

SUPPLEMENTARY INFORMATION

From Doping to Composites: Zirconia (ZrO_2) Modified Hematite Photoanodes for Water Splitting

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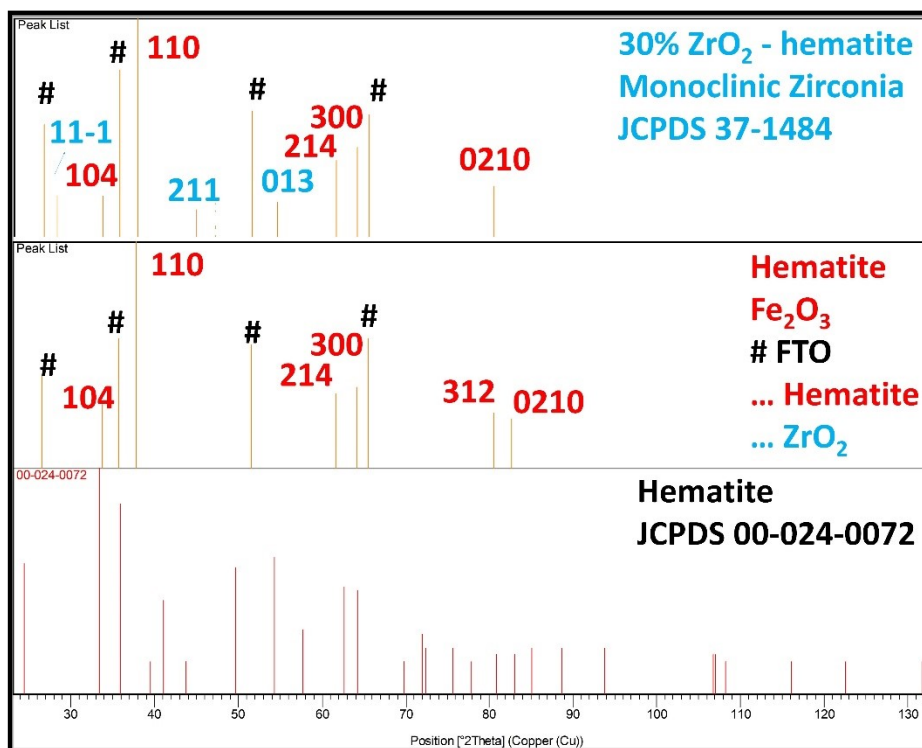


Fig S1(a) XRD line pattern for hematite as taken from the JCPDS (00-024-0072)

,experimental XRD patterns taken for a sample of pristine hematite and a sample of 30 wt.% zirconia/hematite deposited on FTO, respectively.

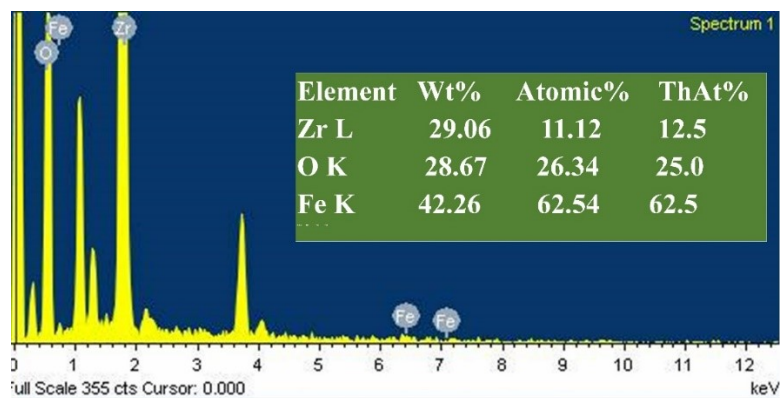
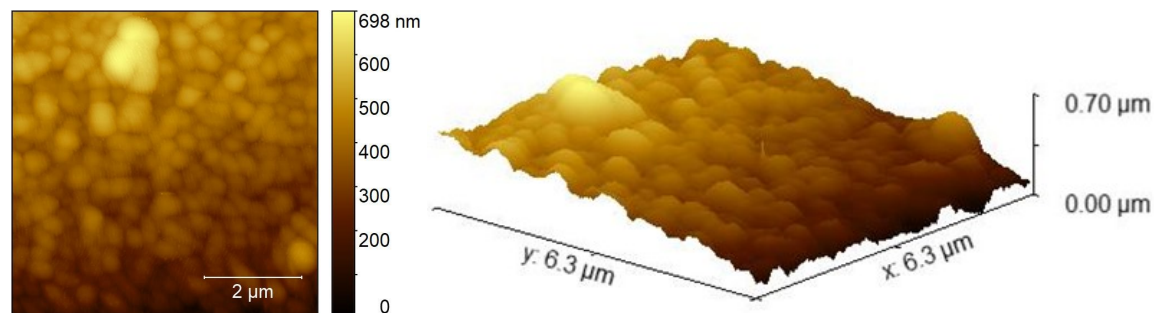


