

# Influence of substrate effect on opto-electrical characteristics of Iron Tungstate photo-anode for solar hydrogen and photo-catalysis applications

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## **ABSTRACT**

Metal Tungstate an inorganic functional materials has high potential in photoluminescence, microwave devices, optics, magnetism, sensors and catalyst applications. In this work monoclinic Iron Tungstate (IT) is synthesized by Solution Combustion Technique. The iron tungstate is characterized by x-ray diffraction to confirm the crystalline phase, size and strain and dislocation density. The band gap of IT is calculated by Kubelka-Munk function is found to be 2.1 eV. The surface morphology of iron tungstate showed flakes like structure and confirmed elemental composition of Fe,W,O. The electrical conductivity studies is performed at different temperatures which reveals that the material is photoactive. The photocatalytic activity oxygen evolution is studied under dark and light conditions. The effect of substrate on photocurrent generation is also evaluated on Stainless Steel, Platinum, Nickel and Copper substrates. The electrical conductivity results shows that iron tungstate coated on Pt substrate has higher current conversion efficiencies. The synthesized iron tungstate is therefore most promising material for catalytic oxygen evolution from water which was intended for solar hydrogen production in tandem cells.

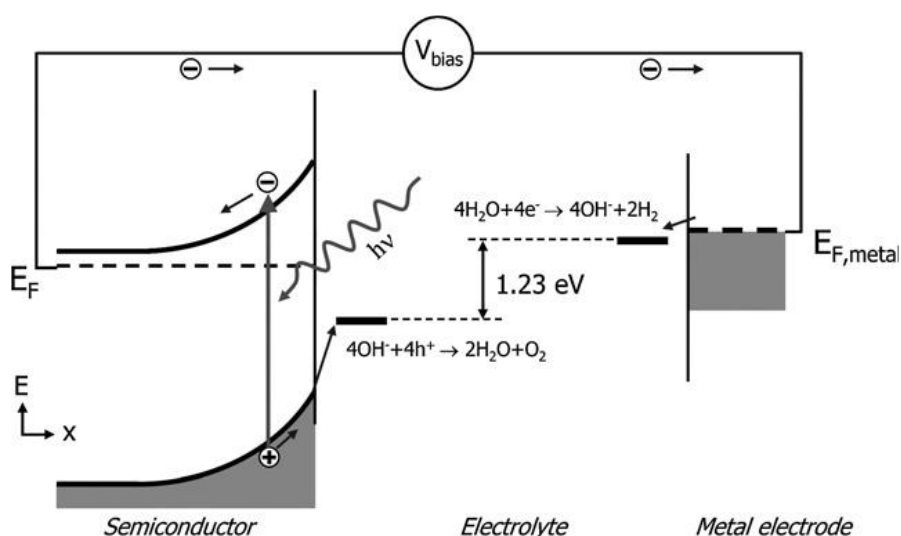
**Keywords** Solution combustion, Iron Tungstate, Photocatalysis, Photo-conductivity.

## **1. INTRODUCTION**

Increasing environmental concerns and energy demands the exploration for sustainable sources of energy. The total energy consumption rate globally is 13.5 TW in 2001 which might increase to

27 TW in 2050. The literatures shows that about 85% of energy demand is met from fossil fuels. Therefore it becomes utmost importance to explore alternative sources of energy. Most of the energy resources that are currently being utilized such as fossil fuels, wind, tide, hydropower and biomass originate from solar energy. Direct utilization of solar energy by thermal or photovoltaic is still limited. Solar energy is intermittent in nature [1]. Solar cells that generate electricity during daytime which remains as one of the major challenge. Hence, large-scale use of solar energy requires an efficient energy storage system. Storing large amount of solar energy in the form of chemical energy is one of the efficient method of energy storage.

Numerous research activities is being carried out to develop new and efficient technologies for the production, storage, utilization, and transport of hydrogen. The principle of photo-electrochemical cell (PEC) for water splitting is shown in Fig. 1.



