Supporting Information

Sulfur ion-exchange strategy to obtaining Bi_2S_3 nanostructures from Bi_2O_3 for better water splitting performance

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S1: Chemical reactions showing the synthesis of the Bi_2O_3 and its conversion to Bi_2S_3 in the presence of different sulphur ion sources

$$HCl \longrightarrow H^{+} + Cl^{-} \quad (1)$$

$$H_2O \longrightarrow H^{+} + OH^{-} \quad (2)$$

$$Bi(NO_3)_3.5H_2O \longrightarrow Bi^{++} + NO_3^{-} \quad (3)$$

$$NH_3 + NO_3^{-} \longrightarrow NH_2^{-} + HNO_3 \quad (4)$$

$$2Bi^{++} + 3NH_2^{-} \longrightarrow Bi(NH_2)_3 \quad (5)$$

$$Bi(NH_2)_3 + OH^{-} \longrightarrow 2Bi(OH)_3 \quad (6)$$

$$2Bi(OH)_3 \longrightarrow Bi_2O_3 + 3H_2O \quad (7)$$

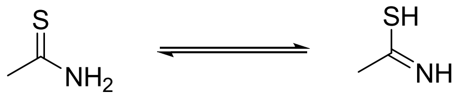
Formation of Bi_2S_3 from Bi_2O_2 in the presence of the sodium sulphate

$$Bi_2O_3 \longrightarrow 2Bi^{++} + 3O^{--} \quad (8)$$

$$Na_2S \longrightarrow 2Na^{+} + S^{--} \quad (9)$$

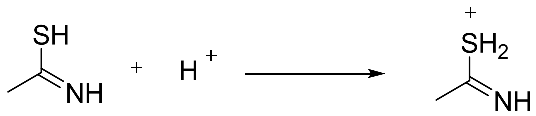
$$2Bi^{++} + 3S^{--} \longrightarrow Bi_2S_3 \quad (10)$$

Formation of Bi_2S_3 from Bi_2O_2 in the presence of the thioacetamide (TAA)



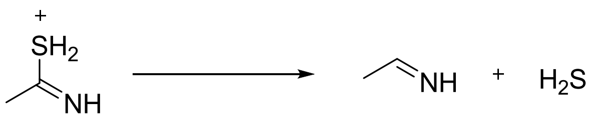
(11)

Protonation gives the following intermediate compound



(12)

Intermediate 12 dissociates to give H_2S



(13)

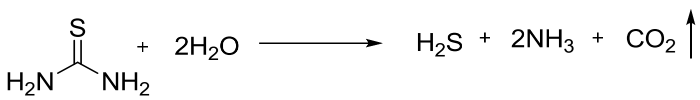
Hydrogen sulphide dissociates to give sulphur ions

$$H_2S \longrightarrow H^{+} + SH^{-} \quad (14)$$

$$SH^{-} \longrightarrow H^{+} + S^{--} \quad (15)$$

$$2Bi^{++} + S^{--} \longrightarrow Bi_2S_3 \quad (16)$$

Formation of Bi_2S_3 from Bi_2O_2 in the presence of the thiourea



(17)

$$H_2S + H_2O \longrightarrow 2H_2O + S^{--} \quad (18)$$

$$2Bi^{++} + S^{--} \longrightarrow Bi_2S_3 \quad (19)$$

*Formation of Bi_2S_3 from Bi_2O_2 in the presence of the s*odium thiosulfate (STS)

The half-cell reaction of reducing agent $Na_2S_2O_3$ is

$$S_2O_3^{--} \longrightarrow S_4O_6^{--} + 2e^{-} \quad (20)$$

Aqueous medium dissociation is shown as follows

$$S_2O_3^{--} + H^+ \longrightarrow HSO_3 + S \qquad (21)$$

Sulfur from reaction 21 captures electrons released in reaction 20 follows

$$S + 2e^- \longrightarrow S^{--} \qquad (22)$$

Finally, S ions react with bismuth ions to form bismuth sulphide

$$2Bi^{++} + S^{--} \longrightarrow Bi_2S_3 \qquad (23)$$

S1:

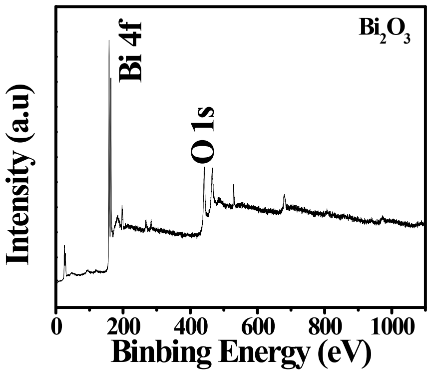


Figure S1: XPS surface analysis Bi_2O_3

S2:

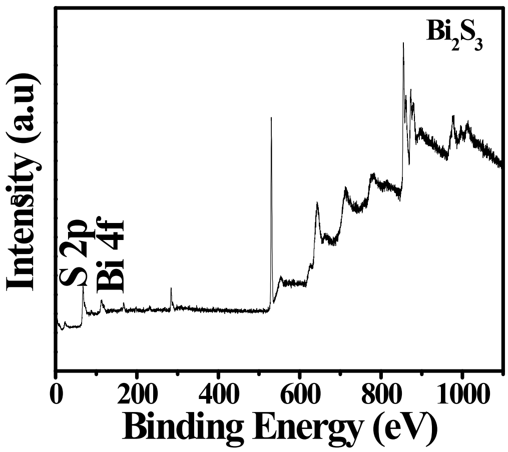


Figure S2: XPS spectrum of the Bi_2S_3 prepared from the thioacetamide.

