Electronic Supporting Information

Visible Light Driven Photoelectrochemical Water Oxidation by Zn- and Ti- doped Hematite Nanostructures

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Table S1. A comparison of parameters for preparation of undoped hematite electrode and the photoelectrochemical activity of the prepared electrode in the water oxidation reaction

Electrodeposition condition				**Photoelectrochemical activity**	
potential range (V) - substrate	scan rate ($mV\ s^{-1}$)	Number of cycle	Annealing temperature and duration (ºC) - (min)	Current density[(a)] and scan rate ($mA\ cm^{-2}$) - ($mV\ s^{-1}$)	Ref.
-0.52 to 0.41 *vs.* SCE[(b)] - FTO	100	100	700 - 30	~ 1.5 at 100	[1]
-0.52 to 0.41 *vs.* Ag/AgCl (1M KCl) - FTO	100	100	800 - 10	~ 0.3 at 50	[2]
-0.49 to 0.41 *vs.* Ag/AgCl - Pt/Ti	100	5	700 - 240	~ 0.8 at 100	[3]
-0.2 to 0 *vs.* SCE - FTO	20	30	450 - 60	~ 0.12	[4]
-0.2 to 0.4 *vs.* Ag/AgCl (saturated KCl) - FTO	200	100	800 - 10	~1.1 at 10	This work

(a) at 1.6 V *vs.* RHE (reversible hydrogen electrode) in 1 M NaOH; (b) saturated calomel electrode

References:

(1) Bak, A.; Choi, W.; Park, H. *Appl. Catal., B* **2011**, *110*, 207-215.

(2) Franking, R.; Li, L. S.; Lukowski, M. A.; Meng, F.; Tan, Y. Z.; Hamers, R. J.; Jin, S. *Energy Environ. Sci.* **2013**, *6*, 500-512.

(3) Hu, Y. S.; Kleiman-Shwarsctein, A.; Forman, A. J.; Hazen, D.; Park, J. N.; McFarland, E. W. *Chem. Mater.* **2008**, *20*, 3803-3805.

(4) Kumar, P.; Sharma, P.; Shrivastav, R.; Doss, S.; Satsangi, V. R. *Int. J. Hydrog. Energy* **2011**, *36*, 2777-2784.

Table S2. Molar ratio % of elements in the electrolyte and electrodeposited film

Sample	Molar ratio % in the electrolyte			Molar ratio % in the film		
	Fe	**Zn**	**Ti**	**Fe**	**Zn**	**Ti**
Pristine hematite	100	0	0	100	0	0
Zn-modified hematite	89.29	10.71[(a)]	0	98.43	1.55[(a)]	0
Ti-modified hematite	98.04	0	1.96[(b)]	99.06	0	0.94[(b)]
Ti + Zn-modified hematite	93.02	5.58[(c)]	1.40[(d)]	96.32	2.75[(c)]	0.93[(d)]

(a) [Zn] / ([Zn] + [Fe]); (b) [Ti] / ([Ti] + [Fe]); (c) [Zn] / ([Ti] + [Zn] + [Fe]); (d) [Ti] / ([Ti] + [Zn] + [Fe]).

Figure S1.

