Supplementary Information

Facile growth of hierarchical hematite (α-Fe_2O_3) nanopetals on FTO by pulse reverse electrodeposition for photoelectrochemical water splitting

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X-diffraction study

Fig.S1 shows the XRD patterns of Fe_2O_3 photoanodes prepared by pulse reverse and normal electrodeposition methods in the diffraction angle (2θ) range of 20-100^o (step size: 0.013^o s^{-1}, dwelling time: 24 s). Both the samples are polycrystalline with hematite crystal structure. However, Fe_2O_3 prepared by pulse reverse electrodeposition is more crystalline since the intensity of hematite peaks at 24.152, 33.164, 35.636^o is enhanced as compared to that of Fe_2O_3 prepared by normal electrodeposition method.

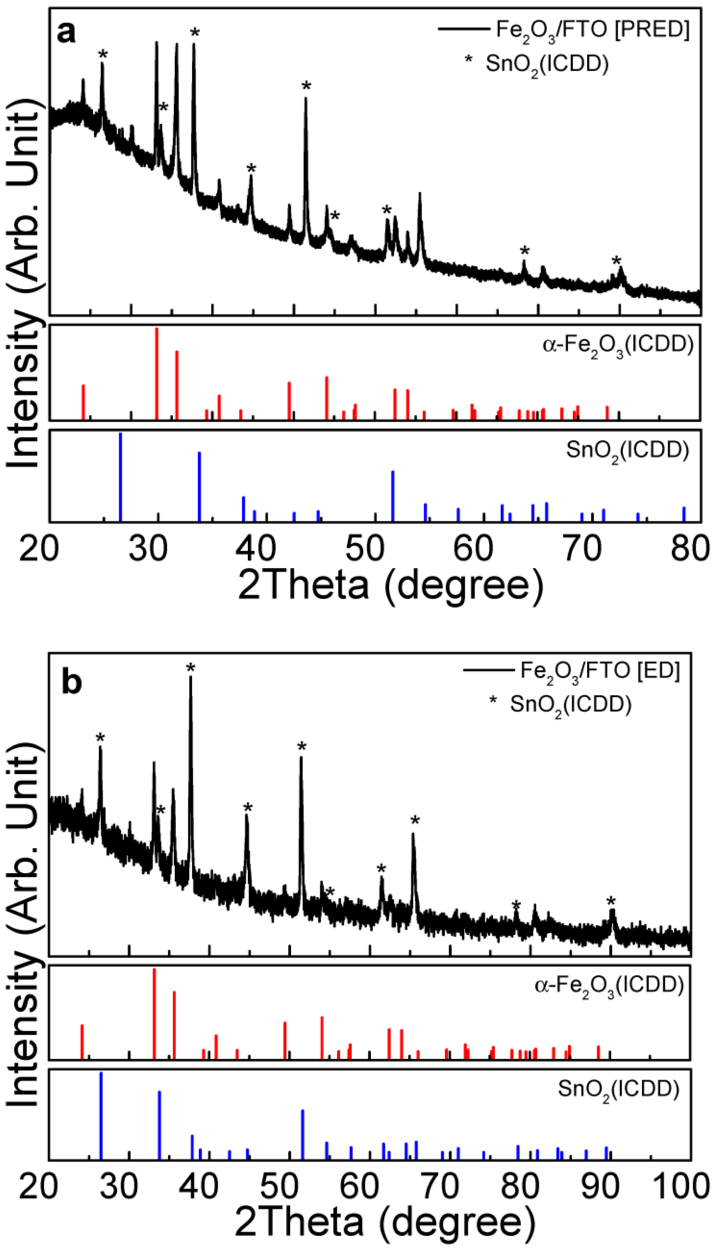


Fig.S1 X-ray diffraction (XRD) patterns of Fe_2O_3/FTO photoanodes prepared by (a) pulse reverse electrodeposition (PRED) and (b) normal electrodeposition (ED).

