

Article

Facile Construction of Three-Dimensional Heterostructured CuCo_2S_4 Bifunctional Catalyst for Alkaline Water Electrolysis

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Abstract: Developing an efficient multi-functional electrocatalyst with high efficiency and low cost to replace noble metals is significantly crucial for the industrial water electrolysis process and for producing sustainable green hydrogen (H_2) fuel. Herein, ultrathin CuCo_2S_4 nanosheets assembled into highly open three-dimensional (3D) nanospheres of CuCo_2S_4 ($\text{Cu}/\text{Co} = 33:67$) were prepared by a facile one-pot solvothermal approach and utilized as a bifunctional electrocatalyst for efficient overall water splitting. The as-prepared CuCo_2S_4 is characterized structurally and morphologically; the BET surface area of the CuCo_2S_4 ($\text{Cu}/\text{Co} = 33:67$) catalyst was found to have a larger specific surface area ($21.783 \text{ m}^2 \text{ g}^{-1}$) than that of other catalysts with a Cu/Co ratio of 67:33, 50:50, and 20:80. Benefiting from a highly open structure and ultrathin nanosheets with excellent exposure to catalytically active sites, CuCo_2S_4 ($\text{Cu}/\text{Co} = 33:67$) is identified as an efficient catalyst for the proton reduction and oxygen evolution reactions in 1 M KOH with an overpotential of 182 and 274 mV at 10 mA cm^{-2} , respectively. As expected, a low cell voltage of 1.68 V delivers a current density of 10 mA cm^{-2} . Stability and durability are also greatly enhanced under harsh alkaline conditions. Therefore, this work provides a simple strategy for the rational design of spinel-based transition metal sulfide catalysts for electrocatalysis.

Keywords: alkaline water electrolysis; solvothermal; CuCo_2S_4 ; electrocatalyst; hydrogen evolution reaction; oxygen evolution reaction; overall water splitting



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1. Introduction

Clean hydrogen energy is a promising alternative to traditional fossil fuels because of its high energy density, light weight, sustainability, and regenerative properties [1,2]. Recently, electrochemical water splitting has been desirable to produce high-purity hydrogen at a low cost and with convenience [3]. A high-performance electrocatalyst is required in the electrode to trigger electrochemical reactions such as the oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode. However, their performance could be improved due to the most energy-consuming anodic oxygen evolution reaction (OER) involving the four-electron transfer process. A high overpotential is needed for the electrolytic cell in electrolyzed water practical applications, resulting in excessive power consumption. The current key challenge of water splitting depends on electrocatalysts, which reduce the energy barrier with improved OER and HER kinetics [4,5]. So far, the most efficient electrocatalysts still rely on noble metals such as Pt, RuO_2 , and IrO_2 ; their low reserve and high cost hinder their further industrial applications. Therefore, developing alternative electrocatalysts for efficient OER and HER from water is challenging. Several high-performance multifunctional electrocatalysts are being explored and designed to efficiently, cheaply, and abundantly replace noble metals [6,7].

An extensive investigation of non-noble metals has been widely conducted in the field of electrocatalysis, such as transition metal oxides [8], carbides [9], and phosphides [10].

Among them, spinel-structured transition metal materials have attracted significant attention due to their competitive cost and excellent performance of HER or OER [11]. As a result, it is desirable to investigate the development of highly effective, low-cost, and environmentally friendly bifunctional electrocatalysts that allow the OER and HER to consume less energy [12,13]. Several ways have been devised to maximize water splitting activity, such as nanostructures, composites, noble metal doping, morphology, and the support of substrates with a high active surface area [14–16]. However, using the earlier techniques to create effective catalysts is still tricky. Ternary sulfide compounds have been reported as highly efficient catalysts due to the strong building of the S-S interface [17,18]. Moreover, the formation of hybrid ternary composites based on AB_2S_4 thiospinel can be an efficient catalyst for water splitting [19–21].

In this view, transition-metal oxides with spinel structures, such as $NiCo_2O_4$ [22,23], $FeCo_2O_4$ [16,24], and $MnCo_2O_4$ [25], have been extensively explored as electrocatalysts in the water-splitting process. However, spinel oxide compounds are used for higher efficiency and encounter typical troubles such as poor conductivity, fewer active sites, limited contact with the electrolyte, and unsatisfactory stability under harsh conditions. Recently, spinel-like transition metal sulfides (AB_2S_4) have been introduced with improved conductivity and redox activity compared to their corresponding oxides. The differing adsorption energies between the active sites of catalysts and catalyzed molecules can significantly affect catalytic efficiency. Earlier work has described a method for altering the crystal plane's adsorption energy and stabilizing the crystal structure by doping with copper ions [14,26–28]. A sufficient amount of crystal surface adsorption energy is anticipated to improve activity and structural stability in binary metal thiospinels simultaneously. It is reported that the octahedral sites of spinels are reactive for OER whereas the tetrahedral sites are rarely active; therefore, {111} plane of spinel with maximum exposure of octahedrally coordinated cations is more catalytically active for OER than other crystal planes. Combining highly conductive reduced graphene oxide with active metal sulfide compounds demonstrates substantial properties to increase the catalytic activity of the reduction process. The substitution of metal atoms in the thiospinel structure effectively improves the d orbital properties that can take electrons or electron pairs and improve the bifunctional properties [29,30].

Motivated by these reports, $CuCo_2S_4$ was chosen as a target material because of the specificity, cost-effectiveness, and performance advantages of copper ion doping. As a typical ternary thiospinel, it has the ideal formula AB_2S_4 , in which Co^{3+} ions occupy the octahedral sites and Cu occupies the tetrahedral sites and was recently reported to be catalytically active for oxygen reduction and evolution reactions [19,31]. $CuCo_2S_4$ is traditionally prepared via solid-state methods at high temperatures and for a prolonged time to overcome the reaction energy barriers. The as-obtained spinels often lead to aggregated sizes, irregular structures, and low surface area, severely affecting their physicochemical performance. More concern has been dedicated to developing alternative strategies under mild conditions. For example, thiospinel $CuCo_2S_4$ nanoparticles were reported via solution synthesis. Cobalt(III) acetylacetonate and copper(II) acetylacetonate were heated to 200 °C in a mixture of oleic acid and oleylamine, then added sulfur powder.

Considering the specific geometric structure and excellent redox chemistry of co-based catalysts and the cost-effectiveness and performance advantages of copper ion doping, spinel-structured cobalt-cobalt-copper ($CuCo_2S_4$) has become a hot topic in electrochemical catalyst research. Due to the poor conductivity of the spinel structure of the catalyst, electron transfer is hindered. Thus, the present study focused on the hydrothermal synthesis of structurally modified $CuCo_2S_4$ by changing the conditions of product formation. In addition, the specific area and the catalytic active sites are also increased by constructing this three-dimensional, flower-like $CuCo_2S_4$ nanosphere. The $CuCo_2S_4$ electrocatalyst exhibits superior activity, achieving current densities of 10 mA cm^{-2} at low overpotentials for HER and OER in alkaline electrolytes. Furthermore, the respective two-electrode alkaline water electrolyzer exhibits a low cell voltage, a higher current density, and remarkable stability over 12 h of continuous electrolysis. This good catalytic performance is caused by doping

the metal cation, which distorts the crystal lattice of the sample. Experiments found that the probabilities of the catalytic properties are closely related to the distribution and quantity of the metal cations in the detailed lattice structure.

