SYNTHESIS STRATEGY OF F:SnO_2 POWDER FOR TCO-LESS DSSCs FABRICATION

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Abstract

In order to improve the photo catalytic properties, fluorine doped tin oxide (F: SnO_2) nanopowder was synthesized by sol-gel auto-combustion process. The X-ray diffraction and SEM analysis have confirmed the formation of structure, the grain size and the morphology of nanoporous F:SnO_2 powder. The synthesis strategy reflected from the microstructure has been investigated. In Dye Sensitized Solar Cells (DSSCs) fabrication, SnO_2 is sensitized with chemical dyes to enhance its efficiency. UV-Vis response of pure and doped (F: SnO_2) were investigated by using UV-1800 Shimadzu spectrophotometer. Some of these materials were applied in the fabrication of Dye Sensitized Solar Cells without Transparent Conductive Oxide layer (TCO-less DSSCs). The current-voltage measurements of the fabricated solar cells revealed the enhancement of energy conversion efficiency, long-term stability and cost effectiveness of DSSCs.

Introduction

In the previous century, it is obvious that the consumption of nonrenewable sources of energy has caused more environmental damage than any other human activity. Energy generated from fossil fuels has led to face many problems such as exhaustion of fossil fuels, ozone depletion, global warming, climate change and social and political risks. Therefore, renewable source of energy such as Hydropower, Wind, Solar, Biomass, Geothermal and others have become very important and relevant to today's world.

Solar photovoltaic cells are a promising form of renewable energy. The primary obstacle to the broader uptake of solar photovoltaic technology is the manufacturing cost of current commercial solar cells. Thus, a new type of dye-sensitized solar cells (DSCs) based on nanoporous F:SnO_2 electrode without TCO layer will be fabricated for low-cost solar cell application.

Experimental Details

Preparing Fluorine Doped Tin Oxide (F:SnO_2) Powder

Fluorine doped SnO_2 powder has been prepared by following sol-gel auto-combustion method. Firstly, 5.2 g of $SnCl_4.5H_2O$, 0.4 g of acetylene black and 0.38 g of HF (50%) were weighed by digital balance. Then $SnCl_4$ and HF were dissolved in 20 ml of deionized water. Acetylene black was added to this solution. NH_4OH aqueous solution was added drop wise during constant stirring. After 15 min stirring, the solution turned to gel. This gel was heated at 120 °C for 10 min to get dry gel. The dry gel was further heated at 500 ˚C in air. After 30 min ignition of the dry gel, auto-combustion process took place as shown in Figure 1 and F doped SnO_2 powder was obtained. The colour of as-burnt powder is gray. The sample was further calcined at 550 °C for 30 min. The colour of the sample is light gray. The sample was sintered at 650 °C for 2 hours. The colour of the simple changed to yellow. The sample was sintered at 750 °C for 2 hours. The colour of the simple changed to white. Finally, the nanoporous F doped

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SnO_2 powder has been successfully obtained. The Flow chart of F:SnO_2 powder preparation is shown in Figure 2. The structure and morphology was investigated by XRD and scanning electron microscopy (SEM). The crystallite size of the particle can be calculated from the XRD peak broadening of the (110) peak using the Scherrer's formula.

$$g_{crystallite} = \frac{0.9\lambda}{D\cos\theta} \quad \text{---------- (1)}$$

(a) (b) (c)

