IIETA International Information and Engineering Technology Association
Advancing the World of Information and Engineering

Journal of New Materials for Electrochemical Systems
Vol.23, No.2, April, 2020, pp. 71-77
http://new-mat.org
http://iieta.org/journals/jnmes

Estimation of Photovoltaic Properties of ZnO nanoparticles and CeO_2- ZnO composite and Electrochemical Determination of Adrenaline Employing Voltammetry Studies

H.A. Deepa[1*], G.M. Madhu[2], B.E. Kumara Swamy[3] and J. Koteswararao [2]

[1] Department of Chemical Engineering, Dayananda Sagar College of Engineering, Bengaluru-560078, India
[2] Department of Chemical Engineering, Ramaiah Institute of Technology, MSR Nagar, Bengaluru-560054, India
[3] Department of Industrial Chemistry, Kuvempu University, Shanakaragatta, Shimoga, India

Corresponding Author Email: deepaha@gmail.com

ABSTRACT

ZnO nano particles and cerium oxide-ZnO composite were synthesized using gel combustion approach. The synthesized ZnO nano particles and CeO_2-ZnO composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). Dye sensitized solar cells (DSSC's) were fabricated by coating the photoanodes with the synthesized nanomaterials employing doctor blade technique. The performance of DSSC fabricated using ZnO nanoparticles was compared with the one which was prepared using CeO_2-ZnO composite. The nanomaterials of ZnO and CeO_2-ZnO were subjected to cyclic voltammetry tests for the electrochemical determination of adrenaline(AD).The DSSC fabricated with ZnO nanoparticles exhibited higher power conversion efficiency when compared to the DSSC fabricated using CeO_2 - ZnO composite but the cerium oxide-ZnO composite showed better sensor properties compared to ZnO nanoparticles for the electrochemical determination of Adrenaline (AD).

Keywords: *Adrenaline (AD), CeO_2 -ZnO composite, dye sensitized solar cells, photoanode, ZnO nano particles*

Received: March-29-2020, Accepted: April-22-2020, https://doi.org/10.14447/jnmes.v23i2.a03

1. INTRODUCTION

Utilization of alternate energy resources to overcome the raising demand for fossil fuels and their environmental impact is a challenging task for the modern world. Many researchers have contributed for the development of techniques related to inexhaustible energy resources utilization. Among the inexhaustible energy resources, solar energy is the most abundantly available resource and it can be considered as an ultimate solution to decrease energy crisis [1]. Solar cells work on the principle of photovoltaic effect, several photovoltaic devices have been developed of which the silicon solar cells have gained the most popularity. A unique solar cell called Dye Sensitized Solar Cell (DSSC) was first produced by Gratzel's and his team [2, 3]. In DSSC, the function of light absorption is accomplished by a dye that is adsorbed on a wide bandgap nanoporous semi conducting photoanode such as TiO_2 which possesses a bandgap of 3.2eV. The charge generation and transfer occur from the photoanode. A counter electrode is employed for the transfer of electrons from an external circuit and a redox electrolyte is introduced amidst the photoanode and the counter electrode [4]. The most important step in the development of DSSC is the selection of appropriate semiconducting material as the photoanode, as it is the component from where the charge production and transference occurs in presence of an illuminated light [5]. As the Zinc oxide (ZnO) possesses better photoelectrochemical properties and stable against photo corrosion, it can be considered as one of the eventual semiconducting materials in converting the solar power into electrical energy [4]. ZnO is a well-known semiconductor having a wide bandgap energy of 3.3eV and a huge binding energy of 60meV at room temperature [6]. Greater conductivity, specific chemical and microstructural characteristics of ZnO nanoparticles renders it a multifunctional material which can be used in gas and electrochemical sensors.

Development of sensors for utilization in biological process control and environmental monitoring is a field of interest for the researchers. Electrochemical based sensors function better than conventional sensors due to their high selectivity and quick response [7]. Liu et al reported an efficiency of 0.25% and open circuit voltage of 0.274 V for the DSSC prepared using ZnO nanoparticles [3]. Suliman et al reported an efficiency of 0.75% and an open circuit voltage of 0.573 V for the DSSC fabricated using ZnO nanoparticles [4]. Rani et al reported an efficiency of 1.11% for the DSSC synthesized using ZnO powder via sol-gel route [6]. Giannouli reported an efficiency of 0.88% and 0.76% for DSSC fabricated using ZnO and ZnO-TiO_2 composites as photoanodes respectively with rose bengal as the dye [8]. The composites may enhance or decrease the photovoltaic performance of DSSC.

Adrenaline is a vital neurotransmitter which is formed by adrenal glands in the cerebrospinal axis. Owing to its significant functions, adrenaline is utilized as a key component of medications which are used in the treatment of ailments like cardiac arrest, bronchitis, anaphylaxis [9]. The presence of optimal amount of adrenaline in human body plays a major role. Therefore, it is essential to determine the presence of adrenaline using an active material.

