A Low-Temperature Molecular Precursor Approach to Copper-Based Nano-Sized Digenite Mineral for Efficient Electrocatalytic Oxygen Evolution Reaction

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Abstract: In the urge of designing noble metal-free and sustainable electrocatalysts for oxygen evolution reaction (OER), herein, a mineral Digenite Cu$_5$S$_9$ has been prepared from a molecular copper(I) precursor, ([PyHS)$_2$Cu(PyHS)$_2$I]$(OTf)$_2$ (1), and utilized as an anode material in electrocatalytic OER for the first time. A hot injection of 1 yielded a pure phase and highly crystalline Cu$_5$S$_9$, which was then electro-phonetically deposited (EPD) on a highly conducting nickel foam (NF) substrate. When assessed as an electrode for OER, the Cu$_5$S$_9$/NF displayed an overpotential of merely 298 ± 3 mV at a current density of 10 mA cm$^{-2}$ in alkaline media. The overpotential recorded here supersedes the value obtained for the best reported Cu-based as well as the benchmark precious-metal-based RuO$_2$ and IrO$_2$ electrocatalysts. In addition, the chronocampertometric OER indicated the superior stability of Cu$_5$S$_9$/NF, rendering its suitability as the sustainable anode material for practical feasibility. The excellent catalytic activity of Cu$_5$S$_9$ can be attributed to the formation of a crystalline CuO overlayer on the conductive Cu$_5$S$_9$, that behaves as active species to facilitate OER. This study delivers a distinct molecular precursor approach to produce highly active copper-based catalysts that could be used as an efficient and durable OER electro(pre)catalysts relying on non-precious metals.

Introduction

Increasing consumption of fossil fuels by mankind leads to a fast depletion of natural abundant fuels and therefore, an urgent requirement of alternative resources to harvest energy. The overpotential recorded here supersedes the value obtained for the best reported Cu-based as well as the benchmark precious-metal-based RuO$_2$ and IrO$_2$ electrocatalysts. In addition, the chronocampertometric OER indicated the superior stability of Cu$_5$S$_9$/NF, rendering its suitability as the sustainable anode material for practical feasibility. The excellent catalytic activity of Cu$_5$S$_9$ can be attributed to the formation of a crystalline CuO overlayer on the conductive Cu$_5$S$_9$, that behaves as active species to facilitate OER. This study delivers a distinct molecular precursor approach to produce highly active copper-based catalysts that could be used as an efficient and durable OER electro(pre)catalysts relying on non-precious metals.

Despite the low cost, environmentally benign, a high electrical conductivity and promising catalytic activity, [6] of copper-based materials, only in a handful of cases, copper-chalcogenides have been used for electrocatalytic OER study. [17c,18] In this direction, Cu$_5$S nanostructure was found to be the best pure Cu-based anode material with considerably good OER activity with a low overpotential of 336 mV (at 10 mA cm$^{-2}$).[18a] A recent study has suggested that the efficiency of Cu$_5$S for OER could be enhanced by the incorporation of second transition metal ion into the structure.[19] Similarly, some of the copper-chalcogenides (Cu$_2$Se) -pnicdies...
analyses indicated the formation of crystalline CuO overlayer on traditional high-temperature techniques. Taking advantage of this approach, we recently demonstrated excellent electrocatalytic water splitting performance of molecularly derived FeSe$_2$, FeP, CoP and NiPt@NiS nanostructures starting from a molecular complex supported by organic nitrogen donor ligands. In this context, 2-mercaptopropionic acid, an organo-sulfur compound, existing as an equilibrium of tautomeric mixture of 2-pyridine-thiol (PySH) and 2-pyridine-thione (PyHS), including a zwitterionic structure (PyH - S$^2$)$^{+}$ (Scheme 1, square box) has been utilized as versatile sulfur donor ligand to isolate diverse transition metal complexes and could be an attractive choice to produce metal sulfide nanostructures.

