mA cm$^{-2}$) shows the same trend as that at 10 mA cm$^{-2}$. The overpotential of the original MoS$_2@Ni_3S_2$/NF is higher than that of the plasma-doped catalysts, and the overpotential of the Ag and Ti plasma-doped catalyst is smaller than those of the other samples, indicating that plasma doping improves the catalytic activity of MoS$_2$. The electrochemical surface area (ECSA) is derived from the CV curves (Figures S29 and S30, Supporting Information). The electric double layer capacitance (EDLC) of Ag$_{500}$-MoS$_2@Ni_3S_2$/NF is 34.6 mF cm$^{-2}$ (Figure 4g) which is significantly bigger than those of MoS$_2@Ni_3S_2$/NF (9.1 mF cm$^{-2}$), Ag$_{250}$-MoS$_2@Ni_3S_2$/NF (11.3 mF cm$^{-2}$), and Ag$_{1000}$-MoS$_2@Ni_3S_2$/NF (24.7 mF cm$^{-2}$). The large EDLC demonstrates that Ag$_{500}$-MoS$_2@Ni_3S_2$/NF has a larger electrochemically active area for HER and more active sites. The EDLCs of the other electrodes with different dopant concentrations are shown in Figure S31, Supporting Information. The EDLCs of Zr$_{500}$-MoS$_2@Ni_3S_2$/NF, Cr$_{500}$-MoS$_2@Ni_3S_2$/NF,
Figure 4.

a) Schematic diagram showing the preparation of plasma doped MoS₂ and HER characteristics on MoS₂@Ni₃S₂/NF doped with different elements; b) LSV curves; c) overpotentials; d) Tafel plots; HER characteristics of Ag-doped MoS₂@Ni₃S₂/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 MoS₂@Ni₃S₂/NF; k) Comparison of polarization curves.
Ti500-MoS2@Ni,S/NF, C1.0-MoS2@Ni,S/NF, and N1.0-MoS2@Ni,S/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 > C > 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 chronocoulometry and cyclic voltammetry (CV). As shown in Figure 4j, compared to Ag1000-MoS2@Ni3S2/NF and Ag250-MoS2@Ni,S/NF with too much or too little Ag dopants, the Ag500-MoS2@Ni,S/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@Ni,S/NF shows negligible loss in the polarization current density after 5000 cycles and compared with the Tafel slope and EIS data of the initial electrode, the results are similar (Figure 4k and Figure S32, Supporting Information) confirming that Ag500-MoS2@Ni3S2/NF exhibits excellent catalytic stability. Chronoamperometry is also performed on Zr-doped MoS2@Ni3S2/NF, Ti-doped MoS2@Ni,S/NF, Cr-doped MoS2@Ni,S/NF, C-doped MoS2@Ni,S/NF, and N-doped MoS2@Ni,S/NF for HER (Figure S33, Supporting Information). A fluence of 5 × 10\(^{16}\) ions cm\(^{-2}\) shows the best stability and the current density retention is basically close to 90% after cycling for 30 h, for example, Zr500-MoS2@Ni,S/NF (97.1%), Ti500-MoS2@Ni,S/NF (88.9%), and Cr500-MoS2@Ni,S/NF (89.3%). The electrodes implanted with a fluence of 2.5 × 10\(^{16}\) ions cm\(^{-2}\) has the worst catalytic stability and the current density retention is only 80%, for instance, Zr250-MoS2@Ni,S/NF (83.3%), Ti250-MoS2@Ni,S/NF (78.8%), and Cr250-MoS2@Ni,S/NF (84.7%). For the non-metallic plasma-doped samples, the samples treated for one hour show 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@Ni,S/NF and N1.0-MoS2@Ni,S/NF are maintained at more than 90% of the initial value, but that of N4.0-MoS2@Ni,S/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 (\(\Delta G_{\text{H^*}}\)) between adsorption and desorption of H\(^{\text{a}}\) on the electrode surface is a key parameter to predict the HER activity and the closer \(\Delta G_{\text{H^*}}\) is to zero, the higher is the HER efficiency.\(^{42,47,48}\) Therefore, \(\Delta G_{\text{H^*}}\) for H\(^{\text{a}}\) adsorbed on the plasma-treated MoS2 surface is first evaluated because H\(^{\text{a}}\) tends to adsorb onto the sulfur (S) sites.\(^{49,50}\) The supercell with the 3 × 3 unit cell top- and side-view H\(^{\text{a}}\) adsorption above the S sites is shown in Figure 5a,b. In the first-principles calculation, H\(^{\text{a}}\) adsorbed on the S sites of the Cr-, Ti-, Zr-, Ag-, Cu-, C-, and N-doped MoS\(_2\) 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 MoS\(_2\) are depicted in Figure 5c,d, respectively, and the calculated \(\Delta G_{\text{H^*}}\) values of the series of MoS\(_2\) samples implanted with different elements are shown in Figure 5e. In order to exclude the surface of Ag-Ni, S\(_x\) as potential active sites, we also calculated the hydrogen adsorption energy on its (110) and (202) surfaces, respectively, and compared them with the hydrogen adsorption energy calculated on the Ag-MoS\(_2\) surface (Figure S35, Supporting Information), which demonstrated that the catalytic activity on the surface of Ag-MoS\(_2\) is better, and it is more reasonable as the active site. \(\Delta G_{\text{H^*}}\) of 22% Ag-doped MoS\(_2\) is closer to zero than the other samples, especially pure MoS\(_2\) (~1.88 eV), indicating that plasma doping can indeed raise the HER activity of the S sites on the basal surface. There is a relationship between \(\Delta G_{\text{H^*}}\) of MoS\(_2\) doped with transition metals (Ag, Cu, Ti, Zr, Cr) and the number of valence electrons of the dopants. The smaller the number of valence electrons, the lower is \(\Delta G_{\text{H^*}}\) at this site, implying that metal dopants can more effectively activate S at the replacement sites. The effects of impurity atoms on valence electrons are also revealed by the density of states (DOSs) in Figure 5f. The valence band of pure MoS\(_2\) is full and the valence orbital of the S atom is saturated. Therefore, it is difficult for H\(^{\text{a}}\) to adsorb to the S site thereby giving rise to a larger \(\Delta G_{\text{H^*}}\).\(^{51}\)