To choose an active material and its development is a challenging task. These dynamic materials may be of a type which performs as a catalyst for sensing a specific analyte. Current progress in the field of nanoscience has created an opportunity for the utilization of novel materials of desirable properties that have applications as biosensors and electrochemical sensors. Many analytical methods such as

HPLC and mass spectroscopy have been utilized for the detection of biological compounds. Although, these techniques provide precise and accurate results, they have detriments such as elevated price and intricate sample pre-treatment procedures required for analysis. Development of electrochemical sensors have gained popularity due to their stability, quick response and low price [10-13]. Cyclic voltammetry analysis is the efficient approach for the determination of sensor properties of nanomaterials.

The aim of the present research work is to determine the photovoltaic properties of the pure ZnO nano particles and CeO_2-ZnO composite and compare the effect of amalgamating CeO_2 with ZnO nanoparticles on both the photovoltaic performance and the electrochemical response for the determination of adrenaline respectively. Accordingly, ZnO nanoparticles and CeO_2-ZnO composite are synthesized using gel combustion approach. The synthesized nano materials are characterized using XRD, SEM, and EDAX. Then, ZnO nano particles and CeO_2-ZnO composite were employed as photoanodes to fabricate dye sensitized solar cells and their performance characteristics (open circuit voltage, short circuit current, efficiency and fill factor) are evaluated under a solar irradiation of 100mW/cm^2. The synthesized nanomaterials are subjected to cyclic voltammetry tests to assess the electrochemical properties and to determine the effect of integrating cerium oxide with ZnO on the peak responses of adrenaline redox reactions. Accordingly, the photovoltaic properties of ZnO nanoparticles and CeO_2-ZnO composite and their and electrochemical properties for the determination of Adrenaline (AD) are estimated and reported.

2. EXPERIMENTAL

2.1 Chemicals Used

The chemicals used for the synthesis of nano particles and the fabrication of DSSC were procured and used directly without further purification. The chemicals procured for the present work include Zinc Nitrate hexahydrate (>96% pure, Sigma Aldrich), Cerium nitrate (98% pure LOBA Chemie), commercial sugar from local market, Acetylacetone (98% pure LOBA Chemie), Triton X-100 (Fisher Scientific), Tertiary butanol (99.5% pure RANKEM), Acetonitrile (99.9% pure RANKEM), N719 dye (Solaronix, Switzerland,) Iodolyte HI-30 (Solaronix, Switzerland), Platisol T/SP (Solaronix, Switzerland).

2.2 Synthesis of ZnO nanoparticles and CeO_2 – ZnO composite using gel combustion method

2.2.1 Synthesis of ZnO

The ZnO nano particles were synthesized using gel combustion approach with Zinc nitrate hexahydrate as a precursor and sugar as a fuel as reported by Venkatesham et al. [14]. 15.7g of Zinc nitrate hexahydrate and 3.7642g of sugar were taken in a glass beaker. The blend was dissolved in 120ml of distilled water and heated on a hot plate in a fume chamber. As the level of the solution in the beaker approached the bottom and when the bubble formation was high, the fume chamber was switched on so that the fumes were exhausted. ZnO nanoparticles were formed with the sudden ignition, which were calcined at 600℃ using a muffle furnace for half an hour for the removal of hydrocarbons and nitrates. The ZnO nanoparticles were obtained according to the following reaction (1):

$$24\ Zn(NO_3)_2\ + 5\ C_{12}H_{22}O_{11} \rightarrow 24\ ZnO + 24\ N_2 + 35\ H_2O + 60\ CO_2 \quad (1)$$

2.2.2 Synthesis of Cerium oxide-ZnO composite

Cerium oxide-ZnO composite was prepared using gel combustion method by taking Zinc nitrate hexahydrate and cerium nitrate hexahydrate as precursors and adding stoichiometric quantities of sugar and distilled water. Zinc nitrate to cerium nitrate were taken in the molar ratio of 0.7:0.3, respectively. 16g of Zinc nitrate hexahydrate, 10g of Cerium nitrate hexahydrate and 14.224g of sugar were taken in a glass beaker. The mixture was dissolved in 120ml distilled water and heated on a hot plate in a fume chamber. When the bubble formation was observed, the fume chamber was switched on so that the fumes were exhausted. The cerium oxide-ZnO composite was formed and calcined at 600^{0}C for half an hour in a muffle furnace for the elimination of hydrocarbons and nitrates. Cerium oxide-ZnO composite was formed according to the following possible reaction (2):

$$24\ Zn(NO_3)_2 + 24\ Ce(NO_3)_3 + 13\ C_{12}H_{22}O_{11} \rightarrow 24\ CeO_2ZnO + 132\ CO_2 + 24\ CO + 60N_2 + 143\ H_2O \quad (2)$$

