Supplementary Information

Eco-friendly Ferrite Nano-Composite Photoelectrode for Improved Solar Hydrogen Generation

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PHYSICO-CHEMICAL CHARACTERIZATION

Table SI-1 : Quantitative elemental analysis of the films showing the variation in Zn:Fe ratio (as estimated from EDS) and corresponding photocurrents generated under simulated solar (AM 1.5G solar simulator) light and white light (Hg-arc lamp-500watt).

Film	**Zn: Fe ratio** (*from EDS*)	**Photocurrent under Solar simulator (*μA/cm²*)**	**Photocurrent under white light (*μA/cm²*)**
Fe_2O_3	X	57	365
A1	1: 5.8	7.9	17.6
A2	1: 2.8	80.0	187.0
FNCP	**1: 2.5**	**143**	**530**
$ZnFe_2O_4$	1: 2.0	24	62
A4	1: 1.6	2.8	5.9

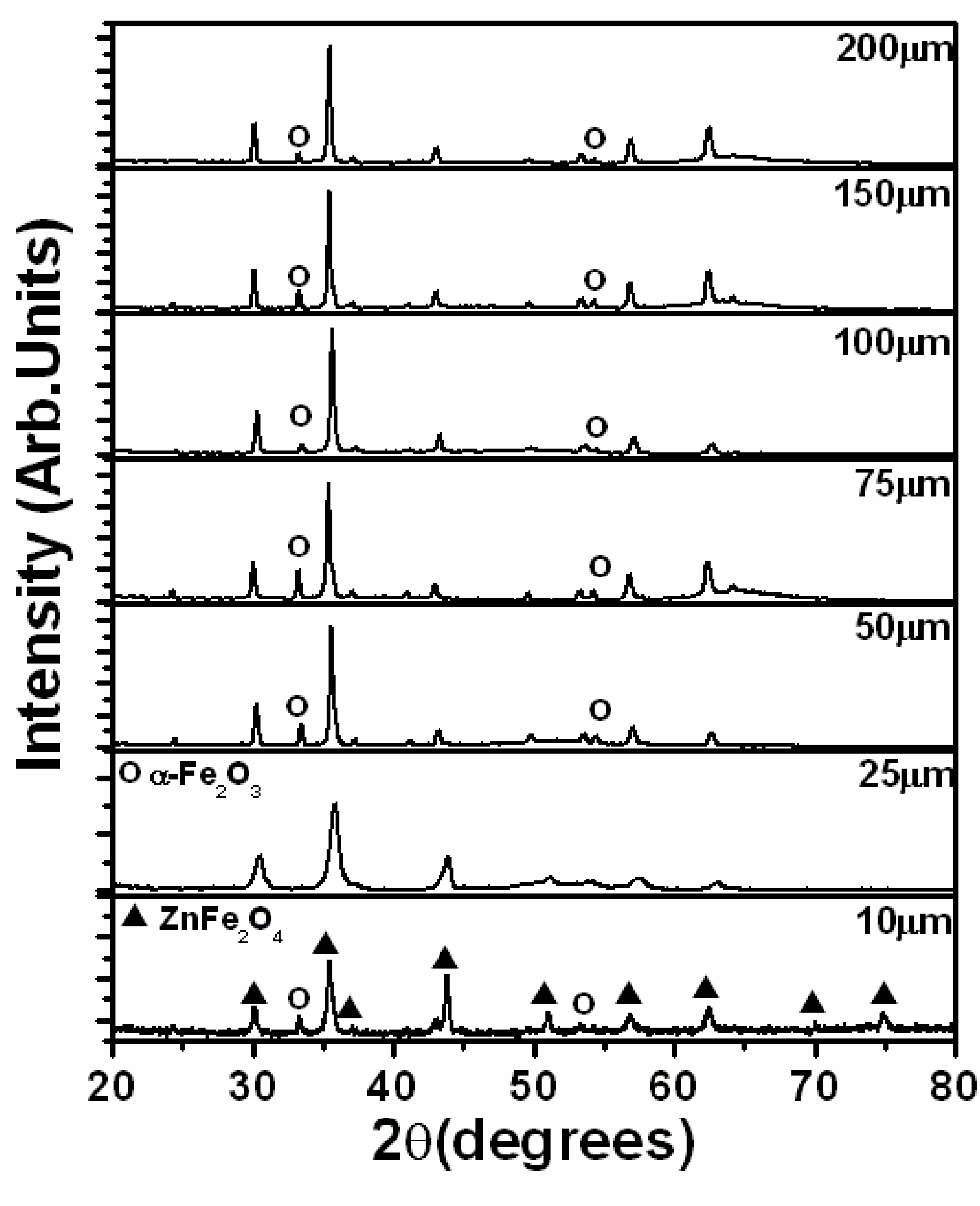

Figure SI-1. The XRD spectra of the films with respect to number of passes (thickness variation -as estimated by FESEM) during the SPPS deposition technique. The unassigned peaks are due to SS substrate.

