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Cobalt–nickel layered double hydroxide on hollow $\text{Co}_3\text{S}_4/\text{CuS}$ derived from ZIF-67 for efficient overall water splitting

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ABSTRACT

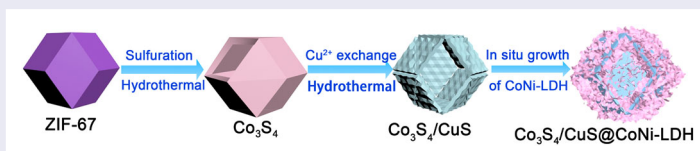
Electrochemical water splitting is one of the most efficient strategies to generate clean energy H_2 . Herein, a novel hollow $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ nanocomposite was designed. This hollow $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ achieved OER overpotential of 220 mV, HER overpotential of 136 mV, respectively, at the current density of 10 mA cm^{-2} . Notably, the hollow $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ serving as both anode and cathode is assembled into a two-electrode water splitting device, and the potential of no more than 1.74 V is required to achieve the overall water splitting efficiency of 10 mA cm^{-2} . This work provides a promising bifunctional catalyst for overall electrochemical water splitting.

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KEYWORDS

Bifunctional catalyst; hydrogen evolution reaction; oxygen evolution reaction; metal sulfide; CoNi-LDH nanosheet



IMPACT STATEMENT

The hollow $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ is prepared by using ZIF-67 as a template and precursor, and the nanosheets are grown on the surface of $\text{Co}_3\text{S}_4/\text{CuS}$ to form a unique heterostructure electrocatalytic catalyst.

1. Introduction

Due to the shortage of energy supply and environmental pressures, it is urgent to develop a new type of clean renewable energy [1–3]. Hydrogen (H_2), as a typical new, clean, efficient and renewable energy with high calorific value, has aroused extensive attention in the preparation process [4–7]. The electrochemical methods of water electrolysis offer a sustainable solution for the production of high-purity H_2 , and the efficient electrocatalyst is required to facilitate the sluggish kinetics of the reaction [8–13]. At present, Pt/C, Ir and Ru precious metal oxide catalysts are ahead of other electrocatalysts in the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), respectively [14–18]. However, the high price and low reserve prevent them from being widely used [19,20]. Therefore, more and more researchers have made tremendous research efforts to prepare an inexpensive and highly active catalyst [21–24].

Metal–organic framework (MOF) catalysts are constructed by coordination between organic ligands and

metal ions/clusters [25]. Materials derived from MOFs generally have the advantages of high electrochemical activity and large specific surface area, which can be used in the design of high-catalytically active electrochemical catalysts [26–29]. For instance, Huo et al. designed a type of hierarchical Fe–Ni LDH/MOF electrocatalyst through in-situ pseudomorphic transformation from heterometallic MOFs [30]. Also, Li et al. reported an electrocatalyst with Co@Ir core–shell nanoparticles derived from MOF [31]. However, the low efficiency of OER limits its application in electrocatalytic water splitting [32]. Therefore, it is of great significance to develop a transition metal-based catalyst with higher efficiency for both HER and OER in alkaline media. The combination of MOF derivatives and layered double hydroxide (LDH) with high OER activity can meet this requirement [33].

Herein, we synthesized a hollow $\text{Co}_3\text{S}_4/\text{CuS}$ via using ZIF-67 as a template and precursor, and then the cobalt–nickel layered double hydroxide (CoNi-LDH) was in situ grown on the hollow $\text{Co}_3\text{S}_4/\text{CuS}$ to obtain the

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dual-functional catalyst for efficient overall water splitting. Compared with monometallic sulfides, bimetallic sulfides have higher electrical conductivity, and the electronic synergy of metal ions increases their reactivity. In addition, the $\text{Co}_3\text{S}_4/\text{CuS}$ material after cation exchange shows that it is rougher, which is more conducive to the growth of nanosheets. It can be seen from the SEM that more CoNi-LDH grown on $\text{Co}_3\text{S}_4/\text{CuS}$ than that supported on Co_3S_4 . The interface interaction generated is stronger, and the more active sites are generated, so the catalytic activity can be significantly improved. Thus, in $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$, the $\text{Co}_3\text{S}_4/\text{CuS}$ shows high catalytic activity on HER, while the CoNi-LDH exhibits excellent catalytic performance on OER. The hollow $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ achieved OER overpotential of 220 mV, HER overpotential of 136 mV, respectively, at the current density of 10 mA cm^{-2} . Moreover, the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ showed outstanding electrochemical stability in 50 h. Finally, the hollow $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ catalysts serving as both anode and cathode are assembled into a two-electrode water splitting device, which delivered a current density of 10 mA cm^{-2} with the cell voltage no more than 1.74 V.

2. Materials preparation

The preparation of the hollow $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ is schematically demonstrated in Figure S1. First, the ZIF-67 nanoparticles were synthesized using cobalt ions and 2-methylimidazole. In TAA solution at 120°C , ZIF-67 formed hollow Co_3S_4 polyhedra. Then, some Co cations in Co_3S_4 were replaced with Cu cations by the cation exchange method to obtain $\text{Co}_3\text{S}_4/\text{CuS}$. Finally, the cobalt-nickel layered double hydroxide nanosheets were in situ grown on the $\text{Co}_3\text{S}_4/\text{CuS}$ to obtain $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$.