2. Results and Discussions

2.1. Structural Characterization of the Catalyst

Highly open CuCo_2S_4 nanosheets were prepared via a one-step solvothermal procedure in the presence of the surfactant CTAB. The morphology and microstructures of CuCo_2S_4 nanospheres with different ratios of Cu and Co have been studied with SEM and XRD analysis. As shown in Figure 1a, a layer-like structure of CuS presents a significant degree of agglomeration (with a Cu/Co ratio of 100:0), showing an average size of 200 nm. For a Cu/Co ratio of 67:33, it persists in a sheet-like structure; however, the size and thickness become larger upon increasing the doping percentage of Co (Figure 1b). For a catalyst with a Cu/Co ratio of 50:50 (Figure 1c), the sheet-like structure gathered into a spherical particle with a size of about 700 nm. Further increasing the doping percentage of Co (Cu/Co ratio of 33:67), there are no changes in the size. In contrast, the nanosheets become thinner and gather into flower-like nanospheres with a particle size of about 100 nm (Figure 1d). Similar observations were obtained for the Cu/Co ratio of 20:80 (Figure 1e) with an increased number of particles. For CoS (with a Cu/Co ratio of 0:100), it can be seen that the particles clumped as a whole block structure (Figure 1f).

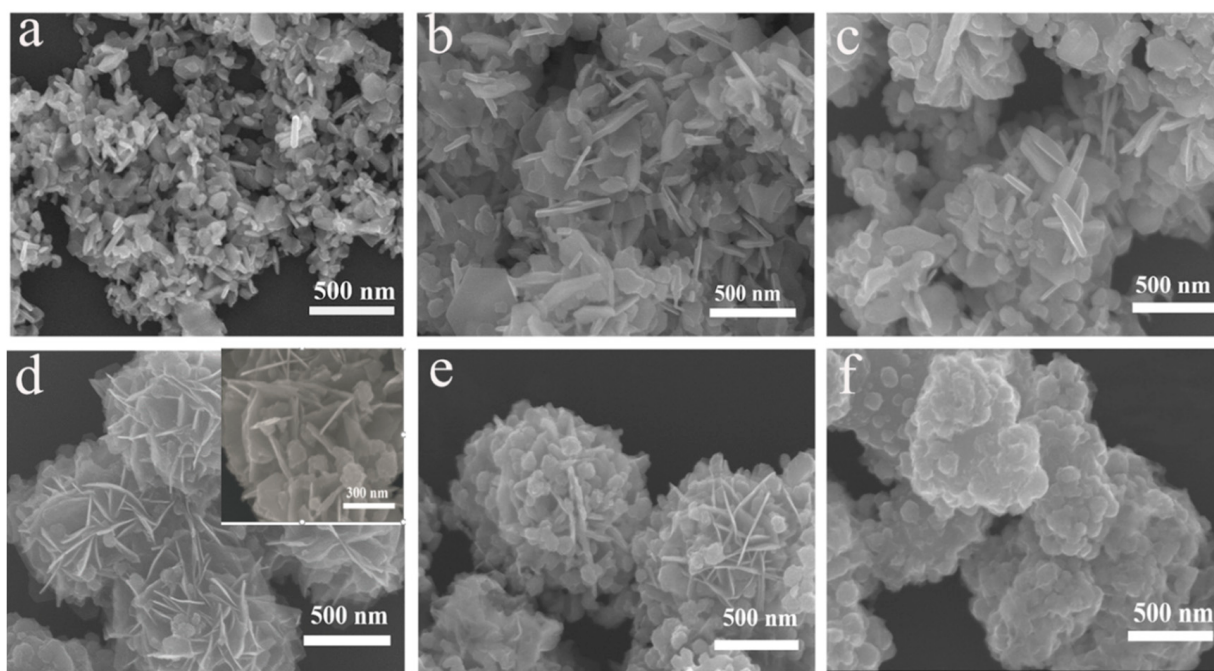


Figure 1. Scanning electron micrograph of CuCo_2S_4 nanospheres with different percentages of Cu/Co. (a) 100:0, (b) 67:33, (c) 50:50, (d) 33:67, (e) 20:80, and (f) 0:100.

The XRD patterns of CuCo_2S_4 nanospheres with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) are presented in Figure 2. The diffraction patterns of CuS (with a Cu/Co ratio of 100:0) are positioned at $2\theta = 27.7^\circ$, 29.3° , 31.80° , and 47.9° , which can be attributed to the (101), (102), (103) and (110) planes of CuS with JCPDS no. 06-0464 (Figure 2a). Similarly, Figure 2b shows the XRD pattern of CoS (with a Cu/Co ratio of 0:100). As shown in Figure 2b, the XRD peaks appearing at $2\theta = 30.9$, 35.6 , 47.0 , and 54.6 can be indexed to the (204), (220), (306), and (330) planes of CoS 1.097 crystals, which are in good agreement with the standard data of JCPDS no. 19-0366). The XRD patterns of other catalysts are presented in Figure 2c. The characteristic peak of CuS at $2\theta = 29.3^\circ$ and 47.9° gradually disappeared upon increasing the Co percentage in CuCo_2S_4 nanospheres.

Further, a shift in the XRD pattern to a lower angle was observed, which thus indicates the formation of a Cu-Co-S compound due to the successive substitution of Co into the crystal lattice of CuS. For the catalyst (with a Cu/Co ratio of 33:67), the diffraction peaks appeared at $2\theta = 26.6^\circ$ (022), 31.3° (113), 38.0° (004), 47.0° (224), 50.0° (115), and 54.8° (044). Furthermore, the XRD pattern of the catalyst (with a Cu/Co ratio of 33:67) was analogous to that of CuCo_2S_4 crystals (JCPDS no. 42-1450). With the further increase in Co percentage, the characteristic peak of CuCo_2S_4 crystals at $2\theta = 38.0^\circ$ has gradually decreased. For CoS (with a Cu/Co ratio of 0:100), the peak at $2\theta = 38.0^\circ$ disappeared utterly, and a new peak appeared at $2\theta = 35.6^\circ$, which is indexed to the characteristics of the diffraction plane (220) of CoS crystal (JCPDS no. 19-0366).

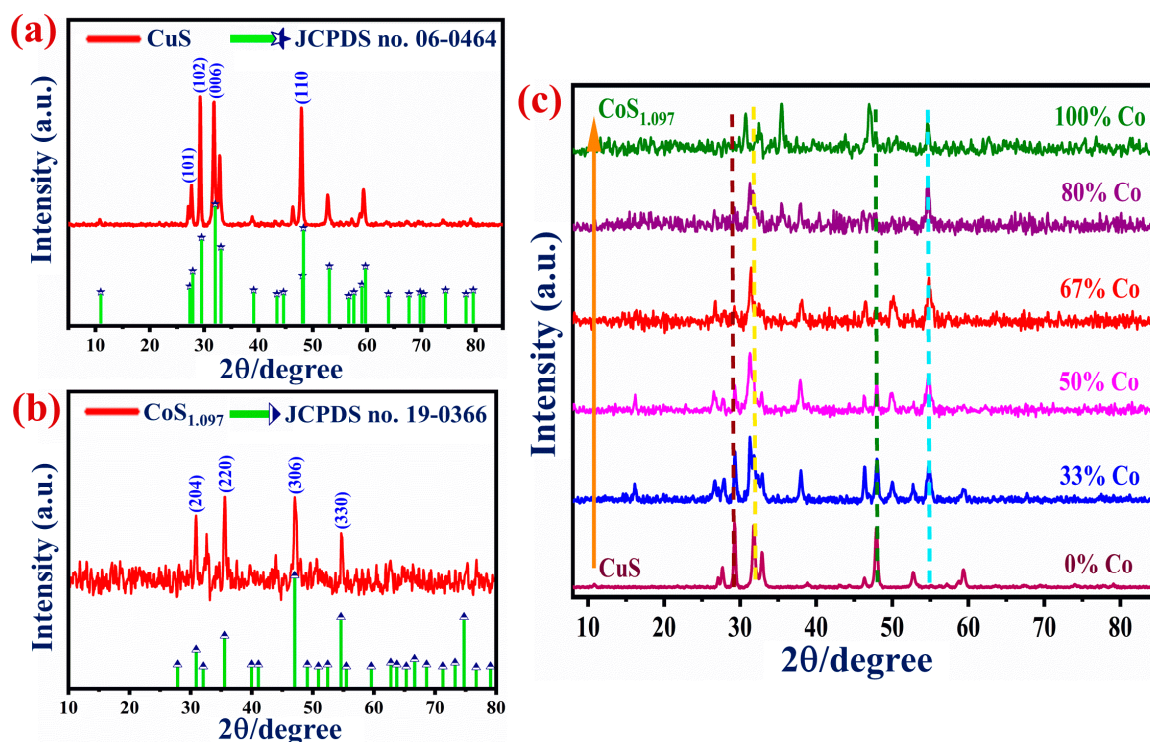


Figure 2. The XRD diffraction of (a) CuS (with a Cu/Co ratio of 100:0), (b) CoS (with a Cu/Co ratio of 0:100), and (c) CuCo_2S_4 nanospheres with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100).