**Fig. 1 Principle of PEC for photo-electrolysis of water.**

In an n-type semiconductor, when the material is exposed to photons the electrons travel to the back contact and to the counter electrode where they reduce water to form hydrogen. The electrons and holes in the valence band move towards to the surface gets oxidized to form oxygen gas [2]. The recombination of electrons and holes is barred by the electric field near to the surface of the

semiconductor. The photo-electrode material used for solar based hydrogen generation should fulfil requirements such as visible light absorption, chemical stability, charge transport under dark and light illumination, low potential for reduction/oxidation reactions and low cost. Some of the materials widely used for the oxygen evolution are TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, CdS, CuO, SrTiO<sub>3</sub> and BaTiO<sub>3</sub> [3]. The band gap energy for various semiconductor materials is shown in Fig. 2.

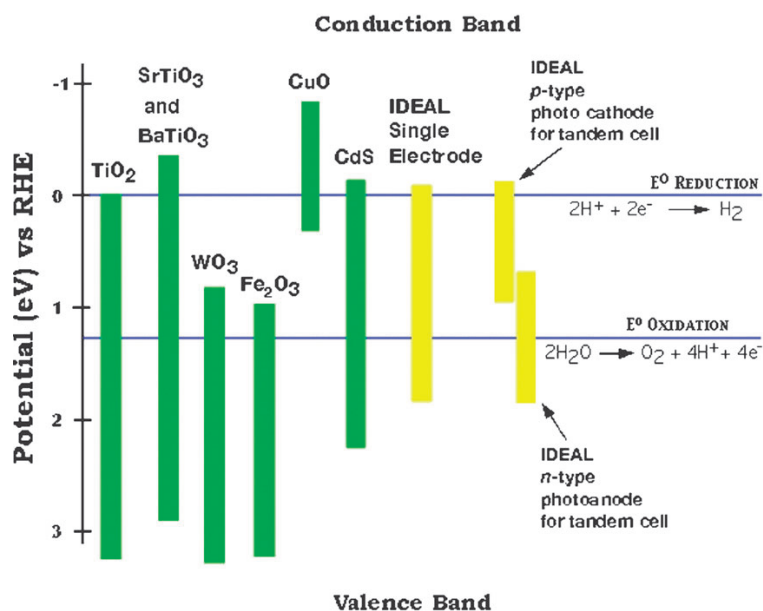


Fig.2 Band gap energy for few semiconductor materials.

TiO<sub>2</sub> is being widely examined material for photo-electrochemical and catalytic applications due to easy availability, chemical stability and low cost. Photo-electrochemical using TiO<sub>2</sub> started with the demonstration on the opportunity to split water using semiconductor based photo-anode. TiO<sub>2</sub> only absorbs UV light due to its bandgap of 3.2 eV. Fine tuning the material properties is being carried out to shift the light absorption in visible spectrum [4]. An alternative approach is integrate TiO<sub>2</sub> with a material that has small band gap, such as α-Fe<sub>2</sub>O<sub>3</sub> (hematite). This material has a band gap of 2.1–2.2 eV and absorbs light of wavelengths below 600 nm. The material also exhibits less photo-corrosion for aqueous solutions. Fe<sub>2</sub>O<sub>3</sub> has high photo-conversion efficiencies for polycrystalline and single crystalline.

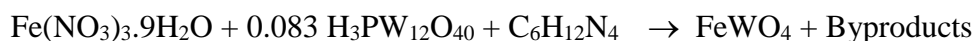
Novel and high efficient visible-light photo catalysts are to be found to come across the energy demand of imminent technologies powered by solar energy. FeWO<sub>4</sub> photo anode material shows increased and stable photo catalytic activity for degradation of toxic chemicals and light to current generation in visible spectrum ( $\lambda > 420$  nm) [5,6]. The material is active for photo oxidation reactions. Low solar radiation or frail indoor lighting can be used as the light source for the oxidation of water to produce current. The FeWO<sub>4</sub> is highly efficient for producing a photo-electrochemical cell that converts optical to chemical energy by decomposition of water (M. Gratzel, 2001). Thus an approach is made to synthesize this mixed metal oxide as FeWO<sub>4</sub> Photo-anode material for oxygen evolution studies from water towards photo-catalysis applications.