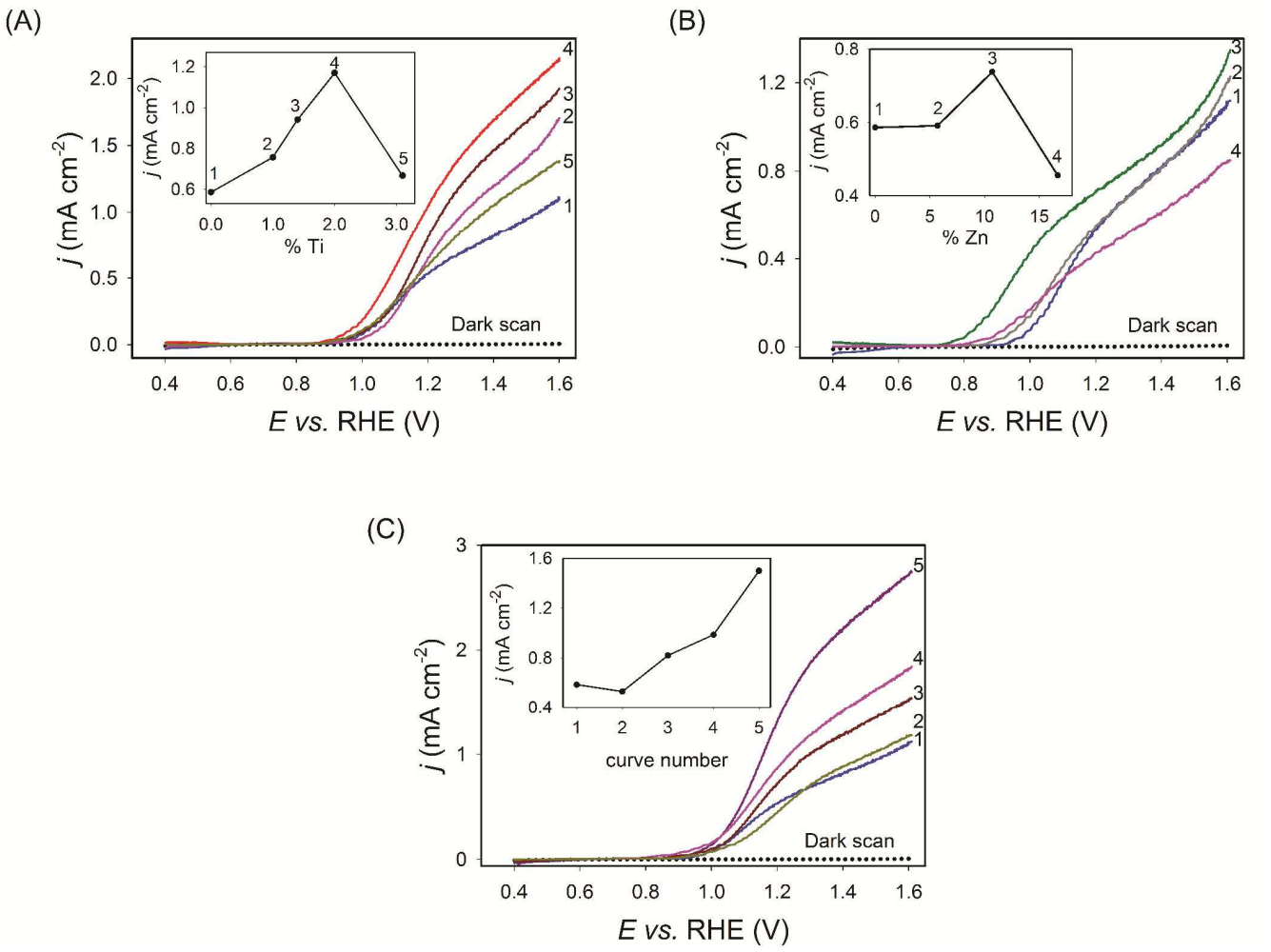

Figure S1. (A) Representative LSV indicating the photocurrent density of the FTO electrode modified in solution of ferric chloride + (1) 0, (2) 0.99, (3) 1.38, (4) 1.96 and (5) 3.10% Ti. (B) Representative LSV indicating the photocurrent density of the FTO electrode modified in solution of ferric chloride + (1) 0, (2) 5.66 , (3) 10.71 and (4) 16.67% Zn. (C) Representative LSV indicating the photocurrent density of the FTO electrode modified in solution of ferric chloride + (1) 0 + 0 , (2) 1.23 + 10.58, (3) 1.85 + 5.56, (4) 1.92 + 1.92 and (5) 1.40% Ti + 5.58% Zn. Dotted lines represent the LSV in the dark condition. Insets of Figure S1A and B represent the plots of the photocurrent density observed at 1.23 V *vs.* RHE as a function of dopant % in the electrodeposition solution whereas insets of Figure S1C represents the plot of the photocurrent density observed at 1.23 V *vs.* RHE as a function of curve number.

