“This chapter summarizes the results of the work presented in the thesis along with the suggested future avenues of investigation.”
6.1 Conclusions

QDSSCs are a promising low cost alternative to existing PV technologies such as crystalline Si and thin inorganic films. The present thesis focuses on the fabrication and characterization of ZnO based quasi solid state QDSSCs. The outcome of the detailed investigations done on various QDSSCs developed in the present work is summarized in the points below -

1. ZnO nanoparticles were synthesized using sol-gel route and solid state reaction method.

2. The results of sol-gel synthesized nanoparticles were found to be more suitable to be used for the fabrication QDSSC. Under the same growth conditions, the size of the nanoparticles obtained by sol-gel method was ~ 24 nm and that obtained by solid state reaction method was ~ 37 nm. Crystallinity of sol-gel synthesized nanoparticles was also better.

3. Because of ease of preparation and control over crystallite size in case of sol-gel synthesized ZnO nanoparticles, the effect of pH variation on sol-gel synthesized ZnO nanoparticles was studied.

4. The size of the ZnO nanoparticles increased with increasing pH. Particle size increased from 28 to 34 nm with increase in pH from 7 to 11. After a certain pH level, the size starts decreasing. At 11 pH, the size was maximum 34 nm. After that, on increasing pH to 12, crystallite size decreased to 32 nm.
The growth mechanism of ZnO particles from zinc acetate dihydrate precursor by the sol-gel process has been discussed in terms of solvation, hydrolysis and polymerization. Aggregation has been found to be dominant growth mechanism of microscopic ZnO particles.

CdS and CdSe QDs were synthesized using chemical colloidal routes.

The CdS QDs were capped by PVA to control the size of the dot and to stabilize the dot formation by increasing the kinetic stability of the reactants. The size of QDs decreased from 5.6 to 2.6 nm with increase in PVA concentration from 2 to 10 wt%. A blue shift (2.5 to 2.74 eV) was found in the bandgap of QDs with decrease in QD size (5.6 to 2.6 nm).

CdSe dots size varied from 0.85 to 2.25 nm with increasing reaction temperature from 225 to 255°C. Bandgap of CdSe QDs decreased from 3.4 to 1.95 eV with increase in size from 0.85 to 2.25 nm.

The synthesized ZnO nanoparticles, CdS and CdSe QDs were used to fabricate QDSSC. ZnO nanoparticles were used as wide bandgap semiconductor electrode and CdS & CdSe QDs were used as light absorbing materials to sensitize the QDSSC.

When CdS QDs were used as sensitizer, then the power conversion efficiency of QDSSC was obtained to be 1.3% at AM 1.5.
When CdSe QDs were used as sensitizer, then the power conversion efficiency of QDSSC was obtained to be 3.6% at AM 1.5. The increased power conversion efficiency may be attributed to the efficient light harvesting and charge collection resulting from enhanced light absorption and faster charge transport in CdSe QDs due to their larger distribution in size.

6.2 Suggestions for Future Work

The development and future of QDSSCs are dependent on the optimal combination of high efficiency, good stability, and low cost, which lie on the design, preparation and modification of materials, especially inorganic materials with excellent properties. The scope of the future work is summarized in the points below -

Improving the light to electric power conversion efficiency in QDSSCs requires that the difference between the absorption onset of the QDs and the photovoltage be minimized. The interface properties within the device are critical for its operation and a fundamental understanding of how to control and engineer their properties is lacking. Research in this direction needs to be progressed. New methods for energy level alignment should boost the QDSSC efficiency to compete with the conversion efficiency of 15–20 %, typical for Si solar cells but at a significant lower cost.

On the material side, future QDSSCs should be fabricated with ZnO nanostructures other than the random fractal-like assembly of nanoparticles. A desirable morphology of the films would have the mesoporous channels or nanorods aligned in parallel to each other and vertically with respect to TCO glass. This would
facilitate pore diffusion, give easier access to the film surface and allow the junction to be formed under better control.

The limited number of semiconducting QDs that have been synthesized up to now leaves the field wide open to identify new semiconducting absorbers.

The \( \Gamma/I_i^3 \) electrolyte redox couple shows good performance in QDSSCs, but with limited success due to photodegradation of the QDs in the presence of very corrosive iodine. Very limited number of electrolytes has been investigated in conjunction with QDSSCs which demonstrates the need for further research.

The work on the fabrication of co-sensitized QDSSCs using colloidal blended solution of CdS and CdSe QDs is in progress. It is expected that these cells would exhibit higher efficiency due to the broadened spectral absorption range i.e. efficient light harvesting process.
ZnO based quantum dot sensitized solar cell using CdS quantum dots

Neetu Singh, R. M. Mehra, Avinashi Kapoor, and T. Soga

Citation: J. Renewable Sustainable Energy 4, 013110 (2012); doi: 10.1063/1.3683531

View online: http://dx.doi.org/10.1063/1.3683531

View Table of Contents: http://jrse.aip.org/resource/1/JRSEBH/v4/i1

Published by the American Institute of Physics.

Related Articles

Suppressed indium diffusion and enhanced absorption in InGaAs/GaAsP stepped quantum well solar cell

High-efficiency thin-film InGaP/InGaAs/Ge tandem solar cells enabled by controlled spalling technology

Mid-gap trap states in CdTe nanoparticle solar cells

Efficiency enhancement of InGaN multi-quantum-well solar cells via light-harvesting SiO2 nano-honeycombs

Band diagrams and performance of CdTe solar cells with a Sb2Te3 back contact buffer layer
AIP Advances 1, 042152 (2011)

Additional information on J. Renewable Sustainable Energy

Journal Homepage: http://jrse.aip.org/
Journal Information: http://jrse.aip.org/about/about_the_journal
Top downloads: http://jrse.aip.org/features/most_downloaded
Information for Authors: http://jrse.aip.org/authors

ADVERTISEMENT

Explore AIP’s new open-access journal
• Article-level metrics now available
• Join the conversation! Rate & comment on articles

Submit Now
**ZnO based quantum dot sensitized solar cell using CdS quantum dots**

Neetu Singh,1 R. M. Mehra,2 Avinashi Kapoor,1 and T. Soga3

1Department of Electronic Science, University of Delhi South Campus, New Delhi 110021, India
2School of Engineering and Technology, Sharda University, Greater Noida 201306, Uttar Pradesh, India
3Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

(Received 29 September 2011; accepted 14 January 2012; published online 8 February 2012)

This paper reports the fabrication of Zinc Oxide (ZnO) based quantum dot sensitized solar cell using Cadmium Sulphide (CdS) quantum dots (QDs) capped by poly vinyl alcohol (PVA). Chemical route was used to synthesize ZnO nanoparticles (NPs) as well as CdS QDs. The crystallite size of ZnO NPs was obtained to be 28 nm at 7 pH. The size of QDs decreased from 5.6 to 2.6 nm with increase in the PVA concentration from 2 to 10 wt. %. There is a blue shift in the band gap of QDs with increase in the concentration of PVA. Current-Voltage characteristic of the cell was obtained and various solar cell parameters were estimated. The efficiency of quantum dot sensitized solar cells was found to be 1.3% at AM 1.5. © 2012 American Institute of Physics. [doi:10.1063/1.3683531]

I. INTRODUCTION

Quantum dot sensitized solar cells (QDSSCs) have attracted extensive interest as a means of fabricating highly efficient, stable and low cost photovoltaic device because of the tuneable bandgap of the quantum dots.1 From the last few decades, most of the research in the field of solar energy are focused on dye sensitized solar cells (DSSCs) in which the problem of wastage of photon energy above the difference between lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energies is dominant, because one photon gives rise to one exciton only and rest of the energy contained in the photon is wasted as heat.2–5 Quantum dots (QDs) have specific advantages over dyes to be used as sensitizers in DSSCs. It is observed that if dye in DSSC is replaced by QDs, then the energy contained in a photon can be fully utilized because in QDs single photon gives rise to multiple excitons.6,7 This effect is known as multiple exciton generation (MEG) effect. The production of multiple excitons by a single photon in quantum-confined systems may improve the efficiency of solar cells. Researchers have already accomplished the production of 2 or more excitons per photon with energy greater than the bandgap in a PbSe QD based system.8

The sensitization in QDSSC is based on the band gap alteration due to the quantum confinement effect (QCE). The absorption edge of QDs can be tailored by exploiting quantum-confined regime of different sized QDs. The bandgap of the QDs can be tuned by controlling their size, and therefore, the absorption spectra of the QDs can be tuned to match the spectral distribution of the sun light.1,8 QDs can be embedded on front TiO2/ZnO electrode to achieve enhanced light harvesting in the visible spectrum. However, in spite of the fact that different sized (different bandgap) QDs are available, the energy conversion efficiency of QDSSCs is still low. The less conversion efficiency of the QDSSCs may be due to the difficulty of embedding the QDs into the mesoporous TiO2/ZnO structure. Another problem is the selection of efficient electrolyte in which the QDSSC can function without degradation. But if suitable linking molecule which could link QDs to TiO2/ZnO surface and electrolyte be used, then QDs can be used to improve the efficiency of DSSCs.
Much research has been done on the fabrication of QDSSCs in which QDs are embedded in mesoporous TiO$_2$/ZnO structure by CBD method. Sudhagar et al. have reported nanospherical TiO$_2$ mesoporous layer combined with CdS QDs as a QDSSC application and the resulting efficiency was 1.2%. Chang et al. have reported an energy conversion efficiency of 1.84% using I$_{-1}$/I$_{3}^-$ electrolyte in CdS based QDSSC. Zhang et al. have reported a maximum power conversion efficiency of 0.34% for 10 CBD cycles of CdS/ZnO nanowire system. Tak et al. have reported the CdS/ZnO nanowire structure as an enhanced photocatalytic activity, because the CdS/ZnO system can efficiently separate photogenerated electron-hole pair and reduce their recombination. Chen et al. have reported an efficiency of 1.4% in CdS and CdSe co-sensitized QDSSC based on ZnO nanowire.

