

The efficiency of ZnO / Platinum Octaethylporphyrin (PtOEP) Nanocomposite Photoanode at Dye-Sensitized Solar Cells

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Abstract:

In the present work, we have been studied the applications of ZnO /Platinum Octaethylporphyrin (PtOEP) Nanocomposites as Photoanodes for Dye-Sensitized Solar Cells (DSSC). The structural properties of ZnO:PtOEP Nanocomposites were examined by X-ray diffraction and Raman spectroscopy analysis which confirm the hexagonal wurtzite ZnO structure. Also, the simultaneous existence of PtOEP and ZnO in XRD and Raman mode was confirmed the formation of nanocomposite. Scanning Electron Microscopy (SEM) image of the surface morphology confirms the presence of PtOEP particle in the film. The variation in the weight ratios of ZnO:PtOEP is taken to optimize the performance of the DSSC. The photovoltaic and electrochemical impedance spectroscopy (EIS) data indicate that the optimum performance can be achieved at ZnO:PtOEP(1:0.009). Also, the (EIS) measurement for ZnO: PtOEP(1:0.009). photoanode shows displayed faster electron transport, significantly increased electron lifetime, and higher charge collection efficiency than those of pure ZnO.

Key words: PtOEP; Dye-sensitized solar cells (DSSC); hexagonal wurtzite; electrochemical impedance spectroscopy (EIS); electron lifetime

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1 **1. Introduction**

2 Dye-sensitized solar cells (DSSCs) or “Grätzel cell” have attracted significant research interest due to
3 their low-cost production, simple manufacturing process, flexibility, transparency, and good performance
4 under diffused light [1, 2, 3]. DSSCs become more, and more remarkable meanwhile an enormous variety of
5 dyes (i.e. dye; e.g. N719, N3 [4], or organic dyes by monolayer adsorption or quantum dots (e.g. CdS, CdSe
6 and PbS) and the also natural dyes [5]. Also, the photovoltaic performance of a DSSC essentially relies on
7 the performance of the photoanode, which plays a fundamental role in the performance of DSSC due to its
8 dye loading, electron transportation, and electron collection characteristics [6]. Wide bandgap
9 semiconductors like TiO₂, ZnO, Nb₂O₅, and SnO₂ [7-9] nanoparticles were used as an efficient photoanode.
10 Due to the small size of the nanoparticles, it can offer a large surface area and a comparatively high
11 absorbency. Several researches have been proposed to control the charge recombination in the DSSC using
12 doping of TiO₂ and ZnO with metal (Al, In, Bi, Cr, Ce, Mg, Au, Ag... etc.) [5, 6, 10, 11, 12]. Recently, new
13 composite systems from hybrid materials of organic materials and metal oxide semiconductors in a
14 nanometer scale have evolved as promising materials for DSSC. Due to the reduced probability of the
15 recombination reaction by void the direct contact between metal oxide semiconductors and the redox
16 electrolyte and reduced the recombination. Also, improved the charge separation and faster interfacial charge
17 transfer than that of the pure metal oxide semiconductors [13, 14, 15, 16, 17, 18]. As examples on the these
18 hybrid composite; polyaniline/ZnO [13], polypyrrole/ZnO [14], NiTPP/ZnO [15] PEDOTPSS/TiO₂ [16],
19 poly(N-vinylcarbazole)/TiO₂ [17] and TiO₂/polyisothianaphthene [18]. The porphyrin and its derivatives have
20 been integrated into of DSSC in several ways. One of the most important advantages of using porphyrin and
21 its derivatives are their redox properties, which aids for generating the porphyrin excited states that can be
22 favorable as excellent dyes for dye DSSCs [19, 20, 21]. According to the best of our knowledge, the
23 composite of ZnO/PtOEP as photoanode has been unexplored in DSSCs application. Therefore, the novel
24 synthesis of ZnO/PtOEP is expected to have significant potential as photoanode in DSSCs.

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26 **2. Experimental techniques**

27 **2.1. Preparation of photoelectrode**

28 PtOEP and ZnO nanoparticle were purchased from Aldrich and were used without further purification.
29 ZnO/PtOEP photoanodes have been prepared by conventional blade coating method. The blade coating paste
30 was consisting of 0.35 g ZnO nanoparticle (< 100 nm) and 2 ml ethanol (99.5%) along with various different
31 weight ratios (as 1:0.00, 1:0.003, 1:0.006, 1:0.009, 1:0.012 and 1:0.015). The solution has been mixed
32 vigorously using a homogenizer (Sonic VCX-130) at 60% amplitude, 1:3 pulse rates for 30 min. Before

1 coating, the prepared uniform paste was deposited on the pre-cleaned FTO substrates (~15 Ω /
2 square) using doctor blade method. The paste thus prepared was coated onto the FTO substrates using
3 polyimide tape as frame and spacer. We coated the layer four times for obtaining a thick, adherent layer
4 photoanode. All the samples were air dried at room temperature for one hour. The thickness of the film was
5 9~10 μm , measured by the surface profilometer (ULVAC alpha step-500). After coating, the films were
6 dried at 100 °C using a hot-plate for 10 min and compressed (Mini TEST Press-10) with 70 MPa
7 compressions at 60 °C for 1 min.