Figure 1 The formation of F doped SnO_2 powder via Auto-combustion process

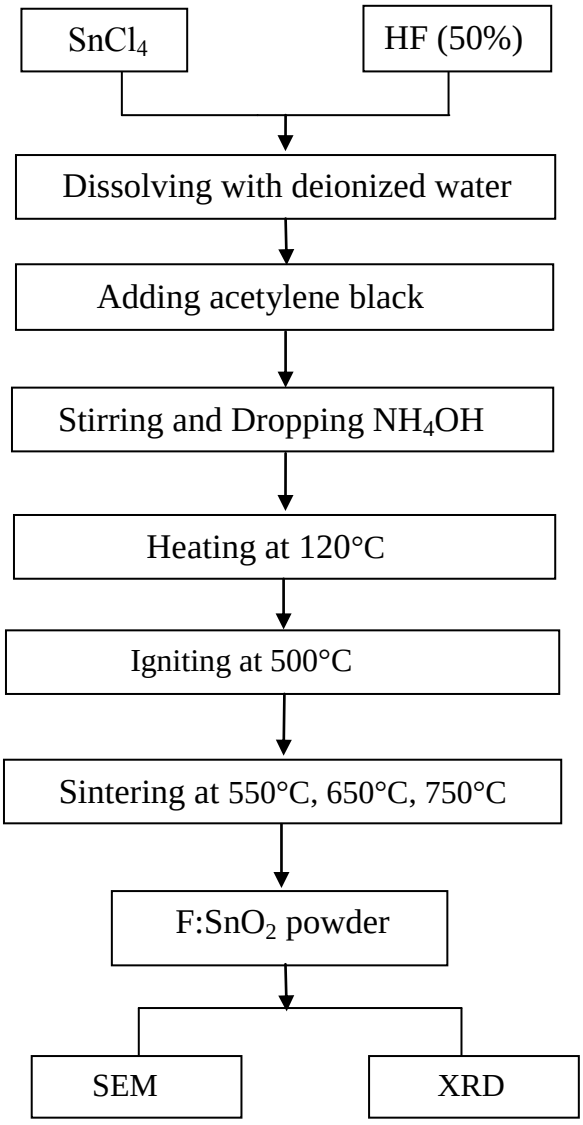


Figure 2 Flow chart of preparation of F:SnO_2 powder

Preparing the Working Electrodes

The well cleaned ordinary glasses have been used as substrates for preparing working electrodes. The scotch tape has been used to cover the three sides of the glass substrates. The nanoporous semiconductor paste was prepared by grinding 2.5 ml of citric acid (pH 2.4) and 1.5 g of fluorine doped tin oxide powder (sintered at 750 ˚C) in the mortar and pestle for about 30 min to break the aggregation of F: SnO_2 powder. One drop of washing powder solution was added to this suspension to reduce surface tension. The resultant paste was put on the masked glass substrates. The flattened paste was distributed by Doctor's Blade Method. These electrodes were put on the hot plate and heated them at approximately 150 ˚C for 30 min and then cooled down slowly.

Preparing Dye Solutions

About 0.2 g of coumarium powder, mercurochrome and methyl blue were dissolved in 100 ml of ethanol in each beaker separately for about 3 hours.

Dipping Working Electrodes in Dye Solutions

The prepared working electrodes were dipped in each dye solution for about (10-30) minutes depending on selected dye solutions and then dried in the dryer. These electrodes were heated mildly at (60-80 ˚C) if coloration is too slow.

Preparing the Counter Electrodes

The cleaned ordinary glasses, silver coated glasses and FTO glasses (which were made in URC lab) were uses as substrates for preparing counter electrodes. The scotch tape was used to cover the three sides of the counter electrodes. The carbon enrich SnO_2 paste was prepared by grinding 2 g of SnO_2 powder, 0.4g of actylene black powder and 0.1 g of graphide powder with 10ml of ethanol and 0.1ml of Triton X-100 in mortar and pestle for about 1 hours. The prepared paste was put and flatten on each glass substrate by doctor's blade method.The counter electrodes were dried on the open hot plate (at about 150 ˚C) and then cooled down slowly.

Preparing the Electrolyte solution

The redox electrolyte solution was prepared by mixing 0.5 M potassium iodide and 0.05 M iodine in unhydrated ethylene glycol. This electrolyte was stored in dark coloured bottle for further use.

Filling Electrolyte solution in the holes and binding two electrodes

The spacers made by cutting plastic film are put on the cooled counter electrodes. Some of the electrolyte solution was dropped into the holes and combine the two electrodes quickly to prevent the solvent from drying out. By fixing them with binder clips the experimental procedure for fabrication of TCO-less and with only TCO glasses involved DSSCs were completed. Figure 3 shows the fabrication processes of DSSCs. Figure 4 shows the prepared working electrodes, counter electrodes and spacers.

