Ternary chalcogenide micro-pseudocapacitors for on-chip energy storage

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Supporting Information

Micro-fabrication

Glass substrates (Fischer) were cut into 1x1″ size, cleaned with a soap solution to remove the dirt or grease followed by sonicating in acetone, isopropanol and deionized water sequentially for 5 minutes each and then dried by blowing nitrogen. Positive photoresist AZ9260 was spun coated at 3000 rpm for 60 seconds over the glass substrates to get 10 μm thick photoresist layer. Photoresist coated substrates were soft baked at 110 ºC for 3 minutes. Ultra-Violet (UV) exposure was done using EVG contact aligner at a constant dose of 1800 mJ/cm^2 through the Cr/Glass mask having the interdigitated patterns. After the exposure, samples were developed in AZ726 developer solution for 6 minutes, which resulted in the formation of patterns in the photoresist layer. Metal layers of 200 nm Au/20 nm Ti were deposited by sputtering (Equipment Support Co., Cambridge, England) technique over the patterned photoresist layer. Before the lift-off process, free-standing rGO film obtained through vacuum filtration was transferred onto metal-coated patterned photoresist followed by electrochemical co-deposition of nickel cobalt sulfide.[25]

Preparation of reduced graphene oxide films

Graphite oxide was prepared from natural graphite source using a modified Hummers method.[30] Thus obtained graphite oxide was exfoliated in de-ionized (DI) water by sonicating using a bath sonicator (UP400S, Ultrasonic processor; Hielscher ultrasound Technology) for 1hr. The resulting graphene oxide was then reduced to graphene by following a method reported by Li et al.[31] The supernatant solution containing thin layers of graphene was used for obtaining free-standing rGO films. The rGO dispersion was filtered using vacuum filtration (VF) method on a porous alumina membrane filter (0.2 μm pore size and 25 mm diameter; Whatman).[32] The alumina membrane was removed by dissolving it into a bath of 3M NaOH solution in order to obtain free-standing rGO film. This film was then transferred to a water bath to remove the traces of adsorbed NaOH over the rGO surface and this step was repeated for several times. Finally, rGO film was transferred onto the Au-coated patterned photoresist chip followed by drying off in a heating oven at 60 ºC for 3 minutes.

Electrochemical co-deposition of $CoNi_2S_4$

An optimized recipe reported in the reference 25 was employed for electrochemical co-deposition, consists of 5 mM $CoCl_2.6H_2O$ with 7.5 mM $NiCl_2.6H_2O$ and 0.75 M thiourea ($CS(NH_2)_2$), resulting in the $CoNi_2S_4$. The pH value of the solution was adjusted with diluted $NH_3{\cdot}H_2O$ to ~6. The potentiodynamic deposition was carried out in a three-electrode cell using rGO/Au coated patterned photoresist, Pt as counter, and Ag/AgCl as reference electrodes by cyclic voltammetry at a scan rate of 5 mV/s for 1-6 cycles within a potential range of -1.2 to 0.2 V vs. Ag/AgCl.[25] After the electrodeposition, substrates were cleaned by rinsing with water to remove unreacted initial precursor solution, followed by drying in air and drying at 60 ºC for 3 min.

Material Characterization

Surface morphology and microstructure were imaged by scanning electron microscope (SEM) (Nova Nano 630 instrument, FEI Co., The Netherlands). The film thicknesses were measured using a Veeco Dektak 150 surface profilometer. X-ray photoelectron spectroscopy (XPS) analysis was carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K_α X–ray source (hν = 1486.6 eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of ~10^{-9} mbar. The high-resolution spectra were collected at fixed analyzer pass energy of 20 eV.