Fig. S2. EDX spectrum for a sample of 30 wt% zirconia added hematite. The corresponding quantitative analysis is provided in the inset table.



Roughness (Ra): 6.076 nm

Root mean square roughness (RMS): 7.641nm

Fig.S3. AFM images of $ZrO_2/\alpha-Fe_2O_3$ (a) 2D and (b) 3D showing topography of the films and an estimation of the surface roughness.

Table S1. Average crystallite size, from XRD data using Scherrer formula, of Zirconia added- α -Fe₂O₃ films prepared by AACVD method.

Amount of added ZrO₂ / wt.%	Crystallite size / nm
2	7
5	13
10	17
20	42
30	14
40	11

Table S2 Direct optical band gaps of zirconia added hematite as a function of composition as calculated from analysis of DR-UV-VIS data from K-M plots

Amount of added zirconia/wt%	Band gap/eV
0 (pure Fe ₂ O ₃)	2.03
2	2.02
5	1.99
10	1.85
20	2.07
30	2.14
40	1.96
100 (<i>m</i> - ZrO ₂)	3.6

Table S3.% IPCE vs wave length and potential of 30% zirconia added hematite.

Photoanode	% IPCE vs. Wavelength	% IPCE vs. Potential
Hematite	18%@265 nm 18%@285 nm	<u>0.53%@0.23 V</u>
30 wt.% ZrO ₂ /Fe ₂ O ₃	48% @ 265 nm 58%@ 285 nm	<u>11%@0.23 V</u>

Table S4. Photocurrents and onset potentials (E_{onset}) for $\text{ZrO}_2/\text{hematite}$ as a function of composition.

Amount of added ZrO_2 / wt. %	$E_{\text{onset}} / \text{V}$	Photocurrent density mA/cm^2 @1.23V
0	0.86	1.23
2	0.95	0.21
5	0.78	0.48
10	0.78	0.63
20	0.74	2.12
30	0.73	3.06
40	1.06	1.03

Table S5. Electron lifetimes for hematite as compared to 30 wt.% zirconia/hematite

Amount of added ZrO₂ / wt.%	Electron lifetime / ms
0	0.175
30	1.690

Table S6. Amounts of hydrogen and oxygen evolved (as determined by GC) as a function of time for pristine hematite and 30 wt.% zirconia/hematite

Time / h	H ₂ evolved / μmol cm ⁻²		O ₂ evolved / μmol cm ⁻²	
	α-Fe ₂ O ₃	30 wt.% ZrO ₂ /α-Fe ₂ O ₃	α-Fe ₂ O ₃	30 wt.% ZrO ₂ /α-Fe ₂ O ₃
1	0	0.27	0.721	4.49
2	0.45	0.47	0.956	5.16
3	0.121	0.69	0.977	6.78
4	0.215	0.74	1.063	7.89
5	0.328	0.94	1.174	9.39
6	0.402	1.02	1.23	11.04