

## Effect of biological template on the performance of SnO<sub>2</sub> dye sensitized solar cell

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This paper reports the role of biological template on the performance of dye-sensitized solar cells (DSSC) fabricated using tin oxide (SnO<sub>2</sub>) nanoparticles. Herein, onion (*Allium cepa*) has been employed as the biological template in the synthesis of tin oxide nanoparticles for the first time and is compared with SnO<sub>2</sub> prepared without the template. The prepared samples were systematically characterised using the state-of-the-art facilities. A sandwich cell was prepared by using the dye soaked SnO<sub>2</sub> film acting as the photoanode and platinum coated on FTO as the counter electrode with I<sub>3</sub><sup>-</sup>/I<sup>-</sup> as the electrolyte. Current-voltage (I-V) characteristics have been studied using solar simulator. Performance of DSSC prepared with and without the template is analysed from the measured I-V curves and it is observed that the DSSC prepared using the biotemplate shows better efficiency (9.54%) and fill factor (0.5352).

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### 1. Introduction

High energy demand in the current scenario force the mankind to use more of renewable energy and among them the widely utilized energy to switch the electrical energy is solar energy. However, the cost of the fabrication of solar cell is extremely high. Researchers work on the fabrication of cost effective and high performance solar cells. In connection, research work focuses on dye sensitized solar cells (DSSCs). But the only disadvantage of available DSSCs is the usage of high cost dyes like N719. The long back invention in 1991 by O'Regan and Gratzel promotes the adsorption of organic dye molecules on the nanocrystalline titanium dioxide film and the use of redox electrolyte. Various other metal oxide semiconductors have been effectively used as a photoanode in DSSCs which include Nb<sub>2</sub>O<sub>5</sub> [1], ZnO [2], SnO<sub>2</sub> [3] and WO<sub>3</sub> [4] which show proficient alternative to TiO<sub>2</sub>. Among them, SnO<sub>2</sub> exhibits high electron mobility compared to that of TiO<sub>2</sub>. Herein it is aimed to use natural dyes such as Alizarine so as to reduce the fabrication cost of DSSCs [5]. This dye could absorb the light photons and create an excited molecular state that can inject electrons into SnO<sub>2</sub>. The best electrolyte so far reported in the literature is I<sub>3</sub><sup>-</sup>/I<sup>-</sup> couple because of slow recombination rate with injected electrons [6] and the commonly employed counter electrode is Pt. This report focuses on the fabrication of DSSC using SnO<sub>2</sub> photoanode, Alizarin dye, I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox electrolyte and Pt counter electrode. Effect of organic template on the properties of SnO<sub>2</sub> nanostructures and their impact on the performance of solar cells are studied and reported herein. SnO<sub>2</sub> nanostructures were prepared using chemical route without any surfactant and also with onion template and were characterized by various techniques.

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## 2. Experimental

Alizarin dye, Chloroplatinic acid Hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), tin chloride (II) dehydrate, FTO Glass Slide, Ethanol, Ethylene glycol and methanol were purchased from sigma Aldrich and were used as such without further purification.

Onions were chopped and dried under shadow for overnight. 5g of the onion was added to 50 ml of distilled water, sonicated for 10 minutes. 50 ml of 0.1M  $\text{Sn}^{4+}$  solution prepared with 2:3 ethanol – water mixture was added to the onion template under sonication, adjusted the pH to 9 using liquid ammonia and was sonicated for 1 hour. The mixture was kept at room temperature for 24 hours, dried at 100°C for 4 hours in hot air oven and calcined at 500° C in muffle furnace and the sample was named as OS9. Without adding template, the procedure was repeated to prepare  $\text{SnO}_2$  nanostructure and the sample was named as ES9.

$\text{SnO}_2$  paste was prepared by mixing  $\text{SnO}_2$  (0.1M), acetic acid (10 drops), Triton X-100 (3 drops) and ethanol (10 drops) thoroughly and was used to fabricate DSSC.  $\text{SnO}_2$  paste was coated onto well-cleaned FTO glass ( $100 \text{ cm}^2$ ) plate using doctor blade method, sintered at 500 °C for 30 minutes and allowed to cool down to room temperature. The sample was then immersed in Alizarine dye solution for 24 hours [7].  $\text{I}_3^-/\text{I}^-$  redox electrolyte was prepared as per the literature [8] and was stored in a black bottle wrapped with aluminium foil. Platinised FTO counter electrode was also prepared as per the reports [9]. The solar cell was assembled by adding the electrolyte in between the working  $\text{SnO}_2$  electrode and a platinised FTO counter electrode.