Scanning electron microscopy study

Fig.S2 shows the low magnification SEM images of Fe_2O_3/FTO photoanode prepared by normal electrodeposition. The Fe_2O_3 film shows agglomerated morphology. Some white impurity overgrowths are seen.

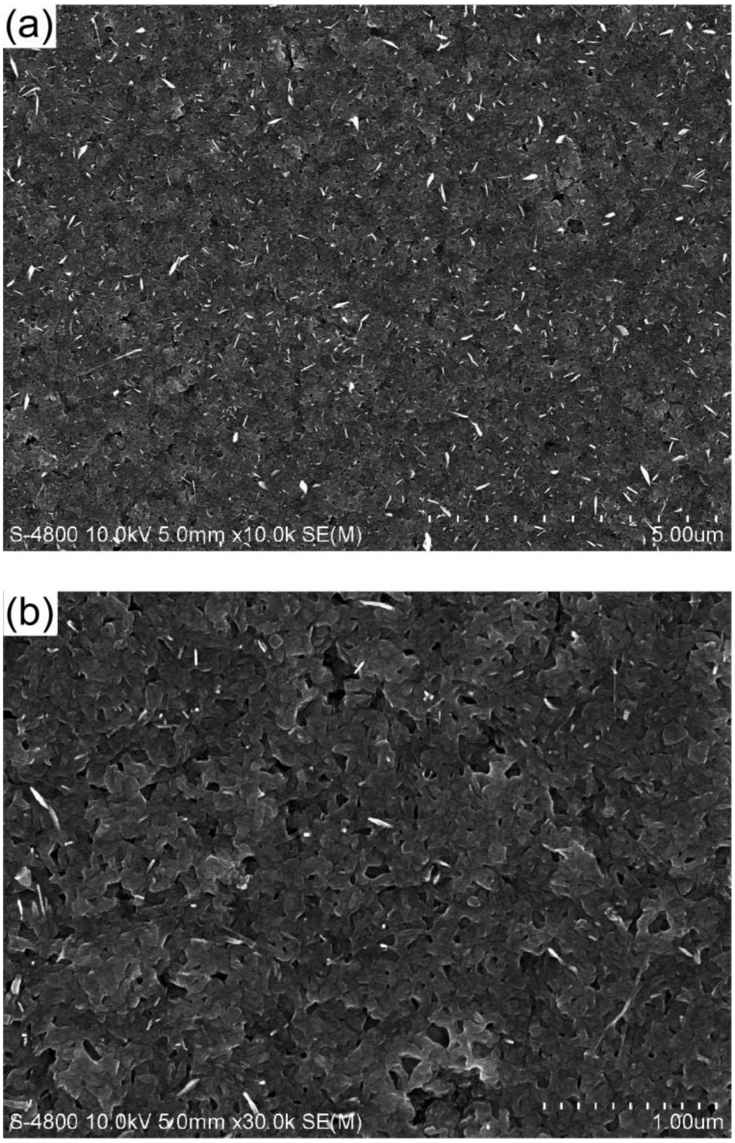


Fig.S2 SEM images of Fe_2O_3/FTO photoanode prepared by normal electrodeposition. Magnification, Scale bar: (a) 10K, 5 μm; (b) 30K, 1 μm;

UV-Vis absorption study

The band gap energy was calculated from the absorbance (αt) data of Fe_2O_3 recorded in the wavelength range of 350-800 nm using Tauc relation (1);

$$\alpha h\nu = A_o(h\nu - E_g)^n \qquad \text{… (1)}$$

where, $$A_o = \left[\frac{e^2}{nch^2 m_e^*}\right](2m_r)^{3/2} \qquad \text{… (2)}$$

Here, α is the measured absorption coefficient (cm^{-1}) near the absorption edge, t is the film thickness, A_o is a constant, hν is photon energy (eV), E_g is optical band gap (eV), n is a constant. The value of n is determined from the nature of optical transition. n=2 or 3 for indirect allowed and indirect forbidden transition, respectively and n=1/2 or 3/2 for direct allowed and direct forbidden transition, respectively. m_e* and m_r are the effective and reduced masses of charge carriers, respectively.