In the present work, ZnO nanoparticles (NPs) and CdS QDs were synthesised via chemical route. Synthesized ZnO NPs were successfully used as front ZnO electrode in QDSSC. Effect of poly vinyl alcohol (PVA) concentration on structural and optical properties of QDs was investigated. Various parameters of CdS sensitized solar cell were calculated.

II. EXPERIMENTAL

All the reagents used were of analytical grade and no further purification was done before use.

A. Synthesis of ZnO NPs

Zinc acetate dihydrate [99.5% Zn(CH$_3$COO)$_2$.2H$_2$O, Alfa Aesar] was used as Zinc precursor. The sol was prepared by dissolving 0.2M of zinc acetate dihydrate in methanol at room temperature. A clear and transparent sol with no precipitate and turbidity was obtained by ultrasonic stirring of the solution for 2 h. NaOH (0.1N, Alfa Aesar) was then added to the sol to adjust the pH level of the sol to 7. The so modified sol was again stirred ultrasonically for 1 h at room temperature. The pH value of the sol was adjusted to add the desired value of OH$^-$ ions in the sol. The clear sol was filtered and kept for complete gelation and hydrolysis process till ZnO precipitate slowly crystallized and settled down at the bottom of the flask. The white precipitate was filtered and washed with excess methanol to remove the starting materials. Precipitate was dried at 80$^\circ$C for 15 min on hot plate and ground for 30 min in mortar pestle. The nanopowder so obtained was annealed at 450$^\circ$C for 4 h in air by microprocessor controlled annealing furnace with the annealing rate 4$^\circ$C/min.

B. Synthesis of CdS QDs

Cadmium chloride (99.9% CdCl$_2$, Alfa Aesar) was used as cadmium source. Sodium Sulphide (99% Na$_2$S, Alfa Aesar) was used as reducing agent. Poly vinyl alcohol (86–89% PVA, Alfa Aesar) was used as capping agent. Nanoparticles formed during the process need to be surface passivated, as colloids formed in liquid have a tendency to coagulate. Therefore, a capping agent is used to achieve stability and avoid coalescence. PVA is used as capping agent because of its excellent emulsifying property because of which it controls and stabilizes the particle formation by increasing the kinetic stability of the reactants. 20 ml of CdCl$_2$ (0.1M), 20 ml of Na$_2$S (0.1M), and 20 ml of 10 wt. % PVA solutions were made in deionized (DI) water. CdCl$_2$ was added to PVA solution and stirred continuously. Na$_2$S was then added to the above solution and again stirred ultrasonically for 1 h. The experiment was repeated for 5 wt. % and 2 wt. % of PVA. The chemical reaction taking place is

\[
\text{CdCl}_2 + \text{Na}_2\text{S} \rightarrow \text{CdS} + 2\text{NaCl}. \tag{1}
\]

The solution was kept undisturbed till the precipitate was collected at the bottom. Precipitate was then filtered and dried on hot plate at 60$^\circ$C for 15 min. The dried precipitate after grinding was annealed at 150$^\circ$C for 30 min. The colour of CdS QDs changed from light yellow to orange with decreasing PVA concentration.
C. Preparation of ZnO electrodes

ZnO nanopowder (1.2 g) was ground by a mortar and pestle with 4 ml DI water and polyethylene glycol (PEG_{20,000}, 0.5 g, Alfa Aesar). PEG was used to break up the aggregated particles into a dispersed paste. Thus, prepared uniform slurry was coated on indium tin oxide (ITO) glass by doctor blade technique using an adhesive scotch tape to control the thickness of the ZnO film\textsuperscript{18,19} and to provide non-coated areas for electrical contact as spacers. After natural drying at room temperature, the film was sintered in air at 450°C for 30 min.

D. Preparation of gel electrolyte

The gel electrolyte was prepared by using 10\% polyethylene oxide (PEO 99\%, Alfa Aesar) solution in acetonitrile and carbon nanotube (CNT, 90+ \%, Alfa Aesar) with LiI 0.1M (9.95\%, Alfa Aesar), and I₂ 0.015M (99.8 \%, Alfa Aesar). The whole mixture was placed for sonication to disperse the CNTs into the matrix of polymer. The mixture was stirred for 10 h by a magnetic stirrer for complete mixing between CNTs and polymer molecules.

E. Fabrication of QDSSC

To fabricate QDSSC, prepared ZnO film electrode was first immersed in mercapto propionic acid, which acts as linker molecule between ZnO film electrode and QDs\textsuperscript{20}. The modified ZnO electrode was immersed in CdS QD colloidal solution consisting of all the three synthesized QDs. The colloidal solution was formed in toluene by ultrasonication for 2 h. The electrode was immersed in QD solution for 24 h at room temperature. The QD adsorbed electrode was then rinsed with toluene and dried at room temperature. To minimize adsorption of impurities from moisture in the ambient air, the electrode was dipped in the QD solution, while it was still warm (\textabout{}80°C). The colour of ZnO electrode changes to yellow after adsorption of CdS QDs. I\textsuperscript{-}/I\textsubscript{3} electrolyte was spread on the QD coated ZnO electrode\textsuperscript{21,22}. A sandwich type QDSSC was fabricated with the CdS QDs sensitized ZnO electrode, a thin platinum sheet as counter electrode, a spacer, and an electrolyte. The schematic diagram of QDSSC is shown in Figure 1.

In QDSSCs, semiconductors such as CdS, CdSe, PbS, and InP which absorb light in visible region work as sensitizers because they are able to transfer electrons to wide bandgap semiconductors such as ZnO, TiO\textsubscript{2}, SnO\textsubscript{2}, etc.\textsuperscript{8–14} The energy level diagram of QDSSC is shown in Figure 2. The working principle of QDSSC is based on excitation of QDs by photons of light and fast electron injection into the conduction band of ZnO\textsuperscript{23}. The injected electron in the conduction band of ZnO percolates through the porous ZnO structure and is fed to the ITO layer which acts as the charge collecting electrode in the cell. The porous ZnO electrode is typically

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{schematic_diagram.png}
\caption{Schematic diagram of QDSSC.}
\end{figure}
10 μm thick. Through ITO, the electron moves to the external circuit. At the Pt counter electrode, triiodide (I\(^{-3}\)) is reduced to iodide (I\(^{-}\)) by taking the electrons from Pt electrode. I\(^{-}\) is transported through the electrolyte towards the ITO photoelectrode, where it reduces the oxidized QD. The QD is then ready for next excitation/oxidation/reduction cycle. We can see that the working mechanism of QDSSC is similar to that of DSSC, the only difference being that in QDSSC dye is replaced by QDs of varying size by which more light can be harvested and hence the overall efficiency of the cell can be improved.

F. Characterization and I-V measurement

X-ray diffraction (XRD) measurements of the ZnO NPs and CdS QDs were carried out using Bruker AXS – D8 discover diffractometer having CuK\(_{α}\) incident beam (λ = 1.54 Å). Structural properties of ZnO NPs and CdS QDs were observed by using TECNAI G\(^2\) T30, u-TWIN TEM. The absorbance of ZnO NPs, CdS QDs, and CdS QD embedded ZnO electrode in the visible region was measured using Shimadzu solidspec-3700 UV-VIS-NIR spectrophotometer. I–V characteristic of the cell was measured using computerised digital 2400 Keithley source meter and a M-91190 Newport class-A solar simulator. The measurement was made at AM 1.5. The active electrode area was typically 1 cm\(^2\).

III. RESULT AND DISCUSSION

A. Analysis of ZnO NPs

The XRD pattern of the synthesized ZnO NPs is shown in Figure 3. The intensity of the diffraction peaks is very high showing that NPs are highly crystalline in nature. The strong diffraction peaks appear at 31.8°, 34.3°, and 36.5°, which correspond to (100), (002) and (101) planes respectively indicating the hexagonal wurtzite structure of ZnO. The preferred orientation corresponding to the plane (101) is shown as the most dominating peak.\(^{24,25}\) Besides these dominant peaks, other characteristic peaks of ZnO are also there, showing that NPs have grown in all these orientations but maximum growth has occurred in (101) plane. All the diffraction peaks coincide with JCPDS card no. 36-1451 for ZnO powder. No characteristic peak of impurity was observed stating the fact that the synthesized NPs are contamination free and will help not degrading the performance of QDSSC due to impurity elements. Crystallite size (D) was calculated by Debye-Scherrer’s formula\(^{26}\).
\[ D = \frac{K \lambda}{\beta \cos \theta}, \] (2)

where, \( K \) is the particle shape factor which depends on the shape of the particles and its value is 0.94 for spherical particles, \( \beta \) is the full width at half maximum (FWHM) of the selected diffraction peak corresponding to (101) plane, and \( \theta \) is the Bragg’s angle obtained from 2\( \theta \) value corresponding to the same plane. Crystallite size of ZnO NPs is calculated to be 28 nm.