The surface areas and pore-size distributions of CuCo_2S_4 nanospheres with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) were investigated by N_2 adsorption-desorption isotherms and are presented in Figure 3a–f. As shown in Figure 3a, it is observed that the nitrogen absorption and desorption curves of CuS (with a Cu/Co ratio of 100:0) appeared at high relative pressure with distinct hysteresis loops of the H4 type, which thus indicates that the catalyst has a mesoporous structure [32]. Further, this H4 hysteresis loop belongs to the slit pore but differs from the pore produced by a layered structure. Moreover, the BET result is in good agreement with the SEM analysis shown in Figure 1. Further, an H3 hysteresis loop with a linear elevation of slope (P/P_0 from 0.3 to 0.8) [33] was obtained for other catalysts (with Cu/Co ratios of 67:33, 50:50, 33:67, 20:80, and 0:100) and thus indicated the presence of a large number of mesopores in the synthesized catalysts. The presence of larger mesopores or macropores in the sample can be confirmed by an abrupt jump (a steep increment in $P/P_0 > 0.8$) in the adsorption of N_2 . For the catalyst (with a Cu/Co ratio of 33:67), the adsorption-desorption curve of nitrogen is not closed, which may be due to the structural changes during the adsorption process. The catalyst with a Cu/Co ratio of 33:67 was found to have a larger specific surface area ($21.783 \text{ m}^2\text{g}^{-1}$) (Figure 3d)

than that of other catalysts with a Cu/Co ratio of 67:33 ($14.794 \text{ m}^2\text{g}^{-1}$) (Figure 3b), 50:50 ($20.031 \text{ m}^2\text{g}^{-1}$) (Figure 3c), and 20:80 ($14.839 \text{ m}^2\text{g}^{-1}$) (Figure 3e), respectively. Thus, it confirms that the catalyst with a Cu/Co ratio of 33:67 contains more active sites, which is beneficial to the further electrocatalytic reaction [34]. For CoS (with a Cu/Co ratio of 0:100), hysteresis loops in the middle and high-pressure regions indicate that large mesopores or macropores are present in the sample. In addition, the specific surface area of CoS was reduced to $11.839 \text{ m}^2\text{g}^{-1}$ (Figure 3f), which may be due to the agglomeration of CoS particles. This result is consistent with SEM analysis (Figure 1). Among the different percentages of Cu/Co, a catalyst with a Cu/Co ratio of 33:67 was an optimized percentage for the synthesis of CuCo_2S_4 nanospheres with structural properties and contained more active sites. Thus, we chose the catalyst with a Cu/Co ratio of 33:67 as the best catalyst for the electrochemical hydrogen evolution (HER) performance analysis.

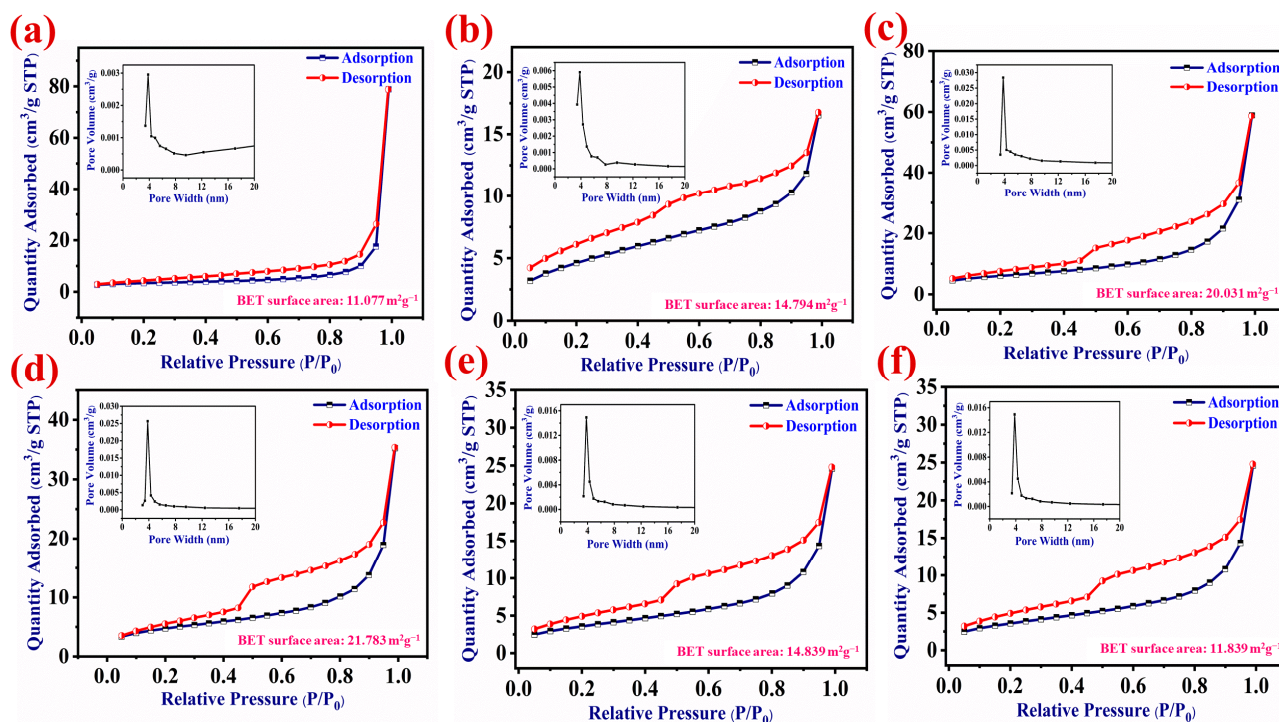


Figure 3. The N_2 adsorption-desorption isotherms of CuCo_2S_4 catalysts with different percentages of Cu/Co. (a) 100:0, (b) 67:33, (c) 50:50, (d) 33:67, (e) 20:80, and (f) 0:100. The insets are corresponding pore size distribution plots.

The HRTEM images of CuCo_2S_4 nanospheres with a Cu/Co ratio of 33:67 are given in Figure 4. It is observed that CuCo_2S_4 nanospheres are composed of sheet-like layers (Figure 4b), and these layers are randomly assembled to form the agglomerated flower-like structure. The inset in Figure 4b shows the high-magnified TEM images of CuCo_2S_4 nanospheres, which confirm that the CuCo_2S_4 nanospheres have a sheet-like structure. Further, Figure 4c clearly shows the lattice fringes in different directions with an interlayer distance of 0.33 nm and 0.28 nm corresponding to the (022) and (113) faces of the cubic phase of CuCo_2S_4 (JCPDS-42-1450) (Figure 4a). The presence of three elements (i.e., Cu, Co, and S) was further confirmed by the appearance of notable signals for elemental Cu, Co, and S in the elemental mapping and X-ray energy spectrum (EDS) of the CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 (Figure 4d,e). It shows that the sample mainly contains the three elements (i.e., Cu, Co, and S) with an even distribution.