8 **2.2. Device fabrication**

9 The prepared photoanodes were immersed into an ethanol solution of the 0.5 mM N719 dye (Ruthenium-535
10 bis TBA, Solaronix). After 1 h the photoelectrodes were removed from the dye solution. The photoelectrodes
11 were then immersed two or three times inside the methanol solution along with slight shaking to remove the
12 extra loaded dye particles from the metal oxide nanoparticles. After cleaning by methanol, all the samples
13 were dried by nitrogen flow. Finally, the DSC was fabricated by using a Pt-coated glass as a counter
14 electrode, and by inserting a polymer film (Himilan, 50 μm) between the electrodes. The electrolyte
15 (Iodolyte AN 50, Solaronix) was inserted into space between two electrodes by capillary action using a glass
16 tube injector.

17 **2.3. Characterization**

18 Structural characterization was performed by XRD system (Rigaku RINT 2100 diffractometer) equipped
19 with Cu target. The Ni-filtered Cu $K\alpha$ radiation ($\lambda=1.5408 \text{ \AA}$) was used. The X-ray tube voltage and current
20 were 40 kV and 30 mA, respectively. The Raman shift of the thin films was investigated by Raman
21 Spectrometer (Jasco NRS-2100) at room temperature .with Ar and Kr laser lines operating at 514.5 nm it has
22 a spectral resolution of 1 cm^{-1} . The morphology of ZnO:(PtOEP) Photoanodes was observed using a
23 scanning electron microscopy (SEM, JSM-6510). The J/V characteristics of the devices were determined
24 under white light illumination using standard solar irradiation of 100 mW/cm^2 (AM 1.5G) with a JASCO
25 CEP-25BX spectrophotometer J/V measurement setup with a xenon lamp as the light source and a computer-
26 controlled voltage-current source meter (Keithley 238) at 25 °C. The impedance spectroscopy was measured
27 at room temperature in the air with the frequency range of 0.02 to 1000 KHz using an impedance analyzer
28 (Agilent 4284A) with a bias voltage of 0.6 V.

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1 3. Results and discussions

2 3.1. Structural studies

3 3.1.1. X-ray powder diffraction analysis

4 A typical XRD pattern of the pure ZnO and ZnO:PtOEP with different weight ratios are shown in **Fig 1**.
5 All of the diffraction peaks, which correspond to the planes (100), (002), (101), and (102) are perfectly
6 indexed to the hexagonal wurtzite ZnO structure (JCPDS 01-1136). The sharp and strong peaks indicate
7 good crystallization of the samples. The diffraction peaks for PtOEP were visible for the lower and higher
8 concentrations with a preferential orientation in the (001) direction [22, 23]. The peaks (001) and (002)
9 related to PtOEP become more intense as the proportion of PtOEP increases in the composite. A small right
10 shift has been observed for the positions of the all three diffraction peaks (100), (002), and (101) of wurtzite
11 structured ZnO, while the percentage of PtOEP has been increased. It means that the spacing between the
12 lattices planes corresponding to the peaks is changed [24]. Also, the increase of the intensities of the XRD
13 peaks with increasing concentrations indicates an improvement in the crystalline quality of the synthesized
14 samples. The crystallite sizes (D) have been estimated by applying the Scherrer formula [22]:

$$15 \quad D = \frac{K_S \lambda}{\beta \cos \theta} \quad (1)$$

16 Where, $K_S = 0.94$ is Scherrer's constant, λ is the X-ray wavelength of CuK α (0.15408 nm), θ is the Bragg's
17 angle and β is the Full Width at Half Maximum (FWMH) in radian. The results show that the average
18 crystallite size increases from 33.7 to 48.3 nm with increasing percentages of PtOEP in the ZnO layer
19 (see **Table 1**). X-ray profile analysis is generally used to estimate the average particle size. Particle size and
20 lattice strain are the two major quantities responsible for change in peak broadening in an X-ray diffraction
21 curve. Lattice strain is a measure of the distribution of lattice constants that arises from the crystal
22 imperfections, such as lattice dislocations. The Williamson-Hall (W-H) analysis of diffraction peaks is used
23 to estimate the crystallite size and lattice strain. Assuming that two terms (particle size and strain) contribute
24 to peak broadening, are independent of each other and hence the observed peak breadth can be written as the
25 sum of the particle size and strain as following equation((W-H) equation)[15]:

$$26 \quad \beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta \quad (2)$$

27 After fitting the data with a straight line to eqn. 2, the crystallite size and the strain ε has been calculated
28 from the intercept and slope of the linear fit respectively (figure not shown). The calculated particle sizes
29 from the W-H plot are from 38.2 to 54.5 nm with increasing percentages of PtOEP in the ZnO layer
30 (see **Table 1**). The crystallite size calculate from W-H analysis is slightly higher than that calculated from
31 the Scherrer formula and this is because of the removal of strain contribution to the FWHM in the XRD peak

1 by W-H analysis. Hence, the resultant peak width is little lower than the same considered in the Scherrer
2 formula. It is evident that the crystallite size increases and the lattice strain decreases with increasing PtOEP
3 content. Grain boundaries, sinter stresses, stacking faults and coherency stress are the possible sources for
4 development of strain in the ZnO host material. Moreover, the photoelectrode films were treated by hot-
5 compression that can be the reason for some crystal disorder and in turn reductions in the lattice strain [15].

