Article

Interfacial Engineering of $CuCo_2S_4/g-C_3N_4$ Hybrid Nanorods for Efficient Oxygen Evolution Reaction

Rathindranath Biswas, Pooja Thakur, Gagandeep Kaur, Shubham Som, Monochura Saha, Vandna Jhajhria, Harjinder Singh, Imtiaz Ahmed, Biplab Banerjee, Deepak Chopra, Tapasi Sen, and Krishna Kanta Haldar*



ABSTRACT: Altering the morphology of electrochemically active nanostructured materials could fundamentally influence their subsequent catalytic as well as oxygen evolution reaction (OER) performance. Enhanced OER activity for mixed-metal spinel-type sulfide (CuCo₂S₄) nanorods is generally done by blending the material that has high conductive supports together with those having a high surface volume ratio, for example, graphitic carbon nitrides (g-C₃N₄). Here, we report a noble-metal-free CuCo₂S₄ nanorod-based electrocatalyst appropriate for basic OER and neutral media, through a simple one-step thermal decomposition approach from its molecular precursors pyrrolidine dithiocarbamate-copper(II), Cu[PDTC]₂, and pyrrolidine dithiocarbamate-cobalt(II), Co[PDTC]₂ complexes.



Transmission electron microscopy (TEM) images as well as X-ray diffraction (XRD) patterns suggest that as-synthesized $CuCo_2S_4$ nanorods are highly crystalline in nature and are connected on the g-C₃N₄ support. Attenuated total reflectance–Fourier-transform infrared (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy studies affirm the successful formation of bonds that bridge (Co–N/S–C) at the interface of $CuCo_2S_4$ nanorods and g-C₃N₄. The kinetics of the reaction are expedited, as these bridging bonds function as an electron transport chain, empowering OER electrocatalytically under a low overpotential (242 mV) of a current density at 10 mA cm⁻² under basic conditions, resulting in very high durability. Moreover, $CuCo_2S_4/g-C_3N_4$ composite nanorods exhibit a high catalytic activity of OER under a neutral medium at an overpotential of 406 mV and a current density of 10 mA cm⁻².

INTRODUCTION

Development of methodologies for advancement of energy resources in sustainable fashion is highly attractive due to its ability to overcome negative outcomes brought about by the utilization of conventional fossil fuels. Consequently, an assortment of energy conversation strategies, for example, PEC water splitting,^{1–3} electrocatalytic water splitting,^{4–7} methanol oxidation,^{8–10} N₂ reduction,^{11–14} CO₂ reduction,^{15–17} and rechargeable metal-air batteries,^{18–21} have been paid increasingly more consideration inferable from their extraordinary potential for reducing the concern of energy needs. Among those, the electrocatalytic water oxidation reaction to produce oxygen can be regarded as a green and sustainable approach for generating alternative energy. It is well established that electrocatalytic OER is engaged with different energy conversion frameworks and has been broadly concentrated in ongoing years.^{22–26} However, the improvement of an effective electrocatalyst toward OER still remains an overwhelming test, as OER catalysts experience a large overpotential and poor sustainability. So far, iridium- and ruthenium-based materials²⁷⁻³¹ were considered to be the

most proficient catalysts in electrochemical OER. However, the significant expense and low abundance of such noble metal electrocatalysts incredibly hinder their huge scope of applications. Therefore, it is exceptionally recommendable to build high-action and noble-metal-free OER catalysts with more extensive adaptability.

To date, enormous attempts have been devoted to readying earth-abundant-based electrocatalysts, especially transition metal oxides,^{32–35} sulfides,^{6,36–38} carbides,^{39–41} hydroxides,^{42–44} phosphides,^{45–47} selenides,^{48–50} etc., for more energy proficient water splitting. Among them, transition metal sulfides, so-called thiospinels, provide great advantages to improve electrochemical execution because they can reveal a substantial number of active surface sites, fast electron transfer

Received: May 25, 2021



Scheme 1. Schematic Representation of Synthesis of PDTC, Co[PDTC]₂, and Cu[PDTC]₂ Complexes



Scheme 2. Schematic Representation for the Synthesis of CuCo₂S₄/g-C₃N₄ Composite Nanostructures



pathways, and narrow band gaps and enhance redox responses.⁵¹⁻⁵⁴ Because of a suitable electrical configuration, thiospinels composed of cobalt and copper have indicated extraordinary assurance for superior OER electrocatalysts because cobalt has suitable water affinity compared to that of other metals. Wiltrout et al. have synthesized CuCo₂S₄ nanoparticles in solution, and they reported that these thiospinels showed high OER activity in a basic medium.⁵⁵ Yang et al. have hydrothermally fabricated a hierarchical CuCo₂S₄ nanoarray on copper foam and shown that these nanoarray catalysts exhibit superior activity for OER.56 Recently, the Wang group demonstrated that various morphologies of CuCo₂S₄ significantly impacted OER activity.⁵⁷ It is also well documented in the literature that solvent can tune the morphology of CuCo₂S₄ for both OER and HER activity.⁵⁸ Again, material fabrication techniques such as multinary metal ion incorporation,^{59,60} surface engineering,⁶¹⁻⁶³ and morphology-controlled nanostructure^{57,64,65} design have been utilized effectively to improve the OER execution of catalysts. Among the various strategies, interfacial engineering of transition metal sulfide nanomaterials with

conductive templates such as graphene, g- C_3N_4 etc., via hybridizing is one of the fundamental and financially savvy approaches to boosting catalytic OER execution.^{66–68} However, the development of rod-shaped CuCo₂S₄ with g- C_3N_4 support was not reported to date. Further, homogeneous inclusion of CuCo₂S₄ nanostructure into g- C_3N_4 templates is not straightforward because of the aggregation of sheets comprising g- C_3N_4 that reduces the electrochemical active surface area and impedes fast electrolyte diffusion, bringing about aggregation of the CuCo₂S₄ nanostructure.⁶⁶ In spite of these recent advances, plenty of scope is there for the improvement of the activity, durability, and sustainability of thiospinels in electrocatalytic OER.

Here, we have carried out a systematic study for the formation of CuCo₂S₄ nanorods (NRs) in solution, and then these CuCo₂S₄ NRs were incorporated onto g-C₃N₄ (CN) sheets (CuCo₂S₄ NRs/CN) by heat treatment achieving synergistically improved catalytic activity for OER under alkaline and neutral conditions. Distinctive starting materials were tried as precursors for CuCo₂S₄ NRs synthesis. Electrochemical investigations were executed on CuCo₂S₄

NRs/CN composites along with their constituents such as $CuCo_2S_4$ NRs, CoS_2 , Cu_2S , $g-C_3N_4$, etc. under same conditions. The results showed that $CuCo_2S_4$ NRs/CN composite catalysts increased the efficiency of oxygen evolution and revealed excellent durability for OER. The heterointerfaces of $CuCo_2S_4$ NRs/CN structures made out of $CuCo_2S_4$ nanorods and $g-C_3N_4$ sheets would enable the well-exposed active sites of $CuCo_2S_4$ and $g-C_3N_4$ both. Furthermore, the hybrid $CuCoS_4$ nanorods with a rough surface and their straight connection to the conducting $g-C_3N_4$ allow effective charge transport pathways during the electrocatalytic process.

RESULTS AND DISCUSSION

 $Cu[PDTC]_2$ and $Co[PDTC]_2$ complexes were synthesized (Scheme 1) as precursors for the fabrication of thiospinel $CuCo_2S_4$ nanorods. In this study, rod-shaped $CuCo_2S_4$ nanostructures are produced by the thermal decomposition of $Cu[PDTC]_2$ and $Co[PDTC]_2$ complexes in the presence of TOP within a hot solution containing coordinating solvent oleyl amine under anaerobic conditions (Scheme 2).

The structural information on PDTC was studied using ¹H NMR, ¹³C NMR, and mass spectroscopic (ESI-MS-TOF) analysis. ¹H NMR (DMSO-d₆, 500 MHz, ppm): 1.81 (mt, 4H); 3.64 (mt, 4H) (Figure S1). ¹³C NMR (DMSO-d₆, 125 MHz, ppm): 209.6, 55.3, and 26.1 (Figure S2). ESI-MS TOF of PDTC: molecular formula, C5H8NNa2S2; calculated mass [M + Na]⁺, 191.9894; experimentally found, 191.9893 (ESI-MS (TOF; Figure S3). The structure of PDTC was further confirmed by single crystal XRD analysis. In the crystal structure of PDTC, ellipsoid plots are shown in Figure S4. Crystal data, data collection, and structure refinement details for PDTC are summarized in Table S1, and the bond angles and lengths are shown in Tables S2 and S3, respectively. It has been found that PDTC crystallized as a monoclinic crystal having the P21/c space group (CCDC no. 2034050). $Co[PDTC]_2$: molecular formula, $C_{10}H_{16}CoN_2S_4$; calculated mass, 350.9528; experimentally found, 350.7915 (ESI-MS (TOF); Figure S5). Cu[PDTC]₂: molecular formula, $C_{10}H_{16}CuN_2S_4$; calculated mass, 354.9492; experimentally found, 354.8520 (ESI-MS (TOF); Figure S6). The structure of Cu[PDTC]₂ was further affirmed by single crystal XRD study and compared with the literature.⁶⁹⁻⁷¹ The crystal structure has been redetermined again to characterize the structure of the synthesized complex. In addition, crystal packing analysis has also been performed. The compound crystallizes in the centrosymmetric space group $P\overline{1}$ with one molecule in the unit cell (Table S4). The ORTEP is shown in Figure S7. The crystal packing is controlled via the formation of C-H...S intermolecular interactions (involving H7A and S2) forming chains along the crystallographic *a* axis (Figure S8, Table S5). Adjacent chains are stacked and connected via the formation of C-H...S centrosymmetric dimers (involving H6B and S2) that provide additional stability to the crystal packing.

