Enhancement of the performance of ZnO based natural dye sensitized solar cells via PVA morphology controlled nanorods

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Abstract. ZnO nanoparticles were synthesized via low temperature hydrothermal synthesis procedures at 90 °C using zinc nitrate hexahydrate as the zinc oxide precursors and hexamethyleneamine as the precipitating agent. The structural, surface morphology and optical studies of the hydrothermally synthesized ZnO nanoparticles revealed that the synthesized products were nano-rods, grown in very high-density with well-crystalline wurtzite hexagonal phase and good optical properties. Polyvinyl alcohol (PVA) was used as surfactant to modify the surface features of the ZnO nanorods. The ZnO nano-rods were employed as photo-anode for dye sensitized solar cell (DSSC) and were sensitized by natural dye extracted from Baphia nitida plant. The photovoltaic characteristics of the cell such as the short circuit current, open circuit voltage as well as the shunt and series resistances of the cell were studied. The incident photon to current conversion efficiency was also studied. The study revealed that the PVA improved the overall photo-conversion efficiency of the DSSC.

Keywords: ZnO, DSSC, Baphia nitida, efficiency, PVA

1. Introduction

Global population is continuously on the increase. Consequently, industrial development and urbanization are posing great challenge in meeting the rising energy demand. This will be highly problematic in the near future. Living standards in various parts of the world and the world's population are increasing proportionately with the rate at which the world consumes fossil fuels. Unfortunately, the fossil fuel reserves such as coal, oil and gas which has been the major sources of global energy supply over the years are inadequate and are quickly depleting [1]. Apart from the
famously known negative environmental impacts of the fossil fuels, it has been empirically estimated that if the world continues to consume fossil fuels at the rates which they were consumed in 2006, then the reserves of oil, coal and gas will approximately last for just a further 35, 107 and 37 years, respectively [2]. Renewable energy resources have thus been widely accepted as best possible alternative to fossil fuel. Solar energy for instance can easily be converted to electrical energy. It has several advantages such as environmental friendliness, availability, accessibility, cheap resources, no moving parts, very high pay pack at long run, remote applications etc. The major issue with this technology is the cost per unit watt of energy generation as compared to the conventional power supply. Due to the high cost of fabrication of the popular silicon solar cells, researchers are recently focused on new innovations to fabricate cheaper and more reliable environmentally friendly solar cells. Dye sensitized solar cell (DSSC) is among such inventions. A DSSC is a photo-electrochemical device which converts the visible portion of the electromagnetic spectrum into electricity without net chemical transformation within the cell. Since the invention of the DSSC by O’Regan and Gratzel [3], several progresses have been made on the improvement of the various components of the DSSCs for better efficiency and cost effectiveness. Major components of the photo-electrochemical cell include the photoanode (working electrode) which consists of wide band gap nanocrystalline metallic oxide semiconductor deposited on a transparent conducting oxide (TCO) substrate; the photosensitizer which absorbs the light energy and injects electrons into the photoanode; the redox electrolyte couple which replenishes electrons ejected by the photosensitizer and the counter electrode coated with a convenient catalyst such as carbon or platinum paste to regenerate the redox couple. Zinc oxide (ZnO) is one of the widely investigated nanocrystalline metallic oxide semiconductor used as the photoanode in DSSC after titanium dioxide (TiO2). It has wide-band-gap energy (3.3 eV) [4] [5] [6] [7] [8]. ZnO normally forms in the hexagonal wurtzite crystal structure with lattice constants of a = 3.25 Å and c = 5.12 Å [9]. Its applications include areas such as transparent electrodes, solar cells, gas sensors and surface acoustic wave devices [10]. Although majority of reported works on DSSC are based on TiO2 porous thin films due to their better efficiencies, various ZnO nanostructures are however recently being explored due to their similar lowest conduction band edge and higher electronic mobility. Although the reported efficiencies of ZnO-based DSSCs are still low compared to the conventional TiO2, it is widely believed that ZnO is highly promising due to its cost, ease of crystallization and anisotropic growth and other advantages over TiO2 [11] [12] [13]. These advantages include higher exciton binding energy (60 MeV) compared to TiO2 (4 MeV), and higher electron mobility (200 cm² V⁻¹ s⁻¹) as against that of TiO2 (30 cm² V⁻¹ s⁻¹) [13]. In addition, ZnO is relatively cheaper than TiO2 [14]. Surfactants such as PVA can be used to achieve higher and relatively steady UV sensitivity in nanostructured ZnO materials. The polymer matrix is capable of modifying the optical and electrical properties of ZnO [15] [16] [17]. This may also lead to modification of the morphology as well as the crystal structure of the nanoparticles [18] [19]. Camwood dye is a red natural dye. It is obtained from the plant Baphia nitida. The plant is predominantly found within the coastal regions of West Africa [20]. It is known to mitigate against different microbial diseases such as ringworm, stiff joints, sprains and rheumatic pains as well as the treatment of constipation, skin and veneral diseases [21] [22]. The dye is also traditionally used by the natives for painting and beatification purposes.