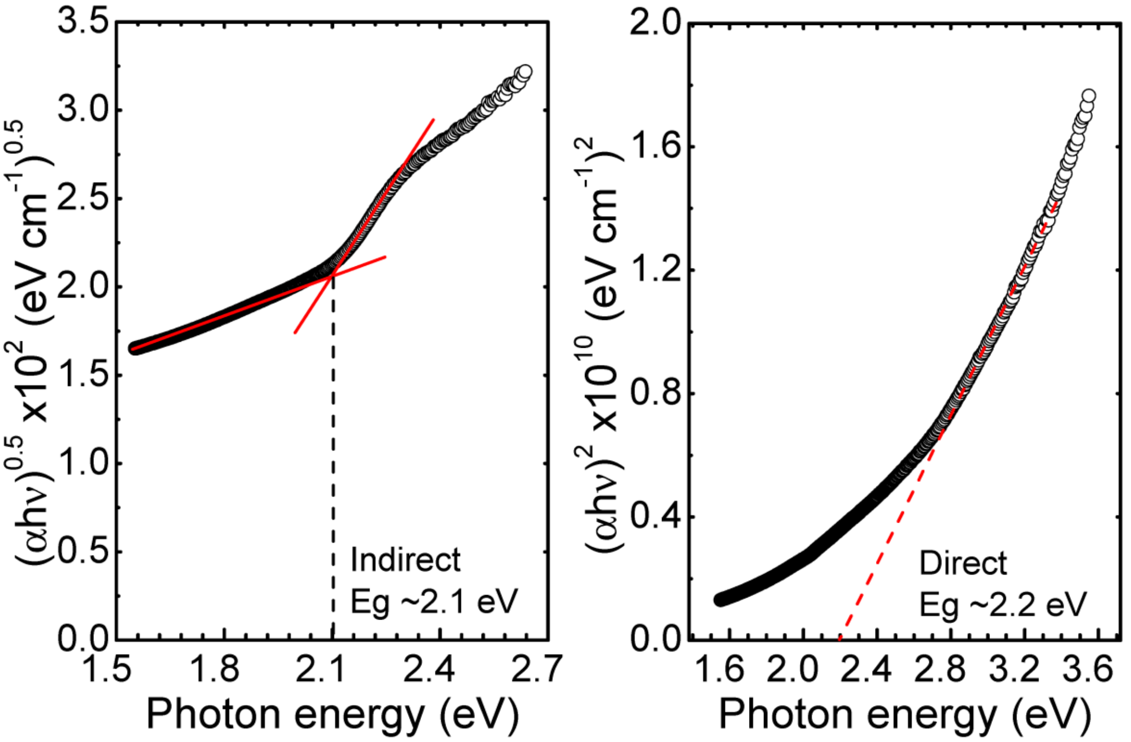


Fig. S3 Tauc plot i.e. plot of $(\alpha h\nu)^{0.5}$ and $(\alpha h\nu)^2$ vs. photon energy (hν) for the Fe_2O_3 film synthesized with +6V/-4V pulse deposition condition, revealing indirect and direct band gap energies of 2.1 and 2.2 eV, respectively.