2.3 DSSC fabrication

The DSSC was fabricated using a similar procedure as reported by Govindaraj et al. [15, 16]. Fluorine doped Tin Oxide (FTO) coated glass slides, TISXZ001 of 0.22 cm thickness, resistivity 7 ohms/sq.cm and transmittance greater than 85% were used as glass substrates for developing photoanode and counter electrode. The FTO glass slides were dipped in deionized water followed by ultrasonicating in ethanol for 10 minutes and dried. The synthesized ZnO nanoparticles and cerium oxide-ZnO composite nanomaterials (in the form of a paste) were coated on the conductive side of the FTO glass slides employing doctor blade technique. These photoanodes were dried and sintered at 450^{0}C for about thirty minutes. The glass substrates thus prepared were soaked in 5mmol/l solution of N719 dye for about a day for dye sensitization. The photoanodes were heated to 80-100℃ before immersing into the dye solution to eliminate adsorbed species. The nanomaterial coated films were then cleansed with ethanol and dried in air after dye sensitization. Platisol T/SP was coated on another FTO glass slide which was used as a counter electrode. The FTO glass substrate coated with Platisol T/SP was sintered at 400^{0}C for half an hour and cooled. The counter electrode was placed over the photoanode and the two electrodes were assembled with a binder clip as shown in Figure 1. The electrolyte (Iodolyte HI-30) was introduced amidst the photoanode and the counter electrode by capillary movement. The active area of the DSSC was nearly 25 mm^2.

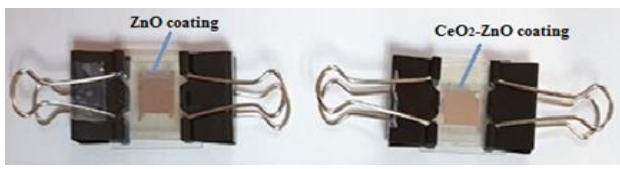

Figure 1. Completed DSSC's coated with ZnO and CeO_2-ZnO composite

2.4 Cyclic Voltammetry

To perform Cyclic voltammetry (CV), an analytical equipment of Model CHI-660C potentiostat was employed. For electrochemical measurements, the conventional tri-electrode cell assemblage comprising of a reference electrode such as Saturated Calomel Electrode (SCE), a carbon paste electrode as a working electrode and a counter electrode consisting of a platinum wire was utilized. During the electrochemical measurements, either an unmodified or modified carbon paste working electrode containing pure ZnO nanoparticles or CeO_2-ZnO composite was used. Measurement of pH was performed using MK VI digital pH meter and the tests were conducted at room temperature [9].

2.4.1 Preparation of bare and modified electrodes employing carbon-paste:

By blending 20% silicon oil and 80% graphite powder in mortar and pestle for nearly half an hour, the bare electrode of carbon-paste was prepared so that a homogenous mix was formed. This blend was packed into the hollow portion of a small cylindrical structure and flattened on a piece of paper. By adding 0.002 g of synthesized nanoparticles to the fused silicon oil and graphite powder, the modified electrode of carbon-paste was synthesized [17]

2.4.2 Description of electrolyte utilized for electrochemical measurements:

The electrolyte employed was Phosphate buffer solution. Phosphate buffer solution (PBS) of 0.2 M were prepared in distilled water by mixing appropriate ratio of $NaH_2PO_4 \cdot H_2O$ and Na_2HPO_4. For the electrochemical measurement 2 mM adrenaline in 0.1M phosphate buffer solution at scan rate of 100 mV/s was selected.

2.5 Characterization

Scanning electron microscopy (Tescan Vega 3) was utilized to determine the morphology of the synthesized ZnO nanoparticles and CeO_2-ZnO composite. X-ray diffraction with CuKα radiation with standard JCPDS (PAN Analytical powder Xpert-3) was utilized to analyze the crystalline phase of the synthesized nanomaterials. To determine the elemental composition of the synthesized nanoparticles, energy dispersive X-ray analysis was performed. The I-V characteristics (current and voltage) of the DSSC fabricated was analyzed using a solar simulator with an irradiation of $100mW/cm^2$ and a Keithley 2400 source meter (computer controlled). The photoelectrical conversion efficiency (η) of the fabricated DSSC is computed utilizing the formula: $\eta = Isc. Voc. FF / P_{in}$, where Isc signifies short circuit current, Voc is the open circuit voltage, P_{in} represents the Incident Power input; FF is the Fill Factor [16]

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

Figure 2 and Figure 3 show the XRD pattern of the ZnO nanoparticles and CeO_2-ZnO composite, respectively. The XRD pattern shown in Figure 2 confirmed the formation of ZnO nanoparticles with the diffraction peak at 2θ=31.7, 34.34, 36.17, 47.45, 56.5, 62.76, 66.28, 67.85, 69.00^0 correlating to standard crystal planes (100), (002), (101), (102), (110), (103), (200), (112), (201) respectively and in agreement with ICDD (International Centre for Diffraction Data) # 36-1451 [18].