## **2. EXPERIMENT**

### **2.1 Materials and Method**

Ferric nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) Phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>), Polyvinylalcohol, Polyvinylidenedifluoride, N-Methyl 2-Pyrrolidone, (Merk, India), Hexamine (C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>, Otto Mann Chem, India) and deionized water. The chemicals purchased are of analytical grade and used as received.

Iron tungstate is synthesized by solution combustion technique. Ferric nitrate, Phosphotungstic acid were used as the precursors and Hexamine is used as the fuel for the synthesis process. All the reactants were weighed according to the stoichiometric proportion to have the desired final product. The precursors are mixed and stirred in deionized water along with the fuel. Metal nitrates are hygroscopic therefore it absorbs moisture and become slurry. The homogeneous slurry mixture of reactants was transferred to a quartz crucible and heated in an open type heater to 300 °C, which follows dehydration and combustion process. After the decomposition of the volatile products, a viscous gel was formed which then swelled and ignited to give the final product of FeWO<sub>4</sub>. The resulting product was then finely grounded and sintered at 550<sup>0</sup> C for 4 hours in air to obtain a fine crystalline single phase Iron Tungstate compound. The chemical reaction involved in the formation of Iron tungstate is shown below,



### **2.2 Pellet preparation**

Iron tungstate is made into a pellet to measure the electrical properties such as semiconducting nature and electrical conductivity. About 0.5 g of material is taken in a mortar and mixed with 1 wt% PVA solution. The mixture is finely grinded and placed in dye with a dia of 10mm. The pellet is prepared using hand pelletiser by applying a pressure of 200kg/cm<sup>2</sup>. The iron tungstate pellet is sintered at 200°C to evaporate the PVA.

### **2.3 Electrode preparation**

The effect of substrate and photocatalytic properties of FeWO<sub>4</sub> towards oxygen evolution studies is studied by coating iron tungstate on different substrates such as stainless steel, copper, nickel and platinum. These electrodes were used as working electrode for the photocatalytic studies in a three cell compartment of Electrochemical cell. The dimension of substrate is 1\*1 cm and washed with metallurgical etchants. Iron tungstate is coated on the substrate with the help of the PVDF and NMP binder in the ratio of 0.75:0.15:0.05 respect on Pt electrode. PVDF acts as binding agent for the material to the corresponding substrate and NMP is used as the solvent for the paste preparation. For Pt substrate iron tungstate is dissolved in ethanol, dispersed over the substrate and annealed at 1200 °C. The electrodes were prepared accordingly to the above procedure and studied for its photocatalytic activity.