In this work, we report a simple single-step synthetic protocol to the homodinuclear copper(I) complex, ([(PyHS)$_2$Cu’(PyHS)$_2$])$_2$(OTf)$_2$ (1) with a square-planar (Cu’$_2$S$_5$) core. Each copper center in 1 adopts a distorted tetrahedral geometry surrounded by four 2-pyridine-SH ligands and both copper centers are connected via two bridging μ$_3$-S donor atoms of two terminal 2-pyridine-thione (PyHS) units. The (Cu’$_2$S$_5$) core complex has been utilized as an suitable low-temperature molecular precursor to isolate the highly crystalline mineral Digenite Cu$_6$S$_5$ as an efficient OER electro(pre)catalyst in an alkaline electrolyte. The Cu$_6$S$_5$ nanostructures acquired through the hot-injection of 1 have been deposited on highly conducting NF electrode substrate through the EPD technique without affecting the chemical identity. The fabricated Cu$_6$S$_5$/NF electrocatalyst requires an overpotential of only 298 ± 3 mV to attain a current density of 10 mA cm$^{-2}$, outperforming benchmark copper-based and even noble metal-based OER catalysts. Apart from low overpotential, the Cu$_6$S$_5$/NF has also been demonstrated to be a stable catalyst on a longer run. Post-OER analyses indicated the formation of crystalline CuO overlayer on Cu$_6$S$_5$, which acts as an active phase for OER while the conductive inner core accelerates the electron mobility. The presented study shows a promising scope to explore new defined transition metal-based molecular structures to derive the unexplored class of functional materials for electrocatalytic applications beyond water splitting.

**Results and Discussion**

The molecular precursor complex, ([(PyHS)$_2$Cu(PyHS)$_2$])$_2$(OTf)$_2$ (1), was isolated as crystalline yellow powder from a mixture of copper(I) triflate and 2-mercaptopropionic acid (with a molar ratio of 1:4) in dichloromethane (Scheme 1). The purity of the isolated complex was verified by elemental analysis, which precisely matched with the calculated values. The Fourier-transform infrared spectrum (FT-IR) of the isolated complex depicts two strong vibrations at 1127 and 1366 cm$^{-1}$ attributed to the vibrations of ν(S=O) and ν(C–F), respectively, of the triflate counter anion (Figure S1). The electrospray ionization (ESI) mass spectrum of 1 (in tetrahydrofuran, positive ion mode) exhibited major molecular ion peaks at m/z value of 284.96, 361.98 and 395.97 with an expected isotopic distribution calculated for the molecular fragments, ([(PyHS)$_2$Cu$^+$], [(PyHS)(PyS)Cu(Py)$^+$] and [(PyHS)$_2$Cu$^+$], respectively (Figure S2). The $^1$H NMR spectrum of 1 in CD$_3$CN revealed resonances of the aromatic protons at the chemically indistinguishable pyridine ring of the 2-mercaptopyridine ligand within the range of 7 to 12.5 ppm, which unambiguously confirms the diamagnetic nature of the complex (Figure S3). Moreover, the high-resolution Cu 2p X-ray photoelectron (XPS) spectra obtained with 1 further confirmed the presence of Cu while the valences of S 2p, N 1s, O 1s, and C 1s are also consistent with the structure determined from the as-synthesized crystalline powders (Figure S4). Although a copper(I) complex, similar to 1, has been isolated previously from a reaction mixture of copper(II) halide and 2-mercaptopropionic acid, the redox non-innocent behavior of 2-mercaptopropionic acid, in-situ reduction of iron(III) to an isolable mononuclear iron(II) complex, [Fe$^2$(PySH)$_3$(ClO$_4$)$_2$]$_2$, was reported only recently.

Single-crystals grown from a concentrated acetone/ethanol solution of 1 belong to a monoclinic space group I2/m (Table S1). X-ray structure determination confirmed the presence of two triflate counter ions along with a dinuclear copper-sulfur cluster as dicaticonic entity, very similar to [Cu$^+$]$^{2+}$.
\((\text{C}_6\text{H}_3\text{NS})_2\)\text{X}_2 \ (\text{X} = \text{Cl}, \text{Br}, \text{NO}_3)\text{Cu}^{2+}(\text{dmpymth})_2\) \((\text{dmpymth} = 4,6\text{-dimethylpyrimidine-2-thione})\). The dication consists of an almost square-planar \([\text{Cu}^2(S)_4]_{\text{core}}\) core where the copper centers are distorted tetrahedral coordinated by two terminal monodentate \(\text{PyHS}\) and two \(\mu_3\)-S-bridging \(\text{PyHS}\) ligands (Figure 1). The \(\text{Cu-S}\) distances and \(\text{S-Cu-S}\) angles are in the range of 2.293(1)-2.496(1) Å and 97.79(4)°-123.42(5)°, respectively, which are in good agreement with metric values of previously reported related transition-metal sulfides (Table S2).