3. Results and discussion

As shown in Figure 1(a), the as-synthesized ZIF-67 nanoparticle is a clear rhombic dodecahedron shape [34], and the nanoparticle size is 289 nm. After the sulfuration, Co_3S_4 still maintains the same shape as ZIF-67 (Figure 1b), and the size is 275 nm. The interior of Co_3S_4 changes from solid to hollow is revealed by transmission electron microscopy (TEM) in the inset of Figure 1(b). The hollow structure of Co_3S_4 is also known as the Kirkendall effect [35] due to the difference in diffusivity of cobalt and sulfide ions. Then, using the cation exchange method, Co cations are replaced partly by Cu cations to obtain $\text{Co}_3\text{S}_4/\text{CuS}$ heterostructure in Figure 1(c), and the morphology still maintained the hollow structure (inset of Figure 1c). The $\text{Co}_3\text{S}_4/\text{CuS}$ heterostructure has a slightly

rougher surface compared to the smooth surface of ZIF-67, which is more conducive to the growth of the CoNi-LDH nanosheets. Finally, the CoNi-LDH nanosheets are grown on the surface of the $\text{Co}_3\text{S}_4/\text{CuS}$, and it can be seen from Figure 1(d) that the interconnected nanosheets are wrapped on the surface of $\text{Co}_3\text{S}_4/\text{CuS}$, and the thickness of CoNi-LDH nanosheets is 11 nm. The resulting $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ still maintains a hollow structure (inset of Figure 1d). The three regions in Figure 1(e) represent the lattice planes of CuS, Co_3S_4 and CoNi-LDH, respectively. The lattice spacings are 0.305, 0.550 and 0.256 nm, which is corresponding to the (102), (111) and (110) lattice planes of CuS, Co_3S_4 and CoNi-LDH, respectively [36], confirming the coexistence of CuS, Co_3S_4 and CoNi-LDH. The selected area electron diffraction (SAED) can also be indexed to the crystal planes of CuS, Co_3S_4 and CoNi-LDH (Figure 1f). Figure 1(g) is the high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and elements mapping of S, Co, Ni and Cu of a $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$, and the uniform distribution of S, Co, Ni and Cu elements is in the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$, especially the presence of Ni element proves that CoNi-LDH grows in the entire hollow structure of $\text{Co}_3\text{S}_4/\text{CuS}$ heterostructure. The morphology and elements mapping of Co_3S_4 , $\text{Co}_3\text{S}_4/\text{CuS}$ and $\text{Co}_3\text{S}_4@\text{CoNi-LDH}$ are shown in Figures S2–S4. The SEM and TEM images of the $\text{Co}_3\text{S}_4@\text{CoNi-LDH}$ are shown in Figure S5–S7.

The X-ray diffraction (XRD) measurement was performed on the Co_3S_4 , $\text{Co}_3\text{S}_4/\text{CuS}$ and $\text{Co}_3\text{S}_4@\text{CoNi-LDH}$ and $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$. As well seen, the XRD pattern of the synthesized ZIF-67 agrees well with the simulated pattern (CCDC deposition No.671073), confirming that the ZIF-67 MOFs have been synthesized successfully with high purity in Figure S8. The representative diffraction peaks located at 16.1° , 31.3° , 47.2° and 55.1° in the XRD pattern of Co_3S_4 in Figure 2(a) are indexed to (111), (311), (422) and (440) planes, respectively [37]. After cation exchange, a diffraction peak of CuS appears at 29.3° , corresponding to the (102) plane [38]. In the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$, the diffraction peak at 31.3° of Co_3S_4 is split into 29.3° and 32.9° corresponding to the (102) and (006) planes of CuS, respectively. When the CoNi-LDH is grown, the diffraction peaks appear at 11.6° and 60.9° , which is corresponding to the (003) and (110) planes of CoNi-LDH [39]. The XRD results state the successful synthesis of $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$.

To further demonstrate the heterostructure in $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$, the Fourier transform infrared (FTIR) spectra of Co_3S_4 , $\text{Co}_3\text{S}_4/\text{CuS}$, $\text{Co}_3\text{S}_4@\text{CoNi-LDH}$ and $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ were obtained, as shown in Figure 2(b). In Co_3S_4 , the peak at 1092 cm^{-1} is indexed to