Electrochemical characterization

The electrochemical performance of $CoNi_2S_4$/rGO MSCs was investigated in a 2-electrode configuration using an electrochemical workstation (CHI 660D, CH Instruments Incorporation). Cyclic voltammetry (CV), galvanostatic charge-discharge (CD), and electrochemical impedance spectroscopy (EIS) measurements were carried out in 1M KOH electrolyte. CV experiments were carried out at different scan rates selected from 0.01 to 50 V/s. CD experiments were performed using current densities selected from 60 to 320 μA/cm^2. The electrochemical impedance spectroscopy (EIS) was measured using a Modulab (Solartron Analytical) electrochemical workstation in the frequency range from 100 kHz to 0.1 Hz at open circuit potential by applying a small sinusoidal potential of 10 mV signal. Electrochemical cycling stability was measured using VMP3 multichannel electrochemical workstation (Bio-Logic). All measurements were done at room temperature.

Areal cell capacitance (C_{cell}) was calculated from the charge-discharge curves according to the following equations.

Areal cell capacitance (C_{cell}) = $(i/A_{two})(\Delta t/\Delta E)$ (for 2-electrode configuration).

Where A_{two} is the total area of both the electrodes, 'i' is the applied current, □t is the discharge time and ΔE is the potential window.

Volumetric cell capacitance (C_{vol}) = $(i/v_t)(\Delta t/\Delta E)$

Volumetric energy density (E) = $\frac{1}{2}C_{vol}\Delta E^2$ (in Wh/cm^3)

Volumetric power density (P) = $E/\Delta t$ (in W/cm^3).

C_{cell} is the areal cell capacitance, C_{vol} is the volumetric cell capacitance, v_t is the total volume of electrodes (including area and thickness of both the electrodes).

