Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

$BiVO_4/Fe_2O_3/ZnFe_2O_4$; Triple Heterojunction for Enhanced PEC Performance for Hydrogen Generation

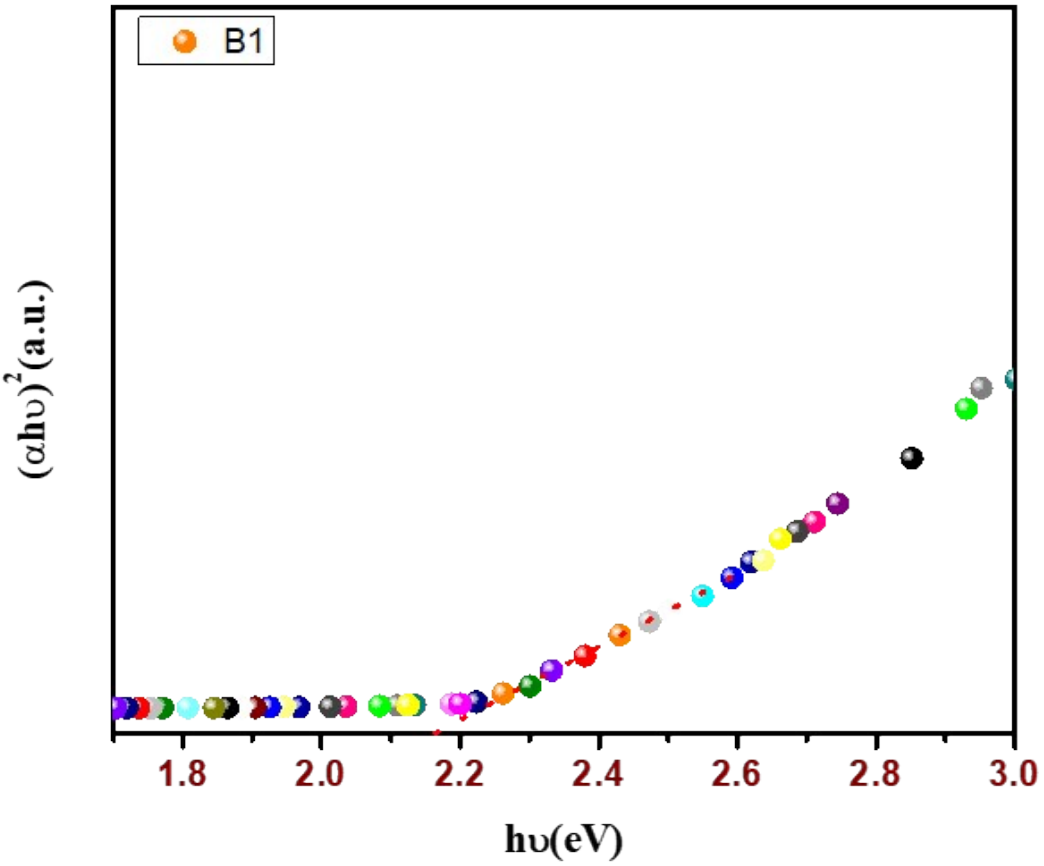

Fig.S1 Tauc plot of pristine B (Zr:W-$BiVO_4$) thin film

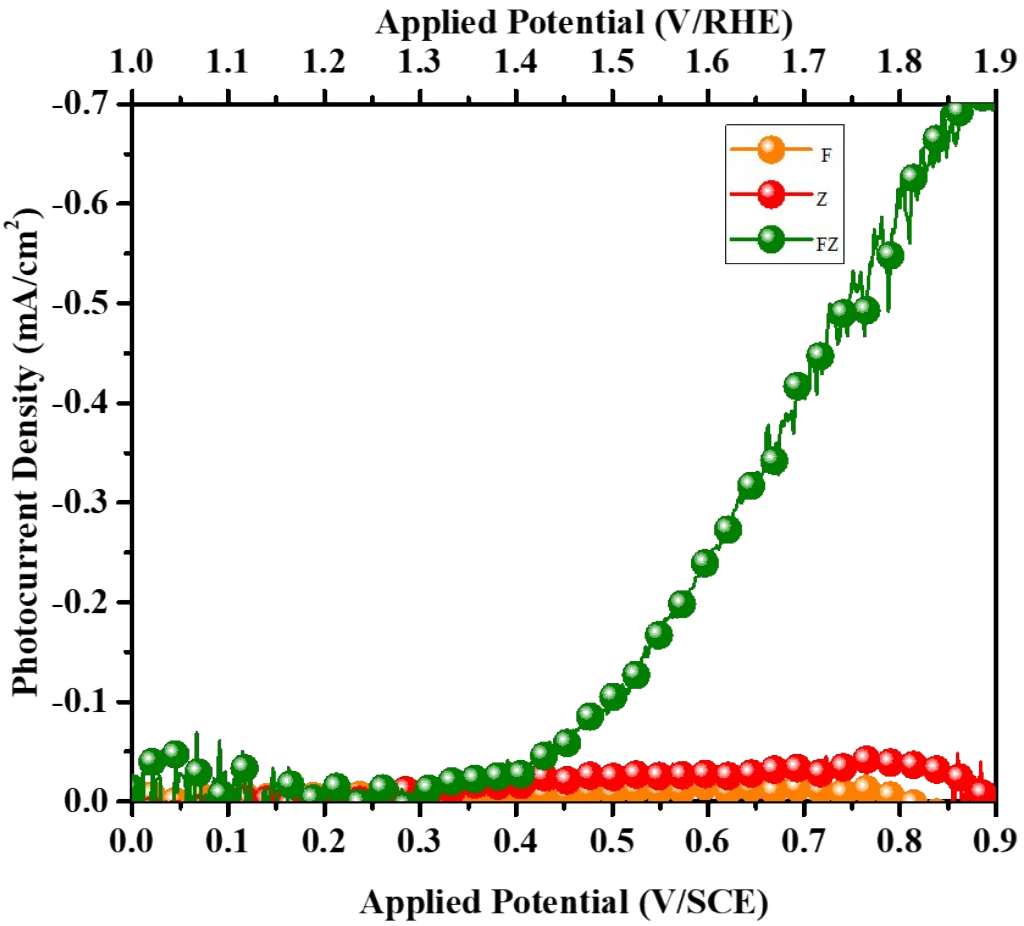