Further, to rationalize the formation of PDTC, Cu[PDTC]₂, and Co[PDTC]₂ complexes, we studied the ATR-FTIR spectroscopy, and the results are shown in Figure 1. In ATR-FTIR spectra of as-synthesized PDTC (Figure 1a), the peaks appearing at 2932 and 2867 cm⁻¹ are due to pyrrolidine–CH₂ stretching vibrations in an asymmetric and symmetric manner.⁷² The C–N stretching vibration bands of the NCS were observed at 1465 and 1328 cm^{-1.73-76} Peaks at 978 cm⁻¹ can be correlated with C=S of the –CSS⁻ group,^{73,75-77}



Figure 1. ATR-FTIR spectra of (a) PDTC, (b) $Co[PDTC]_2$, and (c) $Cu[PDTC]_2$.

whereas the C-S vibration band was found to be centered at 887 cm⁻¹. Further, the characteristic peaks at 549 and 483 cm⁻¹ due to the stretching vibration of the Cu-S bond strongly support the formation of the Cu[PDTC]₂ complex (Figure 1c). From the literature survey, it has been found that the stretching vibration frequency of the metal sulfur (M-S)bond (such as Zn-S,⁷³ Co-S,⁷⁸ Sn-S,⁷⁷ etc.) appears between 475 and 580 cm⁻¹. The peaks appearing at 554 and 489 cm⁻¹ (Figure 1b) can be attributed to the stretching vibration of the Co-S bond⁷⁸ and hence confirm the formation of the Co[PDTC]₂ complex. Both Cu[PDTC]₂ and Co[PDTC]₂ complexes show the characteristic peaks corresponding to -CH₂, C-N, and C=S stretching vibrations (Table S6). It is noteworthy that the stretching frequency of C=S and C-S bonds of both $Cu[PDTC]_2$ and $Co[PDTC]_2$ complexes are observed at a lower range compared to PDTC, which further confirms the formation of Cu-S and Co-S bonds in Cu[PDTC]₂ and Co[PDTC]₂ complexes, respectively. Again, to further confirm the formation of PDTC, Cu[PDTC]₂, and Co[PDTC]₂ complexes and their optical properties, we have investigated using UV-visible absorbance spectroscopy. Figure 2 exhibits the UV-vis absorbance spectra



Figure 2. UV–vis absorbance spectra of (a) PDTC, (b) Co[PDTC]₂, and (c) Cu[PDTC]₂.

pubs.acs.org/IC



Figure 3. (a and b) TEM images with corresponding diameter distribution (inset) for $CuCo_2S_4$ nanorods in different magnifications, (c) HRTEM images of $CuCo_2S_4$ nanorods, (d) FFT pattern, (e) TEM image of Cu_2S nanoparticles, and (f) TEM image of CoS_2 nanoparticles.

of as-synthesized PDTC, Cu[PDTC]₂, and Co[PDTC]₂ complexes. Here, peaks at 253 nm were attributed to $\pi \rightarrow$ π^* transitions related to the N-C=S group where the absorption band at 286 nm was associated with transitions of the S–C=S group present in PDTC (Figure 2a).⁷⁹ The UV– vis spectra of Cu[PDTC]₂ show an additional peak at 432 nm which is due to the electronic transition from C=S π^* orbitals to 3d orbitals of Cu(II) (Figure 2c), whereas the electronic transition from C=S π^* orbitals to the 3d orbital of Co(II) leads to an absorption band at 394 nm for the Co[PDTC], complex (Figure 2b). To get the information regarding the thermal stability and thermal behavior of $Cu[PDTC]_2$ and Co[PDTC]₂ complexes, we have studied the thermogravimetric analysis (TGA), shown in Figure S9. There was no loss of weight % up to 100 °C, indicating the absence of water molecules in both complexes. However, the TGA plot of Cu[PDTC]₂ and Co[PDTC]₂ complexes exhibited a 75% weight loss at 255 and 273 °C, respectively, whereas a 50% weight loss occurred only at 287 and 302 °C for Cu[PDTC]₂ and Co[PDTC]₂ complexes, respectively. The sharp thermal decomposition of Cu[PDTC]₂ and Co[PDTC]₂ complexes occurring from 180 to 308 °C and 206-320 °C was associated with the loss of the organic moiety along with the dithiocarbamate unit of the complexes, respectively.⁷⁵ Steady state weight loss was observed above 308 °C for Cu[PDTC]₂ and 320 °C for the Co[PDTC]₂] complex, which corresponded to the formation of Cu₂S and CoS₂ due to the pyrolysis of Cu[PDTC]₂ and Co[PDTC]₂ complexes, respectively.

Without size sorting, the as-prepared one-dimensional $CuCo_2S_4$ nanorods showed uniform size dispersion. It is observed from TEM images that the synthesis of $CuCo_2S_4$ nanorods was accomplished with high yield (Figure 3a,b). Inplane and out-of-plane HRTEM images of $CuCo_2S_4$ NRs are collected to verify the exposed lattice planes. Clear lattice fringes were observed with the lattice spacing of approximately 0.33 and 0.23 nm (Figure 3c), corresponding to the (022) and (004) planes of the cubic phase of spinel-type $CuCo_2S_4$ (JCPDS-42-1450) nanorods. Clear lattice fringes were also observed from an in-plane HRTEM image (Figure 3c). The

single-crystalline nature of a CuCo₂S₄ nanorods was unambiguously proved from the FFT pattern (Figure 3d) and HRTEM image (Figure 3c). In order to understand the mechanism of growth of CuCo₂S₄ nanorod formation, we carried out detailed TEM studies to investigate the influence of reaction conditions and growth stages associated with formation of the $CuCo_2S_4$ nanorods. First, we have taken fractions of our reaction mixture over time for CuCo₂S₄ nanorods. At 5 min, we found very tiny nanorods (length 7.6 ± 0.4 nm and diameter 0.8 ± 0.1 nm; Figure S10). After 10 min, CuCo₂S₄ nanorods are wider and longer (length 15.2 \pm 0.6 nm and diameter 2.5 ± 0.3 nm; Figure S11). However, at 15 min, we again find larger nanorods (length 38.4 ± 0.8 nm and diameter 6.1 \pm 0.4; Figure S12). Thus, it can be believed that the CuCo₂S₄ nanorods' growth increases as the reaction proceeds. This might indicate that monomer growth is taking place. Further, we studied the effect of reaction temperature on the growth of the CuCo₂S₄ nanorods. Figures S13 and S14 show the TEM images of the CuCo₂S₄ nanorods prepared at 200 and 230 °C, respectively, while other conditions were kept constant. The result demonstrated that CuCo₂S₄ nanorods also form at lower temperatures, only the growth rate is slower. Spherical Cu₂S nanoparticles (Figure 3e) were generated in the absence of the Co[PDTC]₂ complex under the same conditions. We also observed that, in the absence of complex Cu[PDTC]₂ in the reaction mixture under similar reaction conditions, spherical CoS₂ nanoparticles were obtained (Figure 3f). To know the role of oleyl amine and TOP for $CuCo_2S_4$ nanorod formation, we prepared CuCo₂S₄ nanorods in the presence and absence of oleyl amine and TOP. Using only TOP as a solvent without varying other conditions, a mixture of small nanorods and nanoparticles was achieved. (Figure S15) However, in the absence of TOP, aggregated nanorods were obtained under identical conditions (Figure S16). Thus, it is assumed that chelating ligands oleyl amine and TOP used in the synthesis directed the growth of the one-dimensional CuCo₂S₄ nanorod structures. Additionally, further investiga-

tion was done to understand the different morphologies and

microstructures of the $g-C_3N_4$ and $CuCo_2S_4/g-C_3N_4$ compo-

site. It is observed that g-C₃N₄ formed a layered structure, and

pubs.acs.org/IC



Figure 4. TEM images of (a) $g\text{-}C_3N_4$ and (b) $CuCo_2S_4/g\text{-}C_3N_4$ composite nanostructures.

 $g\text{-}C_3N_4$ and $CuCo_2S_4$ resulted in the formation of rod-shaped $CuCo_2S_4$ uniformly dispersed on the surfaces of $g\text{-}C_3N_4$, which eventually created the composite $CuCo_2S_4/g\text{-}C_3N_4$ nanostructure.