Using the single-source precursor approach, a crystalline black powder was isolated via hot-injection of 1 at 250 °C in oleylamine (see Experimental Section). The crystalline structure, composition and phase purity of the as-obtained crystals of the particles was determined by powder X-ray diffraction (PXRD) technique. The XRD analysis of the as-prepared sample confirmed its high crystallinity and the reflections obtained correspond to the pure mineral \(\text{Digenite Cu}_9\text{S}_5\) (JCPDS 47-1748) phase (Figure 2a). The solid-state crystal structure of \(\text{Cu}_9\text{S}_5\) belongs to a rhombohedral, \(R-3m\) with lattice parameters \(a = 3.930(1)\) Å and \(c = 48.143(4)\) Å, respectively.\(^{[27]}\) In \(\text{Cu}_9\text{S}_5\), the mixed-valence copper centers comprise three different coordination geometries varying from trigonal planar to near square pyramidal with \(\text{Cu-S}\) distance of 2.285-2.880 Å resulting in a three-dimensional network (Figure S5).\(^{[27]}\) The information on the atomic structure of \(\text{Cu}_9\text{S}_5\) was provided by the transmission electron microscopy (TEM), which contained hexagon-shaped particles (Figure 2b). The high-resolution TEM image clearly indicated the d(101) lattice fringes with an interplanar distance of 0.33 nm (Figure 2c), further confirming the purity of the \(\text{Cu}_9\text{S}_5\) product.\(^{[28]}\) Additionally, the selected area electron diffraction (SAED) pattern of the particles displayed well-defined diffraction rings corresponding to the Miller indices (101) and (1010) planes of \(\text{Cu}_9\text{S}_5\) (Figure 2c, inset). The morphological features of pristine \(\text{Cu}_9\text{S}_5\) were investigated by scanning electron microscopy (SEM) that exhibited a well-defined morphology in the aggregated particles (Figure 2d) and the subsequent elemental mapping of the particles confirmed the homogeneous distribution of \(\text{Cu}\) and \(\text{S}\) (Figure 2e-2f). The chemical composition of the particles was also evaluated by energy-dispersive X-ray spectroscopy and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses evi-

**Figure 1.** Molecular structure of the dication of 1; thermal ellipsoid plot (40% probability). Colour code: carbon: grey, nitrogen: blue, sulphur: yellow, copper: red. All the hydrogen atoms of the protonated pyridine rings were omitted for clarity. The dicaticonic unit of 1 is symmetry generated from the half of its complete structure with a symmetry \((\cdot) - x+3/2, -y+1/2, -z+1/2\).

**Figure 2.** Structural characterization of as prepared \(\text{Cu}_9\text{S}_5\) derived from molecular complex 1; (a) PXRD pattern displaying sharp reflections, corresponding to \(\text{Cu}_9\text{S}_5\) (JCPDS-47-1748), (b) TEM images of \(\text{Cu}_9\text{S}_5\) showing hexagonal-shaped nanocrystals (c) High-resolution TEM image with atomic fringes associated with the (101) lattice plane of \(\text{Cu}_9\text{S}_5\), and SAED pattern exhibiting diffraction rings of \(\text{Cu}_9\text{S}_5\) (inset), (d) SEM image of \(\text{Cu}_9\text{S}_5\) particles with (e, f) EDX mapping revealing a homogenous distribution of elements \(\text{Cu}\) (orange) and \(\text{S}\) (yellow) (oxygen shown in Figure S6).
dencing the Cu:S ratio of ~1.80:1 (Figure S7, S8 and Table S3), which is consistent with the atomic composition of Cu₅S₅.