6 7 **3.1.2. Raman study**

8 **Fig. 2** displays the Raman spectra of pure ZnO and ZnO:PtOEP with different weight ratios at the range
9 of 300-1000 cm^{-1} . These measurements confirmed the gradual increase of PtOEP content in the ZnO NPs.
10 Two sharp Raman peaks at about 338 and 438 cm^{-1} have been observed for ZnO film. Where the peak at 438
11 cm^{-1} represents the E_2^{high} vibration mode of wurtzite ZnO [25]. Also, all the samples show weak band around
12 438 cm^{-1} is related to the vibration of Zn and O atoms in the hexagonal phase formation. On the other hand,
13 the intensity of the peak at 438 cm^{-1} decreased with increasing concentration which corroborated with the
14 crystallinity behavior observed in XRD data. The presence of the E_2^{high} mode in all samples is the indication
15 of the hexagonal ZnO structure, with the XRD results [26] and the 338 cm^{-1} peak represents the $E_2^{high} - E_1^{low}$
16 vibration mode [26, 27]. For E_2^{high} vibrational peak intensity has been reduced by increasing percentages of
17 PtOEP in the ZnO samples. On the other hand, the $E_2^{high} - E_1^{low}$ peak intensity has been improved with the
18 increasing percentages of PtOEP in the ZnO samples. Nevertheless, Raman vibration modes centered at 677,
19 721, 766, 784 and 818 cm^{-1} with different intensities belong to PtOEP respectively. The composite formation
20 can be further confirmed by the simultaneous existence of PtOEP and ZnO Raman modes

21 **3.2.3. Surface morphology**

22 **Fig. 3** shows the surface morphology for (a) Pure ZnO, (b) ZnO/PtOEP_(0.009), and (c) ZnO/PtOEP_(0.015). In
23 the pure ZnO, the surface looks smooth and homogeneous. While at ZnO/PtOEP_(0.009), the surface
24 morphology has not been changed a lot, only some black dots are visible, which represents some big PtOEP
25 particles. By increasing the percentage of PtOEP in the sample, the PtOEP particles are found to create many
26 big aggregates with different size and shapes with ZnO nanoparticles. This large-scale aggregation at high
27 concentrations from PtOEP was a result of limited solubility of PtOEP in the ZnO blend.

28 **3.2. Photovoltaic properties**

29 Photovoltaic performance of the cells as an effect of weight ratios of ZnO:PtOEP is shown in **Fig. 4**.
30 According to this figure the average device photovoltaic parameters such as open circuit voltage (V_{OC}),
31 short-circuit current density (J_{SC}), fill factor (FF), and power conversion efficiency (PCE, η) for DSSC based
32 on ZnO:PtOEP Photoanodes at different blend ratios are summarized in **Table2**. According to **Fig. 4** and

1 **Table 2**, the control device exhibited a PCE of 2.09% with J_{sc} of 7.27 mA/cm^2 and FF of 0.52. Also, the
2 optimum performance can be achieved at ZnO:PtOEP_(0.009) (J_{SC} of 8.05 mA/cm^2 , FF of 0.57, and PCE of
3 2.58%), where the J_{SC} , and PCE enhanced about 23.44 and 10.72%, respectively compared to the control
4 device. Thus, it is evident that the PtOEP concentration has an obvious effect on the photovoltaic
5 performance. For the higher PtOEP concentration (ZnO:PtOEP_(0.012) and ZnO:PtOEP_(0.015)), the J_{SC} value has
6 been decreased to 7.11 and 6.84 mA/cm^2 , also the PCE value has been reduced to 1.96 and 1.83%. Efficient
7 operation of a DSSC device relies upon the minimization of possible recombination pathways occurring at
8 the ZnO-dye-electrolyte interface, allowing efficient charge transport through the ZnO film, electrolyte, and
9 subsequent charge collection at the device contacts. There are two possible recombination losses are to
10 consider: i) the injected electrons may recombine either with oxidized dye molecules or ii) with the oxidized
11 redox couple [15, 28, 29, 30, 31]. In order to reduce the recombination, at lower concentrations from PtOEP
12 which is favorable for the effective electron transfer because the LUMO of PtOEP is little lower than the
13 LUMO of N719 (see **Fig. 5**), which is nearer to the conduction band of the metal oxide. Thus, it can be the
14 reason for fast electron transfer at the dye-PtOEP/ZnO interface, and higher current density. Besides this, the
15 inducing force in the electron transfer process inside the film might also be the reason for the improvement
16 in the charge separation process as well as lowering the rates for the charge recombination. Without PtOEP
17 the electrons transfer from dye to ZnO at a lower force, therefore there is a possibility of recombination for a
18 couple of the electrons. However, for the higher concentration, the reason for decreasing the electron transfer
19 can be described from the structural defects that have been created due to the formation of the considerable
20 amount of bigger aggregates. These aggregates might be the reason for higher charge transport resistance at
21 the metal oxide-dye to electrolyte interface which in turn reduces the J_{SC} . Another phenomenon is the
22 generation of the singlet exciton to triplet exciton using the smaller amount from PtOEP incorporation and
23 thus PtOEP particles inside the cells would lead to improving the exciton diffusion length, and solar cell
24 performance [32, 33, 34]. Once the aggregation takes place at the higher concentrations from PtOEP in
25 DSSCs, the power conversion efficiency dramatically decreases due to the localization of the triplet excitons
26 in PtOEP phase islands resulting in lower J_{sc} , PCE, and V_{OC} of the cells. Therefore, it gives lower R_{SH} and
27 high R_s with a higher percentage of PtOEP. **Fig. 6** represents the EQE as a function of wavelength. High
28 EQE signifies high optical absorption and hence a higher the incident photon-to-electron conversion
29 efficiency [35]. According to **Fig. 6**, the range of wavelength of the incident light that contributes to photon
30 to current conversion is varied from 350 to 750 nm. Ru-dye provides high quantum efficiency in the range of
31 500 to 550 nm [36, 37]. Therefore, the maximum conversion efficiency was found in this range. EQE curves
32 follow the trends of short-circuit current density obtained from J - V curve measurements.