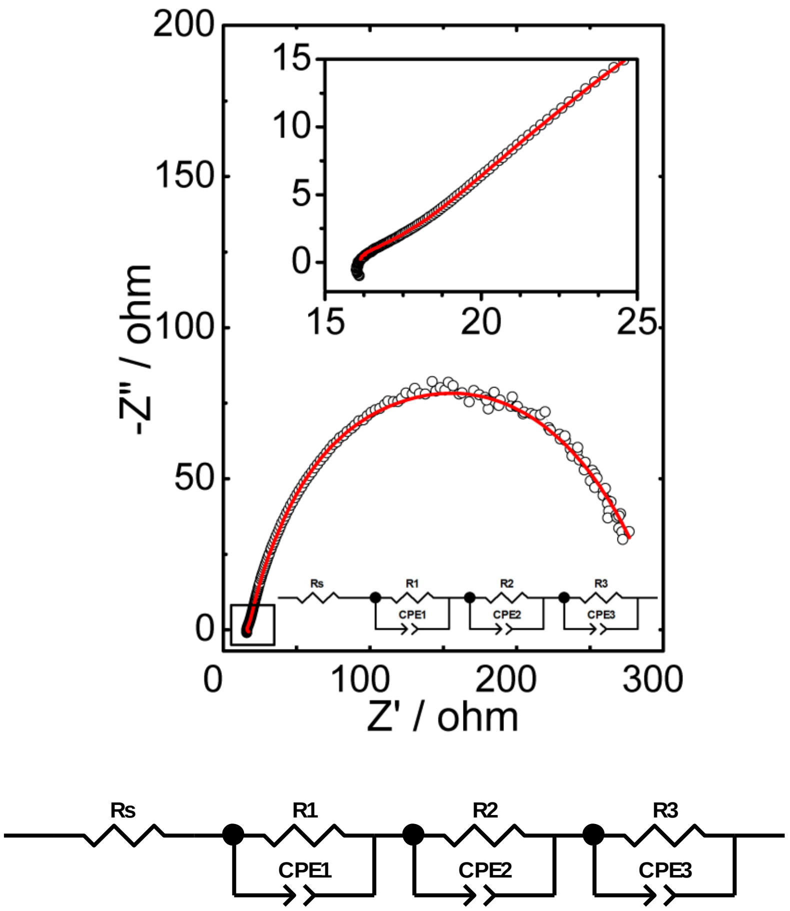
The optical band gap of semiconductor can be estimated from the intercept of the extrapolated linear fit for the plotted experimental data of $(\alpha h\nu)^n$ versus incident photon energy (hν) near the absorption edge. Although, hematite has an indirect band gap [R1, R2], a direct band gap for oriented hematite nanorods is also reported [R3]. Therefore, we determined both indirect and direct band gap energies for Fe_2O_3 by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ versus photon energy, respectively. The indirect allowed and direct allowed band gap energies for Fe_2O_3 film prepared by pulse reverse electrodeposition are 2.1 and 2.2 eV, respectively. The estimated band gap values are in good agreement with the earlier reported values for hematite films [R2].

Electrochemical Impedance Spectroscopy (EIS) study

Potentiostatic electrochemical impedance study of the Fe_2O_3/FTO photoanode was performed with a conventional three-electrode configuration in 1M NaOH electrolyte in dark and under simulated 1 SUN (100 mW cm^{-2}) illumination. The obtained data were fitted using ZView program with equivalent circuit elements such Rs and three parallel RC circuits (See Fig. S4 and S5). Their physical significance is mentioned as follows:

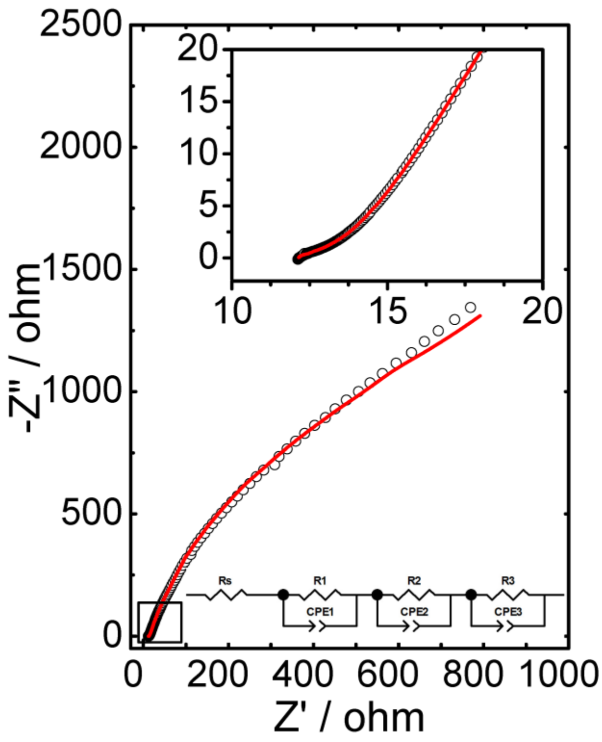
- The Rs represents series resistance (sheet resistance of the FTO and the external contact resistance of the cell such as wire connections).
- First RC circuit comprising R1 and CPE1 (constant phase element) represent Fe_2O_3|FTO contact. CPE is used instead of capacity C if the films are porous in nature.
- Second RC circuit comprising R2 and CPE2 represent interface inside the Fe_2O_3 layer.
- Third RC comprising R3 and CPE3 represent Fe_2O_3|Electrolyte system

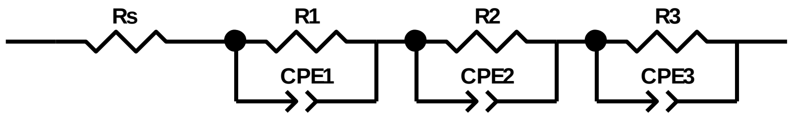
Supplementary Material (ESI) for Journal of Materials Chemistry



Circuit Element	Values	Error	Error %
Rs (Ω)	12.08	0.0054701	0.045282
R1 (Ω)	2.324	0.016949	0.7293
CPE1-T (F)	0.0066136	0.000069839	1.056
CPE1-P	0.54989	0.0012602	0.22917
R2 (Ω)	1018	3.9432	0.38735
CPE2-T (F)	0.0014851	1.2372E-06	0.083308
CPE2-P	0.83031	0.0002208	0.026592
R3 (Ω)	3245	27.265	0.84022
CPE3-T (F)	0.0015608	1.7139E-06	0.10981
CPE3-P	1	0.00040598	0.040598

Fig. S4 Nyquits plot for Fe_2O_3/FTO photoanode in 1M NaOH electrolyte under dark recorded in the frequency range of 0.1-10,000 Hz. Inset shows the magnified curve in the high frequency region depicting a small semicircle.





Circuit Element	Values	Error	Error %
Rs (Ω)	12.16	3.0105E-05	0.00024757
R1 (Ω)	1.465	0.00024267	0.016565
CPE1-T (F)	0.0013104	6.2504E-08	0.0047698
CPE1-P	0.74971	6.0333E-05	0.0080475
R2 (Ω)	397.3	0.03241	0.0081576
CPE2-T (F)	0.00091561	3.0573E-08	0.0033391
CPE2-P	0.87563	1.0596E-05	0.0012101
R3 (Ω)	97.45	0.032993	0.033856
CPE3-T (F)	0.025716	5.5981E-07	0.0021769
CPE3-P	0.67074	6.68E-05	0.0099591

Fig. S5 Nyquits plot for Fe_2O_3/FTO photoanode in 1M NaOH electrolyte under 1 SUN illumination recorded in the frequency range of 0.1-10,000 Hz. Inset shows the magnified curve in the high frequency region depicting a small semicircle.

Mott-Schottky study

Mott-Schottky study of Fe_2O_3 prepared by pulse reverse electrodeposition was carried out in 1M NaOH electrolyte (pH=13.6) with a three-electrode setup. DC potential from -0.6–0.4V vs. Ag/AgCl was applied at the AC frequency of 30000 Hz and AC amplitude of 0.023 V. Space charge layer capacitance values were obtained at each potential (ΔV=0.1V vs. Ag/AgCl). A higher frequency was selected to minimize the contribution of Helmholtz capacitance, which results from the charge redistributions within the solution at the surface.

