

Supplementary Information:

Noble and single source precursor for the synthesis of metal-rich sulphides embedded in N-doped carbon framework for highly active OER electrocatalysts

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Experimental section:

We prepare the metal chelate complex by adding 0.5 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CoSO}_4 \cdot \text{H}_2\text{O}$ aqueous solution in excess volume of ethylenediamine (EDA). It precipitates immediately in the form of $[\text{M}^{\text{II}}(\text{EDA})_3]\text{SO}_4$ complex where $\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}$. We wash the complex with de-ionised water/ethanol and dried at 80°C and collected the solid metal-chelate complex. For the synthesis of metal sulphide embedded N-doped carbon nanostructures, we take 0.5 g of metal complex in quartz tube of 1.0 cm diameter with one end closed and the open end is closed by rubber bladder. Then the complex is pyrolyzed at different temperatures between 750 to 950°C for 2 h. Schematic of the experimental set-up is shown in Fig. 1

ESI-1

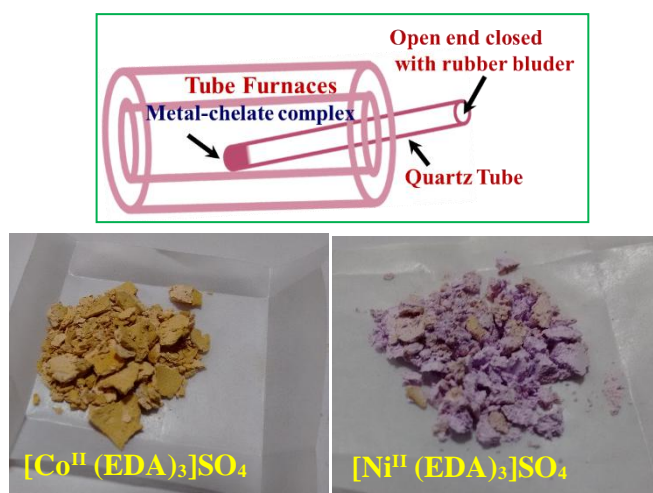


Fig.1. Schematic of the experimental set-up and photographs of $[\text{M}^{\text{II}}(\text{EDA})_3]\text{SO}_4$ precursor.

Physical characterizations

Powder X-ray diffraction (XRD) patterns are recorded using PAN analytical instrument using a Cu K_α ($\lambda = 1.54 \text{ \AA}$) radiation source. Scanning electron microscope (SEM) images and Energy-dispersive X-ray spectroscopy (EDS) are taken on a FE-SEM, FEI-INSPECTF50

instrument. Transmission electron microscope (TEM), high resolution TEM (HRTEM) and selected area electron diffraction (SAED) pattern are obtained with a TEM, JEOL- JEM-2100F operated a 200 kV accelerating voltage. For TEM analysis, the samples are dispersed in ethanol solution and drop-casted on carbon coated copper grid, and dried. Raman spectroscopy experiments are performed on a WITec 300 confocal microscope using a Nd:YAG laser (532 nm) as an excitation source, while X-ray photoelectron spectroscopy (XPS) experiments are performed on an ESCALAB 250 (Thermo Electron) with a monochromatic Al K_{α} (1486.6 eV) source for the elemental analysis. The surface atomic concentrations are determined from the peak areas using the atomic sensitivity factors reported by Scofield. The binding energy is calibrated by placing the principal C1s peak at 284.6 eV.

Electrochemical OER measurements

Electrochemical oxygen evolution reaction (OER) measurements are conducted using electrochemical work station with rotating disk electrode and Bipotentiostat (CH Instruments). An ink of the hybrids or RuO₂ are prepared from ultrasonically dispersed 5 mg catalyst in 1 ml of ethanol solution. Then, 3 μ L of catalyst ink are added with the 10 % of Nafion solution. Subsequently, the ink is dispersed on a glassy carbon rotating disk electrode (RDE) followed by drying at 60 °C. The catalyst loadings on RDE are 0.22 mg/cm² for all hybrids and RuO₂. A conventional three-electrode cell is employed incorporating an AgCl/Ag (3M KCl) as the reference electrode, a Pt wire as the counter electrode and the catalyst film coated RDE as the working electrode. OER measurements were carried out at rotation speed at 600 rpm N₂ saturated 0.1 M and 1 M KOH aqueous solution.