3.3. Impedance spectroscopy

The Electrochemical impedance spectroscopy (EIS) plays a vital role in understanding the interfacial kinetics and reactions of the fabricated DSSCs [20, 21, 38]. The Nyquist plot with the standard equivalent circuit model (at inset) is shown in **Fig. 7**. The fitting data is summarized in **Table 3**. R_s correspond to the overall series resistance of the device. The small semicircle at the high frequency is ascribed to the charge transfer process at the interfaces between the electrolyte and the Pt counter electrode, represented by R_{CE} . The larger semicircle at the lower frequency is related to the combination of i) transport process of the injected electrons within ZnO porous films and ii) the charge transfer process of the injected electrons at the interfaces between dye-loaded ZnO (ZnO/PtOEP) and the electrolyte, represented by R_{AE} . From **Table 3** we find that the values of R_s , R_{CE} , and R_{AE} were decreased by increasing the concentration of PtOEP and the lowest values for R_s , R_{CE} , and R_{AE} have observed at ZnO:PtOEP_(0.009). The lowest values of these resistances of the DSSC at ZnO:PtOEP_(0.009) is consistent with the higher J_{SC} and FF values of the cell, and with its higher performance. Also, the decreasing in R_{CE} with the increase of the concentration of PtOEP until ZnO:PtOEP_(0.009) indicates faster charge migration across Pt-electrolyte interfaces and faster regeneration of the oxidized dye [39]. While the R_s , R_{CE} , and R_{AE} values have been increased to 74.6, 217.4, and 116.2 Ω , respectively at ZnO:PtOEP_(0.015) inside the cell. This may be due to the formation of PtOEP aggregates on the electrode surface, which might have caused a reduction in the surface area and a reduced dye uptake [40], resulting in a low value of current. This is evident from the SEM images shown in **Fig. 3 (c)**. The bode phase plots for the samples are shown in **Fig. 8**. The characteristic time or electron lifetime τ_n in the DSSC based on PtOEP: ZnO nanoparticles is determined as the product of capacitance (C_{AE}) and electron transport resistance R_{AE} at the ZnO/dye/electrolyte interface. From the Bode phase plot (**Fig. 8**) it is observed that the characteristic frequency peak (low-frequency region) shifts to lower frequency, as the concentration of PtOEP is increased until ZnO:PtOEP_(0.009) after that shifts to the higher frequency at higher concentration from PtOEP. The characteristic frequency can be related to the inverse of electron lifetime [14, 41]. This indicates that the electron lifetime is higher at ZnO:PtOEP_(0.009) and decreased at higher concentration. This result clearly explains the higher values of V_{oc} and FF for DSSCs based on ZnO:PtOEP_(0.009) Photoanodes compared to the control cell (0% PtOEP). The improvement in the electron lifetime was attributed to a reduced recombination between PtOEP: ZnO nanoparticles and the electrolyte. The high fill factor indicates the rapid diffusion of ions to the counter electrode as well as rapid transport of electrons through at ZnO:PtOEP_(0.009) [40, 42].

1 **4. Conclusions**

2 The XRD pattern of the pure ZnO and ZnO: PtOEP has the diffraction peaks, which correspond to the planes
3 (100), (002), (101) and (102), are perfectly indexed to the hexagonal wurtzite ZnO structure. Also, the XRD
4 results show that the average crystallite size increases from 33.7 to 48.3 nm with increasing the
5 concentrations of PtOEP. The weak peak at 438 cm^{-1} in Raman spectra of ZnO and PtOEP:ZnO NP samples
6 represents the E_2^{high} vibration mode of wurtzite ZnO. The SEM image shows that higher level of PtOEP
7 concentration creates the considerable number of micro-sized aggregates. This large-scale aggregation at high
8 concentrations of PtOEP was a result of the limited solubility of PtOEP in the ZnO blend. The optimum
9 performance can be achieved at ZnO:PtOEP_(0.009) (JSC of 8.05 mA/cm^2 , FF of 0.57, and PCE of 2.58%),
10 where the JSC, and PCE enhanced about 23.44 and 10.72%, respectively. The smallest values of resistances
11 for equivalent circuit model of impedance spectroscopy at of ZnO:PtOEP_(0.009) based DSSC leads to
12 upgrading in the photocurrent and solar cell performance. The electron lifetime is higher when the
13 concentration of PtOEP is increased (ZnO:PtOEP_(0.009)) and decreased at higher concentrations of PtOEP.
14 Thus, lower level of PtOEP can be a suitable choice for a low-cost efficient DSSC application.

