Influence of pH on the DSSC Performance of Template Assisted SnO2 Nanostructures

vasanthapriya R  
Sri Ramakrishna Engineering College

NEELAKANDESWARI N (✉ neela476@gmail.com)  
Nallamuthu Gounder Mahalingam College

K. Uthayarani  
Sri Ramakrishna Engineering College

M. Chitra  
Sri Ramakrishna Engineering College

Keywords: Dye sensitized solar cells, onion, tin oxide, alizarin

DOI: https://doi.org/10.21203/rs.3.rs-411184/v1

License: © This work is licensed under a Creative Commons Attribution 4.0 International License.  Read Full License
Abstract

This paper reports the performance of alizarin based SnO$_2$ dye-sensitized solar cells. A novel template assisted method has been applied for the preparation of tin oxide nanoparticles. For the first time, onion (*Allium cepa*) was used as a template for the synthesis of tin oxide nanostructures at different pH values. Tin oxide nanostructures were used for the photoanode preparation. A sandwich cell was prepared by using the dye soaked SnO$_2$ film as a photoanode and platinum as a counter electrode. The structural, morphological and optical properties of the nanoparticles were studied using powder X-ray diffraction (XRD), Scanning Electron microscope (SEM), Photoluminescence (PL), Attenuated Total Reflectance (ATR) spectra and UV-visible spectroscopic techniques. Current-voltage (I-V) characteristics have been measured using electrochemical workstation under the presence of solar illumination. Characteristic parameters of the fabricated cell were determined on the basis of the measured I-V curves.

1. Introduction

Current energy requirements can be met by the mankind simply by utilizing renewable energy to extract electrical energy and among the renewable resources; solar plays a vital role and solar cells convert the sun light into electrical energy. However, the fabrication cost of the solar cell is highly expensive. This provides a platform for the researchers to work on the fabrication of cost effective and high performance solar cells. Solar cell or PV cell use solar energy instead of a fuel gives out no waste and produces clean energy. The innovatory works on the DSSC by O'Regan and Gratzel [1] in the field of solar cell stimulated the researchers to work on DSSC. DSSCs have been widely investigated due to their low-cost, fabrication procedure and reasonable efficiency [2]. Furthermore, the green nature of these energy devices has encouraged scientists to pay more attention to DSSCs rather than solar cells made from hazardous materials such as cadmium. In recent years, use of tin oxide based photoanodes for DSSCs has started to accelerate.

Most of the ongoing DSSC research work is based on TiO$_2$ used as Photoanode of dye sensitized solar cell [3]. The photoanode acts as an electron collector and overall performance of device depend on shape, size, porosity, crystallinity, surface area, morphology and band gap of photoanode material. The main drawback of TiO$_2$ DSSCs is the slow electron transport. In order to rectify it the alternative metal oxides with high electron mobility such as Nb$_2$O$_5$ [4], ZnO[5], CeO$_2$ [6] and SnO$_2$[7] are used as photoanode for DSSCs. When compared to all metal oxides SnO$_2$ has two benefits, it has higher electron mobility and has a larger bandgap (3.6eV) when compared to TiO$_2$[8].

Available advanced techniques for the synthesis of nanostructures limit their applicability due to their high cost. Cost effective approach to control the size and morphology of the nanostructures can be achieved with the help of templates. Template is a pattern or mould which transfers its topology or morphology to the material. All kinds of nanomaterials varying from metals to semiconductors can be prepared using the naturally occurring low cost templates. Resulting nanostructures with special morphologies find applications in the fields of sensors, optoelectronics, catalysis etc., Materials like butterfly wings, diatoms, bacteria, virus, wood tissues, vegetable skins, egg shell membrane etc were used as templates and the nanostructures were used for the above mentioned applications. Herein onion is used as a template for the synthesis of SnO$_2$ nanostructures.
Onion possess closely arranged hexagonal cells and can behave like a membrane with three layers namely sugar-chain layer, lipid layer and protein layer. Effect of pH will play role in controlling the structure.

In this present study, SnO$_2$ nanostructures are prepared for the DSSC fabrication by template assisted method and the structure, luminescence properties and morphology are studied by using X-ray diffraction, infrared absorption, UV – Vis, Photoluminescence spectroscopic studies and Field emission scanning electron microscopic studies and reported.

