Atomically Dispersed Platinum Modulated by Sulfide as an Efficient Electrocatalyst for Hydrogen Evolution Reaction

Kai Ling Zhou, Chang Bao Han,* Zelin Wang, Xiaoxing Ke, Changhao Wang, Yuhong Jin, Qianqian Zhang, Jingbing Liu, Hao Wang,* and Hui Yan

Catalytically active metals atomically dispersed on supports presents the ultimate atom utilization efficiency and cost-effective pathway for electrocatalyst design. Optimizing the coordination nature of metal atoms represents the advanced strategy for enhancing the catalytic activity and the selectivity of single-atom catalysts (SACs). Here, we designed a transition-metal based sulfide-Ni$_3$S$_2$ with abundant exposed Ni vacancies created by the interaction between chloride ions and the functional groups on the surface of Ni$_3$S$_2$ for the anchoring of atomically dispersed Pt (Pt$_{SA}$-Ni$_3$S$_2$). The theoretical calculation reveals that unique Pt-Ni$_3$S$_2$ support interaction increases the $d$ orbital electron occupation at the Fermi level and leads to a shift-down of the $d$-band center, which energetically enhances H$_2$O adsorption and provides the optimum H binding sites. Introducing Pt into Ni$_3$S$_2$ system can efficiently enhance electronic field distribution and construct a metallic-state feature on the Pt sites by the orbital hybridization between S-3p and Pt-5d for improved reaction kinetics. Finally, the fabricated Pt$_{SA}$-Ni$_3$S$_2$ SAC is supported by Ag nanowires network to construct a seamless conductive three-dimensional (3D) nanostructure (Pt$_{SA}$-Ni$_3$S$_2$@Ag NWs), and the developed catalyst shows an extremely great mass activity of 7.6 Amg$^{-1}$ with 27-time higher than the commercial Pt/C HER catalyst.

1. Introduction

The noble-metals based catalysts play significant roles in renewable energy utilization, storage, and conversion,$^{[1,2]}$ and have been widely used to drive the various catalytic reactions including nitrogen reduction reaction,$^{[3,4]}$ hydrogen evolution reaction (HER),$^{[5,6]}$ oxygen evolution reaction,$^{[7,8]}$ and the oxygen reduction reaction.$^{[9,10]}$ However, the high cost caused by scarcity hinders the widespread application of these catalysts. Single-atom catalysts (SACs), with atomically distributed noble-metal on supports equipped with extremely high specific activity and significantly large atom utilization efficiency, have attracted considerable attention.$^{[11]}$ The electrochemical activity of single-atom sites highly depends on the chemical and physical properties of the SACs, and specifically, the microenvironments of the single atom, including geometric construction and electronic coordination are extremely critical in determining the performances of the catalysts.$^{[12,13]}$ Therefore, exploring and understanding the structure-activity relationship of the single-atom in SACs is imperative from the aspects of materials synthesis and reaction mechanism.

For the SACs, the strong interaction between the metal atoms and support is required to avoid the formation of aggregated clusters and particles by considering the stability.$^{[14,15]}$ However, the strong metal-support interaction will result in a large charge loss of metal atoms, and gift a cation-like positive electrons states to the metal atom.$^{[16,17]}$ These high-valence metal atoms are more favorable for electro-oxidation reactions rather than electroreduction processes due to the less $d$ orbital electrons of SACs involved in the reaction.$^{[13]}$ Recently, the metal atoms with low-coordinated electrons transfer and the close-to-zero valence state resembling a metallic-state atom were designed by anchoring Pt on the specific site of N-C framework and exhibited a superior activity for electroreduction reactions.$^{[18]}$ Whereas, the application of such metallic-state atoms is embarrassed due to the unaccessible fabrication approach and unsatisfied durability. Further, the local electron distribution around metal sites and $d$-band position of SACs is sensitive to the electron interaction between the metal atom and support.$^{[16,17]}$ and especially, the locally enhanced electron density on the single-metal sites induced by appropriate metal-support interaction has been expected to efficiently accelerate the catalytic reaction kinetics toward HER.$^{[19,20]}$ Nevertheless the development of such unique electronic field distribution feature in SACs are extremely sluggish due to the lack of suitable...
support. Therefore, it is challenging but significant to fabricate the metallic-state single atoms in the catalyst with the optimized d orbital structure and locally enhanced electronic field distribution by increase the local electron density on the metal atoms for satisfactory HER by considering the stability. Apart from the electronic structure factors, the catalytic activity of SACs is also extremely limited by low exposure efficiency of metal atoms sites and inefficient electronic supply ability due to the introduction of insulating binder (e.g., Nafion and polytetrafluoroethylene) in electrode framework,[13,14,19,21,22] leading to the inefficient conversion of the adsorbed hydrogen (M-H_ads) to H₂ in the Heyrovsky or Tafel step.[23–27] Interesting, architectural nanostructure engineering, in the non-noble metal catalysts field, provides an appealing platform to realize a seamlessly conductive system by integrating active materials on current collectors.[28,29] Inspired by the above, the integration of electronic structure adjustment strategy and architectural nanostructure engineering may provide some new avenues and insights for the design of highly efficient SACs.