### **2.4 Characterization**

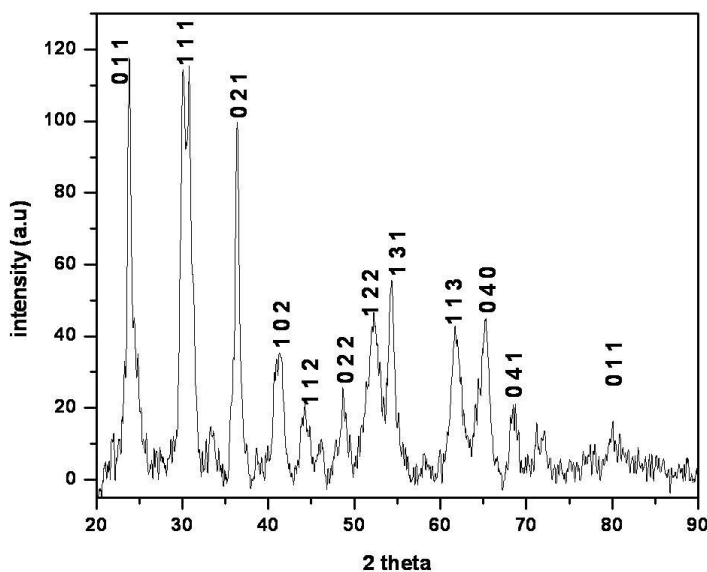
The crystalline nature and phase analysis is carried out using an X-ray diffractometer (Philips 8030 X-Ray Diffractor) with Cu K $\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ). The obtained XRD patterns is compared with the standard JCPDS file. The UV-visible analysis is performed with JASCO model 7800. The surface morphology and elemental composition of the crystalline powders of iron tungstate is analyzed using a scanning electron microscopy (Tescan SEM). The I-V characteristics of iron tungstate is studied on Keithley High Resistance Meter/Electrometer 6517B. The photo-electrochemical measurements were carried out using Bio-logic SA potentiostat /Galvanostat. The Photo-electrochemical measurements is performed in a three electrode system using 0.1M KOH aqueous solution as electrolyte under illumination of 150W metal halide lamp as light source. The working electrode is FeWO<sub>4</sub> coated on stainless steel, Copper, Nickel and Platinum substrate,

whose geometric area is 1 cm<sup>2</sup>. A platinum specimen is used as counter electrode and Hg/HgO as reference electrodes for all the experiments.

**3. RESULTS AND DISCUSSION**

**3.1 Phase evaluation studies**

The FeWO<sub>4</sub> compound is synthesized by solution combustion technique. X-ray Diffraction pattern for the synthesized FeWO<sub>4</sub> is shown in Fig. 3. The average crystallite size is 19 nm and the average lattice strain is found to be 0.63 %. The strong and spiky diffraction peaks signifies that iron tungstate is finely crystallized. All the reflection peaks corresponds to a pure, well –crystalline, monoclinic phase of FeWO<sub>4</sub>. The lattice parameters obtained from the XRD data was consistent with the reported values JCPDS powder diffraction file No. 71-2390) (Jiang Zhang, June2011, Yu-Xue Zhou, June 2009). The crystalline size was calculated from XRD data using Scherrer’s formula and all the other parameters such as strain and density is tabulated in Table 1.



**Fig. 3 X-RAY Diffraction pattern of FeWO<sub>4</sub>.**

**Table 1 Structural parameters determination from XRD Pattern of FeWO<sub>4</sub>.**

3.2 UV-VIS- DRS spectroscopic studies

UV-VIS-DRS studies is used to determine the absorption wavelength of the material. The absorption spectrum of iron tungstate is shown in Fig 4. From the figure it is observed that iron tungstate has a strong absorption edge in the near UV and visible range which confirms the visible light photo-catalyst (Gratian R.Bamwenda,2001). The band gap energy is determined by the kubelka-munk relationship with respect to reflectance and energy gap relation with wavelength. The reflectance spectrum and bandgap energy is shown in Fig. 5 (a) and (b). From the reflectance spectrum, 'K' is calculated by,

$$K = (1-R)^2 / (2R)$$

The band gap is calculated from the graph by interpolating the straight line. The band gap energy was determined to be 2.1 eV.