An X-ray diffraction (XRD) study was performed to confirm the crystallographic structure, phase composition, and purity of as-synthesized samples (Figure 5). XRD diffraction peaks



Figure 5. XRD patterns of (a) g-C₃N₄, (b) Cu₂S₅, (c) CoS₂, (d) CuCo₂S₄, and (e) CuCo₂S₄/g-C₃N₄ composite nanostructure.

related to $2\theta = 16.21^{\circ}$, 26.41° , 31.39° , 38.01° , 46.05° , 50.46° , and 54.77° may be attributed to the (111), (022), (113), (004), (224), (115), and (044) planes of the cubic phase of CuCo₂S₄ (JCPDS card no. 42-1450; Figure 5e). The weak peak around 27.68° indicated the presence of g-C₃N₄ in the composite nanostructures (Figure 5e). This result reveals that the as-obtained sample was constructed with g-C₃N₄ and CuCo₂S₄ NRs. The absence of any other peaks indicates that the prepared nanocomposites did not contain any impurities. XRD analysis of the CuCo₂S₄/g-C₃N₄ was also compared to pure CuCo₂S₄, Cu₂S₂, CoS₂, and g-C₃N₄. Figure 5d shows the XRD pattern of pure CuCo₂S₄ nanorods, and the characteristic peaks appeared at $2\theta = 16.17^{\circ}$, 26.34° , 31.42° , 37.97° , 46.08° , 50.41°, and 54.78°. XRD patterns of Cu₂S were found at 2θ = 27.82°, 29.37°, 32.22°, 37.02, 38.91°, 46.24°, 47.39°, 51.35°, 54.81°, and 69.98° (Figure 5b) and confirmed the formation of

cubic phase Cu₂S (JCPDS no. 84-1770). Peaks at 26.44°, 31.63°, 37.21°, 40.15°, 45.79°, and 55.14° correspond to pure CoS₂ (Figure 5c; JCPDS card no. 65-3322).^{80,81} XRD analysis of pure g-C₃N₄ showed two characteristic peaks at 13.11 and 27.52° , which could be indexed by the (002) and (110) plane of hexagonal g-C₃N₄ (JCPDS no. 87-1526; Figure 5a).⁸² Further, an XPS study was done to obtain detailed information regarding the chemical composition and bonding of $CuCo_2S_4/$ g-C₃N₄ composite nanorods. Figure 6 depicts XPS spectra of $CuCo_2S_4/g-C_3N_4$ composite nanorods. The Cu 2p spectra can be fitted into two different chemical states (Figure 6a). The binding energies at 932.14 and 952.12 eV are attributed to $\rm Cu^+,$ and the binding energies at 935.16 and 953.4 eV are assigned to $\rm Cu^{2+}.^{57,83,84}$ Peaks located in the Cu 2p spectra at 932.14 and 935.16 eV are assigned to Cu $2p_{3/2}$, and the peaks at the binding energies of 952.12, and 553.4 eV may be attributed to the Cu $2p_{1/2}$.⁸³ Two satellite peaks are also observed at the binding energies of 943.91 and 460.37 eV corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. Due to the spin-orbit doublet of $2p_{1/2}$ and $2p_{3/2}$ of Co³⁺ ions⁸³ (Figure 6b), binding energies at 793.53 and 778.36 eV are showm in the XPS. Peaks appearing at 796.22 and 780.47 eV are ascribed to the spin-orbit doublet of $2p_{1/2}$ and $2p_{3/2}$ of Co^{2+} ions.^{57,84} Additionally, satellite peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$ were observed at the binding energy values of 784.89 and 804.77 eV, respectively. These studies proved CuCo₂S₄ has Co²⁺ and Co³⁺ valence states, and the results are consistent with other cobalt-based spinel structures reported. The S 2p spectrum was divided into one shakeup satellite and two prominent peaks. The binding energies at 162.45 and 161.34 eV (Figure 6c) in the S 2p fine spectrum correspond to the spin-orbit doublet of $2p_{1/2}$ and $2p_{3/2}$ peaks, which can be attributed to S_2^{2-} and S^{2-} , respectively.^{84,85} It is noteworthy to mention that sulfur valence states coexist with -1 and -2states, which is due to the $2p_{1/2}$ peak of the S²⁻ ions, partially overlapped with the low-coordinated sulfur ions at the surface or the presence of S_2^{2-} ions. A binding energy of 168.95 eV⁵⁷ corresponds to shakeup of the satellite peak. Notably, the peak at 165.26 eV can be attributed to the C-S-C bond, which indicates the incorporation of S into the $g-C_3N_4$ sheet. Figure 6d presents the corresponding high-resolution spectra of C 1s, which could be fitted to three distinct peaks at binding energies of 284.61, 285.53, and 288.28 eV. These peaks are assigned to pure graphitic sites present in the carbon nitride matrix C-C bonds, an aromatic ring that has a $C-NH_2$ bond formed by sp^2 hybridized carbon atoms bonded to N and triazine having sp² hybridized C atoms, respectively.^{82,85} Figure 6e shows the N 1s spectra where it is clearly observed that N 1s spectra are asymmetrical and broad in feature. This may be due to the presence of distinguishable nitrogen models. The N 1s peak could be deconvoluted into three peaks located at the binding energy values of 398.55, 399.21, and 400.43 eV, which can be attributed to pyridine nitrogen (C=N-C) having sp^2 hybridization, tertiary nitrogen $(N-C_3)$, and a $C-NH_2$ functional group, respectively.^{82,85,86} XRD, XPS, and TEM results confirmed the successful formation of CuCo₂S₄/g-C₃N₄ composite nanorods.

To gain insight into structural and development information, we carried out an ATR-FTIR spectroscopic study of $g-C_3N_4$, and $CuCo_2S_4/g-C_3N_4$ composite nanorods, and the corresponding ATR-FTIR spectra are depicted in Figure 7a. In the FTIR spectrum of $g-C_3N_4$ (Figure 7a,i), two main bonds in the products are correlated to the absorption peaks between 1200



Article



Figure 6. XPS patterns of CuCo₂S₄/g-C₃N₄ composite nanostructure: (a) Cu 2p, (b) Co 2p, (c) S 2p, (d) C 1s, and (e) N 1s.



Figure 7. (a) ATR-FTIR spectra and (b) Raman spectra of (i) pure g-C₃N₄ and (ii) Cu₂CO₂S₄/g-C₃N₄ composite nanostructure.

to 1640 cm⁻¹. The peak due to sp² C=N stretching vibration is observed at 1638 cm⁻¹, whereas the peaks at 1242, 1324, 1365, 1411, and 1464 cm⁻¹ were attributed to the aromatic sp³ C–N bonds.^{87–89} Additionally, the peaks at 887 and 808 cm⁻¹ were due to the deformation mode of N-H bonds and breathing modes of the triazine ring, respectively.⁹⁰ Moreover, all characteristic peaks of g- C_3N_4 were also observed in the composite CuCo₂S₄/ g-C₃N₄ nanorods (Figure 7a,ii and Table S7). It is worth mentioning that the stretching vibration of the C=N bond slightly shifted toward a lower wavenumber in the CuCo₂S₄/g-C₃N₄ composite nanorods compared to pure g-C₃N₄, which further confirmed that close interfacial contact between g-C₃N₄ and CuCo₂S₄ was formed. Peaks observed at 547 and 478 cm⁻¹ were attributed to stretching vibrations of metal sulfide bonds present in the $CuCo_2S_4/g-C_3N_4$ composite nanostructures (Figure 7a,ii).⁷⁸ We have also studied the Raman spectroscopy to further confirm the formation of the CuCo₂S₄/g-C₃N₄ composite nanostructure. Figure 7b shows the Raman spectra of pure g-C₃N₄ and CuCo₂S₄/g-C₃N₄ composite nanostructures. Raman spectra of pure g-C3N4 exhibited two prominent peaks at 1341 and 1598 cm⁻¹ which are associated with the D and G bands of the graphitic nitrogen-bonded carbon structure, respectively (Figure 7b,i).⁹¹⁻⁹³ The $CuCo_2S_4/g-C_3N_4$ composite nanostructure also displayed the D and G bands corresponding to g-C₃N₄ at 1347 and 1602 cm⁻¹, with an intensity ratio of 1.02 (I_D/I_G)

Figure 7b,ii), which is greater with respect to pure $g-C_3N_4$ ($I_D/I_G = 1.01$). Notably, the shifting of the D band from 1341 to 1347 cm⁻¹ and G band from 1598 to 1602 cm⁻¹ confirmed the formation of the CuCo₂S₄/g-C₃N₄ composite nanostructure by combining $g-C_3N_4$ with CuCo₂S₄ nanorods.

OER ACTIVITY

The working electrode was prepared by dissolving the catalyst (3 mg) in double distilled water (680 μ L) and ethanol (400 μ L) and was kept in a 1.5 mL microcentrifuge tube to form a homogeneous ink. The resulting mixture was sonicated for half an hour prior to the addition of 20 μ L of 5% Nafion solution. After that, the solution was again sonicated for another 20 min. Prepared catalyst ink (5 μ L) was drop-casted onto a glassy carbon (GC) electrode, and the electrode was kept overnight in a vacuum desiccator for drying. Thus, the dried electrode prepared was used as a working electrode (WE) in the experiment, keeping the mass loading of the catalyst as 0.19 mg cm⁻² to study the OER activity. All the experiments were carried out at room temperature in an electrochemical cell.