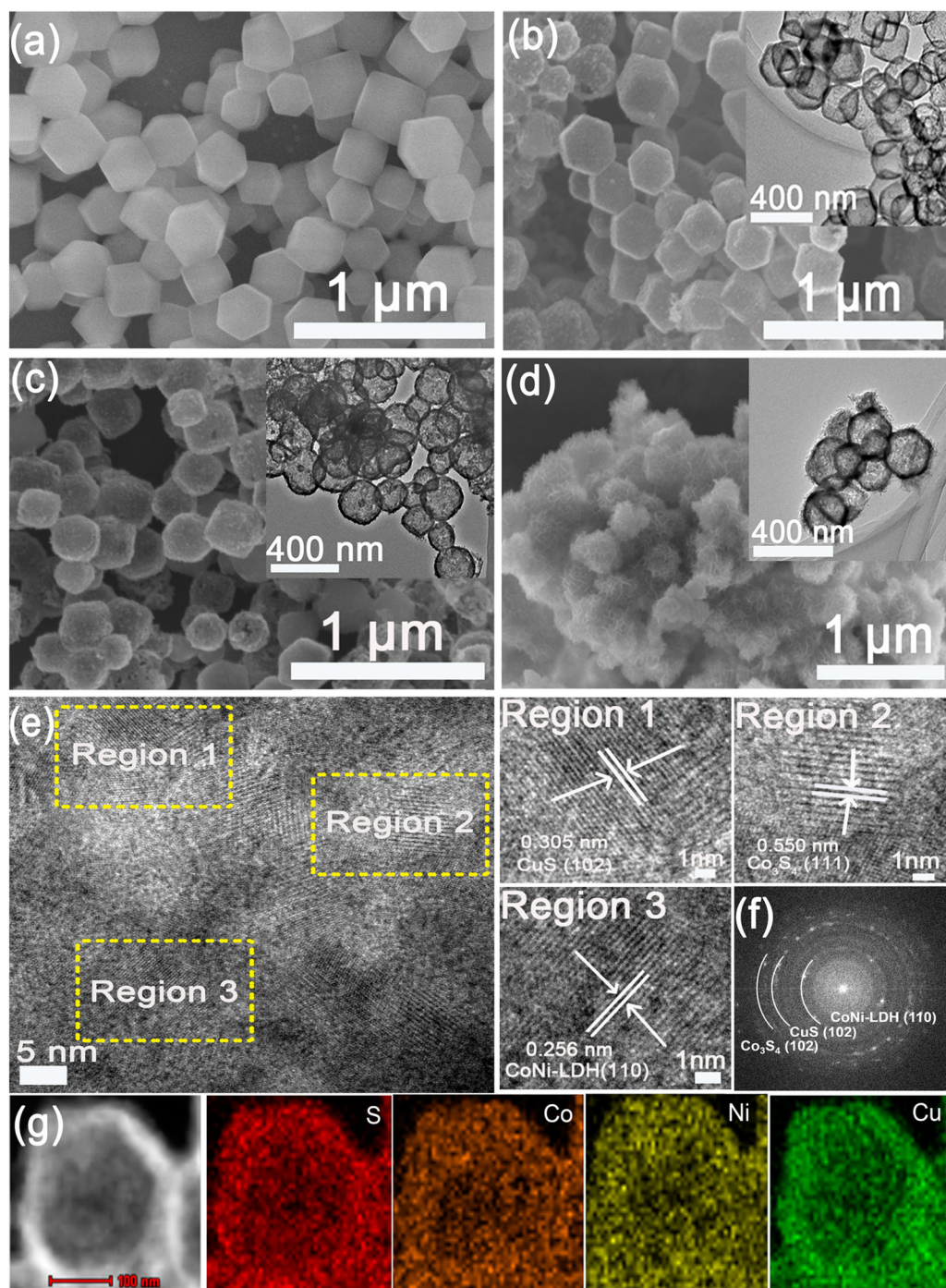


Figure 1. SEM images of (a) ZIF-67, (b) Co_3S_4 , (c) $\text{Co}_3\text{S}_4/\text{CuS}$, (d) $\text{Co}_3\text{S}_4/\text{CuS}@ \text{CoNi-LDH}$ (insets of (b–d) are the corresponding TEM images). (e) HRTEM images and (f) SAED pattern of a $\text{Co}_3\text{S}_4/\text{CuS}@ \text{CoNi-LDH}$. (g) HAADF-STEM and elemental mapping images for S, Co, Ni and Cu of a $\text{Co}_3\text{S}_4/\text{CuS}@ \text{CoNi-LDH}$.

the vibration of the Co–S bond [40]. Compared to Co_3S_4 , $\text{Co}_3\text{S}_4/\text{CuS}$ and $\text{Co}_3\text{S}_4/\text{CuS}@ \text{CoNi-LDH}$ show an obvious blue shift from 1092 cm^{-1} to 1149 cm^{-1} . This shift of the peak position in $\text{Co}_3\text{S}_4/\text{CuS}$ and $\text{Co}_3\text{S}_4/\text{CuS}@ \text{CoNi-LDH}$ is due to the introduction of Cu, where part of S in Co_3S_4 is bound to Cu in the interface of Co_3S_4 and CuS, indicating a strong electronic interaction between Co_3S_4 and CuS. In $\text{Co}_3\text{S}_4/\text{CuS}$ and $\text{Co}_3\text{S}_4/\text{CuS}@ \text{CoNi-LDH}$, the

peak position of Cu–S bond has a clear red shift from 467 cm^{-1} to 430 cm^{-1} compared with the Cu–S bond of CuS in the previous literature [41], which suggests that the $\text{Co}_3\text{S}_4/\text{CuS}$ heterojunction results in a strong interaction between Co_3S_4 and CuS. For $\text{Co}_3\text{S}_4@ \text{CoNi-LDH}$ and $\text{Co}_3\text{S}_4/\text{CuS}@ \text{CoNi-LDH}$, two peaks at 490 and 559 cm^{-1} are assigned to Ni–O and Co–O bond [42,43], respectively. Similarly, Raman spectra of Co_3S_4 ,