Here, by combining theoretical simulation techniques, we design a transition-metal sulfide-Ni₃S₂, with abundant exposed Ni vacancies created by the interaction between chloride ions and the functional groups on the surface of Ni₃S₂, to anchor atomically dispersed Pt for efficiently electrocatalytic hydrogen evolution. Specifically, the Pt atoms undergo a redistribution in the local electronic structure after coordinating with Ni₃S₂ support and lead to a locally enhanced electronic field distribution by increasing the electron density on the top of Pt sites. Meanwhile, metallic-state single Pt atoms are obtained by the orbital hybridization between S-3p and Pt-5d after introducing Pt into Ni position in the Ni₃S₂ system for improved reaction kinetics. Moreover, Pt-Ni₃S₂ support interaction increases the d orbital electron occupation at the Fermi level and leads to a shift-down of the d-band center, which energetically enhances H₂O adsorption and provides the optimum H binding sites. By considering the superiority of architectural nanostructure, Ni₃S₂ toiled Pt single atom is integrated on Ag nanowires network (Pt₅A::Ni₃S₂@Ag NWs) to form a seamlessly conductive nanostructure for the more facile generation and release of H₂. As such, the designed Pt₅A::Ni₃S₂@Ag NWs demonstrate outstanding HER performance with 27-fold higher mass activity than the commercial Pt/C catalyst and long-term durability with 5000 cycles or 30 h.

2. Results and Discussion

First, theoretical investigations were carried out to elucidate the hidden mechanisms of Ni₃S₂ tailored Pt single atom on the electronic structure and HER process of catalyst. According to the optimized crystal structures (Figure S1, Supporting Information), the formation energy of Pt immobilized at surface Ni positions in Ni₃S₂ is −0.33 eV, significantly lower than that at S positions (7.83 eV), bottom Ni site (−0.23 eV), and surface S–S bridge site (−0.26 eV) in Ni₃S₂, suggesting the preference of surface cation occupancy of incorporated Pt. From the charge density difference analysis, the replacement of Ni site by Pt atom causes the redistribution of the local electrons around the Pt site by metal-support coordination due to the different electronegativity among Pt (2.2), S (2.5), and S (2.5) (Figure 1a,b; and Figures S2 and S3, Supporting Information), leading to a locally aggregated electrons area on the top of Pt site (Figure 1c), which is more favorable for boosting HER kinetics.[19] The electrons redistribution could affect the partial density of states (PDOS) of the SACs. Compared with the Ni₃S₂ system, the total DOS (of single-atom Pt immobilized Ni₃S₂) show a higher electronic occupied state near the Fermi level (Figure 1d; and Figure S4, Supporting Information), leading to the higher intrinsic electrical conductivity and larger carrier concentration. Specifically, the improved DOS of the Pt₅A::Ni₃S₂ near the Fermi level mainly derives from the contribution of the Pt 5d orbitals electrons (Figure S5, Supporting Information), suggesting the strong orbital hybridization between S-3p and Pt-5d after introducing Pt into Ni position in the Ni₃S₂ system. Besides, the Pt-5d band in Ni₃S₂ shows a substantially wide range for overlapping with H-1s and H₂O-2pσ orbitals (Figure 1e). Meanwhile, the surface Ni-3d band also exhibits optimal overlapping with H-1s and H₂O-2pσ orbitals. Therefore, the anchored single-atom Pt site plays a protecting role for stabilizing the Ni valence state against corrosion, and also acts as a distributing role for reducing the deactivation of reaction sites by binding H and O species under over-binding of intermediates on the Ni-sites.[30] Further, the reactants-support interaction in Pt₅A::Ni₃S₂ system was explored by performing the d-band center model, and the Pt₅A::Ni₃S₂ shows the lowest d-band center (−1.40 eV, Figure 1f) comparing with that of Ni₃S₂ (−1.22 eV) and V₅A::Ni₃S₂ (−1.26 eV), which could efficiently reduce the adsorption energy and meanwhile promote the desorption ability for H atoms on the catalyst surface.[31,32] Besides, the metal-support interactions could be quantified by performing Bader charge analysis of the Pt atom (Figure 1g), and the charge transfer (absolute value of Bader charge value) between Pt atom and Ni₃S₂ support is only 0.017 e, much smaller than 0.044 e for Pt foil and ever lower than that of reported SACs recently (Table S2 (Supporting Information), 0.188 e for Pt₅A in CoSe₂, 0.32 e for Pt₅A in Co(OH)₂, 0.23 e for Pt₅A in C₆N₄, and 0.47 e for Pt₅A in Co(OH)₂, which suggests a metallic electron state for Pt atom anchoring in Ni₃S₂ support, leading to an extremely active catalytic property for HER.[11,18] From all of the above, the increased electrons occupation near Fermi level, locally enhanced electrons density distribution on the top of Pt sites and shift-down of the d-band center deriving from the metallic-state Pt induced by the orbital hybridization between S-3p and Pt-5d after introducing Pt into Ni position in Ni₃S₂ system are expected to optimize the reactant binding energy and promote the reaction kinetics for HER.