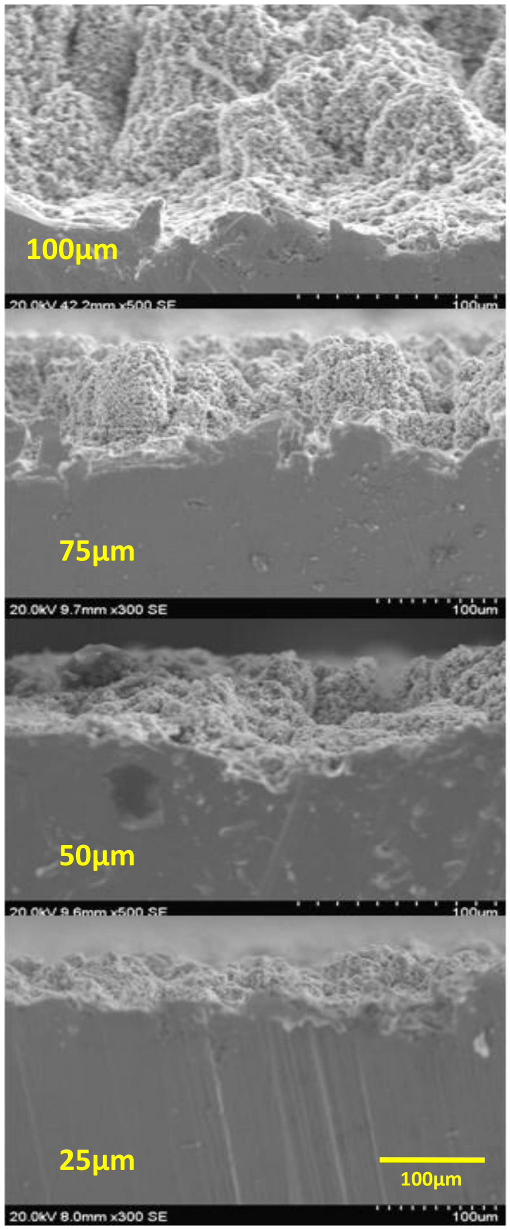

Figure SI-2 Film cross-section as viewed during FESEM for the typical ZFO/SS films deposited with various thickness. The thickness is indicated on left corner of each image. The scale bar is common to all images.