In this report, we employed the relatively low-cost hydrothermal synthesis methods to synthesize highly crystalline hexagonal wurtzite ZnO nanorods for use as photoanode in the fabrication of environmentally friendly dye sensitized solar cell. Polyvinyl alcohol (PVA) was used as surfactant in order to modify the surface features of the ZnO nanorods. Rarely explored natural red dye extract from Baphia nitida was used as dye photosensitizer for the DSSC. The effects of the PVA on the ZnO nanorods as well as its effects on the photovoltaic performances of the fabricated ZnO-based DSSCs were studied.
2. Experimental details

2.1. Deposition of the Photoanode
The deposition of the ZnO photo anodes for the DSSC was performed using zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O) and hexamethylenetetramine (HMTA) as the main precursors. Zinc acetate (Zn(CH$_3$COOH)$_2$·2H$_2$O) and ethanol were used to prepare the seed solution prior to the hydrothermal synthesis. All the chemicals were analytical grade and required no further purifications before use. Initially, fluorine doped tin oxide (FTO) substrates were subjected to ultra-sonic cleansing with acetone, ethanol and distilled water respectively for 600 seconds each. They were dried in moderately hot (60 °C) oven. The seed solution was prepared according to the method described elsewhere [23]. Briefly, 0.1 M ethanolic sol gel was prepared and stirred for 1 hour at room temperature. Spin coating machine adjusted to 2000 rev/min was used to coat the substrates with the seed layers. The ZnO seed-coated glass was heated in the oven at 100 °C for 15 minutes. The procedure was repeated for five times in order to obtain a reasonably thick seed layer. The seed layer was then finally annealed at 350 °C to evaporate the organic solvent from the ZnO films. The seed layers served as nucleation centers on the surface of the substrate to induce the growth of the ZnO nano rods [24]. To prepare the nanocrystalline ZnO photo anode by hydrothermal method, 0.02 M solution of Zn(NO$_3$)$_2$.6H$_2$O and 0.2 M HMT were mixed and was stirred continuously for 2 hours at room temperature (~25 °C). The solution was transferred into and tightly secured in a teflon lined steel autoclave. The autoclave was subsequently placed into an oven at 95 °C and left to deposit for 15 hours. The autoclave was then removed and allowed to gradually cool to room temperature before removing the substrate and rinsing with distilled water. The deposited ZnO nano rods were found to be strongly adhered to the FTO substrate. Similar procedures were followed in order to prepare the PVA-capped ZnO nanoparticles. However, the capping solution was initially prepared by dissolving 9.0 g of PVA in 450 ml of water and vigorously stirred without heating until a clear homogeneous solution is formed. 20 ml of this solution was added to the zinc acetate and HMT solution. The ZnO and ZnO:PVA nano rods were annealed at 450 °C for 60 minutes. Before loading the photoanodes with dye, after annealing, they were characterized for UV-Vis absorbance, scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2.2. Extraction of the natural dye and staining of the ZnO photo anodes
Sample of Baphia nitida obtained from the stem of the tree was dried. The sample was pulverized to obtain large surface area for easy extraction. Sohxlet apparatus was used in the extraction process. 10 g of the pulverized sample was dissolved in 50 ml ethanol solution and refluxed at 80 °C for about 3 hours. The resulting red solution of the camwood dye was filtered to obtain a homogeneous solution. The already prepared ZnO and the PVA-capped ZnO photo anodes were dye-sensitized by immersing it completely into the dye solution and allowed to stand for 24 hour for effective dye loading.