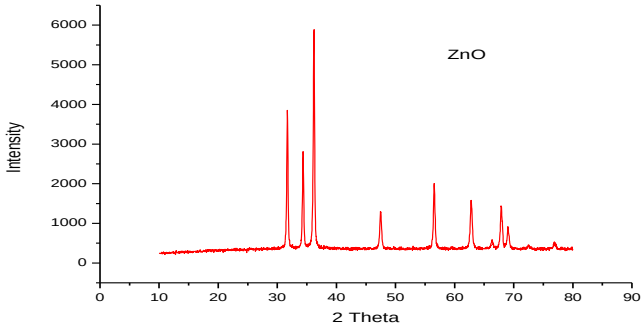

Figure 2. XRD pattern of pure ZnO

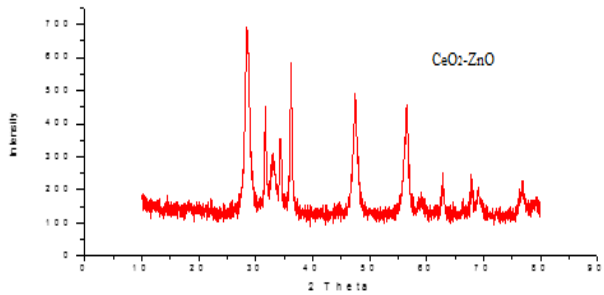

Figure 3. XRD pattern of CeO_2-ZnO composite

The XRD pattern shown in Figure 3 confirmed the formation of CeO_2-ZnO composite with the diffraction peaks at an angle of 2θ=28.58, 31.67, 33.07, 34.34, 36.15, 47.45, 56.28, 59.04, 62.76, 67.85, 69.08, 76.66^0 and the broad peaks indicate the formation of the CeO_2-ZnO composite in the nano meter range [19]. Crystallite size of the synthesized nanopowders were estimated employing Scherrer's formula $D=K\lambda/(\beta)Cos\theta$ Where, D represents the average (mean) size of the particles, λ signifies the X-ray wavelength, θ gives the Bragg's angle, β is the line broadening at half the maximum intensity, K denotes a constant (0.9). The mean particle size of ZnO nanoparticles were determined as 33.57nm and the mean particle size of 15.78 nm was computed for the CeO_2-ZnO composite. The average crystallite size of the synthesized nano particles was higher than the values reported by Sowmya et al. [20] which was determined as 14.1nm.

3.2 EDAX Analysis

EDAX analysis was performed on the synthesized nanomaterials to determine the elemental composition which are represented in Figure 4a and Figure 4b. The EDAX analysis indicated the formation of ZnO nanoparticles in the stoichiometric weight ratio as Zn=78.1 % and O=21.9% respectively. The EDAX analysis also confirmed the absence of impurities in the synthesized nanomaterials.

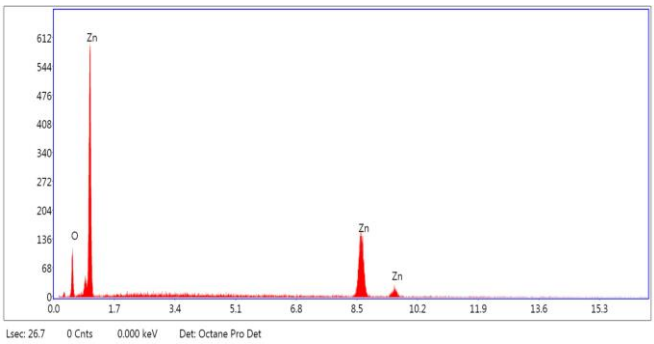

Figure 4a. EDAX analysis of pure ZnO nanoparticles

The EDAX analysis confirmed the formation of CeO_2 - ZnO composite in the stoichiometric weight ratio as Zn=39.42%, O=24.29% and Ce=36.29% respectively. There were no impurities present in the synthesized nano composite.