2. Experimental

2.1 Materials Used

Alizarin dye, Chloroplatinic acid Hexahydrate (H$_2$PtCl$_6$.6H$_2$O), tin chloride (II) dehydrate, FTO Glass Slide, Ethanol, Ethylene glycol and methanol are purchased from sigma Aldrich and used as such without further purification. Onions were chopped and dried under shadow for overnight and the preparation protocol is shown in Figure. 1.

2.2 Characterization

Crystallinity of the samples was identified by X – ray powder diffraction (XRD) using a PANalytical X’pert PRO X-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å) as X-ray source. ATR (Attenuated Total Reflectance) spectra are recorded using Alpha T –Bruker. Surface morphology of SEM images of SnO$_2$ nanostructures were recorded using SIGMA WITH GEMINI COLUMN MODEL, CARL ZEISS (USA) make, Resolution 1.5 field emission Scanning Electron Microscope (FESEM). The elemental composition of the samples was obtained using Nano XFlash Detector MODEL, BRUKER (GERMAN) MAKE Energy Dispersive X-ray (EDAX) Spectrometer .The absorption spectra of the solid samples were recorded using Cary 60 UV-Visible spectrophotometer make Agilent technology. The photovoltaic performance of the fabricated DSSC was measured using electrochemical workstation (Metrohm, Autolab 302NFRA2) under the xenon lamp irradiance (100 mW/cm$^2$ and AM 1.5) of LOT-LS0104 solar simulator.

2.3 Preparation of Electrolyte

0.05 M iodine and 0.5M potassium iodide were mixed thoroughly in 10ml of ethylene glycol. This solution was used as DSSC electrolyte and was stored in a black bottle wrapped with aluminium foil [9].

2.4 Preparation of Pt counter electrode

Initially, Fluorinated tin oxide (FTO) glass substrates were cleaned using ethanol and double distilled water and were subjected for sonication. Isopropanol and H$_2$PtCl$_6$.6H$_2$O. were used as the precursor to obtain metallic nanostructured platinum. A small amount of the precursor was deposited on a FTO plate, of 1 cm X 1 cm dimension and placed on a hot plate at 100$^0$ C. Finally Platinised FTO plate is placed on a muffle furnace at 400 $^0$C for 1 hour [10].

2.5 Fabrication of Dye-Sensitized Solar Cells
As-prepared SnO$_2$ (0.1M), acetic acid (10 drops), Triton X-100 (3 drops) and ethanol (10 drops) were mixed thoroughly and the resulting SnO$_2$ paste was used to fabricate DSSC. SnO$_2$ paste was coated onto well-cleaned FTO glass (1 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 [11], the electrolyte was sandwiched between the working electrode SnO$_2$ and a slightly platinised FTO counter electrode to assemble the solar cell device.

3. Results And Discussion

3.1 X – Ray Diffraction Studies

Powder XRD pattern of template (onion) assisted SnO$_2$ nanostructures at different pH is shown in Fig. 2.. From the diffraction patterns, it is observed that the peaks of OS7(pH-7) matches well with ICDD 78-1063 [12] and ICDD 88-0287 which corresponds to the presence of mixed phases tetragonal and orthorhombic structure respectively. Whereas the peaks obtained for samples OS8, OS9 and OS10 corresponds to Cassiterite SnO$_2$ with tetragonal structure (ICDD 88-0287) [13]. The crystallite size of all the samples were calculated using the equation (1)[14]

$$D = \frac{K\lambda}{\beta \cos \theta} \quad \text{-----------------------(1)}$$

and is tabulated in Table 1. From the table 1, it is observed that upon increasing pH of the reaction medium, crystallite size also increases.

The intensity ratios of the prominent peaks $(110)/(101)$ and $(211)/(101)$ were calculated for all the samples and tabulated in Table 1. From that, it is observed that the ratio of $(211)/(101)$ is relatively more for OS9 when compared to other samples which indicates the growth of SnO$_2$ nanostructures along (211) plane rather than (101) plane. Also, it is inferred that the intensity ratio $(110)/(101)$ is low for OS9 sample, which might be due to the growth of SnO$_2$ nanostructure along (101) plane rather than (110) plane. Such growth of SnO$_2$ nanostructure observed in OS9 along these active planes might be the reason for the formation of polyhedral structures as observed in FESEM.

