In situ establishment of Co/MoS$_2$ heterostructures onto inverse opal-structured N,S-doped carbon hollow nanospheres: Interfacial and architectural dual engineering for efficient hydrogen evolution reaction

Tingyu Lu$^1$ | Tongfei Li$^1$ | Desheng Shi$^1$ | Jialin Sun$^1$ | Huan Pang$^2$ | Lin Xu$^1$ | Jun Yang$^{3,4}$ | Yawen Tang$^1$

$^1$Jiangsu Key Laboratory of New Power Batteries, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing, Jiangsu, China
$^2$School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu, China
$^3$Nanjing IPE Institute of Green Manufacturing Industry, Nanjing, Jiangsu, China
$^4$State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China

**Correspondence**
Lin Xu and Yawen Tang, Jiangsu Key Laboratory of New Power Batteries, School of Chemistry and Materials Science, Nanjing Normal University, 210023 Nanjing, Jiangsu, China.
Email: xulin001@njnu.edu.cn and tangyawen@njnu.edu.cn

Jun Yang, Nanjing IPE Institute of Green Manufacturing Industry, 211100 Nanjing, Jiangsu, China.
Email: jyang@mail.ipe.ac.cn

**Funding information**
National Natural Science Foundation of China, Grant/Award Numbers: 21875112, 21972068, 22075290; Qing Lan Project of Jiangsu Province, Nanjing IPE Institute of Green Manufacturing Industry and Beijing Natural Science Foundation, Grant/Award Number: Z200012

**Abstract**
Rational design of low-cost and high-efficiency non-precious metal-based catalysts toward the hydrogen evolution reaction (HER) is of paramount significance for the sustainable development of the hydrogen economy. Interfacial manipulation-induced electronic modulation represents a sophisticated strategy to enhance the intrinsic activity of a non-precious electrocatalyst. Herein, we demonstrate the straightforward construction of Co/MoS$_2$ hetero-nanoparticles anchored on inverse opal-structured N$_x$S$_x$-doped carbon hollow nanospheres with an ordered macroporous framework (denoted as Co/MoS$_2$@N$_x$S$_x$–CHNSs hereafter) via a template-assisted method. Systematic experimental evidence and theoretical calculations reveal that the formation of Co/MoS$_2$ heterojunctions can effectively modulate the electronic configuration of active sites and optimize the reaction pathways, remarkably boosting the intrinsic activity. Moreover, the inverse opal-structured carbon substrate with an ordered porous framework is favorable to enlarge the accessible surface area and provide multidimensional mass transport channels, dramatically expediting the reaction kinetics. Thanks to the compositional synergy and structural superiority, the fabricated Co/MoS$_2$@N$_x$S$_x$–CHNSs exhibit excellent HER activity with a low overpotential of 105 mV to afford a current density of 10 mA/cm$^2$. The rationale of interface manipulation and architectural design herein is anticipated to be inspirational for the future development of efficient and earth-abundant electrocatalysts for a variety of energy conversion systems.
1 INTRODUCTION

With the ever-growing concerns on energy crisis and environmental pollution, extensive attention has been triggered to develop clean and sustainable energy sources to mitigate the overreliance on nonrenewable fossil fuels.\(^1\)-\(^3\) Undoubtedly, hydrogen (H\(_2\)), as a central energy carrier, is identified as the most promising alternative due to its highest gravimetric energy density (143 MJ/kg), perfect renewability, and carbon-free byproduct during the process of H\(_2\) utilization.\(^4\),\(^5\) Among various approaches for hydrogen production, electrochemical water splitting driven by uninterrupted energy resources, such as solar and wind, has been widely established as an eco-friendly and highly efficient avenue to generate high-purity hydrogen.\(^6\)-\(^8\) In order to enable the water electrolysis more energy saving and rapid, an efficient and durable electrocatalyst is prerequisite to accelerate the sluggish kinetics and reduce the overpotential of the cathodic hydrogen evolution reaction (HER, 2H\(^+\) + 2e\(^-\) → H\(_2\)).\(^9\) Hitherto, the state-of-the-art HER electrocatalysts still mainly rely on the precious platinum (Pt)-based nanomaterials.\(^10\),\(^11\) Unfortunately, their prohibitive price, scarce earth abundance, and insufficient durability have greatly hindered the widespread commercial applications in energy conversion devices.\(^12\) To avert these limitations, it becomes urgent and imperative to develop efficient, robust, and affordable alternatives at a practical level to substitute Pt for the future hydrogen economy.\(^13\)-\(^17\)

