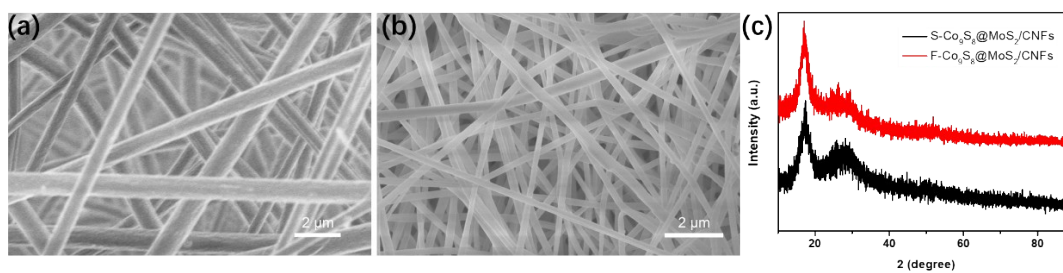


## Supporting Information

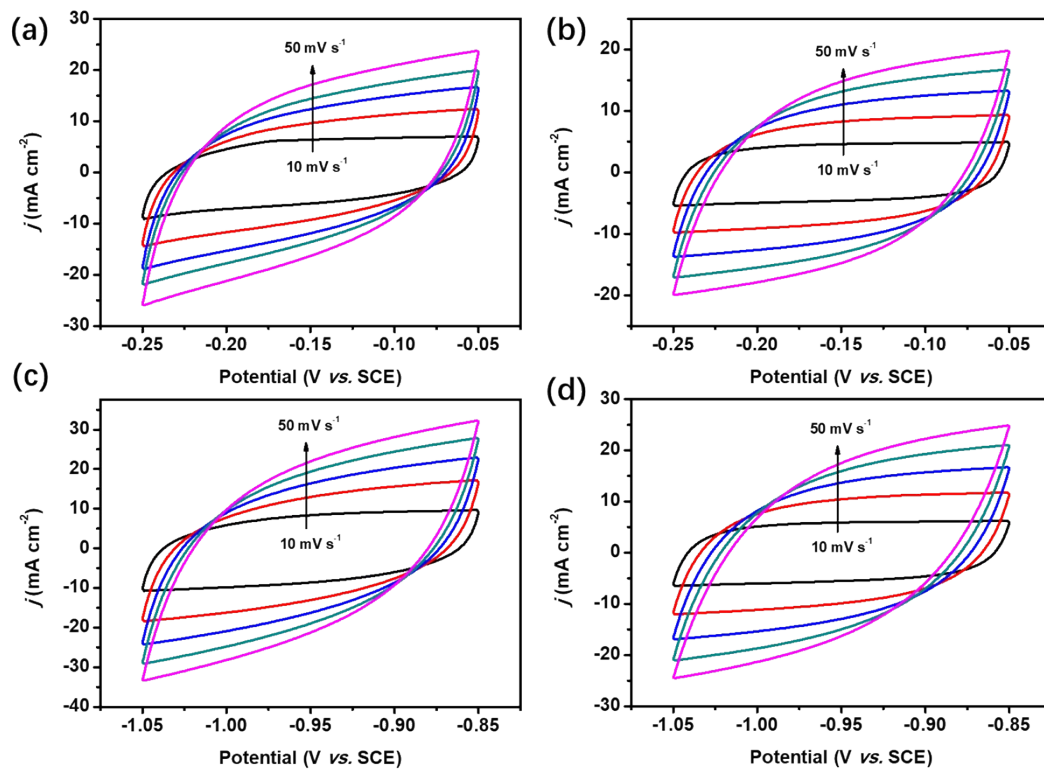
**Interface engineering in core-shell  $\text{Co}_9\text{S}_8@\text{MoS}_2$  nanocrystals induces enhanced hydrogen evolution in acidic and alkaline media**