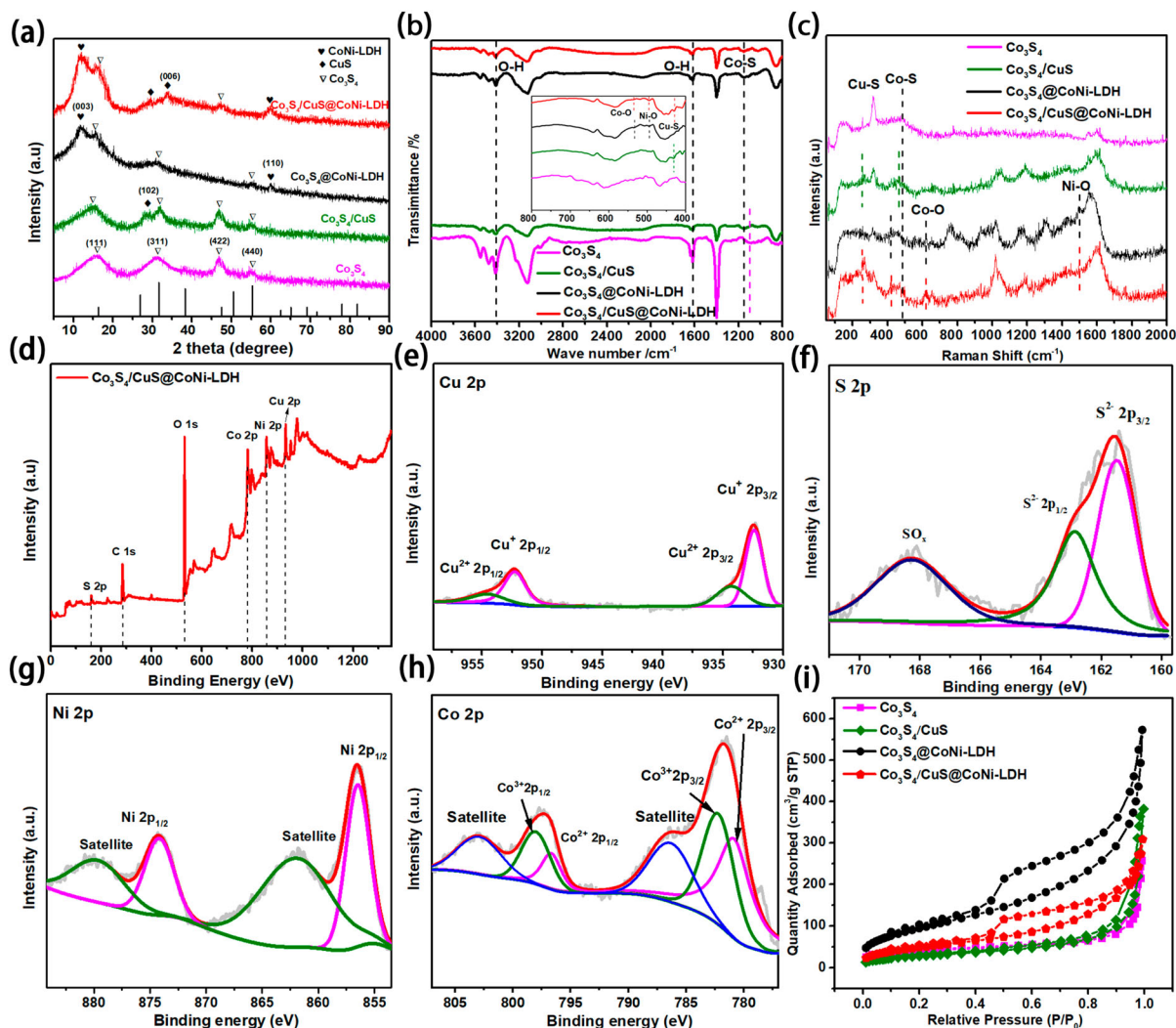


Figure 2. (a) XRD, (b) FTIR, (c) Raman and (i) N_2 adsorption–desorption curves of Co_3S_4 , Co_3S_4/CuS , $Co_3S_4@CoNi-LDH$ and $Co_3S_4/CuS@CoNi-LDH$. (d) XPS survey spectra of $Co_3S_4/CuS@CoNi-LDH$. The XPS spectra of (e) Cu 2p, (f) S 2p, (g) Ni 2p and (h) Co 2p.

Co_3S_4/CuS , $Co_3S_4@CoNi-LDH$ and $Co_3S_4/CuS@CoNi-LDH$ are shown in Figure 3(c). In Co_3S_4 , the peaks at 498 cm^{-1} is corresponding to the F_{2g} of vibration mode of Co_3S_4 [44]. Interestingly, the peaks have obvious red shifts at Co_3S_4/CuS and $Co_3S_4/CuS@CoNi-LDH$. In Co_3S_4/CuS , the peak shifts from 498 cm^{-1} to 463 cm^{-1} indicating that the heterojunction is formed between Co_3S_4 and CuS , which is consistent with the FTIR result. Similar to Co_3S_4/CuS , the Co–S peak in $Co_3S_4/CuS@CoNi-LDH$ has a red shift from 498 cm^{-1} to 423 cm^{-1} . In Co_3S_4/CuS and $Co_3S_4/CuS@CoNi-LDH$, the peak at 251 cm^{-1} is assigned to Cu–S, and the peak has an obvious red shift from 266 cm^{-1} to 251 cm^{-1} compared to the previous literature [45]. The peaks at 627 and 1518 cm^{-1} are attributed to the Co–O stretching and two-magnon (2M) mode of the Ni–O [46,47], respectively, in $CoNi-LDH$.

The element composition and surface chemical environment of $Co_3S_4/CuS@CoNi-LDH$ was also studied via the X-ray photoelectron spectroscopy (XPS) analysis. The XPS survey spectrum (Figure 2d) shows the presence of Cu, S, Ni, and Co as the main components of $Co_3S_4/CuS@CoNi-LDH$. The valence states of Cu in Figure 2(e) and Figure S11 are +1 and +2, indicating that the Cu ions successfully exchanged the Co ions [48]. The binding energy of Cu 2p in Co_3S_4/CuS (Figure S11) and $Co_3S_4/CuS@CoNi-LDH$ (Figure 2e) is lower than Cu 2p of CuS in the previous literature [49], which is due to the electron transfer from Co_3S_4 to CuS in the interface of Co_3S_4/CuS . In the high-resolution XPS spectrum (Figure 2f) of S 2p, the weak peaks at 161.8 and 163.2 eV are S^{2-} , demonstrating the formation of metal sulfides, and the high-energy peak position around 168.6 eV can be assigned to the sulfate groups [50]. Compared with

