

Performance Comparison of Low Cost TiO₂ and ZnO Solar Cells Sensitized with Coumarin C343

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Dye-sensitized solar cells (DSSCs) based on TiO₂ and ZnO nanoparticles using low cost organic dye Coumarin 343 (C343), carbon counter electrode and iodide electrolyte were fabricated and compared. The two types of thin films were deposited on the transparent conducting oxide substrates by doctor Blade technique. The morphological and structural properties of these thin films were studied using SEM and XRD. Current-voltage measurements were carried out to investigate the DSSCs photovoltaic efficiency. The comparative performance study shows that the cell with ZnO/C343 as the photo-anode produces higher short circuit current density (J_{sc}) and open circuit voltage (V_{oc}), which leads to higher energy conversion efficiency than the cell with TiO₂/C343 as the photo-anode. UV-Visible and electrochemical impedance spectroscopy studies revealed the better performance of ZnO cell due to higher light absorption and slower electron recombination compared to TiO₂ solar cell.

Keywords: DSSCs, ZnO, TiO₂, Coumarin 343.

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1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) are the most promising alternative photovoltaic technology due to lower production cost, environmental friendliness [1] and have the advantage of choosing the materials that constitute them among different materials valid to be utilized in this type of solar cells.

A DSSC consists of a wide band-gap semiconductor such as TiO₂, ZnO, NiO and SnO₂ deposited on a conductive substrate, a sensitizer (e.g. ruthenium complexes and organic dyes like Coumarin complexes) anchored on the surface of the semiconductor, a counter electrode (e.g. Pt and carbon materials) deposited on another conductive substrate and an electrolyte (e.g. I⁻/I³⁻ and Co²⁺/Co³⁺ redox couples) injected between the sensitizer and the counter electrode [2].

Dye molecules are responsible for absorbing most of the incoming light. Photo-excitation of the dye results in an electron being inserted into the semiconductor conduction band and transported to the external circuit through the conductive substrate, producing an electric current. The coloring is regenerated by withdrawing electrons from the redox electrolyte and the redox mediator is reduced via the counter electrode [3, 4].

Among all the wide band-gap semiconductors (WBGSs) explored as alternatives to TiO₂ as an electron conductor, ZnO has a similar band gap as TiO₂ and presents excellent bulk electron mobility (more than 1 order of magnitude larger than anatase TiO₂), which should favor electron transport [5-8]. Efficiency of over 11 % has been achieved with films that consist of 20 nm TiO₂ nanocrystallites sensitized by ruthenium-based dyes and platinum counter electrode [9].

The best photovoltaic properties of Ru complexes

are due to absorption of light in the visible spectrum, the excited states of the complexes have long lifetimes and the oxidized Ru complexes have long-term chemical stability. However, they are expensive and their use renders the resulting solar cells expensive [10, 11].

Platinum (Pt) is usually used as the counter electrode of the DSSC which shows high electrical conductivity and catalytic properties, but its limited resources make it undesired for low cost DSSCs [12].

For the fabrication of low cost DSSCs, we should replace Ru complexes by organic dyes. Coumarin complexes, e.g. Coumarin 343 (C343), are environmentally friendly, inexpensive, and easy to synthesize [13, 14].

Carbon electrode is a low cost alternative to Pt one due to its abundance, good catalytic property and excellent corrosion resistance against the redox couple [12, 15].

DSSCs based on ZnO and TiO₂ nanoparticles with approximately identical particle sizes and using the same low cost material C343 as sensitizer and carbon as counter electrode were fabricated and their photovoltaic performance was compared and investigated.

2. EXPERIMENTAL DETAILS

2.1 Preparation of TiO₂ and ZnO Photo-anodes

TiO₂ and ZnO porous films were manufactured by using doctor Blade technique.

The films were deposited on FTO glass (SnO₂: F with a sheet resistance of 25 Ω/sq).

Commercial TiO₂ and ZnO nanopowders were used to prepare a colloidal paste.

