Electronic Supplementary Information

Transition metal sulfides laminated copper wire for flexible hybrid supercapacitor

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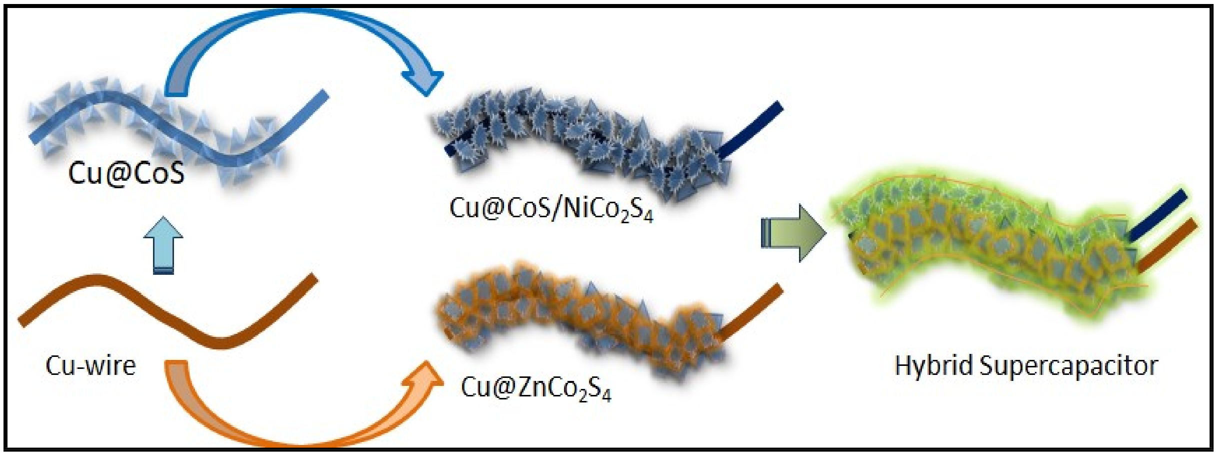
Experimental details:

The chemicals used for the electrodeposition of the nanostructure material were received from Sigma Aldrich reagent quality and used without further purifications. Firstly, Cu-wire was cleaned with distilled water (DW), ethanol, and acetone and then used for deposition. Electrodeposition was conducted in potentiostatic mode through a three-electrode system with a platinum plate, Ag/AgCl and Cu-wire as a counter, reference and working electrodes, respectively at low temperature (50 ºC). **Schema 1** shows the schematic representation for the stepwise formation of $NiCo_2S_4$ nanoflakes and $ZnCo_2S_4$ nanosheets on a Cu-wire for flexible hybrid supercapacitors. In the first step, a single layer of CoS was formed on Cu-wire. In which, working electrolyte solution was prepared by mixing 10 mM $Co(NO)_3.6H_2O$, and 0.10 M thiourea in distilled water (40 mL) and experiment conducted at -1.2 V/SCE for 60 s deposition time, resulting in the formation of the Cu@CoS. Further, $NiCo_2S_4$ formed on a Cu@CoS by following potentiostatic mode of electrodeposition at -1.2 V/SCE for 300 s with electrolyte solution contains, 5 mM $Ni(NO)_3.6H_2O$, 10 mM $Co(NO)_3.6H_2O$, and 0.10 M thiourea mixed in 50 ml DW. The resulting Cu@CoS/$NiCo_2S_4$ thin film rinsed in DI water and dried at 60 ºC for 4 h. For the second electrode preparation, electro-deposition was conducted for $ZnCo_2S_4$. In this case, the experiment was performed the same with $NiCo_2S_4$, only replacing Ni $(NO)_3.6H_2O$ instead of $Zn(NO)_3.6H_2O$ in an electrolyte solution. The Cu@$ZnCo_2S_4$ thin film further formed on Cu-wire at the applied cathodic potential of -1.5 V/SCE for 600s then samples rinsed in DI water and dried 4 h. Finally, Cu@CoS/$NiCo_2S_4$ and Cu@$ZnCo_2S_4$ thin films used for further physico-electrochemical characterizations.



Schema 1 Schematic illustration for the formation of a flexible hybrid supercapacitor on Cu-wire.