2.3. Fabrication of the solar cell
In order to fabricate the ZnO-based dye sensitized solar cells, liquid redox electrolyte consisting of 0.1 M Lithium iodide (LiI) and 0.05 M iodine (I$_2$), dissolved in acetonitrile was prepared. The counter electrode was prepared by applying carbon coating on an FTO of the same dimension with the photo anode substrate. The carbon coated electrode served as catalyst for the tri-iodide to iodide generation reaction in the cell [25]. The DSSC was fabricated by using the already prepared I$_3$~/I$^{-}$ redox couple electrolyte with the carbonized FTO glass as the counter-electrode electrode. Binder clips were used to gently hold the plates together at two opposite edges. Provisions were made for external electrical contacts. Few drops of the iodide electrolyte solution was allowed to percolate between the electrodes by capillary action before measuring the current–voltage ($I$-$V$) characteristics of the fabricated cells in order to study the photovoltaic conversion parameters.
3. Results and discussions

3.1. Structural studies

3.1.1. XRD analysis. The x-ray diffractometry analysis was performed on the ZnO thin films deposited on microscopic glass slides after annealing at 450 °C. The XRD patterns recorded for the nanocrystalline ZnO films grown by hydrothermal synthesis technique is shown in figure 1. The diffraction patterns were obtained with 2θ from 20° to 90°. The results of the analysis revealed that the deposited ZnO thin films are polycrystalline with hexagonal wurtzite phase and a preferential orientation along the c-axis. This is in agreement with the JCPDF card no 00-036-1451. The observable peaks occurred at 2θ angles of 31.77°, 34.42°, 36.33°, 47.58°, 63.03° and 72.57° corresponding to (100), (002), (101), (102), (103) and (004) reflection planes respectively (JCPDF 00-036-1451). However, it shows high preferential orientation in (0 0 2) direction with a uniquely defined peak at 34.42°. The prominent 002 peak is an indication of highly crystalline films. However, the minor peaks were present due to polycrystalline nature of the ZnO thin films [26] [27]. The preferred orientation of crystallites in all cases are in direction perpendicular to the sample surface. By comparing the XRD patterns of the as deposited ZnO and PVA capped ZnO nanoparticles, it was visibly clear that the polymer matrix did not introduce different patterns to the as-deposited ZnO patterns. This is an indication that the PVA did not change the crystalline structure of the ZnO nanoparticle.

![Figure 1: XRD patterns of the nanocrystalline ZnO nano rods](image)

The crystallite size, \( D \) was calculated using the Debye Scherrers’ formula [28],
\[
D = \frac{0.94 \lambda}{\beta \cos \theta}
\]
where \( \lambda \) is the wavelength of the XRD target source (1.54060 Å), 0.94 is a constant (also known as the shape factor), \( \beta \) is the full-width at half-maximum (FWHM) and \( \theta \) is the diffraction angle. Calculations revealed that the average crystallize sizes of the as-deposited ZnO nanostructures was approximately 10.34 nm while the crystallize sizes of the PVA-capped ZnO slightly decreased to about 10.14 nm. The dislocation densities (\( \delta \)) of both nanoparticles were determined using the relationship
\[
\delta = \frac{1}{D^2}
\]
The dislocation density may be used to ascertain the level of defects in the deposited ZnO nanostructures [29]. The dislocation density for the as-deposited and the PVA-capped ZnO nanostructures were estimated as \(9.4 \times 10^{11}\) cm\(^{-2}\) and \(9.7 \times 10^{11}\) cm\(^{-2}\) respectively. The slightly decreased dislocation density and larger crystallite size of the as deposited ZnO thin films is an indication that it was slightly better crystallized than the PVA-capped ZnO which has a dislocation density of \(9.4 \times 10^{11}\) cm\(^{-2}\) and crystallite size of 10.34 nm [30]. The reason for better crystallization and improved grain structure of the as-deposited sample of the ZnO nanoparticles than the PVA-capped sample may be explained as follows. During the hydrothermal growth mechanism on the seeded substrate, the seed layer acted as nucleation points for the growth of the nanoparticles which are stacked on one another to show a strong c-axis of preferred orientation. However, the addition of the PVA surfactant may be seen to have introduced a slight distortion in the growth direction [31].

