

Supporting Information

Spray Pyrolysis Deposition of ZnFe₂O₄/Fe₂O₃ Composite Thin Films on Hierarchical 3-D Nanospikes for Efficient Photoelectrochemical Oxidation of Water

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XRF results:

The surface composition of the prepared composites were analysed by XRF and the results are presented in Figure S1. The simple molar ratio between Zn and Fe in composite ZF3 was kept to be 1:8 which is consistent with the XRF results, Figure S1 (A). The simple mole ratio between ZnFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ in composite ZF3 would be 1:3, and can be justified as follows.

$$\begin{array}{ccc} \text{Zn} & : & \text{Fe} \\ 1 & : & 8 \end{array}$$

So the simple ratio between ZnO and $\alpha\text{-Fe}_2\text{O}_3$ in ZF-3 would be as follows

$$\begin{array}{ccc} \text{ZnO} & : & \text{Fe}_2\text{O}_3 \\ 1 & : & 4 \end{array}$$

One mole of ZnO combine with the one mole of $\alpha\text{-Fe}_2\text{O}_3$ to form one mole of ZnFe_2O_4 as follows.

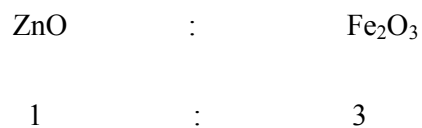


The remaining 3 moles of $\alpha\text{-Fe}_2\text{O}_3$ will remain as such, therefore the simple molar ratio between ZnFe_2O_4 and Fe_2O_3 will be 1:3.

According to XRF results shown in figure S1 (B), the simple molar ratio between Zn and Fe in composite ZF2 was 1:6. The simple mole ratio between ZnFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ in ZF2 would be 1:2 and can be justified as under.

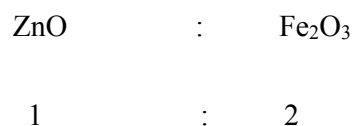
$$\begin{array}{ccc} \text{Zn} & : & \text{Fe} \\ 1 & : & 6 \end{array}$$

Ratio between ZnO and $\alpha\text{-Fe}_2\text{O}_3$ would be as follows.



One mole of $\alpha\text{-Fe}_2\text{O}_3$ out of three moles, combines with ZnO to form ZnFe_2O_4 . Therefore, simple ratio between ZnFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ in composite ZF-2 would be 1:2.

Figure S1 (C) shows the XRF results of composite ZF-1 according to which the simple molar ratio between Zn and Fe is 1:4. So the ratio between ZnO and $\alpha\text{-Fe}_2\text{O}_3$ will be 1:2.



ZnFe_2O_4 is formed by reacting one mole of ZnO with the one mole of $\alpha\text{-Fe}_2\text{O}_3$, so the final ratio between ZnFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ in composite ZF1 would be 1:1.