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Figure caption

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21 **Fig. 1.** The XRD patterns of ZnO and ZnO: PtOEP with different weight ratios photoelectrode films.

22 **Fig. 2.**Raman spectra of ZnO and ZnO: PtOEP with different weight ratios photoelectrode films.

23 **Fig. 3.** SEM image of a) Pure ZnO, (b) ZnO/PtOEP_(0.009), and (c) ZnO/PtOEP_(0.015).

24 **Fig. 4.** The J-V curve for the cells prepared by ZnO and ZnO: PtOEP with different weight ratios
25 photoelectrode.

26 **Fig. 5.** The diagram of interfacial charge-transfer processes in DSSCs based on PtOEP:ZnO nanoparticles.

27 **Fig. 6.**EQE curve for the cells prepared by by ZnO and ZnO: PtOEP with different weight ratios
28 photoelectrode.

29 **Fig. 7.** Nyquist plots of the of DSSC based on ZnO and ZnO: PtOEP with different weight ratios
30 photoelectrode. The inset shows the basic RC model of the equivalent circuit.

31 **Fig. 8.**Bode phase plots of the of DSSC based on ZnO and ZnO: PtOEP with different weight ratios
32 photoelectrode.

Table caption

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34
35 **Table. 1.** Structural parameters of PtOEP:ZnO nanocomposite.

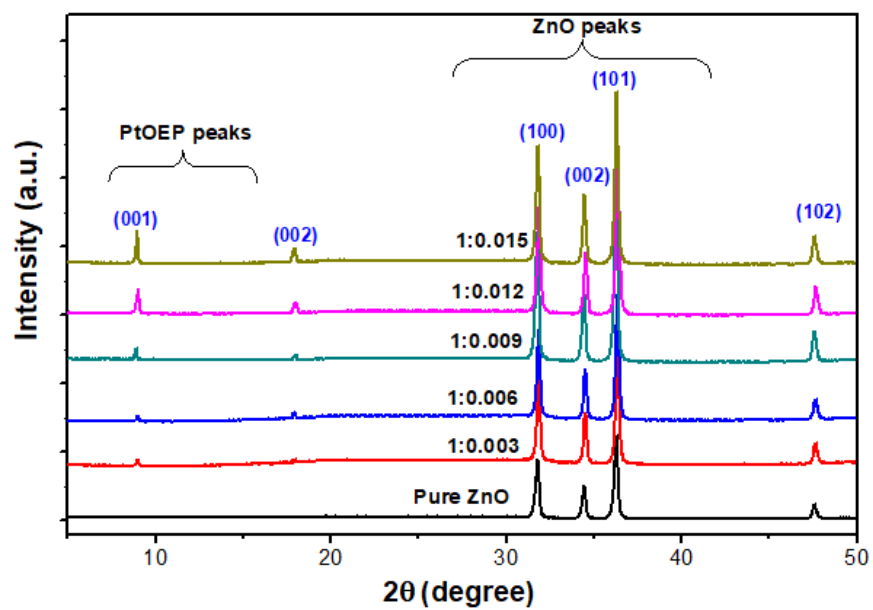
36 **Table. 2.** Photovoltaic parameters of DSSC based on PtOEP: ZnO nanocomposite.

37 **Table.3.** Electrochemical impedance parameters of DSSC based on PtOEP:ZnO nanocomposite.

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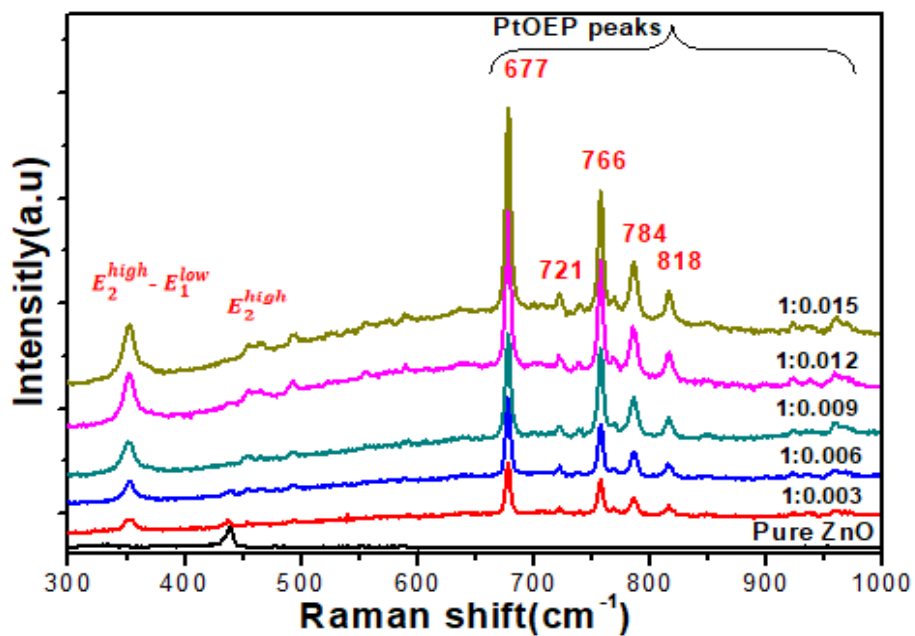
2 FIG.1