A Metrohm Autolab (Multichannel-204) connected to a standard three-electrode system using Nova 2.1.4 software was used to perform the electrochemical measurements. In order to characterize the electrochemical reactions, Ag/AgCl (3 M KCl) and platinum (Pt) electrodes were used as reference and counter-electrodes, respectively. Additionally, the working

80 g-C₃N₄ 2.0 (a) (b)70 Cu₂S Current density (mA cm⁻² 173 mVIdec 143 mV/dec Potential (V vs. RHE) CoS 60 CuCo,S/g-C,N IrO, 124 mV/dec 1.8 CuCo₂S₄ 50 CuCo,S 76 mV/dec IrO. CuCo S /g-C 40 CoS, 69 mV/dec Cu.S 1.6 30 20 57 mV/dec 10 1.4 0 -1.0 -0.5 0.0 0.5 1.0 1.5 1.2 1.4 1.6 1.8 log [j (mA cm⁻²)] Potential (V vs. RHE) 500 300 – g-C₃N₄ (c) (d) Cu,S 400 - CoS 225 - CuCo S 300 R (Ω) (U) ...Z-150 **R**__ 200 R 75 100 Z' (Ω) 100 200 300 400 500 CuCo2S4 CuCo2S4 g-C3 g-C3N4 Cu₂S CoS2 Z' (Ω)

Figure 8. (a) Polarization curves (LSV) plot. (b) Corresponding Tafel plots of $g-C_3N_4$, Cu_2S , CoS_2 , IrO_2 , $CuCo_2S_4$, and $CuCo_2S_4/g-C_3N_4$ composite. (c) EIS at 350 mV (vs Ag/AgCl). (d) Variation of R_s and R_{ct} of $g-C_3N_4$, Cu_2S , CoS_2 , $CuCo_2S_4$, and $CuCo_2S_4/g-C_3N_4$ composite catalyst.

Table 1. Summary of OER Performance of CuCo₂S₄/g-C₃N₄, CuCo₂S₄, Commercial IrO₂, CoS₂, Cu₂S, and g-C₃N₄ Catalysts

system	overpotential at 10 mA $\rm cm^{-2}$	Tafel slope (mV dec^{-1})	$R_{\rm ct} (\Omega)$	$R_{\rm s} (\Omega)$	$C_{\rm dl}~({\rm mFcm^{-2}})$	ECSA (cm ²)	surface area $(m^2 g^{-1})$
g-C ₃ N ₄	472 mV	173	281.7	1.5	0.256	6.4	19.67
Cu ₂ S	425 mV	143	263.4	1.3	0.381	9.5	22.45
CoS_2	385 mV	124	97.6	1.3	0.574	14.35	33.89
IrO ₂	354 mV	76					
CuCo ₂ S ₄	307 mV	69	47.3	1.2	0.738	18.4	41.72
$CuCo_2S_4/g-C_3N_4$	242 mV	57	33.5	1.6	1.705	42.6	64.15

electrode was a GC (3 mm diameter) electrode, which was loaded with the catalyst. A potential range from 0 to 1 V vs the reference potential with a 10 mV s⁻¹ scan rate was set for carrying out a linear sweep voltammetry (LSV) experiment. Further, a potential range of 0.05 to 0.15 V with a scan rate varying from 20 mV s⁻¹ to 100 mV s⁻¹ was used in cyclic voltammetry (CV) experiments. A chronoamperometric method was used to test the durability of the catalyst by applying a constant overpotential of 242 mV for 12 h in an alkaline medium. Further, the stability of the $CuCo_2S_4/g-C_3N_4$ composite was evaluated by calculating the change in overpotential after 2000 LSV cycles at a constant scan rate of 10 mV s^{-1} under both alkaline and neutral conditions. The electrochemical impedance spectroscopy (EIS) was done between 100 kHz and 0.1 Hz frequencies at 350 mV (vs Ag/AgCl) under alkaline conditions. All of the potentials were calibrated versus RHE, and the Nernst equation given below was followed:

$$E_{(RHE)} = E_{(Ag/AgCl)} + 0.059 \text{ pH} + E_{Ref}$$
(1)

The oxygen evolution reaction (OER) performance was evaluated using a conventional three-electrode configuration for the synthesized $CuCo_2S_4/g-C_3N_4$ catalyst in a 1 M KOH

solution. For comparison, the OER activities of CuCo₂S₄, CoS₂, Cu₂S, and g-C₃N₄ were also investigated under identical conditions. For the correlation of OER activity of assynthesized catalysts, commercially available IrO2 was used for a reference catalyst. Figure 8a shows the linear sweep voltammetry (LSV) curves of CuCo₂S₄/g-C₃N₄, CuCo₂S₄, CoS₂, Cu₂S, and g-C₃N₄ catalysts. CuCo₂S₄/g-C₃N₄ composite nanorods indicate that a current density of 10 mA cm⁻² was achieved at an overpotential of only 242 mV, whereas for generating a current density of 10 mA cm⁻², commercial IrO₂ requires 354 mV overpotential. Moreover, CuCo₂S₄/g-C₃N₄ shows premier OER activity over achieving the current density of 10 mA cm⁻², whereas CuCo₂S₄, CoS₂, Cu₂S, and g-C₃N₄ catalysts require overpotentials of 307, 385, 425, and 472 mV, respectively. It is well established that in order to access the reaction kinetics, the Tafel slope is an important parameter in the electrocatalytic OER process. The Tafel slope of $CuCo_2S_4/$ g-C₃N₄ composite nanorods was found to be 57 mV dec⁻¹ whereas the commercial IrO₂ exhibited a Tafel slope of 76 mV dec⁻¹ (Figure 8b). However, CuCo₂S₄, CoS₂, Cu₂S, and g- $\mathrm{C_3N_4}$ possessed Tafel slopes of 69, 124, 143, and 173 mV dec⁻¹, respectively. Analysis of the LSV study as well as the



Figure 9. (a) Polarization curves of the $CuCo_2S_4/g-C_3N_4$ composite after the first and 2000th cycles. (b) Chronoamperometry investigation of the $CuCo_2S_4/g-C_3N_4$ composite catalyst at an overpotential of 242 mV for 12 h. (c) Chronopotentiometric study of $CuCo_2S_4/g-C_3N_4$ for OER in 1.0 M KOH as a function of current density.



Figure 10. (a) Polarization curves (LSV) and (b) corresponding Tafel plot of $g-C_3N_4$, Cu_2S , CoS_2 , $CuCo_2S_4$, and $CuCo_2S_4/g-C_3N_4$ composite nanorods at pH 7. (c) Polarization curves of $CuCo_2S_4/g-C_3N_4$ for the first and 2000th cycles of continuous operation at pH 7.

Tafel slope confirmed the superior OER activity of $CuCo_2S_4/g-C_3N_4$ composite nanorods.

Further, to figure out the superior catalytic activity of $CuCo_2S_4/g-C_3N_4$ composite nanorods and investigate the solution resistance (R_s) and charge-transfer resistance (R_{ct}) during the catalytic process, electrochemical impedance spectroscopy (EIS) was used. The EIS spectra of $CuCo_2S_4/g-C_3N_4$, $g-C_3N_4$, GoS_2 , Cu_2S , and $CuCo_2S_4$ are shown in Figure 8c. It was observed from the EIS that $CuCo_2S_4/g-C_3N_4$ displayed the least charge transfer resistance (R_{ct}) of 33.5 Ω compared to $CuCo_2S_4$ (47.3 Ω), CoS_2 (97.6 Ω), Cu_2S (263.4 Ω), and $g-C_3N_4$ (281.7 Ω ; Table 1 and Figure 8c,d). Presumably, a lower R_{ct} value appeared because the quick charge transfer process was taking place across the $CuCo_2S_4/g-C_3N_4$ composite nanostructures and electrolyte.

Additionally, electrochemically active surface area (ECSA) in terms of double layer capacitance, C_{dl} , was measured to understand the origin of the high OER activity of CuCo₂S₄/g- C_3N_4 composite nanostructures. From the CV curves (Figure S17a-e), both the anodic and cathodic double-layer charging currents $(J_a \text{ and } J_c$, respectively) were calculated at a fixed potential of 0.1 V (vs Ag/AgCl), and the values are plotted against corresponding scan rates (Figure S17f-j). The C_{dl} thus calculated for CuCo₂S₄/g-C₃N₄ was found to be 1.705 mF cm^{-2} , and the corresponding ECSA was found to be 42.6 cm^{2} , which was greater compared to $CuCo_2S_4$ (18.4 cm²), CoS_2 (14.35 cm²), Cu₂S (9.5 cm²), and $g-C_3N_4$ (6.4 cm²) catalysts (Figure S17f-j and Table 1). It was found from the Brunauer-Emmett-Teller (BET) results that CuCo₂S₄/g-C₃N₄ possesses the highest surface area of 64.15 m² g⁻¹ compared to CuCo₂S₄, g^{-0} , g^{-1} , and g^{-1} , g^{-1} , material to be an efficient electrocatalyst, catalyst durability is an important parameter. Accordingly, the long-term stability of the $CuCo_2S_4/g-C_3N_4$ catalyst for the OER activity was

examined by performing and running 2000 continuous LSV cycles using 1 M KOH electrolyte. The LSV curve for the initial and 2000th cycles of CuCo₂S₄/g-C₃N₄ composite nanorods is shown in Figure 9a. It is observed that overpotential change at a current density of 10 mA cm⁻² after 2000 LSV cycles is only 9 mV (from 242 mV to 251 mV), which indicates the superior durability of the $CuCo_2S_4/g-C_3N_4$ composite nanostructures toward OER activity. We have also tested the durability of the CuCo₂S₄/g-C₃N₄ using chronoamperometry techniques at an overpotential of 242 mV for 12 h constantly (Figure 9b). The chronoamperometry study revealed that only 9% of its initial current density was lost after 12 h. We have also studied chronopotentiometric measurements of CuCo₂S₄/g-C₃N₄ in 1 M KOH as a function of current density (20 to 80 mA cm⁻²; Figure 9c). CuCo₂S₄/g-C₃N₄ displayed a current density of 20, 40, 60, and 80 mA cm^{-2} at overpotentials of 272, 323, 375, and 419 mV, respectively (Figure 8a and Figure 9c). The chronopotentiometric stability test showed that, at different applied current densities, the obtained overpotential remained almost constant.