Fig.S2 Current-voltage graph for F, Z and FZ thin films obtained through LSV

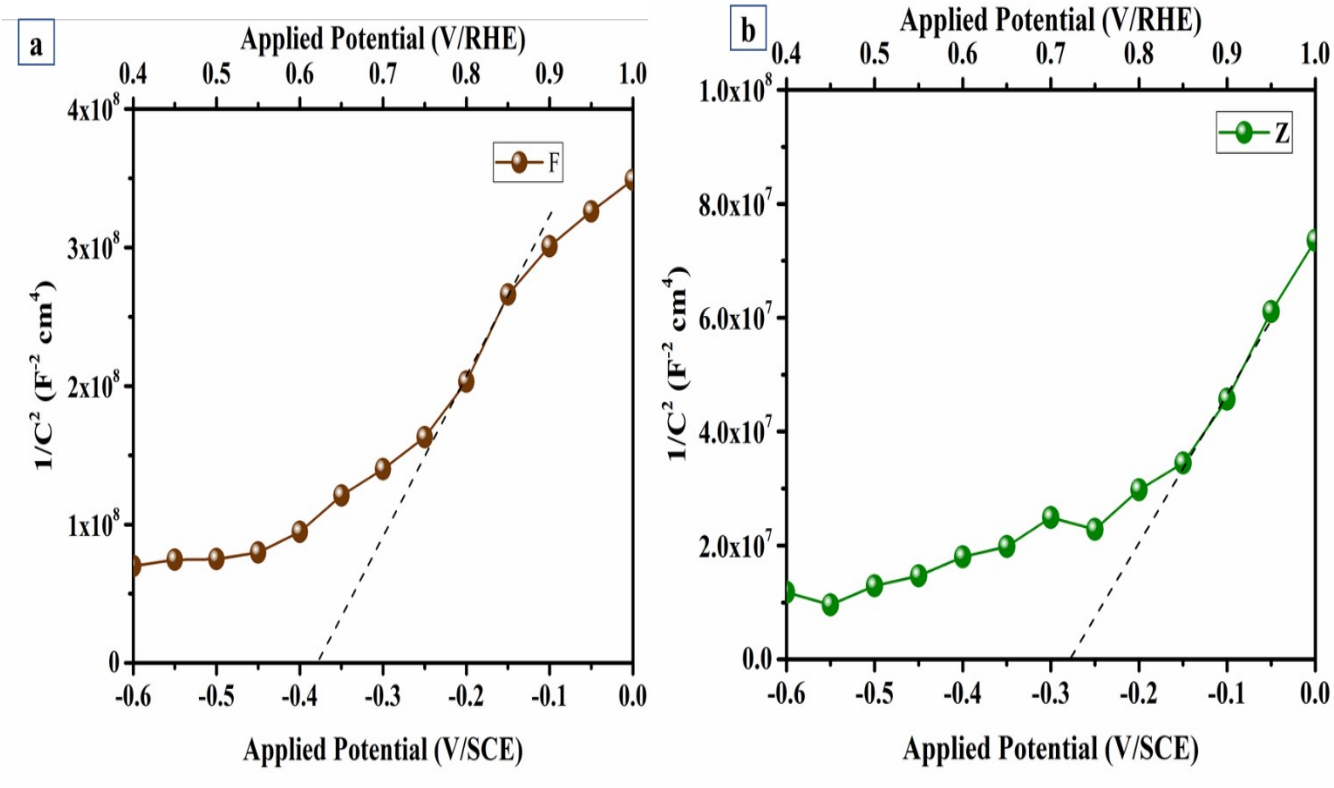

Fig.S3 (a,b) Mott-Schottky plot for F and Z thin film

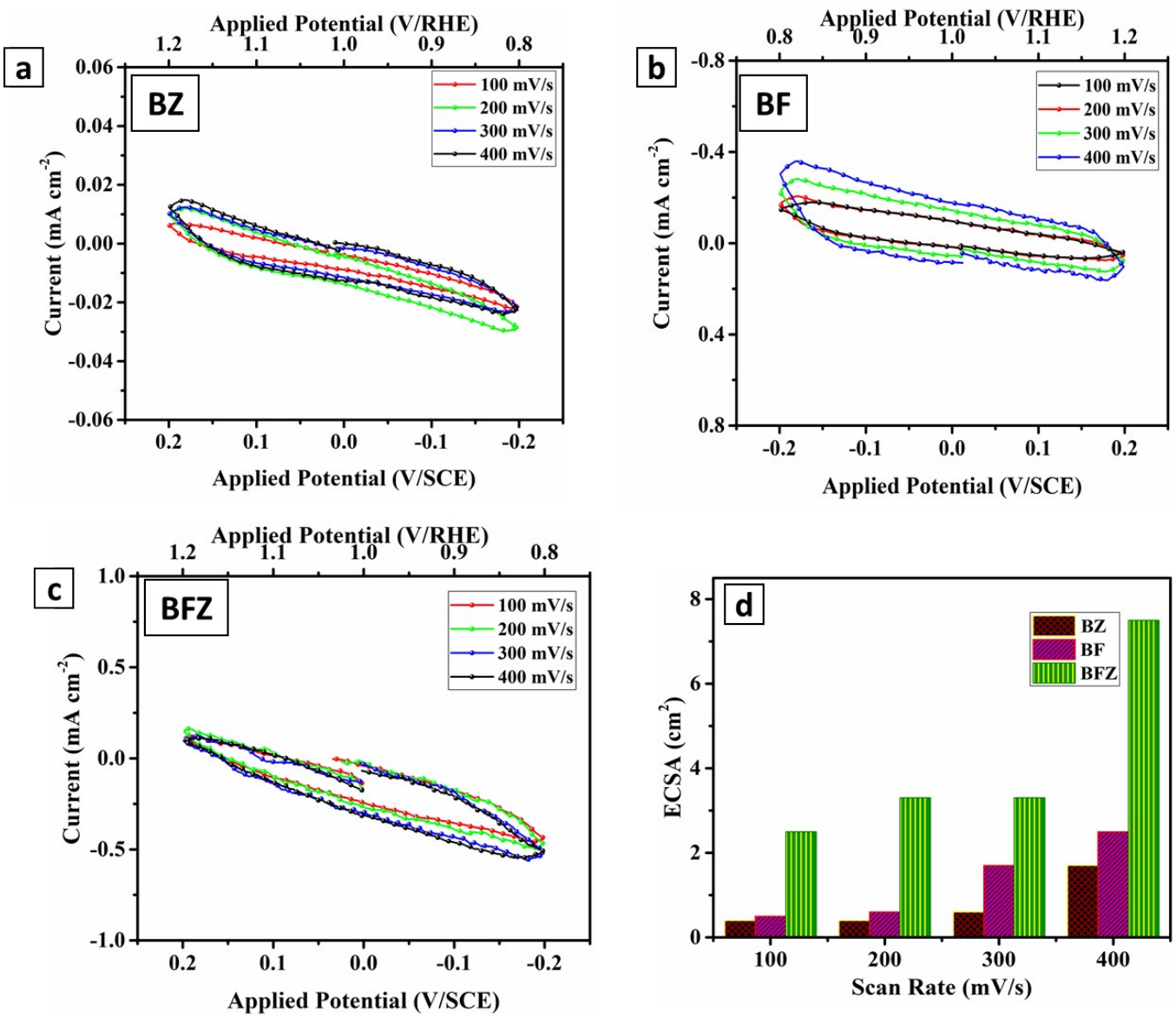

Fig.S4 (a-c) Cyclic voltammetry curve for BF, BZ and BFZ thin film recorded in the potential range of -0.2 V to 0.8 V/SCE at different scan rate: (d) ECSA plot at different scan rate

Table S1: Electrochemical surface area (ECSA) value for BF, BZ and BFZ at different scan rate

Scan Rate (mV/s)	ECSA (cm^2) for different Sample		
	BZ	BF	BFZ
100	0.4	0.5	2.5
200	0.4	0.6	3.3
300	0.6	1.7	3.3
400	1.7	2.5	7.5

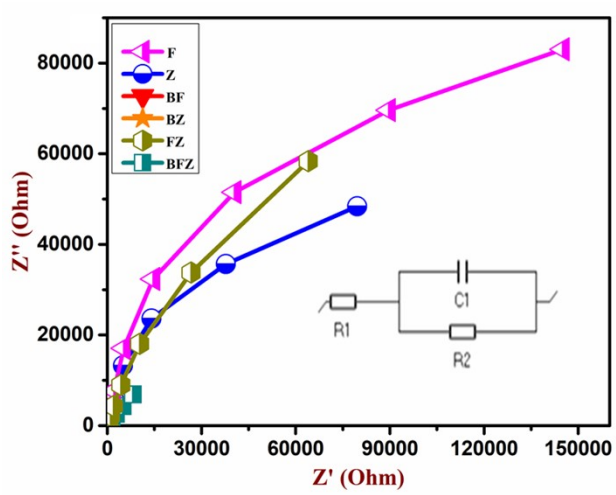

Fig. S5 Nyquist plot for all the prepared thin films; Inset: fitted equivalent circuit

Table S2: Fitted values obtained from the equivalent circuit

Sample	R_s (Ohm)	R_{CT} (Ohm)	C (F)
F	35.47	60.91	45.1×10^{-6}
Z	43.86	45.35	32.27×10^{-6}
BFZ	64.22	33.22	23.45×10^{-6}

