Supporting Information

Electrocatalytic water splitting through the Ni_xS_y self-grown superstructures obtained through a wet chemical sulfurization process

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S1: The possible chemical reaction mechanismsresponsible for the hydrothermal formation of Ni_xS_v considering different S²⁻ ion source precursors

(1) Sodium thiosulfate (STS)

Sodium thiosulfate (Na₂S₂O₃, STS) is a reducing agent and whose half-cell reaction as

$$S_2 O_3^{-2} \rightarrow S_4 O_6^{2-} + 2e^{-} \qquad (1)$$

In aqueous medium, dissociation of STS take place

$$S_2 O_3^{-2} + H^+ \rightarrow HSO_3^- + S$$
 (2)

The electron released (using eq. (1)) reacts with sulphur from reaction (2)

$$S + 2e^{-} \rightarrow S^{-2} \tag{3}$$

$$xNi^{+2} + yS^{-2} \rightarrow Ni_xS_y \tag{4}$$

(2) Thioactetamide (TAA)

TAA solution which gives sulphide ions (S²⁻) and reaction follows

$$\begin{array}{ccc} & & SH \\ CH_3 - \ddot{C} - NH_2 & \longleftrightarrow & CH_3 - \dot{C} = NH \end{array}$$
(5)

In acidic medium protonation gives

$$\begin{array}{ccc} SH & H-S^{+}-H \\ CH_{3}-C=NH+H^{+} \longrightarrow CH_{3}-C=NH \end{array}$$
(6)

The intermediate compound formed dissociates to give H₂S as

$$H-S^{+}-H$$

$$CH_{3}-C=NH \longrightarrow CH_{3}-C=NH^{+}+H_{2}S$$
(7)

In aqueous medium H₂S dissociates to give

$$H_2 S \rightarrow H^+ + S H^- \tag{8}$$

$$SH^- \to H^+ + S^{2-} \tag{9}$$

Finally, S^{2-} ions react with Ni to form Ni_xS_y superestructures.

$$xNi^{+2} + yS^{-2} \rightarrow Ni_xS_v(10)$$

(3) Thiourea (TU)

$$NH_{2}CSNH_{2} + 2H_{2}O \rightarrow 2H_{2}O + H_{2}S + CO_{2}\uparrow$$
(11)
$$H_{2}S + H_{2}O \rightarrow 2H_{2}O^{+} + S^{2-} (12)$$
$$xNi^{+2} + yS^{-2} \rightarrow Ni_{x}S_{y}$$
(13)

(4) Sodium sulfate (SS)

$$Na_2 S \rightarrow 2Na^+ + S^-$$
(14)
$$xNi^{+2} + yS^{-2} \rightarrow Ni_x S_y$$
(15)

S2:Formulas used

All potentials mentioned in this work measured verses Hg/HgO as a saturated calomel electrode (SCE) and converted in to a reversible hydrogen electrode (RHE) scale according to Nernst equationwithout iR-correction. Equation for conversion of potential as

$$E_{RHE} = E_{SCE} + 0.059 \times pH + E^0 SCE \tag{16}$$

where, E_{RHE} , E_{SCE} , and E^0_{SCE} are potential verses RHE, potential vs. SCE, and standard redox potential of SCE at 298 K.

The overpotential (η) at a current density of the prepared samples were calculated from linear sweep voltammetry (LSV) curves using following equation,

$$\eta = E_{RHE} - 1.23 V \tag{17}$$

and Tafel slopes (b) were calculated by fitting linear portion of Tafelplot with Tafel equation as,

$$\eta = b \log j + a - 1.23 V \tag{18}$$

where, ' η ', 'j' and 'a' are overpotential, current density and fitting parameter, respectively.

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Figure. S1:: FE-SEM EDX images for Ni and S mapping on (a-a2) NiF, (b-b2) Ni_xS_y-STS, (c-c2) Ni_xS_y-TAA, (d-d2) Ni_xS_y-TU and (e-e2), Ni_xS_y-SS surfaces.



Figure.S2: FE-SEM images showing an uncomplete growth of; (a) Ni_xS_y-STS (1 gm), (b) Ni_xS_y-TAA (0.15 gm), (c) Ni_xS_y-TU (3 gm), (d) Ni_xS_y-SS (1.5 gm) superstructures at different magnifications.



Figure. S3: XPS spectra of; (a-a1) NiF, (b-b2) Ni_xS_y-TAA, (c-c2) Ni_xS_y-TU, (d-d2)Ni_xS_y-SS.



Figure. S4:(A) EIS spectrums of;(a) NiF, (b) Ni_xS_y -STS, (c) Ni_xS_y -TAA, (d) Ni_xS_y -TU, (e) Ni_xS_y -SS in the frequency range 0.01 HZ to 100 KHz (inset shows its enlarge view EIS spectrum at higher frequency regions), and (B) cyclability test of Ni_xS_y -STS electrocatalyzer at 10 mA.cm⁻² at current density (inset shoes stability curves of 1st and 1000th cycle). (C, D) FESEM images recorded at different magnifications showing the structural loss of Ni_xS_y .



Figure. S5: (a) XRD, (b) O, (c) Ni2p and (d) S 2p XPS spectrums of Ni_xS_y-STS electrode before and after OER test.