The TiO₂ colloidal paste was prepared by mixing 2 g of TiO₂ powder, 5 ml of distilled water, 0.1 ml of acetic acid and 0.2 g of polyethylene glycol (PEG) in order to

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improve the porosity of the film. The colloidal paste was realized in the ambient temperature and under magnetic mixture with a moderate speed for 6 h.

The paste was coated on the conductive glass substrate by doctor-Blade technique. The film was then annealed at 450 °C for 30 min after air drying [16].

The ZnO colloidal paste was prepared by mixing 2 g of ZnO powder, 4 ml of ethanol, 2 ml of distilled water and 0.2 g of PEG.

The ZnO film was prepared using a similar method as the TiO₂ film, but was annealed at 400 °C. The films were immersed in a 0.3 mM solution of C343 dye (Sigma-Aldrich) in ethanol and kept at room temperature for at least 12 h and then washed with ethanol to remove the excess dye. The films have approximately the same thickness (16-18 μm) which was measured by a mechanic profilometer (DEKTAK 6M).

2.2 Fabrication of DSSCs

The electrolyte has been primed by dissolution of 0.5 M KI and 0.05 M I₂ in ethanol [17]. Counter electrodes were prepared by using carbon paste which was coated on the FTO glass by doctor Blade technique and subsequently dried at 180 °C for 1 h.

2.3 Characterizations

Scanning electron microscope (SEM) images were obtained with SEM, JEOL, JSM 6610 LA in order to examine the morphology of the films and determine the average size of the particles. The structures of the TiO₂ and ZnO films were identified by X-ray diffraction (Science RAD-2R) using $\lambda_{\text{Cu-K}\alpha} = 1.54058 \text{ \AA}$. The absorption spectra were analyzed by Ultraviolet-Visible (UV-Vis) spectroscopy using a CARY 500 (VARIAN) spectrophotometer. The current-voltage characteristics were measured using a 400 W xenon light source that was focused to give 100 mW/cm² (one-sun at AM 1.5) at the surface of the test cell. Electrochemical impedance spectra (EIS) analysis of the DSSCs was performed using potentiostat/galvanostat (Metrohm Autolab) with a frequency range of 0.1 Hz to 1 MHz at the open circuit voltage.

3. RESULTS AND DISCUSSION

3.1 Semiconductor Film Morphology

Fig. 1a shows the SEM image of TiO₂ film. It was observed that the film has homogeneous TiO₂ nanoparticles with a porous structure. This porous structure helps to adsorb more dye molecules on the surface of the film, which is needed for efficient light harvesting. Fig. 1b shows the SEM image of ZnO film, it appears to have the same surface morphology of TiO₂ film. The particle size of both TiO₂ and ZnO films was found to be in the range of 100-150 nm.

3.2 XRD

Fig. 2a shows the X-ray diffraction spectrum of the nanostructure TiO₂ film and illustrates peaks characteristic of two phases: anatase and brookite. The particle size, calculated from the peak broadening using the