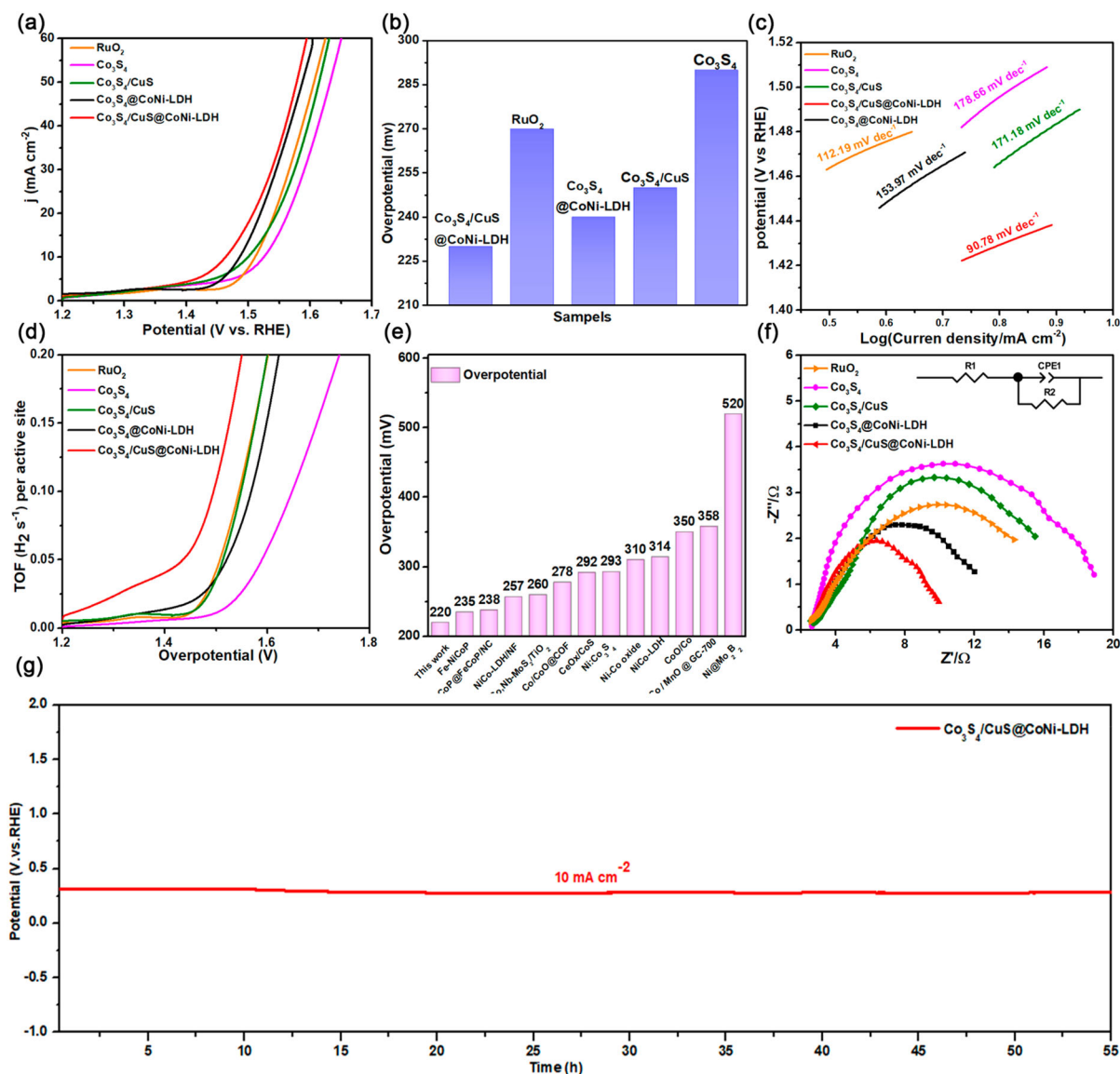


Figure 3. OER electrocatalysis in 1 M KOH. (a) LSV curves, (c) Tafel plots, (d) TOF and (f) Nyquist plots of RuO₂, Co₃S₄, Co₃S₄/CuS, Co₃S₄@CoNi-LDH and Co₃S₄/CuS@CoNi-LDH. (b) Comparison of the overpotential at 10 mA cm⁻². (e) Comparison of the overpotential of previously reported electrocatalysts with that of Co₃S₄/CuS@CoNi-LDH. (g) Potential time curve of Co₃S₄/CuS@CoNi-LDH.

Co₃S₄ (168.2, 162.4 and 161.3 eV), the binding energies of S in Co₃S₄/CuS (168.6, 162.9 and 161.6 eV) are higher, which is due to the formation of Co₃S₄/CuS heterojunctions. The Ni 2p regions are analyzed as Ni 2p_{1/2} (874.2 eV) and 2p_{3/2} (856.4 eV) in Figures 2(g) and S10, proving the existence of CoNi-LDH [51]. The high-resolution spectra of Co 2p in Figure 2(h) and S9-S11 show that the valence states of Co in all samples are +2 and +3, which are same from those in Co₃S₄, further indicating the formation of Co₃S₄ [52]. It is worth noting that the binding energy of Co (798.1 and 796.8 eV) in Co₃S₄/CuS is higher than that in Co₃S₄ (797.8 and 794.7 eV), suggesting that there is the electron transfer from Co₃S₄ to CuS in the interface of Co₃S₄ and CuS. Based on the above experimental results, the Co₃S₄/CuS heterostructure is formed

in the Co₃S₄/CuS@CoNi-LDH. Elemental compositions of Catalysts are determined by XPS in Table S1.

The N₂ adsorption-desorption isotherm (Figure 2i) was carried out, and the obtained results are listed in Table S2. The specific surface area size relationship is as follows: Co₃S₄/CuS@CoNi-LDH (258.10 m² g⁻¹) > Co₃S₄/CoNi-LDH (183.71 m² g⁻¹) > Co₃S₄/CuS (165.55 m² g⁻¹) > Co₃S₄ (150.55 m² g⁻¹). The specific surface area of Co₃S₄/CuS@CoNi-LDH and Co₃S₄/CoNi-LDH is slightly larger than that of Co₃S₄/CuS and Co₃S₄, indicating that the specific surface area is enlarged after loading LDH. Among them, the largest specific surface area of Co₃S₄/CuS@CoNi-LDH contributes to the electrochemical performance due to its more active sites and faster electrolyte diffusion. From the

pore size distribution in Figure S12, indicating that they are all mesoporous structure.