XPS analysis was utilized to study the surface electronic state and the composition of as-prepared Cu₅S₅. High-resolution core-level Cu 2p XPS spectrum displayed two major peaks at binding energy 932.1 and 952.2 eV, for 2p½ and 2p½, respectively. The binding energy values attained here clearly indicated the presence of CuI with minor amounts of CuII, which appeared due to surface oxidation of the materials and is common in non-oxidic Cu-based materials (Figure S9a,19a,29) Furthermore, the spin-orbit coupling spacing value (2p½−2p½) of 19.6 eV also supported the CuI valency in Cu₅S₅ (Figure S9a).29 The S 2p spectrum showed the existence of doublet species with 2p½ binding energy located at 161.53 eV and the 2p½ binding energy at 163.8 eV, consistent with the presence of S²⁻ (Figure S9b).29 The binding energies and the chemical composition attained by XPS analysis are in accordance with the earlier reports of Cu₅S₅ and Cu₅S₅ materials.11b,18a,19a

After a thorough microscopic and spectroscopic analysis, the Cu₅S₅ powder was deposited on NF through the EPD process.11b,30 To ensure the chemical stability, the as-deposited Cu₅S₅ on NF were further analyzed by microscopic and analytical techniques, which demonstrated its unaltered stability upon EPD (Figure S10–S12). The OER activities of the as-synthesized Cu₅S₅/NF were investigated in a 1 M aqueous KOH electrolyte using a three-electrode cell. The polarization curve from the linear sweep voltammetry (LSV) displayed a continuous increment in current density up to 500 mA cm⁻² at 1.7 V vs. RHE (Figure 3a), which clearly revealed catalytic oxidation of water. For comparison, CuO and Cu nanoparticles were also synthesized, electrodeposited and measured in a similar condition. Remarkably, the overpotential of Cu₅S₅/NF electrode attained at 10 mA cm⁻² was only 298 ± 3 mV, which was lower than those of CuO/NF (340 ± 4 mV), Cu/NF (390 ± 3 mV), and bare NF electrode (490 ± 5 mV). Incidentally, the electrocatalytic OER performance of Cu₅S₅/NF at higher current density (360 ± 4 mV at 100 mA cm⁻²) was even better than CuO/NF (440 ± 4 mV), Cu/NF (550 ± 3 mV), and noble metal-based RuO₂/NF (421 ± 5 mV at 100 mA cm⁻²) and IrO₂/NF (419 ± 3 mV at 100 mA cm⁻²) electrocatalysts (Figure S13), making it one of the superior OER catalysts relying on one of the most earth-abundant first-row transition metals. Furthermore, the catalytic activity achieved with Cu₅S₅/NF is much higher than the well-established copper-oxide and/or hydroxides OER catalysts, however, it is comparable to CuₓN, CuₓP, and CuₓSe (Table S4).10c,17e,18a–c,31 Besides, the catalytic activity of the presented catalysts is also almost comparable to highly-active CoOₓ, NiOₓ, and Fe doped NiOₓ NiₓFeₓO_x OER catalysts (Table S4).10a,22

The OER kinetics of Cu₅S₅/NF, CuO/NF and Cu/NF were investigated by the Tafel slope. The Tafel plots (Figure 3b) of all catalysts were calculated by their corresponding LSV polarization curves. As observed in Figure 3b, the Tafel slope of Cu₅S₅/NF electrode (67 ± 3 mV dec⁻¹) is lower than those of CuO/NF (92 ± 4 mV dec⁻¹), and Cu/NF electrode (146 ± 3 mV dec⁻¹), indicating a more efficient electron transfer, more favorable electrocatalytic reaction kinetics, and high catalytic activity toward OER for Cu₅S₅/NF. The electron (or charge) transfer capacity was further evaluated by electrochemical impedance spectra (EIS) where Cu₅S₅/NF exhibited the lowest charge-transfer resistance (Rct) than CuO/NF and Cu/NF imply-