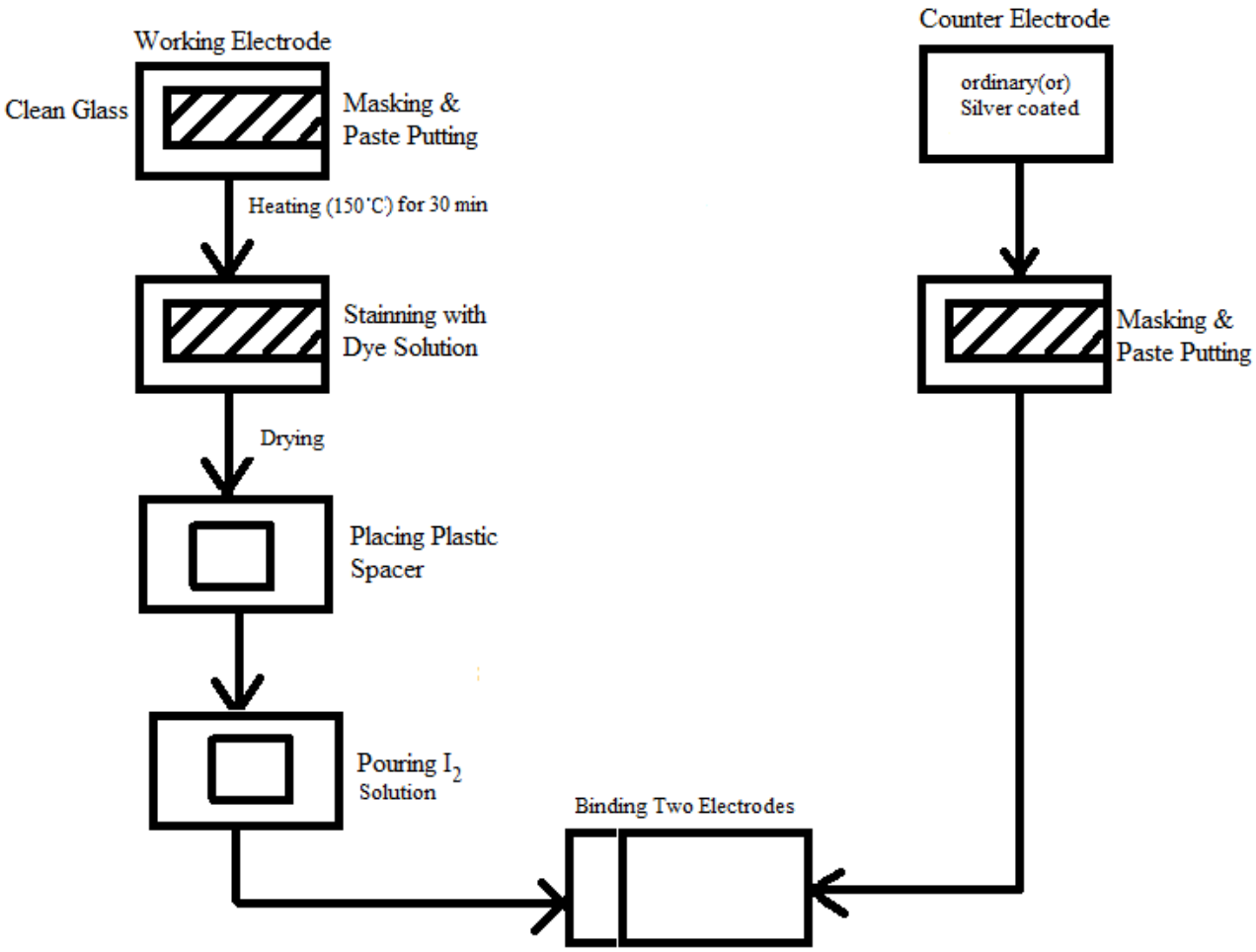


Figure 3 The fabrication processes of DSSCs

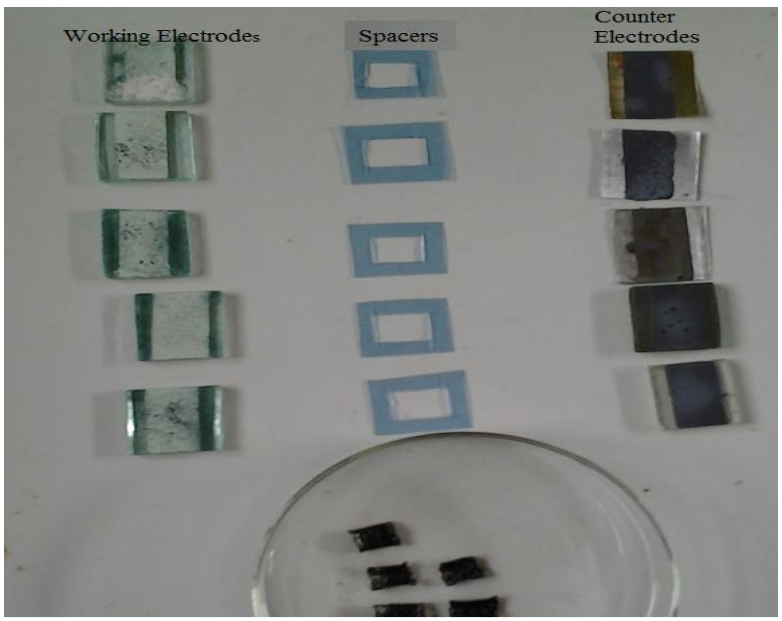


Figure 4 The prepared working electrodes, counter electrodes and spacers

Results and Discussion

Observation on Fluorine Doped Tin Oxide (F:SnO_2) Powder

The phase formation of F: SnO_2 powder is analyzed by X-ray diffraction (XRD) method. XRD patterns of nanoporous F: SnO_2 samples are shown in Figures 5(a), 6(a) and 7(a). Variation of 2θ, d-spacing and FWHM with annealing temperature is listed in Table 1. Crystallite size (g) and lattice parameter (a) is listed in Table 2. According to XRD results, it can be concluded that the annealing temperature can increase crystallization and growing of F: SnO_2 nanocrystallite. The preferred orientation indicates (1 1 0), (1 0 1), (2 1 1) for SnO_2 and (2 0 0) for fluorine, respectively.

The surface morphology of the F:SnO_2 samples has been characterized by Scanning Electron Microscopy (JEOL-JSM 5610LV). The SEM photographs of F doped SnO_2 sample at 550 °C, 650 °C and 750 °C are shown in Figures 5(b), 6(b) and 7(b) respectively. Each photograph exhibits a typical porous structure with many intergrain pores. It is observed that the intergranular pores are linked through the large pores. The pore structure should be regarded as interconnected voids that form a kind of capillary tubes. This structure is preferable for the adsorption of dye solution capable of making photo excitation (pumping out of photo electrons). In the micrograph of F: SnO_2 sintered at 550°C, the grains are spread out and the mean pore size is about 7 nm. After sintering at 750°C, the grains are adhered and the large pores are formed between groups of grains. The mean pore diameter is 7-20 nm. The variation of mean pore size of F: SnO_2 sample with sintered temperature is shown in Table 3.