Over the past several years, tremendous efforts have been continuously devoted to the development of economical, active, and stable earth-abundant HER catalysts, including transition metals (such as Mo, W, Ni, Co, and Fe) and their compounds, spanning from alloys, carbide, nitride, phosphides, to chalcogenides, and so forth.\(^18\)-\(^23\) Among these miscellaneous candidates, molybdenum disulfide (MoS\(_2\)) is a typical 2D layered material composed of S–Mo–S layers that are held together by weak van der Waals forces. It has been well recognized as an attractive nonprecious HER electrocatalyst on account of several fascinating characteristics, for example, easy availability, eco-friendliness, and moderate binding free energy with hydrogen.\(^24\)-\(^26\) Pioneering experimental studies and theoretical calculations have comprehensively elucidated that the exposed edge sites of unsaturated sulfur atoms rather than the basal planes of MoS\(_2\) possess a preferable chemisorption capability for hydrogen in the Volmer process, analogous to Pt-group metals.\(^12\),\(^24\)-\(^27\) Unfortunately, restricted by the poor intrinsic conductivity resulted from the large internal resistance, high sulfur leaching rate, and insufficient exposure of the marginal active sites, the charge-transfer kinetics and available active surface of MoS\(_2\) are greatly suppressed, thus leading to unsatisfied catalytic performance.\(^31\) To circumvent these issues, considerable endeavors have been exerted to optimize the electrochemical performance of MoS\(_2\)-based nanomaterials by augmenting the active sites, improving the intrinsic activity, and enhancing the electrical conductivity. The strategies include nanostructuring, phase engineering, heteroatoms doping, interfacial engineering, and hybridization with conductive substrates, and so on.\(^32\) Among them, the construction of heterostructures is extensively established as a powerful approach to modify the local electronic state of the active site, accelerate the charge transfer rate, facilitate water dissociation, and optimize the adsorption behaviors of reaction intermediates, thus significantly boosting the intrinsic electrocatalytic activity.\(^13\),\(^34\) Particularly, the intimate coupling of MoS\(_2\) with metal species at nanoscale to form metal/semiconductor heterojunctions could effectively induce the electron reconfiguration and vacancy formation between adjacent segments, leading to favorable synergy due to the Mott–Schottky effect.\(^14\),\(^35\)-\(^37\) For example, the establishment of metal/MoS\(_2\) interfaces is conducive to produce H* and OH\(^-\) via accelerating the water dissociation step (H\(_2\)O + e\(^-\) → H + OH\(^-\)) due to the low energy barrier for H adsorption of the metal moiety.\(^38\)-\(^40\) In addition to the aim of the intrinsic activity enhancement, the immobilization of active components onto a nanocarbon substrate could further effectively anchor the active sites and also improve the overall conductivity, significantly reinforcing the long-term stability and improving the electron transfer efficiency.\(^41\) Therefore, nanomaterials of carbon support with a specific geometrical configuration enables to enlarge the number of exposed active sites and facilitate mass transportation, enormously promoting electrocatalytic kinetics. Architecturally, the inverse opal-structured carbon hollow nanospheres with a 3D ordered macroporous framework are of great interest for electrocatalysis in virtue of the prominent structural features, such as periodically interconnected macropore structure, spacious and open internal void, uniform pore size, and large specific surface area.\(^42\) All these merits are collectively conducive to boost the electron transfer
capability, mass diffusion, and electrolyte permeation, ultimately resulting in enhanced electrocatalytic performance.\textsuperscript{31} In light of the above statements, the immobilization of metal/MoS\textsubscript{2} hetero-nanoparticles onto the inverse opal-structured carbon hollow nanospheres is reasonably anticipated to afford satisfactory HER performance.\textsuperscript{15,43,44}