Transmission electron microscope (TEM) image of the ZnO NPs is shown in Figure 4(a). A drop of ZnO solution in methanol was drop-cast on a carbon coated copper grid and dried for 1 h before testing through TEM. TEM image mainly consists of hexagonal shaped NPs having an average particle size of approximately 28 nm confirming the results obtained by XRD. SEM image of ZnO electrode is shown in Figure 4(b). The image clearly exhibits the porous nature of the ZnO layer. This porous structure of ZnO helps in the sensitization of QDs in QDSSC because when QDs are embedded on ZnO electrode, QDs actually go and sit in these pores where they get adsorbed (Fig. 1). That is why the cell is known as quantum dot sensitized solar cell because when light falls on such structure, ZnO electrode on the top does not absorb light in the visible region (large bandgap \( \sim 3.37 \) eV) but passes it into the next QD layer where it gets absorbed and sensitizes the dots.
The optical absorption spectra of ZnO NPs as a function of energy in the visible region are shown in Figure 5. Graph shows that ZnO does not absorb light in the visible region, which means that prepared ZnO samples are transparent to visible light. We can see that proper light absorbance takes place above bandgap energy of approximately 3.4 eV. Below this energy, absorption level decreases stating that below 3.4 eV photons does not possess enough energy to excite the electrons from valence band to conduction band. The overall analysis of the absorbance spectrum concludes that the synthesized ZnO NPs can be successfully used as a photoelectrode in QDSSC.

B. Analysis of CdS QDs

XRD pattern of CdS QDs with different concentration of PVA is shown in Figure 6. XRD pattern reveals that the dot size is dependent on concentration of PVA. As the PVA concentration increases, the FWHM also increases thereby decreasing the dot size. The dominant peak position is observed at 26.6° for (002) plane, which belongs to hexagonal structure of CdS QDs. Two more additional peaks are observed at 43.7° and 51.7° corresponding to (110) and (112) planes, respectively. Dot size is calculated using Debye-Scherrer’s formula. The size of the CdS QDs decreases from 5.6 to 2.6 nm with increase in the PVA concentration from 2 to 10 wt. %. The synthesis of QDs, using polymeric stabilizers such as PVA is very easy and requires ambient laboratory conditions. The three-dimensional network of the polymer chains efficiently restricts the particle formation to nanoscale. For this purpose, a water-soluble monomer or a polymer compound is generally employed, along with the reagents required for the synthesis.
the synthesis of the QDs. Recently researchers have used PVA, to stabilize CdSe QDs. The higher concentration of PVA increases the rate of reaction and thus uniform and smaller sized dots are formed.

The variation in FWHM and dot size with capping agent concentration is shown in Figure 7. FWHM increases with increase in the concentration of PVA thereby decreasing the size of the dot. TEM analysis was further carried out to investigate more about CdS phase. TEM images of CdS QDs with different PVA concentration are shown in Figure 8. From the TEM images, it can be seen that the particle size varies from 5.6 to 2.6 nm with increase in the PVA concentration from 2 to 10 wt. %. Therefore, TEM results confirm that the size of the QDs is similar to the dot size obtained by the XRD measurements. The selected area electron diffraction pattern (SAED) of the QDs is also shown in the inset. From the SAED pattern, it is clear that the QDs are crystalline in nature.

FIG. 7. Effect of PVA concentration on FWHM and size of CdS QDs.

FIG. 8. TEM images CdS QDs with different PVA concentration (a) 2 wt. % (b) 5 wt. %, and (c) 10 wt. %. Inset: SAED of the CdS QDs.
The optical absorption spectra of the CdS QDs of varying size and CdS QDs embedded on ZnO electrode are shown in Figure 9. Absorbance spectra reveal that there is a blue shift in the absorbance as the dot size decreases due to quantum confinement effect. Bandgap of the QDs increases from 2.5 to 2.74 eV with decrease in dot size from 5.6 to 2.6 nm. It is seen from the figure that the absorbance of the CdS QD embedded ZnO electrode covers a wide range of visible spectrum (400–600 nm). Thus using CdS QDs as sensitizers onto ZnO NPs resulted enhanced light harvesting of the solar energy.

The bandgap of CdS QDs can also be calculated using effective mass model. It is the simplest model, which predicts the effective bandgap (E_g^*) due to three dimensional confinements. The blue shift of the bandgap with decrease in dot size is described by the following equation:

$$E_g^* = E_{\text{bulk}}^g + \frac{\hbar^2 \pi^2}{2 \mu R^2}, \quad (3)$$

where, $E_{\text{bulk}}^g$ is the band gap of bulk CdS, $\hbar = h/2\pi$ (h being Planck’s constant), R is the dot size and $\mu$ is the effective reduced mass,

$$\mu = \frac{1}{m_e} \left( \frac{1}{m_e} + \frac{1}{m_h} \right), \quad (4)$$

FIG. 9. Optical absorption spectra CdS QDs for various PVA concentration and CdS embedded ZnO electrode.

FIG. 10. Experimental and theoretical bandgap of CdS QDs as a function of dot size.
where, \( m_e \), \( m_e^* \) (0.2), and \( m_h^* \) (0.8) are the mass of the electron, effective mass of electron, and effective mass of hole, respectively. The second term in Eq. (3) represents the kinetic energy. The effective bandgap of the CdS QDs is found to be varying from 2.49 to 2.78 eV with decrease in dot size from 5.6 to 2.6 nm, which agrees with the confinement regime. The effective and experimental values of the QD bandgap as a function of dot size are shown in Figure 10. It is clear that the bandgap decreases with increase in the CdS QDs size. This is due to the quantum confinement effect in the dots.39,40

C. I-V measurement

QDSSC was fabricated using the synthesized of ZnO NPs and CdS QDs. The cell was illuminated under one sun illumination (AM 1.5, 100 mW/cm\(^2\)) and I-V characteristic of the cell (Figure 11) was obtained by using Keithley source meter. The values of short circuit current (I\(_{sc}\)), open circuit voltage (V\(_{oc}\)), maximum power (P\(_{m}\)), fill factor (FF), and efficiency (\(\eta\)) are 5.43 mA, 0.64 V, 1.3 mW, 0.4 and 1.3%, respectively. When the QDSSC is illuminated, excitons are generated in CdS QDs and charge separation is performed by ZnO/CdS QDs/electrolyte interface. The resultant electrons are conducted to the ITO layer through ZnO layer and the holes are recovered by \( \Gamma^-/I_3^- \) electrolyte. I\(_{sc}\) depends on number of incident photons. Adsorbing PVA capped CdS onto ZnO could result in the hindrance of charge transport. In the present case, the PVA capping molecules were removed by repeated washing30 with DI water before incorporating them in ZnO electrode in QDSSC, which provides a better charge carrier exchange between QDs and the conducting polymer. The overall conversion efficiency is found to be 1.3%.

IV. CONCLUSION

In conclusion, ZnO based QDSSC with an efficiency of 1.3% at AM 1.5 has been successfully fabricated by sensitizing the ZnO electrode by CdS QDs. The CdS QDs of varying size from 5.6 to 2.6 nm with increase in the bandgap from 2.5 to 2.74 eV, respectively, have been chemically synthesized. The use of QDs of varying bandgap resulted in the absorbance of a broader spectrum of visible light in the range 400–600 nm.

ACKNOWLEDGMENTS

This work is done under DST-JSPS sponsored project No. DST/INT/JSPS/PROJ/10. One of the authors, Neetu Singh, gratefully acknowledges the financial support by University Grant Commission (UGC) in the form of JRF. The authors are also thankful to University Science Instrumentation Centre (USIC) for providing XRD and TEM facilities.
Effect of Ageing in Structural Properties of ZnO Nanoparticles with pH Variation for Application in Solar Cells

Neetu Singh¹, Dhruvasi¹, Davinder Kaur¹, R. M. Mehra² and Avinashi Kapoor¹,*

¹Department of Electronic Science, University of Delhi South Campus, New Delhi-110021, India
²School of Engineering and Technology, Sharda University, Greater Noida-201306 Uttar Pradesh, India

Abstract: ZnO nanoparticles were synthesized via novel Sol-gel route. The effects of pH variation as well as ageing were studied. The nanoparticles were synthesized with two different pH levels viz. pH 7 and pH 10. It was found that the size of the nanoparticles increased from 19 to 39.6 nm with increase in pH level from 7 to 10. Further the effect of ageing on the ZnO nanoparticles was studied. It was found that the crystallite size as well as the crystallinity of the nanoparticles increased with ageing. The crystallite size increased from 19 to 32.8 nm for pH 7 and from 39.6 to 42 nm for pH 10 with ageing. The intensity of the XRD peaks increased drastically with ageing primarily due to increase in crystallite size of nanoparticles. The nanoparticles were further characterized using TEM. The particle size obtained by TEM was same as crystallite size obtained by XRD. The synthesized ZnO nanoparticles can be used as a suitable material for application in quantum dot sensitized solar cells (QDSSCs).

Keywords: ZnO nanoparticles, Sol-gel route, pH, ageing, QDSSC.

INTRODUCTION

Zinc oxide (ZnO) is a piezoelectric, dielectric and transparent oxide semiconductor, with a direct band gap of 3.37eV at room temperature and a large excitation binding energy (60 meV), which is 2.4 times the effective thermal energy (25meV) at room temperature [1]. As in most II-VI materials, the bonding in ZnO is largely ionic, which explains its strong piezoelectricity. In addition, ZnO is the hardest of all II-VI semiconductors due to the high melting point (2248 K) and large cohesive energy (1.89 eV), therefore more resistant to wear. Electron mobility in ZnO single crystals is about 200 cm²/V.s [2]. ZnO crystallizes in three forms: hexagonal wurtzite, cubic zinc blende, and the rarely observed cubic rocksalt. Hexagonal wurtzite is the main stable crystal structure of ZnO at room temperature [3]. ZnO has several fundamental advantages over its chief competitor GaN, due to its high energy radiation stability and amenability to wet chemical etching. It is highly transparent and has good electrical conductivity, that is why it is extensively used for various applications such as gas sensor and photovoltaic devices [4-8].