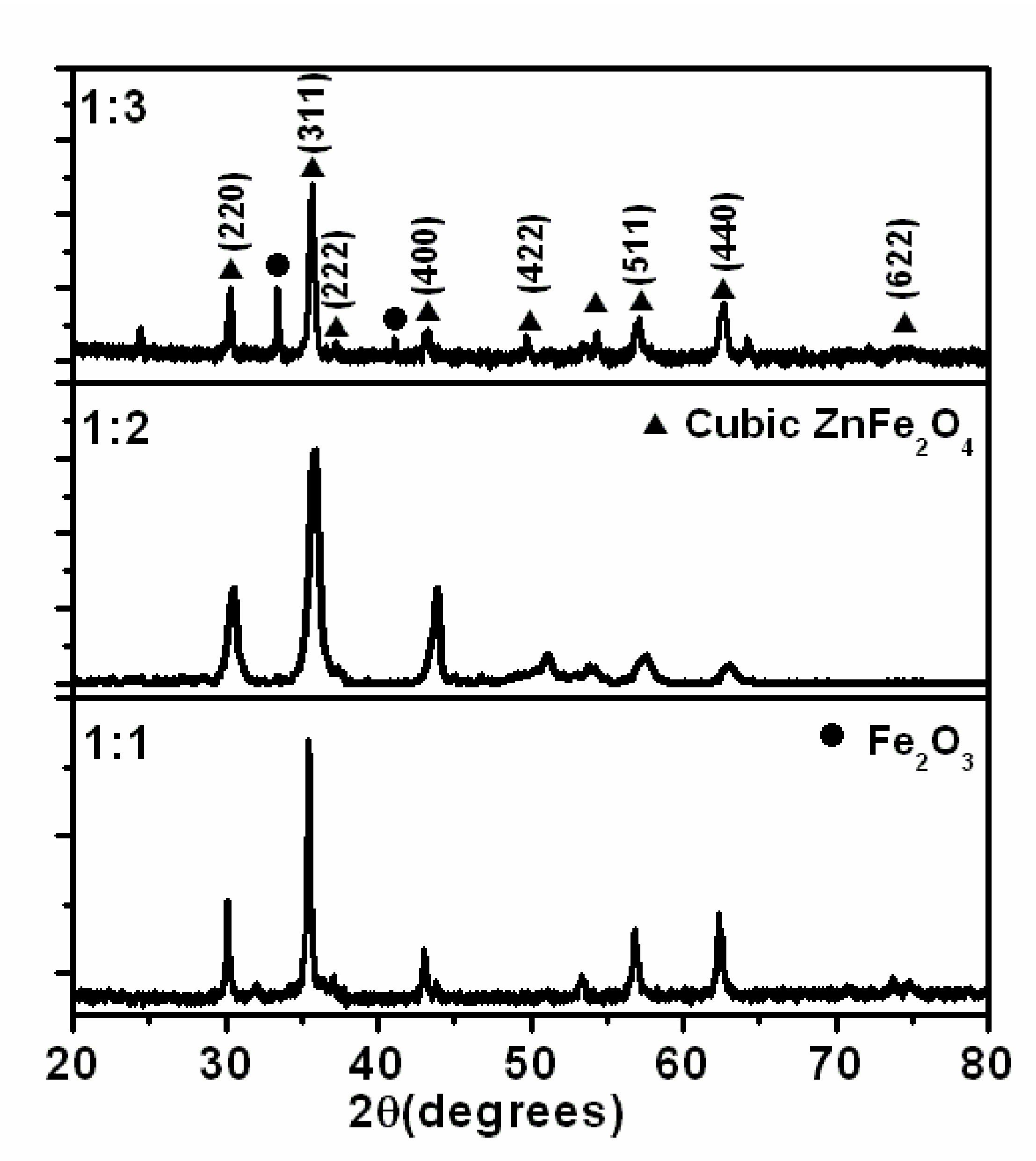

Figure SI-3. The XRD spectra of the FNCP films w.r.t. Zn:Fe stoichiometry variation as deposited by SPPS method.

