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# A Co-MOF-derived Co<sub>9</sub>S<sub>8</sub>@NS-C electrocatalyst for efficient hydrogen evolution reaction†

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The exploitation of efficient hydrogen evolution reaction (HER) electrocatalysts has become increasingly urgent and imperative; however, it is also challenging for high-performance sustainable clean energy applications. Herein, novel Co<sub>9</sub>S<sub>8</sub> nanoparticles embedded in a porous N,S-dual doped carbon composite (abbr. Co<sub>9</sub>S<sub>8</sub>@NS-C-900) were fabricated by the pyrolysis of a single crystal Co-MOF assisted with thiourea. Due to the synergistic benefit of combining Co<sub>9</sub>S<sub>8</sub> nanoparticles with N,S-dual doped carbon, the composite showed efficient HER electrocatalytic activities and long-term durability in an alkaline solution. It shows a small overpotential of −86.4 mV at a current density of 10.0 mA cm<sup>−2</sup>, a small Tafel slope of 81.1 mV dec<sup>−1</sup>, and a large exchange current density (*J*<sub>0</sub>) of 0.40 mA cm<sup>−2</sup>, which are comparable to those of Pt/C. More importantly, due to the protection of Co<sub>9</sub>S<sub>8</sub> nanoparticles by the N,S-dual doped carbon shell, the Co<sub>9</sub>S<sub>8</sub>@NS-C-900 catalyst displays excellent long-term durability. There is almost no decay in HER activities after 1000 potential cycles or it retains 99.5% of the initial current after 48 h.

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## 1. Introduction

Due to the energy crisis and environmental problems, sustainable utilization of renewable energy has shown rapid development in the world. As high efficiency and clean energy, hydrogen energy is giving rise to a new dawn in the future energy systems and is well on the way.<sup>1,2</sup> Thus, exploring numerous HER electrocatalysts to generate sufficient H<sub>2</sub> by water-splitting is an effective and efficient tactic.<sup>1,2</sup> It is known that noble metal Pt is by far the most efficient and benchmark HER electrocatalyst; however, it suffers from resource exhaustion, which blocks its widespread applications.<sup>3,4</sup> Therefore, various alternative noble-metal-free catalysts, such as transition metal derived nanomaterials (Mo, W, Co, Fe, and Ni),<sup>5–10</sup> N, S, P heteroatom-doped carbon materials,<sup>11</sup> and their composites,<sup>12</sup> have been scrutinized due to their high HER electrocatalytic activities, other important energy storage and conversion features,<sup>13</sup> and low cost. Of note, Co(II)-based species are a type of high-profile candidates whose enhanced electrocatalytic activities have recently been noticed.<sup>7,8,14,15</sup> Among them, cobalt and sulfide-rich Co<sub>9</sub>S<sub>8</sub> have been applied in both electrocatalytic ORR and various batteries but scarcely in HER due to its low

conductivity and easy aggregation.<sup>14,15</sup> To improve these defects, encapsulating metal sulfides into N or S doped carbon materials to generate hybrids gave us a profound inspiration.<sup>11</sup> The heteroatom-doped carbon materials not only offer improved electrical conductivity, long-term durability and high selectivity but also can be used as shells to protect metal sulfides from aggregation. More specifically, N,S-dual doped carbon materials themselves have been employed as attractive HER electrocatalysts.<sup>11</sup> Therefore, combining Co<sub>9</sub>S<sub>8</sub> nanoparticles and N,S-dual doped carbon to prepare new composite materials and further improve their HER electrocatalytic activities is indeed an appealing task.<sup>15</sup>

In recent years, metal-organic framework (MOF)-derived hybrids are demonstrated as promoting electrocatalysts for energy storage and conversion.<sup>16,17</sup> By pyrolysis of MOF precursors, the advanced features of MOFs, such as heteroatom-doped carbon skeletons, active metal nodes, adjustable structure components, robust frameworks, and periodic porosities, can be endowed or transferred into the derived hybrids with advantages toward electrocatalysis.<sup>16,17</sup> To promise highly active electrocatalysts, one can also encapsulate small organic molecules containing heteroatoms to introduce and increase multiple active sites. Herein, we incorporated a small thiourea molecule with both N and S into a crystalline Co-MOF (LCU-105)<sup>18</sup> to manage multi-component composites for HER. The skeleton ligands of Co-MOF and thiourea offer N,S-dual doped carbon substrates, which can not only favour electrical conductivity and improve potential active sites but can also embed Co(II) species to increase stability. As a result, Co<sub>9</sub>S<sub>8</sub>

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nanoparticles wrapped in the N,S-dual doped carbon composite (abbreviated as Co<sub>9</sub>S<sub>8</sub>@NS-C-900) were fabricated. The Co<sub>9</sub>S<sub>8</sub>@NS-C-900 composite displays efficient HER electrocatalytic activities and long-term durability. It showed a small overpotential of -86.4 mV at a 10.0 mA cm<sup>-2</sup> current density, a small Tafel slope of 81.1 mV dec<sup>-1</sup>, and a large exchange current density (*J*<sub>0</sub>) of 0.40 mA cm<sup>-2</sup>, performance comparable to Pt/C.