ZnO is being extensively used in the fabrication of a new class of solar cells namely quantum dot sensitized solar cells (QDSSCs) [9]. It is expected to be an alternating material for TiO₂ because of its properties such as being environment friendly, stability, and that it can be synthesized into different shapes and sizes very easily. The schematic diagram of a sandwich type QDSSC using ZnO nanoparticles as front electrode, a thin platinum sheet as counter electrode, quantum dots (QDs) as sensitizer and an electrolyte (I⁻ / I₃⁻) is shown in Fig. (1). The front ZnO electrode passes the photons in the visible range to the underlying QD layer. QDs are excited by uptake of energy contained in photons. The excitation process creates excitons in the QDs. The electrons are then fastly injected into the conduction band of ZnO. The injected electron in the conduction band of ZnO percolates through the porous ZnO structure and is fed to the ITO layer. Through ITO, the electron moves to the external circuit. At the Pt counter electrode, triiodide (I₃⁻) is reduced to iodide (I⁻) by taking the electrons from Pt electrode. I⁻ is transported through the electrolyte towards the ITO photoelectrode, where it reduces the oxidized QD. The QD is then ready for the next excitation/oxidation/reduction cycle. So, here we can see that ZnO layer plays a major role in functioning of QDSSC.
As compared to other techniques for the synthesis of ZnO nanoparticles such as solid state reaction method and hydrothermal synthesis, sol-gel technique has a number of advantages such as simplicity, low cost, excellent homogeneity as well as purity of the product (due to availability of highly pure raw materials that can be mixed to atomic levels), relatively low processing temperatures such as room temperature. The other advantages of sol-gel process are that the composition and size of the nanoparticles can be controlled. Sol-gel processing has been found to be an economical, convenient and non-vacuum method to synthesize homogenous and high quality nanoparticles. This technique is especially useful for growth of ZnO nanoparticles as well as films, since zinc belongs to the group of elements, that form polymeric hydroxides easily, a fundamental requirement for sol-gel chemistry.

In the present work, we have synthesized ZnO nanoparticles via novel sol-gel route. Effect of pH variation and aging on the structural properties of synthesized ZnO nanoparticles were studied. As the demand of renewable energy sources is increasing day by day, solar cells such as QDSSCs are extensively researched for better efficiency. As discussed earlier also, the front transparent conducting oxide (TCO) layer of QDSSC is made up of wide bandgap semiconductors such as ZnO. So the synthesized ZnO nanoparticles will be used in QDSSCs.

MATERIALS AND METHODOLOGY

Sol-gel is one of the well known techniques for the synthesis of ZnO nanoparticles as it is easy, has good control over particle size and low cost processing [10]. Nanoparticles were prepared by dissolving 0.2M Zinc acetate dihydrate \([\text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O}]\) in methanol at room temperature. Then the solution was mixed ultrasonically for 2 hours at 25°C to obtain transparent and clear solution. NaOH was then added for the desired pH level (pH 7 and 10) in the sol [11]. The solution was again stirred ultrasonically for 60 min. The resulting solutions were divided into two parts and kept undisturbed for different time periods. Precipitates collected at the bottom were filtered and washed with excess methanol to remove the starting material. Precipitates were dried for 15 min at 80°C on hot plate.

The XRD measurements were carried out using Bruker AXS – D8 discover diffractometer. The crystallite size calculated from the XRD measurements was confirmed by using TECNAI G² T30, u-TWIN TEM.

RESULTS AND DISCUSSION

The XRD spectra of ZnO nanoparticles are shown in Fig. (2). The nanoparticles are highly crystalline as can be seen from the XRD pattern in which broad peaks with high intensity are extended over the 2θ scale. The diffraction peaks are observed at 2θ value of 36.25, 47.54, 56.55, 62.87, 66.38, 67.91, 69.05 and 76.95° corresponding to the lattice planes (101), (102), (110), (103), (200), (112), (201) and (202) respectively, indicative of hexagonal wurtzite structure of ZnO [12]. All the peaks are matched with standard JCPDS card no. 50-0664. The broadening of the diffraction peaks gives an idea about the small particle size of the synthesized ZnO. Crystallite size \((D)\), was calculated by using Debye Scherrer’s formula,

\[
D = \frac{K\lambda}{\beta \cos \theta_p}
\]

(1)

Where, \(K\) is the particle shape factor which depends on the shape of the particles and its value is 0.94 for spherical particles, \(\lambda\) is the CuKα radiations (1.54 Å), \(\beta\) is the full width at half maximum (FWHM) of the selected diffraction peak corresponding to 101 plane and \(\theta_p\) is the Bragg angle obtained from 2θ value corresponding to the same plane. The
crystallite size for pH 7, pH 10, ageing pH 7 and ageing pH 10 are obtained to be 19, 39.6, 32.8 and 42 nm respectively.

EFFECT OF pH

The ZnO nanoparticle growth from zinc acetate dihydrate precursor using sol–gel process undergoes four stages; solvation, hydrolysis, polymerization and transformation into ZnO nanoparticles. The zinc acetate dihydrate precursor was first solvated in methanol, and then hydrolyzed which results in a colloidal–gel of zinc hydroxide (Eq. 2). This zinc hydroxide splits into Zn$^{2+}$ cation and OH$^{-}$ anion (Eq. 3), followed by polymerization of hydroxyl complex to form “Zn–O–Zn” bridges and finally transformed into ZnO (Eq. 4).

\[ \text{ZnO(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{Zn(OH)}_2 \cdot 2\text{CH}_3\text{COONa} + 2\text{H}_2\text{O} \]  
\[ \text{Zn(OH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_4^{2+} + 2\text{H}_2\text{O} \]  
\[ \text{Zn(OH)}_4^{2+} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^{-} \]

When pH is low i.e. concentration of OH$^{-}$ is low, the growth of ZnO particle does not proceed due to lack of Zn(OH)$_2$ formation in the solution. In this study, the growth of ZnO nanoparticles in zinc acetate solution was observed from a solution having pH of 7. A solution with a pH 7 would have less OH$^{-}$ concentration, so the crystallite size is small (19 nm) and the diffraction peaks are less intense which can also be seen from XRD pattern. Since pH controls the rate of ZnO formation, it affects the size and their way of combination to get stable state. The larger crystallite size (39.6 nm) was obtained when the pH of the solution was increased to 10. As the freshly formed nuclei in the solution are unstable, it has a tendency to grow into larger particles.

EFFECT OF AGEING

XRD patterns of the nanoparticles having pH 7 and 10, after ageing are shown in Fig. (2c) and (2d) respectively. By increasing the ageing period, the FWHM and intensity is observed to be changed. Intensity of the diffraction peak increases due to grain growth of the zinc oxide, due to the Ostwald ripening [13]. Ostwald ripening is an observed phenomenon in solid solutions or liquid sols which describe the change of an inhomogeneous structure over time. Due to large ageing period, small sol particles dissolve and redeposit into larger sol particles and hence the grain size increases [14].

TEM images of the ZnO nanoparticles with different pH levels and ageing period are shown in Fig. (3). The results from TEM images are consistent with the observations from XRD. Hexagonal shaped ZnO nanoparticles have been observed. The particle size is increasing with increase in pH value as well as with ageing period.

CONCLUSION

In summary, the effects of pH variation as well as ageing on the structural properties of Sol-gel synthesized ZnO nanoparticles were studied. It was found that the size of the nanoparticles increased from 19 to 39.6 nm with increase in pH level from 7 to 10. The crystallite size as well as the crystallinity of the nanoparticles increased with ageing. The crystallite size increased from 19 to 32.8 nm for pH 7 and from 39.6 to 42 nm for pH 10 with ageing. The synthesized ZnO nanoparticles will be used as front wide-bandgap electrode in QDSSCs.

CONFLICT OF INTEREST

None declared.

ACKNOWLEDGEMENTS

One the authors, Ms. Neetu Singh gratefully acknowledge University Grant Commission (UGC), India for provid-
The authors are also thankful to University Science Instrumentation Centre (USIC) for providing XRD and TEM facility.

REFERENCES


SYNTHESIS AND CHARACTERIZATION OF ZnO NANOPARTICLES

N. Singh1, R.M. Mehra2, A. Kapoor1

1 Department of Electronic Science, University of Delhi south Campus, New Delhi-110021, India
E-mail: Singhneetu1985@gmail.com
2 School of Engineering and Technology, Sharda University, Greater Noida-201306 Uttar Pradesh, India

In this paper, we report the comparison between ZnO nanoparticles prepared via two different routes; i) via sol-gel route and ii) by solid state reaction method. It was found that when prepared under the same ambient conditions viz temperature, pressure etc. and keeping all the parameters same viz precursors, molarity, solvent etc; the nanoparticles prepared via Sol-gel route were highly crystalline and had smaller crystallite size (~24 nm) as compared to the one prepared by Solid state reaction method (~37 nm). The crystallinity and the crystallite size were examined by XRD and TEM. Variation in the bandgap as a function of size of the particles was determined using the absorption spectra obtained by UV-Vis-NIR spectrophotometer. Photoluminescence (PL) was also recorded in the visible region for the two types of particles and results have been analysed.

Keywords: SYNTHESIS, ZnO, NANOPARTICLES.