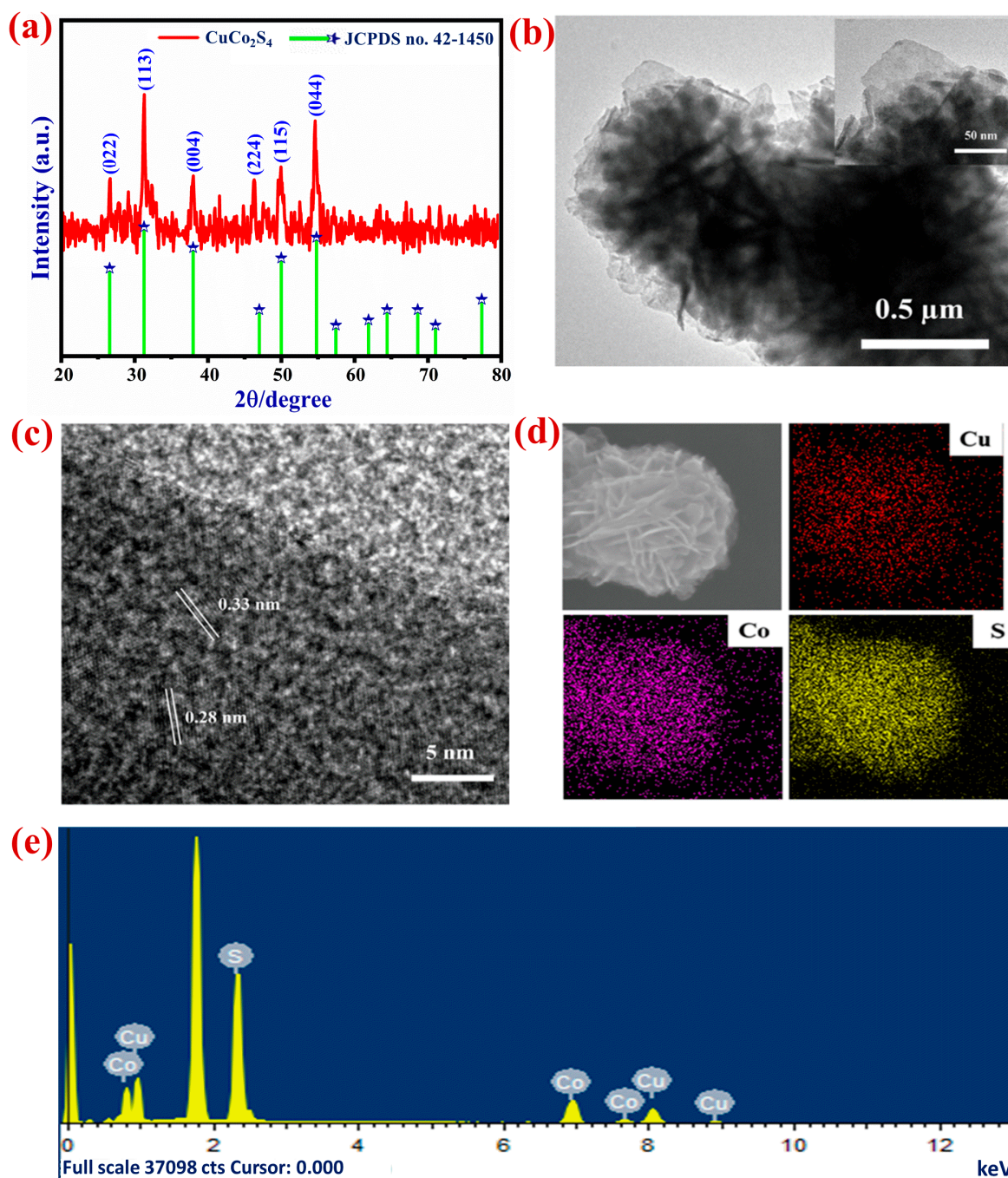


Figure 4. (a) XRD diffraction, (b) TEM images, (c) HRTEM, (d) elemental mapping, and (e) EDS spectra of CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67.

The chemical composition and chemical state of the CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 are detected by X-ray photoelectron spectroscopy (XPS). Figure 5a shows the survey spectrum of the CuCo_2S_4 catalyst and infers the existence of Cu, Co, S and C elements. As revealed in Figure 5b, two distinct peaks at 932.0 eV and 952.0 eV were attributed to the binding energy of Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. The peak at 956.2 eV was ascribed to the characteristic satellite peak of Cu (II) ions [35]. Similarly, the binding energies at 795.3 and 779.6 eV are attributed to the spin-orbit bimodal of the $2p_{1/2}$ and $2p_{3/2}$ peaks of the Co (II) ion. Furthermore, the signal peaks at 793.9 and 778.6 eV can be assigned to the spin-orbit bimodal of the $2p_{1/2}$ and $2p_{3/2}$ peaks of the Co (III) ion. In addition, the small peaks at 803.0 eV and 786.3 eV were attributed to the characteristic

satellite peaks of Co (III) and Co (II) ions (Figure 5c), respectively [36]. This result indicates the coexistence of Co^{2+} and Co^{3+} , which is consistent with the previous reports on cobalt-based spinel structure compounds. Figure 5d shows the XPS spectra of S 2p, with two characteristic peaks at 162.3 and 161.1 eV ascribed to the spin-orbit bimodal peaks of the $2p_{1/2}$ and $2p_{3/2}$ peaks of the S 2p ion [37].

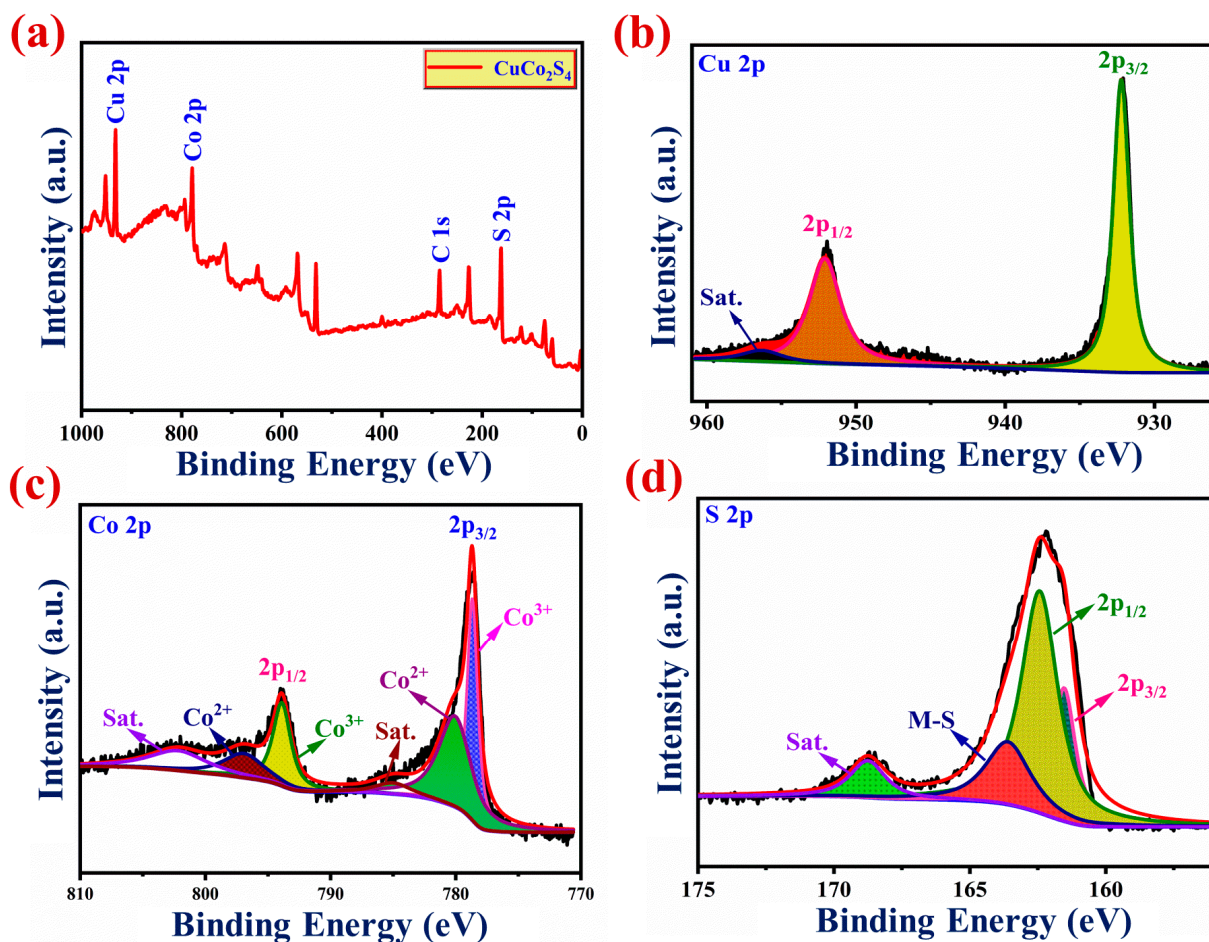


Figure 5. X-ray photoelectron spectroscopy (XPS) of CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67. (a) Survey scan spectra; (b) high-resolution Cu 2p; (c) high-resolution Co 2p; and (d) high-resolution S 2p of CuCo_2S_4 .