![Figure 3. Electrochemical OER activities of Cu₅S₅/NF, CuO/NF, and Cu/NF; (a) OER polarization curves from LSV, (b) Tafel plot, (c) Nyquist plot from EIS analysis (inset: equivalent RC circuit) and (d) double-layer capacitance (Cdl) determination from CV scans in a non-Faradaic potential range. (The LSV and Tafel slopes were recorded at a scan rate of 1 mV s⁻¹ in 1 M aqueous KOH solution).](image-url)
ing the smallest electron and charge transfer resistance and thus fast electrode kinetics of Cu$_{2}$S$_{4}$/NF (Table S5). A better OER activity of Cu$_{2}$S$_{4}$/NF was achieved due to low $R_{CT}$, which indicates a spontaneous electron transfer between the electrode surface and electrolyte (Figure 2c).$^{[3]}$ To gain insights into the intrinsic activity of the presented catalysts, we measured the double-layer capacitances ($C_{dl}$), which could be associated with electrocatalytic active surface areas (ECAS). A $C_{dl}$ of 1.51 mF cm$^{-2}$ was determined for Cu$_{2}$S$_{4}$/NF by collecting CVs in a non-faradic region (Figure S14), which is higher than CuO/NF (1.05 mF cm$^{-2}$) and Cu/NF (0.98 mF cm$^{-2}$) (Table S6, Figure 3d).$^{[2,2a,2c,2e]}$ From $C_{dl}$, ECSA was calculated and an ECSA of 0.89 cm$^{2}$ was obtained for Cu$_{2}$S$_{4}$/NF, which is the best among the other copper materials reported herein (Table S6). The ECSA normalized current density obtained for Cu$_{2}$S$_{4}$ is also higher compared to other copper catalysts used herein, proving a superior intrinsic activity of the Cu$_{2}$S$_{4}$ catalyst (Figure S14d). Eventually, the long-term durability of Cu$_{2}$S$_{4}$/NF was assessed by a chronomperometry (CA) measurement conducted at 1.55 V (vs. RHE), which maintained a current density above 10 mA cm$^{-2}$ (Figure S15) over 12 h indicating the inherent stability of the catalyst on a longer run. Faradaic efficiency of ~96% for OER was calculated by quantifying the evolved O$_{2}$ (gas) during electrolysis at a constant current of 50 mA cm$^{-2}$ using Cu$_{2}$S$_{4}$/NF as a working electrode (Table S7).

To uncover the role of electrode substrate in electrocatalysis, additionally, Cu$_{2}$S$_{4}$ was also deposited (via EPD) on fluorine-doped tin oxide (FTO) substrate. Microscopic and analytical studies confirmed the structural integrity of materials deposited on FTO (Figure S16–S18). Under a similar electrochemical condition (in 1 M aqueous KOH electrolyte, three-electrode set-up), the LSV of Cu$_{2}$S$_{4}$/FTO showed an overpotential of 380 ± 3 mV at a current density of 10 mA cm$^{-2}$ while an overpotential of 455 ± 5 and 610 ± 5 mV was required for CuO/FTO and Cu/FTO to achieve the same current density (Figure S19). Interestingly, the presented Cu-based materials deposited on FTO followed a similar trend as that of NF in the electrochemical condition the transition metal-based (non-oxide) materials undergo transformation/corrosion forming an overlayer, which is considered as the active species for water oxidation.$^{[10a,d,11,12–14,15e]}$ To understand the structure of active species generated during alkaline OER with Cu$_{2}$S$_{4}$, we conducted a post electrochemical analysis of the (pre)catalyst using multiple ex-situ microscopic and spectroscopic techniques. The SEM images (Figure S20–21) and successive EDX elemental mapping indicated a considerable amount of oxygen incorporation into the structure, in addition to the initial Cu and S of Cu$_{2}$S$_{4}$ (Figure 4a-d). High-resolution TEM images of the material, carefully isolated from the electrode surface, indicated the presence of Cu$_{2}$S$_{4}$, with a thin crystalline overlayer (Figure S22). This thin layer consisted of highly crystalline CuO (JCPDS 72-629) as depicted by the atomic fringes of d(111) planes (Figure 4e). However, atomic fringes at the core displayed d (1010) planes, which belonged to the crystalline core of Cu$_{2}$S$_{4}$ (JCPDS 47–1748),$^{[27]}$ and substantiated the formation of CuO@Cu$_{2}$S$_{4}$ core-shell type structures.$^{[14b,15]}$ The SAED pattern further affirmed this claim with well-defined rings of CuO and Cu$_{2}$S$_{4}$ (Figure 4f). The elemental composition obtained from the EDX measurement (Figure S23–S24) provided a Cu to S ratio ~1.6:1 and which is due to loss of S from the surface and concomitant incorporation of O into the structure. The surface leaching of S (~20%) in the electrolyte solution was also confirmed by ICP-AES analysis (Table S8).