## 2. Experimental section

### 2.1. Chemicals and material characterization

All chemicals were purchased commercially and used as received. The powder X-ray diffraction (PXRD) was obtained on a D/MAX-rA (Rigaku) diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ) at a scan rate of 4° min<sup>-1</sup>. Raman spectrum was collected using Monovista CRS500. X-ray photoelectron spectra (XPS) were collected using ESCALAB Xi+. N<sub>2</sub> adsorption experiments were performed on a Micrometrics ASAP 2020M instrument. FT-IR spectra were recorded on a NICOLET 6700F-IR spectrometer using the KBr disc method in the range of 400–4000 cm<sup>-1</sup>. Electron microscopy measurements were performed on a field-emission scanning electron microscope (SEM, JSM-6360). Transmission electron microscopy (TEM) was performed on a JEM-2100 at 200 kV.

### 2.2. Syntheses and structure of the Co-MOF precursor

The pure single crystals of the Co-MOF (LCU-105) precursor were synthesized according to our recently reported reference and for the detailed synthesis process see ESI†<sup>18</sup>. The pure phase was confirmed by single-crystal X-ray diffraction (Table S1, ESI†) and PXRD (Fig. S2, ESI†) measurements. The Co-MOF structure displays a three-dimensional (3D) microporous framework (see Scheme 1 and Fig. S1†), which can well enclose small organic molecules, such as thiourea, presenting it as an excellent candidate as a precursor to fabricate multi-component composites. The crystallographic data of Co-MOF are listed in Table S1 (ESI†). The synthesis details of Co<sub>9</sub>S<sub>8</sub>@NS-C composites can be found in Scheme 1 and are discussed below.

### 2.3. Fabrication of Co<sub>9</sub>S<sub>8</sub>@NS-C composites

The Co<sub>9</sub>S<sub>8</sub>@NS-C composites were synthesized using the above Co-MOF as a precursor *via* the pyrolysis route in Ar atmosphere, followed by the acid etching treatment (Scheme 1): (i) a mixture of crystalline Co-MOF and thiourea was carefully ground in an agate mortar to obtain the thiourea@Co-MOF precursor. (ii) The precursor was transferred to a tube furnace and carbonized under an Ar atmosphere at different temperatures (1000, 900 and 800 °C) for 3 h. The N,S-dual doped carbon composite wrapping both the CoO<sub>x</sub> and Co<sub>9</sub>S<sub>8</sub> nanoparticles was formed. (iii) The obtained three samples were thoroughly etched with 3 M HCl solutions 3 times to remove the residual CoO<sub>x</sub> (Scheme 1), and then repeatedly rinsed in ultra-pure water and ethanol. After drying at 60 °C in a vacuum for 8 h, black catalyst powder was synthesized (Scheme 1). These samples are abbreviated as Co-MOF-1000, Co-MOF-900 and Co-MOF-800. The calcined Co-

MOF-900 (or named as Co<sub>9</sub>S<sub>8</sub>@NS-C-900) sample displays good HER performance and was selected to study its other characteristics.

### 2.4. Electrochemical measurements

The HER electrocatalytic properties including EIS (electrochemical impedance spectroscopy) were evaluated using the Gamry references 3000 electrochemical workstation. A typical experimental procedure was performed as follows: 2.0 mg of the Co<sub>9</sub>S<sub>8</sub>@NS-C-900 composite catalyst (or 20% Pt/C) was dispersed in 1 mL ultra-pure H<sub>2</sub>O under ultrasound to obtain a homogeneous catalyst ink. Then, 20  $\mu$ L of the catalyst ink was dropped on the glassy carbon electrode (0.196 cm<sup>2</sup>). Afterwards, 5  $\mu$ L of Nafion aqueous solution (0.5 wt%) was dropped on the electrode and naturally air-dried. A three-electrode cell system was worked out using glassy carbon as the working electrode, Ag/AgCl (4 M) as the reference electrode, graphite rod as the counter electrode, and 70 mL KOH (1 M) as the electrolyte. Linear sweep voltammogram (LSV) tests were performed at a scan rate of 10 and 5 mV s<sup>-1</sup>, respectively. The long-term durability test was performed using chronopotentiometric measurements. All the potentials were calibrated to a reversible hydrogen electrode (RHE) using the equation  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.205 \text{ V} + 0.0591 \text{ pH}$  and without an IR-correction.