Thus, based on the optimized electronic structure of Pt₅A::Ni₃S₂ as the above analysis, the potential HER activity is predicted. Generally, the HER pathway consists of three main steps comprising the initial water adsorption H₂O*, the generated intermediate H⁺ as well as final molecular H₂ (Figure 1h). The free energy (ΔG_H₂ in hydrogen atom adsorption is a reasonable descriptor to estimate HER activity for various catalysts. According to the density functional theory (DFT) calculation, the ΔG_H₂ of Pt₅A::Ni₃S₂ (~0.06 eV) are closer to 0 eV than that of Ni₃S₂ (0.49 eV), Pt foil (~0.10 eV), and recently reported SACs (Table S2, Supporting Information), benefiting from the promoted electrons occupation near Fermi level, down-shift d-band center as well as local-enhance electrons density on Pt site due to the orbital hybridization between S-3p and Pt-5d after introducing Pt into Ni position in Ni₃S₂ system as above discussion. In the alkaline condition, the water molecular splitting kinetics from the
Figure 1. Theoretical investigations. a) Top view of the computational model of PtSA–Ni3S2. b) The local electron density distribution on the Pt site in the PtSA–Ni3S2 system and the isosurface value is 0.0014 e Å\(^{-3}\). c) Two-dimensional (2D) isosurface map of the cross-section consisting of Pt, S, and S atoms in PtSA–Ni3S2 with a unit of e Å\(^{-3}\). d) Calculated PDOS of PtSA–Ni3S2, PtSA–Ni3S2, and Pt foil with aligned Fermi level \(E_F\). e) The \(d\)–\(p\) orbital alignment of the surface Pt, Ni sites for PtSA–Ni3S2. f) Calculated \(d\)-band center \((E_d)\) of Ni3S2, PtSA–Ni3S2, VNi–Ni3S2, and Pt foil. g) Bader charge numbers of Pt atom in PtSA–Ni3S2 and Pt foil. h) The free energy diagram of \(H_2O\) and \(H\) adsorbing on the surface of PtSA–Ni3S2, Ni3S2, and Pt foil.

Volmer step (step 2 in Figure 1h) determine the overall HER rate. Based on the DFT simulation, PtSA–Ni3S2 shows more favorable \(H_2O\) adsorption with \(-0.67\) eV comparing with Ni3S2, Pt foil, and recently reported SACs (Table S2, Supporting Information), and the improved \(H_2O\) adsorption on PtSA–Ni3S2 site derives from the more \(d\) electrons as the real active centers of catalyst contributed by metallic-state Pt \(5d\) orbital (Figure 1g; and Figure S5, Supporting Information).\(^{[13]}\) Thus, transition-metal based sulfide-Ni3S2 immobilized Pt single atom provides an efficient approach to modulate the electronic structure of SACs and is predicted to show the most outstanding HER catalytic activity.

Experimentally, we designed Ni3S2 immobilized Pt single-atom catalyst with a 3D cable-shape structure on cloth fiber-loaded Ag NWs support (PtSA–Ni3S2@Ag NWs) by a four-step route illustrated in Figure 2a, in which Pt atoms immobilized at Ni positions in Ni3S2 is realized by Ni vacancies creation and subsequent Pt single atom anchoring. In detail, metal Ni was electrodeposited on Ag NWs by chronoamperometry method (Figure S6, Supporting Information). Then, the Ag NW supported Ni was converted into Ni3S2 (Ni3S2@Ag NWs) by the selective sulfuration process in Thioacetamide (TAA) aqueous solution. Finally, the formation of Ni vacancies and single-atom Pt...
immobilization was performed by an electrochemical process with 400 cyclic voltammetry between 0 and −0.4 V in 1 M KOH solution with 50 × 10⁻⁶ M PtCl₆²⁻.