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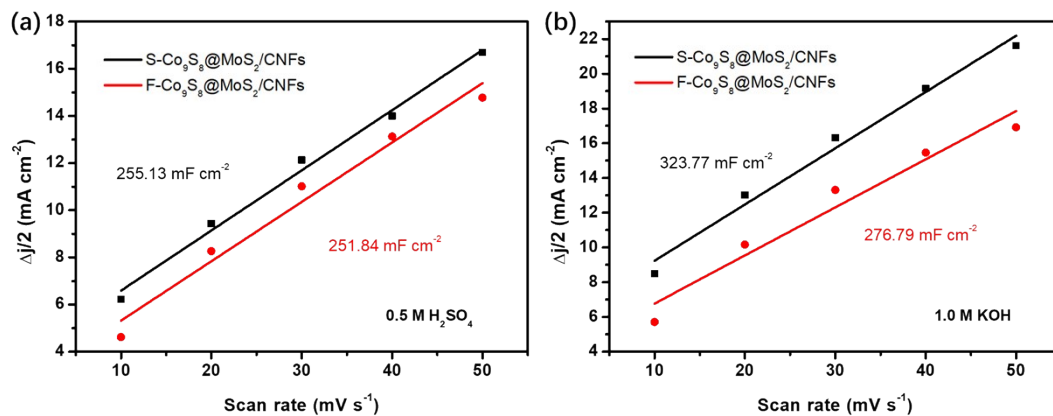
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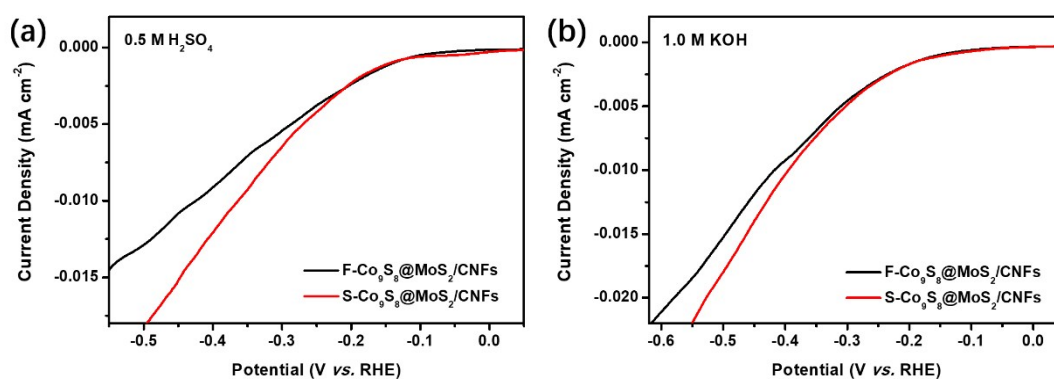
**Figure S1.** SEM images of PAN/CoMo precursor nanofibers of F-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs (a) and S-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs (b). (c) XRD patterns of PAN/CoMo precursor nanofibers of F-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs and S-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs.



**Figure S2.** Electrochemical cyclic voltammograms curves of S-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs and F-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs in 0.5 M H<sub>2</sub>SO<sub>4</sub> (a, b) and 1.0 M KOH (c, d) at scan rates of 10, 20, 30, 40, and 50 mV s<sup>-1</sup>.



