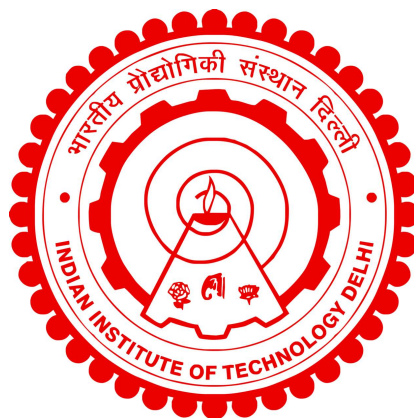


**DETECTION OF ELECTROACTIVE SPECIES
DERIVED FROM TRANSITION METAL
CHALCOGENIDES DURING
ELECTROCATALYSIS**

AVINAVA KUNDU



DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

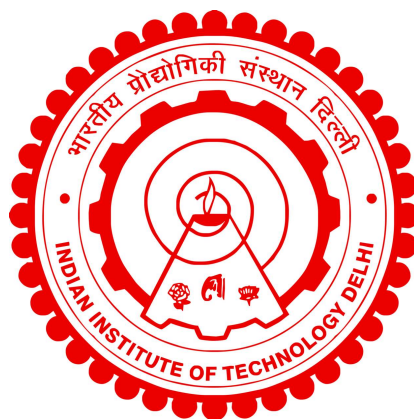
AVINAVA KUNDU

Department of Chemistry

Submitted

in partial fulfilment of the requirements of the degree of Doctor of Philosophy

to the



**INDIAN INSTITUTE OF TECHNOLOGY
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*Dedicated to my Elder Brother, Mother, Father and
Teachers*

Certificate

This is to certify that the thesis entitled “**Detection of Electroactive Species Derived from Transition Metal Chalcogenides During Electrocatalysis**”, submitted by **Mr. Avinava Kundu** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of the original, bona fide research work carried out by him under my supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

The results in this thesis have not been submitted in part or in full to any other University or Institute for awarding any degree or diploma to the best of my knowledge.

Date:

Prof. Biswarup Chakraborty
Department of Chemistry,
Indian Institute of Technology Delhi.

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Avinava Kundu

Abstract

Even after 200 years of the industrial revolution, fossil fuels remain the dominant source of energy for the modern society. However, fossil fuel combustion releases a significant amount of greenhouse gases, contributing to the global warming and a yearly temperature increase of 1.5 °C. At this moment, the atmospheric CO₂ level has reached to a critical point of nearly 400 ppm and is continuously increasing. Although photosynthesis has played a crucial role in balancing the atmospheric CO₂ levels close to the global average of 350 ppm, building a sustainable society hinges on adopting alternative energy sources with minimal environmental impact. The conversion of CO₂ into valuable chemicals is a vital path toward achieving a green and sustainable future. On the other side, hydrogen can be considered a zero-emission fuel, an alternative to fossil fuels. However, industrial-scale hydrogen production relies on energy-intensive pathways with substantial carbon emissions. Water electrolysis is a green approach to hydrogen production. However, with high thermodynamic energy requirements and sluggish kinetics for the anodic oxygen evolution reaction (OER), the counter reaction of hydrogen evolution reaction (HER) during water electrolysis becomes energetically less probable. Development of an electrocatalyst that reduces the thermodynamic and kinetic barrier is crucial for achieving cost-effective hydrogen production through HER. In this context, the transition metal chalcogenides (TMCs) have emerged as promising electrocatalysts due to their unique electronic structure and properties. Despite the notable electrochemical performance of TMCs in water splitting or CO₂ reduction, the TMCs, under

alkaline pH and anodic potential, are not stable. Under electrochemical conditions, TMCs often transform into metal oxides, hydroxides, or oxyhydroxides. In-situ and ex-situ spectroscopic have been useful tools for the identification of the chemical and morphological changes during electrocatalysis.

This thesis, entitled “**Detection of Electroactive Species Derived from Transition Metal Chalcogenides During Electrocatalysis**”, deals with the detection of electroactive species derived from the TMC-based electrocatalyst during electrochemical performances. The identification of the electroactive species provides a detailed understanding of the reaction mechanism.