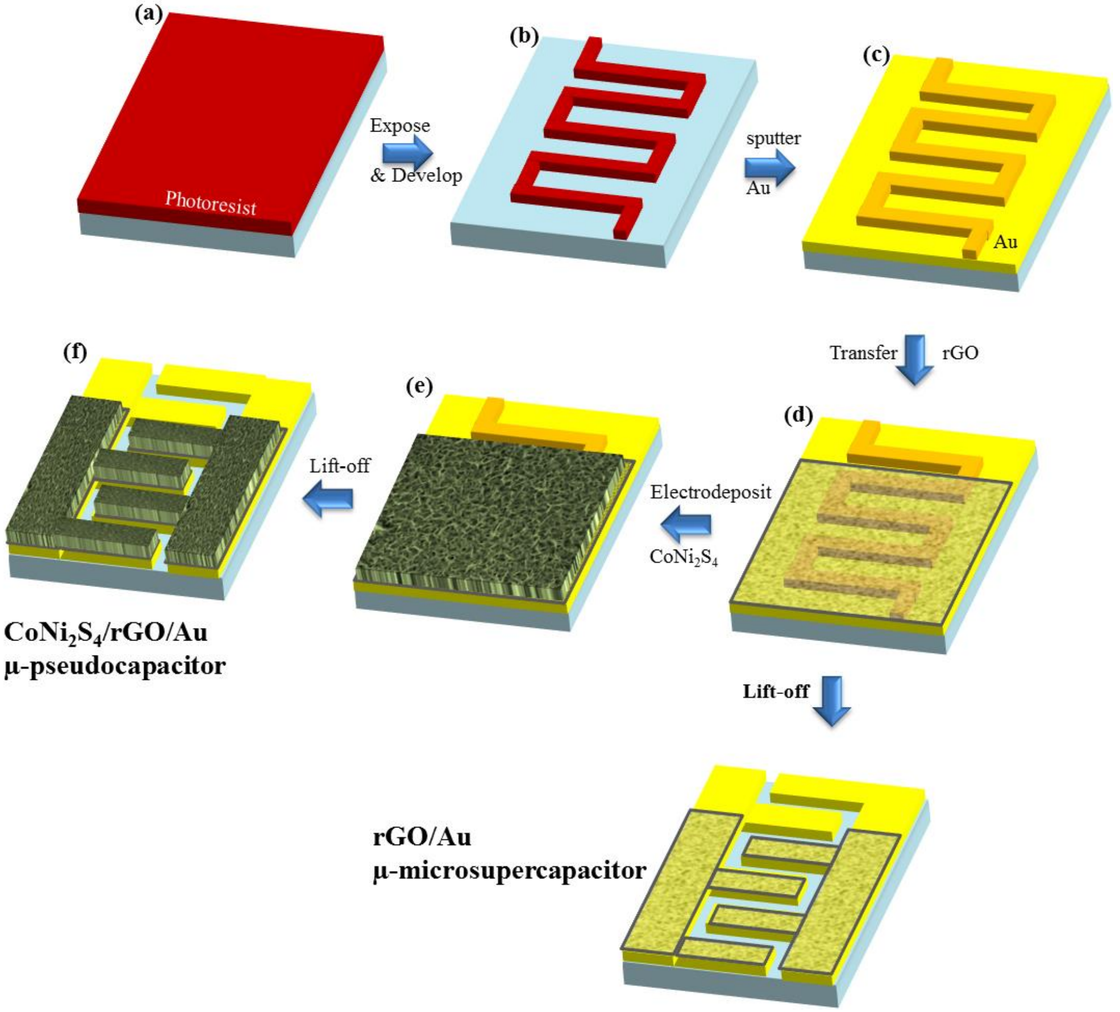

Fig. S1 (a-f) Schematic depicting the process flow for fabricating $CoNi_2S_4$/rGO/Au micro-pseudocapacitor.

Briefly, spin coating of positive photoresist (see Fig. S1a) followed by exposure and developing will give patterned photoresist as shown in Fig. S1b. Metal layers of Au (200 nm)/ Ti(20 nm) were deposited by sputtering technique as shown in Fig. S1c. Free-standing rGO films were obtained through vacuum filtration of rGO dispersion as described in Fig. 1 of main manuscript. This rGO film was transferred onto the metal coated patterned photoresist layer as shown in Fig. S2d. Lift-off at this stage has resulted in the rGO microsupercapacitor. Further, electrodeposition of $CoNi_2S_4$ over the rGO fingers may result in the extraneous deposits in the interspaces. In order to have clean and neat finger electrodes while not employing second step of photolithography; after transferring rGO layer, electrochemical deposition was carried out over the entire substrate (rGO/Au/patterned photoresist/substrate), as shown in Fig. S1e. Now the final step of lift-off has resulted in the interdigitated finger electrodes comprising of $CoNi_2S_4$/rGO/Au (see Fig. S1f). This is how rGO film has turned out be the part of patterns of hybrid electrodes with $CoNi_2S_4$/rGO.

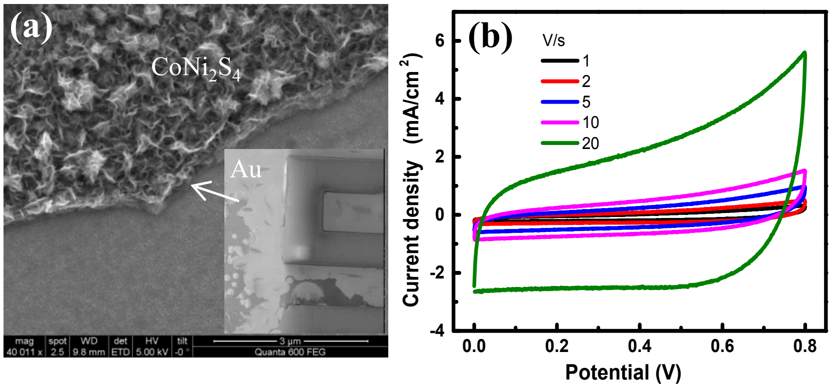

Fig. S2 (a) SEM image showing the growth of $CoNi_2S_4$ on Au surface, inset shows the non-uniform growth over the Au finger electrodes. (b) CV curves of $CoNi_2S_4$/Au micro-pseudocapacitor (deposited for 6 cycles under potentiodynamic conditions as described in the experimental section) in 1M KOH electrolyte.