We have further investigated the OER activity of CuCo₂S₄/ g-C₃N₄, CuCo₂S₄, CoS₂, Cu₂S, and g-C₃N₄ catalysts in a neutral medium, i.e., phosphate buffer (0.1 M PBS; pH = 7.0) electrolyte. Figure 10a represents the LSV curves of CuCo₂S₄/ g-C₃N₄, CuCo₂S₄, CoS₂, Cu₂S, and g-C₃N₄ catalysts in a neutral medium. It is seen from Figure 10a that, for the generation of a current density of 10 mA cm⁻², CuCo₂S₄/g-C₃N₄, CuCo₂S₄, CoS₂, and Cu₂S catalysts exhibited overpotential values of 406, 465, 591, and 654 mV, respectively. Tafel slopes of CuCo₂S₄/g-C₃N₄, CuCo₂S₄, CoS₂, Cu₂S, and g-C₃N₄ catalysts were calculated to be 95, 108, 241, 253, and 346 mV dec⁻¹, respectively (Figure 10b). So the LSV and Tafel plot analysis confirmed that CuCo₂S₄/g-C₃N₄ showed very good activity toward OER even in a neutral medium. The stability of CuCo₂S₄/g-C₃N₄ was also performed in a neutral medium by 2000 contentious cycles of LSV analysis, and it has been found that after 2000 cycles of LSV analysis that the overpotential is 429 mV, which is 23 mV higher than the initial overpotential (406 mV) at a current density of 10 mA cm⁻² (Figure 10c). Hence, $CuCo_2S_4/g-C_3N_4$ exhibited long-term superior stability toward OER activity even in a neutral medium. All of these electrochemical studies indicate that $CuCo_2S_4/g-C_3N_4$ composite nanorods are good catalysts for OER activity under both alkaline and neutral conditions. Therefore, the results confirmed that the incorporation of g-C₃N₄ is very beneficial for creating more active sites for efficient electron transfer in the catalytic OER process in $CuCo_2S_4/g-C_3N_4$ composite nanorods. From an OER efficiency point of view, the presence of g-C₃N₄ provides an additional direct conduction of electrons to CuCo₂S₄ nanorods and improves O₂ production. Thus, the surface complexity of CuCo₂S₄ nanorods via g-C₃N₄ incorporation showed better OER efficiency. In addition to the chronoamperometric stability test, we conducted powder XRD analysis (Figure S19) to study any changes in crystalline structure of the CuCo₂S₄/g-C₃N₄ composite. From the XRD pattern, it was found that all of the diffraction peaks related to CuCo₂S₄/g-C₃N₄ composite nanorods were observed with almost the same intensity ratio. As the OER reaction mechanism of CuCo₂S₄/g-C₃N₄ composite nanorods has not been thoroughly investigated yet, we utilized XPS at different applied potentials to understand the reaction process and modification of the catalyst to some extent. We picked CuCo₂S₄/g-C₃N₄ composite nanorods to execute a chronoamperometry test for 1 h at four stages: before the catalytic reaction and after three different applied potentials to get a current density of 10, 20, and 40 mÅ cm⁻², to examine the impact of surface modification of $CuCo_2S_4$ nanorods by $g-C_3N_4$ on the OER process. These are displayed in Figure S20. Concerning the XPS range of Co 2p (Figure S20a), the moving of the peak position to bring down the binding energy (in all of the stages) has illustrated that Co2+ changes into Co3+ as the reaction proceeds. Again, moving of the Cu peaks toward a lower binding energy (Figure S20b) seems to be consistent with the electronic charge equilibrium of Cu in advancement of a synergistic response. After catalytic activity, the intensity of the peaks at 160.93 eV for S 2p (Figure S20c) is significantly reduced, which indicates that most of the S sites detected had been replaced by O centers. In the XPS spectra of O 1s, it was found that there is an appearance of a new peak at 535.48 eV for $CuCo_2S_4/g$ - C_3N_4 composite nanorods that indicates the presence of surface oxygen imperfection (Figure S20d). Moreover, as the reaction continues, a few little, sharp peaks at the binding energy values of 529.92 and 532.03 eV appeared, which correspond to various oxides and hydroxides of Co and Cu, respectively (Figure S20d).94 Moreover, the appearance of O 1s peaks with applied potential toward a lower binding energy shows that water molecules respond with the dynamic site of Co (Figure S20d).⁹⁴

In the summary, spinel-type sulfide $CuCo_2S_4$ nanorods have been successfully synthesized using their molecular precursors via a simple colloidal approach. Various TEM studies were conducted to realize the reaction conditions and growth stages associated with the formation of $CuCo_2S_4$ nanorods. Microscopic analysis affirmed that the utilization of $Cu[PDTC]_2$ and $Co[PDTC]_2$ complex precursors provides an advantage in preparing homogeneous CuCo₂S₄ nanorods. In addition, these CuCo₂S₄ nanorods coupled with g-C₃N₄ conductive support were examined for OER activity under alkaline and neutral media as well. The CuCo₂S₄/g-C₃N₄ was found to be a more active electrocatalyst for OER catalysis compared to its various constituents and other reported CuCo₂S₄-based catalysts (Table S8)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01566.

Additional data such as name of chemicals used; detailed instrumentation; experimental procedure; ¹H and ¹³C NMR; HRMS of PDTC, Cu[PDTC]₂, and Co-[PDTC]₂; summary of crystallographic details of PDTC; Cu[PDTC]₂; TGA; additional TEM images; cyclic voltammograms (CV) and corresponding electrochemical double layer capacitance; details of fabrication of working electrode; BET study; XPS; XRD; and OER activity comparative table (PDF)

Accession Codes

CCDC 2034050 and 2082152 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Krishna Kanta Haldar – Department of Chemistry, Central University of Punjab, Bathinda 151001 Punjab, India; orcid.org/0000-0002-0675-8299; Email: krishankant.haldar@cup.edu.in

Authors

- Rathindranath Biswas Department of Chemistry, Central University of Punjab, Bathinda 151001 Punjab, India; orcid.org/0000-0002-0909-1442
- **Pooja Thakur** Department of Chemistry, Central University of Punjab, Bathinda 151001 Punjab, India
- Gagandeep Kaur Institute of Nano Science and Technology, Mohali 140306 Punjab, India
- Shubham Som Department of Chemistry, Indian Institute of Science Education and Research, Bhopal 462066 Madhya Pradesh, India
- Monochura Saha Indian Institute of Science Education and Research, Kolkata, Nadia 741246 West Bengal, India
- Vandna Jhajhria Department of Chemistry, Central University of Punjab, Bathinda 151001 Punjab, India
- Harjinder Singh Department of Chemistry, Central University of Punjab, Bathinda 151001 Punjab, India; orcid.org/0000-0002-9203-427X
- Imtiaz Ahmed Department of Chemistry, Central University of Punjab, Bathinda 151001 Punjab, India
- Biplab Banerjee Department of Chemistry, Central University of Punjab, Bathinda 151001 Punjab, India
- **Deepak Chopra** Department of Chemistry, Indian Institute of Science Education and Research, Bhopal 462066 Madhya Pradesh, India; orcid.org/0000-0002-0018-6007

Tapasi Sen – Institute of Nano Science and Technology, Mohali 140306 Punjab, India; o orcid.org/0000-0003-0243-178X

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.1c01566

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support was provided by the Department of Science and Technology, DST (Project No. EEQ/2017/000467), and is gratefully acknowledged. R.B. is thankful to the DST for providing an INSPIRE fellowship for the Ph.D. programme (DST/INSPIRE Fellowship/ [IF190052]). H.S. and I.A. thank CSIR for awarding a fellowship. S.S. acknowledges CSIR for a JRF fellowship. D.C. and S.S. acknowledge the CIF at IISERB for research facilities and infrastructure. We are thankful to Dependu Dolui, IIT Gandhinagar, Gujarat-382355 for helping with the HRMS studies. The paper was written through contributions of all authors.

REFERENCES

(1) Sarkar, A.; Karmakar, K.; Khan, G. G. Designing Co-Pi Modified One-Dimensional n-p $TiO_2/ZnCo_2O_4$ Nanoheterostructure Photoanode with Reduced Electron-Hole Pair Recombination and Excellent Photoconversion Efficiency (> 3%). *J. Phys. Chem. C* **2017**, 121, 25705–25717.

(2) Huang, J.; Liu, T.; Wang, R.; Zhang, M.; Wang, L.; She, H.; Wang, Q. Facile loading of cobalt oxide on bismuth vanadate: Proved construction of pn junction for efficient photoelectrochemical water oxidation. *J. Colloid Interface Sci.* **2020**, *570*, 89–98.

(3) Kim, J. S.; Kim, B.; Kim, H.; Kang, K. Recent progress on multimetal oxide catalysts for the oxygen evolution reaction. *Adv. Energy Mater.* **2018**, *8*, 1702774.

(4) Yue, Q.; Sun, J.; Chen, S.; Zhou, Y.; Li, H.; Chen, Y.; Zhang, R.; Wei, G.; Kang, Y. Hierarchical Mesoporous MXene–NiCoP Electrocatalyst for Water-Splitting. *ACS Appl. Mater. Interfaces* **2020**, *12*, 18570–18577.

(5) Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* **2009**, *38*, 253–278.