The dislocation density and crystallite size of the as deposited ZnO thin films is an indication that it was slightly better crystallized than the PVA-capped ZnO which has a dislocation density of \(9.4 \times 10^{11}\) cm\(^{-2}\) and crystallite size of 10.34 nm [30]. The reason for better crystallization and improved grain structure of the as-deposited sample of the ZnO nanoparticles than the PVA-capped sample may be explained as follows. During the hydrothermal growth mechanism on the seeded substrate, the seed layer acted as nucleation points for the growth of the nanoparticles which are stacked on one another to show a strong c-axis of preferred orientation. However, the addition of the PVA surfactant may be seen to have introduced a slight distortion in the growth direction [31].

The lattice constants were determined from the most prominent peak (002) by the following equations [32].

\[
a = \left(\frac{1}{2} c^2\right)^{1/2}; \quad c = \lambda \left[\sin(\theta)\right]^{-1/3}.
\]

In addition, the corresponding inter-planar spacing \((d\text{ value})\) based on the hexagonal structure was estimated using the Miller indices \((h k l)\) and the lattice constants \((a\text{ and } c)\) in conjunction with the equation,

\[
d_{hkl} = \left(\frac{4(h^2 +hk +k^2)}{3a^2} + \frac{l^2}{c^2}\right)^{1/2}.
\]

Using the most prominent peak, the lattice constants were estimated as \(c = 5.2052\) Å and \(a = 3.0052\) for the as-deposited ZnO nanostructures while \(c = 5.1946\) Å and \(a = 2.9991\) Å for the PVA-capped ZnO sample. Both samples has ratio \(c/a = 1.7321\). The observed figure fairly agrees with some published data [32] [33] [34]. The d-spacing were estimated as 2.6026 Å and 2.5973 Å respectively for the as grown and the PVA-capped ZnO thin films. Table 1 shows the lattice parameters of the ZnO photoanodes.

**Table 1:** Miller Indices and lattice parameters of the ZnO grown by the two methods

| Sample   | 2 \(\theta\) (°) | \(h\ k\ l\) | \(a\) (Å) | \(c\) (Å) | \(c/a\) | \(d_{hkl}\) (Å) | \(D\) (nm) | \(\delta\) cm\(^{-2}\) |
|----------|----------------|-------------|-----------|-----------|---------|----------------|-----------|---------------------|
| ZnO      | 34.44         | 0 0 2       | 3.0052    | 5.2052    | 1.7321  | 2.6026         | 10.34     | 9.4 x 10\(^{11}\) |
| ZnO:PVA  | 34.44         | 0 0 2       | 2.9991    | 5.1946    | 1.7321  | 2.5973         | 10.14     | 9.7 x 10\(^{11}\) |

3.1.2 Surface morphology study. The scanning electron microscope (SEM) images of the ZnO nanorods at two different magnifications are shown in figure 2. The surface of the thin films is almost homogeneous hexagonal nanorods oriented perpendicularly to the plane of the substrate which confirmed the XRD results. The seed layer induced the growth to vertical direction to the plane [23]. The ZnO also reveals porous structures which could be highly advantageous in providing maximum surface area for dye loading and photosensitization in the DSSC. The quantity of dye adsorption is defined by pore volume which is affected by the porosity of crystal structures [35]. In addition, vertically aligned ZnO nanorods arrays has been noted to be beneficial to the performance of devices like solar cells [36].
Although both the as-grown and the PVA-capped ZnO revealed hexagonal nanostructures, it can however be noted that the PVA actually modified the surfaces of the nanorods by introducing rough surfaces on the nanorods. The smooth surfaces observed from the as-deposited ZnO nanorods became extremely distorted, giving rise to irregularly shaped nanorods. Cracks and holes were observed in some of the nanoparticles while some particles appeared to broken into tiny fragments. The hexagonal structures could hardly be observed. This is likely because PVA molecules offer abundant active OH groups forming a metal ion-polymer complex by means of a kind of ligand reaction. These OH groups adsorb the metal cations in a specific pattern. The polymer skeleton eventually limits the growth in a specific shape of the lattice [16]. The average diameter of the PVA-modified ZnO nanoparticles were larger than the as deposited sample. While the as-deposited ZnO has average particle sizes between 50 nm and 200 nm, the average range of the particle sizes of the PVA-capped ZnO increased to about between 150 nm and 900 nm. The nano-tips observed on the as-deposited nano-rods were also not seen on those nanoparticles capped with the PVA. The observed rough surfaces of the ZnO nanorods may be seen as advantageous property in DSSCs applications. This is because larger surface area will be available to the photosensitizing dye molecules to be easily loaded to the photoelectrodes. Also the increased diameter of the irregularly shaped nano-rod could also be advantageous as the nanoparticles will more likely offers direct transport pathways for photo-excited electrons. It was earlier reported [37] that the efficiency of DSSC fabricated using ZnO nano-tube increased as the diameter of the ZnO nanotubes increased.