The X-ray diffraction (XRD) patterns (Figure 2b) confirm the phase evolution of metallic Ni to Ni₃S₂, and the diffraction peaks of Pt₃SA-Ni₃S₂ @ Ag NWs mainly derive from Ni₃S₂ and metallic Ag. The absence of Pt characteristic peaks implies the single-atom distribution of Pt instead of nanoparticles or clusters in Ni₃S₂. Scanning electron microscopy (SEM, Figure 2c; and Figure S7, Supporting Information) suggests the densely packed Pt₃SA-Ni₃S₂ nanoparticles uniformly grow on Ag NWs to form a seamless contact nanoarchitecture via sulfuration and subsequent electrochemical process, which shows a different appearance with bare Ag NWs (Figure S8, Supporting Information) and Ni coated Ag NWs (Figure S9, Supporting Information). Further, the Pt₃SA-Ni₃S₂ @ Ag NWs were characterized by transmission electron microscopy (TEM), and a distinct cable-shape configuration is presented (Figure S10a, Supporting Information). Besides, interconnected pores were observed in the Pt₃SA-Ni₃S₂ shell layer (Figure S10b, Supporting Information), which is favorable for hydrogen generation and release. The high-resolution TEM (HRTEM, Figure 2d) image of Pt₃SA-Ni₃S₂ @ Ag NWs demonstrates well-resolved lattice fringes with 0.20 and 0.24 nm, corresponding to the exposed (202) and (003) crystallographic plane of Ni₃S₂, respectively. The derived fast Fourier transform (FFT) image (the inset in Figure 2d) also shows the related crystallographic plane of (101), (003), (202), and (015) from the Ni₃S₂ phase, suggesting the surface coupling of Pt-support does not change the crystal structure of Ni₃S₂.

The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image presents uniformly dispersed bright spots on the Ni₃S₂ substrate (Figure 2e), corresponding to the heavy constituent atoms anchoring in Ni₃S₂, which verifies the formation of single-atom Pt species. Furthermore, the atomic-resolution HAADF-STEM (Figure 2f; and Figure S10c,d, Supporting Information) demonstrates that the Pt
atoms are fixed in Ni₃S₂. Subsequently, a STEM simulation based on the DFT-optimized structure was performed to verify the microstructure of single-atom Pt immobilized Ni₃S₂ (Figure 2g,h). The simulated result suggests that the single Pt atoms were anchored in the sites of Ni vacancies by binding with the nearest S atoms in Ni₃S₂ support. The corresponding energy-dispersive spectroscopy (EDS) mapping analysis corroborates well the uniform dispersion of Pt atoms throughout the Ni₃S₂ (Figure 2i–l; and Figure S11, Supporting Information). While increasing the electrodeposition cyclic voltammetry (CV) cycle to 500 will result in the formation of Pt nanoclusters during the Pt immobilization process (PtNC-Ni₃S₂@Ag NWs, Figures S12–S14, Supporting Information), suggesting the continuous deposition of Pt atoms during the repeated polarization scanning, and the optimal HER catalytic performance could be obtained.

The corresponding mechanism was unraveled by theoretical investigations and experimental characterization. As shown in Figure 3a, the formation of Ni vacancies and Pt single atoms anchoring results from the facilitation of electrochemical reaction in alkaline media altering the chemical composition of Ni₃S₂@Ag NWs surface. Based on the theoretical calculation, the Ni-terminated Ni₃S₂ provides the optimal site for water absorption (Figure 3b; and Figure S15, Supporting Information) and hydrogen evolution (Figure S16, Supporting Information). By capturing electrons, the Ni-terminated basal planes are capable to reduce water into H₂, and the generated −OH was grafted to the Ni terminal by the Ni−O band, causing the formation of Ni−OH intermediate confirmed by X-ray photoelectron spectroscopy (XPS) (Figure 3b). Further, the following reactions on Ni−OH intermediate include two possible routes. One is the restoration of Ni−OH intermediate to the original Ni−Ni₃S₂ terminal by the deabsorption of the −OH due to the weak binding between Ni and −OH comparing with the strong Ni−S bond. Another route involves the local corrosion of low-valence Ni in Ni−OH intermediate supported by Ni₃S₂ induced by the chloride ions originating from PtCl₆²⁻ in alkaline media to form high-valence Ni²⁺−OH due to the strong depassivation ability and penetrating performance of Cl⁻ ions. Subsequently, by combining OH⁻ ions, the Ni²⁺−OH intermediate was transformed to the metal hydroxide Ni(OH)₂ in the alkaline electrolyte to form a chemistry-stable OH−Ni−OH leaving group. Consequently, the Ni vacancies on the surface of the Ni₃S₂ (VNi−Ni₃S₂) were created for subsequent
immobilization of Pt atoms. X-ray near-edge absorption spectra (XANES) for Ni K edge of \( V_{\text{Ni}}-\text{Ni}_3\text{S}_2 \) are depicted in Figure S17a (Supporting Information) and show that the white line intensity of \( V_{\text{Ni}}-\text{Ni}_3\text{S}_2 \) is lower than that of NiO, but higher than that of the pure \( \text{Ni}_3\text{S}_2 \). This proves that Ni atoms in \( V_{\text{Ni}}-\text{Ni}_3\text{S}_2 \) are positively charged, implying Ni vacancies formation. By Bader charge analysis deriving from DFT calculation (Figure S17b, Supporting Information), the average charge value of Ni atoms in \( V_{\text{Ni}}-\text{Ni}_3\text{S}_2 \) (+0.28 e) is higher than that of Ni atoms in \( \text{Ni}_3\text{S}_2 \) (+0.10 e), further implying the increased degree of nickel oxidation state and Ni vacancies formation. As shown in the HAADF-STEM (Figure 3c; and Figure S17c, Supporting Information) image, after the same electrochemical process with Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \)@Ag NWs but replacing PtCl\(_6\)\(^{2-}\) by NaCl in KOH solution to avoid the deposition of Pt species, the obtained Ni\(_3\text{S}_2 \) shows a large number of Ni vacancies (\( V_{\text{Ni}}-\text{Ni}_3\text{S}_2 \)). By comparing the STEM results of Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \)@Ag NWs and \( V_{\text{Ni}}-\text{Ni}_3\text{S}_2 \)@Ag NWs, the Pt atoms are finely anchored in the sites of Ni vacancies. Combining the analysis in theoretical investigations (Figure 1e), the anchored Pt atoms at Ni positions under cathodic potential will protect adjacent Ni against corrosion. Consequently, a stable single-atom Pt-Ni\(_3\text{S}_2 \) support system could be obtained. Besides, the release of reduced H\(_2\) will serve as the dynamic template to generate interconnected pores in the Ni\(_3\text{S}_2 \) layer, leading to more accessible basal planes for Ni vacancies defects creation and Pt atoms immobilization.