The mechanistic pathway of the OER consistently varies depending on the surface structure of the catalyst, making it challenging to visualize. Regarding the mechanistic interpretation of the rate-limiting step, the reaction order, and other intrinsic parameters, electrokinetic studies are particularly interesting. However, the OER electrokinetics on *Greigite* (Fe_3S_4) is relatively less explored. Given that, in the first work chapter of the thesis, a detailed study on Fe_3S_4 has been carried out. *Greigite* (Fe_3S_4) nanosheets synthesized by the solvothermal method recorded an overpotential of 251 (± 6) mV at a current density (j) of 10 mA cm^{-2} . The ex-situ post-OER analysis of $\text{Fe}_3\text{S}_4/\text{NF}$ anode confirmed the formation of $\alpha\text{-FeO(OH)}$ as an electroactive species. The experimentally derived transfer coefficient α (1.90), exchange current density j'_s ($3.06 \times 10^{-6} \text{ mA cm}^{-2}$), and a Tafel slope of 45.9 mV dec^{-1} indicate O-O bond formation as the rate-limiting step. The nucleophilic attack of OH^- on the Fe(IV)=O leads to the generation of iron(III) hydroperoxo (Fe(III)-OOH) species.

The electroactive species has a low OER activation energy (E_a) of 53 (± 2.1) kJ mol⁻¹, following a 2nd order reaction kinetics.

In the subsequent chapter, a detailed electrochemical study of Fe₃X₄ type TMCs has been performed. Mixed-valence iron chalcogenide with a typical formula Fe₃X₄ where X can be O, S, and Se exhibit unique electronic properties due to the presence of Fe^{II} and Fe^{III} in their sub-lattices. Despite both Fe₃O₄ and Fe₃S₄ possessing an inverse spinel structure with cubic lattice and iron atoms in both tetrahedral (T_d) and octahedral (O_h) sites, Fe₃Se₄ adopts a monoclinic crystal system, where iron atoms occupy only the O_h sites. Notably, the bulk morphology and exposed facets of the solvothermally prepared Fe₃X₄ nanomaterials are different. Fe₃Se₄ and Fe₃S₄ possess (002) and (400) planes, respectively, while (311) remained the exposed facets for Fe₃O₄. Lattice correlation to the exposed facets confirmed the presence of only Fe^{III} centres in the case of Fe₃Se₄, while Fe^{II} and Fe^{III} centres are present as exposed in the case of Fe₃S₄ and Fe₃O₄. The cyclic voltammetry (CV) study with Fe₃S₄ and Fe₃Se₄ reveals that both Fe^{II} and chalcogenide anions (S²⁻/Se²⁻) show irreversible oxidation within -0.2 to 1.0 V (vs RHE). CV cycling (10 cycles) within this potential window and concomitant ex-situ Raman spectra identified the formation of trigonal-Se (t-Se) on the electrode surface. Chronoamperometry at 1.47 V and subsequent post-CA characterization reveal the formation of α -FeO(OH)@t-Se as the electroactive species. The electrochemically derived α -FeO(OH)@t-Se delivered OER activity with 219 mV overpotential (@ 10 mA cm⁻²). The better OER activity of α -FeO(OH)@t-Se is evident from the low Tafel slope, low charge-transfer resistance (R_{ct}), and high exchange current density (j_0). The difference in the lattice

structure of Fe_3Se_4 and Fe_3S_4 and the electrochemical potential of S^{2-} and Se^{2-} and the stability of the elemental state of the chalcogenide counterpart play an intriguing role in the formation of electroactive species and a distinct reconstruction pathway is followed for the Fe_3X_4 .