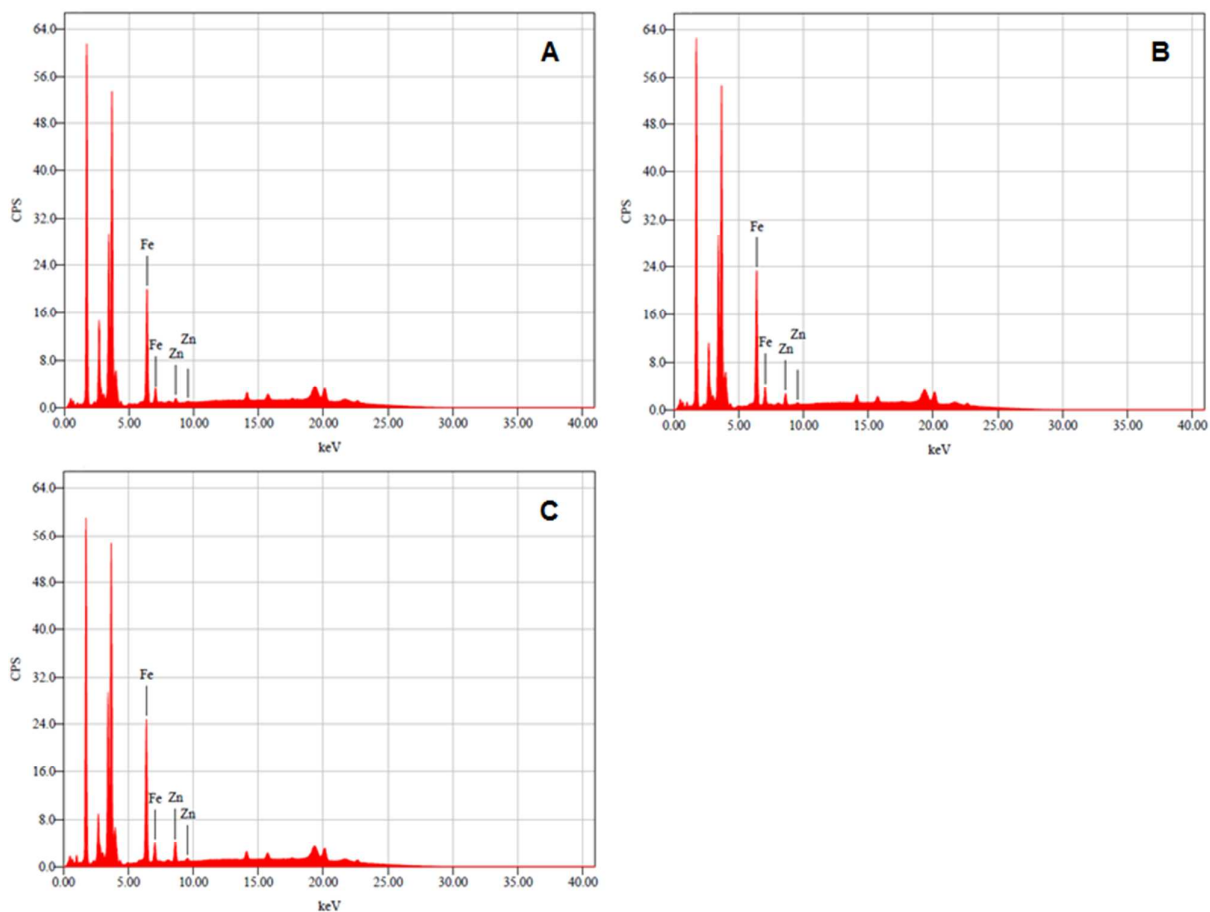


Figure S1: XRF results of $\text{ZnFe}_2\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ composites, ZF3 (A), ZF2 (B), ZF1 (C)

Energy dispersive X-Ray spectroscopic (EDS) mapping

The elemental mapping for Zn, Fe, O, Sn, Ti, Pt and Al are shown in figure S2. The protective layers of Ti and Pt against basic electrolyte are clear in their respective elemental mapping shown in Fig S2 (G) and (H). The mapping of Sn of FTO layer can also be seen in section (I) of figure S2. The mapping of other fundamental elements of the composites like Fe and Zn are shown in section (D) and (E) of figure S2.