Inspired by the aforementioned considerations, we herein present a feasible SiO\textsubscript{2} template-engaged strategy for the in situ immobilization of Co/MoS\textsubscript{2} hetero-nanoparticles onto inverse opal-structured N,S-doped carbon hollow nanospheres with an ordered porous framework (abbreviated as Co/MoS\textsubscript{2}@N,S–CHNSs hereafter) as a high-performance HER electrocatalyst. The intimate combination of Co/MoS\textsubscript{2} hetero-nanoparticles with N,S-doped hollow carbon nanospheres renders the as-fabricated hybrid catalyst with modified electronic structure, abundant exposed active sites, and promoted mass diffusion/charge transfer. As such, the formed Co/MoS\textsubscript{2}@N,S–CHNSs exhibit excellent electrocatalytic performance for the HER in 1.0 mol/L KOH medium, which is reflected by the low overpotential of 105 mV at a current density of 10 mA/cm\textsuperscript{2}, exceeding most of the previously reported MoS\textsubscript{2}-based HER electrocatalysts. Moreover, the Co/MoS\textsubscript{2}@N,S–CHNSs exhibit highly electrochemical and structural robustness with a negligible attenuation of current density for 11 h of continuous operation and excellent selectivity with a Faradaic efficiency of nearly 100%. Density functional theory (DFT) calculations further verify that the formation of Co/MoS\textsubscript{2} heterojunctions can effectively increase the conductivity, modulate the electronic configuration, and optimize the adsorption free energies for reaction intermediates, leading to considerably boosted HER intrinsic activity.

**RESULTS AND DISCUSSION**

Figure 1 schematically depicts the overall synthetic procedure of Co/MoS\textsubscript{2}@N,S–CHNSs. Briefly, glucose, Co(NO\textsubscript{3})\textsubscript{2}, (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4}, and preformed SiO\textsubscript{2} nanospheres (~130 nm in diameter; Figure S1) are substantially mixed via a facile solid-phase grinding technique in a mortar. The uniform SiO\textsubscript{2} nanospheres are employed as a hard and removable template to precisely define the morphology and size of the final product. Through sufficient grinding, glucose, Co(NO\textsubscript{3})\textsubscript{2}, and (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} are uniformly coated on the surface of SiO\textsubscript{2} nanospheres. Subsequently, the mixed solid precursor undergoes a pyrolysis treatment at 900°C under Ar/H\textsubscript{2} atmosphere. During this annealing step, (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} is decomposed into MoS\textsubscript{2} residue, H\textsubscript{2}S, and NH\textsubscript{3} gases according to the following chemical equation: (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} + H\textsubscript{2} \rightarrow MoS\textsubscript{2} + 2NH\textsubscript{3}↑ + 2H\textsubscript{2}S↑.\textsuperscript{45} Simultaneously, glucose molecules are carbonized into N,S-codoped graphitic carbon in the presence of NH\textsubscript{3} and H\textsubscript{2}S, and Co\textsuperscript{2+} ions are reduced into metallic Co species. Through atomic migration and rearrangement, the generated MoS\textsubscript{2} would combine with Co to form Co/MoS\textsubscript{2} hetero-nanoparticles. Thanks to the space-confinement effect of the voids in SiO\textsubscript{2} opal templates, the overgrowth of Co/MoS\textsubscript{2} hetero-nanoparticles can be greatly suppressed, effectively avoiding the coarsening of active components and thus enlarging the exposure of active sites. Finally, the annealed product is subjected to the leaching treatment by NaOH to completely eliminate the SiO\textsubscript{2} template, leading to the formation of Co/MoS\textsubscript{2} hetero-nanoparticles anchored on inverse opal-structured N,S-doped carbon hollow nanospheres with an ordered macroporous

![Figure 1](https://example.com/figure1.png)
framework. For comparison, a set of controlled samples, including the single component-decorated carbon hollow nanospheres and bare carbon hollow nanospheres, are also synthesized according to the standard protocol, except adjusting the precursor types while the other preparation parameters are kept identical. The absence of Co(NO₃)₂ leads to the generation of N,S-codoped carbon hollow nanospheres decorated with MoS₂ (denoted as MoS₂@N,S–CHNSs; Figure S2). Whereas, the product obtained without the involvement of (NH₄)₂MoS₄ turns out to be carbon nanospheres decorated with Co₃O₄ (denoted as Co₃O₄@CHNSs; Figure S3). The presence of neither Co(NO₃)₂ or (NH₄)₂MoS₄ results in the formation of uniform and regular carbon hollow nanospheres (denoted as CHNSs; Figure S4).