In another work chapter, the electrochemical activity of α -NiS based electrode has been explored. Nanocrystalline α -NiS, synthesized via solvothermal methods, has been selected as an electrode material in pursuit of electrode materials with multifunctional capabilities. α -NiS deposited onto conductive nickel foam (NF) as an anode, where, upon application of anodic potential, the α -NiS transform amorphous electro-derived $\text{NiO}(\text{OH})$ ($\text{NiO}(\text{OH})_{\text{ED}}$). The in-situ transformation of α -NiS to amorphous $\text{NiO}(\text{OH})_{\text{ED}}$ enhances the electrochemical surface area, enabling efficient OER catalysis at a moderate overpotential of 264 mV (at 20 mA cm^{-2}), while also converting organic compounds such as 2-hydroxymethylfurfural (HMF), 2-furfural (FF), ethylene glycol (EG), and glycerol (Gly) to essential feedstocks. During these organic oxidations, $(\text{NiO}(\text{OH})_{\text{ED}})/\text{NF}$ engages in a multiple-electron oxidation process, including C-C bond cleavages, while the structural integrity of the α -NiS/NF electrode remains intact, demonstrating superior cathodic performance for alkaline hydrogen evolution reaction (HER) and CO_2 reduction (CO_2R). Upon pairing, α -NiS and its electro-oxidized ($\text{NiO}(\text{OH})_{\text{ED}}$) counterpart in a fabricated cell, α -NiS/NF(-)/(+)NiO(OH)ED/NF, facilitates an artificial photosynthetic scheme wherein the $(\text{NiO}(\text{OH})_{\text{ED}})/\text{NF}$ anode oxidizes water to O_2 . At the same time, the α -NiS cathode reduces CO_2 at a moderate cell potential.

In another work, *Covellite* (CuS) has been chosen as the anode material, and its structural reformation to evolve the reactive species under anodic conditions has been done. A facile hydrothermal method is utilized to prepare Covellite (CuS) nanoplates, where copper exists in a mixed-valent state. The as-synthesized CuS serves as an efficient electro(pre)catalyst for alkaline water oxidation when deposited on glassy carbon (GC) and nickel foam (NF) electrodes, exhibiting electrochemical and irreversible oxidation to CuO during cyclic voltammetry, as evidenced by a redox feature at 1.2 V (vs RHE) and confirmed by ex-situ Raman study. Electrochemically activated CuS (CuS_{EA}) to the CuO is a copper-based catalyst with 349 (± 5) mV overpotential at a current density of 20 mA cm⁻². The CuS_{EA}/NF anode can sustain a stable current output of approximately 15 mA cm⁻² for 10 hours. The integrated water electrolyzer configuration, Pt(-)/(+)CuS_{EA}/NF, achieved a current density (j) of 10 mA cm⁻² at 1.58 V cell potential and was utilized further for the electrochemical conversion of ethanol, furfural, and 5-hydroxymethylfurfural to their respective acids.

In the final work chapter of the thesis, the structure and electrochemical activity of Cu₉S₅ have been compared with an analogous mixed-valence CuS to infer the effect of electronic structure to regulate the electrochemical activity. Nanostructured Cu₉S₅ and CuS are synthesized and employed as electrode materials for electrochemical investigation, with powder X-ray diffraction (PXRD) and microscopic analyses revealing the exposed surface of Cu₉S₅ as d(0015) and CuS as d(002). The d(0015) surface of Cu₉S₅ comprises tetrahedral (T_d) Cu^{II}, distorted octahedral (O_h) Cu^{II}, and trigonal planar (T_p) Cu^I sites, while the (002) surface of CuS consists solely of

tetrahedral (T_d) Cu^{II} . The variation in the electrochemical behaviour between Cu_9S_5 and CuS originates from the distinct copper sites on their exposed surfaces and their respective redox states. In-situ Raman spectra reveal that Cu_9S_5 exhibits greater electrochemical lability than CuS . Contact-angle and BET analyses suggest that the high surface energy and macroporous nature of the Cu_9S_5 surface facilitates electrolyte diffusion, resulting in a notable redox response. Post-chronoamperometric (CA) analyses reveal the potential-dependent structural transformation of Cu_9S_5 and Cu_9S_5 to $\text{CuO}/\text{Cu}_2\text{O}/\text{Cu}(\text{OH})_2$ electroactive species. The performance of these in-situ formed copper oxides in electrocatalytic water-splitting surpasses that of the pristine copper sulfides. The correlation between structure and activity offers comprehensive insights into interpreting the electrochemical properties of metal sulfides and their potential-driven surface/bulk transformation pathway to develop the active phase.