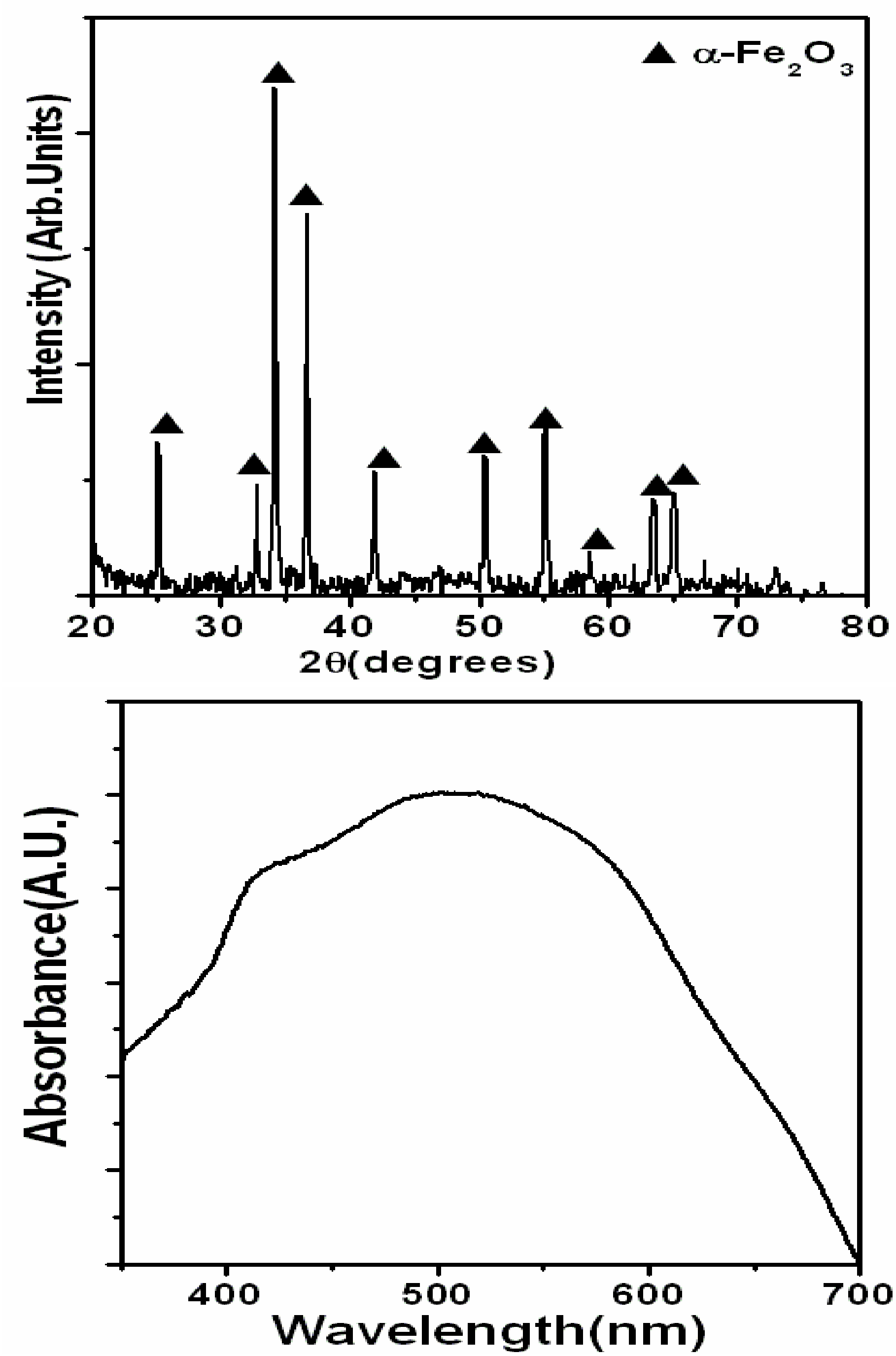

Figure SI-4. XRD and DRS spectra of Fe_2O_3 film deposited by SPPS deposition method, keeping all other deposition parameters same as used for FNCP deposition.