From UV-Vis Spectroscopy, it was noticed that F:SnO_2 powder has lower absorbance value(<1) and wider band gap value(4.11eV-5.31eV). Therefore it can be used as electron transport mediator semiconductor at working electrode of DSSCs. The VU-Vis spectrum of pure and doped SnO_2 powder is shown in Figure 8. The estimated band gap values and the corresponding wavelengths are listed in Table 4. The band gap values are calculated by

$$E_g = 1240/\lambda. \text{ eV nm /nm} \qquad \text{---------- (2)}$$

Measuring DSSCs' Parameter

To measure open circuit voltage (V_{OC}) and the short circuit current (I_{SC}) for each cell, the cell was connected with external circuits shown in Figure 8(a). Figures 8(b) and 8(c) show the photographs for measuring currents and voltages under sunlight and illuminations. The open circuit voltage (V_{OC}) and the short circuit current (I_{SC}) for each cell were measured under illumination of (1000 W/cm^2) neon bulb and the effective cells' area is 1cm^2.

The measured open circuit voltage (V_{OC}) and short circuit current (I_{SC}), the estimated maximum voltage (V_{MPP}) and maximum current (I_m) and the calculated energy conversion efficiency (η) and fill factor (FF)for each cells were listed in Table 5. The energy conversion efficiency (η) can be calculated by Equation 3.

$$\eta = \frac{MPP}{E \times A_C} \qquad \text{---------- (3)}$$

$$MPP = I_m \times V_m \quad \text{----------} \quad (4)$$

The Fill factor (FF) can calculated by equation 5.

$$FF = \frac{MPP}{I_{sc} \times V_{oC}} \quad \text{----------} \quad (5)$$

η = energy conversion efficiency, MPP = maximum power point

E = illumination, A_C = area of cells, I_m = maximum current, V_m = maximum voltage

The working principles of DSSCs can demonstrate as the following Equations 6,7,8,9 and 10.