सारांश

200 वर्षों के औद्योगिक क्रांति के बाद भी, जीवाश्म ईंधन आधुनिक समाज के लिए प्रमुख ऊर्जा स्रोत बने हुए हैं। हालांकि, जीवाश्म ईंधन के दहन से भारी मात्रा में ग्रीनहाउस गैसों निकलती हैं, जो ग्लोबल वार्मिंग में योगदान देती हैं और सालाना तापमान में 1.5°C की वृद्धि करती हैं। इस समय, वायुमंडलीय CO_2 स्तर लगभग 400 पीपीएम के महत्वपूर्ण बिंदु तक पहुँच गया है और लगातार बढ़ रहा है। हालाँकि प्रकाश-संश्लेषण ने वायुमंडलीय CO_2 स्तर को वैश्विक औसत 350 पीपीएम के करीब संतुलित रखने में महत्वपूर्ण भूमिका निभाई है, एक सतत समाज का निर्माण पर्यावरणीय प्रभाव को कम करने वाले वैकल्पिक ऊर्जा स्रोतों को अपनाने पर निर्भर करता है। CO_2 को मूल्यवान रसायनों में परिवर्तित करना एक हरित और सतत भविष्य प्राप्त करने का एक महत्वपूर्ण मार्ग है। दूसरी ओर, हाइड्रोजन को शून्य-उत्सर्जन ईंधन माना जा सकता है, जो जीवाश्म ईंधनों का एक विकल्प है। हालाँकि, औद्योगिक पैमाने पर हाइड्रोजन उत्पादन ऊर्जा-गहन मार्गों पर निर्भर करता है जिनमें महत्वपूर्ण कार्बन उत्सर्जन होता है। जल विद्युत अपघटन (वॉटर इलेक्ट्रोलिसिस) हाइड्रोजन उत्पादन के लिए एक हरित दृष्टिकोण है। हालाँकि, उच्च ताप-गतिकीय ऊर्जा आवश्यकताओं और एनोडिक ऑक्सीजन विकास प्रतिक्रिया (OER) के लिए धीमी गति के कारण, जल विद्युत अपघटन के दौरान हाइड्रोजन विकास प्रतिक्रिया (HER) की प्रति प्रतिक्रिया ऊर्जा की दृष्टि से कम संभव हो जाती है। HER के माध्यम से लागत-प्रभावी हाइड्रोजन उत्पादन प्राप्त करने के लिए एक इलेक्ट्रोकेटालिस्ट का विकास महत्वपूर्ण है जो ताप-गतिकीय और गतिकीय अवरोध को कम करता है। इस संदर्भ में, संक्रमण धातु चैल्कोजेनाइड्स (TMCs) अपने अद्वितीय इलेक्ट्रॉनिक संरचना और गुणों के कारण आशाजनक इलेक्ट्रोकेटालिस्ट के रूप में उभरे हैं। जल विखंडन या CO_2 कमी में (TMCs) के उल्लेखनीय विद्युत रासायनिक प्रदर्शन के बावजूद, क्षारीय pH और एनोडिक संभावनाओं के तहत, (TMCs) स्थिर नहीं होते हैं। विद्युत रासायनिक परिस्थितियों के तहत, (TMCs) अक्सर धातु ऑक्साइड, हाइड्रॉक्साइड, या ऑक्सीहाइड्रॉक्साइड में परिवर्तित हो जाते हैं। इलेक्ट्रोकेटलिसिस के दौरान रासायनिक

और रूपात्मक परिवर्तनों की पहचान के लिए इन-सिचु और एक्स-सिचु स्पेक्ट्रोस्कोपिक उपयोगी उपकरण रहे हैं।

इस शोध प्रबंध, जिसका शीर्षक “इलेक्ट्रोकेटलिसिस के दौरान ट्रांजिशन मेटल चाल्कोजेनाइड्स से व्युत्पन्न इलेक्ट्रोएक्टिव प्रजातियों का पता लगाना” है, का विषय इलेक्ट्रोकेटलिटिक अनुप्रयोग के लिए इलेक्ट्रोएक्टिव प्रजातियों का पता लगाना है और यह इलेक्ट्रोएक्टिव प्रजातियों की पहचान के महत्व को विस्तार से समझाता है।