It was observed that the growth of $CoNi_2S_4$ was non-uniform over the Au current collectors as evident from the SEM micrographs shown in Fig. S2a. As shown in Fig. S2b, CVs of $CoNi_2S_4$/Au micro-pseudocapacitor are of rectangular type (areal capacitance of < 1 mF/cm^2), revealing that the pseudocapacitive contribution of $CoNi_2S_4$ towards overall capacitance of the device is minimal. Hence, we have chosen rGO as a nucleation layer for the uniform growth of

$CoNi_2S_4$ which further can contribute to the enhanced values of areal capacitance of $CoNi_2S_4$/rGO/Au micro-pseudocapacitor. It appears that the functional rGO surface can facilitate better nucleation and growth of $CoNi_2S_4$ over the Au surface.

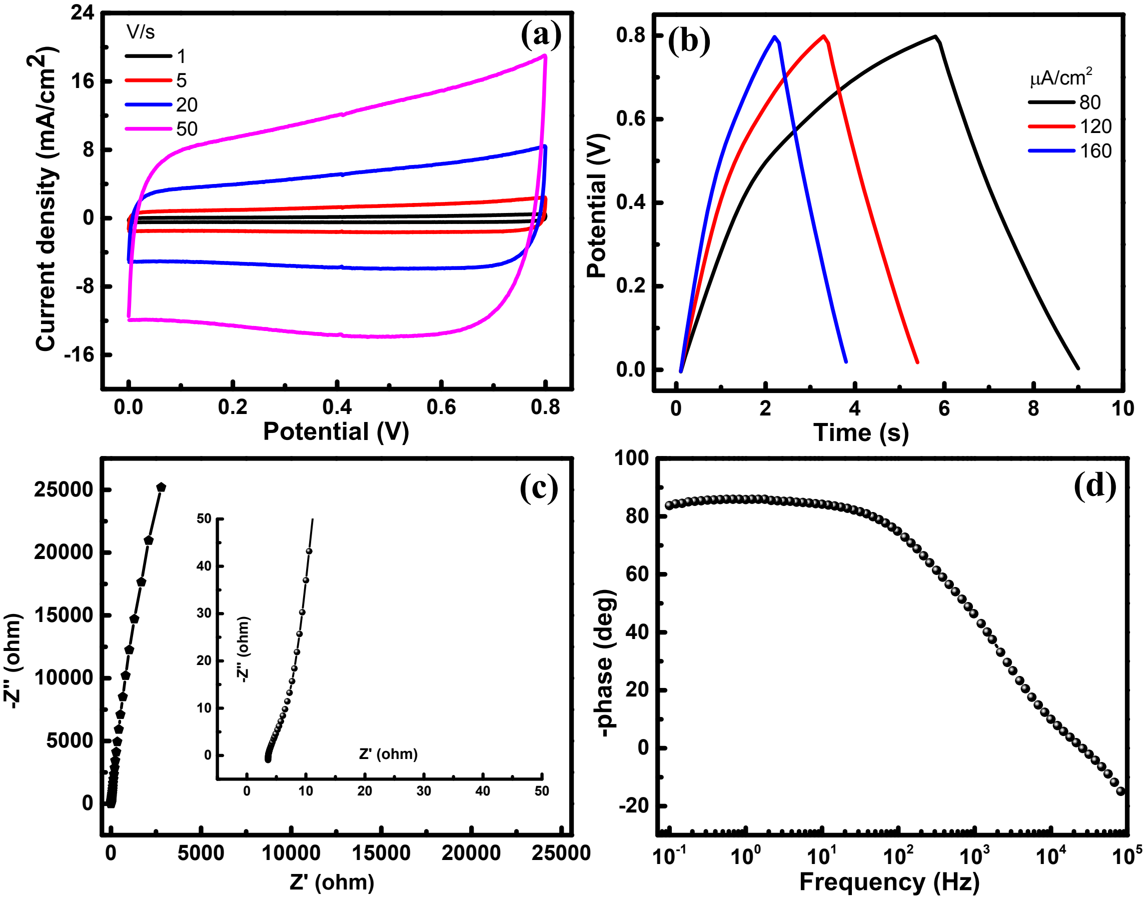

Fig. S3 (a) CV scans rGO MSC at different scan rates 1-50 V/s (b) CDs at different current densities. (c) Nyquist spectrum of RGO MSC, inset shows the high frequency region of the spectrum. (d) Phase angle vs. frequency of rGO MSC.