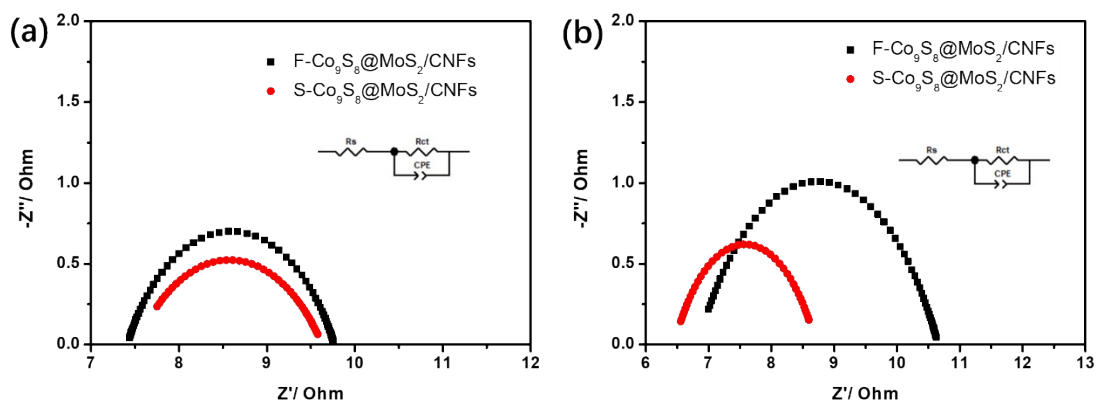
**Figure S3.** Calculation of  $C_{dl}$  by plotting Capacitive currents ( $\Delta j$ ) against scan rates in 0.5 M H<sub>2</sub>SO<sub>4</sub> (a) or 1.0 M KOH (b).



**Figure S4.** Polarization curves of F-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs and S-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs normalized by ECSA in 0.5 M H<sub>2</sub>SO<sub>4</sub> (a) or 1.0 M KOH (b).

Table S1. Comparison of sulfide-based electrocatalysts.

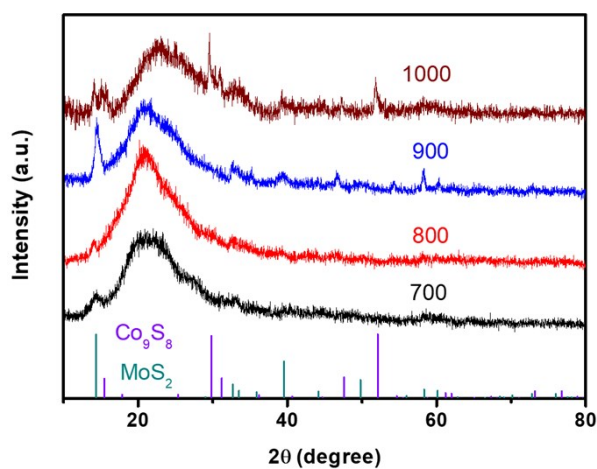
| Catalysts  | Electrolyte                          | $\eta_{10}$ (mA cm <sup>-2</sup> ) | $\eta_{100}$ (mA cm <sup>-2</sup> ) | Tafel Slope (mV dec <sup>-1</sup> ) | Reference |
|--|--------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|-----------|
| Co <sub>9</sub> S <sub>8</sub> /MoS <sub>x</sub> nanotubes | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 161                                | /                                   | 78                                  | [1]       |
| Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub> HNBS      | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 106                                | /                                   | 51.8                                | [2]       |
| Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub> hybrids   | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 171                                | /                                   | 123                                 | [3]       |
|  | 1.0 M KOH                            | 143                                | /                                   | 117                                 |           |
| Co <sub>9</sub> S <sub>8</sub> -30@MoS <sub>x</sub> /CC    | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 98                                 | 165                                 | 64.8                                | [4]       |
| MoS <sub>2</sub> /Ni <sub>3</sub> S <sub>2</sub>           | 1.0 M KOH                            | 110                                | /                                   | 83.1                                | [5]       |
| CoMoS-2-C  | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 135                                | /                                   | 50                                  | [6]       |
| Hollow CoS <sub>x</sub> @MoS <sub>2</sub> microcubes       | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 239                                | /                                   | 103                                 | [7]       |
|  | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 117                                | /                                   | 68.8                                |           |
| Co <sub>9</sub> S <sub>8</sub> /NC@MoS <sub>2</sub>        | 1.0 M KOH                            | 67                                 | /                                   | 60.3                                | [8]       |
|  | 1.0 M PBS                            | 261                                | /                                   | 126.1                               |           |
|  | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 230                                | /                                   | 111.7                               |           |
| Co <sub>9</sub> S <sub>8</sub> -MoS <sub>2</sub> @3DC      | 1.0 M KOH                            | 177                                | /                                   | 83.6                                | [9]       |
|  | 1.0 M PBS                            | 474                                | /                                   | 172                                 |           |
| Co <sub>9</sub> S <sub>8</sub> /1L MoS <sub>2</sub>        | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 97                                 | /                                   | 71                                  | [10]      |
| Co <sub>9</sub> S <sub>8</sub> /CNFs                       | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 165                                | /                                   | 83                                  | [11]      |
| Pd <sub>16</sub> S <sub>7</sub> /MoS <sub>2</sub> /CNFs    | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 83                                 | /                                   | 113                                 | [12]      |
| Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub> /CNFs     | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 190                                | /                                   | 110                                 | [13]      |
| Co <sub>9</sub> S <sub>8</sub> HMs-140/C                   | 0.1 M KOH                            | 250                                | /                                   | 98                                  | [14]      |
| Co <sub>9</sub> S <sub>8</sub> /HWS <sub>2</sub> /CNFs     | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 83                                 | 235                                 | 56                                  | [15]      |
|  | 1.0 M KOH                            | 87                                 | 375                                 | 72                                  |           |
| S-Co <sub>9</sub> S <sub>8</sub> @ MoS <sub>2</sub> /CNFs  | 0.5 M H <sub>2</sub> SO <sub>4</sub> | 77                                 | 236                                 | 83                                  | This work |
|  | 1.0 M KOH                            | 122                                | 322                                 | 66                                  |           |



