

Bifunctional electrocatalyst of low-symmetry mesoporous titanium dioxide modified with cobalt oxide for oxygen evolution and reduction reactions

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Supporting materials

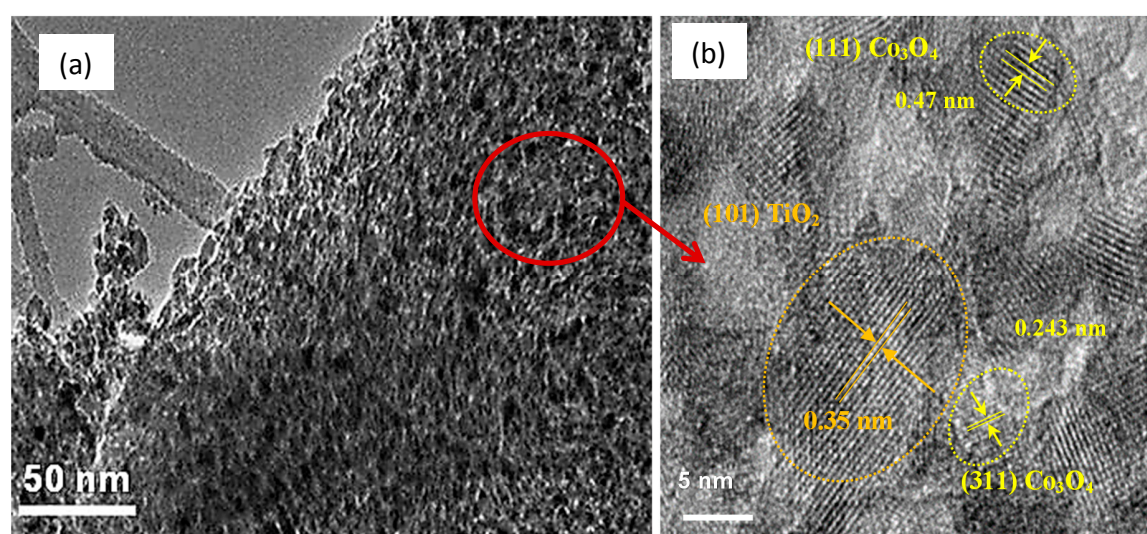


Figure S1 (a) TEM image for $\text{Co}_3\text{O}_4(7)/\text{lsm-TiO}_2$ with cobalt oxide nanoparticles, and (b) High magnification TEM showing the crystal fringes of the TiO_2 and Co_3O_4 nanoparticles.

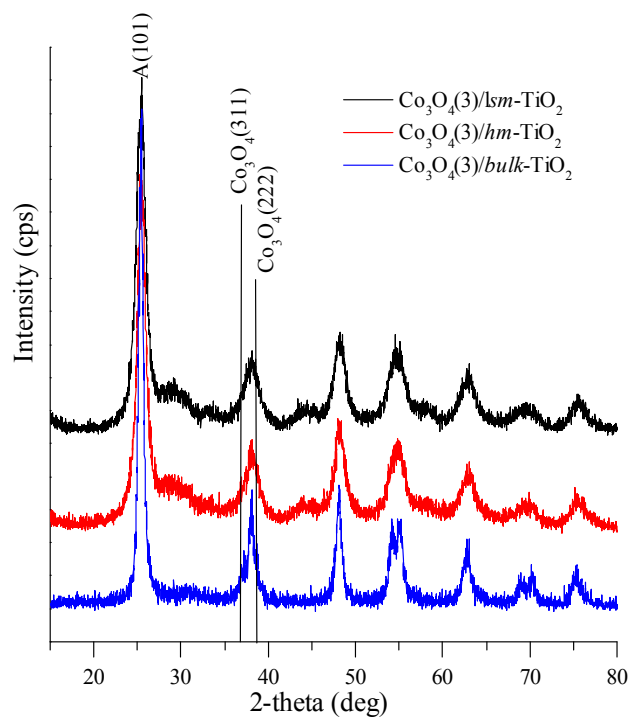


Figure S2 XRD spectra of $\text{Co}_3\text{O}_4(3)/\text{lsm-TiO}_2$, $\text{Co}_3\text{O}_4(3)/\text{hm-TiO}_2$ and $\text{Co}_3\text{O}_4(3)/\text{bulk-TiO}_2$.