ऑक्सीजन इवोल्यूशन रिएक्शन (OER) का यांत्रिक मार्ग उत्प्रेरक की सतह संरचना के आधार पर लगातार बदलता रहता है, जिससे इसे समझना चुनौतीपूर्ण हो जाता है। दर-सीमित चरण की यांत्रिक व्याख्या, प्रतिक्रिया क्रम, और अन्य अंतर्निहित पैरामीटरों के संदर्भ में, इलेक्ट्रोकाइनेटिक अध्ययन विशेष रूप से दिलचस्प हैं। हालांकि, ग्रेगाइट (Fe_3S_4) पर OER इलेक्ट्रोकाइनेटिक्स की तुलनात्मक रूप से कम जांच की गई है। इसे ध्यान में रखते हुए, इस शोध प्रबंध के पहले अध्याय में (Fe_3S_4) पर एक विस्तृत अध्ययन किया गया है। सॉल्वोथर्मल विधि द्वारा संश्लेषित ग्रीगाइट (Fe_3S_4) नैनोशीट्स ने 10 mA cm^{-2} की धारा घनत्व (j) पर $251 (\pm 6) \text{ mV}$ का ओवरपोटेंशियल दर्ज किया। $\text{Fe}_3\text{S}_4/\text{NF}$ एनोड का एक्स-सिटू पोस्ट-OER विश्लेषण $\alpha\text{-FeO}(\text{OH})$ के इलेक्ट्रोएक्टिव प्रजाति के रूप में गठन की पुष्टि करता है। प्रयोगात्मक रूप से व्युत्पन्न ट्रांसफर गुणांक α (1.90), एक्सचेंज करंट घनत्व j'_s ($3.06 \times 10^{-6} \text{ mA cm}^{-2}$), और 45.9 mV dec^{-1} का टैफल ढलान O-O बंध निर्माण को दर-सीमित चरण के रूप में इंगित करते हैं। $\text{Fe}(\text{IV})=\text{O}$ पर OH^- के न्यूक्लियोफिलिक हमले से आयरन(III) हाइड्रोपेरोक्साइड ($\text{Fe}(\text{III})\text{-OOH}$) प्रजातियों का निर्माण होता है। इलेक्ट्रोएक्टिव प्रजाति का OER सक्रियण ऊर्जा (E_a) $53 (\pm 2.1) \text{ kJ mol}^{-1}$ है, जो 2nd ऑर्डर प्रतिक्रिया गतिकी का पालन करता है।

अगले अध्याय में, Fe_3X_4 प्रकार के (TMCs) का एक विस्तृत विद्युत रासायनिक अध्ययन किया गया है। मिश्रित-वलेन्स आयरन चाल्कोजेनाइड जिसकी सामान्य सूत्र Fe_3X_4 है, जहाँ X=O, S, और Se हो सकते हैं, उनकी उप-लटाइसेस में Fe^{II} और Fe^{III} की उपस्थिति के कारण अद्वितीय इलेक्ट्रॉनिक गुण प्रदर्शित

करते हैं। Fe_3O_4 और Fe_3S_4 दोनों में इनवर्स स्पिनेल संरचना के साथ क्यूबिक लटाइस और टेट्राहेड्रल (T_d) और ऑक्टाहेड्रल (O_h) साइटों में लोहे के परमाणु होने के बावजूद, Fe_3Se_4 एक मोनोक्लिनिक क्रिस्टल सिस्टम को अपनाता है, जहाँ लोहे के परमाणु केवल O_h साइटों पर स्थित होते हैं। विशेष रूप से, सॉल्वोथर्मल विधि द्वारा तैयार किए गए Fe_3X_4 नैनोमटेरियल्स का थोक आकार और अनावृत्त पहलू अलग-अलग होते हैं। Fe_3Se_4 और Fe_3S_4 क्रमशः (002) और (400) प्लेन्स रखते हैं, जबकि Fe_3O_4 के लिए (311) अनावृत्त पहलू बने रहते हैं। अनावृत्त पहलुओं से लटाइस संबंध ने Fe_3Se_4 के मामले में केवल Fe^{III} केंद्रों की उपस्थिति की पुष्टि की, जबकि Fe_3S_4 और Fe_3O_4 के मामले में Fe^{II} और Fe^{III} केंद्र अनावृत्त होते हैं। Fe_3S_4 और Fe_3Se_4 के साथ साइक्लिक वोल्टमेट्री (CV) अध्ययन से पता चला कि Fe^{II} और चाल्कोजेनाइड आयनों ($\text{S}^{2-}/\text{Se}^{2-}$) दोनों में -0.2 से 1.0 V (RHE के विरुद्ध) के भीतर अपरिवर्तनीय ऑक्सीकरण होता है। इस संभावित विंडो के भीतर CV साइक्लिंग (10 साइकिल) और साथ ही एक्स-सिट्र रमन स्पेक्ट्रा ने इलेक्ट्रोड सतह पर ट्रिगोनल-Se (t-Se) के-Se (t-Se) गठन की पहचान की। 1.47 V पर क्रोमोएम्पेरोमेट्री और इसके बाद के पोस्ट-CA चरित्रण ने $\alpha\text{-FeO(OH)}@t\text{-Se}$ के इलेक्ट्रोएक्टिव प्रजातियों के गठन का खुलासा किया। इलेक्ट्रोकेमिकल रूप से व्युत्पन्न $\alpha\text{-FeO(OH)}@t\text{-Se}$ ने 219 mV ओवरपोटेंशियल (@ 10 mA cm⁻²) के साथ OER गतिविधि प्रदान की। $\alpha\text{-FeO(OH)}@t\text{-Se}$ की बेहतर OER गतिविधि निम्न टैफल ढलान, निम्न चार्ज-ट्रांसफर प्रतिरोध (R_{ct}), और उच्च एक्सचेंज करंट घनत्व (j_0) से स्पष्ट होती है। Fe_3Se_4 और Fe_3S_4 की लटाइस संरचना में अंतर और S^{2-} और Se^{2-} की इलेक्ट्रोकेमिकल संभाव्यता और चाल्कोजेनाइड समकक्ष के तत्वमूलक अवस्था की स्थिरता इलेक्ट्रोएक्टिव प्रजातियों के गठन में एक रोमांचक भूमिका निभाती है और Fe_3X_4 के लिए एक विशिष्ट पुनर्निर्माण मार्ग का पालन करती है।