The OER activity of $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ was investigated in 1 M potassium hydroxide (KOH). Figure 3(a) shows the linear sweep voltammetry (LSV) curves of $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ with IR compensation, which exhibits a low overpotential of 220 mV at the current density of 10 mA cm^{-2} . The comparative samples overpotential are shown in Table S3. Besides, $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ shows better OER performance than the state-of-the-art RuO_2 . In addition to this, it can be observed that the LDH-supported catalyst is more active than the unsupported one. It is speculated that LDH provides more OH^- to participate in the OER reaction. Figure 3(b) shows the overpotential comparison of $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ and the control sample. It can be seen that $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ has a relatively low OER overpotential. The $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ has a lower Tafel slope of $90.78 \text{ mV dec}^{-1}$ in OER (Figure 3c), which is lower than that of the state-of-the-art RuO_2 catalyst, revealing the higher OER rate and favorable kinetics of it. The turnover frequency (TOF) can reflect the intrinsic activity of the catalyst, and it can be found that the catalytic activity of $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ is higher than that of other samples in Figure 3(d). Impressively, the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ exhibits superior electrocatalytic performance over other previously reported CoNi-based catalysts (Figure 3e).

Electrochemical impedance spectroscopy (EIS) measurements are shown in Figure 3(f). The EIS data are all fitted by an equivalent circuit (inset of Figure 3f), consisting of a resistor (R_1) in series with a parallel combination of a resistor (R_2) and a constant-phase element [53]. The lower R_2 value corresponds to the faster reaction rates. The $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ in OER shows the smallest R_2 , which is consistent with the low overpotential and small Tafel slope in the above analysis. The resulting R_2 values are shown in Table S4. Figure 3(g) shows that $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ maintains a current density of 10 mA cm^{-2} for at least 50 h, the overpotential only changed slightly by 1.0%. As a comparison, the overpotential of RuO_2 , Co_3S_4 , $\text{Co}_3\text{S}_4/\text{CuS}$, and $\text{Co}_3\text{S}_4@\text{CoNi-LDH}$ (Figure S13–S16) at the current density of 10 mA cm^{-2} changed by 10.9%, 1.8%, 13.6% and 1.7%, respectively. It is worthwhile noting that the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ shows outstanding catalytic stability, and the high catalytic activity is still maintained even after 50 h of continuous operation. The cyclic voltammetric (CV) scans with different rates were performed to determine the double-layer capacitance C_{dl} , which can be used to estimate the ECSA and the corresponding intrinsic activity [54]. The CV curves were measured in N_2 -saturated 1 M KOH in Figure S17, and

C_{dl} calculated from CV is shown in Figure S18. The C_{dl} value of $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ is much higher than that of other catalysts and RuO_2 , further indicating that $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ can expose more catalytic active site. The durability of the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ after the OER test was confirmed by TEM and XRD (Figures S19 and S20), and no prominent change was found.

The electrocatalytic HER performance of each material was also investigated in Figure 4. Figure 4(a) shows the LSV curves of samples with IR compensation, which shows that the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ has high HER activity. The overpotential of $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ is 136 mV at a current density of 10 mA cm^{-2} , which is slightly higher than the commercial Pt/C and lower than other comparative sample in Figure 4(b) and Table S5. Therefore, the enhanced activity of $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ is related to the heterostructure of $\text{Co}_3\text{S}_4/\text{CuS}$. To study the kinetic activity of each catalyst, the Tafel slope curve of each catalyst is plotted in Figure 4(c). The Tafel slope of $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ in HER is $126.3 \text{ mV dec}^{-1}$, which is slightly larger than the commercial Pt/C, but smaller than $\text{Co}_3\text{S}_4/\text{CuS}$, $\text{Co}_3\text{S}_4@\text{CoNi-LDH}$ and Co_3S_4 , consistent with the results measured above. The TOF of $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ is higher than that of other samples in Figure 4(d). Moreover, $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ exhibits superior electrocatalytic HER performance over other previously reported CoNi-based catalysts in Figure 4(e). Similarly, the catalyst kinetics at the electrode interface was investigated by EIS measurements in Figure 4(f). The order of R_2 values obtained in HER indicates that the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ has a more optimized charge transfer ability than other catalysts, and the resulting R_2 values are shown in Table S6. Figure 4(g) shows that $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ maintains a current density of 10 mA cm^{-2} for at least 50 h, and the overpotential only changed slightly by 1.8%. As a comparison, in Figures S22–S24, the potentials of $\text{Co}_3\text{S}_4/\text{CuS}$, Co_3S_4 , and $\text{Co}_3\text{S}_4@\text{CoNi-LDH}$ at 10 mA cm^{-2} changed by 5.0%, 3.2%, and 3.8%, respectively. After 35 h, the potential of Pt/C decreased sharply by 23.0% in Figure S21. Therefore, the above experimental results prove the excellent stability of the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ as a water electrolysis catalyst. As shown in Figure S25, the CV curves in N_2 -saturated 1 M KOH. The results of C_{dl} calculated by CV are shown in Figure S26. The results of C_{dl} indicate the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ has higher ECSA and more catalytic active sites. The durability of the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ after the HER test was confirmed by TEM and XRD (Figures S27 and S28), and no prominent change was found.