Electrochemical charge storage and impedance evaluations of electrodeposited material were evaluated using cyclic voltammetry (CV), and galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) using an IVIUM Tech potentiostat with the help of the three-electrode and a two-electrode system. For three-electrode system, electrochemical performances of the separate electrode were performed in 1M KOH electrolyte. In the case of a two-electrode system, the flexible wire-type hybrid supercapacitor was fabricated using Cu@CoS/$NiCo_2S_4$ and Cu@$ZnCo_2S_4$ electrodes assembled in polymeric gel electrolyte (PVA-KOH). The fabricated supercapacitor cell noted as $NiCo_2S_4$//$ZnCo_2S_4$ FWHSCs.

Formulas:

The specific capacity of the electrode was calculated from the cyclic voltammetry curve using formula (1) in a three-electrode configuration. From the charge/discharge study, the specific capacity, specific capacitance, power, and energy density of the electrode were calculated using the following formulae (2)-(5).

1. $$Specific capacity = \frac{\int i(v)dv}{m \times v \times 3600}$$

2. $$Specific capacity = \frac{i \times \Delta t \times A}{3600 \times m}$$

3. $$Specific capacitance = C_{cd} = \frac{specific capacity \times 3600}{\Delta V(V)}$$

4. $$P = \frac{E \times 3600}{\Delta t}$$

5. $$E = \frac{0.5 \times C_{cd} \times (\Delta V)^2}{3600}$$

Where, $\int i(v)dv$ (mA.V): average integrated area under the CV curves, ν (mV s^{-1}): scan rate, and m (g): loading mass of the electrode material. *I* (mA cm^2)*:* current density, *Δt* (s): discharge time, *ΔV (V):* potential window and *A* (cm^2)*:* active area of the electrode. P (W kg^{-1}): power density, E (Wh kg^{-1}): energy density,

XRD studies

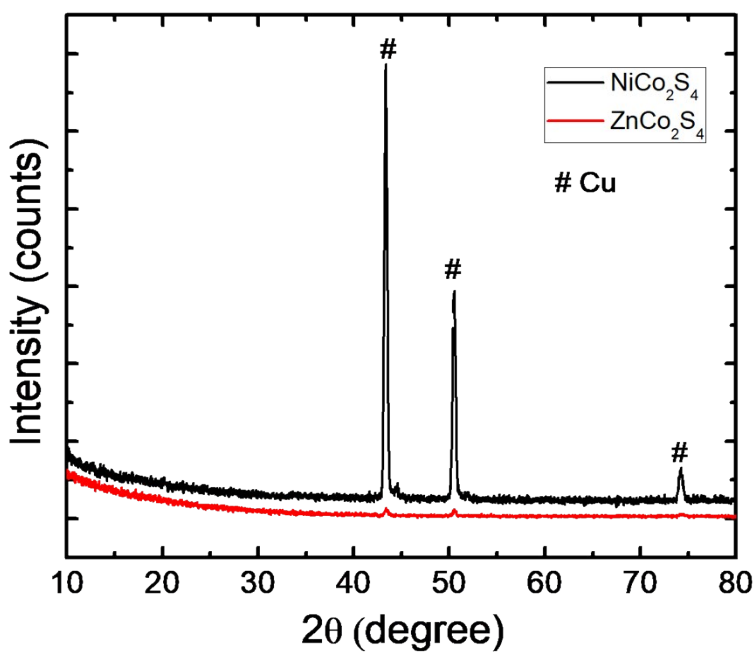


Figure S1 The XRD patterns of the electrodeposited materials.

XPS studies

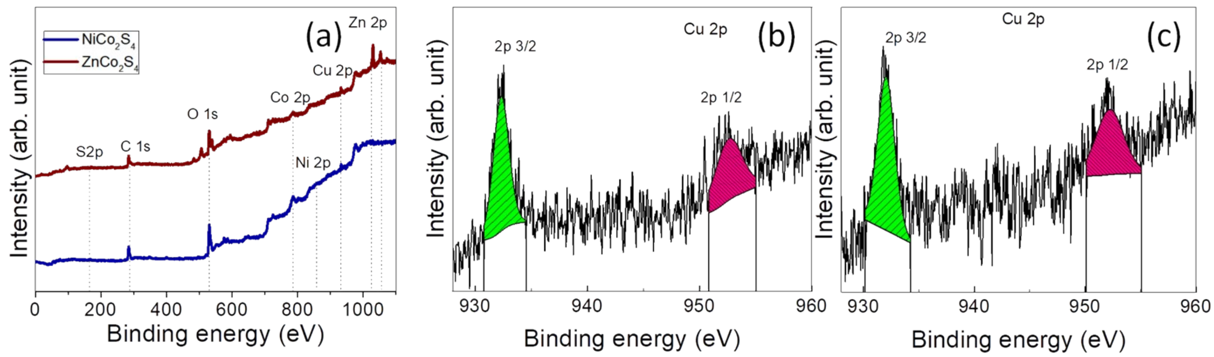


Figure S2 (a) The wide XPS scan spectra of $CoS/NiCo_2S_4$ and $ZnCo_2S_4$ materials. The XPS narrow scan spectra of Cu 2p in **(b)** $Cu@CoS/NiCo_2S_4$ and **(c)** $Cu@ZnCo_2S_4$ materials.