एक अन्य कार्य अध्याय में, $\alpha\text{-NiS}$ आधारित इलेक्ट्रोड की विद्युत रासायनिक गतिविधि का अन्वेषण किया गया है। सॉल्वोथर्मल विधियों के माध्यम से संश्लेषित नैनोक्रिस्टलीय $\alpha\text{-NiS}$ को इलेक्ट्रोड सामग्री के रूप में चुना गया है, जिनमें बहुउद्देशीय क्षमताओं वाली इलेक्ट्रोड सामग्री की खोज की जा रही है। $\alpha\text{-NiS}$ को प्रवाहकीय निकेल फोम (NF) पर एनोड के रूप में जमाया गया है, जहां एनोडिक पोर्टेंशियल के अनुप्रयोग

पर α -NiS, अमोर्फ इलेक्ट्रो-व्युत्पन्न NiO(OH) (NiO(OH)_{ED}) में बदल जाता है। α -NiS से अमोर्फ NiO(OH)_{ED} में इन-सीटू रूपांतरण इलेक्ट्रोकेमिकल सतह क्षेत्र को बढ़ाता है, जो मध्यम ओवरपोटेंशियल (264 mV पर 20 mA cm⁻²) पर कुशल OER (ऑक्सीजन इवॉल्यूशन रिएक्शन) कैटालिसिस को सक्षम बनाता है, साथ ही साथ 2-हाइड्रोक्सीमिथाइलफुरफुराल (HMF), 2-फुरफुराल (FF), एथिलीन ग्लाइकॉल (EG), और ग्लिसरॉल (Gly) जैसे कार्बनिक यौगिकों को आवश्यक फीडस्टॉक्स में परिवर्तित करता है। इन कार्बनिक ऑक्सीडेशन के दौरान, NiO(OH)_{ED}/NF एक बहु-इलेक्ट्रॉन ऑक्सीडेशन प्रक्रिया में संलग्न होता है, जिसमें C-C बॉन्ड टूटना भी शामिल है, जबकि α -NiS/NF इलेक्ट्रोड की संरचनात्मक अखंडता बरकरार रहती है, जो क्षारीय हाइड्रोजन इवॉल्यूशन रिएक्शन (HER) और CO₂ न्यूनीकरण (CO₂) के लिए उत्कृष्ट कैथोडिक प्रदर्शन प्रदर्शित करती है। एक निर्मित सेल में α -NiS और इसके इलेक्ट्रो-ऑक्सीडाइज्ड NiO(OH)_{ED} समकक्ष की जोड़ी, α -NiS/NF(-)/(+)NiO(OH)_{ED}/NF, एक कृत्रिम प्रकाश संश्लेषण योजना को सुगम बनाती है जिसमें NiO(OH)_{ED}/NF एनोड पानी को O₂ में ऑक्सीडाइज करता है, जबकि α -NiS कैथोड मध्यम सेल पोटेन्शियल पर CO₂ को कम करता है।