Further, the priority of S 2p in CuCo_2S_4 was confirmed by the appearance of a weak satellite peak at 168.6 eV [38]. The peak at 163.8 eV is attributed to the typical metal-sulfur (MS) bond peak in the CuCo_2S_4 material [36]. The XPS analysis confirmed the chemical composition of the CuCo_2S_4 catalyst. By XRD analysis, the result is consistent with forming a Cu-Co-S composite with a CuCo_2S_4 phase on the Ni foam.

2.2. Characterization of Electrochemical Performance

2.2.1. Electrochemical Hydrogen Evolution (HER) Performance Analysis

The HER electrocatalytic behavior of the CuCo_2S_4 catalyst was evaluated by linear sweep voltammetry (LSV) curves using 1 M KOH (pH = 14) as the electrolyte, and the results are presented in Figure 6. Before that, the performance of the CuCo_2S_4 catalyst was stabilized by several cycles of cyclic voltammetry. The catalytic activity of the present catalysts was compared with that of blank Ni foam (NF), and standard Pt/C electrodes for HER were also investigated. Figure 6a shows that the current density increases rapidly with an increase in applied potential. The commercial Pt/C showed the optimum HER activity, providing a near-zero onset potential at 10 mA cm^{-2} . Bare nickel foam does not

have HER activity due to its lower electrochemical surface area and fewer active sites. The CuCo_2S_4 catalyst exhibited an overpotential of 182 mV at 10 mA cm^{-2} , which thus indicated the efficient catalytic activity of the CuCo_2S_4 catalyst. Since the measured data comprises intrinsic catalytic activity and the effect of ohmic contact, we applied “ohmic loss” (iR) correction to all the data before performing the data analysis (Figure 6b).

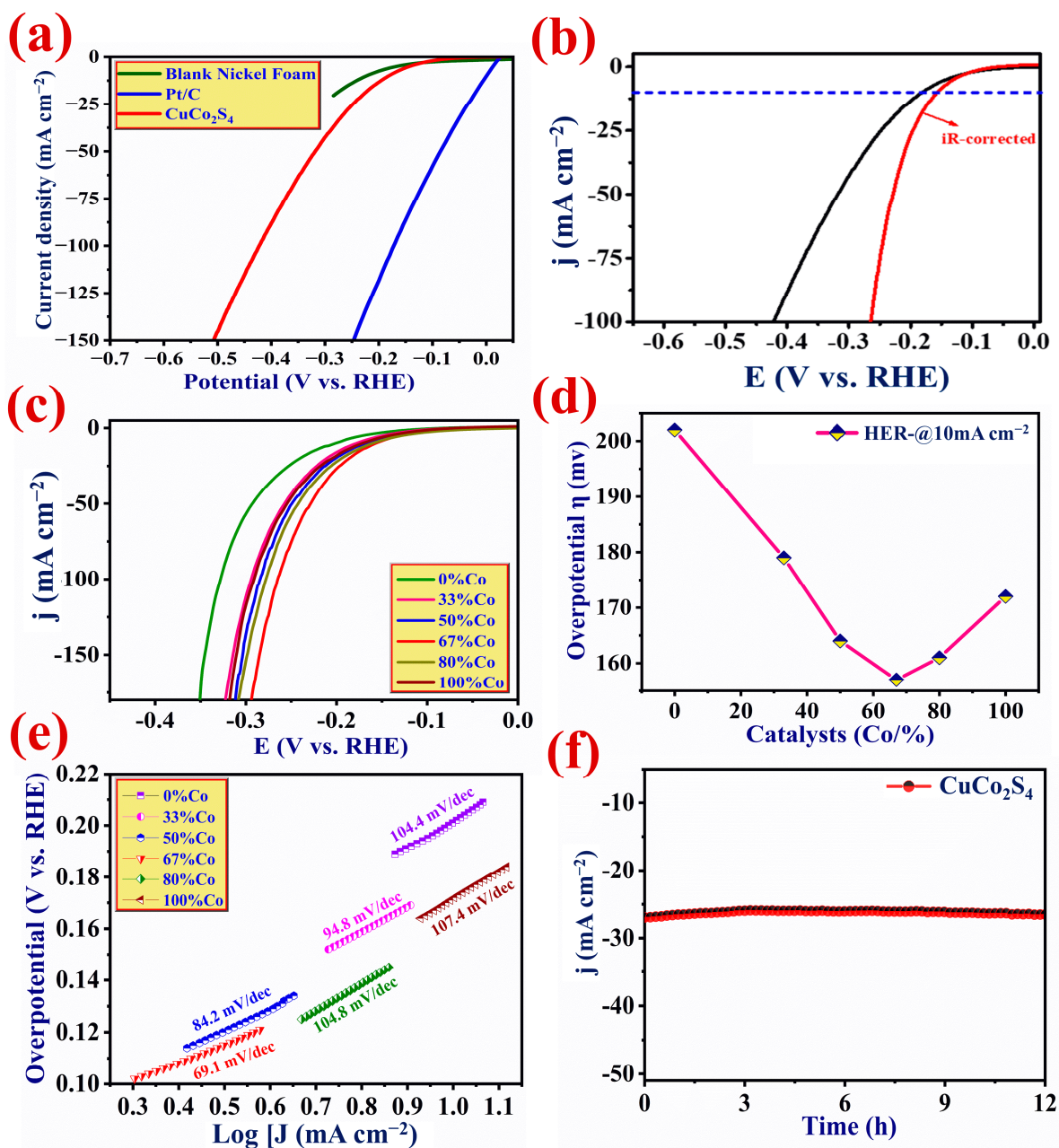


Figure 6. Electrocatalytic activity of CuCo_2S_4 for HER activity. HER polarization curves (a) with Pt/C, blank foam nickel, and CuCo_2S_4 , (b) the linear sweep volt-ampere curve before and after iR compensation for CuCo_2S_4 , (c) the LSV curve of CuCo_2S_4 catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) (d) the overpotentials of CuCo_2S_4 catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) at a current density of 10 mA cm^{-2} ; (e) the Tafel for CuCo_2S_4 catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100); and (f) the time-dependent current density curve for CuCo_2S_4 under static overpotential for 12 h.

The HER electrocatalytic behavior of CuCo_2S_4 catalyst with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) was investigated by the LSV curve at a current density of 10 mA cm^{-2} and is presented in Figure 6c,d. As we can see, the overpotential for the CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 (157 mV) was found to be lower than that of other Cu/Co ratios, suggesting that the CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 could be the optimum concentration for enhanced electrocatalytic performance. The reaction kinetics for the CuCo_2S_4 catalysts were further analyzed by Tafel slopes and are presented in Figure 6e. As shown in Figure 6e, the Tafel slope value of the CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 is found to be smaller than that of other Cu/Co ratios. Thus, the CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 has the best electrocatalytic activity and exhibits faster catalytic kinetics in a primary medium. Figure 6f shows the electrochemical stability of the CuCo_2S_4 catalyst at a 255 mV overpotential for 12 h. The current density of the catalyst remains almost constant during the continuous operation for 12 h, and the retention rate is more than 87% after 12 h, indicating that the CuCo_2S_4 catalyst has good catalytic stability during the alkaline HER process.