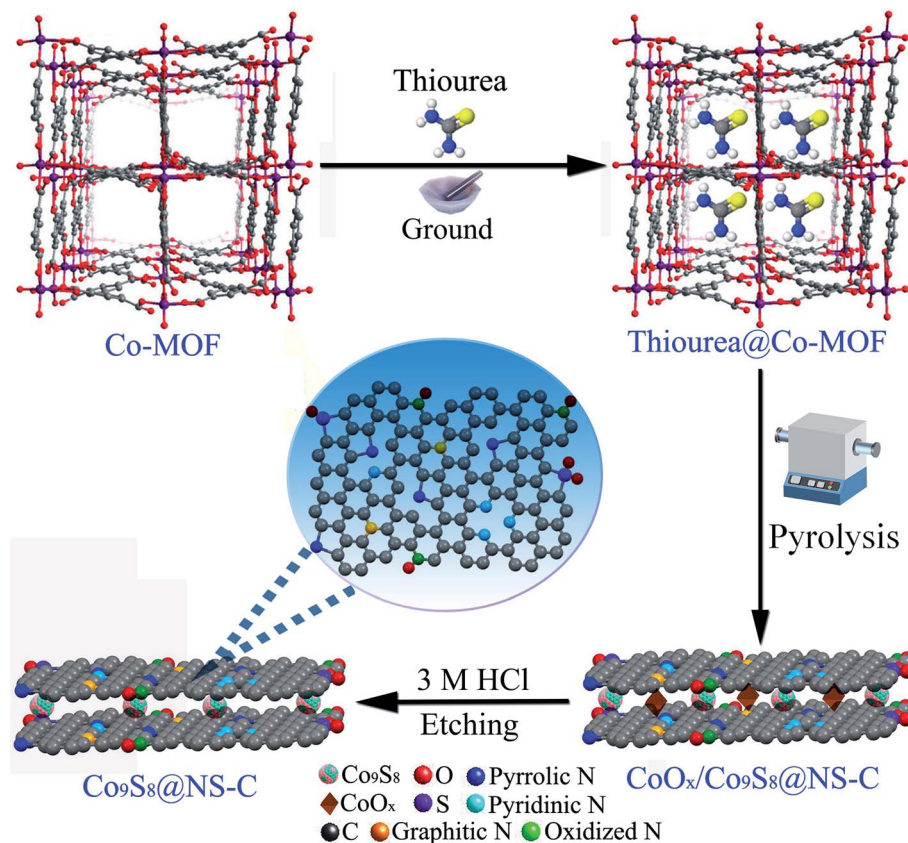
## 3. Results and discussions

### 3.1. Structural characterizations of the Co<sub>9</sub>S<sub>8</sub>@NS-C-900 composite

The phase composition of the as-prepared Co<sub>9</sub>S<sub>8</sub>@NS-C-900 was detected *via* PXRD. As shown in Fig. 1a, the characteristic peaks are well assigned to the cubic Co<sub>9</sub>S<sub>8</sub> phase (PDF#73-1442). The peaks at *ca.*  $2\theta = 15.43^\circ, 17.84^\circ, 29.80^\circ, 31.81^\circ, 39.52^\circ, 40.61^\circ, 44.66^\circ, 52.06^\circ, 54.62^\circ$  and  $55.5^\circ$  are ascribed to the (111), (200), (311), (222), (331), (420), (422), (440), (531) and (600) diffraction planes of cubic Co<sub>9</sub>S<sub>8</sub>, respectively. Therefore, the Co<sub>9</sub>S<sub>8</sub> nanoparticles embedded in NS-C was confirmed by the PXRD results. Raman spectra (Fig. 1b) of the Co<sub>9</sub>S<sub>8</sub>@NS-C-900 catalyst also displayed the characteristic C-C absorption signals at 1449 and 1624 cm<sup>-1</sup>, indexing to D (defects or amorphous of graphitic carbon) and G (ordered sp<sup>2</sup> bonded graphitic carbon) bands of carbon materials, respectively. Therefore, the small *I*<sub>D</sub>/*I*<sub>G</sub> confirms that NS-C is partially graphitized and generates multiple defects as active sites by N,S-dual doping modification.<sup>19a</sup> These features of carbon-based catalysts may not only effectively improve the electronic conductivity and anti-corrosion, but also enhance the electrocatalytic efficiency.<sup>11,12</sup> Moreover, a broad peak with a maximum value at 2573 cm<sup>-1</sup> further proved the evidence of the 2D N,S-dual doped carbon materials. The peaks at 863, 1165 and 1300 cm<sup>-1</sup> can be attributed to the Co<sub>9</sub>S<sub>8</sub> species.<sup>19b,c,d</sup> Raman spectroscopy results also further demonstrate the formation of the Co<sub>9</sub>S<sub>8</sub>@NS-C-900 composite. The chemical model of Co<sub>9</sub>S<sub>8</sub> by the combination of PXRD and Raman is demonstrated in Fig. 1b.

As the porous framework of Co-MOF can be easily transmitted to its derived material, the porous feature of the





Scheme 1 The fabrication of  $\text{Co}_9\text{S}_8@\text{NS-C}$  composites by pyrolysis and etching.

$\text{Co}_9\text{S}_8@\text{NS-C-900}$  composite was evaluated by  $\text{N}_2$  adsorption studies (Fig. 2a). The  $\text{N}_2$  adsorption capacity rises rapidly at the beginning, afterward it grows slowly to reach a maximum of  $90.7 \text{ cm}^3 \text{ g}^{-1}$ . The isotherm displays a clear reversible adsorption behaviour, which shows a typical type-I porous feature.<sup>20</sup> The corresponding BET (Brunner–Emmet–Teller) was calculated as *ca.*  $239 \text{ m}^2 \text{ g}^{-1}$  using the above  $\text{N}_2$  adsorption data.<sup>20</sup> This high BET surface area supplies the exposure of additional active sites, which are beneficial for the HER activity. The diameters of pores are between 4.4 and 19 Å, and the pore

maximum is at 7.9 Å, indicating the easy transportation of  $\text{H}_2$  in the electrocatalytic process appropriately.