एक अन्य कार्य में, कोवेलाइट (CuS) को एनोड सामग्री के रूप में चुना गया है, और एनोडिक परिस्थितियों के तहत प्रतिक्रियाशील प्रजातियों को विकसित करने के लिए इसकी संरचनात्मक पुनर्रचना की गई है। एक साधारण हाइड्रोथर्मल विधि का उपयोग करके कोवेलाइट (CuS) नैनोप्लेट्स तैयार किए जाते हैं, जहां तांबा मिश्रित-मानक अवस्था में मौजूद होता है। तैयार CuS को ग्लासी कार्बन (GC) और निकेल फोम (NF) इलेक्ट्रोड पर जमाकर क्षारीय जल ऑक्सीकरण के लिए एक कुशल इलेक्ट्रो(प्री)कैटालिस्ट के रूप में उपयोग किया जाता है, जो साइक्लिक वोल्तामेट्री के दौरान 1.2 V (RHE के विरुद्ध) पर एक रिडॉक्स विशेषता द्वारा प्रदर्शित होता है और एक्स-सिचू रमन अध्ययन द्वारा CuO के रूप में अपरिवर्तनीय ऑक्सीकरण की पुष्टि होती है। इलेक्ट्रोकेमिकल रूप से सक्रिय CuS (CuS_{EA}) से CuO में परिवर्तित होने पर यह एक तांबा-आधारित कैटालिस्ट है जो 20 mA cm⁻² धारा घनत्व पर 349 (±5) mV ओवरपोटेंशियल दिखाता है। CuS_{EA}/NF एनोड 10 घंटे के लिए लगभग 15 mA cm⁻² की स्थिर धारा आउटपुट बनाए रख सकता है। एकीकृत जल इलेक्ट्रोलाइजर विन्यास, Pt(-)/(+)CuS_{EA}/NF, 1.58 V सेल पोटेन्शियल पर 10 mA

cm^{-2} धारा घनत्व (j) प्राप्त करता है और इसे इथेनॉल, फुरफुराल, और 5-हाइड्रोक्सीमिथाइलफुरफुराल के उनके संबंधित एसिडों में विद्युत रासायनिक रूपांतरण के लिए आगे उपयोग किया गया।

शोध प्रबंध के अंतिम कार्य अध्याय में, Cu_9S_5 की संरचना और विद्युत रासायनिक गतिविधि की तुलना समान मिश्रित-अपचय CuS के साथ की गई है ताकि विद्युत रासायनिक गतिविधि को नियंत्रित करने के लिए इलेक्ट्रॉनिक संरचना के प्रभाव का निष्कर्ष निकाला जा सके। इस अध्ययन में, नैनोस्ट्रक्चर्ड Cu_9S_5 और CuS का संश्लेषण किया गया है और इन्हें विद्युत रासायनिक जाँच के लिए इलेक्ट्रोड सामग्रियों के रूप में उपयोग किया गया है, जिसमें पाउडर एक्स-रे विवर्तन (PXRD) और सूक्ष्म विश्लेषणों से यह सामने आया है कि Cu_9S_5 की उजागर सतह $d(0015)$ है और CuS की $d(002)$ है। Cu_9S_5 की $d(0015)$ सतह में टेट्राहेड्रल (T_d) Cu^{II} , विकृत ऑक्टा-हेड्रल (O_h) Cu^{II} , और ट्राइगोनल प्लेनर (T_p) Cu^{I} साइट्स होती हैं, जबकि CuS की (002) सतह में केवल टेट्राहेड्रल (T_d) Cu^{II} होती है। Cu_9S_5 और CuS के बीच विद्युत रासायनिक व्यवहार में अंतर उनके उजागर सतहों पर विभिन्न तांबा साइट्स और उनके संबंधित रिडॉक्स अवस्थाओं से उत्पन्न होता है। इन-सिटू रमन स्पेक्ट्रा से पता चलता है कि Cu_9S_5 की विद्युत रासायनिक लबिलिटी CuS की तुलना में अधिक है। संपर्क-कोण और BET विश्लेषण बताते हैं कि Cu_9S_5 सतह की उच्च सतह ऊर्जा और मैक्रोपोरस प्रकृति इलेक्ट्रोलाइट प्रसार को सुगम बनाती है, जिसके परिणामस्वरूप एक उल्लेखनीय रिडॉक्स प्रतिक्रिया होती है। पोस्ट-क्रोमोएम्पेरोमेट्रिक (CA) विश्लेषण से Cu_9S_5 और CuS के $\text{CuO}/\text{Cu}_2\text{O}/\text{Cu}(\text{OH})_2$ विद्युत सक्रिय प्रजातियों में संभावित-निर्भर संरचनात्मक परिवर्तन का पता चलता है। इन इन-सिटू बने तांबा ऑक्साइड्स का इलेक्ट्रोकेटलिटिक जल-विभाजन में प्रदर्शन अप्रदूषित तांबा सल्फाइड्स से बेहतर है। संरचना और गतिविधि के बीच संबंध धातु सल्फाइड्स की विद्युत रासायनिक विशेषताओं की व्याख्या करने और सक्रिय अवस्था को विकसित करने के लिए उनके संभावित-संचालित सतह/बल्क परिवर्तन मार्ग को समझने के लिए व्यापक अंतर्दृष्टि प्रदान करता है।