(Received 04 February 2011, in final form 17 March 2011)

1. INTRODUCTION

Zinc Oxide is a member of II-VI semiconducting compounds and occurs naturally as the mineral zincite. It is a hexagonal wurtzite type crystal exhibiting anisotropy. ZnO is a well-known n-type semiconductor and has got a wide band gap of 3.3 eV at 300 K. Some of its important properties are listed in Table 1 [10-16]. ZnO is considered a good candidate for transparent conducting electrodes in solar cells because it is transparent to the visible light [1]. It is also considered as a prime candidate for UV and blue light-emitting devices such as blue LED and Lasers due to its large exciton binding energy of 60 meV [2, 3]. Due to such large exciton binding energy, the excitons remain dominant in optical processes even at room temperature. Due to its vast industrial applications such as electrophotography, electroluminescence phosphorus, pigment in paints, flux in ceramic glazes, filler for rubber products, coatings for paper, sunscreens, medicines and cosmetics, ZnO is attracting considerable attention in powder as well as thin film form. Its resistance to radiation damages also makes it useful for space applications. The fabrication of ZnO nanostructures have attracted intensive research interests [4-5] as these materials have found uses as transparent conducting oxides (TCO) [8-9]. Since it is the hardest of the II-VI family of semiconductors with a large shear modulus, its performance is not degraded as easily as the other compounds through the
appearance of defects. Since Zinc, the main constituent is cheap, non-toxic and abundant, ZnO has become commercially viable.

In the present work, we have synthesized ZnO nanoparticles via two different routes (sol-gel route and solid state reaction method) and tried to analyze the two on the basis of their crystallinity, crystallite size, bandgap and structural properties. X-ray diffraction (XRD) is used to calculate crystallite size. Variation in the bandgap as a function of size of the particles is determined using the absorption spectra obtained by UV-Vis-NIR spectrophotometer. Photoluminescence (PL) is also recorded in the visible region. Transmission electron micrograph (TEM) and Scanning electron micrograph (SEM) images are shown to clearly see the particle size and grain size respectively.

**Table 1 – Properties of zinc oxide**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Rock salt, Zinc blende and Wurtzite</td>
</tr>
<tr>
<td>Energy Bandgap, eV</td>
<td>3.2-3.3</td>
</tr>
<tr>
<td>Electr. Mobility, cm²Vs⁻¹</td>
<td>2.5-300 (Bulk ZnO), 1000 (Single nanowire)</td>
</tr>
<tr>
<td>Exciton Binding Energy, meV</td>
<td>60</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>5.606</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.0041</td>
</tr>
<tr>
<td>Electr. Effective Mass (mₑ)</td>
<td>0.26</td>
</tr>
<tr>
<td>Relative Dielectric Constant</td>
<td>8.5</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>1975</td>
</tr>
<tr>
<td>Boiling point, °C</td>
<td>2360</td>
</tr>
<tr>
<td>Electron Diffusion Coefficient, cm²s⁻¹</td>
<td>5.2 (Bulk ZnO), 1.7 × 10⁻⁷ (Particulate Film)</td>
</tr>
</tbody>
</table>

### 2. EXPERIMENTAL

#### 2.1 Sol-gel route

All the reagents used were of analytical grade and no further purification was done before use. ZnO nanopowder was prepared by dissolving 0.2M Zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] in methanol at room temperature and then mixing this solution ultrasonically at 25 °C for 2h. Clear and transparent sol with no precipitate and turbidity was obtained. 0.02 M of NaOH was then added in the sol and stirred ultrasonically for 60 min. The sol was kept undisturbed till white precipitates were seen in the sol. After precipitation, the precipitates were filtered and washed with the excess methanol to remove starting material. Precipitates were then dried at 80 °C for 15 min on hot plate.

#### 2.2 Solid state reaction method

The chemical reagents used in this work were Zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] and NaOH powders of analytical grade purity. In solid-state reaction method, 0.2 M of Zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] was ground for 10 min and then mixed with 0.02 M of NaOH. After the mixture was ground for 30 min, the product was washed many times with
deionized water and methanol to remove the by-products. The final product was then filtered and dried into solid powders at 80 °C for 15 min on hot plate.

The XRD measurements were carried out using Bruker AXS-D8 discover diffractometer. The absorbance of the powder in the visible region was measured using Shimadzu UV-VIS-NIR spectrophotometer (solidspec-3700). PL measurements were carried out using Shimadzu RF-5301 PC spectrophotometer under 325 nm excitation wavelength. The crystallite size calculated from the XRD measurements was confirmed by TEM Morgagni-268D FEI.

3. RESULTS AND DISCUSSION

The XRD patterns of the nanoparticles obtained by sol-gel route and solid state reaction method are shown in Fig. 1 and 2 respectively. The nanoparticles synthesized by both methods showed crystalline nature with 2θ peaks lying at 31.750° (100), 34.440° (002), 36.252° (101), 47.543° (102), 56.555° (110), 62.870° (103), 66.388° (200), 67.917° (112), 69.057° (201), 72.610° (004), 76.95° (202), 81.405° (104), and 89.630° (203). The preferred orientation corresponding to the plane (101) is observed in both the samples. These peak positions coincide with JCPDS card no. 36-1451 for ZnO powder. Crystallite size was obtained by Debye-Scherrer formula given by equation

$$D = \frac{0.94 \lambda}{\beta \cos \theta},$$

where $D$ is the crystallite size, 0.94 is the particle shape factor which depends on the shape of the particles, $\lambda$ is the CuKα radiations (1.54 Å), $\beta$ is full width at half maximum (FWHM) of the selected diffraction peak corresponding to 101 plane and $\theta$ is the Bragg angle obtained from 2θ value corresponding to maximum intensity peak in XRD pattern. The crystallite size obtained using this formula is 23.585 nm for sol-gel derived particles and 37.344 nm in case of solid state reaction method derived particles.

![Fig. 1 – XRD pattern of ZnO nanoparticles synthesized via sol-gel route](image-url)
The absorbance curve of the sol-gel derived nanoparticles in the visible region is shown in Fig. 3(a). The graph shows that ZnO does not absorb light in the visible region. This result is in accordance with the bandgap value of the bulk ZnO (3.37 eV) according to which ZnO absorbs light in ultra violet (UV) range. Band gap energy is calculated using Tauc’s plot Fig. 3b which comes out to be 3.23 eV in case of sol-gel derived nanoparticles. Tauc’s equation (2) is given by [17]

\[ \alpha h \nu = A(h \nu - E_g)^n, \]  

(2)

where \( \alpha \) is the absorption coefficient, \( h \nu \) is the photon energy, \( A \) is the constant, \( E_g \) is the bandgap energy of the sample. The value of \( n \) is 1/2 or 2 depending upon whether the transition from valence band to conduction band is direct or indirect. The value is 1/2 in case of direct transition and 2 in case of indirect transition. Since ZnO is a has a direct band structure, the value of \( n \) is 1/2 in this case. So, the equation takes the form

\[ (\alpha h \nu)^2 = B(h \nu - E_g), \]  

(3)

where, \( B \) is a constant related effective masses of charge carriers associated with valence and conduction bands. Intersection of the slope of \((\alpha h \nu)^2 \) vs \( h \nu \) curve provides bandgap energy of the samples. According to the experimentally calculated bandgap, the synthesized ZnO nanoparticles should absorb light below 383 nm and absorbance graph is in agreement with this.

The absorbance curve of the solid state reaction derived nanoparticles in the visible region is shown in Fig. 4a. Tauc’s plot is shown in Fig. 4b. The band gap energy comes out to be 3.15 eV from the Tauc’s plot. According to the experimentally calculated bandgap, the synthesized ZnO nanoparticles should absorb light below 393 nm in this case and absorbance graph shows this thing. The band gap values validates our crystallite size results according to which smaller crystallite size should have larger band gap (23.585 nm, 3.23 eV for sol-gel derived nanoparticles) and large crystallite size should have smaller band gap (37.344 nm, 3.15 eV for solid state reaction derived nanoparticles).
Photoluminescence (PL) spectra of the nanoparticles obtained by both the processes are shown in Fig. 5. The first peak in PL spectra corresponds to band to band transition and the spectra between 420-500 nm are showing blue luminescence. ZnO nanoparticles prepared via solid state reaction method show high luminescence than sol-gel derived nanoparticles. This could be due to the chemical instability caused during the fabrication process. As can be seen from the PL spectrum of sol-gel derived nanoparticles, the intensity peak is observed at 388.6 nm. If we calculate the band gap value from this wavelength, it comes out to be 3.2 eV. The PL intensity peak in case of solid state reaction derived nanoparticles is observed at 391.5 nm. From this value, band gap comes out to be 3.16 eV. The band gap energies calculated using PL spectra are approximately same as the ones calculated using Tauc’s plot.

TEM images of sol-gel derived nanoparticles are shown in Fig. 6a. Clear hexagonal structures can be seen in the Fig. 6c having diameter ~ 23 nm. Selected area diffraction is shown in Fig. 6b which clearly indicates that the ZnO nanoparticles are highly crystalline in nature.
Fig. 5 – Photoluminescence peak of ZnO nanoparticles obtained via different method

Fig. 6 – TEM image of the sol-gel derived nanoparticles (a) Selected area diffraction (b) Hexagonal structure of the sol-gel derived nanoparticles (c)

TEM image and selected area diffraction pattern of the solid state reaction derived nanoparticles are shown in Fig. 7a and 7b respectively. Selected area diffraction pattern of the nanoparticles indicates that the ZnO nanoparticles prepared via solid state reaction method are crystalline in nature. However the diffraction rings in this case are not properly aligned as in the case of sol-gel derived nanoparticles. No clear hexagonal structures can be seen in the TEM image. Nanoparticles obtained in this case are adhering to one another. Agglomeration of nanoparticles is more in this case than the former one. As can be seen from the TEM image that the average particle size is ~ 37 nm which is in agreement with the crystallite size obtained from XRD.
SEM images of the nanoparticles prepared via both the routes are shown in Fig. 8. Fig. 8a shows the SEM image of sol-gel derived nanoparticles. Clear nanostructures can be seen having grain size of ~ 70 nm. The crystallite size as observed from TEM in this case is ~ 24 nm. This shows that one grain in sol-gel derived nanoparticles is approximately equal to three crystallites. So it is clear that the nanoparticles seen by SEM image consist of a number of crystallites which are seen by TEM image. SEM image of nanoparticles prepared by solid state reaction method is shown in Fig. 8b. Grain size in this case is ~ 200 nm. Crystallite size as seen from TEM image is ~ 37 nm in this case. This shows that one grain in solid state reaction derived nanoparticles consists of approximately five crystallites. XRD results are confirmed by the combined study of these SEM and TEM images.