XPS characterization of FNCP and ZFO films

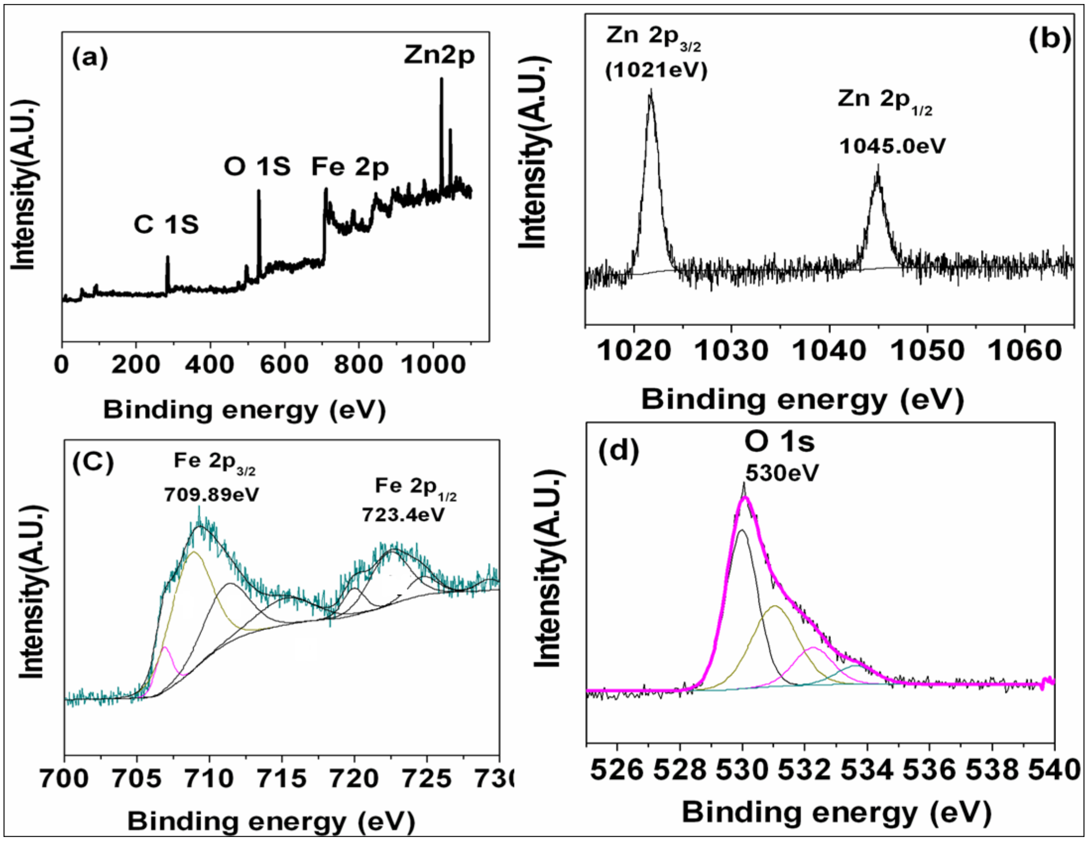

Figure SI-5a. XPS of FNCP Film (a) survey scan; and region scan for (b) Zn-2*p*; (c)Fe-2*p* and (d) O-1*s*. It clearly validates the existence of Fe_2O_3 component along with the ZFO.

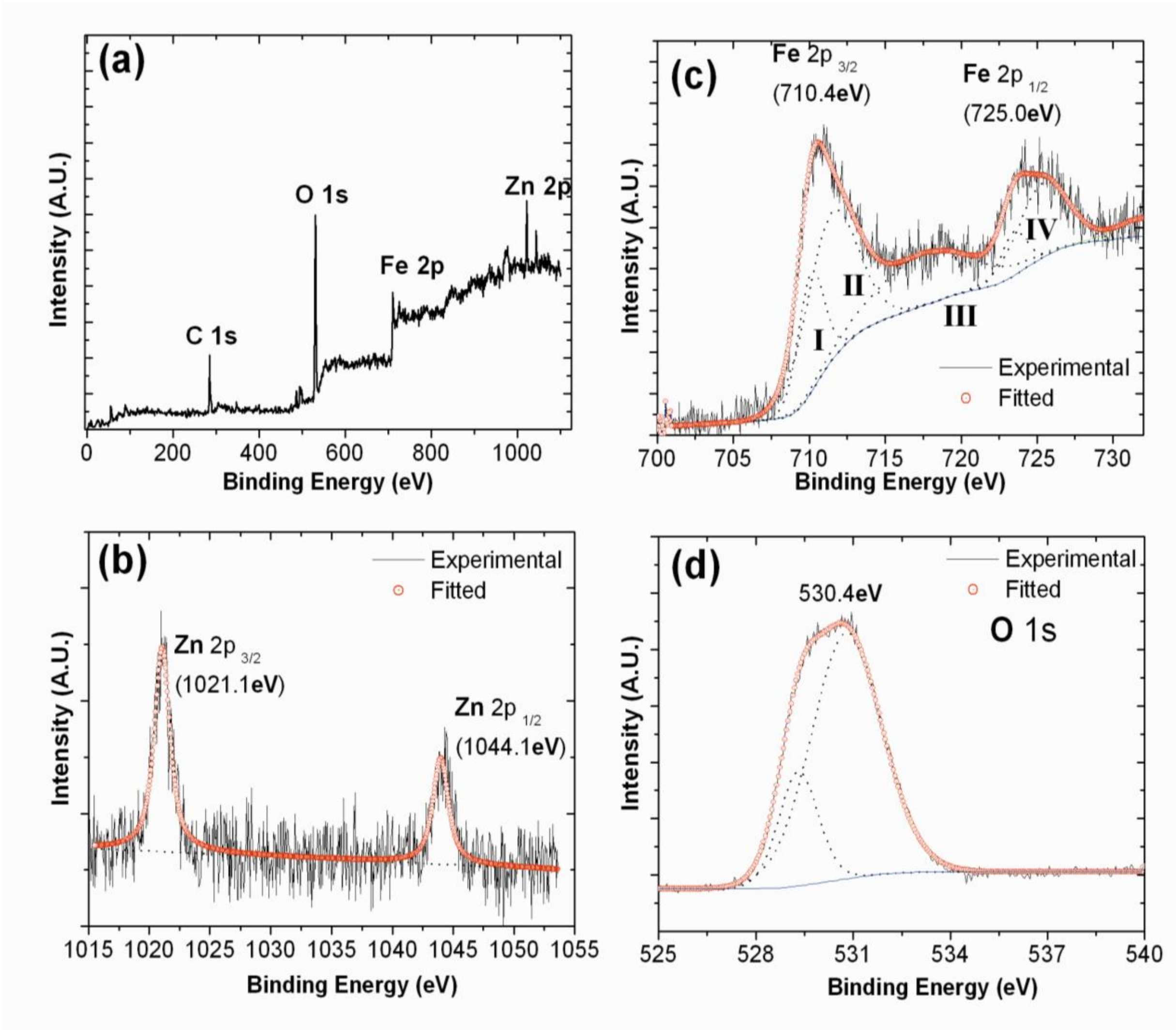

Figure SI-5b. XPS of typical ZFO Film (a) survey scan; and region scan for (b) Zn-2*p*; (c)Fe-2*p* and (d) O-1*s*.