ESI-2: Ni₃S₂@NC

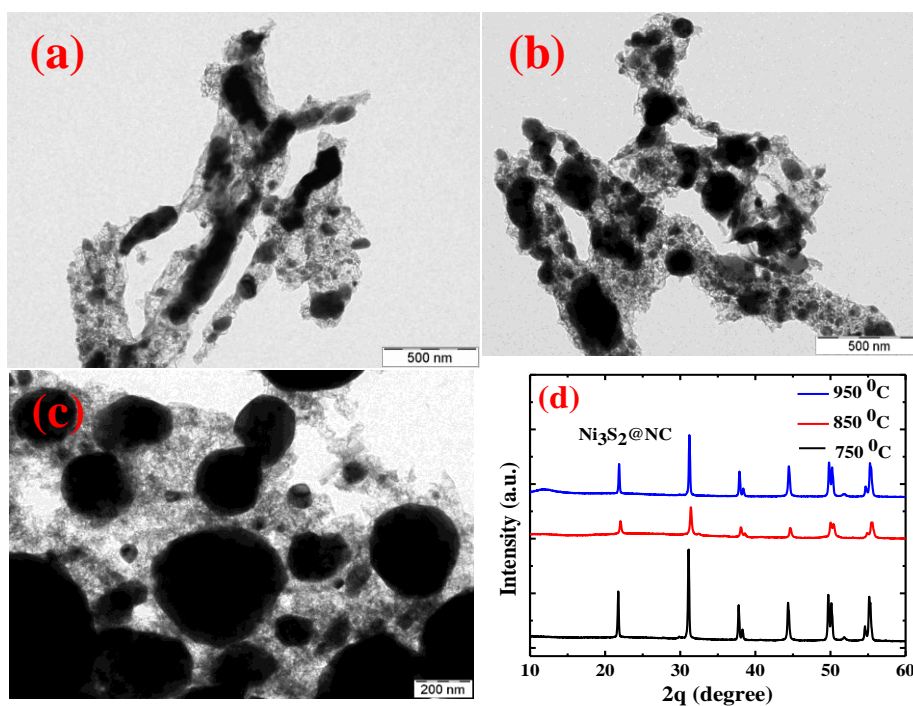


Fig.2 (a, b and c) TEM images of Ni₃S₂@NC which are synthesized at 750 °C, 850 °C and 950 °C reaction temperature for 2h. (d) Powder XRD pattern of the corresponding sample.

ESI-3: Co₉S₈@NC

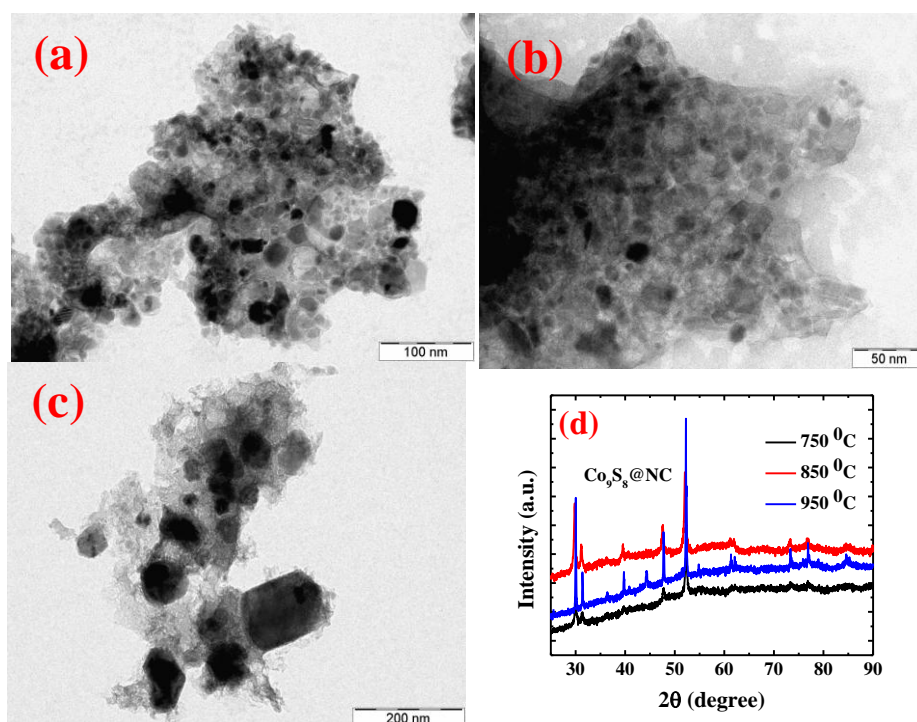


Fig.3 (a, b and c) TEM images of Co₉S₈@NC which are synthesized at 750 °C, 850 °C and 950 °C reaction temperature for 2h. (d) Powder XRD pattern of the corresponding sample.