4. CONCLUSION

ZnO nanoparticles were prepared via sol-gel and solid state reaction methods. The ZnO nanoparticles prepared via sol-gel route were highly crystalline and had smaller crystallite size (~ 24 nm) as compared to the one prepared by Solid state reaction method (~ 37 nm). The bandgap of the synthesised nanoparticles was found to be size dependent. Photoluminescence (PL) study confirms the results obtained by XRD and TEM.
ACKNOWLEDGMENTS

This work is done under the DST-JSPS sponsored project DST/INT/JSPS/PROJ/10. Financial support by University Grant Commission, India in the form of JRF is also acknowledged. The authors are thankful to University Science Instrumentation Centre (USIC) for providing XRD facility, All India Institute of Medical Sciences (AIIMS) for providing TEM facility and Prof. P.K. Bhatnagar from Department of Electronic Science, Delhi University for providing PL facility.

REFERENCES

Modeling of Dye Sensitized Solar Cells

NEETU SINGH1*, R.M. MEHRA2 and AVINASHI KAPOOR3
1Department of Electronic Science, University of Delhi South Campus, New Delhi-110 021
2School of Engineering and Technology, Sharda University, Greater Noida-201306, Uttar Pradesh
*E-mail: singhneetu1985@gmail.com

Abstract

The article brings out the need for switching onto Dye Sensitized Solar Cells (DSSCs) over traditional solid state solar cells. It also features several different equivalent circuit models for DSSC reported by various research groups based on Electrochemical Impedance Spectroscopy (EIS). By listing these equivalent circuits, the article tries to make out the difference in the equivalent circuits of the traditional solid state solar cells and DSSCs. Since the principle and working mechanism of the traditional solid state solar cells and DSSCs are different, the equivalent circuit models for the two cannot be the same. They differ with each other in various circuit parameters and when operated in high frequency range. EIS is a powerful technique to study the kinetics of electrochemical and photoelectrochemical processes taking place inside the cell. So EIS is used by the researchers to model the equivalent circuits for DSSCs. Based on the comparison between various models featured, the article lists those parameters of the cell which have to be optimized and taken care of before making a cell for getting maximum efficiency.

Key words: DSSC, modelling, EIS.

1. Introduction

The increasing global demand of inexpensive and large scale solar energy conversion has led to very fast development in the field of photovoltaics. Solar cell technology has shown much promise over the last many decades to replace the use of fossil fuels. However, because of the high cost of manufacturing silicon-based solar cells, research is being carried out on many new varieties of solar cells including organic, hybrid organic-inorganic and DSSCs to fulfill this upcoming never ending demand of energy. Among all these varieties of solar cells DSSCs have attracted researchers the most due to their low manufacturing cost, increase in the amount of power output for the same cost and good long term stability [1, 2]. Traditional solar cells rely on a single semiconductor (typically silicon) for both light absorption and charge transport. DSSC separates these functions. Organic dyes (sensitzers) which are sensitive to light can absorb a broader range of the sun's spectrum and a separate wide band gap semiconductor electrode, electrolyte and their interface is used for charge transport [3]. When a photon hits the dye, an electron in the dye becomes excited and is injected into the conduction band of a nanocrystalline semiconductor oxide, where charge transport takes place. Electrons lost from the dye, are regenerated by a redox electrolyte, usually an inorganic solvent (I\textsubscript{-}/I\textsubscript{+}). These components are sandwiched between substrates of a transparent conducting oxide (TCO) and platinum counter electrode. This configuration has shown promise in the laboratory. It appears that the enormous surface area per unit volume of the nanoparticles can increase the photon to current ratio. Research is being focused on controlling the order and shape of the particles to increase the photon to current ratio even further.

The construction and working mechanism of traditional solid state solar cells and DSSCs are entirely different. So, the equivalent circuits of the two cannot be exactly same. There has to have some difference in the equivalent circuit models of the two [4]. The DSSC is generally characterized by using the single diode model as equivalent circuit which is similar to treating it as traditional solid state solar cells in working. But this is not the case. Ideally
thinking, the same circuit model having one current source parallel to a diode with one series and shunt resistance is impractical for DSSC. The real structure of DSSC is much more complicated corresponding to the multi diode model that takes into account different charge transport processes taking place in the cell. Also, since DSSC is a photoelectrochemical cell, it has many photoelectrochemical processes and reactions taking place into it. DSSC has got a layered structure with one layer stacking on the top of other. Due to these layers and their interfaces, a number of series and shunt resistances (two, three or more) are present in the device. Recombination losses at the oxide/dye/electrolyte interface are also found to play a major role in the working of DSSC. Single diode model does not take into account all these parameters (recombination diode due to recombination losses, multiple resistances due to layered structure, photoelectrochemical effects, capacitive and inductive effects).

This article discusses new equivalent circuit models for DSSCs which also take into account the effect of recombination losses, multiple resistances due to layered structure, photoelectrochemical reactions taking place into the cell, capacitive and inductive elements. EIS is used to investigate the internal resistances, analyze the voltage dependence of the internal resistance elements and get an equivalent circuit model for DSSCs. EIS is a method for measuring current on application of an ac voltage as a function of frequency to study the kinetics of electrochemical and photoelectrochemical processes. Since frequency is involved in the measurement, we can see the changes in I-V characteristics as a function of frequency which indicate the existence of capacitive effects in DSSCs. In EIS, we get Nyquist plot, in which the respective electrochemical steps are represented by semicircles. In case of DSSC, usually there are three to four semicircles indicating that atleast three to four photoelectrochemical process are taking place in the device. The equivalent circuits developed for DSSCs using EIS provide a more accurate presentation and a better fit to the experimental I-V curves.

1.1 Why do We Need DSSC

DSSC is a class of low-cost solar cell belonging to the group of thin film solar cells. It is based on a semiconductor formed between a photo-sensitized anode and an electrolyte; a photoelectrochemical system. This cell was invented by Michael Gratzel and Brian O'Regan in 1991. So these cells are also known as Gratzel cells.

Because it is made up of low-cost materials (dye) and does not require any elaborate apparatus to manufacture, this cell is technically attractive. Likewise, manufacture can be significantly less expensive than older solid-state cell designs. It can also be engineered into flexible sheets and is mechanically robust, requiring no protection from minor events like hail or tree strikes. Although its conversion efficiency is less than the best thin-film cells, in theory its price-performance ratio (kWh/(m² annum · dollar)) should be high enough to allow them to compete with fossil fuel electrical generation by achieving grid parity.

1.2 Fundamental Differences between PN Junction Solar Cells and DSSCs

1.2.1 Si based PN junction solar cells

PN junction solar cell is made from two doped crystals, one doped with n-type impurities (n-type semiconductor), which has "extra free" electrons, and the other doped with p type impurities (p-type semiconductor), which is lacking free electrons. PN junction is formed by diffusing an n-type dopant into one side of a p-type wafer (or vice versa). Diffusion of electrons occur from the region of high electron concentration (N type side) into the region of low electron concentration (P type side). Eventually enough electrons will flow across the boundary to equalize the Fermi levels of the two materials. The result is a region at the interface, the p-n junction, where charge carriers are depleted and/or accumulated on each side of the interface. In silicon, this transfer of electrons produces a potential barrier of about 0.6 to 0.7 V. When placed in the sun, photons of the sunlight can excite electrons on the n-type side of the semiconductor, a process known as photoexcitation. In silicon, sunlight can provide enough energy to push an electron out of the lower-energy valence band into the higher-energy conduction band. As the name implies, electrons in the conduction band are free to move about the silicon. When a load is placed across the cell as a whole, these electrons will flow out of the n-type side into the p-type side, lose energy while moving through the external circuit, and then back into the n-type material where they can once again re-combine with the valence-band hole they left behind. In this way, sunlight creates an electrical current.
1.2.2 Limitations of PN junction solar cells

In any semiconductor, the band gap means that only photons with that amount of energy, or more, will contribute to producing a current. In the case of silicon, the majority of visible light from red to violet has sufficient energy to make this happen. Unfortunately higher energy photons, those at the blue and violet end of the spectrum, have more than enough energy to cross the band gap; although some of this extra energy is transferred into the electrons, the majority of it is wasted as heat. Another issue is that in order to have a reasonable chance of capturing a photon, the n-type layer has to be fairly thick. This also increases the chance that a freshly ejected electron will meet up with a previously created hole in the material before reaching the p-n junction. These effects produce an upper limit on the efficiency of silicon solar cells, currently around 12 to 15% for common examples and up to 25% for the best laboratory modules.

Moreover silicon is an indirect bandgap semiconductor, meaning that valence band maximum and conduction band minimum are not opposite to each other in k-space. Light absorption is much weaker in an indirect gap semiconductor than in a direct semiconductor.

By far the biggest problem with the conventional approach is cost. Silicon processing is expensive because of high temperature and high vacuum processes. There have been a number of different approaches to reduce this cost over the last decade, notably the thin-film approaches. DSSC is one among these approaches.