(6) Chandrasekaran, S.; Yao, L.; Deng, L.; Bowen, C.; Zhang, Y.; Chen, S.; Lin, Z.; Peng, F.; Zhang, P. Recent advances in metal sulfides: from controlled fabrication to electrocatalytic, photocatalytic and photoelectrochemical water splitting and beyond. *Chem. Soc. Rev.* **2019**, *48*, 4178–4280.

(7) Tiwari, A. P.; Yoon, Y.; Novak, T. G.; An, K.-S.; Jeon, S. Continuous network of phase-tuned nickel sulfide nanostructures for electrocatalytic water splitting. *ACS Appl. Nano Mater.* **2019**, *2*, 5061–5070.

(8) Wang, F.; Fang, B.; Yu, X.; Feng, L. Coupling ultrafine Pt nanocrystals over the Fe₂P surface as a robust catalyst for alcohol fuel electro-oxidation. *ACS Appl. Mater. Interfaces* **2019**, *11*, 9496–9503.

(9) Biswas, R.; Singh, S.; Ahmed, I.; Patil, R. A.; Ma, Y. R.; Haldar, K. K. Rational Design of Bimetallic Au/Cu Nanostructure: An Efficient Catalyst for Methanol Oxidation. *ChemNanoMat* **2021**, *7*, 158–164.

(10) Yaqoob, L.; Noor, T.; Iqbal, N. Recent progress in development of efficient electrocatalyst for methanol oxidation reaction in direct methanol fuel cell. *Int. J. Energy Res.* **2021**, *45*, 6550–6583.

(11) Chen, P.; Zhang, N.; Wang, S.; Zhou, T.; Tong, Y.; Ao, C.; Yan, W.; Zhang, L.; Chu, W.; Wu, C.; Xie, Y. Interfacial engineering of cobalt sulfide/graphene hybrids for highly efficient ammonia electrosynthesis. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 6635–6640.

(12) Qing, G.; Ghazfar, R.; Jackowski, S. T.; Habibzadeh, F.; Ashtiani, M. M.; Chen, C.-P.; Smith, M. R., III; Hamann, T. W. Recent advances and challenges of electrocatalytic N_2 reduction to ammonia. *Chem. Rev.* **2020**, 120, 5437–5516.

(13) He, C.; Wu, Z.-Y.; Zhao, L.; Ming, M.; Zhang, Y.; Yi, Y.; Hu, J.-S. Identification of FeN₄ as an efficient active site for electrochemical N_2 reduction. *ACS Catal.* **2019**, *9*, 7311–7317.

(14) Chu, K.; Liu, Y.-p.; Wang, J.; Zhang, H. NiO nanodots on graphene for efficient electrochemical N_2 reduction to NH3. ACS Appl. Energy Mater. **2019**, 2, 2288–2295.

(15) Raciti, D.; Livi, K. J.; Wang, C. Highly dense Cu nanowires for low-overpotential CO₂ reduction. *Nano Lett.* **2015**, *15*, 6829–6835.

(16) Yang, Y.; Ajmal, S.; Zheng, X.; Zhang, L. Efficient nanomaterials for harvesting clean fuels from electrochemical and photoelectrochemical CO_2 reduction. *Sustainable Energy & Fuels* **2018**, *2*, 510–537.

(17) Han, J.; Li, S.; Chen, J.; Liu, Y.; Geng, D.; Wang, D.; Zhang, L. Dendritic Ag/Pd alloy nanostructure arrays for electrochemical CO_2 reduction. *ChemElectroChem* **2020**, *7*, 2608–2613.

(18) Jung, K.-N.; Jung, J.-H.; Im, W. B.; Yoon, S.; Shin, K.-H.; Lee, J.-W. Doped lanthanum nickelates with a layered perovskite structure as bifunctional cathode catalysts for rechargeable metal—air batteries. *ACS Appl. Mater. Interfaces* **2013**, *5*, 9902–9907.

(19) Xu, N.; Nie, Q.; Luo, L.; Yao, C.; Gong, Q.; Liu, Y.; Zhou, X.-D.; Qiao, J. Controllable hortensia-like MnO_2 synergized with carbon nanotubes as an efficient electrocatalyst for long-term metal-air batteries. ACS Appl. Mater. Interfaces **2019**, 11, 578–587.

(20) Cheng, F.; Chen, J. Metal-air batteries: from oxygen reduction electrochemistry to cathode catalysts. *Chem. Soc. Rev.* 2012, 41, 2172-2192.

(21) Xiong, M.; Ivey, D. G. Synthesis of bifunctional catalysts for metal-air batteries through direct deposition methods. *Batteries & Supercaps* **2019**, *2*, 326–335.

(22) Zou, H.; He, B.; Kuang, P.; Yu, J.; Fan, K. Metal-organic framework-derived nickel-cobalt sulfide on ultrathin mxene nanosheets for electrocatalytic oxygen evolution. *ACS Appl. Mater. Interfaces* **2018**, *10*, 22311–22319.

(23) Han, H.; Kim, K. M.; Choi, H.; Ali, G.; Chung, K. Y.; Hong, Y.-R.; Choi, J.; Kwon, J.; Lee, S. W.; Lee, J. W.; Ryu, J. H.; Song, T.; Mhin, S. Parallelized reaction pathway and stronger internal band bending by partial oxidation of metal sulfide–graphene composites: important factors of synergistic oxygen evolution reaction enhancement. ACS Catal. **2018**, *8*, 4091–4102.

(24) Wu, Z. P.; Lu, X. F.; Zang, S. Q.; Lou, X. W. Non-noble-metalbased electrocatalysts toward the oxygen evolution reaction. *Adv. Funct. Mater.* **2020**, *30*, 1910274.

(25) Yuan, X.; Ge, H.; Wang, X.; Dong, C.; Dong, W.; Riaz, M. S.; Xu, Z.; Zhang, J.; Huang, F. Controlled phase evolution from Co nanochains to CoO nanocubes and their application as OER catalysts. *ACS Energy Lett.* **2017**, *2*, 1208–1213.

(26) Biswas, R.; Kundu, A.; Saha, M.; Kaur, V.; Banerjee, B.; Dhayal, R. S.; Patil, R. A.; Ma, Y.-R.; Sen, T.; Haldar, K. K. Rational design of marigold-shaped composite Ni₃V₂O₈ flowers: a promising catalyst for the oxygen evolution reaction. *New J. Chem.* **2020**, *44*, 12256–12265.

(27) Reier, T.; Oezaslan, M.; Strasser, P. Electrocatalytic oxygen evolution reaction (OER) on Ru, Ir, and Pt catalysts: a comparative study of nanoparticles and bulk materials. *ACS Catal.* **2012**, *2*, 1765–1772.

(28) Menzel, N.; Ortel, E.; Mette, K.; Kraehnert, R.; Strasser, P. Dimensionally stable $Ru/Ir/TiO_2$ -anodes with tailored mesoporosity for efficient electrochemical chlorine evolution. *ACS Catal.* **2013**, *3*, 1324–1333.

(29) Hu, W.; Zhong, H.; Liang, W.; Chen, S. Ir-surface enriched porous Ir–Co oxide hierarchical architecture for high performance water oxidation in acidic media. *ACS Appl. Mater. Interfaces* **2014**, *6*, 12729–12736.

(30) Reier, T.; Pawolek, Z.; Cherevko, S.; Bruns, M.; Jones, T.; Teschner, D.; Selve, S.; Bergmann, A.; Nong, H. N.; Schlogl, R.; Mayrhofer, K. J. J.; Strasser, P. Molecular insight in structure and activity of highly efficient, low-Ir Ir–Ni oxide catalysts for electrochemical water splitting (OER). J. Am. Chem. Soc. 2015, 137, 13031–13040.

(31) Retuerto, M.; Calle-Vallejo, F.; Pascual, L.; Lumbeeck, G.; Fernandez-Diaz, M. T.; Croft, M.; Gopalakrishnan, J.; Pena, M. A.; Hadermann, J.; Greenblatt, M.; Rojas, S. La_{1.5}Sr_{0.5}NiMn_{0.5}Ru_{0.5}O₆ double perovskite with enhanced ORR/OER bifunctional catalytic activity. *ACS Appl. Mater. Interfaces* **2019**, *11*, 21454–21464.

(32) Meng, Y.; Song, W.; Huang, H.; Ren, Z.; Chen, S.-Y.; Suib, S. L. Structure–property relationship of bifunctional MnO_2 nanostructures: highly efficient, ultra-stable electrochemical water oxidation and oxygen reduction reaction catalysts identified in alkaline media. *J. Am. Chem. Soc.* **2014**, *136*, 11452–11464.

(33) Esswein, A. J.; McMurdo, M. J.; Ross, P. N.; Bell, A. T.; Tilley, T. D. Size-dependent activity of Co_3O_4 nanoparticle anodes for alkaline water electrolysis. *J. Phys. Chem. C* **2009**, *113*, 15068–15072.

(34) Lee, D. U.; Kim, B. J.; Chen, Z. One-pot synthesis of a mesoporous $NiCo_2O_4$ nanoplatelet and graphene hybrid and its oxygen reduction and evolution activities as an efficient bi-functional electrocatalyst. *J. Mater. Chem. A* **2013**, *1*, 4754–4762.

(35) Gao, D.; Liu, R.; Biskupek, J.; Kaiser, U.; Song, Y. F.; Streb, C. Modular design of noble-metal-free mixed metal oxide electrocatalysts for complete water splitting. *Angew. Chem., Int. Ed.* **2019**, *58*, 4644–4648.