Table 1. Structural properties of SnO$_2$ nanostructures synthesized at different pH
| Sample | Crystallite size (nm) | Intensity ratio | Intensity ratio | Lattice constant (Å) | Lattice strain ε = β_{hkl} / 4\tanθ |
|--------|----------------------|----------------|----------------|---------------------|----------------------------------|
|        |                      | (211)/(101)     | (110)/(101)    | a = b               | (101) plane (110) plane (211) plane |
| OS7    | 22                   | -              | -              | -                   | 4.7079 3.1761 0.00322 0.00429 0.002188 |
| OS8    | 34                   | 0.9612         | 1.0428         | 4.7093 3.1704      | 0.00160 0.00442 0.002193 |
| OS9    | 35                   | 1.078          | 1.0089         | 4.7093 3.1704      | 0.00160 0.00442 0.002193 |
| OS10   | 39                   | 1.037          | 1.0379         | 4.7186 3.2508      | 0.00313 0.00197 0.002065 |

Figure 3. shows the ATR spectra of template assisted SnO₂ nanostructures. Sharp absorption centered around 615cm⁻¹ is due to Sn-O framework vibrations (symmetric stretching of Sn-O-Sn) and confirms the formation of SnO₂ during the preparation process [15,16,17]. In addition, there were no absorptions corresponding to hydroxyl groups which indicates that all the organic impurities from the template were completely removed from the metal oxide during calcination at 500°C.

### 3.3 UV-Visible Spectral analysis and UV-DRS

UV-Vis absorption spectra of all the samples are depicted in Figure 4. From the spectra, it is observed that as pH increases, the absorbance edge gets shifted towards lower wavelength region. Band gap is also calculated from the plot (shown in Figure 5) between \((αhν)^2\) and \(hν\) [18] and is tabulated in Table 2. It is inferred that as pH increases, band gap value decreases. This may be due to the quantum confinement effect [19]. This is accordance with the increase in crystallite size as evidenced from XRD data.

**Table 2. Band gap of SnO₂ nanostructures synthesized at different pH values**

| Sample | Band gap (eV) |
|--------|---------------|
| OS7    | 4.00          |
| OS 8   | 3.75          |
| OS 9   | 3.30          |
| OS 10  | 3.00          |

Diffused reflectance spectra of SnO₂ nanostructures is shown in Figure 6. Percentage of reflectance increases with increase in pH this increased reflectance will decrease the pathway for the reflective light to reach the dye absorbed underlayer of the nanostructure and hence enhance the light flux [20] and hence this could be one of the reason for better photovoltaic efficiency of the samples.

### 3.4 Photoluminescence spectral analysis
Defects in the prepared SnO$_2$ nanostructure is identified using the photoluminescence spectra at 385 nm excitation and presented in Figure 7. Complex emissions observed indicate the existence of more defects in the lattice. Emissions at 424 nm and 432 nm could be correlated to the lattice stress due to lattice distortion. A small hump at 433 nm could be due to the interstitial Sn. An intense emission at 488 nm and the low intense emissions at 461 nm were correlated to the oxygen deficiency. These oxygen deficient sites were trapped by the holes, tunnel back into the particle to recombine with an electron in the conduction band. This recombination results in the intense blue emission [21]. Low intense green emissions at higher wavelengths were correlated to the recombination of electron sites to the holes at the oxygen vacant sites [22].

OS7 shows both blue and green emissions with relatively higher intensity and could be due to the presence of multiple crystalline phases in the material as evidenced from powder XRD. Intensity of blue emission decreases with pH and could be ascribed to the increased OH$^-$ ion concentration. Results are in agreement with the lattice strain observed for OS9 (Table 1). Relative intensities of green emissions originated at 570 nm and 601 nm are very low for OS9 than the other 3 samples and indicates the minimum recombination of electron hole pair in this sample.