The chemical composition of the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  composite was further checked *via* XPS (Fig. 2b–f). The survey spectrum displays that the composite consists of Co, S, N, C and O elements (Fig. 2b). The Co 2p high-resolution spectrum after fitting displays that it comprises four typical characteristic peaks (Fig. 2c): the peaks at 777.04 and 796.75 eV are assigned to  $\text{Co}^{3+}$ ; the peaks at 781.40 and 798.03 eV are ascribed to  $\text{Co}^{2+}$ . However, the peaks at 785.94 eV and 802.97 eV are indexed to satellite peaks.<sup>21,22</sup> The S 2p high-resolution spectrum is

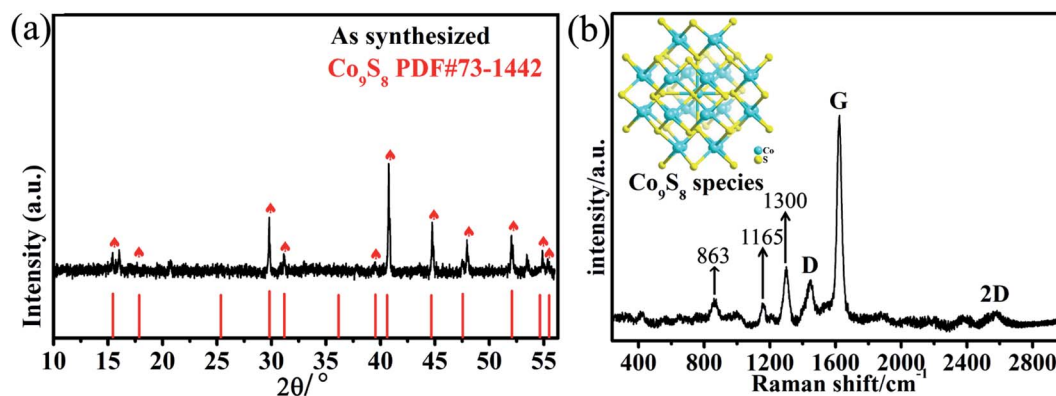


Fig. 1 The PXRD pattern (a) and (b) Raman spectrum of the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  composite (inset: the chemical model of  $\text{Co}_9\text{S}_8$ ).



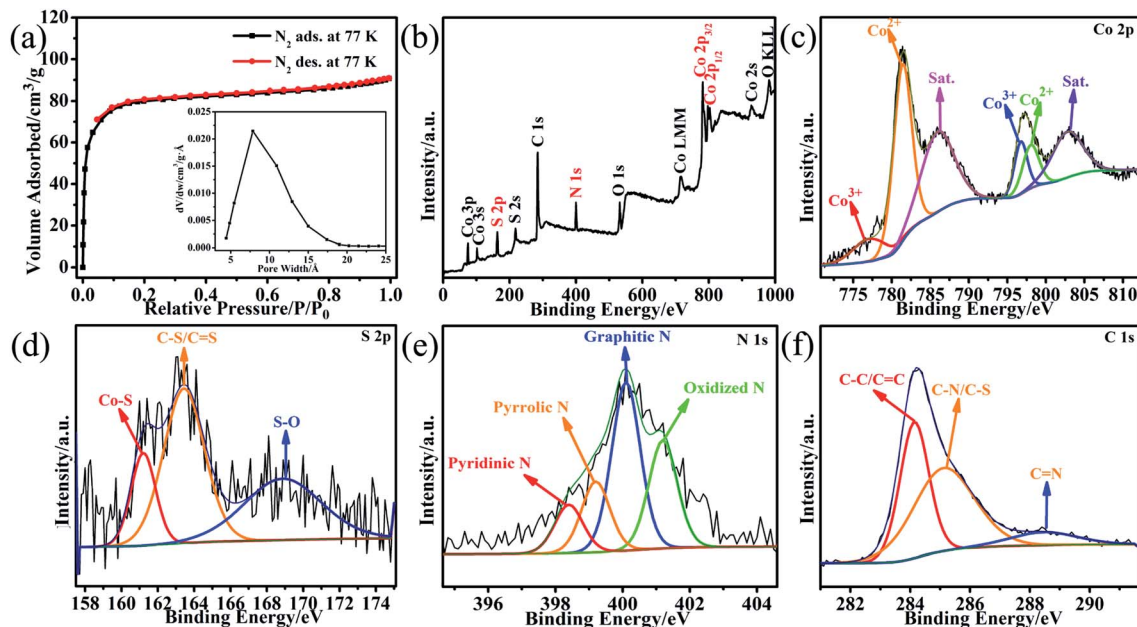


Fig. 2 (a) The  $N_2$  sorption isotherm (inset: the pore size distribution). (b) The XPS survey spectrum. High-resolution XPS: (c) Co 2p. (d) S 2p. (e) N 1s. (f) C 1s of the  $Co_9S_8@NS-C-900$  composite.