When dopants with less valence electrons than Mo are incorporated, empty states emerge from the valence band and the smaller the number of valence electrons, the larger is the number of empty states. Accordingly, as shown by the DOS of S atoms in the plasma-treated MoS\(_2\) in Figure 5f, introduction of metal dopants with less electrons makes the valence orbitals of S atoms unsaturated and the empty states in the valence orbitals also increase, so that it is relatively easy for H\(^{\text{a}}\) to adsorb to the active sites of S and \(\Delta G_{\text{H^*}}\) is closer to zero. In contrast, Cr has the same valence electrons as Mo and so \(\Delta G_{\text{H^*}}\) of Cr-doped MoS\(_2\) is similar to that of pure MoS\(_2\). Regarding non-metallic dopants, N doping produces empty states in the valence orbitals of S leading to a lower \(\Delta G_{\text{H^*}}\) than undoped MoS\(_2\), whereas C doping does not produce empty states in the valence band and consequently a large \(\Delta G_{\text{H^*}}\).

Structural strain is also an important factor for \(\Delta G_{\text{H^*}}\), 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) is larger than the Mo–S bond length (2.42 Å) before H adsorption on S, leading to stretch strain in the bond between the impurity atom and S. As shown in Figure 5h, the bond length between the Ag atom directly connected to the H\(^{\text{a}}\)-adsorbed S atom increases from 2.59 to 3.00 Å, while the other Ag–S bond length decreases from 2.59 to 2.55 Å, implying that H adsorption releases this strain and therefore lowers \(\Delta G_{\text{H^*}}\). \(\Delta G_{\text{H^*}}\) in Figure 5e corresponds to adsorption of one H atom on one S atom which directly bonds with impurity metal atoms as shown in Figure 5d,h. \(\Delta G_{\text{H^*}}\) at the S site that does not bond with metal atoms is higher than zero (Figure S36, Supporting Information), meaning that the S site that directly bonds with the impurity atom is the active site for hydrogen evolution, while the S site far away from the impurity atom is basically inactive. Therefore, the S atoms that do not bond with the metal atoms will not be discussed in the following section.