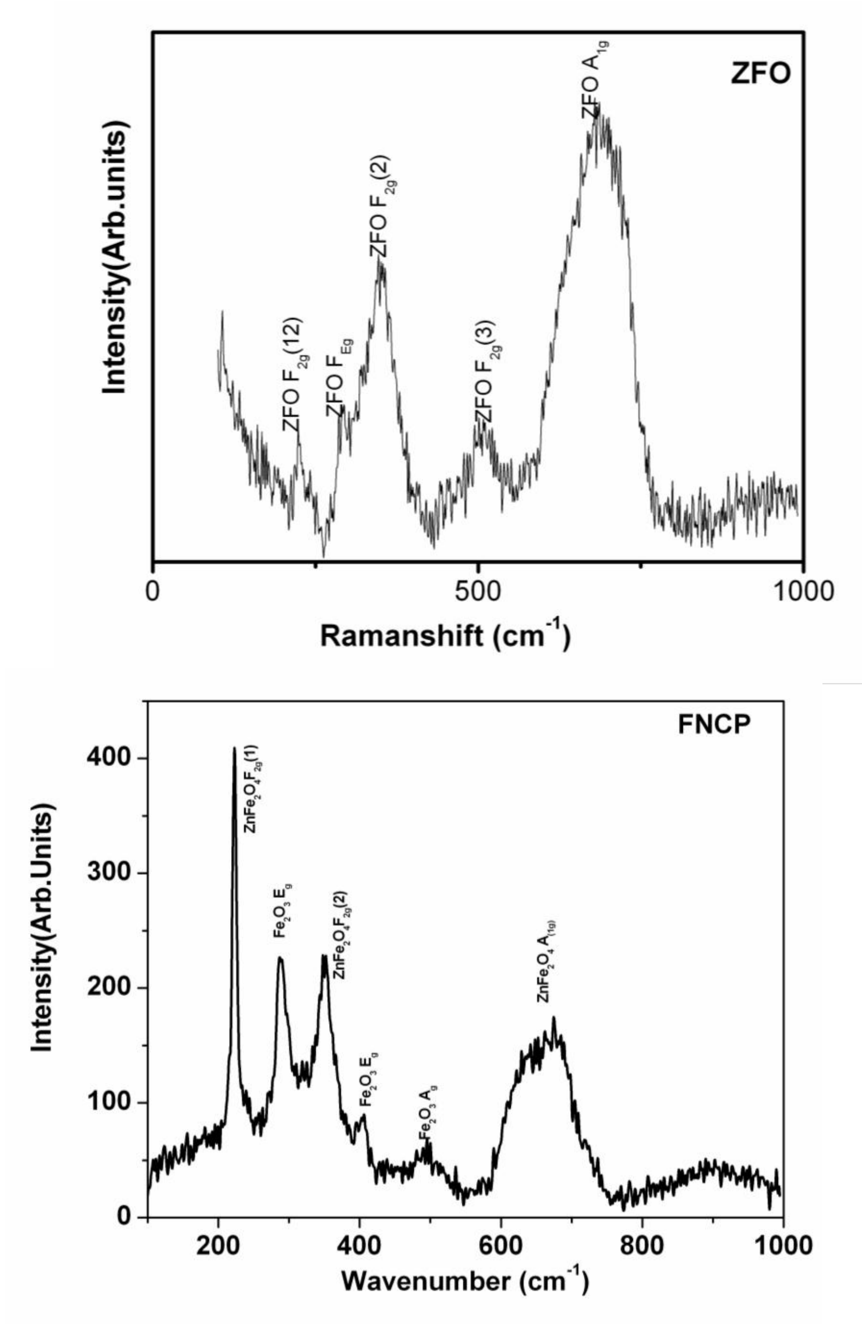

Figure SI-6. Raman spectra of typical ZFO and FNCP films

Optical characterization of the photoanodes: Estimation of Band gap energy using UV-Visible absorption study

The band gap energy was calculated from the absorbance data of the films recorded in the range 350-700nm using Tauc relation(1);

$$\alpha h\nu = A(h\nu - E_g)^q \quad \dots\dots\dots\dots\dots \quad (1)$$

Where $$A = [\frac{e^2}{qch^2 m_e^*}]x^2(2m_r)^{3/2} \dots\dots\dots\dots\dots (2)$$