The electrochemical performance of rGO MSC was investigated in a 2-electrode configuration in 1M KOH electrolyte. The CV curves are seen quite rectangular until high scan rates up to 50 V/s, due to its EDLC behavior. The areal capacitance was found to be 0.3 mF/cm^2 at a scan rate of 1 V/s.

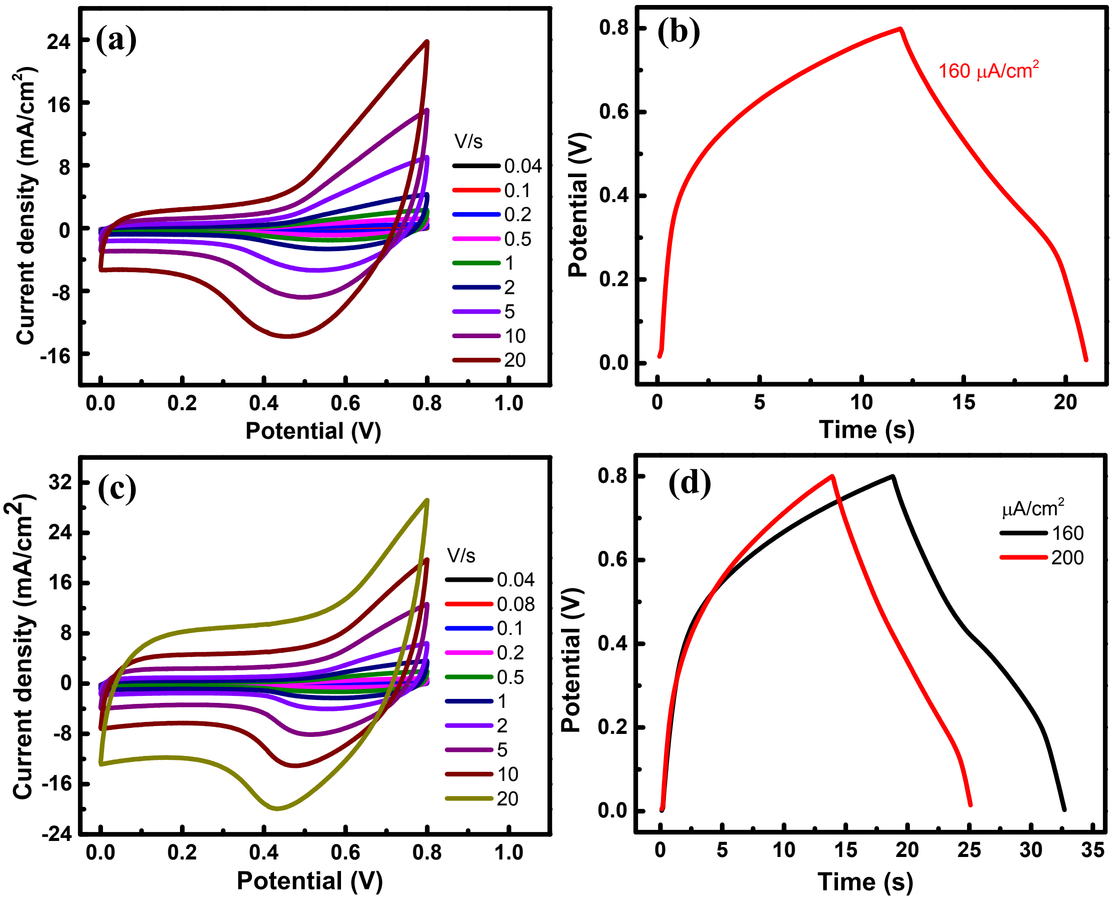

Fig. S4 (a, c) CVs and (b,d) CDs of $CoNi_2S_4$ micro-pseudocapacitors deposited for 1 and 4 cycles, respectively.