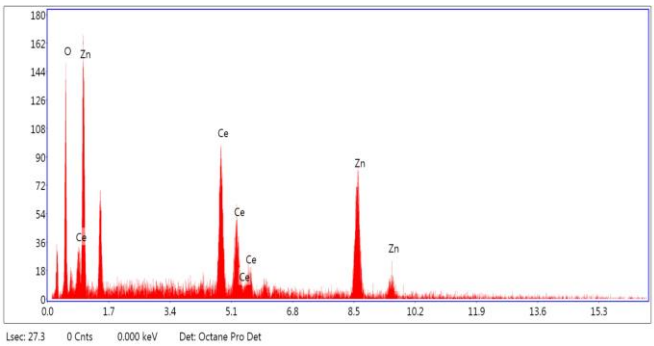

Figure 4b. EDAX analysis of CeO_2 -ZnO composite

3.3 SEM Analysis

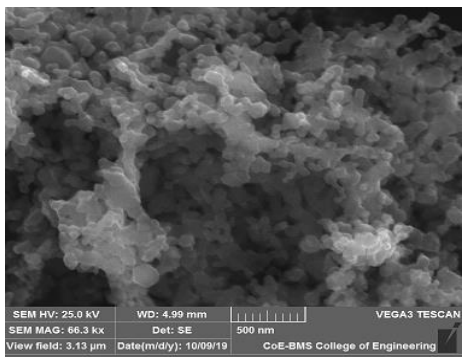

Figure 5a. SEM image of pure ZnO nanoparticles

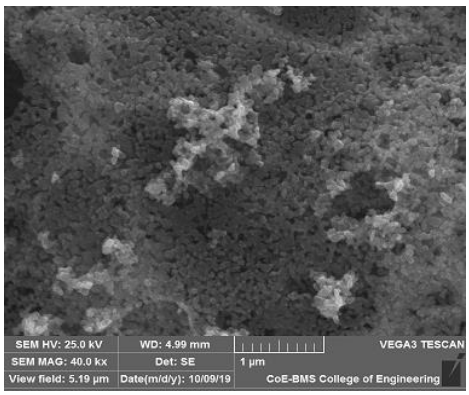

Figure 5b. SEM image of CeO_2 -ZnO composite

Figure 5a and 5b exhibit the SEM images of the ZnO nanoparticles (with 66.3kX magnification) and CeO_2-ZnO composite (with 40kX magnification) respectively. The ZnO nanoparticles were found to be roughly spherical in shape, agglomerated and uniform distribution of particles was observed from the SEM image analysis. The CeO_2-ZnO composites were seen more agglomerated when compared to the pure ZnO nanoparticles, roughly spherical in shape.

3.4 I-V Characterization:

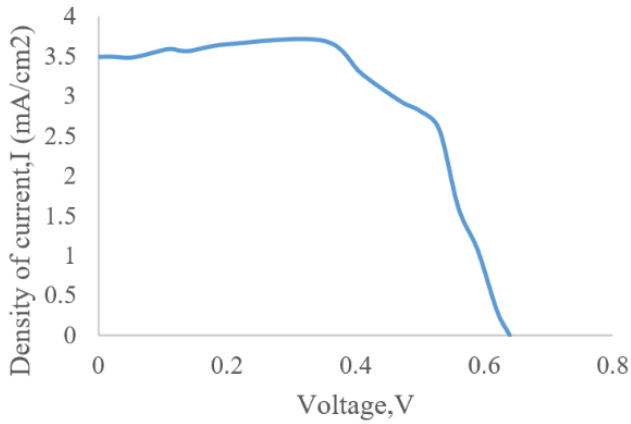

Figure 6a. Current-Voltage characteristics of the DSSC fabricated with pure ZnO nanoparticles

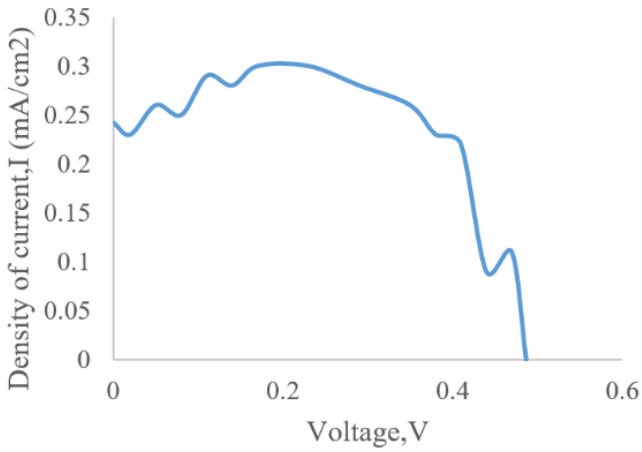

Figure 6b. Current-Voltage characteristics of the DSSC fabricated with CeO_2 – ZnO composite

Figures 6a and 6b represent the I-V (current-voltage) characteristics of the DSSC fabricated using ZnO nano particles and CeO_2-ZnO composite as the photoanodes, respectively. From Figure 6a we can infer that the DSSC fabricated using ZnO nanoparticles as photoanode is conductive in nature whereas from Figure 6b we can deduce that the DSSC fabricated using CeO_2-ZnO composite is having a low conductivity.