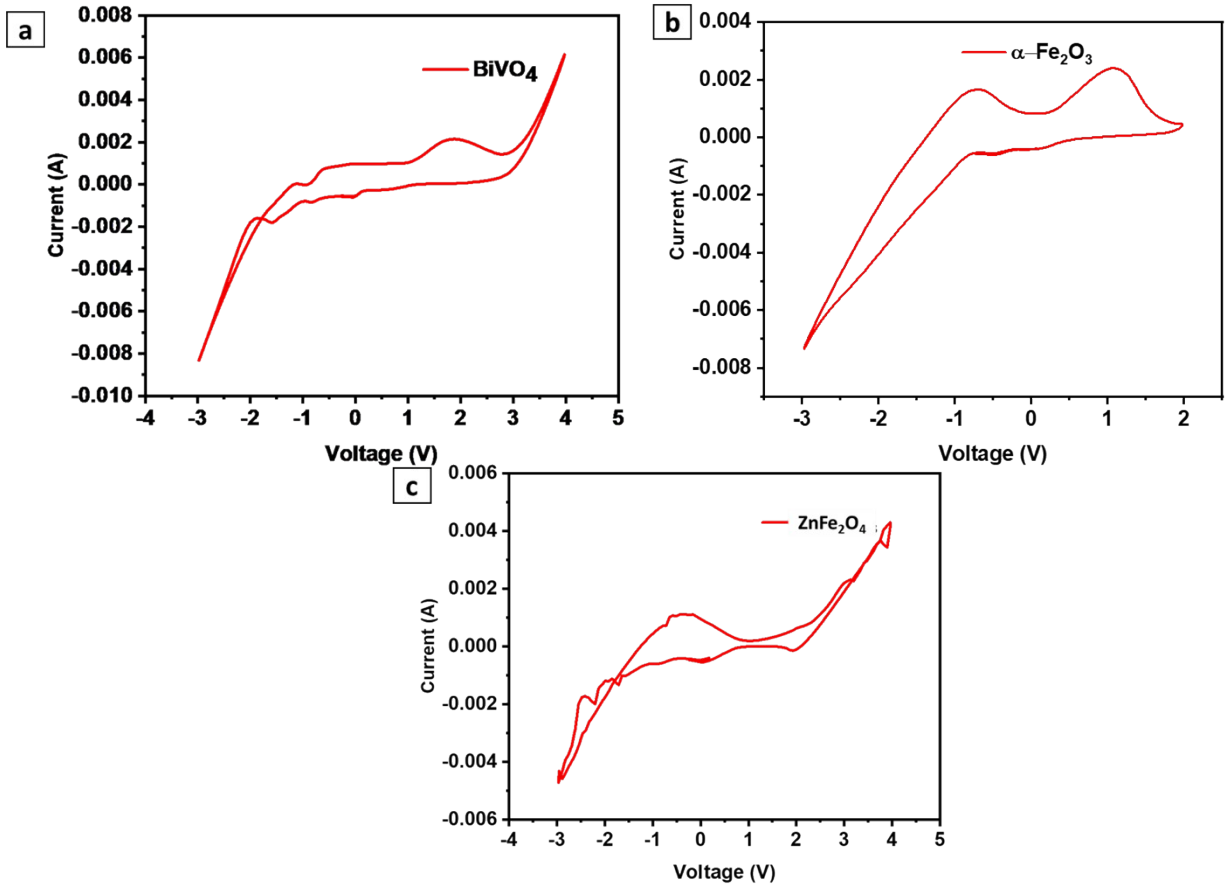

Fig. S6 (a-c) Cyclic voltammetry curve for B, F and Z

Cyclic Voltammetry analysis for calculating the energy levels

Cyclic voltammetry was executed in 0.1M of tetrabutylammonium phosphorus hexafluoride (TBAPF6) in anhydrous acetonitrile (CH_3CN) in order to estimate the energy levels (HOMO and LUMO). The redox potentials (E_{red} and E_{ox}) obtained from cyclic voltammetry graphs was used to calculate the HOMO & LUMO using the following equations:

$$E\ (HOMO) = -e\ [E_{ox}{}^{onset} + 4.4]$$

$$E\ (LUMO) = -e\ [E_{red}{}^{onset} + 4.4]$$

From the graphs it is clear that pristine $BiVO_4$ (B) shows E_{HOMO} at 3.2 eV and E_{LUMO} at 5.4 eV, Fe_2O_3(F) shows E_{HOMO} at 3.14 eV and E_{LUMO} at 5.2 eV and $ZnFe_2O_4$ (Z) shows E_{HOMO} at 3.0 eV and E_{LUMO} at 5.09 eV. The estimated band gap values for B, F and Z comes out to be 2.2 eV, 2.06 eV and 2.09 eV which matches well with the literature reported values. This shows that sample exhibited the type-II heterojunction formation which facilitates the charge transfer kinetics at interface.

Reference:

1. Shafiee A, Salleh MM, Yahaya M. Determination of HOMO and LUMO of [6, 6]-phenyl C61-butyric acid 3-ethylthiophene ester and poly (3-octyl-thiophene-2, 5-diyl) through voltametry characterization. Sains Malaysiana. 2011 Feb 1;40(2):173-6.

2. Leonat L, Sbarcea G, Branzoi IV. Cyclic voltammetry for energy levels estimation of organic materials. UPB Sci Bull Ser B. 2013 Jan 1;75(3):111-8.