(36) Mohanty, B.; Ghorbani-Asl, M.; Kretschmer, S.; Ghosh, A.; Guha, P.; Panda, S. K.; Jena, B.; Krasheninnikov, A. V.; Jena, B. K. MoS₂ quantum dots as efficient catalyst materials for the oxygen evolution reaction. *ACS Catal.* **2018**, *8*, 1683–1689.

(37) Chen, J. S.; Ren, J.; Shalom, M.; Fellinger, T.; Antonietti, M. Stainless steel mesh-supported NiS nanosheet array as highly efficient catalyst for oxygen evolution reaction. *ACS Appl. Mater. Interfaces* **2016**, *8*, 5509–5516.

(38) Chauhan, M.; Reddy, K. P.; Gopinath, C. S.; Deka, S. Copper cobalt sulfide nanosheets realizing a promising electrocatalytic oxygen evolution reaction. *ACS Catal.* **2017**, *7*, 5871–5879.

(39) Kawashima, K.; Shin, K.; Wygant, B. R.; Kim, J.-H.; Cao, C. L.; Lin, J.; Son, Y. J.; Liu, Y.; Henkelman, G.; Mullins, C. B. Cobalt metal-cobalt carbide composite microspheres for water reduction electrocatalysis. *ACS Appl. Energy Mater.* **2020**, *3*, 3909–3918.

(40) Jiang, J.; Liu, Q.; Zeng, C.; Ai, L. Cobalt/molybdenum carbide@ N-doped carbon as a bifunctional electrocatalyst for hydrogen and oxygen evolution reactions. *J. Mater. Chem. A* 2017, *5*, 16929–16935.

(41) Kim, J.-H.; Kawashima, K.; Wygant, B. R.; Mabayoje, O.; Liu, Y.; Wang, J. H.; Mullins, C. B. Transformation of a cobalt carbide (Co₃C) oxygen evolution precatalyst. *ACS Appl. Energy Mater.* **2018**, *1*, 5145–5150.

(42) Luan, C.; Liu, G.; Liu, Y.; Yu, L.; Wang, Y.; Xiao, Y.; Qiao, H.; Dai, X.; Zhang, X. Structure effects of 2D materials on α -Nickel hydroxide for oxygen evolution reaction. *ACS Nano* **2018**, *12*, 3875–3885.

(43) Wang, M.; Wang, J.-Q.; Xi, C.; Cheng, C.-Q.; Zou, C.-Q.; Zhang, R.; Xie, Y.-M.; Guo, Z.-L.; Tang, C.-C.; Dong, C.-K.; Chen, Y.-J.; Du, X.-W. A hydrogen-deficient nickel–cobalt double hydroxide for photocatalytic overall water splitting. *Angew. Chem.* **2020**, *132*, 11607–11612.

(44) Chen, X.; Wang, H.; Meng, R.; Xia, B.; Ma, Z. Cadmium hydroxide: a missing non-noble metal hydroxide electrocatalyst for the oxygen evolution reaction. *ACS Appl. Energy Mater.* **2020**, *3*, 1305–1310.

(45) Chang, J.; Xiao, Y.; Xiao, M.; Ge, J.; Liu, C.; Xing, W. Surface oxidized cobalt-phosphide nanorods as an advanced oxygen evolution catalyst in alkaline solution. *ACS Catal.* **2015**, *5*, 6874–6878.

(46) Dutta, A.; Pradhan, N. Developments of metal phosphides as efficient OER precatalysts. *J. Phys. Chem. Lett.* **201**7, *8*, 144–152.

(47) Liu, K.; Zhang, C.; Sun, Y.; Zhang, G.; Shen, X.; Zou, F.; Zhang, H.; Wu, Z.; Wegener, E. C.; Taubert, C. J.; Miller, J. T.; Peng, Z.; Zhu, Y. High-performance transition metal phosphide alloy catalyst for oxygen evolution reaction. *ACS Nano* **2018**, *12*, 158–167. (48) Zhang, J.-Y.; Lv, L.; Tian, Y.; Li, Z.; Ao, X.; Lan, Y.; Jiang, J.; Wang, C. Rational design of cobalt—iron selenides for highly efficient electrochemical water oxidation. *ACS Appl. Mater. Interfaces* **2017**, *9*, 33833–33840.

(49) Masud, J.; Liyanage, W. P.; Cao, X.; Saxena, A.; Nath, M. Copper selenides as high-efficiency electrocatalysts for oxygen evolution reaction. *ACS Appl. Energy Mater.* **2018**, *1*, 4075–4083.

(50) Fang, Z.; Peng, L.; Lv, H.; Zhu, Y.; Yan, C.; Wang, S.; Kalyani, P.; Wu, X.; Yu, G. Metallic transition metal selenide holey nanosheets for efficient oxygen evolution electrocatalysis. *ACS Nano* **2017**, *11*, 9550–9557.

(51) Fu, G.; Lee, J.-M. Ternary metal sulfides for electrocatalytic energy conversion. J. Mater. Chem. A 2019, 7, 9386–9405.

(52) Hu, X.; Wang, R.; Sun, P.; Xiang, Z.; Wang, X. Tip-welded ternary $FeCo_2S_4$ nanotube arrays on carbon cloth as binder-free electrocatalysts for highly efficient oxygen evolution. *ACS Sustainable Chem. Eng.* **2019**, *7*, 19426–19433.

(53) Hao, Z.; Wei, P.; Yang, Y.; Sun, J.; Song, Y.; Guo, D.; Liu, L. Self-assembled $CuCo_2S_4$ nanosheets with rich surface Co^{3+} as efficient electrocatalysts for oxygen evolution reaction. *Appl. Surf. Sci.* **2021**, 536, 147826.

(54) Selvaraj, S.; Moon, H.; Kim, D.-H. Combined effect of nanostructured NiCo₂S₄ coated hematite photoanodes for efficient photoelectrochemical water oxidation. *Catal. Today* **2020**, 347, 63– 69.

(55) Wiltrout, A. M.; Read, C. G.; Spencer, E. M.; Schaak, R. E. Solution synthesis of thiospinel $CuCo_2S_4$ nanoparticles. *Inorg. Chem.* 2016, 55, 221–226.

(56) Yang, L.; Xie, L.; Ren, X.; Wang, Z.; Liu, Z.; Du, G.; Asiri, A. M.; Yao, Y.; Sun, X. Hierarchical $CuCo_2S_4$ nanoarrays for high-efficient and durable water oxidation electrocatalysis. *Chem. Commun.* **2018**, 54, 78–81.

(57) Lu, M.; Cui, X.; Song, B.; Ouyang, H.; Wang, K.; Wang, Y. Studying the effect of $CuCo_2S_4$ morphology on the oxygen evolution reaction using a flexible carbon cloth substrate. *ChemElectroChem* **2020**, 7, 1080–1083.

(58) Zequine, C.; Bhoyate, S.; Wang, F.; Li, X.; Siam, K.; Kahol, P.; Gupta, R. K. Effect of solvent for tailoring the nanomorphology of multinary $CuCo_2S_4$ for overall water splitting and energy storage. *J. Alloys Compd.* **2019**, 784, 1–7.

(59) Ding, S.; Cao, D.; Liu, D.; Lin, Y.; Wang, C.; Wu, C.; Zhou, Y.; Chen, S.; Song, L. Modulating electronic structure of cobalt phosphide precatalysts via dual-metal incorporation for highly efficient overall water splitting. *ACS Appl. Energy Mater.* **2019**, *2*, 8022–8030.

(60) Gao, Z.; Gong, L. L.; He, X. Q.; Su, X. M.; Xiao, L. H.; Luo, F. General strategy to fabricate metal-incorporated pyrolysis-free covalent organic framework for efficient oxygen evolution reaction. *Inorg. Chem.* **2020**, *59*, 4995–5003.

(61) Wang, M.; Fu, W.; Du, L.; Wei, Y.; Rao, P.; Wei, L.; Zhao, X.; Wang, Y.; Sun, S. Surface engineering by doping manganese into cobalt phosphide towards highly efficient bifunctional HER and OER electrocatalysis. *Appl. Surf. Sci.* **2020**, *515*, 146059.

(62) Ou, G.; Yang, C.; Liang, Y.; Hussain, N.; Ge, B.; Huang, K.; Xu, Y.; Wei, H.; Zhang, R.; Wu, H. Surface engineering of perovskite oxide for bifunctional oxygen electrocatalysis. *Small Methods* **2019**, *3*, 1800279.

(63) Liu, P. F.; Zhang, L.; Zheng, L. R.; Yang, H. G. Surface engineering of nickel selenide for an enhanced intrinsic overall water splitting ability. *Mater. Chem. Front.* **2018**, *2*, 1725–1731.

(64) Joo, J.; Kim, T.; Lee, J.; Choi, S. I.; Lee, K. Morphologycontrolled metal sulfides and phosphides for electrochemical water splitting. *Adv. Mater.* **2019**, *31*, 1806682.

(65) Devaguptapu, S. V.; Hwang, S.; Karakalos, S.; Zhao, S.; Gupta, S.; Su, D.; Xu, H.; Wu, G. Morphology control of carbon-free spinel $NiCo_2O_4$ catalysts for enhanced bifunctional oxygen reduction and evolution in alkaline media. *ACS Appl. Mater. Interfaces* **2017**, *9*, 44567–44578.

(66) Hong, Y.-R.; Mhin, S.; Kwon, J.; Han, W.-S.; Song, T.; Han, H. Synthesis of transition metal sulfide and reduced graphene oxide hybrids as efficient electrocatalysts for oxygen evolution reactions. *R. Soc. Open Sci.* **2018**, *5*, 180927.