## 3. Characterization

Crystallinity of the samples were identified by X – ray powder diffraction (XRD) using a PANalytical X'pert PRO X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) as X-ray source. ATR (Attenuated Total Reflectance) spectra are recorded using Alpha T –Bruker. Surface morphology of SEM images of  $\text{SnO}_2$  nanoparticles were recorded using SIGMA WITH GEMINI COLUMN MODEL, CARL ZEISS (USA) make, Resolution 1.5 field emission Scanning Electron Microscope (FESEM). The absorption spectra of the solid samples were recorded using Cary 60 UV-Visible spectrophotometer make Agilent technology. The DSSC performance of the prepared cell was measured by electrochemical workstation (Metrohm, Autolab 302NFRA2) under the xenon lamp irradiance ( $100 \text{ mW/cm}^2$  and AM 1.5) of LOT-LS0104solar simulator.

## 4. Results and discussion

### 4.1. ATR

ATR spectra of  $\text{SnO}_2$  nanostructures prepared with and without onion template is presented in Fig. 1. A band appeared between  $400\text{--}700\text{cm}^{-1}$  is assigned to Sn–O antisymmetric vibrations and confirms the formation of  $\text{SnO}_2$  [10]. The band at  $613 \text{ cm}^{-1}$  corresponds to Sn-O lattice vibration. It got widened due to the addition of onion template during the synthesis of  $\text{SnO}_2$  nanostructures [11]. Absence of vibrations corresponding to other organic moiety in the OS9 spectrum indicates complete removal of organic template during calcinations at 500°C.

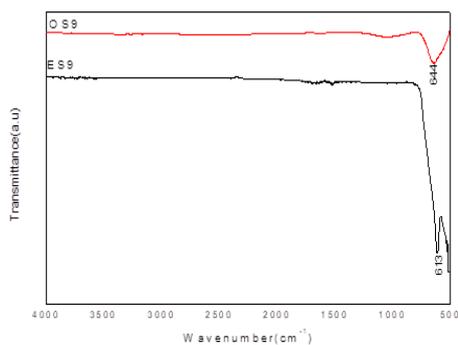


Fig. 1. ATR spectra of  $\text{SnO}_2$  nanostructures.

#### 4.2. Powder XRD

XRD patterns for  $\text{SnO}_2$  nanostructures prepared with and without template is given in Fig. 2 and the prominent peaks were indexed to (110), (101), (111), (211), (220), (002), (310), (112), (301), (202) and (321) planes corresponding to the tetragonal crystal structure of  $\text{SnO}_2$  based on the ICDD No. 77-0449[12].

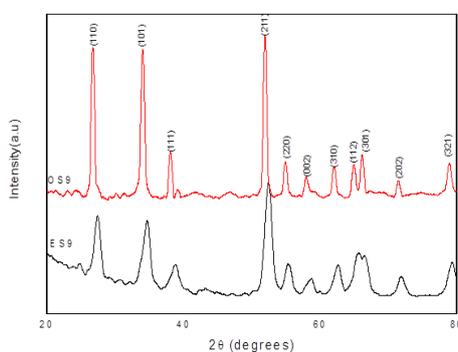


Fig. 2. XRD pattern of Synthesized  $\text{SnO}_2$  nanostructure.

Peak intensity of  $\text{SnO}_2$  increases with onion template, which indicates the increase in crystallinity. The crystallite size was determined using Scherrer formula [13] and it was found to be 20 nm and 36 nm respectively for ES9 and OS9. In addition, the pores present in the template could lead to the agglomeration of nuclides inside them and could result in the increased crystallite size compared to the sample prepared without template.

#### 4.3. UV –DRS

Fig.3 represents the absorption spectra of  $\text{SnO}_2$  nanostructures prepared in the presence of onion and without template. The optical energy band gap is calculated using Tauc's relation [14] by plotting the graph between  $(\alpha h\nu)^2$  and incident photon energy ( $h\nu$ ) which is depicted in the inset of fig. 3. It is observed that the value of  $E_g$  for OS9 is 3.30 eV and is similar to the reported value for bulk  $\text{SnO}_2$  [15], while the value of  $E_g$  for ES9 was increased to 3.76 eV. Since it was well renowned that the reduction of particle size could increase the bandgap of  $\text{SnO}_2$  [16] as evidenced from powder XRD results.

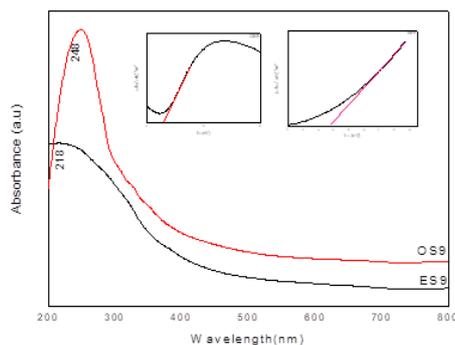


Fig. 3. UV- DRS and (inset) the corresponding  $(ah\nu)^2$  versus photon energy  $(h\nu)$  plot.