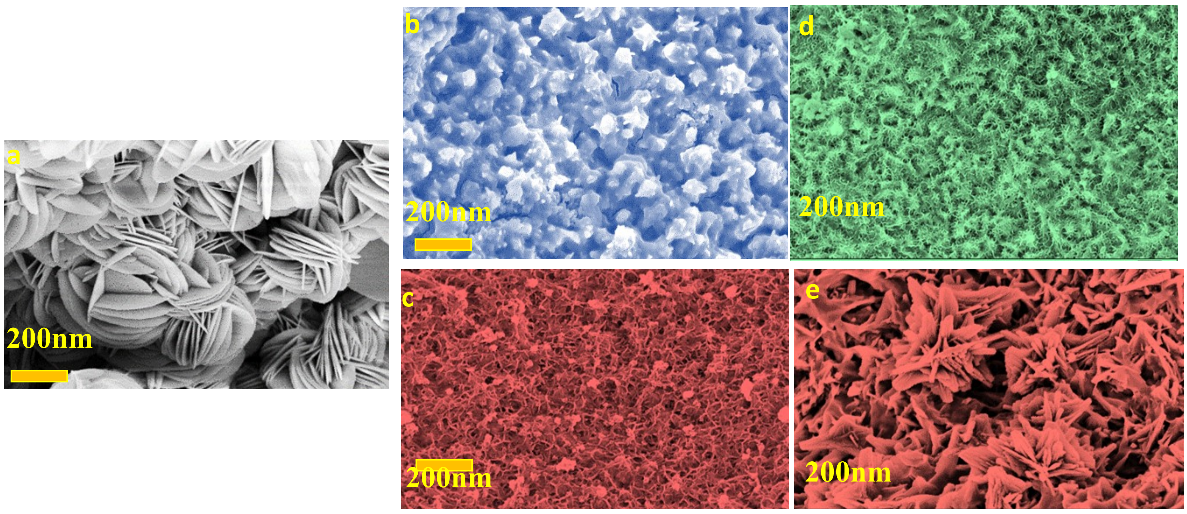


Figure S3. FE-SEM images of; (a) Bi_2O_3 and its conversion to Bi_3S_3 from SS(b), TAA (c), TU (d), and STS (e) sulphur sources at the same magnifications. Also, the bar scales on both sides are the same.

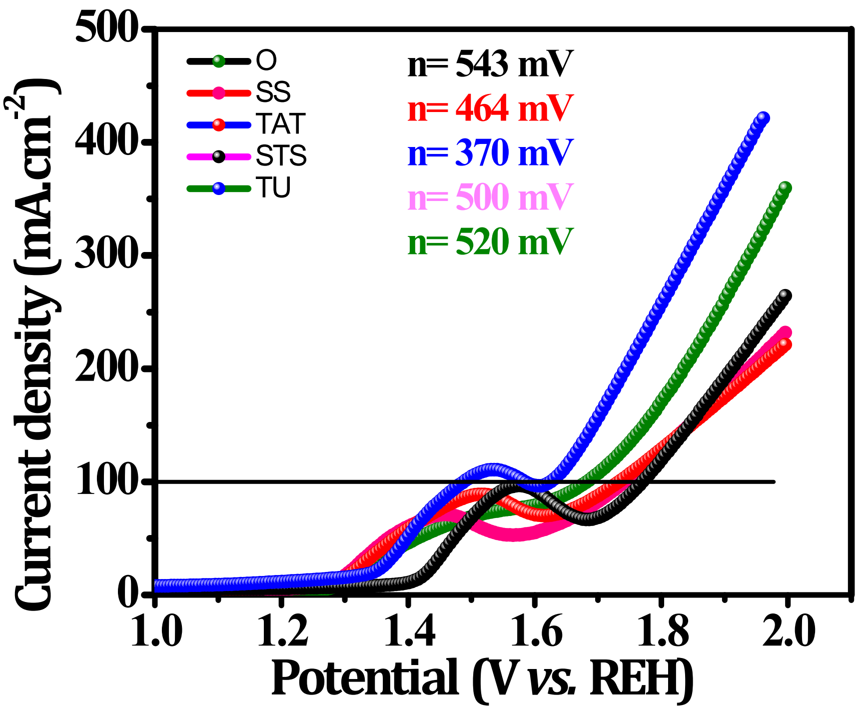


Fig. S4. OER performance for all electrodes.

S5

$$TOF = j*NA (F*n*I) \quad (24)$$

where j, NA, F, n, and I represent current density, the Avogadro constant, the Faraday constant, the number of electrons transferred to generate one molecule of the product, and the surface concentration or exact number of active sites catalyzing the reaction (m^{-2}), respectively.

Table S1. Comparison of surface area, pore-diameter, and performance of electrode.

Electrode	**Morphology**	**Surface area m^2 g^{-1}**	**Pore Diameter**
Bi_2O_3	Nanoplates	7.4	2.98
Bi_2S_3-SS	walnut-like	12.79	3.49
Bi_2S_3- TAA	Network	22.020	2.186
Bi_2S_3-TU	Nanowires	5.716	4.0
Bi_2S_3-STS	Nanoflowers	14.8	3.6