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4 FIG.2

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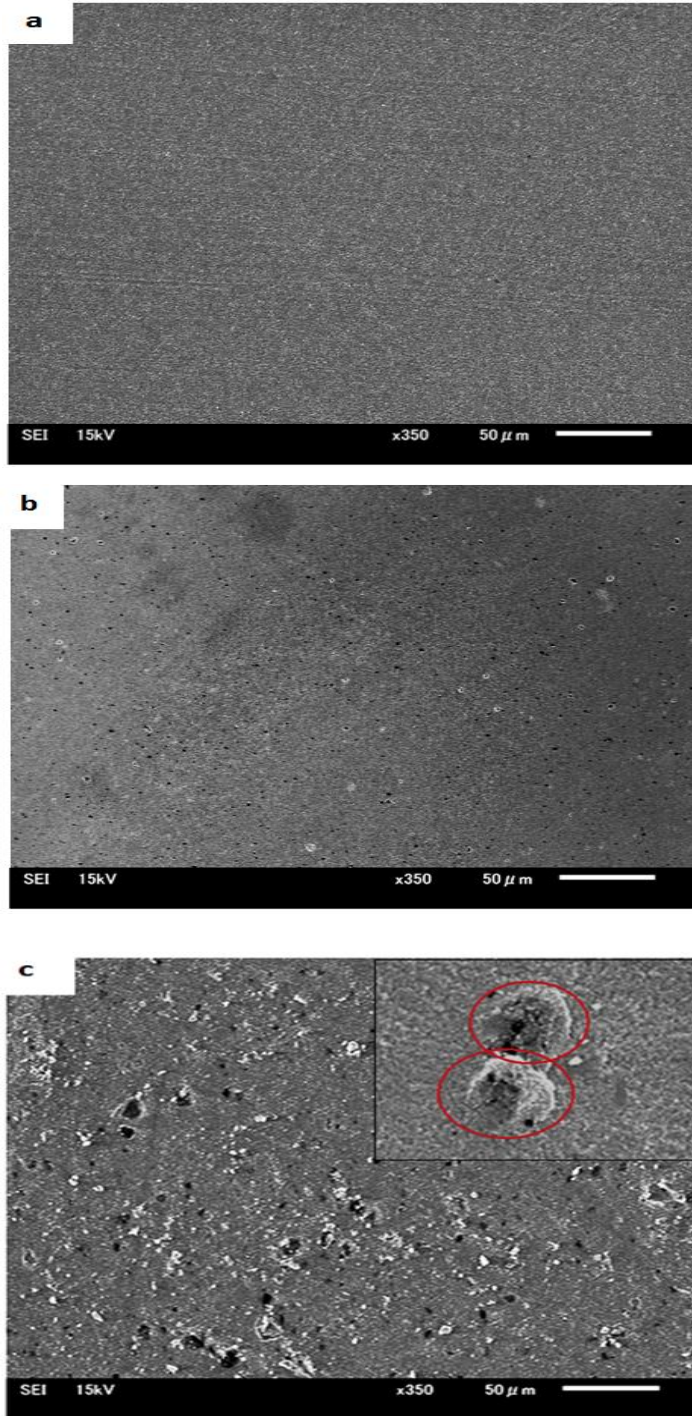
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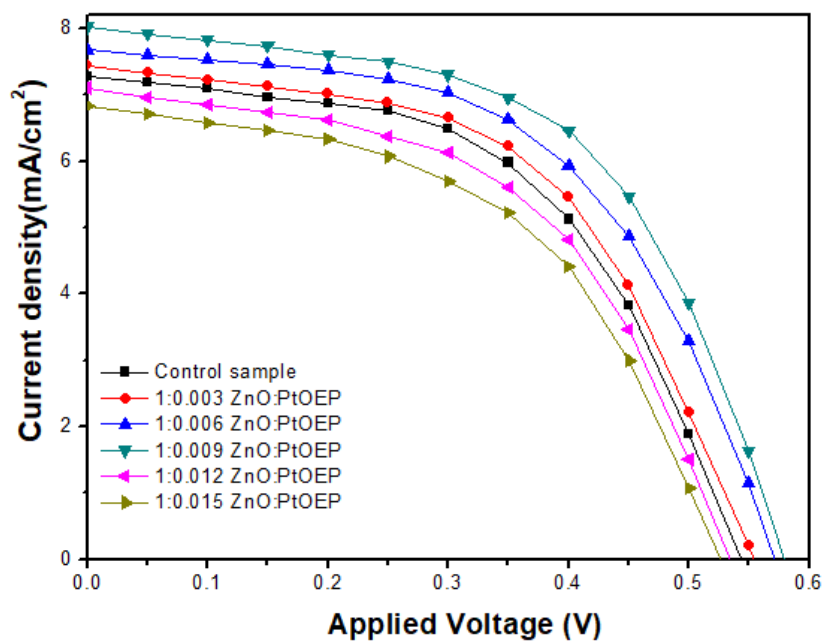
FIG.3