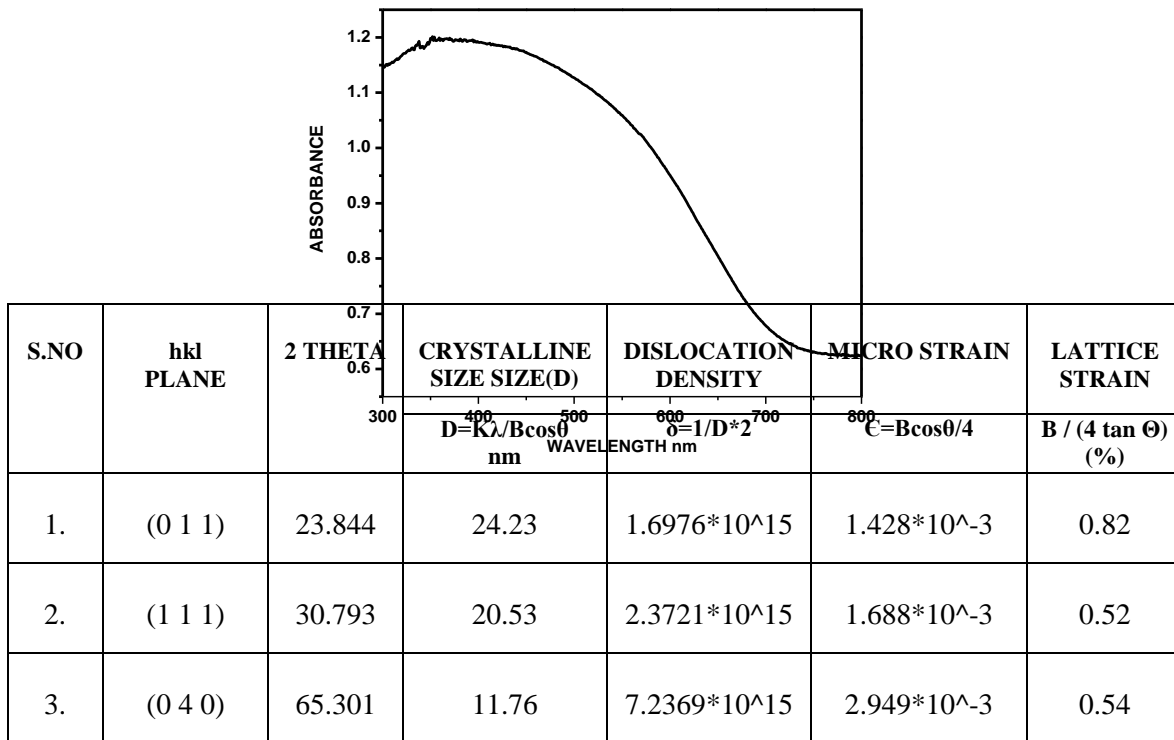
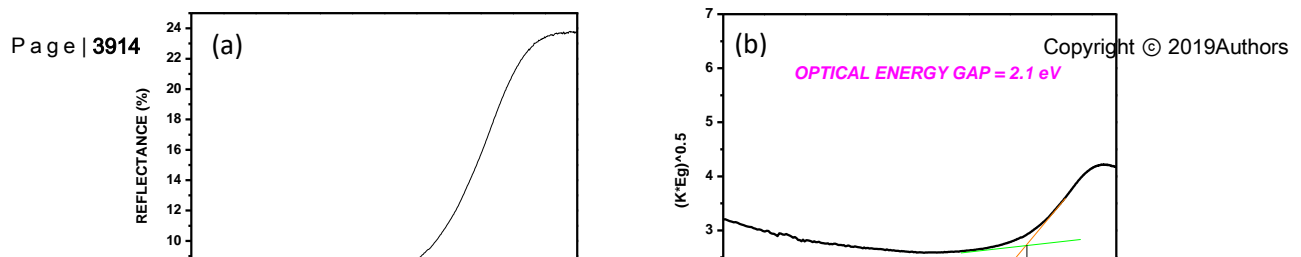