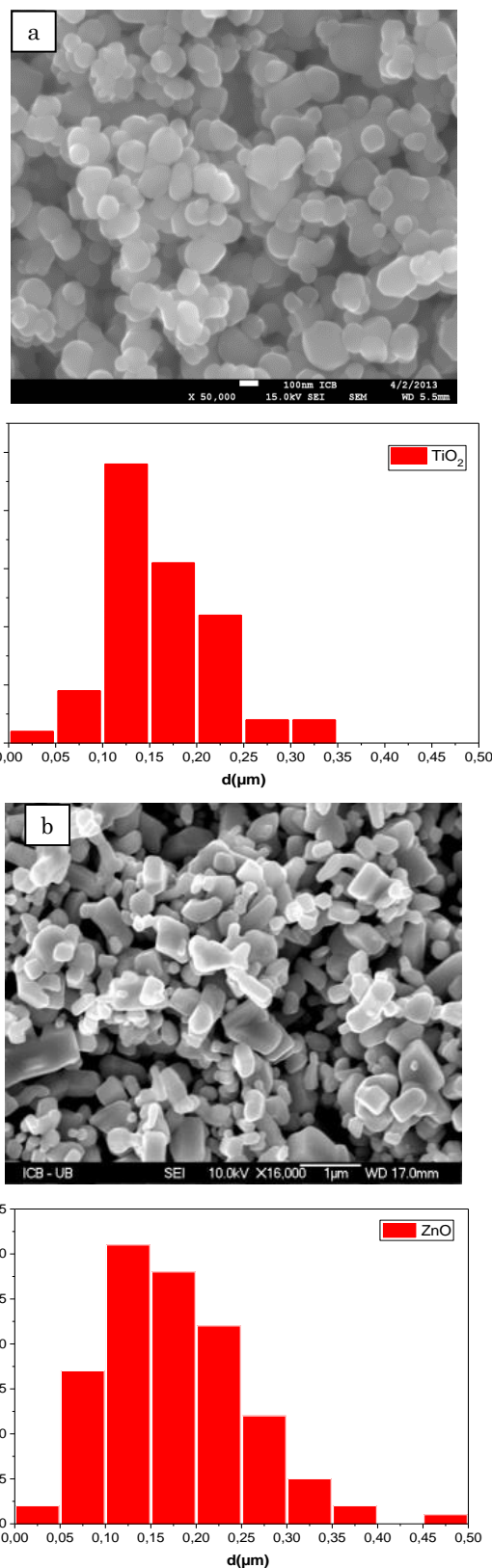


Fig. 1 – SEM images and a particle size of (a) TiO₂ film and (b) ZnO film

Scherrer formula, was 77 nm for anatase particles and 180 nm for brookite. X-ray diffraction spectrum of the nanostructure ZnO film is shown in Fig. 2b and presents peaks characteristic of wurtzite. The particle size,

calculated from the peak broadening, was 105 nm. These sizes are in agreement with SEM results.

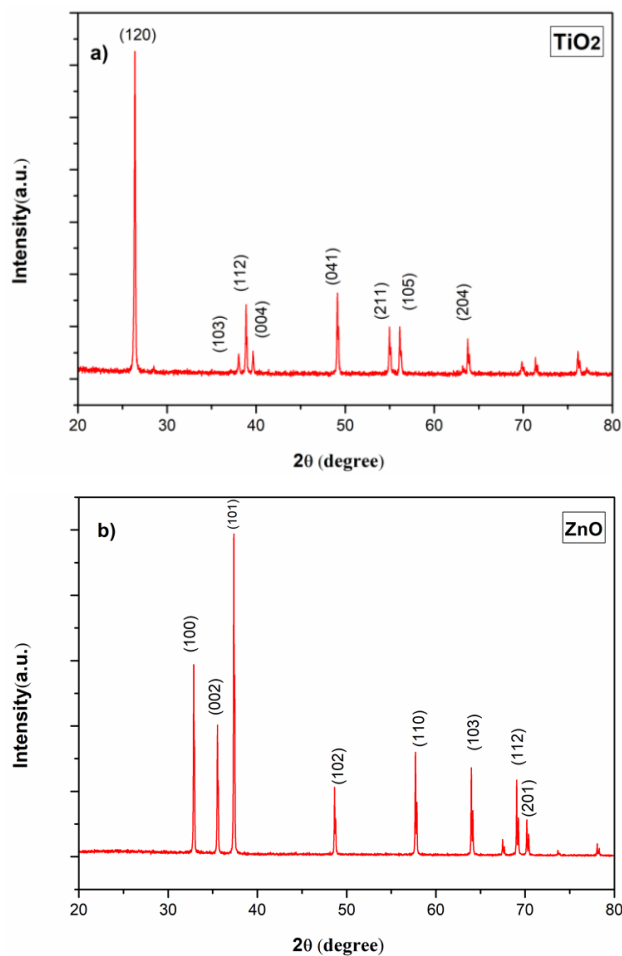


Fig. 2 – X-ray diffractogram of (a) TiO₂ film and (b) ZnO film

3.3 UV-Vis Absorption Spectra

The UV-Vis absorption spectrum of Coumarin 343 dye in ethanol shown in Fig. 3a exhibits one peak at 435 nm corresponding to the intermolecular π - π^* transition.