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3 FIG.4

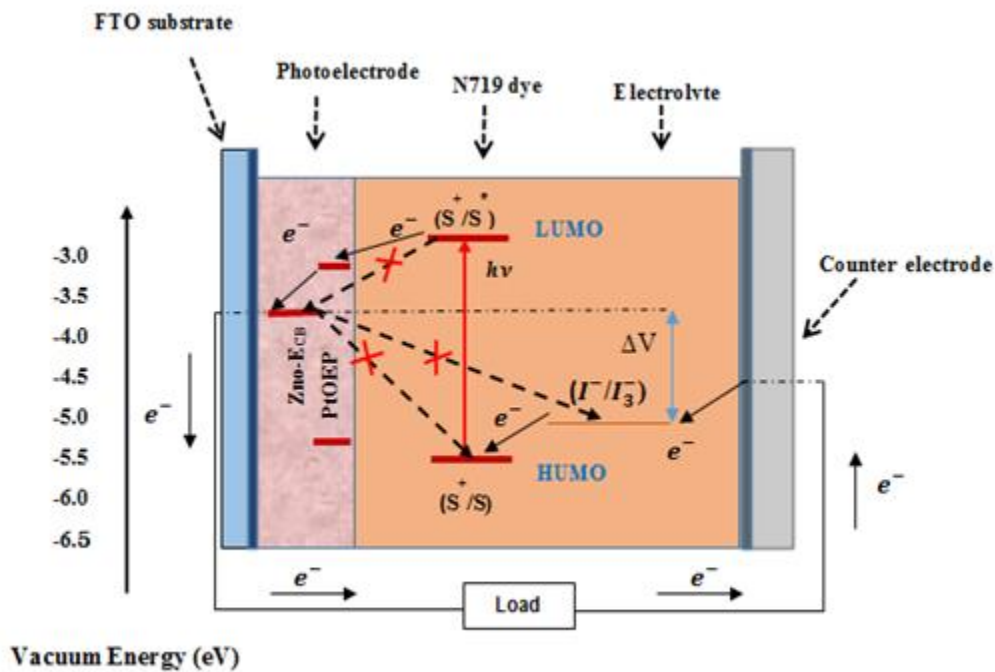


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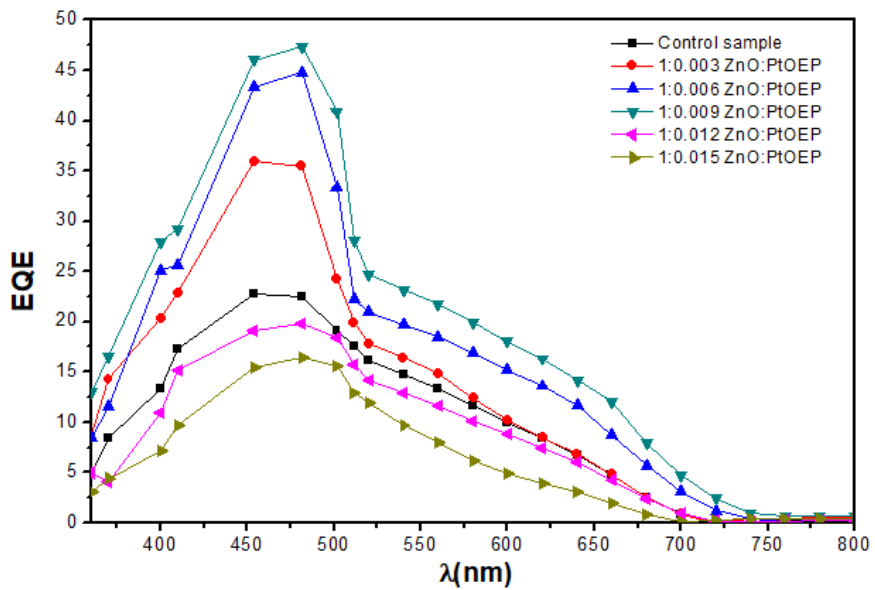
6 FIG.5