Further, the electronic states of Pt atoms in Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \) were verified by XPS, X-ray absorption near-edge spectroscopy (XANES), and extended X-ray absorption fine spectroscopy (EXAFS) measurements. The binding energy in high-resolution Pt 4f XPS spectra (Figure 4a) shows a slightly positive shift for Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \) compared to Pt foil. Moreover, the Ni 2p and S 2p XPS peaks show an apparent evolution in the binding energy after Pt anchoring (Figure S18, Supporting Information), suggesting a weak electron transfer between Pt atoms and Ni\(_3\text{S}_2 \) support. The corresponding electronic states of Pt atoms in Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \) were further explored by XANES measurements (Figure 4b), in which Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \) show slightly enhanced intensity than Pt foil but extremely lower than PtO\(_2\), proving less electron loss of Pt atoms in Ni\(_3\text{S}_2 \) as theoretical calculation in Figure 1g.\(^{[13]}\) The Fourier transform spectrum of the k-weighted EXAFS oscillations of Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \) exhibits a prominent peak in the region 1.8–2.4 Å (Figure 4c), corresponding to the Pt–Cl and Pt–S first coordination shell.\(^{[41,42]}\) The absence of Pt–Pt contribution peaks at about 2.7 Å confirms atomically dispersed Pt in Ni\(_3\text{S}_2 \). The fitting results of the Fourier transform curves give a coordination number of 3 for Pt–S contribution (Figure 4c; and Table S1, Supporting Information). To further verify the coordination conditions of Pt atoms, the wavelet transforms (WT, Figure 4d–f) analysis was performed, which can provide powerful resolution in the radial distance in the \( R \) and \( K \) space. A WT intensity maximum at about 5 and 12 Å\(^{-1}\) are attributed to the Pt–O and Pt–Pt contributions, respectively.\(^{[43]}\) In contrast, the intensity maximum of Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \) near 8 Å\(^{-1}\), assigned to the Pt–S contribution, and the Pt–Pt coordination with an intensity maximum at \( \approx 12 \) Å\(^{-1}\) is not detected, confirming the presence of isolated Pt atoms in Ni\(_3\text{S}_2 \).