At Cathode:

$$S + h\upsilon \rightarrow S^* \quad \text{Absorption} \quad \text{----------} \quad (6)$$

$$S^* \rightarrow S^+ + e^- (F:SnO_2) \quad \text{Electron injection} \quad \text{----------} \quad (7)$$

$$2S^+ + 3I^- \rightarrow 2S + I_3^- \quad \text{Regeneration} \quad \text{----------} \quad (8)$$

At Anode:

$$I_3^- + 2e^- (carbon) \rightarrow 3I^- \quad \text{----------} \quad (9)$$

Cell:

$$e^- (carbon) + h\upsilon \rightarrow e^- (F:SnO_2) \quad \text{----------} \quad (10)$$

Table 1 Variation of 2θ, d-spacing and FWHM with annealing temperature

$F:SnO_2$ Powder	**(hkl)**	**2θ (deg)**	**D (Å)**	**FWHM (deg)**
550˚C	(110)	26.676	3.3389	0.326
650 ˚C	(110)	27.139	3.2831	0.546
750 ˚C	(110)	26.498	3.3610	0.641

Table 2 Variation of Crystallite size (g) and lattice parameter (a)

$F:SnO_2$ Powder	Crystallite Size g (nm)	Lattice Parameter a (Å)
550˚C	24.76	4.72
650 ˚C	14.79	4.64
750 ˚C	12.59	4.75

Table 3 Variation of mean pore size with sintering temperature

Sintering temperature (˚C)	Mean pore size (nm)
550	7
650	10
750	12

Table 4 Band gap values calculated from respective wavelength values

sample	First scan (200-400)nm		Second scan (190-1100)nm		Mean value E_g (eV)
	λ	E_g(eV)	λ	E_g(eV)	
Pure SnO_2	230	5.31	237	5.23	5.27
F:SnO_2(550 ˚C)	237	5.23	297	4.175	4.70
F:SnO_2(750 ˚C)	236	5.24	302	4.106	4.67

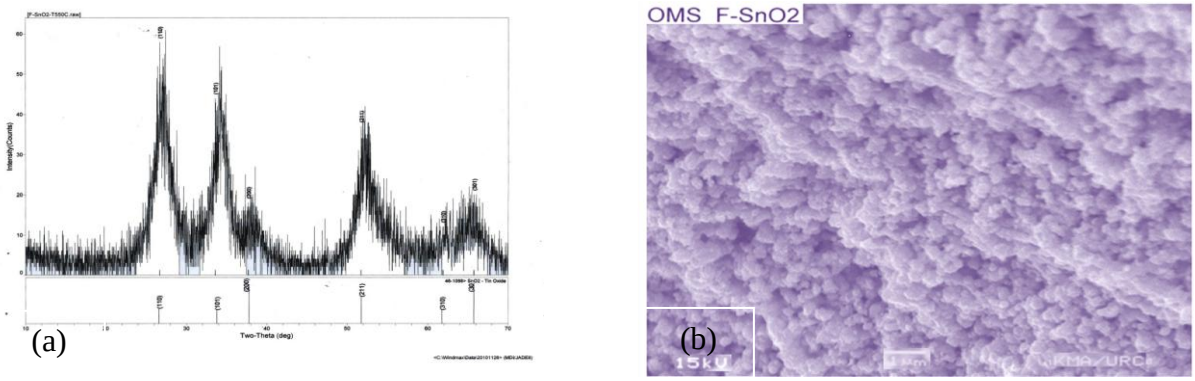


Figure 5 (a) XRD pattern and (b) SEM photograph of nanoporous F:SnO_2 Sample (550°C)