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E.56	GC chromatogram for the evolved H_2 in the cathodic compartment of the Cell 2 ($CuO-Cu_9S_5@NF(-)/(+)CuO-Cu_2O@NF$) during the electrolysis performed at a cell potential of 2.5 V for 2 h. The peak at retention time 1.5 due to H_2 and peak at retention time 1.9 and 9.7 due to the N_2 and O_2 , respectively.	299
E.57	Gas chromatogram for the evolved H_2 in the cathodic compartment of the Cell 3 ($Cu_9S_5(-)/(+)Cu_9S_5$) during the electrolysis performed at a cell potential of 2.5 V for 2 h. The peak at retention time 1.5 due to H_2 and peak at retention time 1.9 and 9.7 due to the N_2 and O_2 , respectively.	299

Abbreviations

2FA	2-Furoic Acid
APS	Artificial Photo-synthetic Scheme
BET	Brunauer–Emmett–Teller
CA	Chronoamperometry
CE	Counter Electrode
CV	Cyclic Voltammetry
DFT	Density Functional Theory
EDX	Energy Dispersive X-ray
EG	Ethylene Glycol
EIS	Electrochemical Impedance Spectroscopy
ECSA	Electrochemical Surface Area
FDCA	2,5-Furandicarboxylic Acid
FE	Faradaic Efficiency
FESEM	Field Emission Scanning Electron Microscopy
FF	Furfural
GC	Glassy Carbon
Gly	Glycerol
HER	Hydrogen Evolution Reaction
HMF	Hydroxymethylfurfural
HRTEM	High Resolution Transmission Electron Microscopy
ICDD	International Centre for Diffraction Data
IPA	Iso Propyl Alcohol
LSV	Linear Sweep Voltammetry
NF	Nickel Foam
OER	Oxygen Evolution Reaction
OOR	Organic Oxidation Reaction

Abbreviations

OWS	O verall W ater S plitting
PCET	P roton C oupled E lectron T ransfer
PXRD	P owder X -ray D iffraction
RE	R eference E lectrode
RHE	R eversible H ydrogen E lectrode
SAED	S electd A rea E lecron D iffraction
SEM	S canning E lectron M icroscopy
SSP	S ingle S ource P recursor
TEM	T ransmission E lectron M icroscopy
TMC	T ransition M etal C halcogenides
TMS	T ransition M etal S ulphides
TOF	T urnover F requency
WE	W orking E lectrode
XPS	X -ray P hotoelectron S pectroscopy

Symbols

C	Celcius
cm	centimetre
α	Charge transfer co-efficient
R_{ct}	Charge transfer resistance
j	Current density
C_{dl}	Double-layer capacitance
e^-	electron
eV	electronvolt
F	Faraday
h	hour
K	Kelvin
keV	kilo electronvolt
kV	kilovolt
μm	micrometre
mA	miliAmpere
mL	mililitre
mol	mole
min	Minute
nm	nanometre
Ω	resistance
η	overpotential
v	scan rate
s	seconds
sec	seconds
R_s	Solution resistance
T	Temperature