Based on the theoretical calculation and structural characterizations, for the first time, we reveal that Ni\(_3\text{S}_2 \) tuned single-atom Pt tends to present a promising activity for HER by the integration of electronic structure adjustment strategy and architectural nanostructure engineering. Experimentally, the electrocatalytic performance of seamlessly conductive Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \)@Ag NWs with 3D architecture for HER was verified in alkaline electrolyte, and the original Ni\(_3\text{S}_2 \)@Ag NWs, Ag NWs, and Ni foam supported commercial Pt/C (Pt/C@Ni foam) were also measured for comparison. Besides, Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \)@Ni foam was fabricated under the same conditions as Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \)@Ag NWs but replacing Ag NWs with Ni Foam. As demonstrated in Figure 5a, the Pt\(_{\text{SA}}\)-\( \text{Ni}_3\text{S}_2 \)@Ag NWs shows the highest HER performance among all catalysts, and only needs 33 and 137 mV to achieve...
the current density of 10 and 150 mA cm$^{-2}$, respectively, suggesting significantly superior activity than the Pt$_{SA}$–Ni$_3$S$_2$@Ni foam, Ni$_3$S$_2$@Ag NWs, Ag NWs, and Pt/C@Ni foam. Even the commercial Pt/C on Ni foam at an overpotential of >80 mV (Figure S19, Supporting Information), in which the decrease of the current density of Pt/C at the high potential should be attributed to the application of Nafion as the binder and poor nanostructure morphology of Pt/C electrode, hindering the rapid generation and release of H$_2$. Besides, the Pt$_{SA}$–Ni$_3$S$_2$@Ag NWs exhibit a similar Tafel slope (34.70 mV dec$^{-1}$) with Pt$_{SA}$–Ni$_3$S$_2$@Ni foam and Pt/C@Ni foam towards HER (Figure S20, Supporting Information), suggesting Pt-like kinetics deriving from the introduction of single-atom Pt. Moreover, the single-atom Pt anchored Ni$_3$S$_2$@Ag NWs also possess higher activity than the Ni$_3$S$_2$@Ag NWs supported Pt particles (Figure S12, Supporting Information) due to the more efficient synergy of the single Pt atom and the Ni$_3$S$_2$ host. Apart from the outstanding metal-support interaction, the Ag NWs are introduced to provide facile electron transport pathways through the entire catalyst, and consequently, the charge transfer resistance ($R_s$) between Pt$_{SA}$–Ni$_3$S$_2$@Ag NWs and reactants (H$_2$O*, M–H$_{ads}$ and H*) reach a significantly low value of 0.95 $\Omega$ (Figure S21, Supporting Information), leading to a faster faradaic reaction.$^{26,27}$ Moreover, Pt$_{SA}$–Ni$_3$S$_2$@Ag NWs exhibits a 5.1-time increase in double-layer capacitance ($C_{dl}$) over Ni$_3$S$_2$@Ag NWs (Figure S22, Supporting Information), suggesting more exposed sites for Pt atoms immobilization and HER due to the formation of a large number of voids in Ni$_3$S$_2$ during Pt anchoring process (Figure S10, Supporting Information). Considering the actual applications, Pt$_{SA}$–Ni$_3$S$_2$@Ag NWs also shows excellent stability with negligible decay in HER activity for 5000 cycles or 30 h (Figure 5b). The corresponding structural measurements including SEM, STEM images, EDS mapping, XRD, and XPS data (Figures S24 and S25, Supporting Information) are performed to confirm the single-atom dispersion and intact structure of Pt$_{SA}$–Ni$_3$S$_2$@Ag NWs after the stability test, suggesting the high stability of Ni$_3$S$_2$@Ag NWs immobilized single-atom Pt by Ni vacancies. Furthermore, the mass activity of Pt$_{SA}$–Ni$_3$S$_2$@Ag NWs normalized to the Pt loading mass (1.47 wt%, measured by inductively coupled plasma-mass spectrometry) at an overpotential of 150 mV is 7.6 A mg$^{-1}$ (Figure 5c), which is 27-fold higher than that of the commercial Pt/C catalyst (20 wt% Pt/C, 0.28 A mg$^{-1}$). As a result, a large hydrogen generation rate was observed at room temperature for Pt$_{SA}$–Ni$_3$S$_2$@Ag NWs (Figure 5d) comparing with Pt$_{SA}$–Ni$_3$S$_2$@Ni foam (Figure 5e) and Pt/C@Ni foam (Figure 5f). Especially, an aggregative H$_2$ cloud was presented on the top of the Pt$_{SA}$–Ni$_3$S$_2$@Ag NWs electrode, indicating the high efficiency of M–H$_{ads}$ generation and facile conversion to H$_2$. Besides, comparing with Ni foam supported commercial Pt/C electrode (Figure 5f) fabricated by using Nafion as the binder, no large bubble absorbs on the surface of Pt$_{SA}$–Ni$_3$S$_2$@Ag NWs electrode, which could be attributed to the shift-down of the $d$-band center (Figure 1f), more optimal $\Delta G_{H^*}$ with $-0.06$ eV than that of Pt foil ($-0.10$ eV, Figure 1h), as well as the formation of abundant voids (Figure 2c; and Figures S10 and S23, Supporting Information) of Ni$_3$S$_2$ immobilized single-atom Pt coating on Ag NWs network for facile desorption and release of H$_2$. To quantify the output...
efficacy of H₂, the turnover frequency (TOF, Note S1, Supporting Information) per Pt atom was performed. As shown in Figure 5g, Pt SA–Ni₃S₂@Ag NWs catalyst shows a high TOF value of 2.91 H₂ s⁻¹, which is 1.6 and 19.4 times higher than that of Pt SA–Ni₃S₂@Ni foam and Pt/C@Ni foam, respectively, demonstrating the extremely high activity of Pt SA–Ni₃S₂@Ag NWs for HER. For the Faradaic efficiency, we roughly collect the H₂ by a drainage method to estimate the experimental gas amount. Faradaic efficiency can be determined by the ratio of H₂ (experimental) to H₂ (theoretical) in a percentage form. To determine the Faradaic efficiency of the Pt SA–Ni₃S₂@Ag NWs hybrid catalyst for HER, the electrolysis was performed in 1 M KOH with an applied constant current density of 100 mA cm⁻² for 100 s. The Faradaic efficiency of about 90% was obtained for HER, indicating that the generated charges were almost consumed for H₂ generation.