The electrochemically active specific surface area (ECSA) of CuCo_2S_4 catalysts was investigated using double-layer capacitance (C_{dl}). The cyclic voltammetry curves of CuCo_2S_4 catalysts at different scanning rates (5, 10, 20, 40, 60 and 80 mV s^{-1}) are presented in Figure 7a–f. The more significant C_{dl} value results in the enhancement of ECSA, and thus the HER performance is also enhanced. The C_{dl} of CuCo_2S_4 catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) are presented in Figure 7g. The C_{dl} value of CuCo_2S_4 , the catalyst with a Cu/Co ratio of 33:67, is found to be higher than that of other ratios, suggesting an increased ECSA and thus the expected higher charge and mass transport capability. The larger ECSA indicates that the sample has more active sites per unit area, thus having better electrocatalytic activity [39]. The EIS was used to evaluate the catalytic kinetics of the CuCo_2S_4 catalyst within the frequency range of 0.1 Hz to 10 MHz at a potential of -0.3 V vs. RHE . The Nyquist plots of CuCo_2S_4 catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) are presented in Figure 7h, where all the catalysts show hemicycles at high frequencies. The CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 exhibited a low charge-transfer resistance (R_{ct}) ($<2 \Omega$) when compared to other catalysts. Thus, the CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 possesses a faster charge transfer, which enhances HER catalytic performance.

2.2.2. Analysis of Electrochemical Oxygen Evolution (OER) Performance

The electrocatalytic OER performance of the CuCo_2S_4 catalysts was evaluated (CuCo_2S_4 loading: 1.02 mg cm^{-2}) using a standard three-electrode system in 1 M KOH (pH = 14) solution at a scanning rate of 2 mV s^{-1} (see Figure 8). The OER activities of blank NF, RuO_2 , and CuCo_2S_4 catalysts were also investigated under optimum conditions. From Figure 8a, it can be seen that CuCo_2S_4 catalysts exhibit much higher current density and a lower onset potential than blank NF and RuO_2 . The RuO_2 requires an overpotential of 340 mV to drive a current density of 10 mA cm^{-2} , while the CuCo_2S_4 requires only 276 mV to operate a current density of 10 mA cm^{-2} . Further, the overpotential of the CuCo_2S_4 catalyst at 10 mA cm^{-2} was reduced from 274 mV to 254 mV upon iR-compensation (Figure 8b), and thus the electrochemical data was then measured under calibration conditions. The OER electrocatalytic performance of CuCo_2S_4 catalyst with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) was investigated by LSV curve at a current density of 10 mA cm^{-2} and is presented in Figure 8c,d. As we can see, the overpotential for the CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 (254 mV) was found to be lower than that of other Cu/Co ratios, suggesting that the CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 could be the optimum concentration for enhanced electrocatalytic performance. The OER reaction kinetics (Tafel slope) for the CuCo_2S_4 catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) are presented in Figure 8e. The Tafel slope of a CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 is 59 mV dec^{-1} , which is less than that of other percentages of the Cu/Co ratio. Thus, it indicates that the OER rate of the

CuCo_2S_4 catalyst with a Cu/Co ratio of 33:67 is much faster than that of other electrodes. In addition, the long-term electrochemical durability of the CuCo_2S_4 catalyst was evaluated by the chronoamperometry method under a certain voltage (Figure 8f). As evident from Figure 8e, the current density remains almost unchanged before and after the test, implying its electrochemical durability. OER analysis in alkaline electrolyte, which outperforms the samples of CuCo_2S_4 , was compared with the recently reported transition metal-based electrocatalysts, demonstrating good electrocatalytic performance and kinetics, respectively, as summarized in Table 1.

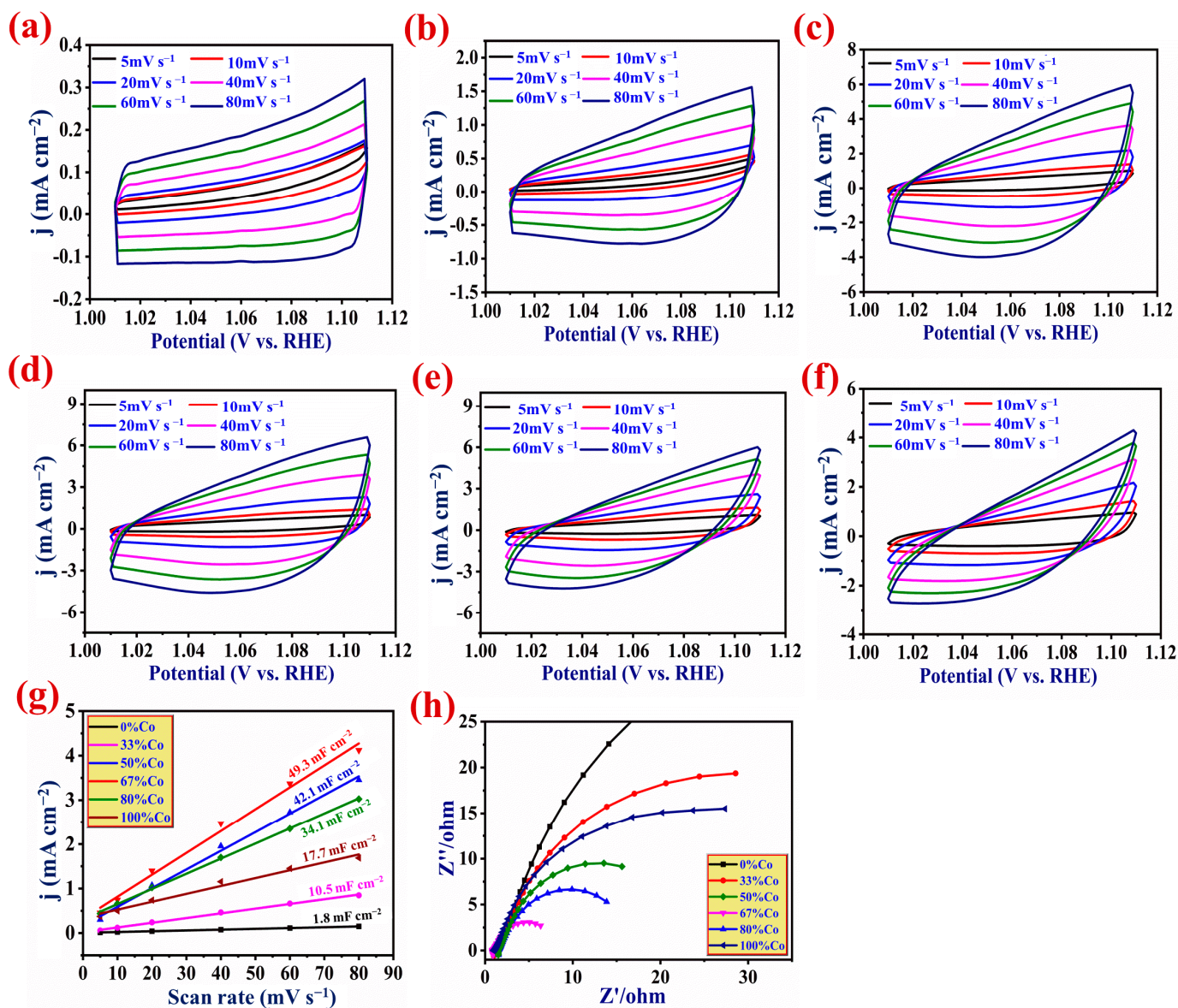


Figure 7. The cyclic voltammogram (CV) curves of CuCo_2S_4 catalysts with different percentages of Cu/Co. (a) 100:0, (b) 67:33, (c) 50:50, (d) 33:67, (e) 20:80, and (f) 0:100 with different scan rates at the applied voltage of 1.055 V vs. RHE, (g) The double-layer capacitance (C_{dl}) of CuCo_2S_4 catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) and (h) Nyquist plots of CuCo_2S_4 catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) recorded at an applied potential with a frequency range of 0.1 Hz to 10 MHz in the electrolyte is 1 M KOH.