The representative scanning electron microscopy (SEM) images (Figure 2A,B) distinctly illustrate the inverse opal structure of Co/MoS₂@N,S–CHNSs. The hollow carbon nanospheres are closely stacked and highly interconnected with each other, generating plentiful cavities and robust 3D ordered macroporous frameworks. Apparently, such intriguing architecture could drastically enlarge the surface area, facilitate the electrolyte permeation, and accelerate the gas release during the electrolytic HER process. The magnified SEM image (Figure 2C) discloses that the average diameter of the hollow carbon nanospheres.

**FIGURE 2** Morphological characterization of the obtained Co/MoS₂@N,S–CHNSs. (A–C) scanning electron microscopy images, (D–F) transmission electron microscopy images, (G–I) high-resolution transmission electron microscopy images, and (J) high-angle annular dark-field scanning transmission electron microscopy image and corresponding energy-dispersive X-ray spectroscopy elemental mapping images.
nanospheres is measured to be ~130 nm, which is in good accordance with the SiO₂ template. The typical transmission electron microscopy (TEM) images (Figure 2D–F) further confirm the spherical hollow structure of the resultant Co/MoS₂@N,S–CHNSs with a wall thickness as thin as ~3.6 nm. From Figure 2F, it can be clearly seen that the decorated nanoparticles are evenly distributed on the carbon nanosphere substrate. The high-resolution transmission electron microscopy (HRTEM) image of the carbon nanosphere wall (Figure 2G) exhibits the interplanar distance of 0.34 nm, corresponding to the (002) plane of graphitic carbon. The HRTEM images (Figure 2H,I) of the anchored Co/MoS₂ nanoparticles unambiguously corroborate the successful formation of Co/MoS₂ heterojunctions. The well-resolved lattice fringes with interplanar spacing of 0.206 and 0.62 nm can be readily assigned to Co(111) and MoS₂(002) planes, respectively. As indicated by the blue dashed lines, the Co and MoS₂ domains are tightly adjacent to each other, building well-defined heterointerfaces. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping images (Figure 2J) reveal the uniform distribution of C, N, O, S, Mo, and Co elements in Co/MoS₂@N,S–CHNSs.

Figure 3A shows the X-ray diffraction (XRD) pattern of the fabricated Co/MoS₂@N,S–CHNSs, affirming the coexistence of Co and MoS₂ components. The broad peak positioned at around 26° is attributed to the (002) plane of graphitic carbon. The diffraction peaks marked by the red stars correspond to the (111), (200), and (220) planes of the face-centered cubic Co phase (JCPDS no. 15-0806), while the rest diffraction peaks indicated by the blue blossoms are associated with hexagonal-phased 2H–MoS₂ (JCPDS no. 37-1492). The thermogravimetric analysis (TGA) curve (Figure 3B) indicates that the weight percentage of Co/MoS₂ in Co/MoS₂@N,S–CHNSs is calculated to be 38.3 wt% based on the final residue of CoMoO₄ and MoO₃ after the TGA test (Figure S5). Raman spectrum (Figure 3C) of Co/MoS₂@N,S–CHNSs exhibits two distinct peaks located at 1324 and 1596 cm⁻¹, corresponding to the D and G bands of carbon, respectively. The relative intensity ratio of the D band to the G band (I_D/I_G) is estimated to be ~1.04, signifying the presence of a large number of defects caused by the N,S-codoping.
into the carbon lattice. The abundant defects are believed to play a positive role in electrocatalysis. According to the \( \text{N}_2 \) adsorption/desorption measurements (Figure 3D), the adsorption–desorption isotherms of Co/MoS\(_2@N,S\)-CHNSs can be categorized as type I with an impressively steep uptake at a low relative pressure range of \( p/p_0 < 0.01 \), implying the existence of a large number of micropores in Co/MoS\(_2@N,S\)-CHNSs. The Brunauer–Emmett–Teller (BET) surface area of Co/MoS\(_2@N,S\)-CHNSs is measured to be 869.4 m\(^2\)/g. The pore-size distribution curve (inset of Figure 3D) further corroborates the microporous feature of the formed Co/MoS\(_2@N,S\)-CHNSs. The inverse opal-structured Co/MoS\(_2@N,S\)-CHNSs with a high BET specific surface and rich macro/micropores can provide abundant exposed active sites and gas–solid–liquid tri-phase reaction interfaces for accelerating the electrocatalytic reaction kinetics.