ESI-4: Raman spectra

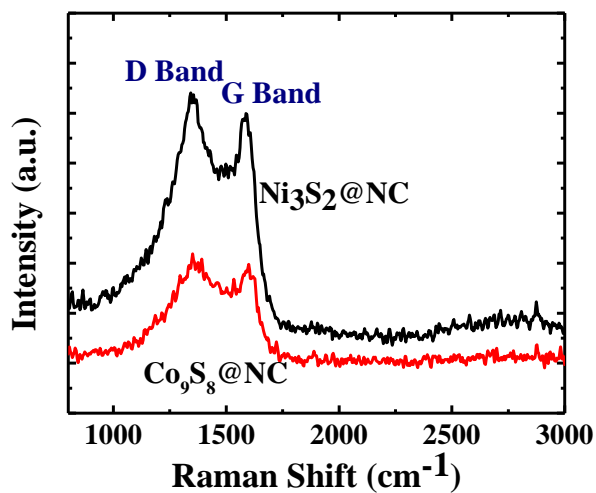


Fig. 4 Raman spectra of Ni₃S₂@NC and Co₉S₈@NC.

ESI-5: XPS survey spectrum of Co₉S₈@NC hybrid

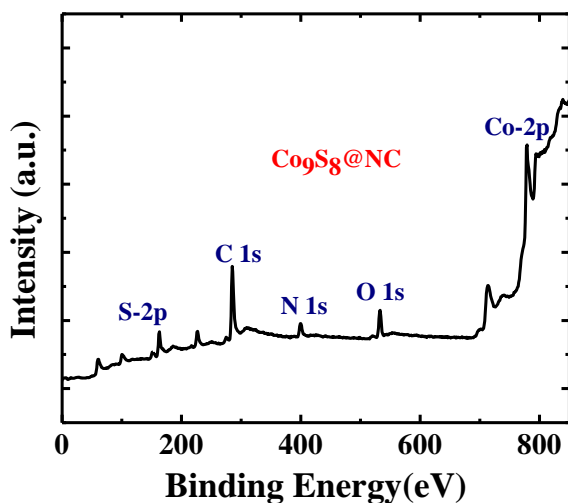


Fig. 5 XPS survey spectrum of Co₉S₈@NC synthesized from [Co^{II} (EDA)₃]SO₄ complex at 850 °C for 2 h.

ESI-6: XPS survey spectrum of Ni₃S₂@NC hybrid

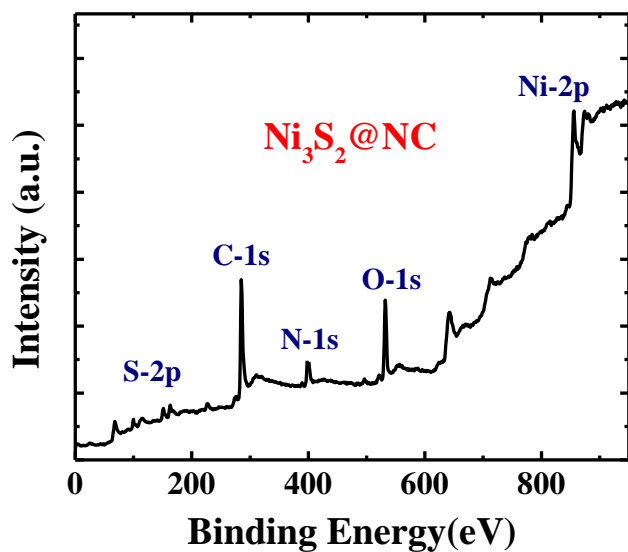


Fig. 6 XPS survey spectrum of Ni₃S₂@NC synthesized from [Ni^{II} (EDA)₃]SO₄ complex at 850 °C for 2 h.