The V_{oc} value of the DSSC fabricated with ZnO nanoparticles was found to be 0.64 V which is a higher value than the open circuit voltage values testified by Liu et al. and Suliman et al. [3,4]. Liu et al have reported the synthesis of ZnO nanoparticles utilizing hydrolyzation method whereas Suliman et al have synthesized the ZnO nanoparticles by hydrothermal method. Liu et al. [3] have sensitized the DSSC using both N3 and N719 dyes whereas Suliman et al. [4] have

incorporated N719 dye for the sensitization of the DSSC fabricated in their work. However, the open circuit voltage values obtained by the DSSC fabricated using CeO_2-ZnO composite in the present work was found to be 0.48V which is a lower value when compared with the open circuit voltage of 0.573V reported by Suliman et al. [4].

The Isc value of the DSSC fabricated with ZnO nanoparticles was determined as 3.485 mA/cm^2 which is a higher value than the current density values reported by Liu et al. [3] Suliman et al. [4] Giannouli et al. [8] but slightly lower than the current density values reported by Rani et al. [6]. Rani et al have utilized the ZnO powders of pH 9 synthesized via solgel route in their work. However, the short circuit current density values are lower for the DSSC fabricated using CeO_2-ZnO composite as the photoanode.

An efficiency of 1.71% was achieved using ZnO nanoparticles as photoanode for the fabrication of DSSC which is a very promising higher value than the efficiencies reported by Liu et al. [3], Suliman et al. [4], Giannouli et al. [6] and Rani et al. [8]. But the efficiency achieved using CeO_2-ZnO composite as the photoanode of DSSC was 0.10% which is an exceptionally low power conversion efficiency value. The reduction in Isc and power conversion efficiency might have resulted because of more aggregated CeO_2-ZnO composite which may have caused resistance for the mobility of electrons. The lower efficiency might have also resulted because of poor dye loading on the photoanode coated with CeO_2 -ZnO composite which would have impeded the dye sensitization process due to the low surface area.

From Table 1, it can be observed that the ZnO nano particles based DSSC has shown better performance when compared to the CeO_2-ZnO composite based DSSC with Voc=0.64V, Isc=3.485 mA/cm^2, FF=76.51% and Efficiency=1.71%. The CeO_2 -ZnO based DSSC has exhibited a Voc value of 0.48 V with an extremely low power conversion efficiency of 0.1%.The drastic decrease in the photovoltaic performance of CeO_2-ZnO composite based DSSC may be due to an increase in the number of oxygen vacancies caused due to the reduction of cerium particles which might have resulted in the inhibition of electron transfer and hence resulted in lower power conversion efficiency.

Table 1. I-V parameters of the DSSC's fabricated with ZnO nano particles and CeO_2 -ZnO composite

Photoanode	Isc (mA/cm^2)	Voc (V)	FF (%)	PCE (%)
ZnO	3.485	0.64	76.51	1.71
CeO_2-ZnO	0.243	0.48	85.43	0.10

3.5 Cyclic Voltammetry

Cyclic Voltammetry analysis of pure ZnO nanoparticles and CeO_2- ZnO composite are presented in the following Figures 7a and 7b, respectively.

Electrochemical detection of adrenaline (AD) by employing a working electrode made of carbon paste, was studied by cyclic voltammetry (CV) technique. Figure 7a exhibits the cyclic voltammetry analysis of 1X10^{-3} M AD at bare as well as ZnO nanoparticle modified working electrode of carbon paste at a scan rate of 100 mV/s. A rise in peak current at ZnO nanoparticles modified electrode of carbon paste was observed as an electrochemical response of adrenaline (AD). The only Zinc Oxide nanoparticle plays important role in the sensor property with and without doped metal ions. But in the presence of composite materials it has shown better property when compared to bare ZnO nanoparticles. The modified electrode of carbon paste has exhibited a rise in current with a reduced peak potential difference. In Figure 7a, the solid line indicates the rise in redox peak current and a formation of a pair of redox waves of AD can be observed at modified carbon paste electrode prepared using ZnO nanoparticle. An insignificant shift in the peak potential was detected which is the distinctive of quasi reversible nature. Enhancement in peak current was noticed at modified carbon paste electrode providing high surface area of the ZnO nanoparticle which increased the electrode contacting area of adrenaline and its electrochemistry of reaction product.