deconvoluted into three peaks at 161.20, 163.44 and 168.86 eV (Fig. 2d), assigning to Co-S, C-S/C=S, and C-S-O, respectively.<sup>21,22</sup> These peaks also verify the existence of the  $Co_9S_8$  and N,S-dual doped carbon substance. The N 1s high-resolution spectrum contains four peaks (Fig. 2e). The peak at 398.4 eV is assigned to the pyridinic-N species, showing the formation of  $CoN_x$  active sites. The peak located at 399.2 eV corresponds to the pyrrolic-N species with another mode of  $CoN_x$  active sites. The peak at 400.1 eV is indexed to the graphitic-N species. The peak located at 401.2 eV is regarded as the oxidized-N species.<sup>21,22</sup> According to the literature, both pyridinic-N and pyrrolic-N can effectively regulate HER active sites.<sup>21,22</sup> The C 1s high-resolution spectrum is also divided into three peaks located at 284.14, 285.16 and 288.46 eV (Fig. 2f), illustrating the coexistence of C=C/C-C, C-S/C-N, and C=N, respectively.<sup>21,22</sup> These XPS analyses are in agreement with the above PXRD and Raman results.<sup>19a</sup> Such  $CoN_x$  and N,S-dual-doped carbon often offer plentiful electrochemically active sites for HER and are further responsive to better HER performance and long-term durability.<sup>7,8,15,21,22</sup>

FT-IR was performed to identify the chemical bonds and groups present in the  $Co_9S_8@NS-C-900$  composite, and it confirmed the above compositional analysis results. As shown in Fig. S4 (ESI<sup>†</sup>), the weak peak at *ca.* 456  $cm^{-1}$  and the moderate peak at 580  $cm^{-1}$  are ascribed to Co-S and Co-N bonds, indicating the existence of  $Co_9S_8$  and  $CoN_x$  active sites in the catalyst, respectively. A broad peak at 1039  $cm^{-1}$  is probably the overlap bending vibrations of C-N, N-H and C-S bonds. The peak at 1402  $cm^{-1}$  is ascribed to C-N and C-H groups. The spike peak at 1630  $cm^{-1}$  and the broad strong peak at 3422  $cm^{-1}$  are both identified as the bending vibrations of N-H bonds. The small peaks at 2848 and 2915  $cm^{-1}$  are ascribed to

the C-H bonds stretching vibrations.<sup>19d,23</sup> These results all confirm the formation of the  $Co_9S_8@NS-C-900$  composite by encapsulating  $Co_9S_8$  nanoparticles in the porous N,S-dual doped carbon substrate.

### 3.2. Morphological analysis of the $Co_9S_8@NS-C-900$ composite

The morphology and microstructure of the  $Co_9S_8@NS-C-900$  composite were evaluated using SEM and TEM, respectively. The SEM morphology of the  $Co_9S_8@NS-C-900$  composite displays interconnected aggregates composed of nanoflakes, and their sizes were within about 10–40  $\mu m$  (Fig. 3a–c). These carbon nanoflakes intertwine each other to generate porous aggregates, providing transport channels for HER. From Fig. 3c, it can be seen that  $Co_9S_8$  nanoparticles are clearly embedded into the N,S-dual-doped nanoflakes. Furthermore, the EDS mapping proves the coexistence of Co, S, N and C elements in these carbon nanoflakes (Fig. 3d), and they are uniformly doped in the entire carbon structure. From the EDS mapping of Co and S elements,  $Co_9S_8$  nanoparticles can be brightly shown by highlights. TEM was also performed to further characterize the detailed structural features of the as-obtained  $Co_9S_8@NS-C-900$  composite (Fig. 4a–i). It can be observed that highly crystalline block-like  $Co_9S_8$  nanoparticles are wrapped by the amorphous N,S-dual-doped carbon nanoflakes (Fig. 4b). High-resolution TEM images also indicate that the composite coexists in two types of planes: one is the  $Co_9S_8$  crystalline phase and the other is the N,S-dual doped carbon amorphous phase (Fig. 4c,d). From Fig. 4c and d, a characteristic lattice plane distance *ca.* 0.497 nm was observed, which can be ascribed to the (200) plane of the cubic  $Co_9S_8$  phase.<sup>14,15</sup> This analysis coincides with PXRD results. Moreover, from the