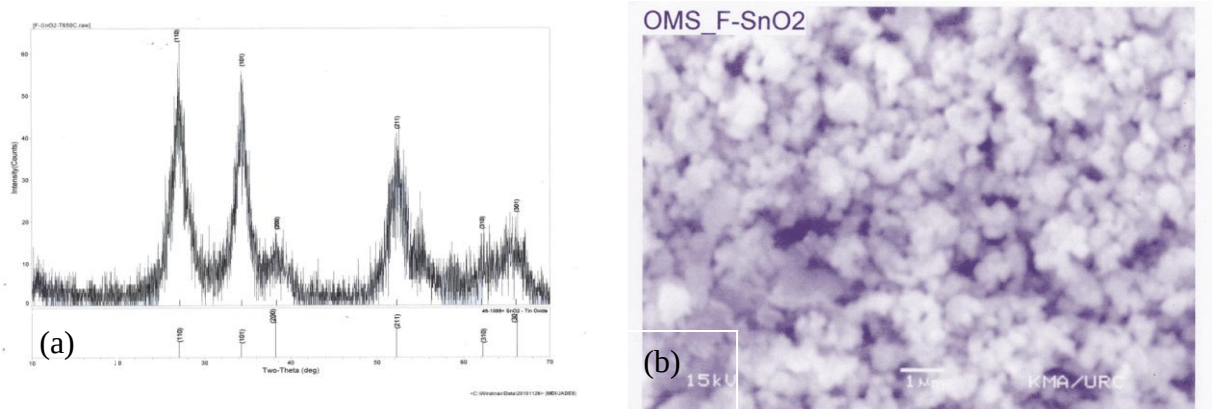


Figure 6 (a) XRD pattern and (b) SEM photograph of nanoporous F:SnO_2 Sample (650°C)

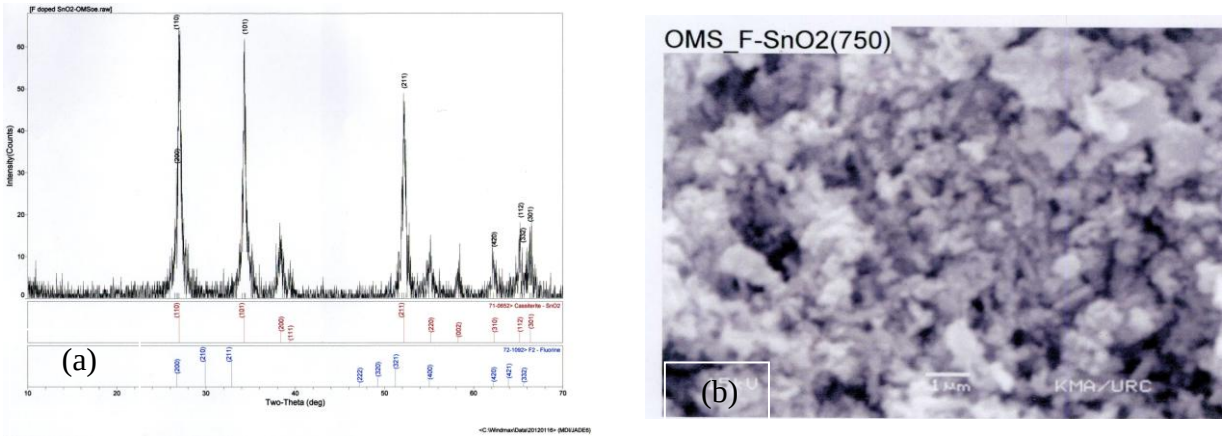


Figure 7 (a) XRD pattern and (b) SEM photograph of nanoporous F:SnO_2 Sample (750°C)