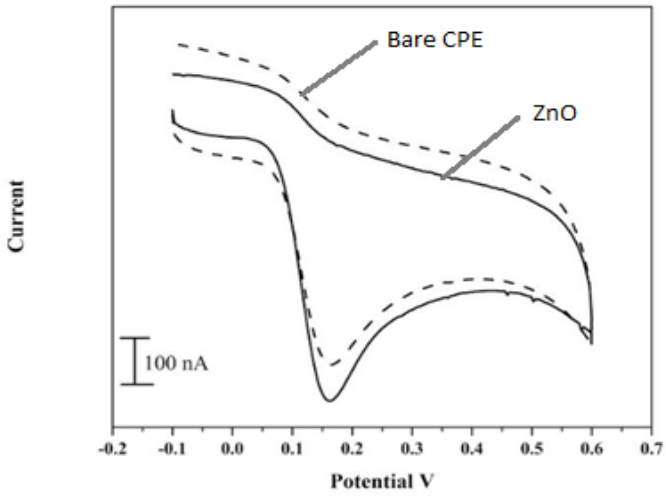

Figure 7a. Cyclic Voltammetry of adrenaline response of carbon paste electrode (CPE) with and without pure ZnO nanoparticles

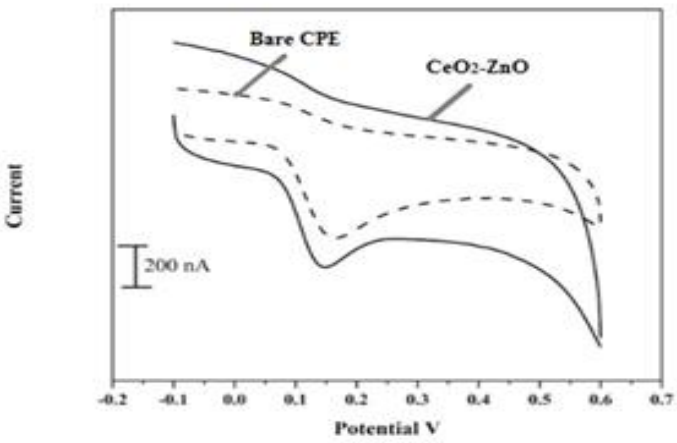

Figure 7b. Cyclic Voltammetry of adrenaline response of carbon paste electrode (CPE) with and without CeO_2-ZnO composite.

Figure 7b demonstrates the cyclic voltammetry analysis of 1X10^{-3} M AD at bare and cerium oxide- ZnO composite modified electrode of carbon paste at 100 mV/s of scan rate. An enhance in peak current at cerium oxide-ZnO composite modified carbon paste electrode was observed which is the electrochemical response of adrenaline. The integrated Zinc plays a vital role in the sensor property with Cerium nanoparticles. The modified carbon paste electrode shows

sensor property and it can act as electro catalyst. In Figure 7b, the thick solid line specifies a rise in redox peak current and a pair of redox waves of adrenaline can be observed at cerium oxide-ZnO composite modified carbon paste electrode. A trivial shift in the peak potential was noted. Rise in peak current was detected at modified carbon paste electrode prepared from cerium oxide-ZnO composite providing high surface area which increased the electrode contacting area of adrenaline and its electrochemistry of reaction product.

Integrating the zinc oxide nano particles with cerium oxide nano particles reduces its band width from 3.3 eV to 2.4eV. Since DSSC necessitates a wide band gap semiconductor photoanode, a reduction in power conversion efficiency has been observed for the cerium oxide-ZnO composite based cell when compared to the efficiency of pure zinc oxide photoanode cell. On the other hand, combining the zinc oxide nano particles with cerium oxide nano particles have increased the surface to volume ratio of the nano particles which facilitates in enhancing the sensor properties. Hence the cerium oxide-ZnO composite has exhibited better sensing property for the determination of Adrenaline when compared to pure Zinc oxide nano particles.

4. CONCLUSIONS

DSSC'S were fabricated employing pure ZnO nanoparticles and CeO_2-ZnO composite as the photoanodes. The performance of DSSC's were studied and compared under the solar simulator of incident power 100 mW/cm^2. The DSSC fabricated using pure ZnO nano particles showed a higher conductivity and power conversion efficiency when compared to the DSSC fabricated using CeO_2-ZnO composite. With cyclic voltammetry tests, the cerium oxide-ZnO composite showed a better sensor property for the electrochemical detection of adrenaline. Incorporation of cerium oxide nanoparticles with ZnO nanoparticles has resulted in the reduction in photovoltaic properties due to drop in band width. An increase in surface to volume ratio for the CeO_2-ZnO composite has been observed which has favored the electrochemical determination of adrenaline.

ACKNOWLEDGEMENT

This work is supported by IIChE, Bengaluru Regional Centre (BRC). The authors express sincere thanks to Mr.Santosh Narendiran , SSN college of Engineering, Chennai, Tamilnadu for valuable discussions.

REFERENCES

[1] Zhang, Q., Dandeneau, C. S., Zhou, X., & Cao, G. (2009). ZnO nanostructures for dye-sensitized solar cells. *Advanced Materials, 21*(41), 4087-4108.

[2] Grätzel, M. (2003). Dye-sensitized solar cells. *Journal of photochemistry and photobiology C: Photochemistry Reviews*, *4*(2), 145-153.