3.5 Field Emission Scanning Electron Microscopic Analysis

FESEM image of all the samples is shown in Figure 8. From that, FESEM of OS7 reveals agglomerated spherical nanostructures, whereas OS8 and OS9 formed as agglomerated polyhedral structures. But OS10 is observed as polyhedron with pyramid top [23].

Among all the samples, the growth of OS9 nanostructures along the active planes ((110), (101) and (211)) is responsible for the formation of their polyhedral structures. Especially the intensity ration of OS9 is relatively more along the active planes and hence polyhedral structures get nucleated. In the case of OS10, (101) and (211) grows along with (110) under excess OH$^-$ concentration resulting in a pyramid like top. The purity of the samples is further confirmed from EDAX spectrum.

3.6 DSSC performance of fabricated photovoltaic cells using Alizarine red dye

DSSC fabricated using SnO$_2$ nanostructures and alizarin dye was subjected to Current-voltage measurements (I-V measurements) under solar spectrum to determine the efficiency of solar cells and presented in Figure 9.

Fill factor of the device is calculated by the equation

\[
FF = \frac{V_m I_m}{V_{oc} I_{sc}}
\]  \(\text{(3)}\)

\(V_m\) – Maximum voltage in volts,

\(I_m\) – Maximum current in Amp,

\(V_{oc}\) – Open circuit voltage in volts,

\(I_{sc}\) – Short circuit current in Amp.[24]
The conversion efficiency of the device was calculated using the equation

\[
\eta(\%) = \frac{V_{oc}I_{sc}FF}{P_{in}} \times 100 \quad \text{----------------------------------------(4)}
\]

\(P_{in}\) is the power input (in this case, it is 100 mW/cm\(^2\)).

\(V_{oc}\), \(I_{sc}\), calculated FF, and photo efficiency of the fabricated DSSCs are presented in Table 3

### Table 3: Photovoltaic performance of DSSC fabricated using SnO\(_2\) nanostructures and alizarin

| pH | \(V_{oc}\) (Volt) | \(J_{sc}\) (mA/cm\(^2\)) | FF | \(P_{max}\) (watt) | Efficiency (%) |
|----|-------------------|---------------------------|----|-------------------|----------------|
| OS7 | 0.185             | 15.5                      | 0.37 | 0.0010          | 1.06           |
| OS8 | 0.318             | 16.3                      | 0.43 | 0.0023          | 2.25           |
| OS9 | 0.419             | 17.1                      | 0.54 | 0.0039          | 3.86           |
| OS10 | 0.453             | 15.0                      | 0.46 | 0.0031          | 3.14           |

It is observed from Table 3 that the open circuit voltage (\(V_{oc}\)) of the fabricated DSSCs increases with pH of the preparation medium. \(V_{oc}\) increases from 0.185V to 0.453V for the samples moving from OS7 to OS10 respectively. This increase could be due to increase in electron density of the samples and is in accordance with the literature [19]. However \(J_{sc}\) (Short Circuit Current density) increases from OS7 to OS9 (15.5mA/cm\(^2\) to 17.1 mA/cm\(^2\)) and decreases for sample OS10. This could be related to the mobility of electrons in the prepared SnO\(_2\) nanostructures. Though the electron density is more, electron mobility depends on the defects. In general high surface energy plane of SnO\(_2\) is (101) and the defects on this plane under high oxygen concentration (i.e at higher pH conditions) could be mainly of oxygen excess defects. Presence of these defects will decrease the electron mobility [25,26]. (101) plane with minimum strain is observed for OS9 (from Table 2) and hence may have maximum \(J_{sc}\). Minimum defect on (101) may lead to the effective conversion of incident photon to electron and thus the sample OS9 shows maximum photoconversion efficiency (3.86%) than the other 3 samples. This could also be due to minimum electron hole pair recombination in OS9 as evidenced from PL analysis. In addition to the defects, existence of more hierarchical spherical structures with aggregates of SnO\(_2\) polyhedral (Figure 7) is also responsible for the maximum observed DSSC efficiency of OS9. Besides OS10 has the aggregates of polygons with pyramid surfaces of SnO\(_2\), (101) planes of the neighboring polygons are not orienting towards each other and possess maximum defect (Table 2). As a result OS10 has lower efficiency than OS8 and OS9. Existences of polymorphism in OS7 due to the oxygen deficient atmosphere lead to poor photoconversion efficiency than the other 3 samples.

