Supporting Information

3D Urchin-like Hierarchical Black TiO_2 Hollow Nanospheres: A Highly Active and Stable Electrocatalyst for Water Oxidation in Alkaline and Neutral Medium

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Turnover frequency (TOF) calculation:

The TOF value was calculated using the equation 1. [1]

$$TOF = \frac{J \times A}{4 \times F \times m} \quad (1)$$

J = current density at fixed overpotential

A = area of the glassy carbon electrode (0.0706 cm^{-2})

F = faraday constant (96485 C mol^{-1})

m = number of moles of the catalyst deposited onto glassy carbon electrode

The ECSA was calculated according to the equation 2.[2]

$$\text{ECSA} = \frac{C_{dl}}{C_s} \quad (2)$$

C_{dl} = double layer capacitance

C_s = specific capacitance

The faradaic efficiency (ε) of the OER system is proportional to the ratio of the ring current to the disk current and was calculated by using the equation 3.[2]

$$\text{Faradaic efficiency} = \frac{2 \times I_r}{I_d \times N} \quad (3)$$

where, I_r = ring current

I_d = disk current

N = collection efficiency (0.37)

Mass activity was calculated according to the equation 4. [2]

$$\text{Mass activity} = \frac{current\ density\ at\ a\ fixed\ potential}{catalytic\ loading} \quad (4)$$

Calibration of Hg/HgO

LSV was obtained for converting the electrode potentials into the reversible hydrogen electrode (RHE) scale. LSV (Figure S1) has been recorded in H_2-saturated 1 M KOH solution at a scan rate of 1 mVs^{-1} with Pt as the working electrode, graphite rod as the counter electrode and Hg/HgO as the reference electrode.[2] The correction factor obtained was 0.912, where the current crosses the zero line.

$$\text{So, E (RHE)} = \text{E (Hg/HgO)} + 0.912 \quad (5)$$

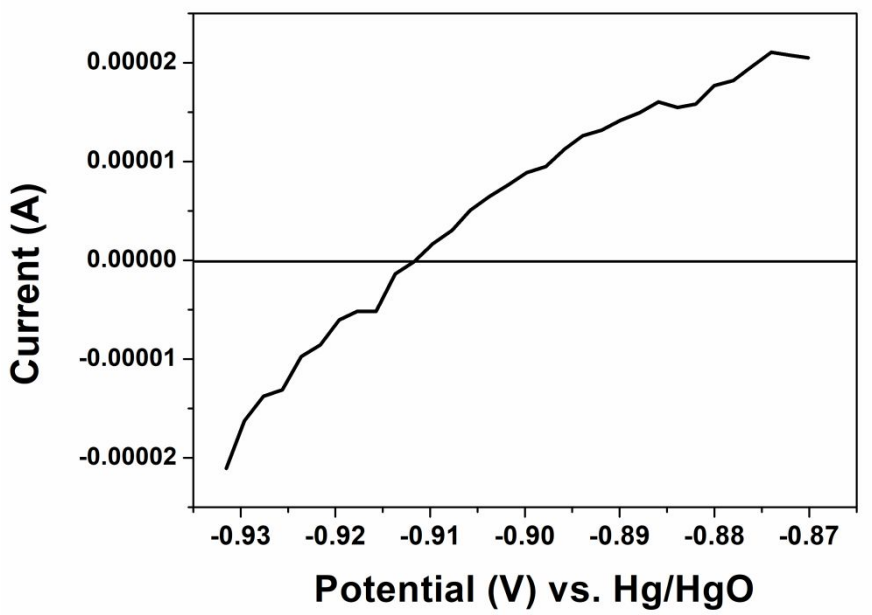

Figure S1. LSV for Hg/HgO to RHE calibration in H_2-saturated 1 M KOH solution recorded at a scan rate of 1 mVs^{-1}.

In alkaline medium, OER process follows four step reaction mechanisms.

$$M + OH^- \longrightarrow M\text{–}OH^* + e^- \quad (6)$$

$$M\text{–}OH^* + OH^- \longrightarrow M\text{–}O^* + H_2O + e^- \quad (7)$$

$$M\text{–}O^* + OH^- \longrightarrow M\text{–}OOH^* + e^- \quad (8)$$

$$M\text{–}OOH^* + OH^- \longrightarrow M + O_2 + H_2O + e^- \quad (9)$$

REFERENCES

(1) Yu, L.; Zhu, Q.; Song, S.; McElhenny, B.; Wang, D.; Wu, C.; Qin, Z.;, Bao, J.; Yu, Y.; Chen, S.; Ren, Z. Non-Noble Metal-Nitride Based Electrocatalysts for High-Performance Alkaline Seawater Electrolysis. *Nat. Comm.* **2019**, *10*, 5106.

(2) Vadakkekara, R.; Illathvalappil, R.; Kurungot, S. Layered TiO_2 Nanosheet-Supported $NiCo_2O_4$ Nanoparticles as an Efficient Bi-Functional Electrocatalyst for Overall Water Splitting. *ChemElectroChem* **2018**, *5(24)*, 4000-4007.