ESI-7: C-1s and N-1s of Co₉S₈@NC hybrid

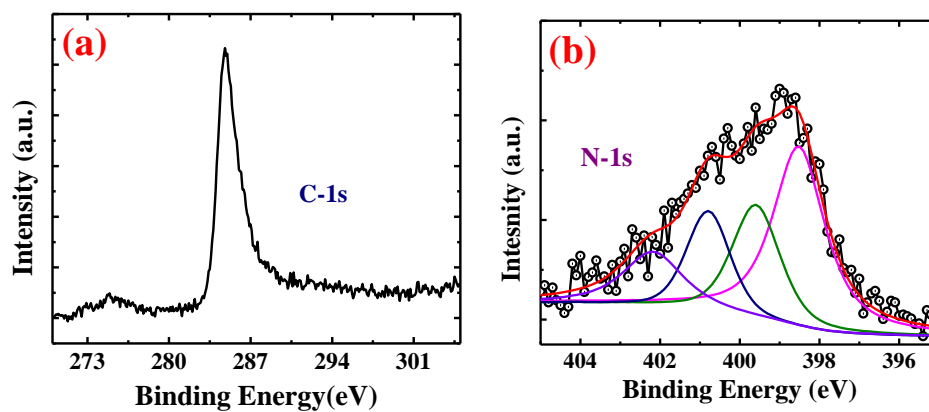


Fig. 7 (a and b) HR C1s and N 1s XPS spectrum of Co₉S₈@NC hybrid synthesized at 850 °C.

ESI-8: C1s and N1s XPS spectra of Ni₃S₂@NC hybrid

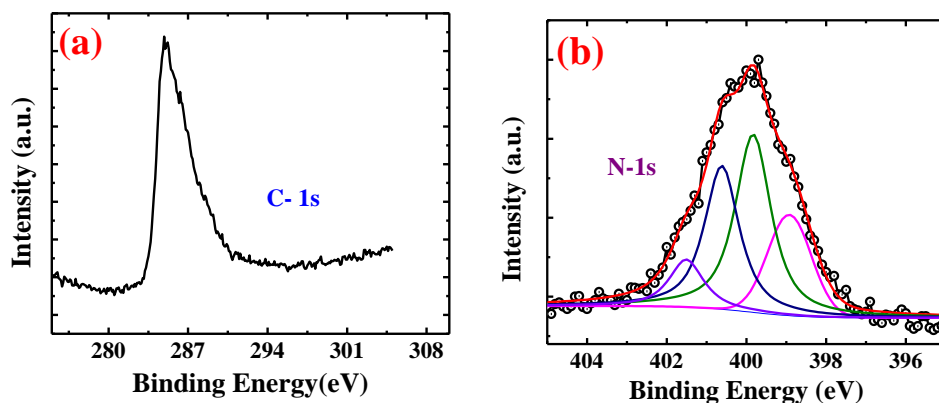


Fig. 8 (a and b) HR C1s and N1s XPS spectra of Ni₃S₂@NC hybrid synthesized at 850 °C.

ESI-9: OER study

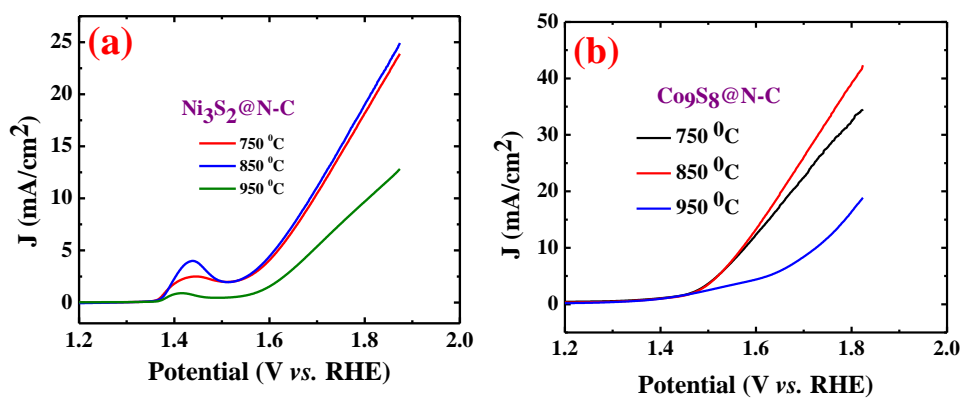


Fig.9 (a and b) OER activity of Ni₃S₂@N-C and Co₉S₈@N-C which are synthesized at different temperature.