#### 4.4. FE-SEM

Fig. 4 shows the FESEM images of  $\text{SnO}_2$  nanostructures of OS9 and ES9. The nanoparticles have spherical morphologies with the sizes 20 nm in ES9 whereas for OS9, the grain size is around 40 nm. OS9 particles are found to be irregular in shape and the agglomeration of such particles resulted in large grain size. This is in agreement with our XRD analysis. The agglomeration could be due to presence macro-sized pores in the onion template. [17].

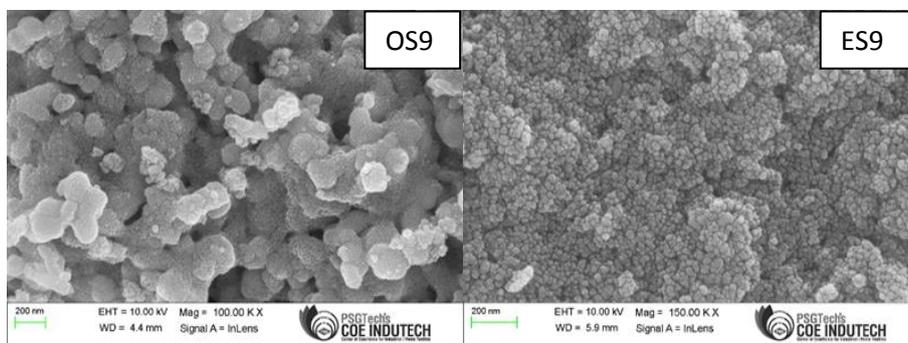


Fig.4.FE SEM image of  $\text{SnO}_2$  nanostructure.

#### 4.5. PL Spectra

Defects in the prepared  $\text{SnO}_2$  nanostructure is identified using the photoluminescence spectra at 385 nm excitation and presented in Fig. 5. Complex emissions observed for both the samples indicate the existence of more defects in the lattice. Oxygen deficiency in the lattice is identified from an intense emission at 488 nm and the low intense emissions at 461 nm. In addition to these emissions, existences of low intense green emissions at higher wavelengths were correlated to the recombination of electron sites to the holes at the oxygen vacant sites [18, 13].

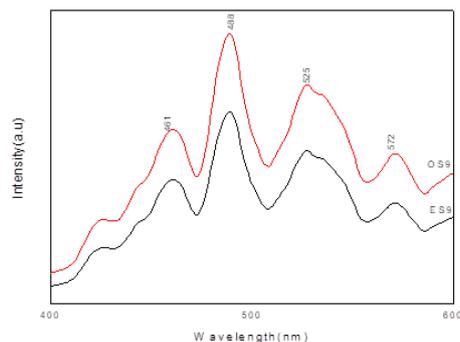


Fig.5.PL spectra of  $\text{SnO}_2$  nanostructure.

#### 4.6. I-V characteristics of fabricated photovoltaic cells using Alizarine red dye

Fig.6 shows the I-V characteristics of DSSC fabricated using  $\text{SnO}_2$  photoanodes and alizarin dye. Photovoltaic conversion efficiency  $\eta$ , is calculated from the formula [3]. The fill factor is calculated using the formula[3]. Onion templated  $\text{SnO}_2$  shows better performance than  $\text{SnO}_2$  prepared without template even with high crystallite size.This result is the highest efficiency reported so far for pure  $\text{SnO}_2$ -based DSSCs involving Alizarine as sensitizer along with  $\text{I}_3^-/\text{I}^-$  electrolyte [19].

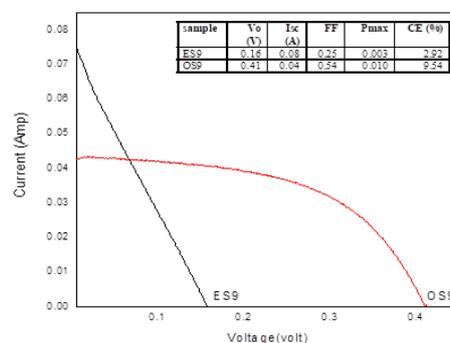


Fig. 6. I-V characteristics of fabricated photovoltaic cells using Alizarine red dye.

## 5. Conclusion

DSSCs were fabricated with  $\text{SnO}_2$  photoanode prepared with and without onion template, platinumized FTO counter electrode and  $\text{I}_3^-/\text{I}^-$  electrolyte. Due to the agglomeration of the crystallites inside the pores of the template, the size of the particles prepared with the template were larger than those prepared without template. Though the particle size is more, DSSC performance is also more for the OS9 sample. Reason for the better performance of the template samples even with larger size will be investigated in future.

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