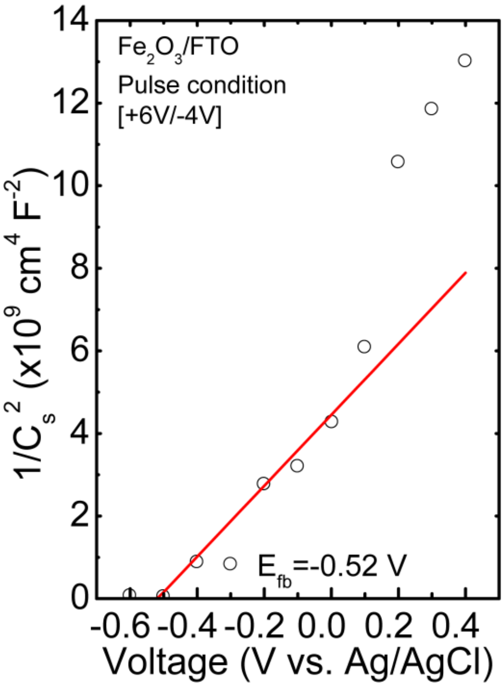


Fig. S6 Mott-Schottky ($1/C_s^2$ vs. potential) plot for Fe_2O_3 film measured at an AC frequency of 30 kHz under dark condition in 1M NaOH solution (pH 13.6) and with AC amplitude of 0.023 V. The reference electrode was Ag/AgCl.

Flat band potential (V_{fb}) can be calculated using Mott-Schottky relation (3),

$$\frac{1}{C_s^2} = \frac{1}{e_0 N_D \varepsilon_0 \varepsilon_r A^2}\left(\left|V - V_{fb}\right| - \frac{kT}{e}\right) \qquad \ldots (3)$$

where, C_s is space charge capacitance (F cm^{-2}), e_0 is the electron charge (1.602177×10^{-19} C), ε_r is the dielectric constant (ε_r=80 for α-Fe_2O_3) [R4], ε_0 is the permittivity of vacuum (8.8542×10^{-14} F cm^{-1}), N_D is donor density (cm^{-3}), V is the applied potential (V), T is the absolute temperature, k is Boltzmann's constant and A is the surface area of the photoanode. At room temperature, Value of V_{fb} determined by extrapolating the linear fit of $1/C_s^2$ versus

V plot to C=0 is -0.4V vs. Ag/AgCl. The positive slope of the plot indicates that Fe_2O_3 is n-type semiconductor with electrons as majority charge carriers. At room temperature, the value of kT/e is negligibly small (0.025V) and can be omitted. According to relation (3), the slope determined from the Mott-Schottky plot can be used to estimate the carrier density using following relation,

$$N_{\mathrm{D}} = \frac{2}{e_0 \varepsilon_0 \varepsilon_{\mathrm{r}} A^2} \left[\mathrm{d}\left(1 / C_s^2 \right) / \mathrm{d}V \right]^{-1} \quad \dots (4)$$

References

[R1] J. E. Turner, M. Hendewerk, J. Parmeter, D. Neiman and G. A. Somorjai, *J.* Electrochem. Soc., 1984, **131**, 1777.

[R2] H. Jun, B. Im, J. Y. Kim, Y-O. Im, J-W. Jang, E. S. Kim, J. Y. Kim, H. J. Kang, S. J. Hong, J. S. Lee, *Energy Environ. Sci.*, 2012, **5**, 6375.

[R3] N. Beermann, L. Vayssieres, S.-E. Lindquist and A. Hagfeldt, *J. Electrochem. Soc.*, 2000, **147**, 2456.

[R4] I. Cesar, K. Sivula, A. Kay, R. Zboril and M. Grätzel, J. Phys. Chem. C, 2009, **113**, 772.