Here, α is the measured absorption coefficient (cm^{-1}) near the absorption edge, A is the constant, hν is the photon energy(eV), Eg is the optical band gap(eV), q is a constant. The value of q is determined from the nature of optical transition. *q* is the index that characterizes the optical absorption process and is theoretically equal to 2 for allowed indirect, ½ for allowed direct, 3 for forbidden indirect, and 3/2 for forbidden direct electronic transitions. m^*_e and m_r are the effective and reduced masses of charge carriers, respectively. The optical band gap can be estimated from the intercept of the extrapolated linear fit for the plotted experimental data of $(\alpha h\nu)^q$ versus incident photon energy (hν) near the absorption edge.

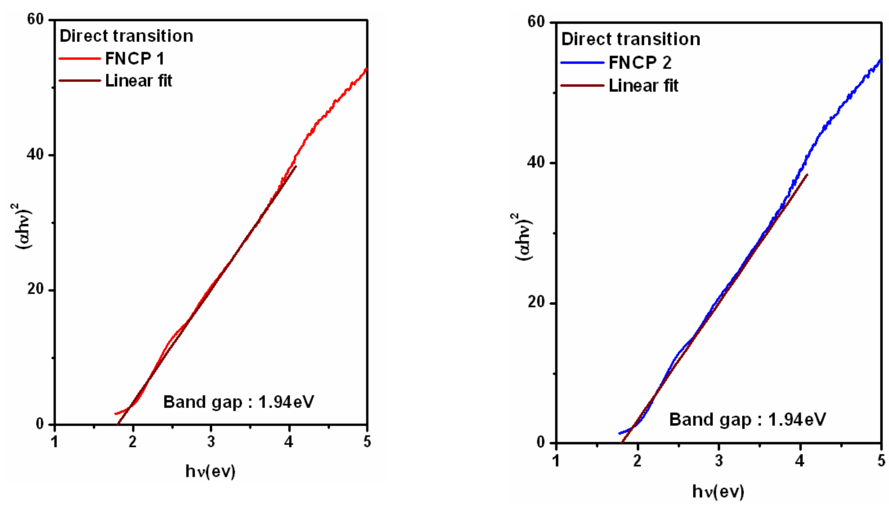

Figure SI-7. Tauc plots of typical FNCP films revealing direct band gap energies

Mott-Schottky characterization of FNCP

The impedance measurements allow the derivation of capacitance at the semiconductor-electrolyte- interface, which can be described by a Mott-Schottky (MS) plot (*i.e.* graph of $1/C^2$ *vs* V). The Mott-Schottky equation is described by relationship

$$\frac{1}{C_{sc}^2} = \frac{2}{(\varepsilon_s \varepsilon_0 e N_D S^2)(V_B - V_{fb})} \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

ε_S is the dielectric constant of the semiconductor 100

ε_0 is the vacuum permittivity and is 8.85 X $10^{-12} C^2/Nm^2$

N_D is the Donor density and S the surface area of the electrode in cm^2.

Mott-Schottky study of FNCP films deposited by SPPS method was carried out in 1M NaOH electrolyte (pH-13.6) with a three-electrode set up. DC potential from -1.0-1.0V vs SCE was applied at the AC frequency of 10kHz and AC amplitude of 10mV.

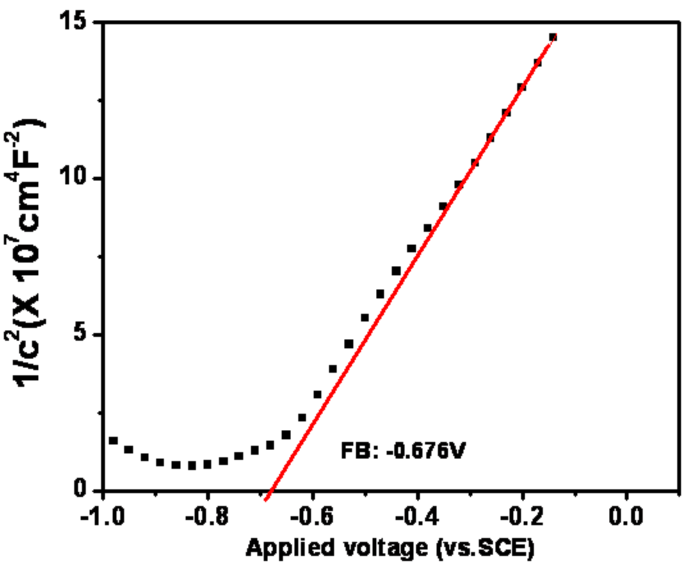

Figure SI-8(a). Mott-Schottky plot for FNCP film measured at an AC frequency of 10kHz under dark conditions in 1M NaOH (pH-13.6) and with AC amplitude of 10mV.The reference electrode was SCE.