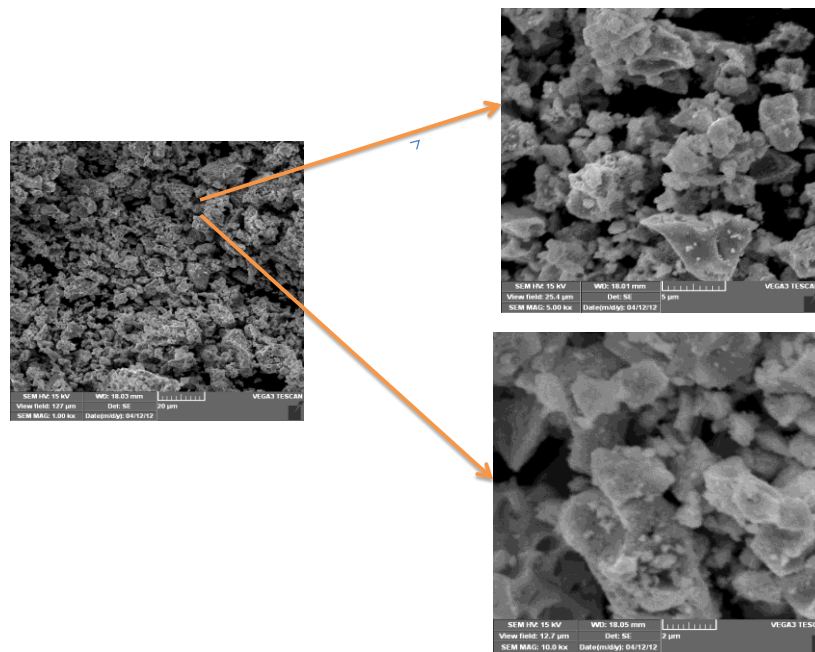
Fig. 4 UV-Vis Absorption Spectrum of FeWO4.



**Fig. 5 (a) Reflectance Spectrum of FeWO<sub>4</sub> and (b) Bandgap Energy Determination Using Kubelka-Munk Function.**

**3.3. SEM and EDAX analysis**

Scanning electron microscope (SEM) is used to observe the morphology of synthesized powders with respect to their particle size and texture. The surface morphology of the samples of FeWO<sub>4</sub> materials is shown in Fig. 6. The SEM micrograph shows the clusters of nanostructured particles synthesized by combustion process has flake like morphology. It is noticed that the grain size derived from SEM photograph is larger than the estimated values from XRD data. This suggests





**Fig. 6 Surface Morphology of FeWO<sub>4</sub>.**

the fact that every particle is shaped by aggregation of larger number of grains. Besides the crystalline size was confirmed with XRD data.

The elemental composition of the synthesized monoclinic FeWO<sub>4</sub> was assessed by EDAX spectral analysis. EDAX spectrum of FeWO<sub>4</sub> is shown in Fig. 7. According to the L series the weight percentage of W is 80.09 % and similarly the weight percentage of Fe and O is found to be 25.78% and 7.44% respectively. Thus the EDAX spectrum confirmed the presence of Fe, W, O in the final compound of monoclinic FeWO<sub>4</sub>.

**3.4 Electrical conductivity studies**

The DC conductivity studies for FeWO<sub>4</sub> at different temperatures from 30°C to 120°C is analyzed using Keithely. The results observed that by increasing the temperature from 30°C to 120°C the current also increases which is an evident for the semiconducting nature of the material. The I-V characteristics follow the ohmic law at lower voltages and on increasing the voltages it followed non-ohmic behavior. The temperature dependent I-V characteristics of FeWO<sub>4</sub> is shown in Fig. 8.