The surface chemical changes of Cu$_{2}$S$_{4}$ film post-OER were determined by XPS. The comparison of the binding energy values of Cu 2p, S 2p and spin-orbit splitting of Cu 2p (2p$_{3/2}$–2p$_{1/2}$) of the as-deposited Cu$_{2}$S$_{4}$ and post-OER films, confirmed a surface structural change under prolonged electrochemical condition. The core level Cu 2p spectra for the post-OER film showed two prominent peaks at 933.3 eV and 953.6 eV for Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$, respectively, indicating the formation of a substantial amount of Cu$^{II}$ on the surface compared to as-deposited film (Figure 5a).$^{[20b,29]}$ Additionally, the presence of two strong satellite peaks at 942.2 eV and 962.1 eV strongly supports the formation of Cu$^{II}$ on the surface. The S 2p core-level spectra showed a broad and weak signal indicating a negligible amount of sulfur on the surface (Figure 5b). However, the O 1s spectrum after OER displayed a sharp peak at 529.8 eV, suggesting the formation of CuO on the surface to act as an active catalyst along with some amount of surface hydroxides (Figure S25).$^{[33]}$ The results attained from XPS are in good agreement with the X-ray diffraction studies as CuO was detected on the surface of Cu$_{2}$S$_{4}$ after OER (Figure 5c).
agreement with the conclusions achieved from SEM, elemental mapping, EDX, ICP-AES, TEM, and SAED.

Overall, the higher catalytic activity of Cu\textsubscript{S}S\textsubscript{S} for OER in strongly alkaline conditions could be attributed to the formation of an in-situ crystalline CuO overlayer under applied oxidation potentials that could form Cu\textsuperscript{II}O(OH)\textsuperscript{−} species to facilitate O–O bond formation to catalyze the reaction of OER.\cite{19,20,21,22} While Cu\textsubscript{S}S\textsubscript{S} could act as a highly conducting core structure.\cite{23,24,25,26} This observation is in analogy to various Cu-based heterogeneous catalysts applied for OER. Besides, the high ECSA of Cu\textsubscript{S}S\textsubscript{S} exposes more active sites for OER while a low charge transfer resistance of Cu\textsubscript{S}S\textsubscript{S} signifies better change transport across electrode/electrolyte and vice versa. Finally, the NF was found to be a good choice as an electrode substrate due to its improved conducting nature, increased mass transport and enhancing the dissipation of evolved O\textsubscript{2} gas.

Conclusion

A facile low-temperature molecular precursor route was presented to give the crystalline Cu\textsubscript{S}S\textsubscript{S} nanostructure of the Digenite mineral. The respective dicopper(I) precursor complex 1 is easily accessible through a simple synthetic protocol using 2-mercapto pyridine as supporting ligand and [Cu(OTf)]\textsubscript{2} as Cu source. The dinuclear Cu\textsubscript{1}S\textsubscript{2} core 1 is ideal for building the structurally versatile Cu\textsubscript{S}S\textsubscript{S} nano-sized particles, where mixed-valence copper centers are present in three different coordination geometries. The distinct Cu\textsubscript{S}S\textsubscript{S} nanostructure, when deposited on electrode substrates, behaves as a potent anode for performing OER in alkaline media displaying considerably low overpotential. A systematic post-OER study revealed that the as-prepared Cu\textsubscript{S}S\textsubscript{S} is a pre-catalyst and under applied potentials, forming an in-situ crystalline CuO overlayer that acts as active sites for OER while the superior conductivity of the Cu\textsubscript{S}S\textsubscript{S} core promotes a facile charge transport between the catalytic sites to the electrode surface. This facile synthetic method can easily be modified and expanded to the design of high-performance catalysts based on earth-abundant non-noble metal-based systems for widespread use in various applications, especially for CO\textsubscript{2} reduction, supercapacitors, and lithium-ion batteries.