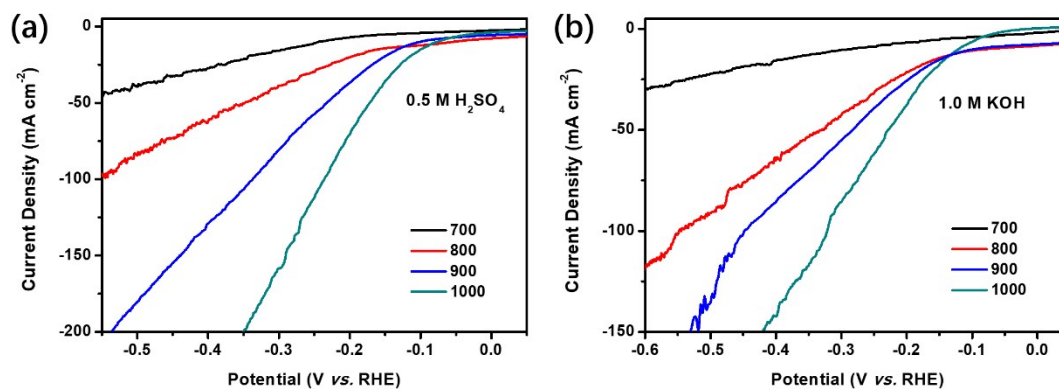
**Figure S5.** The Nyquist plots of F-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs and S-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs in 0.5 M H<sub>2</sub>SO<sub>4</sub> (a) and 1.0 M KOH (b) at  $\eta = 10$  mV.

**Table S2.**  $R_{ct}$  values of F-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs and S-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M KOH at  $\eta = 10$  mV.

| $R_{ct}$                             | F-Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub> /CNFs | S-Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub> /CNFs |
|--------------------------------------|--|--|
| 0.5 M H <sub>2</sub> SO <sub>4</sub> | 2.36   | 2.11   |
| 1.0 M KOH                            | 3.83   | 2.26   |



**Figure S6.** XRD patterns of the S-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs prepared at different temperatures.



**Figure S7.** HER LSV curves of S-Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs prepared at different temperatures obtained in (a) 0.5 M H<sub>2</sub>SO<sub>4</sub> and (b) 1.0 M KOH.

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