The surface chemical composition and elemental states of Co/MoS\(_2@N,S\)-CHNSs are examined by the X-ray photoelectron spectroscopy (XPS) technique. The XPS survey spectrum (Figure 4A) confirms the presence of C, N, O, S, Mo, and Co elements in Co/MoS\(_2@N,S\)-CHNSs. The high-resolution Mo 3d spectrum (Figure 4B) can be deconvoluted into three peaks, which are corresponding to Mo\(^{4+}\) 3d\(_{5/2}\) (229.31 eV), Mo\(^{4+}\) 3d\(_{3/2}\) (232.48 eV), and Mo\(^{6+}\) (235.6 eV), respectively. The peak at 226.77 eV originates from the S 2s characteristic peak, verifying the formation of Mo–S bond. It is noteworthy that the binding energies of Mo\(^{4+}\) in Co/MoS\(_2@N,S\)-CHNSs exhibit a negative shift of \(-0.18\) eV relative to MoS\(_2@N,S\)-CHNSs, signifying the strong electronic interaction between Co and MoS\(_2\) domains caused by the establishment of Co/MoS\(_2\) interfacial heterojunctions. The altered electronic state is believed to induce unique surface reactivity for HER. For the high-resolution spectrum of S 2p region (Figure 4C), the fitted peaks positioned at 162.14 and 163.6 eV are ascribed to S 2p\(_{3/2}\) and S 2p\(_{1/2}\) peaks of the S–S bridging divalent sulfide ions, respectively. Additionally, the peak centered at 164.95 eV is associated with C–S bond, suggesting the S-doping into the carbon substrate. The high-resolution Co 2p spectrum (Figure 4D) can be well fitted into metallic Co (779.9 and 795.37 eV), Co\(^{3+}\) (781.02 and 797.1 eV), Co\(^{2+}\) (782.9 and 798.45 eV), and satellite peaks (786.9 and 803.66 eV), respectively. The metallic Co has been well recognized as an HER promoter due to its low energy barrier for H adsorption and favorable kinetics in the Volmer process. The high-resolution C 1s spectrum (Figure 4E) can be well-fitted into four characteristics peaks, including C–C (284.6 eV), C–S (285.29 eV), C–N (286.36 eV), and C=O (289.09 eV) bonds. The high-resolution N 1s region (Figure 4F) shows three predominant peaks, which are associated with pyridinic-N (395.23 eV), pyrrolic-N (399.2 eV), and graphitic-N (400.78 eV), respectively. Of note, the N-
doping, especially the pyridinic-N and pyrrolic-N, can effectively activate the neighboring carbon atoms by altering their electron environment, creating more defects in the carbon surface, and enhancing their HER activity by interacting with H.