3.2. Optical studies
3.2.1 Absorbance. The optical absorption of the ZnO nanorod photoanode for the fabrication of the dye sensitize solar cells were investigated using spectrophotometer within the wavelength range of 200 nm – 1100 nm of the electromagnetic spectrum at normal incident at room temperature. The optical absorbance data was used to determine the band gap energy of both the as deposited and the PVA capped ZnO nanostructures. Figure 3 (a, b) shows the plot of absorbance against the wavelength and the plot to determine the band gap energy of the ZnO. The PVA capped ZnO showed relatively higher absorbance than the as deposited ZnO thin films within the same range of the electromagnetic spectrum. The absorbance of the as-grown ZnO photo-anode decreased gradually from about 30% to about 15% in the visible region and further decreased to about 5% towards the near-infra-red region. However, the PVA-capped ZnO showed stronger absorbance of about 75% which decreased to about 25% in the visible region then further decreased to about 5% in the near-infra-red region of the electromagnetic spectrum. The higher absorbance of the PVA-capped ZnO is an indication that the modified nanoparticles could better be applied as a pho-anode for dye sensitized solar cell applications.
3.2.2. Band gap energy. In order to estimate the optical energy band gap for the ZnO photo-anodes, the absorbance data in the wavelength range between 350 nm and 800 nm covering the visible region of the electromagnetic spectrum was used to estimate the absorption coefficient ($\alpha$). The photon energy ($h\nu$) was also calculated. The graph of the absorption coefficient with respect to the photon energy was plotted according to the Tauc’s relationship [38],

$$\alpha h\nu = A (h\nu - E_g)^n$$  

(4.10)

where $A$ is a constant which depends on the effective masses of the electrons and holes in the semiconductor material [39]. $n$ is $\frac{1}{2}$ for direct transition in polycrystalline thin films.

The energy band gap was extrapolated using the band gap plots (see figure 3b) The plots show that there was no significant alteration of the band gap energy as a result of the capping agent. The band gap energy is approximately 3.25 eV in each case which reasonably agrees with some published data for ZnO nanostructures [32] [34] [40] [41] [42]. The introduction of the polyvinyl alcohol to the ZnO does not affect the gap between bottom of the conduction band and top of the valence band of the nanoparticles.

![Figure 3: (a) Plots of the absorbance against wavelength and (b) plots to obtain the energy band gaps of the as-grown and the PVA-capped ZnO photoelectrodes.](image)

3.2.3. Photovoltaic performance of the cells. Figure 4(a) shows the absorption spectrum of the *Baphia nitida* natural dye extract. The UV-Vis absorption spectra were studied using spectrophotometer in the wavelength region between 300 nm and 1100 nm. The graph shows that the *Baphia nitida* natural dye extract absorbs strongly at the visible spectrum with peak absorptions at wavelengths of 479 nm and 507 nm respectively. However, the dye shows very low absorption beyond 550 nm and the near infrared regions of the electromagnetic spectrum. Good absorption in the visible region of the electromagnetic spectrum is necessary for efficient light to electricity conversion.