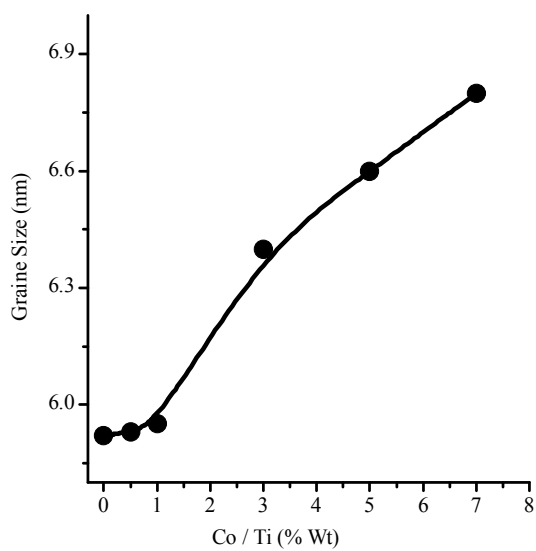


Figure S3 plot for the effect of varying cobalt content on the average crystallite size of the $\text{Co}_3\text{O}_4(x)/\text{lsm-TiO}_2$ catalysts.

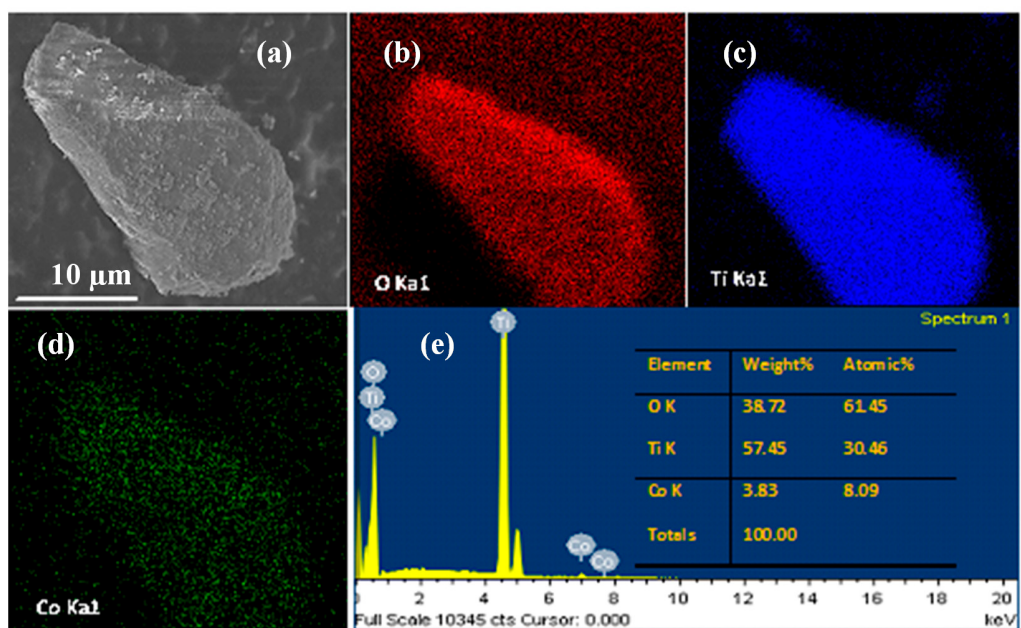


Figure S4 SEM-EDX elements mapping of Co(3)/hm-TiO₂.