The strong immobilization of Co/MoS2 heteronanoparticles onto inverse opal-structured N,S-doped carbon hollow nanospheres with an ordered macroporous framework enables the resultant Co/MoS2@N,S-CHNSs as a distinguished HER electrocatalyst. Due to the wide application of alkaline water electrolysis in industry, the electrocatalytic HER performance of the as-fabricated Co/MoS2@N,S-CHNSs is evaluated by recording the linear sweep voltammetry (LSV) curves in 1.0 mol/L KOH electrolyte using a standard three-electrode configuration. For fair comparison, MoS2@N,S-CHNSs, Co3O4@CHNSs, CHNSs, and commercial Pt/C (20 wt%) are also assessed as references under the identical test conditions. Figure 5A displays the LSV curves of different catalysts with a scan rate of 5 mV/s. Unquestionably, the commercial Pt/C catalyst exhibits the best HER activity with the onset potential of nearly 0 mV, and the smallest overpotential of 45 mV to deliver a current density of 10 mA/cm². The pristine CHNSs are almost catalytically inert for HER even at a very large overpotential. In comparison with the single-component decorated counterparts (MoS2@N,S-CHNSs and Co3O4@CHNSs), the Co/MoS2@N,S-CHNSs exhibit the smallest overpotential and the largest current density, emphasizing the superiority of Co/MoS2 heterointerfaces for HER. As illustrated in Figure 5B, the overpotential of Co/MoS2@N,S-CHNSs at 10 mA/cm² is 105 mV, which is drastically lower than those of MoS2@N,S-CHNSs (332 mV), Co3O4@CHNSs (369 mV), and a majority of previously reported MoS2-based HER electrocatalysts in alkaline media (Table S1). The HER kinetics and reaction mechanism are further studied by the Tafel plot. A small Tafel slope generally implies favorable HER kinetics. As shown in Figure 5C, the Tafel slope of the standard Co/MoS2@N,S-CHNSs is identified as 112 mV/dec, significantly lower than those of MoS2@N,S-CHNSs.
Furthermore, the Tafel slope value also suggests that the HER proceeding on Co/MoS2@N,S–CHNSs might follow a Volmer–Heyrovsky mechanism with a rate-determining step of desorption of discharged proton.

To further understand the origin of the excellent HER activity of Co/MoS2@N,S–CHNSs, the electrochemical double-layer capacitance ($C_{dl}$) values, which are proportional to their electrochemical active surface areas (ECSAs) of different electrocatalysts, are calculated according to the cyclic voltammograms (CVs; Figure S6) recorded within non-Faradic potential region at various scan rates. As displayed in Figure 5D, the $C_{dl}$ value of 30.7 mF/cm$^2$ for Co/MoS2@N,S–CHNSs is considerably higher than those of MoS2@CHNSs (14.1 mF/cm$^2$), Co$_3$O$_4$@CHNSs (5.0 mF/cm$^2$), and CHNSs (2.0 mF/cm$^2$). Thus, the ECSAs of Co/MoS2@N,S–CHNSs, MoS2@N,S–CHNSs, Co$_3$O$_4$@CHNSs, and CHNSs samples are estimated to be 767.5, 352.5, 125.0, and 50 cm$^{-2}$, respectively, which affirming that the formation of Co/MoS2 heterojunctions can substantially create more active sites and thereby boost the HER activity. The electrochemical impedance spectroscopy (EIS) measurements are performed to gain deep insight into the HER kinetics for different catalysts. As reflected by the Nyquist plots (Figure 5E), the Co/MoS2@N,S–CHNSs exhibit the smallest charge-transfer resistance ($R_{ct}$), as compared with MoS2@CHNSs, Co$_3$O$_4$@CHNSs, and CHNSs. This finding indicates that the generation of Co/MoS2 heterointerfaces enables improvement of the charge-transfer efficiency and expedite the Faradaic process. The long-term durability of the Co/MoS2@N,S–CHNSs is appraised by the chronoamperometric method. As depicted in Figure 5F, the current density of Co/MoS2@N,S–CHNSs remains relatively stable without obvious attenuation after continuous electrolysis for 11 h at a constant overpotential of 150 mV, demonstrating their excellent electrochemical stability.

Moreover, TEM images (Figure S7a,b) suggest that the hollow spherical structure of Co/MoS2@N,S–CHNSs can be perfectly retained after the long-term stability test. XPS spectra (Figure S7c,d) manifest that the binding energy peaks of Mo 3d and Co 2p after the stability test tend to be nearly unchanged as compared with the as-fabricated sample. The above results strongly underline the outstanding electrochemical and structural robustness of Co/MoS2@N,S–CHNSs. The Faradaic efficiency for HER is determined by measuring the volume of generated H$_2$ through a simple water drainage method (Figure 5G). As shown in Figure 5H, the measured gas volumes coincide well with the calculated values for each 10 min interval in 1 h. The
experimental H₂ volume–time curve (Figure 5I) shows a perfect linear correlation, hinting a nearly 100% Faradaic efficiency of the HER process occurred on Co/MoS₂@N,S–CHNSs. As a whole, the above electrochemical results solidly certify that the formed Co/MoS₂@N,S–CHNSs may serve as an affordable yet competent candidate toward the HER.