**Experimental Section**

**General considerations and instrumentation:** Synthesis of molecular precursor 1 and Cu\textsubscript{S}S\textsubscript{S} manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Organic solvents (CH\textsubscript{3}CN, diethyl ether) were dried by standard methods and freshly distilled prior to use. Commercially available reagents; 2-mercaptopryidine, Cu(OTf)\textsubscript{2} (98 %) were purchased from Sigma-Aldrich and used as received. The commercial RuO\textsubscript{2} (99 %), IrO\textsubscript{2} (99 %), were purchased from Alfa Aesar. NF and FTO, resistivity (8–12 Ω/cm) were obtained from Racemat BV and Sigma Aldrich respectively. The solution NMR spectrum was recorded on Bruker Sumbomors AV 500 with residual solvent signals as internal reference (CD\textsubscript{3}CN). The following abbreviations were used to describe peak patterns when appropriate: br = broad singlet, s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Fisher Nicolet iS 50 IR spectrometer (ATR-Diamond) under inert conditions. High-resolution ESI-MS, APC-MRS were measured on a Thermo Scientific LTQ orbitrap XL. Elemental analyses were recorded in a Thermo FlashEA 1112 Organic elemental analyzer. Related details of crystallographic measurement and the materials characterizations have been discussed in the supporting information.

**Preparation of [(PyHS)\textsubscript{2}Cu(PyHS)]\textsubscript{2}OTf \textsubscript{2} (1).** To a well stirred solution of Cu(OTf)\textsubscript{2} (0.500 g, 1.38 mmol) in dichloromethane (10 mL), was added a dichloromethane solution (15 mL) of 2-mercaptopryidinethiol (0.615 g, 5.52 mmol). After stirring the resultant yellow suspension for 8 h under inert atmosphere, solvent was evaporated under vacuum. The residue was washed twice with diethyl ether (2 × 20 mL), filtered and dried under vacuum. X-ray quality crystals were obtained by keeping concentrated acetonitrile solution of 1 at −20 °C overnight. Yield: 0.990 g (89 %). Elemental analysis calculated for Cu\textsubscript{2}H\textsubscript{10}Cu\textsubscript{2}F\textsubscript{2}N\textsubscript{4}O\textsubscript{3}S\textsubscript{8} (1092.19 g mol\textsuperscript{−1}): C 35.26; H 2.59; N 7.71; S 23.53; found: C 34.9, H 2.7, N 7.6, S 22.9 %. IR (ATR, diamond): ν = 3183(br), 3056-m (m), 1571(s), 1499(s), 1441(s), 1366(s), 1269(m), 1222(s), 1127(s), 1028(s), 750(s), 636(s). ESI-MS (positive ion mode, THF): m/z = 284.96 [Cu\textsubscript{2}O\textsubscript{2}S\textsubscript{6}H\textsubscript{4}]. 2099 / 158522 © 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA

Figure 5. High resolution (a) Cu 2p and (b) S 2p core-level XPS spectra obtained for Cu\textsubscript{S}S\textsubscript{S} as-deposited (black curves) and post OER films (red curves). After OER, the Cu 2p indicated the oxidation of Cu to Cu\textsuperscript{II} to Cu\textsuperscript{II} with typical satellite peaks and spin-orbit splitting distance while the negligible amount of S was found on the surface illustrating the concomitant incorporation of O into the structure (Figure S24) forming CuO@Cu\textsubscript{S}S\textsubscript{S}.
Synthesis of Cu and CuO

Solid copper(II) acetate monohydrate (300 mg) was heated to 300 °C with a heating rate of 5 °C min⁻¹ and maintained the temperature for 2 hours in an atmosphere of flowing \( H_2 \) (slow, 2–3 L h⁻¹). The resulting black powder product was washed with water and ethanol (3 × 50 mL) and dried overnight at 60 °C to obtain 100 mg (yield > 90%) of phase pure Cu. Following a very similar procedure, CuO (yield > 95%) nanoparticles (NP) were obtained whereas the heating was done in presence of \( O_2 \) flow.