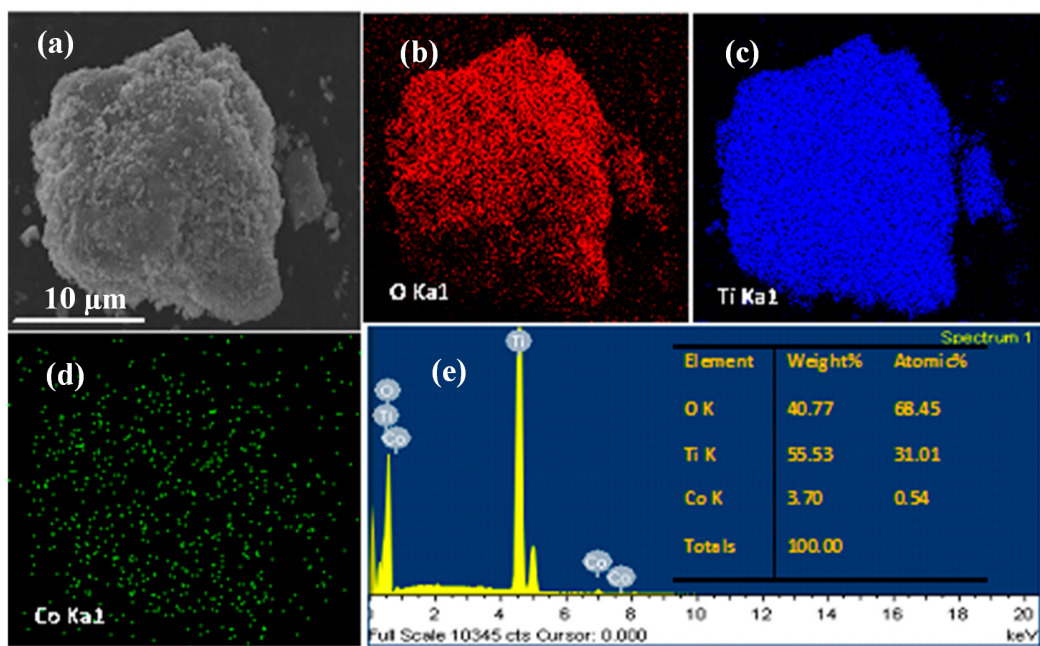


Figure S5 SEM-EDX elements mapping of Co(3)/lsm-TiO₂ catalyst.

Table S1. The atomic contents of Co, Ti, O in *lsm*-TiO₂ and Co₃O₄/*lsm*-TiO₂ according to the XPS reports.

Catalyst	O /atom %	Ti /atom %	Co /atom %	Co/(Co+Ti) %
<i>lsm</i> -TiO ₂	64.57	35.43	0	0
Co ₃ O ₄ (3)/ <i>lsm</i> -TiO ₂	70.90	28.25	0.85	2.92

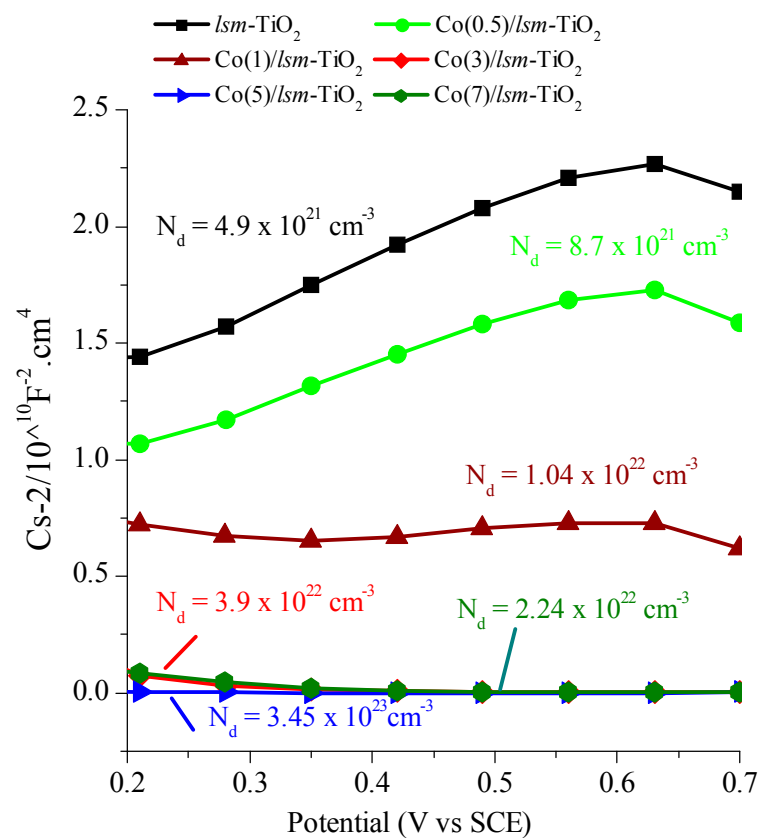


Figure S6 Mott-Schottky plot of pure *lsm*-TiO₂ and Co₃O₄ modified *lsm*-TiO₂ electrodes measured at 500 Hz.