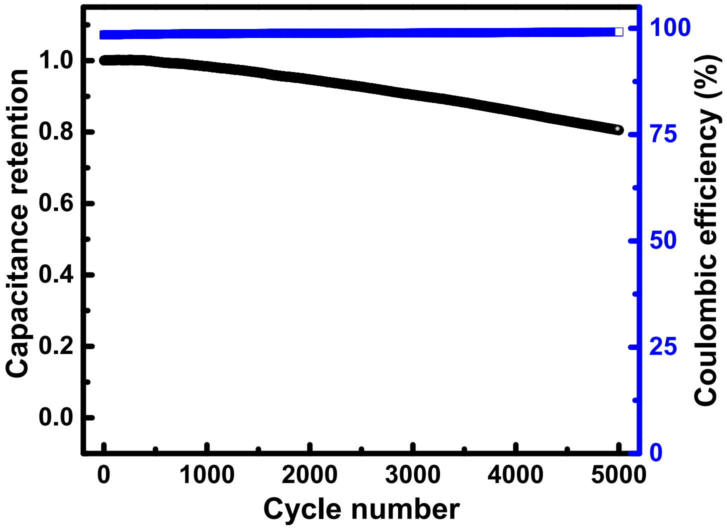

Fig. S5 Cycling stability and Coulombic efficiency of $CoNi_2S_4$ micro-pseudocapacitor over 5000 cycles at a current density of 320 μA/cm^2.

Cycling stability of $CoNi_2S_4$ MSC was tested by continuous charging/discharging at a current density of 320 μA/cm^2 which showed capacitance retention of 80% after 5000 cycles with a coulombic efficiency above 95%.

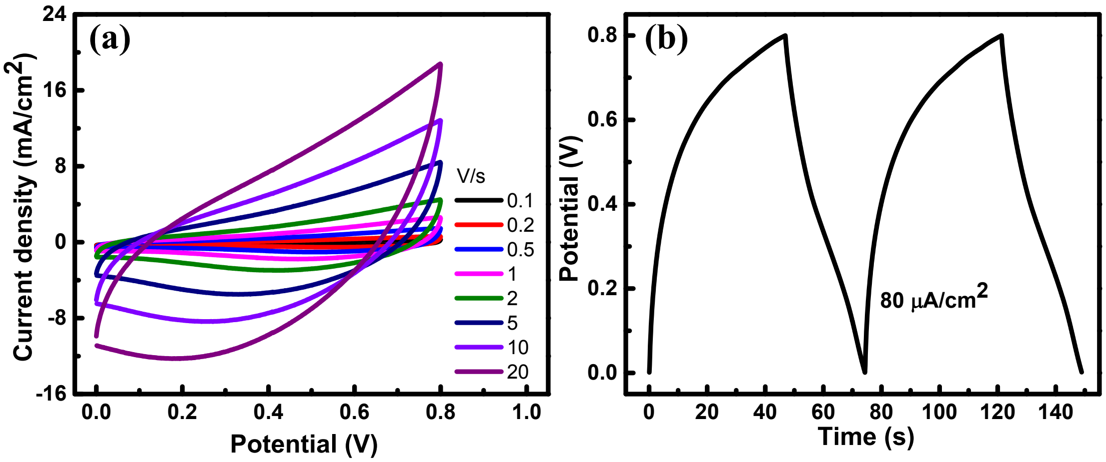

Fig. S6 (a) CVs and (b) CD of $CoNi_2S_4$ solid state micro-pseudocapacitor employing PVA/KOH gel electrolyte.

Table S1. Comparison table for Sulfide based micro-pseudocapacitors

Reference	System	Thickness (μm)	Volumetric capacitance (F/cm^3)	Current density (A/cm^3)	Voltage window (V)	Volumetric energy density (mWh/cm^3)	Volumetric Power density (W/cm^3)
Cao et al., small 2013, 9, 2905	MoS_2	0.45	178	0.5	0.4	6	1.1
Feng et al., J. Am. Chem. Soc. 2011, 133, 17832	VS_2	0.15	317 (per electrode)	0.66	0.6	12	1.1
Our work	**$CoNi_2S_4$**	**0.55**	**211**	**3**	**0.8**	**18.7**	**1.2**