Electrochemical measurements.

Electrocatalytic OER was carried out in an open three-electrode setup consisting of a Hg/HgO as a reference electrode (RE), a Pt wire (0.5 mm diameter × 230 mm length; A-002234, BioLogic) as a counter electrode (CE) and the catalyst-modified working electrode (WE) using an aqueous electrolyte (1 M KOH, Sigma Aldrich). A potentiosstat (SP-200, BioLogic Science Instruments) controlled by the EC-Lab v10.20 software package was used for all the electrochemical measurements and further data analyses. Two different substrates NF and FTO were used as electrode support. The investigated materials were deposited electrochemically by a well-established method on both, NF and FTO. A potential difference of –10 V in a mixture of iodine and acetone on a 1 × 1 cm² area was applied. The electric charge on the catalyst in acetone is insufficient for EPD, as minimal amounts of free ions exist in acetone. When iodine is used as the dispersant, it can react with acetone through the keto-enol tautomerization to produce protons as per the following equation:

\[
\text{C} = \text{C} + \text{H} + \text{H}^+ + \text{I}^- + \text{H}_2O
\]

Thus, formed protons are adsorbed on the surface of the suspended particles by making them positively charged. The applied electric field induces the positively charged particles to migrate towards and deposit on the cathode. Typically, 30–40 mg of the catalyst powder was suspended in 10 mL acetone and sonicated for 1 h, then 3 mg of iodine was added and the suspension sonicated for another 3 min. The EPD was conducted at –10 V for 2 min over a 1 × 1 cm² surface area of the electrode and thin uniform films were obtained. The sample loading on each NF and FTO was ~0.6 and ~0.5 mg cm⁻², respectively. A similar procedure was also followed to deposit other materials (Cu, CuO, RuO₂, and IrO₂) on NF.

LSV measurements were performed with an applied iR compensation of 85%, applied before each experiment. The potentials of the reference electrodes in this work were referenced to the reversible hydrogen electrode (RHE) through calibration, and in 1 M aqueous KOH the potential was calculated using the following equations: \( E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 \text{V} + (0.059 \times p) \text{V} \). The potential ranges were 1.2 to 1.8 V vs. RHE for OER. The overpotentials were determined from the resulting polarization curves. The chronoamperometry measurements were performed in 1 M aqueous KOH, and a constant potential 1.55 V vs RHE was applied for 10 h. The polarization curves were plotted as overpotential (\( \eta \)) versus the logarithm of current density (log \( j \)) to obtain Tafel plots. The Tafel slope was calculated according to the Tafel equation \( \eta = \log j + a \), where \( \eta \) is the overpotential (V), \( j \) is the current density (mA cm⁻²), and \( a \) is the Tafel slope (mV dec⁻¹). Tafel plots were constructed for OER on samples deposited on NF. The region considered for Tafel was on the kinetically controlled region. The double-layer capacitance (Cdl) was determined to calculate the active surface area of the materials deposited on the electrode surface. Cdl was calculated from cyclic voltammogram (CV) curves recorded in a potential range with no Faradaic current at different scan rates from 10 to 200 mV s⁻¹ (cycled between 0.875 and 0.925 V vs. RHE). The ECSA of the catalysts was calculated using the equation \( \text{ECSA} = C_{\text{dl}}/C \), where \( C \) can be defined as the specific capacitance of the material per unit area under identical electrolyte conditions. The specific capacitance (C) value of 1.7 mF cm⁻² based on the literature reported values of NF in 1 M KOH solution is considered to calculate the ECSA. EIS was recorded at 1.51 V vs. RHE for samples deposited on NF to obtain the Nyquist plots. The amplitude of the sinusoidal wave was examined in a frequency range of 100 kHz to 1 mHz. All impedance spectra were fitted using an equivalent RC circuit model. The charge-transfer resistance (Rct) was then obtained from the diameter of the semicircle in the Nyquist plots.

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Copper as the topper. The Digenite mineral Cu$_3$S$_5$ phase has been produced from a molecular Cu$_2$S$_2$ precursor complex and applied for efficient electrocatalytic alkaline oxygen evolution reaction, displaying competent catalytic activity and stability.