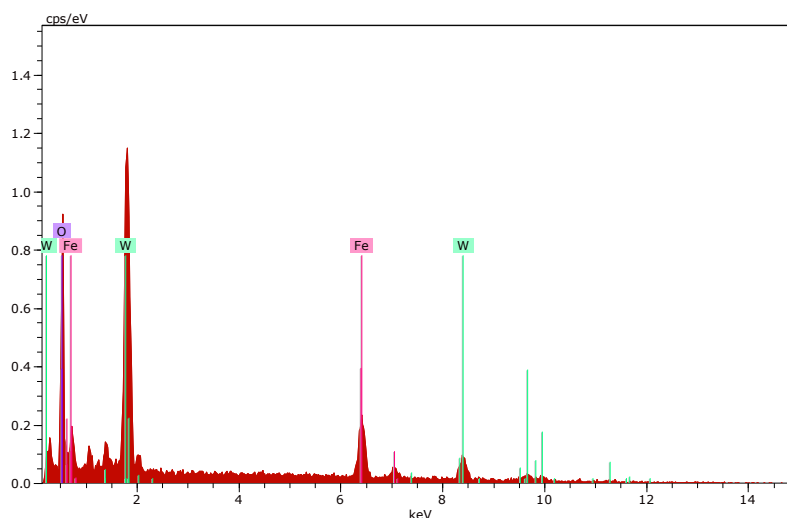
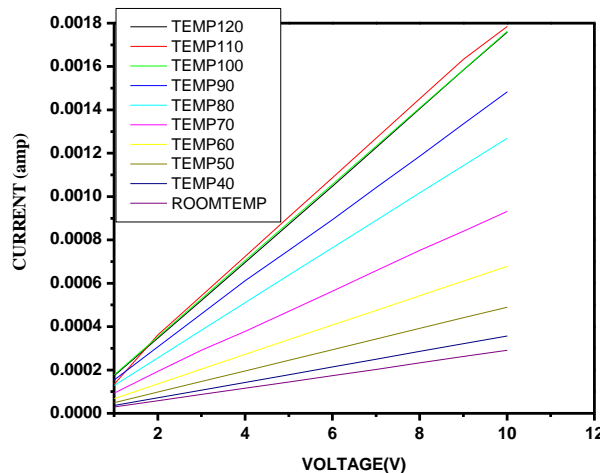


Fig. 7 EDAX spectrum of FeWO<sub>4</sub>.

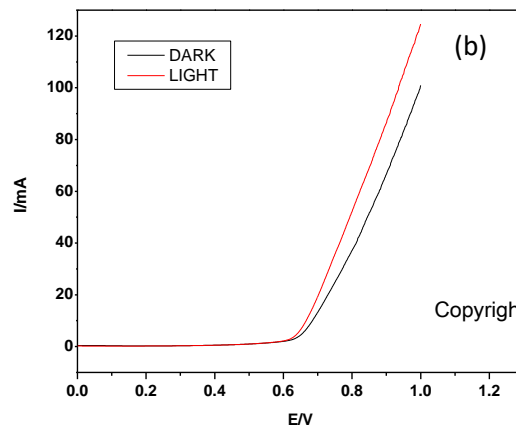
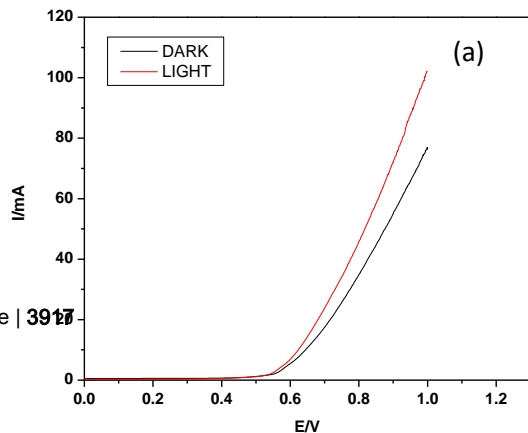
Fig. 8 DC conductivity studies of FeWO<sub>4</sub> at different temperatures.