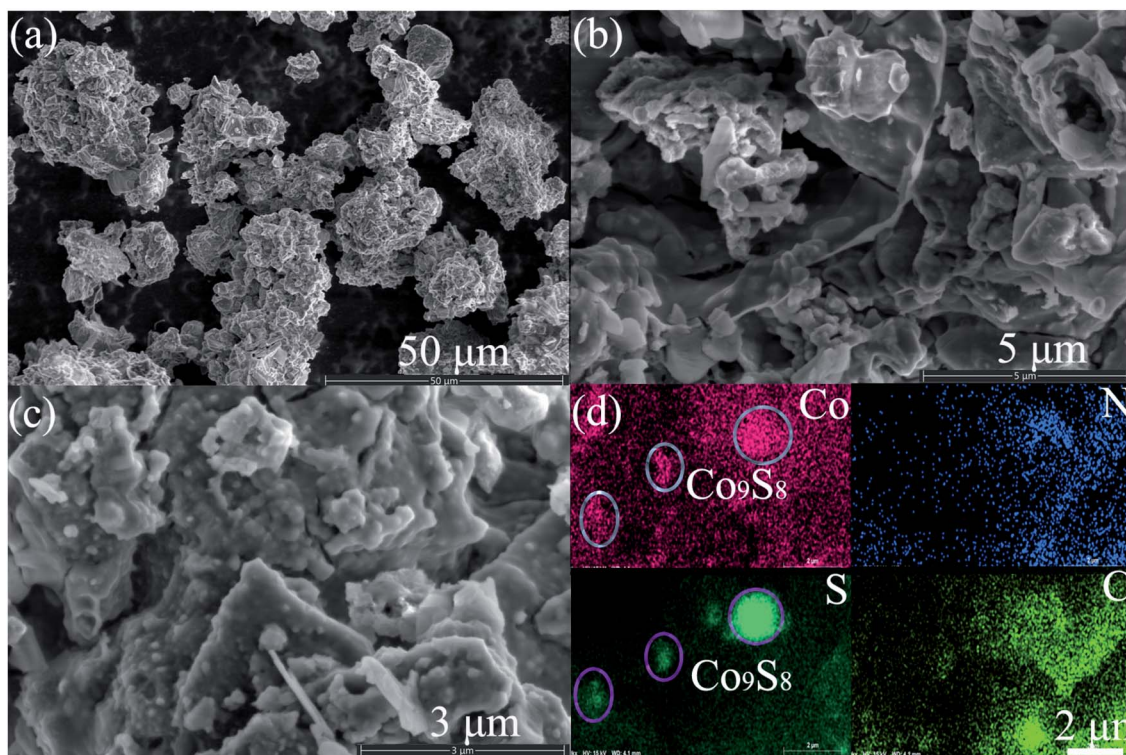


Fig. 3 (a–c) The SEM images of the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  composite under different magnifications. (d) The EDS mapping images of selected regions: Co, S, N, and C.

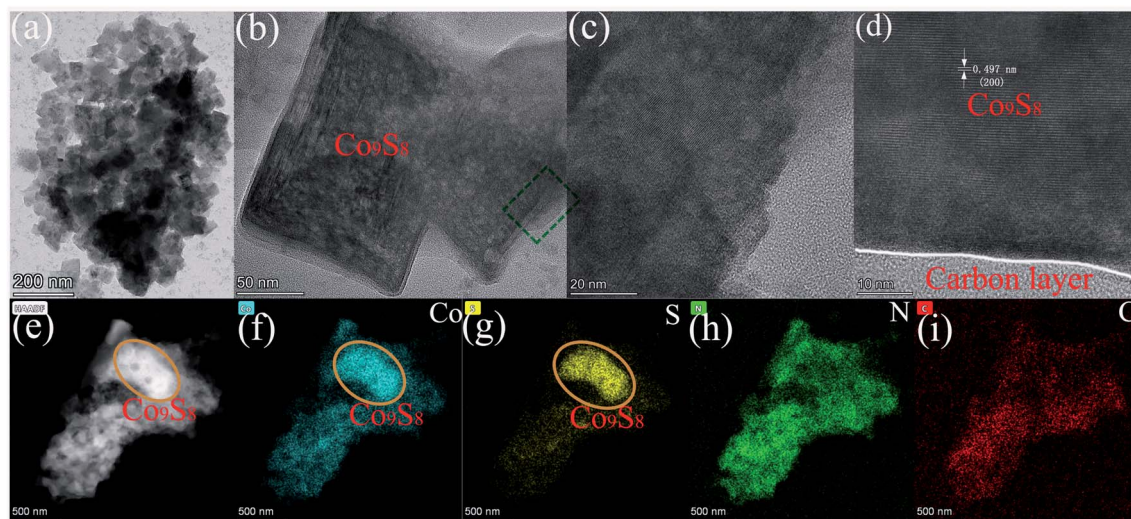


Fig. 4 (a–d) The TEM images of the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  composite under different magnifications. (e–i) The HAADF and EDS mapping images of selected regions: Co, S, N, and C.

HAADF (high-angle annular dark-field) image and EDS mappings displayed in Fig. 4e–i, it can be seen that Co, S, N and C elements are uniformly distributed in the N,S-dual-doped carbon nanoflakes. From both HAADF image and EDS mappings of Co and S elements (Fig. 4e–g),  $\text{Co}_9\text{S}_8$  nanoparticles are also clearly visible by highlights. Based on SEM and TEM results, it can be concluded that  $\text{Co}_9\text{S}_8$  nanoparticles are successfully embedded in N,S-dual-doped carbon nanoflakes.