Figure S2.

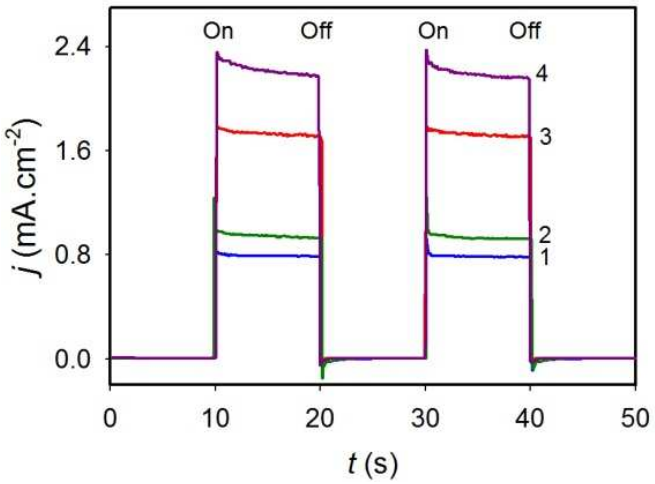

Figure S2. Representative photocurrent density at 1.4 V *vs.* RHE under simulated illumination recorded for the (1) pristine hematite (2) 10.71% Zn-, (3) 1.96% Ti- and (4) 1.40% Ti + 5.58% Zn-modified hematite electrode.

Figure S3.