ESI-10: OER stability of RuO₂

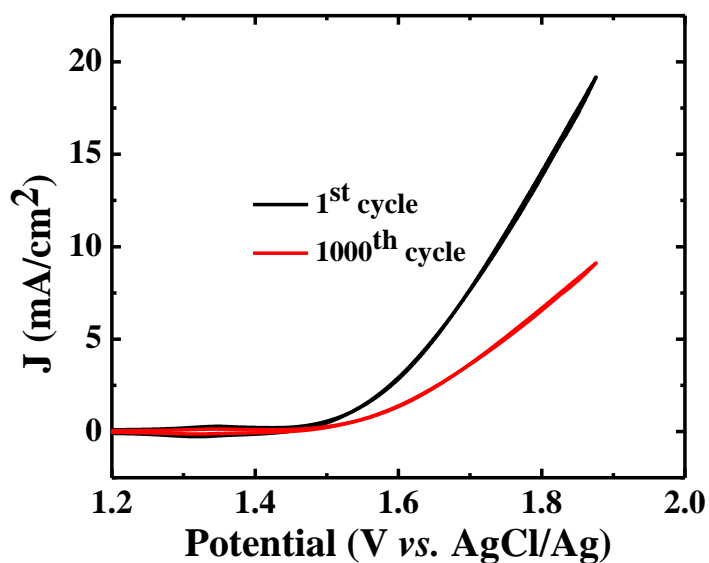


Fig. 10 Stability curve for commercial RuO₂ representing 1st and after 1000th cycle (scan rate 100 mV/s and rotation speed of 600 rpm).

ESI-11: OER stability of Ni₃S₂@NC

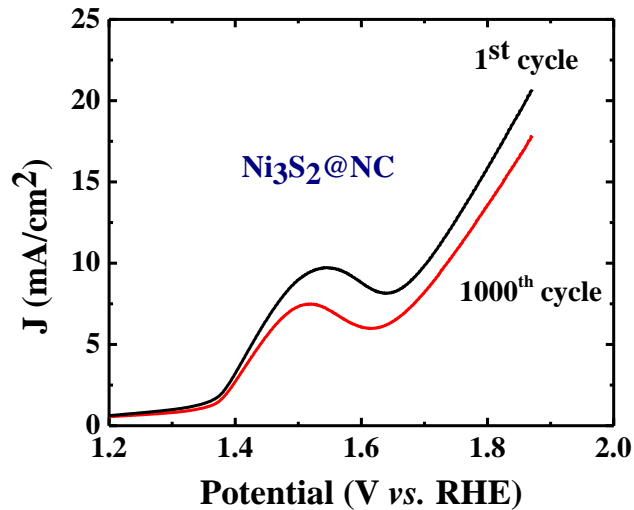


Fig. 11 Stability curve for Ni₃S₂@NC hybrid representing 1st and after 1000th cycle (scan rate 50mV/s and rotation speed of 600 rpm).

ESI-12: Capacitance

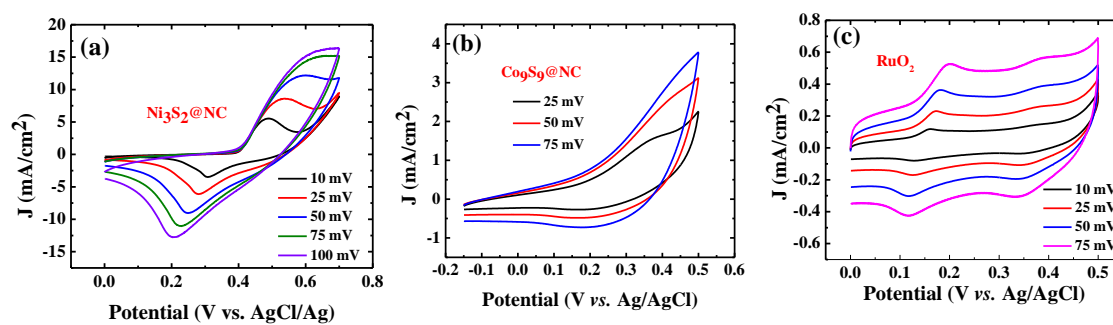


Fig. 12 (a, b and c) Electrochemical cyclic voltammetry curves of capacitance performances of Ni₃S₂@NC, Co₉S₈@NC and RuO₂ at different scan rate in 0.1M KOH solution as electrolyte.