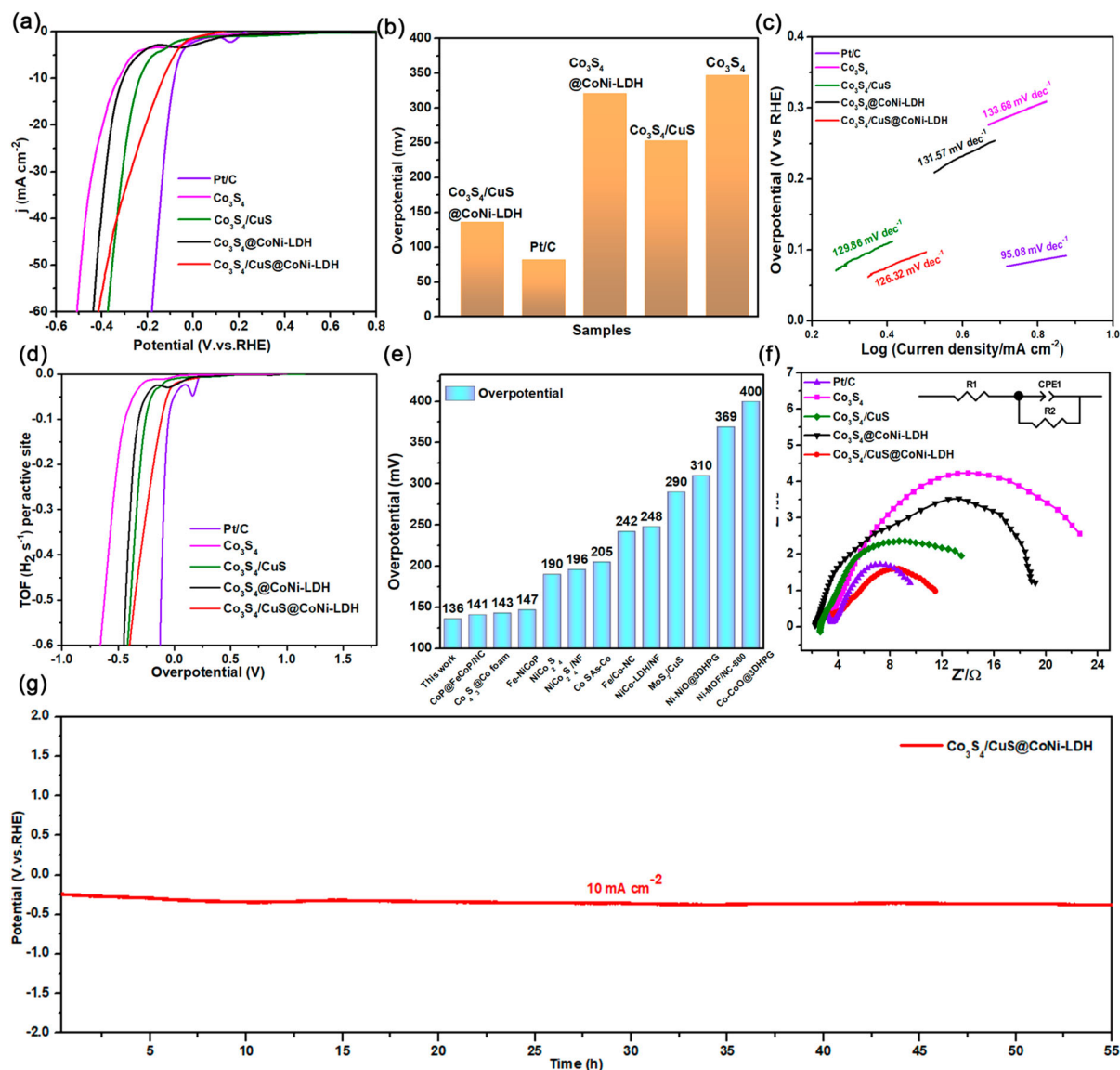


Figure 4. HER electrocatalysis in 1 M KOH. (a) LSV curves, (c) Tafel plots, (d) TOF and (f) Nyquist plots of Pt/C, Co₃S₄, Co₃S₄/CuS, Co₃S₄@CoNi-LDH and Co₃S₄/CuS@CoNi-LDH. (b) Comparison of the overpotential of achieving a current density of 10 mA cm⁻². (e) Comparison of the overpotential values of previously reported electrocatalysts with that of Co₃S₄/CuS@CoNi-LDH. (g) Potential-time curve of Co₃S₄/CuS@CoNi-LDH.

Inspired by the excellent electrocatalytic properties of HER and OER, the Co₃S₄/CuS@CoNi-LDH serves as anode and cathode to prepare electrolyzers for overall water splitting in an alkaline solution. As shown in Figure 5(c), the dual-functional Co₃S₄/CuS@CoNi-LDH and Co₃S₄@CoNi-LDH achieved a current density of 10 mA cm⁻² at potentials of 1.74 and 1.84 V, respectively, which is lower than the overall hydrolysis potential (1.88 V) of RuO₂||Pt/C. The calculated potential of total hydrolysis and the actual measurement are shown in Figure 5(d). The overall hydrolysis potential calculated based on HER and OER is slightly lower than the

actual measured. In addition to the high catalytic efficiency, the Co₃S₄/CuS@CoNi-LDH||Co₃S₄/CuS@CoNi-LDH was tested at 10 mA cm⁻² for 50 h, only a weak potential decay was observed, and the potential can maintain 99.9%, which further proves the durability. In Figures S29 and S30, the overall water splitting stability of Co₃S₄@CoNi-LDH||Co₃S₄@CoNi-LDH and RuO₂||Pt/C is compared. After 50 h, the Co₃S₄@CoNi-LDH||Co₃S₄@CoNi-LDH and RuO₂||Pt/C remain at 89.5% and 90.0% of their original values, respectively. To realize the efficient utilization of green resources, the assembled electrolyzer is driven by solar cells. Figure 5(a)