The plots of the current density against the voltage of the DSSCs fabricated using the ZnO and ZnO:PVA photoanodes sensitized with the *Baphia nitida* (camwood) natural dye extract are shown in figure 4(b). The curves were subsequently used to determine the short circuit current ($I_{sc}$), open circuit voltage ($V_{oc}$), maximum power point ($P_{mp}$), current at the maximum power point ($I_{mp}$) and voltage at the maximum power point ($V_{mp}$) in each case. These values were then used to calculate the fill factor ($FF$) and the overall light to electricity conversion efficiency ($\eta$) of the solar cell. The inverse of the slopes near the short circuit current and open circuit voltage were used to estimate the nature of the shunt and series resistances respectively.
Figure 4: (a) Absorption spectrum of the Baphia nitida natural dye extract, (b) the plot of the current density against the voltage of the DSSCs fabricated using the as-grown ZnO and the PVA-capped ZnO as the photo-electrodes

The fill factor (FF) and the overall power conversion efficiency (η) were respectively calculated using the following mathematical relationships.

\[ FF = \frac{I_{MP} \cdot V_{MP}}{I_{sc} \cdot V_{oc}} = \frac{P_{MP}}{I_{sc} \cdot V_{oc}} \]  
\[ \eta = \frac{P_{out}}{P_{in}} = \frac{I_{sc} \times V_{oc} \times FF}{E \times A_{c}} \]

where \( E \) stands for the intensity of the solar radiation and \( A_{c} \) is the effective area of the solar cell exposed to the light.

The open circuit voltage for DSSCs fabricated with the as-deposited and the PVA-capped ZnO photo-anodes showed no significant difference. The two samples however revealed open circuit voltage values of 336.5 mV and 328.2 mV respectively. The DSSC fabricated using the as deposited ZnO photo-electrode has a slightly lower fill factor (0.51) than the fill factor (0.56) of the DSSC fabricated using PVA capped ZnO. The overall power-conversion efficiency of the DSSC fabricated using the PVA capped ZnO photo-anode displayed an enhanced efficiency of 1.2% whereas an efficiency of 0.7% was estimated for the DSSC fabricated using the as-deposited ZnO photo-electrode.

This can be attributed to the modification of the surface morphology due to the introduction of the PVA surfactant which slightly reduced the crystallite sizes, improved the absorbance of the ZnO nanoparticles and also enhanced the dye loading ability of the photo-electrode. The resultant effect is increase in injection yields and collection efficiencies of photo-generated carriers from photo-sensitizer to the conduction band of the PVA capped ZnO photo-anode. The presence of the PVA may also be seen to inhibit the agglomeration of the ZnO nanoparticles during the process of calcination. This helps to improve both the specific surface area for enhanced dye loading and the porosity for easy percolation of the electrolyte solution [11]. Consequently, there was an enhanced photo-current density for the PVA capped ZnO DSSC as compared with DSSC fabricated using the as-grown ZnO photo-anode. Table 2 gives a summary of the photo-conversion parameters.
Table 2: Photovoltaic parameters for the DSSCs fabricated using the different photoanodes

| Parameter | $V_{oc}$ (mV) | $I_{sc}$ (mA) | $J_{sc}$ (mA cm$^{-2}$) | $R_{sh}$ (Ω) | $R_{s}$ (Ω) | FF | η (%) |
|-----------|---------------|---------------|----------------------|-------------|-------------|----|------|
| ZnO/As-grown | 336.5 | 7.6 | 1.81 | 193.9 | 9.8 | 0.51 | 0.65 |
| ZnO/PVA | 328.2 | 9.7 | 2.31 | 115.4 | 7.0 | 0.56 | 1.17 |

3. Conclusions

Highly crystalline ZnO nanorods were synthesized via a low temperature hydrothermal synthesis technique. Modification of the properties of the thin films were done by the addition of polyvinyl alcohol as surfactant. The ZnO nanoparticles which were crystalized in hexagonal wurtzite structure and vertically aligned perpendicular to the plane of the substrate with nanorods of average diameter of 95 μm and length of 300 μm were sensitized with Baphia nitida natural dye extract and used to fabricate dye sensitized solar cells. The Baphia nitida plant showed a reasonably high absorbance in the visible spectrum. The overall photo-conversion efficiency of the DSSC fabricated using the PVA capped ZnO photo-anode displayed an enhanced efficiency of 1.2 % against 0.7% for the DSSC fabricated using the as-deposited ZnO photo-electrode. This was attributed to the modification of the surface morphology as a result of the introduction of the PVA surfactant, improving not only the absorbance of the ZnO nanoparticles but also enhanced the dye loading ability of the photo-electrode. Hence there was an increase in the injection yields and collection efficiencies of photo-generated carriers from photo-sensitizer to the conduction band of the PVA capped ZnO photo-anode as compared to the as grown ZnO photoanode used for the fabrication of the DSSC.

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