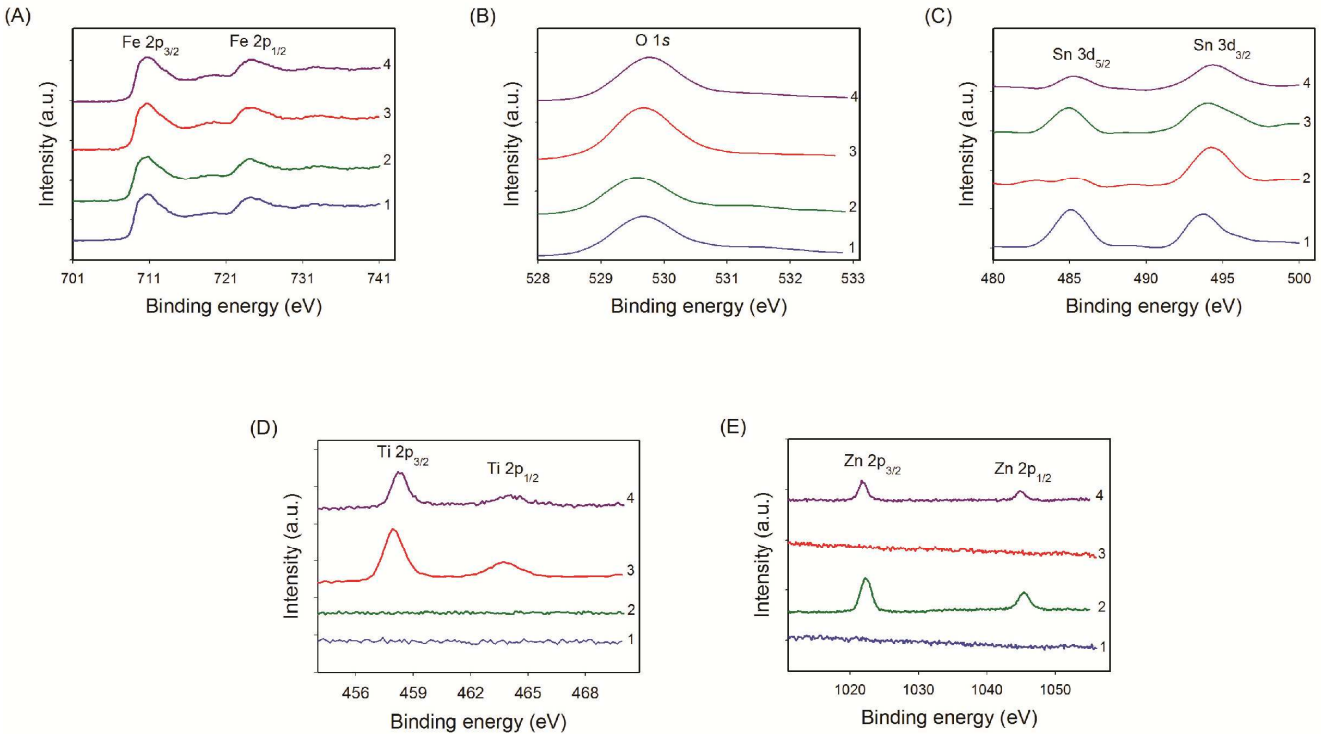

Figure S3. The XPS spectrum of: (A) Fe 2p, (B) O 1s, (C) Sn 3d, (D) Ti 2p and (E) Zn 2p recorded for the (1) pristine hematite, (2) Zn-, (3) Ti- (3) and (4) Ti + Zn-modified hematite electrode. The tin signals were collected from the survey data.

Figure S4.