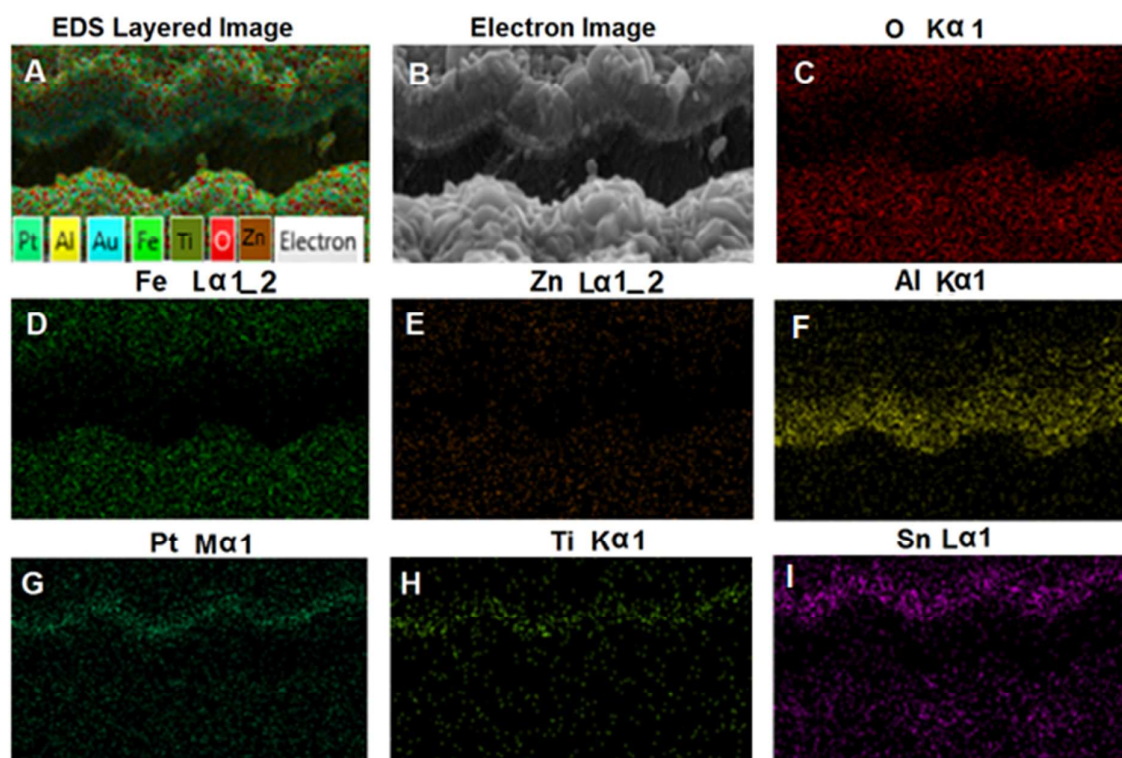


Figure S2: Energy dispersive X-Ray spectroscopic images of composite ZF2 deposited on 3D template.

UV-Vis Study:

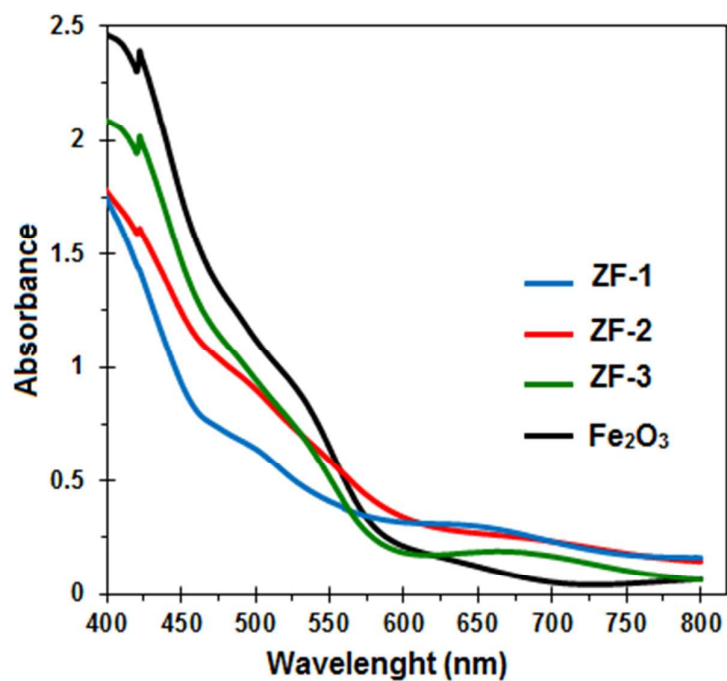


Figure S3: UV-Vis absorption spectra of composites, α -Fe₂O₃ (Black), ZF3 (Green), ZF2 (Red), and ZF1 (Blue) deposited on FTO coated glass.