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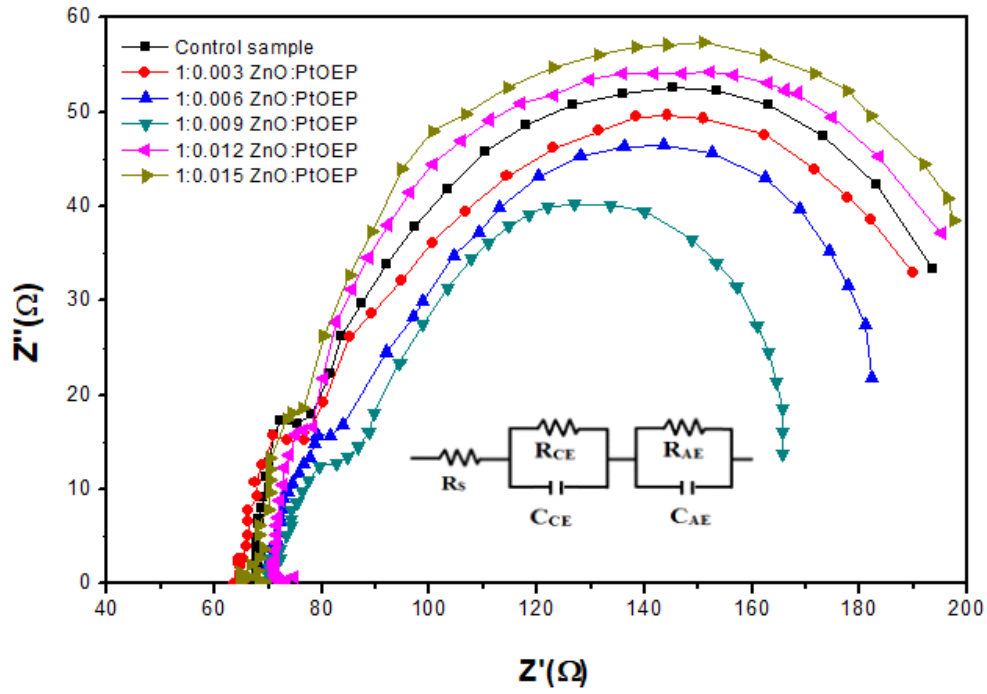
FIG.6



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FIG.7

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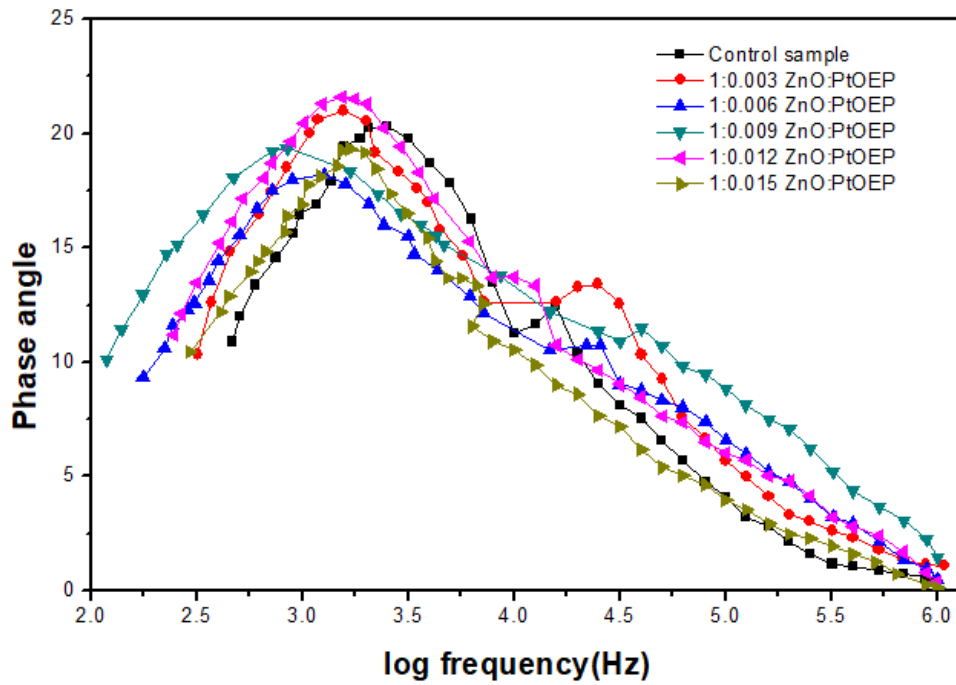


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4 **FIG.8**

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photoelectrode	Crystallite size (nm) (Scherrer)	(W-H analysis)	
		Particle size (nm)	Strain (ϵ) $\times 10^{-4}$
ZnO	33.78	38.23	9.32
1:0.003 ZnO:PtOEP	42.96	47.12	8.23
1:0.006 ZnO:PtOEP	45.54	49.46	7.75
1:0.009 ZnO:PtOEP	46.84	51.32	7.56
1:0.012 ZnO:PtOEP	46.98	52.45	7.47
1:0.015 ZnO:PtOEP	48.32	54.5	7.35

1 **Table.2**

Cells	VOC(Volt)	Jsc(mA/cm ²)	FF%	η%
ZnO	0.54	7.27	0.52	2.09
1:0.003 ZnO:PtOEP	0.55	7.44	0.53	2.18
1:0.006 ZnO:PtOEP	0.56	7.68	0.54	2.37
1:0.009 ZnO:PtOEP	0.58	8.05	0.57	2.58
1:0.012 ZnO:PtOEP	0.53	7.11	0.52	1.96
1:0.015 ZnO:PtOEP	0.52	6.84	0.51	1.83

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18 **Table.3**

Cells	R _S (Ω)	R _{CE} (Ω)	R _{AE} (Ω)	τ _n (ms)
ZnO	69.6	15.2	115.2	0.063
1:0.003 ZnO:PtOEP	68.1	14.58	111.7	0.101
1:0.006 ZnO:PtOEP	67.5	14.1	99.32	0.159
1:0.009 ZnO:PtOEP	65.8	13	82.5	0.201
1:0.012 ZnO:PtOEP	70.2	15.4	112.9	0.101
1:0.015 ZnO:PtOEP	74.62	17.4	116.2	0.079

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