Electrochemical results

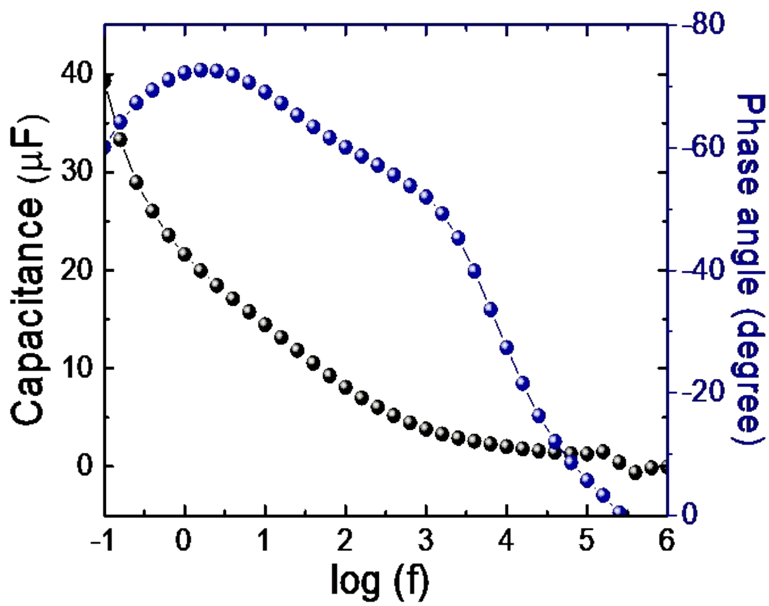


Fig S3 Bode plot of the $NiCo_2S_4//ZnCo_2S_4$ FWHSCs.

Table S1 The atomic percentages of the elements obtained from the EDX spectra for the $Cu@CoS$, $Cu@NiCo_2S_4$, $Cu@CoS/NiCo_2S_4$, and $Cu@ZnCo_2S_4$ materials.

Cu@CoS		$Cu@NiCo_2S_4$		$Cu@CoS/NiCo_2S_4$		$Cu@ZnCo_2S_4$	
Element	***At%***	***Element***	***At%***	***Element***	***At%***	***Element***	***At%***
OK	50.18	***OK***	14.48	***OK***	13.69	***OK***	12.08
SK	3.65	***SK***	39.47	***SK***	42.69	***SK***	39.53
CoK	22.13	***CoK***	21.33	***CoK***	19.84	***CoK***	20.46
NiK	0.00	***NiK***	09.34	***NiK***	8.88	***ZnK***	12.84
CuK	24.04	***CuK***	15.38	***CuK***	14.9	***CuK***	15.09

Table S2 The table shows the electrochemical performance of the fabricated wire-type $NiCo_2S_4//ZnCo_2S_4$ HSCs compared with the previous literature report.

Electrode material	**Capacitance**	**Power density**	**Energy density**	**Ref.**
3D-$NiMoO_4$/Ni@CW//rGO/CF	0.504 F cm^{-2}	4050 μW cm^{-2}	0.202 mWh cm^{-2}	[1]
CuO@CoFe-LDH	468.75 mF cm^{-2}	45720 μW cm^{-2}	93.75 μWh cm^{-2}	[2]
pErGO@Cuf/Cu wire	283.5 mF cm^{-2}	7.6 mW cm^{-2}	39.3 μWh cm^{-2}	[3]
NiVS/NiCuP/CW/rGO/CF	13.4 F cm^{-2}	4.3 mW cm^{-2}	295 μWh cm^{-2}	[4]
Cu@Ni@NiCoS NFs	-	11.15 μW cm^{-2}	0.48 μWh cm^{-2}	[5]
$CoNi_2S_4$/E-NZP film @CW//rGO/CF	8.9 F cm^{-2}	9280 μW cm^{-2}	108.4 μWh cm^{-2}	[6]
$NiCo_2S_4//ZnCo_2S_4$ HSCs	4.8 mF cm^{-2}	1125 mW cm^{-2}	1.5 mWh cm^{-2}	**Present work**

References:

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