### 3.3. HER electrocatalytic activity of the $\text{Co}_9\text{S}_8@\text{NS-C-900}$ composite

As the porous feature of the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  composite is suitable for electrolyte transportation, HER electrocatalytic activities of the as-prepared sample were tested in the KOH (1 M) solution. HER polarization curves of various catalysts (including benchmark 20% Pt/C, Co-MOF-1000, Co-MOF-900 and Co-MOF-800) were obtained from LSV ( $5 \text{ mV s}^{-1}$ ). From



Fig. 5a, it can be seen that  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  shows the smallest onset potential ( $E_{\text{onset}}$ ) of ca.  $-4.8$  mV at  $1 \text{ mA cm}^{-2}$  current density, smaller than that of **Co-MOF-1000** ( $E_{\text{onset}} = -54$  mV) and **Co-MOF-800** ( $E_{\text{onset}} = -108$  mV), and close to Pt/C ( $E_{\text{onset}} = 0$  mV). To deliver a  $10.0 \text{ mA cm}^{-2}$  current density, the operating overpotential of  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  is  $-86.4$  mV. This is lower than that for **Co-MOF-1000** ( $-176$  mV), **Co-MOF-800** ( $-292$  mV), several reported noble-metal-free HER catalysts,<sup>5–12,15,17</sup> and also close to most Pt/C catalysts ( $-41.6$  mV). To evaluate the HER kinetics of these catalysts for comparing with the benchmark Pt/C, Tafel slopes were extracted from the LSV curves. From Fig. 5b, it can be seen that the Tafel slopes obey the following sequence: Pt/C ( $44.8 \text{ mV dec}^{-1}$ ) <  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  ( $81.1 \text{ mV dec}^{-1}$ ) < **Co-MOF-1000** ( $116.3 \text{ mV dec}^{-1}$ ) < **Co-MOF-800** ( $182.2 \text{ mV dec}^{-1}$ ), which is consistent with the results from Fig. 5a. The  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  composite has the smallest Tafel slope among the three **Co-MOF**-derived catalysts and is close to that of Pt/C, showing efficient HER kinetics. The Tafel value of  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  also confirms that the HER mechanism abides by a Volmer–Heyrovský pathway, which means that the HER rate-determining progress depends on  $\text{H}_2$  desorption by  $\text{H}_{\text{ads}}$  reacting with  $\text{H}_3\text{O}^+$ . The HER inherent activities of these catalysts were evaluated by the exchange current densities ( $J_0$ ) extracted from the Tafel slopes by applying the extrapolation method. The  $J_0$  value of  $0.40 \text{ mA cm}^{-2}$  for  $\text{Co}_9\text{S}_8@\text{NS-C-900}$

outperforms the values of  $0.30 \text{ mA cm}^{-2}$  for **Co-MOF-1000**, and  $0.26 \text{ mA cm}^{-2}$  for **Co-MOF-800**, and only a little lower than that of Pt/C with the value of  $0.54 \text{ mA cm}^{-2}$ , but the value is higher than that for most of the reported noble-metal-free HER catalysts.<sup>5–12,15,17</sup> Therefore, the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  catalyst has a small overpotential, a small Tafel slope and a large  $J_0$  value, which was integrated to evaluate its efficient electrocatalytic activity towards HER. The comparison of the HER activity for some cobalt-based materials reported in literature is listed in Table S2 (ESI†). From the table, the HER catalytic performance of  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  is better than that of most of similar  $\text{Co}_9\text{S}_8$ , and its composite catalysts under alkaline conditions. It can also match most of the other cobalt-based HER catalysts, but is lower than that for some high-performance materials.

Long-term durability is a key factor to evaluate the catalyst performance. Therefore, the cyclability of the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  catalyst was tested. In Fig. 5c, the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  catalyst displays excellent cycling stability, and there is almost no loss in the HER activity after 1000 potential cycles. Furthermore, the long-term durability of the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  catalyst was also evaluated by chronoamperometric measurements. As displayed in the  $i-t$  (current–time) plot (Fig. 5c, inset), the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  catalyst retains 99.5% of the initial current after 48 h, also indicating that it exhibits excellent cycling stability in the KOH solution. Furthermore, the EIS of three **Co-MOF**-derived