1.2.3 Dye sensitized solar cells

Gratzel cell consists of a porous layer of titanium dioxide nanoparticles, covered with a molecular dye that absorbs sunlight. The titanium dioxide is immersed under an electrolyte solution, above which is a platinum-based catalyst. Sunlight passes through the transparent electrode into the dye layer where it can excite electrons, which then flow into the titanium dioxide. The electrons flow towards the transparent electrode where they are collected for powering a load. After flowing through the external circuit, they are re-introduced into the cell on a metal electrode on the back, flowing into the electrolyte. The electrolyte then transports the electrons back to the dye molecules.

Dye-sensitized solar cells separate the two functions provided by silicon in a traditional cell design. Normally the silicon acts as both the source of photoelectrons, as well as providing the electric field to separate the charges and create a current. In the dye-sensitized solar cell, the bulk of the semiconductor is used solely for charge transport, the photoelectrons are provided from a separate photosensitive dye. Charge separation occurs at the surfaces between the dye, semiconductor and electrolyte.

The dye molecules are quite small (nanometer sized), so in order to capture a reasonable amount of the incoming light the layer of dye molecules needs to be made fairly thick, much thicker than the molecules themselves. To address this problem, a nano-material is used as a scaffold to hold large numbers of the dye molecules in a 3-D matrix, increasing the number of molecules for any given surface area of cell. In existing designs, this scaffolding is provided by the semiconductor material, which serves double-duty.

1.2.4 Differences between PN junction solar cell and DSSC based on their working

In PN junction solar cells, light absorption and charge transport occurs in the same material, whereas in DSSC, photons are absorbed by the dye molecules and transport of charges is carried out in a separate wide band gap semiconductor electrode (ZnO or TiO2) and electrolyte. Also the charge separation in PN junction cells is induced by the electric field across the junction. No such long-range electric field exists in the DSSC. In DSSC, charge separation occurs via other kinds of kinetic and energetic reasons at the dye-covered semiconductor-electrolyte interface. In the DSSC the generated electrons travel in the nanoporous ZnO (TiO2) network and holes in the electrolyte, which means that the requirement for a pure and defect free semiconductor material as in case of PN junction solar cell is relaxed for DSSC, where the recombination can occur only at the semiconductor electrolyte interface. The first reported efficiency for DSSC was 7.1%.

1.3 Physics of DSSC

The working of every photovoltaic cell is based on the following three steps [3]:
1. Photon Absorption
2. Charge Separation
3. Charge Collection
DSSC has three main parts (Fig. 1). On top is a transparent conducting anode made of Indium tin dioxide (ITO) deposited on the back of a glass plate. On the back of this conductive plate is a thin layer of wide band gap semiconductor material (ZnO, TiO$_2$), which forms a highly porous structure with an extremely high surface area. ZnO absorbs only a small fraction of the solar photons (those in the UV). The plate is then immersed in a mixture of a photosensitive dye and a solvent. After soaking the film in the dye solution, a thin layer of the dye is left covalently bonded to the surface of the ZnO.

Meanwhile, the dye molecule which has lost an electron will decompose if another electron is not provided to it. The dye strips one electron from iodide in electrolyte below ZnO, oxidizing it into triiodide. This reaction occurs quite quickly compared to the time that it takes for the injected electron to recombine with the oxidized dye molecule, preventing this recombination reaction that would effectively short-circuit the solar cell.

The triiodide then recovers its missing electron by mechanically diffusing to the bottom of the cell, where the counter electrode re-introduces the electrons after flowing through the external circuit.

2. Various Models of DSSC Based on Experimental Evidence

The equivalent circuit diagram (single diode model) for PN junction solar cell is shown below (Fig. 2).

In this circuit, the resistance $R_s$ in series with diode represents electrical properties of PN junction. Shunt resistance and constant current source are parallel to the junction. $R_s$ is due to the bulk resistance of the semiconductor material, metallic contacts and their interconnections, and the contact resistance between the metallic contacts and the semiconductors. $R_{sh}$ is due the leakage across the PN junction around the edge of the cell, and the presence of crystal defects and/or impurities in the junction region. Current source $I_{ph}$ is due to the excitation of charge carriers by solar radiation.

Liyuan Han et al., 2005 reported an equivalent circuit model for DSSC based on EIS analysis and showed its comparison to the single diode model as

![Fig. 3. Single diode model for traditional solid state solar cell [3]](image)
shown [4]. He reported the EIS spectrum for two cells, one containing N3 dye as sensitizer and other black dye as sensitizer. The semicircles in impedance spectroscopy represent different electrochemical processes taking place in the cell and hence tell us about the no. of impedance elements present in the cell. Figure below (Fig. 4) shows the EIS of DSSC using N3 dye.

![EIS of DSSC using N3 dye as sensitizer](image)

**Fig. 4. EIS of DSSC using N3 dye as sensitizer [4]**

We can see in this plot that there are three semicircles each corresponding to a different electrochemical process taking place in the cell and hence three different impedance elements should be present as a result of which we get three different resistances [5, 6]. Here Z₂ plays the role of diode. As we know, a solar cell must contain a diode. But here we have three impedances (Z₁, Z₂, and Z₃). Now to determine which impedance element gives diode like behavior under open circuit conditions, let us see the diode equation which is given by

\[
I = I_o \left\{ \exp \left( \frac{qV}{nkT} \right) - 1 \right\}
\]

(1)

Where I_o, q, V, n, k and T are diode saturation current, electronic charge, voltage, ideality factor, Boltzman constant and temperature respectively. The resistance R is described by the equation

\[
\frac{1}{R} \propto \exp \left( \frac{qV}{nkT} \right)
\]

(2)

In this equation, q, n, k, T are constants. Therefore 1/R should be proportional to the exponential function of V. The dependence of Rᵣ, Rᵥ, Rₑ and Rₙ on applied bias voltage around Voc was investigated. The graph shows that 1/Rᵥ, 1/Rₑ and 1/Rₙ remain almost unchanged but 1/Rᵣ increases linearly with applied bias voltage (Fig. 5). This suggests that R acts as diode in DSSCs and Rᵥ, Rₑ and Rₙ act as series resistances. Zₑ is assigned to the carrier transport resistance of TiO₂/dye/electrolyte interface.

![Dependence of R₂ on applied bias voltage](image)

**Fig. 5. Dependence of R₂ on applied bias voltage [4]**

Rₑ is the high frequency resistance which is in direct proportion to the sheet resistance of TCO layer. Rᵥ decreases with increase in the roughness factor of the platinum counter electrode (Fig. 6) which suggests that Rᵥ is related to the carrier transport resistance at the surface of Pt counter electrode.

![Dependence of R₁ on roughness factor of platinum counter electrode](image)

**Fig. 6. Dependence of R₁ on roughness factor of platinum counter electrode [4]**
$R_3$ depends on the distance between TCO and platinum counter electrode (Fig. 7). From the graph we can see that $R_3$ is in direct proportion to the cell gap which is the distance between the TCO and platinum counter electrode. Therefore we can say that $R_3$ is related to the diffusion of $I^-/I_3^-$ ions within the electrolyte.

Based on the above analysis the equivalent circuit diagram which the author gave is shown in the fig below (Fig. 8)

Since capacitance plays role in high frequency operation, $C_1$ and $C_2$ can be eliminated under direct current applications. In that case

$$R_s = R_1 + R_3 + R_h \quad (3)$$

So the circuit takes the form (Fig. 9) as shown

A similar equivalent circuit was proposed by Naoki Koide at el. in 2006 [7]. In this paper, besides giving the equivalent circuit model for DSSC, the author tries to co-relate the diode I-V equation with electrochemistry’s famous Butler-Volmer equation to show the similarities between the single diode model and circuit obtained by him when operated under direct current conditions. The Nyquist plot he obtained also had three semicircles in the frequency range of 0.1 Hz-1 MHz (Fig. 11). The three semicircles are attributed to the redox reaction at the platinum counter electrode ($Z_1$), the electron transfer at the TiO$_2$/dye/electrolyte interface ($Z_2$), and the carrier transport by...
ions within the electrolyte ($Z_3$). The resistance elements $R_1$, $R_2$, and $R_3$ are described as the real part of $Z_1$, $Z_2$, and $Z_3$ respectively.

$R_h$ is the resistance element in high frequency range over 1 MHz and it is influenced by the sheet resistance of transparent conducting oxide (TCO) and contact resistance between the TCO and TiO$_2$. Sheet resistance of TCO is the main factor of $R_h$. The value of $R_h$ increases in direct proportion to the sheet resistance (Fig. 12).

Here also $Z_2$ plays the role of a diode (Fig. 13) using the similar analogy reported by Liyuan Han et al.

The equivalent circuit for DSSC is as shown (Fig. 14). In this $Z_2$ functions as diode to rectify the current. Shunt resistance $R_{sh}$ was added to the circuit to describe the back electron transfer across the TiO$_2$/dye/electrolyte junction. $R_{sh}$ cannot be determined from the impedance spectrum. But is found by the slope of the I-V curve at the short-circuit current point, which is typically of the order of $10^3$ $\Omega$. A constant current source ($I_{ph}$) describes the latent ability in $J_{sc}$. As we can see, the equivalent circuit is exactly same in the previous case. Here also $C_1$ and $C_2$ can be eliminated under direct current applications.