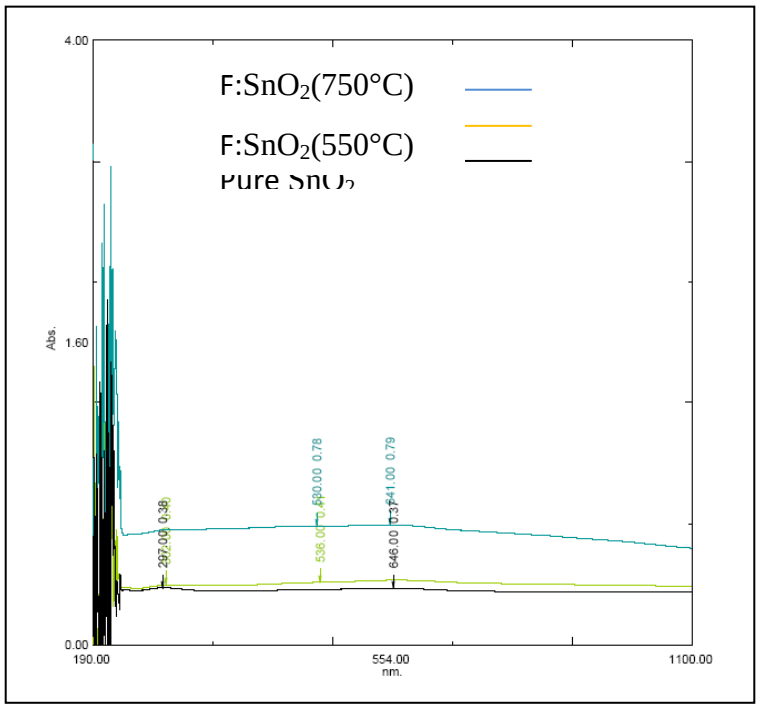
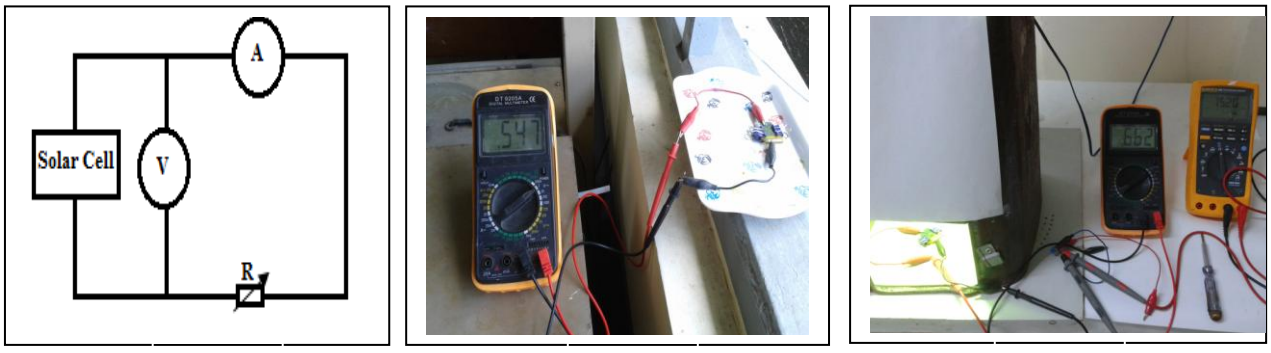


Figure 8 UV-Vis spectrum of pure and F doped SnO_2 Samples



(a) (b) (c)

Figure 9 (a) The experimental setups for measuring the current-voltage characteristics of DSSCs, (b) under Sunlight and (c) under illumination

Table 5 The values of open circuit voltage V_{oc}, short circuit current I_{sc}, estimated maximum voltage V_{MPP}, maximum current I_{MPP}, calculated cells' efficiency (η) and fill factor(FF)

Sample	Type of Counter Electrode	Type of Dye solution	V_{oc} (V)	I_{sc} (mA)	η (%)	V_{MPP} (V)	I_{MPP} (mA)	FF (%)
1	Ordinary	Mecurochome	0.59	0.13	0.0300	0.50	0.060	39.11
2	Ordinary	Methyl blue	0.55	0.11	0.0263	0.47	0.056	43.50
3	Ordinary	Coumarium	0.52	0.09	0.0210	0.42	0.050	44.87
4	Silver	Mecurochome	0.56	0.25	0.060	0.40	0.15	48.00
5	Silver	Methyl blue	0.53	0.22	0.0546	0.42	0.130	46.80
6	Silver	Coumarium	0.46	0.21	0.043	0.33	0.130	44.40

Conclusion

The auto-combustion assisted sol-gel method has been proven as synthesis route for F doped SnO_2 powder. XRD patterns have confirmed that F: SnO_2 powder has been possessing single phase nanocrystalline structure. SEM images (Microstructures) obtained at sintering temperature, 550°C, 650°C and 750°C have proved that a typical porous structure with many intergrain pores has been produced by this method. Since a higher temperature of 750°C can provide larger pore size of around 12 nm, F: SnO_2 powder must be fabricated with this sintering temperature to replace both TCO and TiO_2 layer in Dye Sensitized Solar Cells (DSSCs). It was proved that fluorine doped tin oxide powder can be used in the place of working electrodes of TCO glasses in DSSCs' fabrication. The DSSCs without TCO layer has lower efficiency but higher fill factor. Therefore, it needs further study to increase cells' efficiency.

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