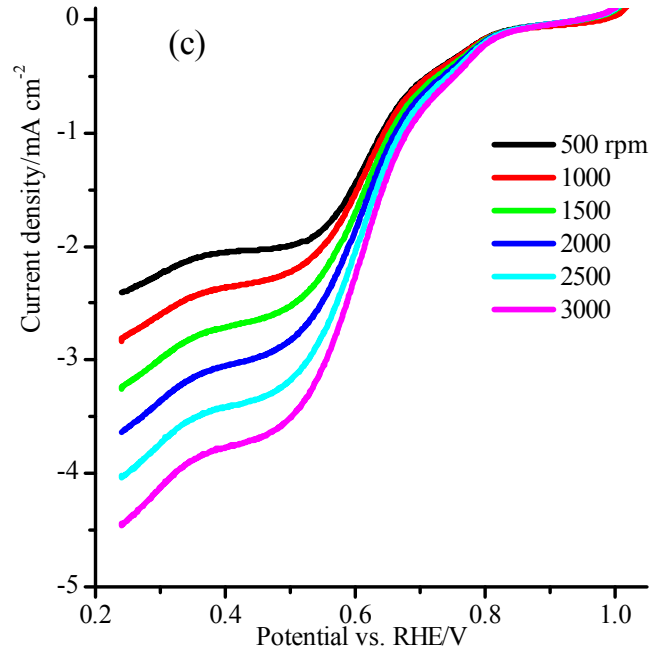


Figure S7 LSV curves of $\text{Co}_3\text{O}_4(3)/\text{lsm-TiO}_2$ at a scan rate of 10 mV s^{-1} and a rotation speed of 500, 1000, 1500, 2000, 2500, and 3000 rpm in O_2 -saturated 1.0 M KOH,

Turnover frequency (TOF) calculation method

The calculation of mass activity, specific activity, and turnover frequency (TOF) in this work is based on literature published by Gao *et al.* [52], and the details are shown below.

The values of mass activity (A g^{-1}) were calculated from the catalyst loading m ($0.8 \text{ mg cm}_{\text{geo}}^{-2}$) and the measured current density j ($\text{mA cm}_{\text{geo}}^{-2}$) at $\eta = 0.370 \text{ V}$:

$$\text{mass activity} = \frac{j}{m}$$

The values of specific activity (mA cm^{-2}) were calculated from the BET surface area S_{BET} ($\text{m}^2 \text{ g}^{-1}$), catalyst loading m ($0.8 \text{ mg cm}_{\text{geo}}^{-2}$), and the measured current density j ($\text{mA cm}_{\text{geo}}^{-2}$) at $\eta = 0.370 \text{ V}$:

$$\text{specific activity} = \frac{j}{10 \cdot S_{\text{BET}} \cdot m}$$

The values of turnover frequency (TOF) were calculated by assuming that every metal atom is involved in the catalysis (lower TOF limits were calculated):

$$\text{TOF} = \frac{j S_{\text{geo}}}{4F \cdot n}$$

Here, j ($\text{mA cm}_{\text{geo}}^{-2}$) is the measured current density at $\eta = 0.370 \text{ V}$, S_{geo} (1.0 cm^2) is the surface area of FTO electrode, the number 4 means 4 electrons per mole of O_2 , F is Faraday's constant ($96485.3 \text{ C mol}^{-1}$), and n is the moles of the metal atom on the electrode calculated from m and the molecular weight of the coated catalysts.

Table S2 comparison of OER performance for $\text{Co}_3\text{O}_4(3)/\text{lsm-TiO}_2$ with other reported OER electrocatalysts in alkaline media.

Catalyst	[KOH]/mole	Onset potential (V vs RHE)	η at 10 mA cm^{-2} (mV)	Tafel slope mV dec^{-1}	Mass activity at 1.6 V vs RHE (A g^{-1})	Ref.
$\text{Co}_3\text{O}_4(3)/\text{lsm-TiO}_2$	0.1	1.65	445	87	4.25	This Work
	1.0	1.48	350	54	41.8	
	5.0	1.45	243	71	88.9	
Co-TiO ₂ NCs	0.1	1.60	N/A	67	N/A	S1
Cobalt- Black TiO ₂ NAs	1.0	1.582	352	65	N/A	S2
Co-S/Ti mesh	1.0	1.549	361	64	N/A	S3
$\text{Co}_3\text{O}_4/\text{MWCNT}$	0.1	1.51	390	65	N/A	S4
<i>meso</i> - Co_3O_4 -35	0.1	1.520	411	80	63	S5
<i>meso</i> - Co_3O_4 -100	0.1	1.53	426	66	53	S5
Co_3O_4 NPs	0.1	~ 1.57	449	63	31	S5
CoO/CNT	1.0	1.54	550	108	43	S6
<i>meso</i> - Co_3O_4	1.0	N/A	476	N/A	22	S7
6 nm Co_3O_4 NPs	1.0	-	328	~70	35	S8
<i>meso</i> - Co_3O_4	1.0	1.58	353	84	21.3 at 0.4 V	S9
$\text{Co}_3\text{O}_4/\text{Fe}_3\text{O}_4$ mesoporous	1.0	-	322	78	34.4 at 0.4 V	S9
$\text{Co}_3\text{O}_4/\text{CoO}$ SC	0.5	-	430	89	234 at 0.4 V	S10
$\text{NiCo}_2\text{O}_4/\text{NiO}$	1.0	1.55	361	61	29.31 at 1.65 V	S11
NiCo_2O_4	1.0	-	431	139	8.05 at 1.65 V	S11

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