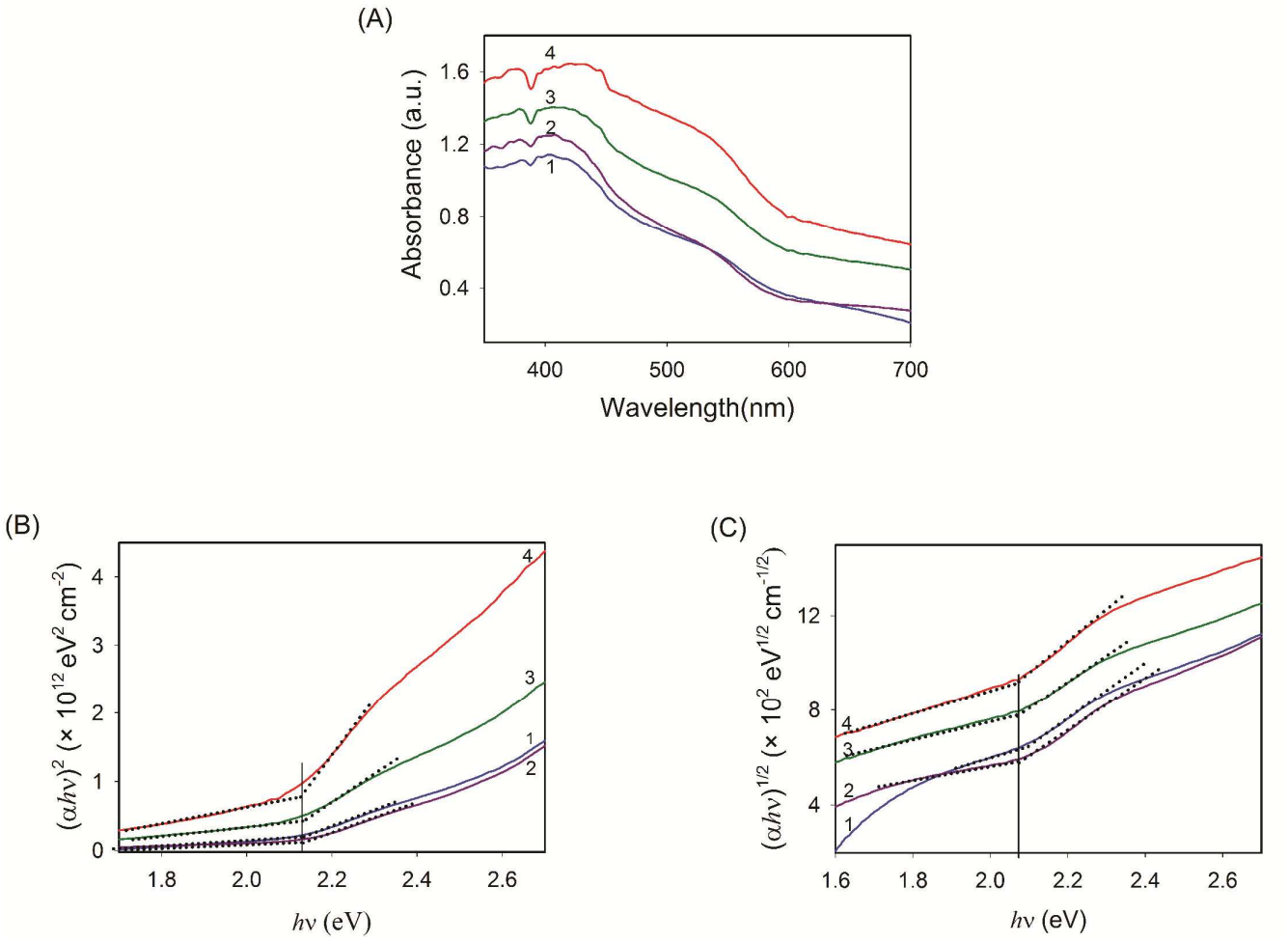

Figure S4. (A) Representative UV-vis spectra and Tauc-Plots used for evaluation of the optical band gap for (B) direct and (C) indirect case of the (1) pristine hematite, (2) Ti + Zn-, (3) Zn- and (4) Ti-modified hematite electrode.

Figure S5.

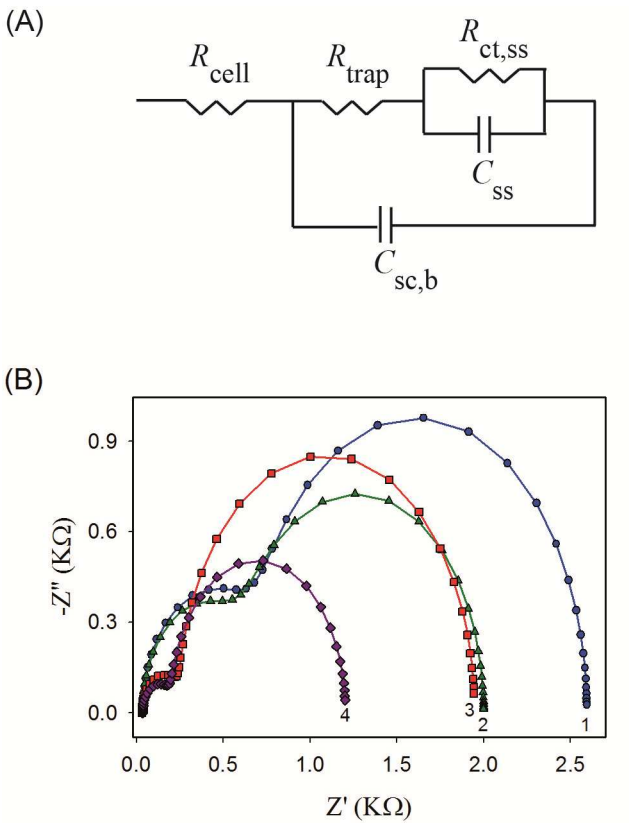

Figure S5. (A) Equivalent circuit used to fit EIS data measured under illumination condition. (B) Nyquist plots measured at 1 V *vs.* RHE for the (1) pristine hematite, (2) Zn- , (3) Ti- and (4) Ti + Zn-modified hematite electrode under standard illumination condition.