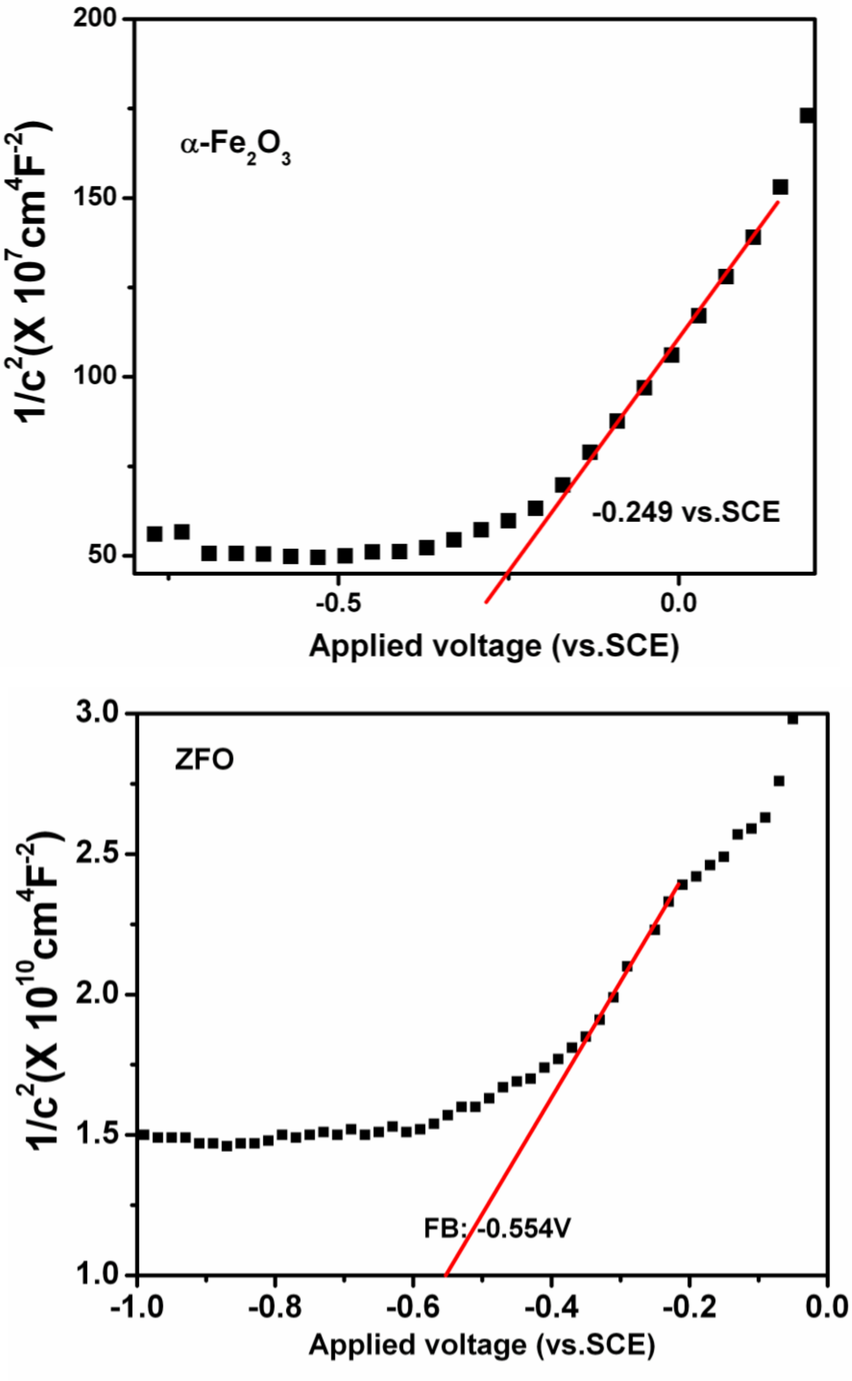

Figure SI-8(b). Mott-Schottky plots for α-Fe_2O_3 and ZFO films measured at an AC frequency of 10kHz under dark conditions in 1M NaOH (pH-13.6) and with AC amplitude of 10mV.The reference electrode was SCE.