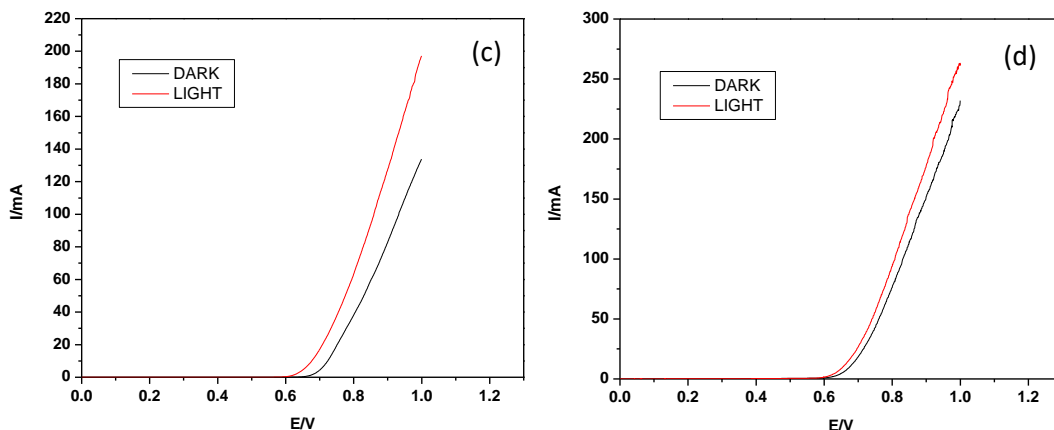
### 3.5 Photo-catalysis of FeWO<sub>4</sub> towards oxygen evolution from water

The photo-electrochemical water splitting towards oxygen evolution was done in a three cell compartment electrochemical cell with Hg/HgO reference electrode, Pt as counter electrode and working electrode using FeWO<sub>4</sub> coated on Ni, Cu, SS, Pt substrates. 1M KOH is used as electrolyte. Linear sweep voltammetry is performed at 1mV/sec in the anodic site with a potential



of -0.6 to 1 V under dark and light conditions (150mW halide lamp). The current potential curves of FeWO<sub>4</sub> on different substrates is shown in Fig. 9.





**Fig. 9 Current Potential Curves of FeWO<sub>4</sub> coated on (a) Nickel (b) Copper (c) Platinum (d) Stainless steel substrate under dark and light conditions.**

The substrate plays a major role in photocatalytic oxygen evolution. The photocurrent generation rates are higher at Pt substrate on comparing with Ni, SS and Cu. The generation rates were in the increasing order of Pt>SS>Ni>Cu. The Pt substrate effectively absorbs the photon and helps in fast carrier generation and transport, which results in the increase of current under light conditions. The photon to current conversion rates were much faster on Pt coated substrates and it was found to be 0.012 sq.units. The photo-oxidation of water towards oxygen evolution is faster in Pt coated samples. The current and voltage raises due to the higher absorption of photons. The current conversion area also follows the same order of Pt>SS>Ni>Cu. Thus the present data show that FeWO<sub>4</sub> powders were promising material for Photo-anodes for the catalytic oxygen evolution from water and best suited for solar hydrogen generation process in tandem cells.

**Table 2 Effect of substrate on photocurrent.**

VOLTAGE (V)	INCREASE IN CURRENT BY PHOTONS (mA)			
	NICKEL SUBSTRATE	COPPER SUBSTRATE	PLATINUM SUBSTARATE	STAINLESS STEEL SUBSTRATE

0.6	2.032	2.83	6.12	7.21
0.7	5.84	9.1	16.7	5.24
0.8	4.98	22.64	19.7	28.83
0.9	14.03	20.72	4.86	31.37
1.0	27.17	23.1	62.84	33.92

## CONCLUSION

Solution Combustion synthesis is found to be a convenient method for the preparation of fine crystalline compounds of Iron Tungstate. The synthesized powders were characterized by XRD and the crystalline size is found to be 19 nm with monoclinic structure and 0.63% lattice distortion. The band gap energy is calculated from reflectance spectrum and is found to be 2.1 eV. Flake like structures is observed from the morphological studies and confirms the elemental composition through EDAX analysis. The DC Conductivity, photoconductivity measurements gave an idea regarding the conductivity of the material. The in depth study of oxygen evolution from water was analyzed by potentiostat and found to be greater photocurrents for the material coated on Pt substrate than Stainless steel, Nickel and copper substrate. The experimental results conclude that the iron tungstate based photo-anode is highly recommended for photo-catalysis for solar hydrogen production in tandem cell applications.

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