It has been shown that the dopant concentration in the catalyst plays an important role in adjusting \(\Delta G_{\text{H^*}}\).\(^{54}\) Figure 5e displays the \(\Delta G_{\text{H^*}}\) values of C, N, Ti, Zr, Ag, and Cu plasma-doped MoS\(_2\) for concentrations of 11, 22, and 33 mol%. As the dopant concent-
Figure 5. a) Optimized structure of H* adsorption on bare MoS2(002); Top views of H* adsorption on b) bare MoS2; c) N–MoS2, and d) Zr–MoS2; e) Calculated ΔG_{H*} of MoS2 doped with different elements; f) DOS of S sites on MoS2 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-MoS2; k–n) Top-view schematic of different H* coverages on 22 mol% Ag-MoS2.

As the dopant concentration increases from 11 to 33 mol%, ΔG_{H*} approaches zero initially and then increases, especially Ag, Cu, Ti doped MoS2, 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%, ΔG_{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 MoS2 with concentration of 11% and 22%, the ΔG_{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, ΔG_{H*} for additional H atom adsorption for 11 mol% H coverage and ΔG_{H*} for second H* adsorption after one H* has already adsorbed to the 3 × 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, ΔG_H* is defined as follows: \( \Delta G_{H^*} = E_{surf+H^*} - (E_{surf+H^*} + 0.5E_{H2}) + 0.24 \text{eV} \), where \( E_{surf+H^*} \) is the total energy of the supercell with one adsorbed H* and \( E_{surf+2H^*} \) is the total energy of the supercell with two adsorbed H*.[55] 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 ΔG_H* for second H* adsorption is only −0.18 eV. With increasing H coverage from 11 to 22%, ΔG_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 ΔG_H* of the second H*. ΔG_H* for adsorption of the second H* atom increases compared to that for the first H*. Remarkably, ΔG_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 atom 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 ΔG_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@Ni₃S₄/NF is also assessed in the same alkaline electrolyte. Figure S38a, Supporting Information, shows the polarization curves of Ag500-MoS₂@Ni₃S₄/NF, Zr500-MoS₂@Ni₃S₄/NF, N1.0-MoS₂@Ni₃S₄/NF, Ti500-MoS₂@Ni₃S₄/NF, C1.0-MoS₂@Ni₃S₄/NF, bare MoS₂@Ni₃S₄/NF and corresponding Tafel slopes and overpotentials are shown in Figure S38b, Supporting Information. Compared with other electrodes, the Ag500-MoS₂@Ni₃S₄/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@Ni₃S₄/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 curve 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 Ni1.0-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 fluences 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. \(\Delta G_{\text{H\*}}\) 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 \(\times\) 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.

**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 determined using 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. The electrocatalytic tests were performed using the three-electrode configuration of 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 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\(d\)) 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 (\(\Delta G_{\text{H\*}}\)) between adsorption and desorption of H atoms on the electrode surface. The closer \(\Delta G_{\text{H\*}}\) is approaching zero, the higher is the HER efficiency. To investigate how \(\Delta G_{\text{H\*}}\) on MoS2 surface varies with the different dopants (C, N, Cr, Ti, Zr, Ag, and Cu), \(\Delta G_{\text{H\*}}\) and H coverage was derived by first-
principles calculation (Supporting Information). The MoS₂ surface was modeled with a supercell with 3 × 3 surface unit cell (Figure S34, Supporting Information). If only the last step of the reaction was considered and the desorption state of H₂ 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. ΔG_H₂ is defined as ΔG_H₂ = E_{surf+H₂} - (E_{surf} + 0.5E₀H₂) + 0.24 eV[25,26] where E_{surf} is the total energy of the supercell without any adsorbed H atom, E_{surf+H₂} is the total energy of the supercell with an adsorbed H atom, E₀H₂ is the binding energy of a H₂ 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.[39]

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.

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Research data are not shared.

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