Maximum efficiency reported with Alizarin Red dye was 2.40% [27] on TiO\(_2\) DSSC. The flower-like SnO\(_2\) prepared by using hydrothermal method shows high power conversion efficiency (2.50%) with a \(J_{sc}\) of 7.20 mAcm\(^{-2}\) and a \(V_{oc}\) of 630 mV using N3 dye[28]. The simple organic surfactant free hydrothermal synthesis
method was used for preparation of SnO$_2$ nanoflowers for dye sensitized solar cell (DSSC). DSSC with flower-like SnO$_2$ nanostructures with EY dye solution exhibited good photovoltaic performance with \( \text{Voc}, \text{Jsc} \) and \( \eta \) about 0.43V, 4.36 mA/cm$^2$ and 1.11\% respectively [29].

The results obtained with the DSSC fabricated using SnO$_2$ nanostructure prepared with onion template at pH 9 were found to be better than the other reports.

4. Conclusion

SnO$_2$ nanostructures were prepared at different pH conditions (7,8,9 &10) using onion as template, characterised by various techniques and is used to fabricate a DSSC with alizarin dye. From XRD, OS7 shows polymorphism due to the availability of low OH$^-$ ions during the preparation whereas OS8, OS9 and OS10 possess tetragonal structure. From UV analysis, the bandgap decreases with increase in crystallite size which is attributed to quantum confinement effect. Increase in pH modulates the formation of polyhedral aggregates rather than microspheres which are due to the growth of SnO$_2$ nanostructure along the active planes are identified from FE SEM analysis. DSSC efficiency was analysed for all the 4 samples with alizarin dye and it was found that OS9 shows better photon conversion efficiency of 3.86 \%.

Declarations

Funding

Authors wish to thank DST, India for creating characterisation facilities under DST-FIST(SR/FST/COLLEGE-154/2013 scheme in Sri Ramakrishna Engineering College, Coimbatore, Tamilnadu, India).

Conflicts of interest/Competing interests

There is no conflict of interest

Availability of data and material

Not Applicable

Code availability

Not Applicable

References

1. Brian O’Regan & Michael Gratzel, Nature 353 (1991) 737-739. https://doi.org/10.1038/353737a0

2. Yukimi Ichikawa, Takashi Yoshida, Toshio Hama, Hiroshi Sakai, Kouichi Harashima, Sol. Energy Mater. Sol. Cells 66 (2001) 107-115. https://doi.org/10.1016/S0927-0248(00)00163-X.

3. Pooja Agarwala, Preeti Makkar, Sarika Sharma, and Rajnish Garg, Mater. Eng. Perform. 23 (2014) 3703–3709. https://doi.org/10.1007/s11665-014-1131-4
4. Riccardo Panetta Alessandro Latini, Ida Pettiti, Carmen Cavallo, Chem. Phys. 202 (2017) 289-301. https://doi.org/10.1016/j.matchemphys.2017.09.030.

5. Iwantonolwantono, Siti Khatijah Md Saad, Rischi Yuda, Mohd Yusri Abd Rahman, Akrajas Ali Umar, Superlattices Microstruct. 123(2018)119-128. https://doi.org/10.1016/j.spmi.2018.05.041.

6. Abirami Rajendran & Sivakumar Kandasamy, Res. Innov., 23(2019) 1-6. https://doi.org/10.1080/14328917.2017.1349060.

7. Asdim, Kazuhiro Manseki, Takashi Sugiura and Tsukasa Yoshida, New J. Chem. 38(201) 598-603. https://doi.org/10.1039/C3NJ01278F

8. Thirumal Krishnamoorthy, Mu Zhi Tang, Akshara Verma, A. Sreekumaran Nair, Damian Pliszka, Subodh G. Mhaisalkard and Seeram Ramakrishna, J. Mater. Chem., 22 (2012) 2166-2172. https://doi.org/10.1039/C3NJ01278F

9. Khalid Hossain, M. F. Pervez, S. Tayyaba, M. Jalal Uddin, A. A. Mortuza, M. N. H. Mia, M. S. Manir, M. R. Karim, Mubarak A. Khan, MATER SCI-POLAND, 35(4), (2017) 816-823.