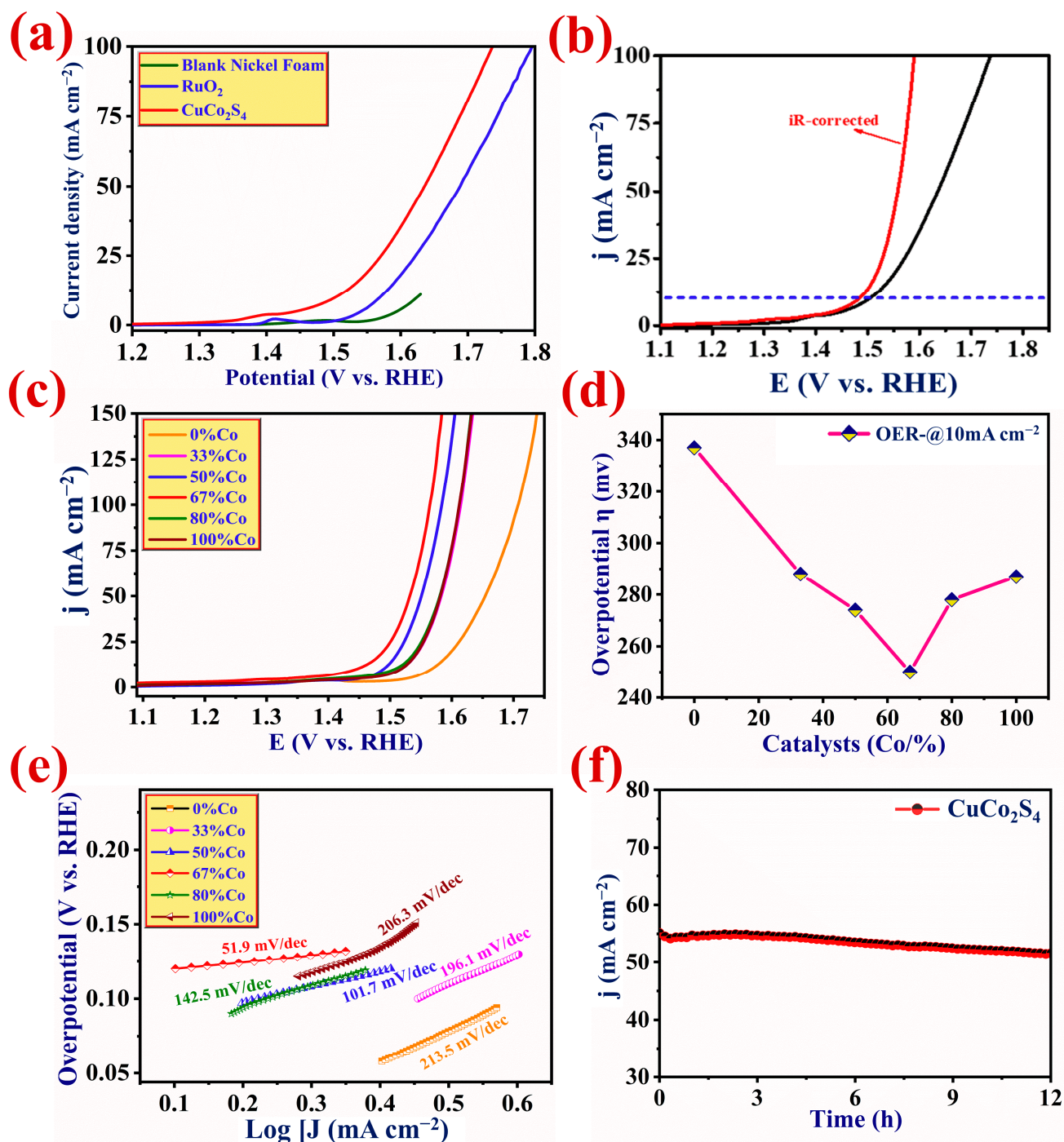


Figure 8. Electrocatalytic activity of CuCo_2S_4 for OER activity. OER polarization curves (a) with RuO_2 , blank nickel foam, and CuCo_2S_4 , (b) a linear sweep volt-ampere curve before and after iR compensation for CuCo_2S_4 , (c) the LSV curve of CuCo_2S_4 catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100). (d) the overpotentials of CuCo_2S_4 catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) at a current density of 10 mA cm^{-2} ; (e) a Tafel plot of CuCo_2S_4 catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100); and (f) a time-dependent current density curve for CuCo_2S_4 under static overpotential for 12 h.

Table 1. Comparison of the electrocatalytic performance of CuCo_2S_4 with other transition metal-based electrocatalysts in an alkaline medium.

Electrocatalyst	Current Density (mA cm^{-2})	Overpotential (mV)	Tafel Slope (mV dec^{-1})	Reference
CuCo_2S_4	10	274	59	This work
carbon-Ni/NiO-Pd	10	380	72	[40]
NiFe-LDH	10	290	33.4	[41]
$\text{Co}_9\text{S}_8/\text{Zn}_{0.8}\text{Co}_{0.2}\text{S@C}$	10	292	52	[42]
$\text{Co}_3\text{O}_4/\text{MnCo}_2\text{O}_4$	10	540	N/A	[43]
$\text{K}_{0.04}[\text{Co}_{0.42}\text{Mn}_{0.58}\text{O}_2]$	10	420	110	[44]
$\text{Co}_9\text{S}_8@\text{MoS}_2/\text{CNFs}$	10	430	61	[45]
Mesoporous Co_3O_4	10	411	80	[46]

2.3. Characterization of Overall Water Electrolysis

All the electrochemical characterizations demonstrate the superior electrochemical performance of the CuCo_2S_4 catalyst for OER and HER applications in 1.0 M KOH. Accordingly, we fabricated an alkaline water electrolyzer using a CuCo_2S_4 catalyst as a cathode and an anode simultaneously to simulate water electrolysis using a two-electrode system. For comparison, we prepared the electrolyzers with the structures $\text{CuCo}_2\text{S}_4 \parallel \text{CuCo}_2\text{S}_4$ and $\text{Pt/C} \parallel \text{Pt/C}$. Figure 9a displays the OER LSV curves of the CuCo_2S_4 electrocatalyst. As shown in Figure 9a, the $\text{CuCo}_2\text{S}_4 \parallel \text{CuCo}_2\text{S}_4$ electrolyzer exhibited the lowest cell voltage of 1.6 V at 10 mA cm^{-2} , with an overpotential of about 370 mV to induce the overall water electrolysis. Furthermore, the long-term durability of the $\text{CuCo}_2\text{S}_4 \parallel \text{CuCo}_2\text{S}_4$ electrolyzer was evaluated in 1.0 M KOH with a cell voltage of 1.50 V. As shown in Figure 9b, it exhibits excellent stability with slight performance degradation during 12 h of continuous electrolysis. However, we investigated and found that there was no significant structural change (inset in Figure 9b) occurring after the long-term performance of the electrodes, which reveals the stability of the catalyst.