Further to correlate this equivalent circuit with single diode model, Koide and his co-workers, rewrite the eq. 1 (diode's I-V equation) in terms of electrochemistry’s well known Butler-Volmer equation (Eq. 3) [8].

$$I = I_0 \left\{ \exp \left( \frac{qV}{nkT} \right) - 1 \right\}$$

$$i = -i_0 \left\{ \exp \left( -\alpha mFE \frac{RT}{RT} \right) - \exp \left( (1-\alpha) mFE \frac{RT}{RT} \right) \right\}$$

Electrochemistry’s equation because DSSC is a photoelectrochemical cell. In this equation $i_0$ is the
exchange current, \( m \) is the stoichiometric number of the electron involved in the electrode reaction, \( F \) is the Faraday constant which is \( q \) times the Avogadro constant, \( E \) is the electric potential at the electrode, and \( R \) is the gas constant which is defined as \( K \) times the Avogadro constant. Now since the electric potential \( E \) is much larger than the \( RT/(\alpha mF) \) in DSSC operations, Eq. 3 can be simplified to Tafel equation (eq. 4)

\[
i = i_0 \left\{ \exp \left( \frac{(1\alpha - n)FE}{RT} \right) \right\} = i_0 \left\{ \exp \left( \frac{\alpha \text{qE}}{kT} \right) \right\}
\]

Now if we assume the equations 5 & 6, then above equation coincides with diode I-V characteristic equation

\[
(1\alpha m) = \left( \frac{1}{n} \right)
\]

\[
E = V >> \left( \frac{nkT}{q} \right)
\]

The above analogy shows that Tafel equation is able to describe a rectifying device like diode, while the ideality factor (\( n \)) in the diode is related to the stoichiometric number of electrons involved in the electrode reaction (\( m \)) and the transfer coefficient (\( \alpha \)).

Now if we compare the equivalent circuits reported above with single diode equivalent circuit model, the only difference is in series resistance. In case of DSSC series resistance \( R_s \) and \( R_2 \) are parallel to large capacitances. Due to these capacitances, a large time constant is added to DSSC. So, I-V curves for DSSCs are not accurately measured when using the same measurement conditions as for PN junction solar cells. This time constant slows down the response to the applied voltage. To get the correct results of the I-V curves in DSSCs based on the equivalent circuit described above, measurements should be carried out with a prolonged delay time [9]. But these capacitance elements can be eliminated since the solar cells are generally operated under direct current conditions. As a result of which \( R_s \) can be written as

\[
R_s = R_1 + R_3 + R_h
\]

Another equivalent circuit for photovoltaic cell having layer by layer assembly (LBL) is proposed by Basudev Pradhan et al. in 2005 [10]. An LBL assembly provides donor/acceptor (D/A) interfaces at molecular scale. The cells were having \( D_m/(D/A)_n/A_m \) structure, where \( m+n=15 \) and number of D/A interfaces (\( n \)) varied from 1 to 11. Current-Voltage and impedance characteristics of the device under dark and illumination conditions were carried out. Short circuit current (\( J_{sc} \)) was found to be dependent on number of interfaces. The author says that since the functioning of a photovoltaic cell involves exciton dissociation, charge separation and carrier transport, the device behavior can be explained in terms of its dielectric properties. In fact when he compared the changes in bulk resistance \( R_p \) and dielectric constant of the active material with short circuit current under illumination condition, he found that photovoltaic devices should be designed in such a way that dielectric constant of the active material should decrease upon illumination. He studied the dielectric properties of LBL photovoltaic devices with controlled number of interfaces (\( n \)) and found that open circuit voltage (\( V_{oc} \)) remained almost same in these devices, but \( J_{sc} \) was higher with moderate number of interfaces (Fig. 15). The reason he gave for such dependence was

![Fig. 15. Dependence of short circuit current, dielectric constant of active layer and bulk resistance on number of interfaces [10]](image)
opposing contribution of the D/A interfaces on exciton dissociation and charge transport.

Above graph shows that J_{sc} is higher with moderate number of interfaces and when J_{sc} is high, dielectric constant value is low. Real and imaginary parts of complex impedance as a function of frequency (1-12 MHz) under illumination and dark conditions were measured (Fig. 16). In the inset is shown the magnified view near the origin of the plot. The magnified view shows the presence of another semicircle with a shift from the origin.

The author says that due to the presence of another semicircle near the origin, the device can be represented as series combination of resistance R_{s} and two parallel resistor-capacitor networks. The radii of semicircles may represent bulk resistance (R_{p}) of the cell and resistance due to organic metal interfaces (R). We can see from the graph above that diameter (and radius) of the semicircle under dark condition is larger than under illumination. Decrease in the diameter of the plots and hence the bulk resistance of the device was due to illumination. Under illumination the dissociated excitons are more, thereby increasing the carrier concentration in the cell resulting in an increase in the mobility of charge carriers. The author suggests that decrease in bulk resistance of the cell could be due to the increase in carrier mobility. The circuit he reported is shown in the figure (Fig. 17).

Virginia Yong at el. in 2008 also reported one such equivalent circuit for DSSC based on EIS [11]. The circuit he reported contained a rectifying diode (D_{r}), double layer capacitance (C_{i}), photogenerated current (I_{ph}), shunt resistance (R_{sh}), recombination resistance (R_{sc}), an inductor (L), charge transfer resistance at the FTO electrode (R_{E}), interfacial capacitance at FTO electrode (C_{E}), charge transfer resistance at electrolyte/Pt interface (R_{CE}), interfacial capacitance at electrolyte/Pt interface (C_{CE}), bulk and contact resistive losses such as sheet resistance of FTO/ITO glass (R) and Warburg impedance (W). The circuit is as shown below (Fig. 18).

In the circuit the interfacial charge transfer at the TiO_{2}/dye/electrolyte is represented by a rectifying diode (D_{r}) and a double-layer capacitance (C_{i}). A recombination diode D, with an ideality factor generally considered as equal to 2 is employed to denote the interfacial charge recombination losses to both the dye cation and the redox electrolyte [12, 13]. Shunt resistance R_{sh} takes into account all parallel resistive losses across the photovoltaic device including leakage current.

The photogenerated current I_{ph} is in parallel with the rectifying diode. An inductive recombination pathway as a result of a charge-transfer current is
incorporated into the circuit, consisting of a recombination resistance \( R_{\text{rec}} \) in series with an inductor \( L \) [14]. The charge-transfer resistance and interfacial capacitance at the FTO electrode and electrolyte/Pt-FTO interface are represented by \( R_e \) and \( C_{ef} \) and \( R_{ce} \) and \( C_{ce} \), respectively. The Nernst diffusion of the carrier transport by ions within the electrolyte is denoted by the Warburg impedance \( W \) [15]. In EIS Nernst diffusion is denoted by \( W \). Resistance element \( R_s \) designates the bulk and contact resistive losses present in a practical DSSC, such as the sheet resistance of the FTO glass.

3. Comparative Study of These Models

So far we have seen some equivalent circuit models for DSSC reported by various research groups containing a number of series and shunt resistors, capacitors, inductors, diodes in addition to photogenerated current source. On the basis of this, we can say that modeling helps improving the overall efficiency of the solar cells because the impedance spectrum of the cell tells us about the various impedance elements playing role in the device. Liyuan Han at el. in his paper reported that \( R_1 \) decreases with increasing roughness factor of counter electrode which was related to the carrier transport resistance at the surface of platinum counter electrode. So, to have minimum value of \( R_1 \), roughness of the counter electrode should be more. A similar analogy was given by Naoki Koide at el. to have minimum value of \( R_1 \). He said that roughness factor is a measure of surface area of the counter electrode and it should increase by increasing the surface area of the electrode. He defined the roughness factor as the ratio of the total surface area to the projected area of the counter electrode. Increase in Roughness factor results in an accelerated rate of \( I_- \) reduction, thereby increasing the overall efficiency of the cell. In both the papers, \( R_s \) is found to vary linearly with applied bias voltage. So impedance element \( Z_2 \) is thought to be acting as diode. About \( R_3 \), both papers said it depends on the distance between TCO and Platinum counter electrode. Liyuan Han at el. said that \( R_3 \) increases with cell gap i.e. the distance between TCO and platinum counter electrode. Naoki Koide at el. relates this thing to the carrier transport by the ions within the electrolyte. He said that the value of \( R_3 \) increases with the thickness of the electrolyte layer. Increasing electrolyte layer thickness means that we are increasing the cell gap. Virginia Yong at el. also say this thing but in a different manner. He introduced the concept of Warburg impedance which is related to the Nernstian diffusion of \( I_3^- \)-ions within the electrolyte. And again the electrolyte thickness is related to the cell gap only. \( R_h \) is proportionally related to the sheet resistance of the TCO layer, but it is a high frequency resistance and comes into picture only when measurements are taken in the high frequency range (over 1 MHz). Basudev Pradhan at el. reported that for getting higher values of short circuit current of LBL photovoltaic devices, dielectric constant of the active material in the device should decrease upon illumination. Device should be designed in such a way that recombination losses should be as low as possible. Virginia Yong at el. tried to explain the device physics on the basis of equivalent circuit model. He showed the existence of recombination diode also in the circuit. So while fabricating DSSC, care should be taken to have recombination losses as less as possible. Further he explained the Nernst diffusion of carrier transport by ions within the electrolyte by Warburg impedance \( W \).

4. Conclusion

In the article, we featured some equivalent circuit models based on EIS. We found that modeling helps improving the overall efficiency of the cell because by using EIS, we can investigate the role of various series and shunt resistances, capacitances and inductances, and diodes; and also see their dependence on the various parameters of the cell such as sheet resistance of TCO layer, roughness factor of platinum counter electrode, thickness of the electrolyte layer (cell gap), dielectric constant of active material, number of interfaces in the device etc. Photovoltaic devices should be designed in such a way that dielectric constant of the active material should decrease upon illumination. Number of interfaces should be moderate. Sheet resistance of the TCO should be less. Roughness of Platinum counter electrode should be more. So while fabricating a DSSC, we should keep these factors in mind and choose the materials having properties which give the best results. Cell can be fabricated using the optimized properties to have maximum efficiency.

Acknowledgement

One of the author, Neetu Singh would like to acknowledge University Grant Commission for financial support.
References