To further elucidate the enhanced catalytic efficacies of the Co/MoS₂@N,S–CHNSs, DFT calculations are performed to investigate the HER process at the atomic level. The computational model of Co/MoS₂ heterojunction is built by coupling the Co(111) facet with the MoS₂(002) facet (Figure 6A). The optimized geometry structure of Co/MoS₂ indicates that metallic Co strongly connects with MoS₂ through the S-edge atoms at the interface. The control model of pure MoS₂(002) is also built for comparison (Figure S8). Figure 6B displays the difference in the charge density near the interface of the Co/MoS₂ nanocomposites. Evidently, the 3D isosurface indicates that coupling of Co with MoS₂ produces the redistribution of electron density, and the electron transfer occurs from Co to MoS₂ in the interfacial region, which is consistent with the XPS results. The electron depletion on Co moiety and electron accumulation on MoS₂ side is believed to strengthen the activation of H₂O molecule and expedite the electron-transfer process in the Volmer and Heyrovsky steps, thus leading to the significantly enhanced electrocatalytic activities. As revealed by the total density of states (DOS) of Co/MoS₂ and MoS₂ in Figure 6C, the electronic states of Co/MoS₂ near the Fermi level increase noticeably as compared with the pristine MoS₂ counterpart, evidencing higher charge carrier density and thus expedited charge transfer upon the formation of Co/MoS₂ heterojunctions. As is well known, the activity of the HER electrocatalyst is closely associated with its capability toward the adsorption of H₂O molecule, and the Gibbs free energy of water adsorption (ΔG_H₂O) is generally considered as a vital parameter of the rate-limiting Volmer step in alkaline conditions. As reflected by Figure 6D, the ΔG_H₂O on Co/MoS₂ is calculated to be −1.69 eV, which is drastically lower than that of MoS₂ (−0.21 eV). This finding indicates that the formation of Co/MoS₂ heterojunctions is favorable for water affinity. As displayed in Figure 6E, the water dissociation barriers for pristine MoS₂ and Co/MoS₂ are determined to be 0.447 and 0.025 eV, respectively, indicating that the cleavage of H–OH bond to form OH* and H* intermediates on Co/MoS₂ is enormously accelerated. In addition, upon the formation of Co/MoS₂ heterojunctions, the Gibbs free energy for H* adsorption (ΔG_H*) on Co/MoS₂ is −0.048 eV, which is noticeably more thermo-neutral than that on MoS₂ (0.145 eV) and implies the much boosted HER intrinsic activity upon the heterojunction construction. As a whole, the DFT simulation findings corroborate that the Co/MoS₂ formation is beneficial to increase the conductivity, regulate the electronic configuration, and thus optimize the reaction pathways, resulting in considerably promoted HER intrinsic activity.

On the basis of the experimental results and theoretical calculations, the distinguished HER performance of Co/MoS₂@N,S–CHNSs can be ascribed to the Co/MoS₂ heterostructure synergy and intriguing architectural superiority. First, the intimate coupling of Co with MoS₂ to form Co/MoS₂ nanointerfaces could effectively modify the electron states of each component, which causes the rapid charge transportation at the interface, creates more active sites, and optimizes the reaction pathways, leading to boosted intrinsic activity. Second, as an excellent current collector, the unique inverse opal-structured N,S-doped carbon hollow nanospheres with open, uniform, and interconnected macropores greatly facilitate the mass diffusion, electrolyte permeation, and gas release, greatly accelerating the reaction kinetics. Third, as a robust substrate, the carbon nanosphere support can effectively prevent the active Co/MoS₂ components from possible agglomeration and migration, ensuring favorable mechanical and electrochemical stability.

