

## Facile Synthesis of Novel $\text{Cu}_2\text{NiBiX}_4$ (X= Se, S) Chalcogenides as Bifunctional Electrocatalysts for Oxygen Evolution Reaction (OER) and Supercapacitive Performance

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### Abstract:

Greatly efficacious catalytically active materials to produce and store sustainable fuels to fulfill global energy demand is highly required, and design of cost-effective multifunctional electrocatalysts for oxygen evolution reaction (OER) and supercapacitors have become prominent. Herein, quaternary chalcogenides of  $\text{Cu}_2\text{NiBiS}_4$  and  $\text{Cu}_2\text{NiBiSe}_4$  have been fabricated by a facile solvothermal method and applied for electrocatalytic OER and supercapacitance performance. The material characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and UV-Visible spectroscopy. The  $\text{Cu}_2\text{NiBiSe}_4$  catalyst shows a low overpotential of 175 at  $10 \text{ mA cm}^{-2}$  current density and a low Tafel slope of  $61 \text{ mV dec}^{-1}$  for OER. Whereas,  $\text{Cu}_2\text{NiBiS}_4$  electrocatalyst retains overpotential 212 mV and Tafel slope  $78 \text{ mV dec}^{-1}$  for the OER at  $10 \text{ mA cm}^{-2}$ . The long-term durability test of  $\text{Cu}_2\text{NiBiSe}_4$  for 12h at  $10 \text{ mA cm}^{-2}$  current density suggests that it may suitably substitute for noble-metal-based electrocatalysts for the oxidation of water in alkaline media. Moreover,  $\text{Cu}_2\text{NiBiSe}_4$  delivers a boosted supercapacitive behavior with an exceptional specific capacity ( $1443 \text{ F g}^{-1}$  at  $2.5 \text{ A g}^{-1}$ ) as compared to  $\text{Cu}_2\text{NiBiS}_4$  ( $1221 \text{ F g}^{-1}$  at  $2.5 \text{ A g}^{-1}$ ). Furthermore,  $\text{Cu}_2\text{NiBiSe}_4$  exhibits admirable energy density of  $24.3 \text{ Wh kg}^{-1}$  at a power density of  $450.7 \text{ W kg}^{-1}$  together with 98% retention after 100 cycles.

## **Material and Methods:**

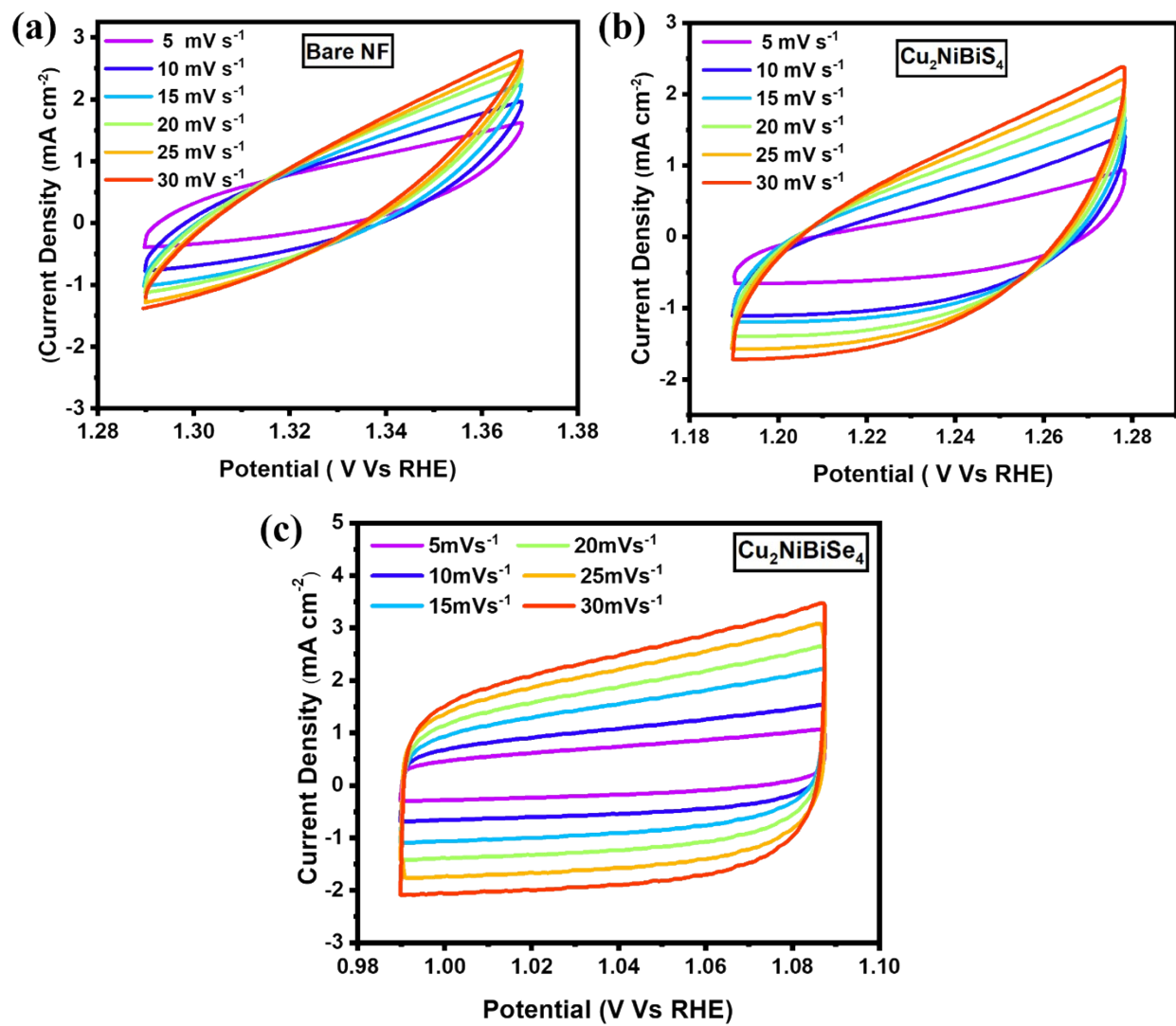
Salts of analytical grade chemicals have been used for the synthesis of  $\text{Cu}_2\text{NiBiX}_4$  ( $\text{X}=\text{S}, \text{Se}$ ) nanostructures. The stoichiometric amounts of each salt were taken along with reducing and stabilizing agents for uniform morphology. The following salts were used for the preparation of  $\text{Cu}_2\text{NiBiX}_4$  ( $\text{X}=\text{S}, \text{Se}$ ) nanostructures; Copper (II) chloride-2-hydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), Iron (III) Chloride-6-hydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), Nickel (II) Chloride Hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), Bismuth Nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), Thiourea ( $\text{CH}_4\text{N}_2\text{S}$ ), Sodium Sulfide Flakes ( $\text{Na}_2\text{S}$ ), Sodium Dodecyl Sulphate (SDS)  $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$ , Ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ).