10. Syrrokostas, A. Siokou, G. Leftheriotis, P. Yianoulis, Sol. Energy Mater. Sol. Cells 103 (2012) 119–127. https://doi.org/10.1016/j.solmat.2012.04.021.

11. Anju Ramachandran, C. O. Sreekala, K. S. Sreelatha, I. Jinchu, IOP Conf. Series: Materials Science and Engineering 310 (2018) 012151. https://iopscience.iop.org/article/10.1088/1757-899X/310/1/012151.

12. Hala K. Farag and Hussein Abbas, Phys. Chem. 2018; 232(2): 245–256. https://doi.org/10.1515/zpch-2017-0966.

13. F. Mohammad, M. A. A. Sooud, S. M. Abed, J. Ovonic Res. 16(2) (2020) 107 – 113.

14. Vignesh, R. Hariharan, M. Rajarajan, A. Suganthi, Solid State Sci. 21 (2013) 91-99. http://dx.doi.org/10.1016/j.solidstatesciences.2013.04.017.

15. C. Abruzzi, B. A. Dedavid, M. J. R. Pire, Cerâmica 61 (2015) 328-333. http://dx.doi.org/10.1590/0366-69132015613591919.

16. Simin Tazikeh, Amir Akbari, Amin Talebi, Emad Talebi, MATER SCI-POLAND 32 (2014) 98–101. https://doi.org/10.2478/s13536-013-0164-y.

17. Huaming Yang, Yuehua, Aidong Tang, Shengming Jin, Guanzhou Qiu, Alloys Compd. 363(2004)276-279. https://doi.org/10.1016/S0925-8388(03)00473-0.

18. Abebe G. Habte, Fekadu Gashaw Hone, Francis B. Dejene, Physica B Condens. Matter. 580(2020) 411832. https://doi.org/10.1016/j.physb.2019.411832.

19. Jayapandi, P. Packiyaraj, S. Premkumar, J. Mayandi, K. Anitha, Ionics volume 23(2017), 2909–2917. https://doi.org/10.1007/s11581-017-2121-y.

20. Wenqin Peng, Xudong Yang, Zhenhua Chen, Jing Zhang, Han Chen, Kun Zhang and Liyuan Han, Chem Sus Chem 7(2014) 172 – 178. https://doi.org/10.1002/cssc.201300644.

21. A. Gondal, Q.A. Drmosha, T.A. Salehb, Appl. Surf. Sci. 256 (2010) 7067–7070. https://doi.org/10.1016/j.apsusc.2010.05.027.

22. Brajesh Nandan, B. Venugopal, S. Amirthapandian, B.K. Panigrahi, P. Thangadurai, J Nanopart Res 10 (2013) 15:1999, https://doi.org/10.1007/s11051-013-1999-1.
Figures

Figure 1

5g of Chopped and dried Onion + 50ml distilled water

Tin(II) Chloride + 20 ml Ethanol+30 ml distilled water

pH of the suspension was adjusted to 7,8,9 and 10

Final mixture of solution

mixture was kept at room temperature for 24 hours

dried at 100°C for 3 hrs and calcined at 500°C for 3 hrs and named as OS7, OS8, OS9 and OS10
Flowchart for the preparation of template assisted SnO2 nanostructures

Figure 2

X-ray diffraction patterns of OS7, OS8, OS9 and OS10
Figure 3

ATR spectra of OS7, OS8, OS9 and OS10
Figure 4

UV-visible absorbance spectra of OS7, OS8, OS9 and OS10
Figure 5

Plot of $(a h u) / (e V) / m^2$ vs. photon energy $(h u)$ for SnO2 nanostructures
Figure 6

Reflectance spectra of OS7, OS8, OS9 and OS10
Figure 7

PL Spectra of SnO2 nanostructures
Figure 8

FE SEM image of SnO2 nanostructures
Figure 9

J-V characteristics of fabricated photovoltaic cells using Alizarin