(67) Li, J.; Yan, M.; Zhou, X.; Huang, Z. Q.; Xia, Z.; Chang, C. R.; Ma, Y.; Qu, Y. Mechanistic insights on ternary $Ni_{2-x}Co_xP$ for hydrogen evolution and their hybrids with graphene as highly efficient and robust catalysts for overall water splitting. *Adv. Funct. Mater.* **2016**, *26*, 6785–6796.

(68) Tahir, M.; Mahmood, N.; Pan, L.; Huang, Z.-F.; Lv, Z.; Zhang, J.; Butt, F. K.; Shen, G.; Zhang, X.; Dou, S. X.; Zou, J.-J. Efficient water oxidation through strongly coupled graphitic C_3N_4 coated cobalt hydroxide nanowires. *J. Mater. Chem. A* **2016**, *4*, 12940–12946.

(69) Engelhardt, L. M.; Patrick, J. M.; White, A. H. Crystal Structures of Bis (pyrrolidinedithiocarbamato)-nickel (II) and-copper (II)(Redeterminations). *Aust. J. Chem.* **1985**, *38*, 1413–1416.

(70) Fang-Fang, J.; Ting, X.; Kui, J.; Shu-Sheng, Z. Crystal structures and characterizations of bis (pyrrolidinedithiocarbamato) Cu (II) and Zn (II) complexes. *Chin. J. Chem.* **2003**, *21*, 50–55.

(71) Newman, P. W.; Raston, C. L.; White, A. H. Crystal structures of bis (pyrrolidonecarbodithioato)-nickel (II) and-copper (II). *J. Chem. Soc., Dalton Trans.* **1973**, 1332–1335.

(72) Dash, L.; Biswas, R.; Ghosh, R.; Kaur, V.; Banerjee, B.; Sen, T.; Patil, R. A.; Ma, Y.-R.; Haldar, K. K. Fabrication of mesoporous titanium dioxide using azadirachta indica leaves extract towards visible-light-driven photocatalytic dye degradation. *J. Photochem. Photobiol., A* **2020**, 400, 112682.

(73) Biswas, R.; Singh, H.; Banerjee, B.; Haldar, K. K. Zn (II) diisobutyldithiocarbamate complex enabled efficient synthesis of Au/ ZnS nanocomposite core-shell in one pot. *ChemistrySelect* **2019**, *4*, 4003–4007.

(74) Biswas, R.; Mete, S.; Mandal, M.; Banerjee, B.; Singh, H.; Ahmed, I.; Haldar, K. K. Novel green approach for fabrication of $Ag_2CrO_4/TiO_2/Au/r$ -GO hybrid biofilm for visible light-driven photocatalytic performance. J. Phys. Chem. C **2020**, 124, 3373–3388.

(75) Kun, W. N.; Mlowe, S.; Nyamen, L. D.; Ndifon, P. T.; Malik, M. A.; Munro, O. Q.; Revaprasadu, N. Heterocyclic bismuth (III) dithiocarbamato complexes as single-source precursors for the synthesis of anisotropic Bi_2S_3 nanoparticles. *Chem. - Eur. J.* **2016**, 22, 13127–13135.

(76) Selvaganapathi, P.; Thirumaran, S.; Ciattini, S. Synthesis, spectra, crystal structures and anticancer studies of 26-membered macrocyclic dibutyltin (IV) dithiocarbamate complexes: Single-source precursors for tin sulfide nanoparticles. *Appl. Organomet. Chem.* **2019**, 33, e5089.

(77) Meyer, E. L.; Mbese, J. Z.; Agoro, M. A.; Taziwa, R. Optical and structural-chemistry of SnS nanocrystals prepared by thermal decomposition of bis (N-di-isopropyl-N-octyl dithiocarbamato) tin (II) complex for promising materials in solar cell applications. *Opt. Quantum Electron.* **2020**, *52*, 90.

(78) Kochuparampil, A.; Joshi, J.; Joshi, M. Growth, structural, spectroscopic, thermal, dielectric and optical study of cobalt sulphidedoped ADP crystals. *Mod. Phys. Lett. B* **201**7, *31*, 1750246.

(79) Ajibade, P. A.; Paca, A. M. The Effects of temperature on iron sulfide nanocrystals prepared from thermal decomposition of bis-(N-methylbenzyldithiocarbamato) iron (II) complex. *J. Inorg. Organomet. Polym. Mater.* **2020**, *30*, 1327–1338.

(80) Hong, X.; Li, S.; Tang, X.; Sun, Z.; Li, F. Self-supporting porous CoS_2/rGO sulfur host prepared by bottom-up assembly for lithium-sulfur batteries. J. Alloys Compd. **2018**, 749, 586–593.

(81) Shanmugaratnam, S.; Velauthapillai, D.; Ravirajan, P.; Christy, A.; Shivatharsiny, Y. CoS_2/TiO_2 nanocomposites for hydrogen production under UV irradiation. *Materials* **2019**, *12* (23), 3882.

(82) Song, G.; Chu, Z.; Jin, W.; Sun, H. Enhanced performance of g- C_3N_4/TiO_2 photocatalysts for degradation of organic pollutants under visible light. *Chin. J. Chem. Eng.* **2015**, *23*, 1326–1334.

(83) Long, J.; Hou, Z.; Shu, C.; Han, C.; Li, W.; Huang, R.; Wang, J. Free-standing three-dimensional $CuCo_2S_4$ nanosheet array with high

catalytic activity as an efficient oxygen electrode for lithium-oxygen batteries. ACS Appl. Mater. Interfaces **2019**, 11, 3834–3842.

(84) Ge, Y.; Wu, J.; Xu, X.; Ye, M.; Shen, J. Facile synthesis of $CoNi_2S_4$ and $CuCo_2S_4$ with different morphologies as prominent catalysts for hydrogen evolution reaction. *Int. J. Hydrogen Energy* **2016**, *41*, 19847–19854.

(85) Wang, X.; Hong, M.; Zhang, F.; Zhuang, Z.; Yu, Y. Recyclable nanoscale zero valent iron doped $g-C_3N_4/MoS_2$ for efficient photocatalysis of RhB and Cr (VI) driven by visible light. ACS Sustainable Chem. Eng. **2016**, 4, 4055–4063.

(86) Tan, L.; Xu, J.; Li, S.; Li, D.; Dai, Y.; Kou, B.; Chen, Y. Direct growth of cuo nanorods on graphitic carbon nitride with synergistic effect on thermal decomposition of ammonium perchlorate. *Materials* **2017**, *10*, 484.

(87) Chen, X.; Kuo, D.-H.; Lu, D. Nanonization of gC_3N_4 with the assistance of activated carbon for improved visible light photocatalysis. *RSC Adv.* **2016**, *6*, 66814–66821.

(88) Shen, L.; Xing, Z.; Zou, J.; Li, Z.; Wu, X.; Zhang, Y.; Zhu, Q.; Yang, S.; Zhou, W. Black TiO_2 nanobelts/gC₃N₄ nanosheets laminated heterojunctions with efficient visible-light-driven photocatalytic performance. *Sci. Rep.* **2017**, *7*, 41978.

(89) Biswas, R.; Banerjee, B.; Saha, M.; Ahmed, I.; Mete, S.; Patil, R. A.; Ma, Y.-R.; Haldar, K. K. Green Approach for the Fabrication of Au/ZnO Nanoflowers: A Catalytic Aspect. *J. Phys. Chem. C* **2021**, *125*, 6619–6631.

(90) Zhu, B.; Xia, P.; Li, Y.; Ho, W.; Yu, J. Fabrication and photocatalytic activity enhanced mechanism of direct Z-scheme g- C_3N_4/Ag_2WO_4 photocatalyst. *Appl. Surf. Sci.* **2017**, *391*, 175–183.

(91) Miao, X.; Shen, X.; Wu, J.; Ji, Z.; Wang, J.; Kong, L.; Liu, M.; Song, C. Fabrication of an all solid Z-scheme photocatalyst g- $C_3N_4/$ GO/AgBr with enhanced visible light photocatalytic activity. *Appl. Catal., A* **201**7, *539*, 104–113.

(92) Xu, Z.; Li, H.; Wu, Z.; Sun, J.; Ying, Z.; Wu, J.; Xu, N. Enhanced charge separation of vertically aligned CdS/gC_3N_4 heterojunction nanocone arrays and corresponding mechanisms. *J. Mater. Chem. C* **2016**, *4*, 7501–7507.

(93) Deng, Y.; Chi, B.; Tian, X.; Cui, Z.; Liu, E.; Jia, Q.; Fan, W.; Wang, G.; Dang, D.; Li, M.; Zang, K.; Luo, J.; Hu, Y.; Liao, S.; Sun, X.; Mukerjee, S. gC_3N_4 promoted MOF derived hollow carbon nanopolyhedra doped with high density/fraction of single Fe atoms as an ultra-high performance non-precious catalyst towards acidic ORR and PEM fuel cells. *J. Mater. Chem. A* **2019**, *7*, 5020–5030.

(94) Zheng, Y.; Gao, R.; Qiu, Y.; Zheng, L.; Hu, Z.; Liu, X. Tuning Co²⁺ coordination in cobalt layered double hydroxide nanosheets via Fe³⁺ doping for efficient oxygen evolution. *Inorg. Chem.* **2021**, *60*, 5252–5263.