## **Synthesis of Quaternary $\text{Cu}_2\text{NiBiX}_4$ ( $\text{X}=\text{Se}, \text{S}$ ):**

CNBS ( $\text{X}=\text{Se}, \text{S}$ ) particles were fabricated at  $200^\circ\text{C}$  for 24 hours via the solvothermal method. In a typical reaction mixture, 2 mmol copper chloride-2-hydrate, 1 mmol nickel nitrate hexahydrate, and 1 mmol bismuth nitrate pentahydrate, 8mmol thiourea, 8mmol sodium selenite were added into 40 ml of ethylene glycol (EG) solvent in a beaker. 8mmol Thiourea was used as a sulfide source whereas 8mmol sodium selenite was used as a selenium source. Then sodium sulfide flakes were added as precipitating agent. Sodium dodecyl sulfate was added as a surfactant to obtain the nanocrystals with well-fashioned morphology. To produce a clear solution, the precursor mixture was stirred at  $60^\circ\text{C}$  for 0.5 hours. The solution was then transferred to a Teflon liner (100 ml). Finally, a stainless-steel autoclave is used to store the Teflon liner. The solvothermal reaction was conducted at  $200^\circ\text{C}$  for 24 hours in a hot air oven. The supernatant was separated from the Teflon liner and mixed with ethanol before being discharged from the autoclave and then allowed to cool down to room temperature. The impurities and byproducts were removed from the dispersed precipitates by centrifuging them for 30 minutes at 6,000 rpm. Finally, to obtain well-structured  $\text{Cu}_2\text{NiBiS}_4$  and  $\text{Cu}_2\text{NiBiSe}_4$  particles, the precipitates were additionally dried at  $65^\circ\text{C}$  for 6 hours in a vacuum oven and then finally grinded to fine powder.

## **Electrode preparation:**

A homogenous slurry was prepared by thoroughly mixing 3 mg of catalyst powder with a solution containing 0.5 mL of deionized water, and 20  $\mu\text{L}$  of Nafion (5 wt%, Sigma Aldrich). The mixture was then sonicated for 40 minutes to achieve an even dispersion. Subsequently, the slurry was carefully drop-casted onto a nickel foam substrate and dried at  $60^\circ\text{C}$  for 30 minutes.



**Figure S1.** Electrochemical surface area of (a) Bare Ni-foam, (b)  $\text{Cu}_2\text{NiBiS}_4$  and (c)  $\text{Cu}_2\text{NiBiSe}_4$