[3] Liu, Z., Liu, C., Ya, J., & Lei, E. (2010). Preparation of ZnO nanoparticles and characteristics of dye-sensitized solar cells based on nanoparticles film. *Solid State Sciences*, *12*(1), 111-114.

[4] Suliman, A. E., Tang, Y., & Xu, L. (2007). Preparation of ZnO nanoparticles and nanosheets and their application to dye-sensitized solar cells. *Solar Energy Materials and Solar Cells*, *91*(18), 1658-1662.

[5] Leonat, L., Sbarcea, G., & Branzoi, I. V. (2013). Cyclic voltammetry for energy levels estimation of organic materials. *UPB Sci Bull Ser B*, *75*, 111-118.

[6] Rani, S., Suri, P., Shishodia, P. K., & Mehra, R. M. (2008). Synthesis of nanocrystalline ZnO powder via sol–gel route for dye-sensitized solar cells. *Solar Energy Materials and Solar Cells*, *92*(12), 1639-1645.

[7] Karimi-Maleh, H., Rostami, S., Gupta, V. K., & Fouladgar, M. (2015). Evaluation of ZnO nanoparticle ionic liquid composite as a voltammetric sensing of isoprenaline in the presence of aspirin for liquid phase determination. *Journal of Molecular Liquids*, *201*, 102-107.

[8] Giannouli, M. (2013). Nanostructured ZnO, TiO2, and composite ZnO/TiO2 films for application in dye-sensitized solar cells. *International Journal of Photoenergy*, *2013*.

[9] Madhuchandra, H. D., & Swamy, B. K. (2019). Poly (vanillin) modified carbon paste electrode for the determination of adrenaline: A voltammetric study, Materials Science for Energy Technologies, 2(3), 697-702.

[10] Liu, X., Luo, L., Ding, Y., Wu, Q., Wei, Y., & Ye, D. (2012). A highly sensitive method for determination of guanine, adenine and epinephrine using poly-melamine film modified glassy carbon electrode. *Journal of Electroanalytical Chemistry*, *675*, 47-53.

[11] Corona-Avendaño, S., Alarcón-Angeles, G., Ramírez-Silva, M. T., Rosquete-Pina, G., Romero-Romo, M., & Palomar-Pardavé, M. (2007). On the electrochemistry of dopamine in aqueous solution. Part I: The role of [SDS] on the voltammetric behavior of dopamine on a carbon paste electrode. *Journal of Electroanalytical Chemistry*, *609*(1), 17-26.

[12] Harisha, K. V., Swamy, B. K., Jayadevappa, H., & Ganesh, P. S. (2016). Electrochemical sensor for the determination of adrenaline in presence of acetaminophen at poly (alanine) modified carbon paste electrode: a cyclic voltammetric study. *J. Biosens. Bioelectron.*, *7*, 1-6.

[13] Ganesh, P. S., & Swamy, B. E. K. (2016). Voltammetric investigation of catechol and hydroquinone at Triton X-100 modified carbon paste electrode. *Anal. Bioanal. Electrochem.*, *8*(5), 615-628.

[14] Venkatesham, V., Madhu, G. M., Satyanarayana, S. V., & Preetham, H. S. (2013). Adsorption of lead on gel combustion derived nano ZnO. *Procedia Engineering*, *51*, 308-313.

[15] Govindaraj, R., Santhosh, N., Pandian, M. S., Ramasamy, P., & Sumita, M. (2018). Fabrication of stable dye-sensitized solar cell with hydrothermally synthesized titanium dioxide nanorods as a photoanode material. *Journal of Materials Science: Materials in Electronics*, *29*(5), 3736-3743.

[16] Govindaraj, R., Santhosh, N., Pandian, M. S., & Ramasamy, P. (2018). Preparation of titanium dioxide nanorods/nanoparticles via one-step hydrothermal method and their influence as a photoanode material in nanocrystalline dye-sensitized solar cell. *Applied Surface Science*, *449*, 166-173.

[17] Reddy, S., Swamy, B. K., & Jayadevappa, H. (2012). CuO nanoparticle sensor for the electrochemical determination of dopamine. *Electrochimica Acta*, *61*, 78-86.

[18] Raoufi, D., & Raoufi, T. (2009). The effect of heat treatment on the physical properties of sol–gel derived ZnO thin films. *Applied surface science*, *255*(11), 5812-5817.

[19] Sani, Z. K., Ghodsi, F. E., & Mazloom, J. (2017). Photoluminescence and electrochemical properties of transparent CeO2–ZnO nanocomposite thin films prepared by Pechini method. Applied Physics A, 123(2), 121.

[20] Sowmya, S. R., Madhu, G.M., & Hashir, M. (2018, February). Studies on Nano-Engineered TiO2 Photo Catalyst for Effective Degradation of Dye. In IOP Conference Series: Materials Science and Engineering (Vol. 310, No. 1, p. 012026). IOP Publishing.