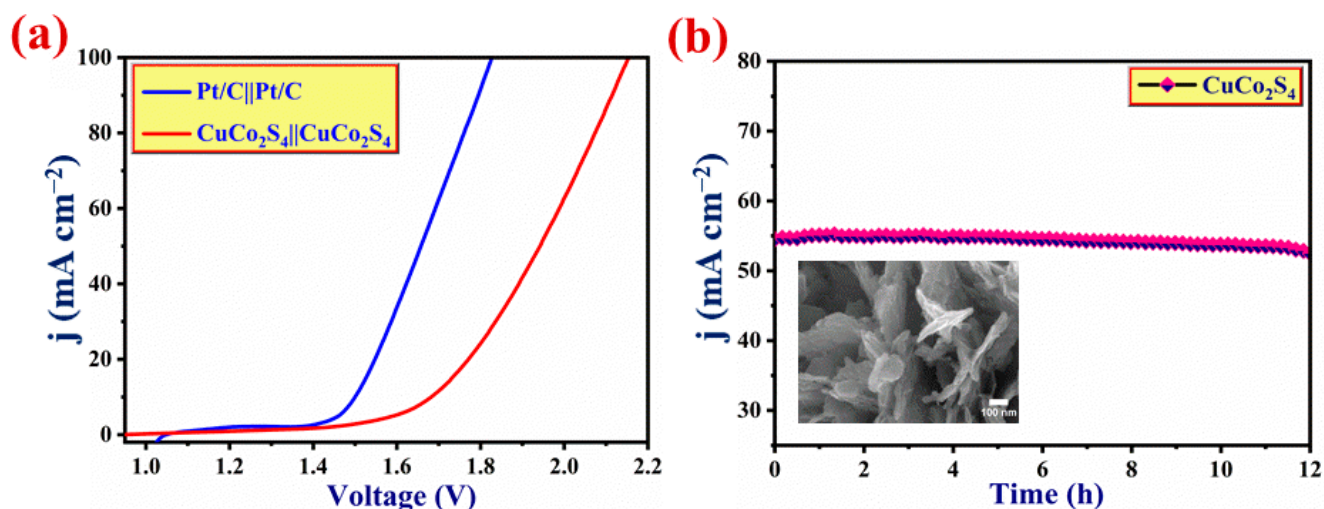


Figure 9. (a) Polarization curves of $\text{CuCo}_2\text{S}_4 \parallel \text{CuCo}_2\text{S}_4$ and $\text{Pt/C} \parallel \text{Pt/C}$ for overall water splitting at a scan rate of 2 mV s^{-1} in 1.0 M KOH. (b) The chronoamperometric curve of CuCo_2S_4 with a constant voltage of 1.98 V. Inset shows a FESEM image of the electrode after the long-term durability test.

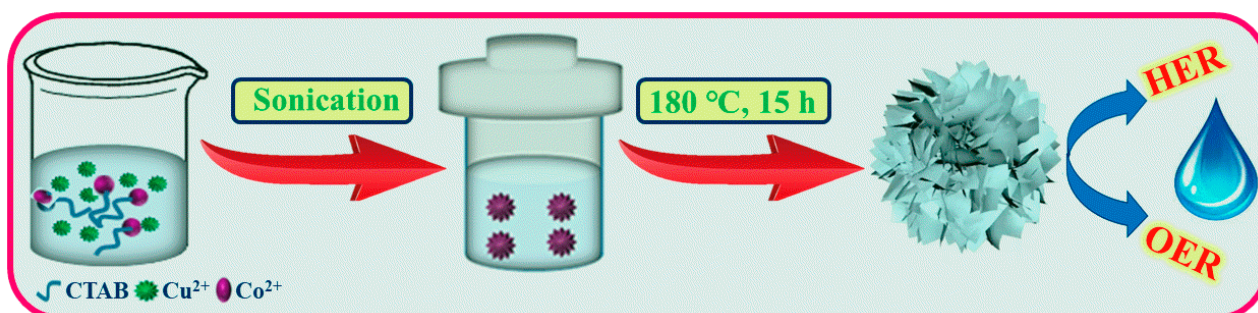
3. Experimental Section

3.1. Materials

Copper(II) nitrate hexahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Cetyltrimethylammonium bromide (CTAB), ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$), Thioacetamide ($\text{TAA C}_2\text{H}_5\text{NS}$), and ethanol were received from Nacalai Tesque Reagent Co. (Kyoto, Japan). All the chemicals were used as procured without any purification. Deionized water was used throughout the entire experiment.

3.2. Synthesis of CuCo_2S_4 Nanosphere Catalyst

The CuCo_2S_4 nanospheres were synthesized via the one-step solvothermal method. In brief, 0.25 mM of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.5 mM of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 30 mL of ethylene glycol under sonication. The sonication was continued until the formation of a homogenous solution. Then, 1.5 mM of CTAB was added and stirred for 6 h. Then, 0.001 M of TAA was added to the above suspension with constant stirring for 30 min. After 30 min, the resultant suspension was transferred into an autoclave (stainless steel) and thermally treated to 180 °C for 15 h in a hot air oven. Finally, the solid black powder was separated by centrifugation, repeatedly washed with water and ethanol, and dried at 60 °C overnight. The schematic illustration for the synthesis of CuCo_2S_4 nanospheres was presented in Scheme 1. Furthermore, catalysts with different percentages of Cu/Co (100:0, 67:33, 50:50, 33:67, 20:80, and 0:100) were also synthesized under similar experimental conditions.



Scheme 1. Schematic illustration for the synthesis of CuCo_2S_4 nanospheres.

3.3. Characterization

The morphology of the prepared sample was investigated using a JEOL JEM-2100F scanning electron microscope (SEM) (Tokyo, Japan) operated at 2.0 kV, accompanied by Oxford INCA EDS software (High Wycombe, UK) for elemental mapping analysis. JEOL JEM-2010 transmission electron microscopy (TEM) (Tokyo, Japan) was used to obtain the TEM and high-resolution TEM images operating at 300 kV. The X-ray D8 Advance instrument (Bruker, Bremen, Germany) was used to obtain the powder X-ray diffraction (XRD) patterns of the prepared samples ($\text{Cu K}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$). A Thermo Scientific Escalab 250Xi photoelectron spectrometer (Waltham, MA, USA) was used to obtain X-ray photoelectron spectroscopy (XPS) spectra. Textural properties (BET surface areas) were obtained from the Quantachrome Nova-1000 surface analyzer (Osaka, Japan).

3.4. Electrochemical Measurements

The CHI660D electrochemical workstation (Shanghai Chenhua Co., Shanghai, China) was used to analyze the electrochemical properties using a three-electrode electrochemical setup. A platinum wire electrode (as a counter) and a saturated calomel electrode (SCE) (as a reference) were used. The modified Ni foam substrate was used as a working electrode. The clean Ni foam substrate (1 cm $\times$ 1 cm) was modified with a homogenous dispersion of electrocatalysts (2 mg) dispersed (sonicated for 60 min) in 400 μL of ethanol and 20 μL of Nafion solution (5 wt%). They were subsequently dried at 60 °C for 3 h. The cyclic voltammogram (CV) and linear sweep voltammetry (LSV) were used to record the polarization

curves (in 1.0 M KOH) for HER. Electrochemical impedance spectroscopy (EIS) was carried out with a 5 mV amplitude at current open circuit voltage in the frequency range of 0.1 Hz to 10 MHz. The reversible hydrogen electrode (RHE) was used as a reference for all the potentials reported here with iR compensation. All the electrochemical characterizations were carried out at room temperature.

4. Conclusions

We have synthesized the flower-like CuCo_2S_4 nanospheres through the one-step solvothermal method. In this process, highly open three-dimensional nanospheres are composed of ultrathin CuCo_2S_4 nanosheets, which expose more catalytic active sites. With certain Co doping, the divalent Co ions replace the divalent Cu ions, leading to specific changes in the lattice structures and thus improving the catalytic performance of the catalyst. The catalysts prepared in this work exhibit excellent stability throughout water electrolysis and are explored as highly effective bifunctional electrocatalysts for enhanced water splitting. The CuCo_2S_4 electrocatalyst shows superior activity, achieving current densities of 10 mA cm^{-2} at low overpotentials of 182 mV and 274 mV for HER and OER, respectively, in 1 M KOH electrolyte. Furthermore, the respective two-electrode alkaline water electrolyzer exhibits a low cell voltage of 1.68 V at a current density of 10 mA cm^{-2} and remarkable stability over 12 h of continuous electrolysis (at 1.68 V at 10 mA cm^{-2}). This simple and effective synthesis method provides new research ideas for synthesizing spinel-like catalysts with different catalytic properties to be used in many renewable energy areas.

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