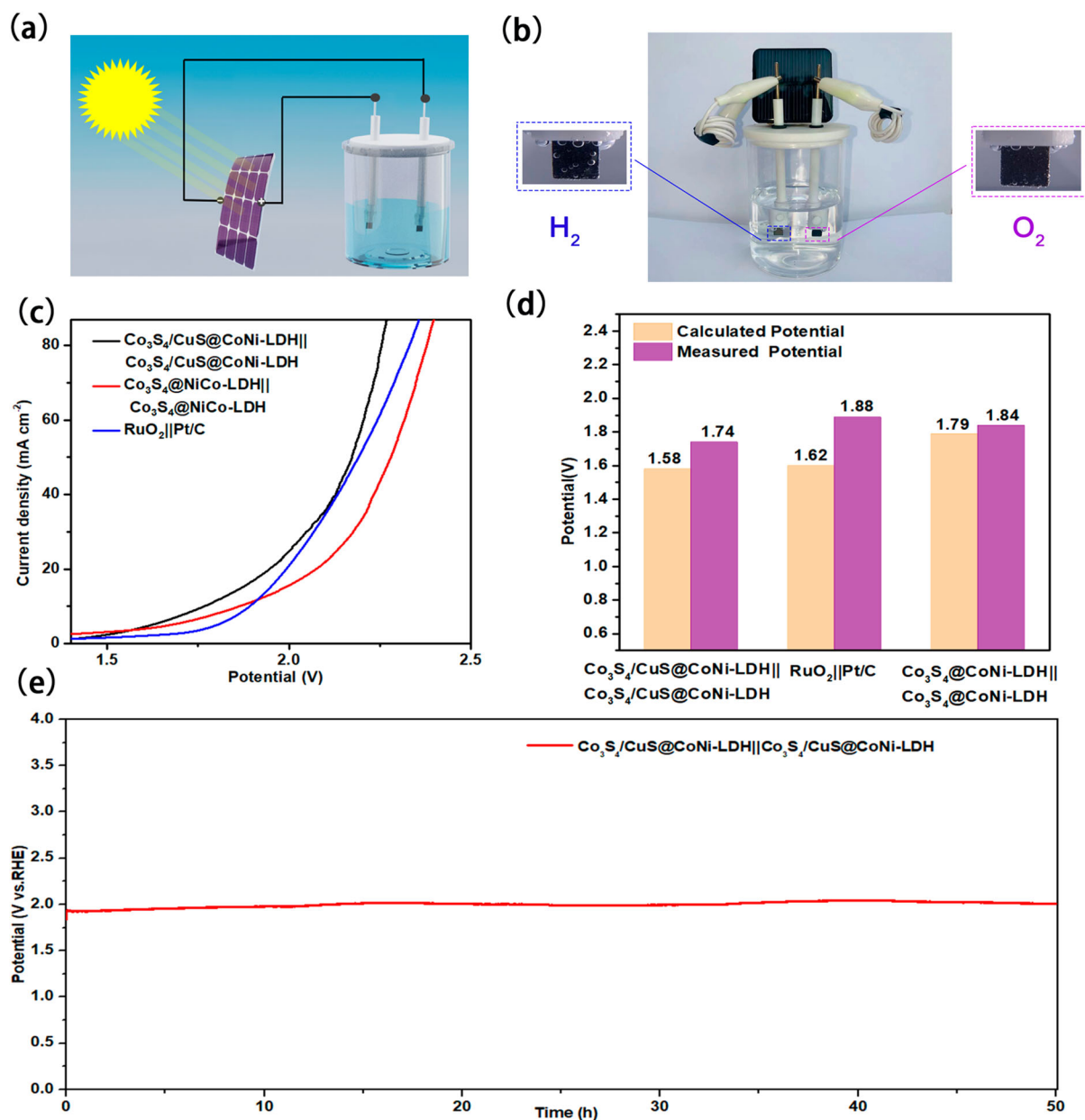


Figure 5. (a) Scheme of water-splitting device powered by a solar panel. (b) Real photo of solar panel measuring total hydrolysis. (c) The catalytic performance of the $\text{RuO}_2||\text{Pt/C}$, $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}||\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$, $\text{Co}_3\text{S}_4@\text{CoNi-LDH}||\text{Co}_3\text{S}_4@\text{CoNi-LDH}$. (d) Comparison of the potential of achieving a current density of 10 mA cm^{-2} . (e) Total hydrolytic stability of $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}||\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ for 50 h.

is a schematic diagram of overall hydrolysis under the driving conditions of solar panels. When the assembled cell was exposed to sunlight, bubbles were generated at both the cathode and anode of the two-electrode system in Figure 5(b). The potential of the solar panel was measured by the voltmeter in Figure S31, the solar panel produced a potential of 1.97V. And the attached video shows the overall water splitting dynamics and the bubble generation and accumulation process driven by the solar panel, proving that the $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ has excellent bifunctional catalytic performance.

4. Conclusion

The hollow $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ is prepared by using ZIF-67 as a template and precursor, and the CoNi-LDH nanosheets are uniformly grown on the surface of hollow $\text{Co}_3\text{S}_4/\text{CuS}$ to form a unique heterostructure electrocatalytic catalyst. The hollow $\text{Co}_3\text{S}_4/\text{CuS}@\text{CoNi-LDH}$ achieved OER overpotential of 220 mV, HER overpotential of 136 mV, respectively, at the current density of 10 mA cm^{-2} . The excellent OER and HER activities can be attributed to the abundant active sites from hollow structures and heterojunctions. The hollow structure can

provide a larger surface area, exposing more catalytical active sites, and the heterostructure improves the structural stability, and the synergistic effect of the bimetal sulfides increases the catalytical activity. This work opens a novel avenue for designing the bifunctional catalyst for overall electrochemical water splitting.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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