3 | CONCLUSION

In summary, we have reported the in situ establishment of Co/MoS₂ hetero-nanoparticles onto inverse opal-structured N,S-doped carbon hollow nanospheres with an ordered macroporous framework through a simple template-assisted approach. The systematical experiments and DFT calculations collectively manifest that the formation of Co/MoS₂ heterojunctions could noticeably induce the electronic redistribution of active sites, promote the conductivity, create abundant exposed active sites, and optimize the adsorption free energies for reaction intermediates, bringing about the enhanced intrinsic activity. Furthermore, the inverse opal-structured N,S-doped carbon hollow nanosphere substrate with open, uniform, and interconnected macropores allows the sufficient exposure of active sites, efficient mass/electron transfer, and rapid gas evolution/release, enabling to accelerate the reaction kinetics. Benefitting from the compositional synergy and morphological advantages, the formed Co/MoS₂@N,S–CHNSs could serve as an economical, efficient, and durable HER electrocatalyst, only requiring a low overpotential of 105 mV at 10 mA/cm² and exhibiting a Faradaic efficiency of nearly 100% as well as excellent long-term stability. These findings may provide a new perspective...
for the design and exploration of advanced electrocatalysts by the interfacial and architectural dual regulation strategy.

ACKNOWLEDGMENTS
The authors are grateful for the financial supports from the National Natural Science Foundation of China (21972068, 21875112, and 22075290), Qing Lan Project of Jiangsu Province, Nanjing IPE Institute of Green Manufacturing Industry and Beijing Natural Science Foundation (No. Z200012).

CONFLICT OF INTERESTS
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ACKNOWLEDGMENTS
The authors are grateful for the financial supports from the National Natural Science Foundation of China (21972068, 21875112, and 22075290), Qing Lan Project of Jiangsu Province, Nanjing IPE Institute of Green Manufacturing Industry and Beijing Natural Science Foundation (No. Z200012).

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ORCID
Lin Xu http://orcid.org/0000-0002-9070-7266
Jun Yang http://orcid.org/0000-0002-8993-0655

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**AUTHOR BIOGRAPHIES**

**Tingyu Lu** obtained her B.S. degree at Nanjing Normal University in 2020. Then, she joined the School of Chemistry and Materials Science at Nanjing Normal University as a graduate. Her current research interests are in the fields of
Tongfei Li received his Master's degree from Nanjing Normal University in 2018. He is currently a joint training Ph.D. student at Southeast University and Nanjing Normal University under the supervision of Prof. Lin Xu, Prof. Yiwei Zhang, and Prof. Yawen Tang. His current research interests include the design and synthesis of functional nanomaterials and their applications toward energy conversion and storage.

Dr. Lin Xu is currently an associate professor at Nanjing Normal University. He gained his Ph.D. degree in Chemistry from Nanjing University in 2010. After that, he conducted postdoctoral research at the Indiana University Bloomington until December of 2011 and at Nanyang Technological University until April 2015. His current research interests mainly focus on rational design and synthesis of nanomaterials toward energy-related applications, including electrocatalysis, lithium batteries, and supercapacitors. Hitherto, he has published more than 60 papers, in journals such as *Adv. Mater.*, *Adv. Funct. Mater.*, *Adv. Sci.*, *Appl. Catal. B*, *Chem. Eng. J.* and *J. Mater. Chem. A*. He also serves on the advisory board for *Nanoscale* and *Nanoscale Advances*.

Jun Yang received his Ph.D. in Chemical and Biomolecular Engineering in 2006 from the National University of Singapore (with Prof. Jim Yang Lee). After postdoctoral research at Boston College and the University of Toronto, he joined the Institute of Bioengineering and Nanotechnology, Singapore in 2007. In 2010, he moved to the Institute of Process Engineering, Chinese Academy of Sciences as the leader of Group of Materials for Energy Conversion and Environmental Remediation (MECER). His main research interests include (i) electrocatalysis, (ii) nanocomposites for energy conversion, (iii) synthesis and application of novel nanocrystalline materials, and (iv) separation techniques.

Yawen Tang received his B.S. degree and M.S. degree from Nanjing Normal University in 1992 and 2002, respectively, and his Ph.D. from Nanjing University of Science & Technology in 2011. He is currently a professor at the College of Chemistry and Materials Science at Nanjing Normal University. His main research interests are the synthesis and assembly of nanomaterials, and their applications in batteries, fuel cells, and photocatalysis.

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**How to cite this article:** Lu T, Li T, Shi D, et al. In situ establishment of Co/MoS2 heterostructures onto inverse opal-structured N,S-doped carbon hollow nanospheres: interfacial and architectural dual engineering for efficient hydrogen evolution reaction. *SmartMat*. 2021;2:591-602.

https://doi.org/10.1002/smm2.1063