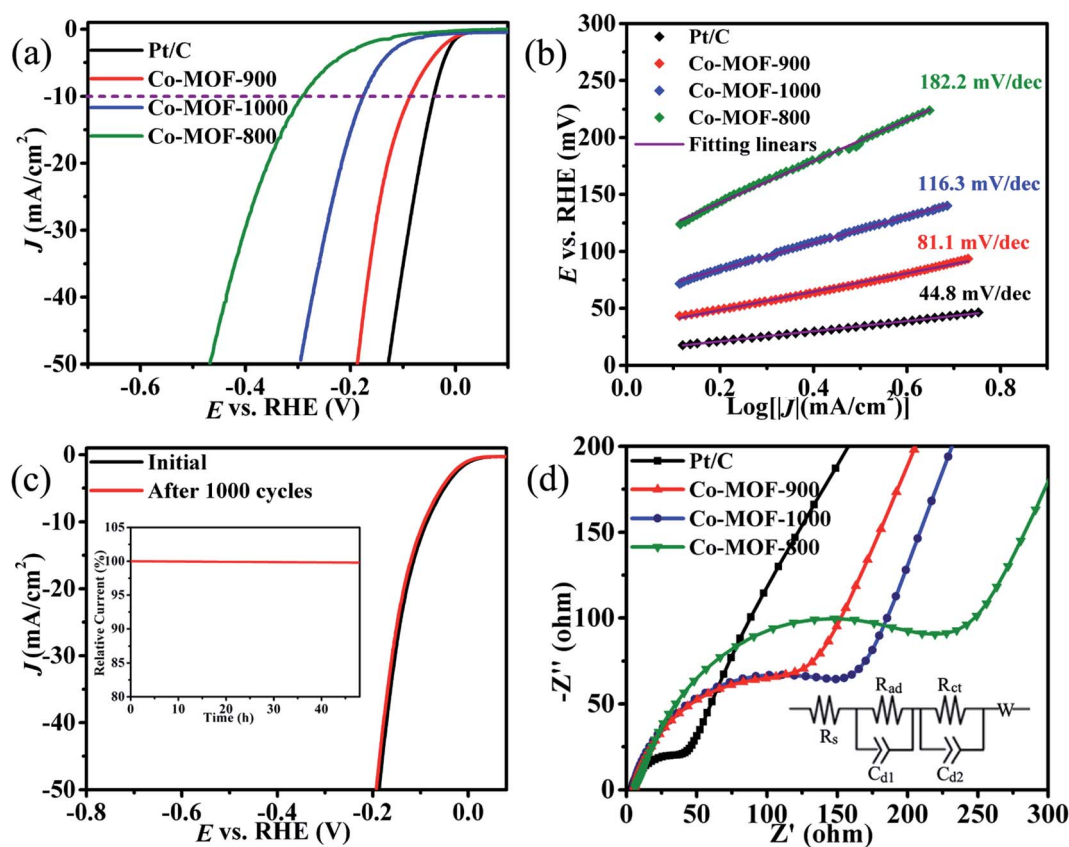


Fig. 5 (a) LSV curves of three **Co-MOF**-derived materials and Pt/C (1 M KOH). (b) Tafel slopes were obtained from the LSV curves of three **Co-MOF**-derived catalysts and Pt/C. (c) LSV plots of the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  catalyst before and after 1000 cycles (inset: the  $i-t$  (current–time) chronoamperometry plot). (d) EIS plots of three **Co-MOF** derived catalysts and 20% Pt/C (inset: simulated equivalent circuit).



catalysts and Pt/C were also tested to estimate their catalytic kinetics. From Fig. 5d, Nyquist curves are presented for these electrocatalysts. We know that Nyquist radius could respond to  $R_{ct}$  (charge transfer resistance) and can effectively estimate the electrocatalytic activities. From Fig. 5d, 20% Pt/C has the smallest radius among all catalysts, which is consistent with its best electrocatalytic activity as a commonly accepted benchmark of HER. In three Co-MOF-derived catalysts, the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  catalyst has the smallest radius than that of others and a little larger than that of Pt/C, which displayed slightly worse HER performance than Pt/C and the best HER electrocatalytic performance among three Co-MOF-derived species. The simulated equivalent circuit (Fig. 5d inset) was also built by fitting the ESI data, and it is composed of three resistances: the solution resistance ( $R_s$ ), hydrogen adsorption resistance ( $R_{ad}$ ), and  $R_{ct}$ . Due to the same equipment and outer solutions,  $R_s$  and  $R_{ad}$  are supposed to be quite similar.  $R_{ct}$  of Co-MOF-1000, Co-MOF-900, and Co-MOF-800 are 361.2, 145.8 and 663.2  $\Omega$ , respectively. The smallest  $R_{ct}$  of the Co-MOF-900 electrode among them suggests its fastest reaction kinetics during the HER process. All told, the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  composite is an efficient HER catalyst possessing excellent cycling stabilities and superior electrocatalytic activities.

## 4. Conclusion

In conclusion, a porous  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  composite was fabricated by the pyrolysis of crystalline Co-MOF involving thiourea. The N,S-dual-doped carbon shell can protect  $\text{Co}_9\text{S}_8$  nanoparticles from corrosion and aggregation by encapsulating them, and further prompt the stability and conductivity of the whole electrocatalyst. Therefore, benefiting from the synergistic interaction of  $\text{Co}_9\text{S}_8$  nanoparticles and N,S-dual-doped carbon substrate, the  $\text{Co}_9\text{S}_8@\text{NS-C-900}$  composite exhibits efficient electrocatalytic activities and long-term durability towards HER in alkaline electrolytes. In particular, the electrocatalyst requires a small overpotential of  $-86.4$  mV at a  $10.0$  mA  $\text{cm}^{-2}$  current density, a small Tafel slope of  $81.1$  mV  $\text{dec}^{-1}$ , and a large exchange current density ( $J_0$ ) of  $0.40$  mA  $\text{cm}^{-2}$ , representing a promising noble-free-metal electrocatalyst that approaches the performance of the state-of-the-art Pt/C electrocatalyst.

## Author contributions

Yun-Wu Li: conceptualization, investigation, funding acquisition, writing-original draft. Qian Wu: data curation, project administration. Rui-Cong Ma: project administration, validation. Xiao-Qi Sun: investigation, data curation. Dan-Dan Li: formal analysis, resources. Hong-Mei Du: methodology, writing-review & editing. Hui-Yan Ma: supervision, conceptualization, visualization, writing-review & editing. Da-Cheng Li: writing-review & editing. Su-Na Wang: supervision, validation, funding acquisition, writing-review & editing. Jian-Min Dou: conceptualization, writing-review & editing. All the authors gave their final approval for publication.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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