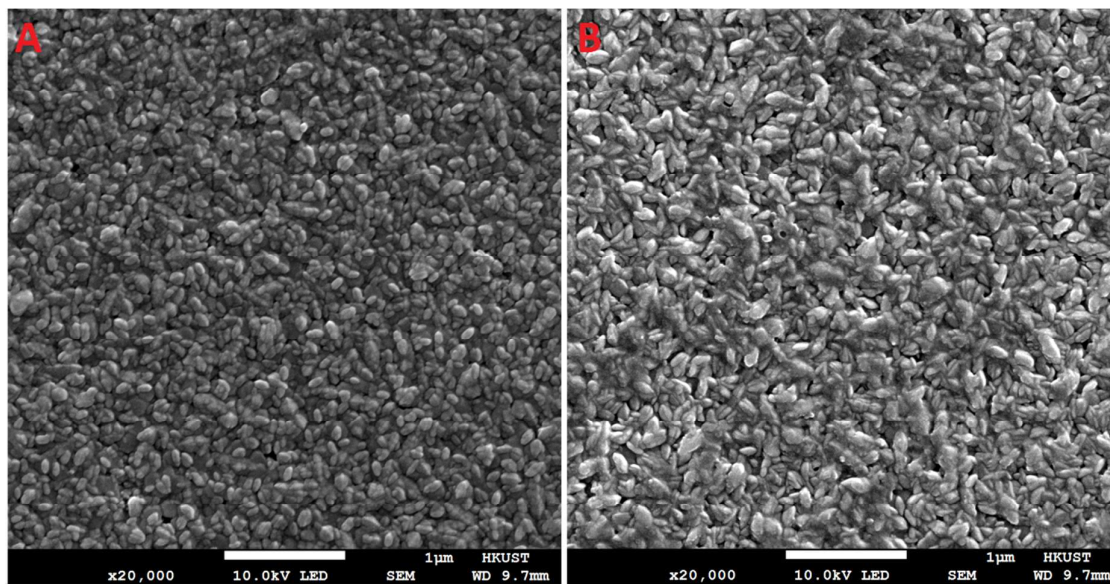


Figure S4: (A) Low magnification SEM images of ZnFe₂O₄/α-Fe₂O₃ composite (ZF2), (B) Low magnification SEM images of ZnFe₂O₄/α-Fe₂O₃ composite (ZF1).

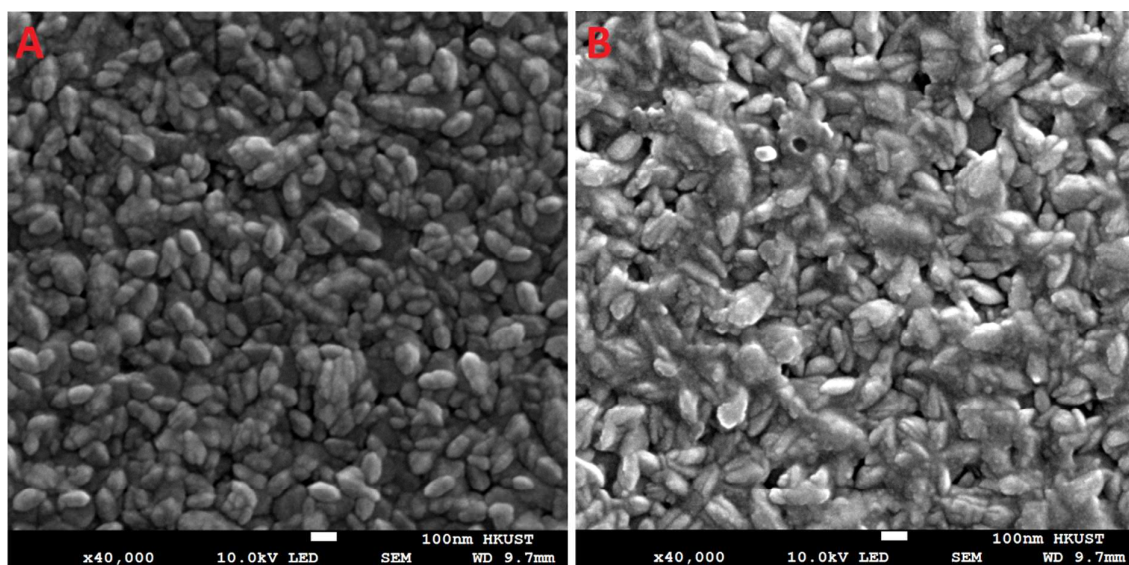


Figure S5: (A) High magnification SEM images of $\text{ZnFe}_2\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ composite (ZF2), (B) High magnification SEM images of $\text{ZnFe}_2\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ composite (ZF1).

Table S1: Molar concentrations of the precursor solutions used and percent composition obtained from XRF analysis.

Code	Molar Concentration of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Molar Concentration of $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$	Composition: Fe : Zn		Composition: ZnFe_2O_4 , Fe_2O_3	
			Fe	Zn	ZnFe_2O_4	Fe_2O_3
ZF1	0.05	0.25	4	1	1	1
ZF2	0.05	0.15	6	1	1	2
ZF3	0.05	0.1	8	1	1	3