As summarized in Table S2 (Supporting Information), our Pt SA–Ni₃S₂@Ag NWs also show superior HER performances than the recently reported SACs, confirming that the improved HER activity of the fabricated Pt SA–Ni₃S₂@Ag NWs mainly derives from the more favorable reconstruction of the electronic-state structure after single-atom Pt anchoring on Ni₃S₂ support.

3. Conclusion

Based on the theoretical simulation, we design a transition-metal sulfide-Ni₃S₂, with abundant exposed Ni vacancies created by the interaction between chloride ions and the functional groups on the surface of Ni₃S₂, to anchor atomically dispersed Pt for efficiently electrocatalytic hydrogen evolution. Specifically, Ni₃S₂ tailored Pt single atom shows a weak metal-support interaction, increasing the d orbital electron occupation near Femi level and shift-down of the d-band center for optimizing the reactants adsorption during HER. The unique coordination environment of Pt sites is constructed by the orbital hybridization between S-3p and Pt-5d after introducing Pt into Ni position in Ni₃S₂ system, inducing a locally enhanced electronic field distribution by increasing the electron density and metallic-state feature on the Pt sites, promoting the electrochemical HER kinetics. By integrating single-atom modification strategy and architectural nanostructure engineering, the fabricated 3D Pt SA–Ni₃S₂@Ag NWs exhibits outstanding HER catalytic activity in terms of high turnover frequencies (2.91 H₂ s⁻¹ at 95 mV) and extremely great mass activity of 7.6 A mg⁻¹, exceeding the commercial Pt/C catalyst and the advanced SACs reported recently. This work presents a new avenue for developing high-activity single-atom electrocatalyst by tailoring the electronic structure and geometrical construction of SACs via transition-metal based sulfides.

4. Experimental Section

Synthesis of Ni₃S₂@Ag NWs: First, an oil bath process was carried out to synthesize Ag nanowires (Ag NWs). In detail, an ethylene glycol solution containing FeCl₃ (7.19 × 10⁻³ M), AgNO₃ (0.051 M), and polyvinylpyrrolidone (0.012 M) was kept at 110 °C for 12 h by oil bath pan. Then, the generated yellow precipitate was collected and washed with acetone and alcohol to obtain Ag NWs. Subsequently, the cleaned Ag NWs were dispersed and stored in an alcohol solution. A conductive network was fabricated by spray coating Ag NWs on a flexible cloth fabric. Finally, the metallic Ni layer is grown on Ag NWs network by a facile electrodeposition process. Specifically, the solution consisting of 0.10 M NiCl₂, 0.09 m H₂BO₃, and a solvent containing ethanol and deionized water with 2.5% in volume ratio. Then the electrodeposition of metallic Ni was performed by chronoamperometry with 1.2 V for 400 s in a standard three-electrode system on a workstation (CHI660E), in which graphite sheet acted as a counter electrode, saturated calomel electrode (SCE) acted as a reference electrode. Finally, the Ag NWs supported metallic Ni was cleaned and dried for stand-by.

Synthesis of Ni₃S₂@Ag NWs: Ni₃S₂@Ag NWs were prepared by performing a hydrothermal treatment on obtained Ni@Ag NWs. In brief, the Ni@Ag NWs coated cloth pieces were immersed in a 50 mL Teflon reaction vessel containing 30 mL of 3 mmol TAA aqueous solution and then kept at 120 °C for 90 min. The obtained samples were cleaned with water and alcohol, and finally drying at room temperature, marking as Ni₃S₂@Ag NWs material.

Synthesis of VNi–Ni₃S₂@Ag NWs: VNi–Ni₃S₂@Ag NWs were fabricated by an electrochemical process in the three-electrode system, in which Ni₃S₂@Ag NWs coated cloth was performed as the working electrode, graphite sheet acted as a counter electrode, SCE acted as a reference electrode. The corresponding electrochemical process was carried out by multicycle cathode polarization in 1 M KOH solution containing 0.5 M NaCl with a scan rate of 50 mV s⁻¹ between 0.00 and −0.50 V versus reversible hydrogen electrode (RHE) for 400 cycles.

Synthesis of Pt SA–Ni₃S₂@Ag NWs: Pt SA–Ni₃S₂@Ag NWs were fabricated by an electrochemical process in the three-electrode system, in which Ni₃S₂@Ag NWs coated cloth was performed as the working electrode, graphite sheet acted as a counter electrode, SCE acted as a reference electrode. The corresponding electrochemical process was carried out by multicycle cathode polarization in 1 M KOH solution containing 50 × 10⁻⁶ m H₂PtCl₆ with a scan rate of 50 mV s⁻¹ between 0.00 and −0.50 V versus RHE for 400 cycles.

Characterizations: The morphology of the fabricated catalysts in this study was observed by SEM (GeminiSEM 300), HRTEM images, HAADF-STEM images, and STEM-EDX mapping images were obtained by a TEM coupled with an energy spectrum analyzer (JEOL JEM2100). The Pt contents in Pt SA–Ni₃S₂@Ag NWs were measured by inductively coupled plasma optical emission spectrometry. The XPS spectra of elements in Pt SA–Ni₃S₂@Ag NWs were tested by a surface analysis system (ESCA-LAB250X). The phase and crystal information of the fabricated catalysts were obtained by Cu Kα radiation in an XRD (Shimadzu). The E-AFS measurement of the Pt SA–Ni₃S₂@Ag NWs at the Pt L₁-edge was performed at 1W1B station at the Beijing Synchrotron Radiation Facility. The cloth-supported Pt SA–Ni₃S₂@Ag NWs were directly subjected to measurements. Data analysis and fitting were performed with Athena and Artemis in the Demeter package.

Electrochemical Measurements: All electrochemical tests were finished by an electrochemical workstation (CHI 660E) with a three-electrode configuration, in which fabricated catalysts in this work were employed as the working electrode, graphite sheet acted as a counter electrode, SCE acted as a reference electrode. All the presented potential in this work was calibrated versus RHE according to the experimental method. HER performance tests were performed in 1 M KOH aqueous solution. Linear sweep voltammograms (LSV) with 95% iR-corrections were tested with a potential range from 0.05 to −0.5 V under a scan rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was obtained by a frequency range from 100 kHz to 0.1 Hz with 200 mV of initial voltage. For the preparation of Pt/C@Ni foam, 5 mg 20 wt% Pt/C was dispersed in 0.9 mL alcohol containing 0.1 mL 5 wt% Nafion solution to form a homogeneous ink. Then, the obtained ink was coated on the Ni foam and dried in air to form a porous Pt/C@Ni foam electrode.

DFT Theoretical Calculations: All the DFT simulations were performed by the Vienna Ab-initio Simulation Package (VASP)[44–45] with the projector-augmented-wave method.[46–47] And the method DFT-D3 developed by Grimme et al.[48,49] was also employed to account for the dispersion correction and van der Waals’ interaction into the conventional Kohn–Sham DFT potential energy calculation. The exchange-correlation energy was described by the Perdew–Burke–Ernzerhof (PBE) implementation of generalized gradient approximation (GGA-PBE).[51] Spin-polarized calculations have been performed with plane wave expansion truncated at
500 eV. 2 x 4 x 1 k-mesh grids were set for the self-consistent field calculation and structural relaxation. Electronic relaxation utilized the conjugate-gradient (CG)\[52\] with the energy convergence being 10-5 eV. Geometry optimization was conducted by using the quasi-Newton algorithm\[33,34\] with residual forces on atoms low than 0.01 eV Å\(^{-1}\). In all calculations, spin polarization was considered. A vacuum region thickness of 20 Å was investigated by comparing the formation energy of different sites. The equation for calculating adsorption enthalpy \(\Delta E_{\text{ads}}\) as the following

\[
\Delta E_{\text{ads}} = E_{\text{slab}+\text{H}} - E_{\text{slab}} - \frac{1}{2} E_{\text{H}_2}
\]

where the \(E_{\text{slab}+\text{H}}\) is the total enthalpy of H adsorbing on the catalysts, the enthalpy of the catalysts is \(E_{\text{slab}}\), the \(H_2\) enthalpy is \(E_{\text{H}_2}\). As similar, the equation for calculating the \(H_2O\) adsorption enthalpy \(\Delta E_{\text{ads2}}\) as the following

\[
\Delta E_{\text{ads}2} = -E_{\text{slab}+\text{H}_2\text{O}} - E_{\text{slab}} - E_{\text{H}_2\text{O}}
\]

The free energy of adsorbed H and \(H_2O\) as follows

\[
\Delta G_{\text{H}} = \Delta E_{\text{H}} + \Delta E_{\text{ZPE}} - T\Delta S
\]

\[
\Delta G_{\text{H}_2\text{O}} = \Delta E_{\text{H}_2\text{O}} + \Delta E_{\text{ZPE}} - T\Delta S
\]

where \(\Delta E_{\text{ads}}\) represent the H adsorption energy and \(\Delta E_{\text{ads2}}\) represent the \(H_2O\) adsorption energy, and \(\Delta E_{\text{ZPE}}\) represents the difference related to the zero-point energy between the gas phase and the adsorbed state.

**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.

**Keywords**

architectural nanostructure engineering, hydrogen evolution reaction (HER), metal-support interaction, single-atom catalysts (SACs), sulfides

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