Fig. 3b, c shows the UV-Vis absorption spectra of photo-anodes ZnO and TiO₂ before and after C343 dye sensitization. Before dye loading (Fig. 3b), no significant absorption was observed in the wavelength range 400-800 nm consistent with the absence of light-scattering phenomena in ZnO and TiO₂ films. After dye loading (Fig. 3c), an absorption band for the two photo-anodes appears which is related to the absorbance by the C343 dye in the visible region.

Moreover, the absorption spectra of the two photo-anodes show the broad tail towards the red edge, which is desirable for harvesting light. As it can be observed, the absorption spectrum of ZnO/C343 photo-anode is broader than the absorption spectrum of TiO₂/C343 photo-anode, which indicates that more of C343 dye was adsorbed by ZnO film. This gives evidence that there is appreciable interaction between C343 dye and ZnO surface.

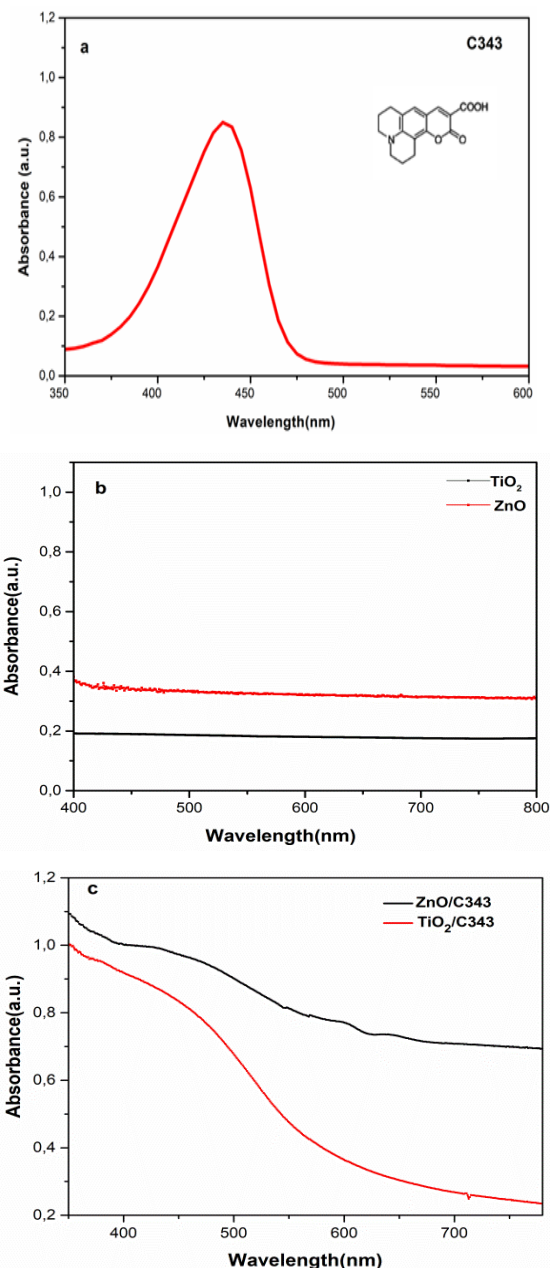


Fig. 3 – Absorption spectra of (a) C343 dye in ethanol, (b) ZnO and TiO₂ films, (c) ZnO/C343 and TiO₂/C343 films

3.4 Photovoltaic Characterization

The photocurrent density-voltage (J - V) curves of ZnO and TiO₂ cells sensitized with C343 are shown in Fig. 4. The open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and solar conversion efficiency (η) of the DSSCs are presented in Table 1.

Table 1 – Photovoltaic parameters of ZnO and TiO₂ cells sensitized with C343

DSSC	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η %
ZnO	2.40	0.50	0.47	0.56
TiO ₂	1.40	0.46	0.44	0.28

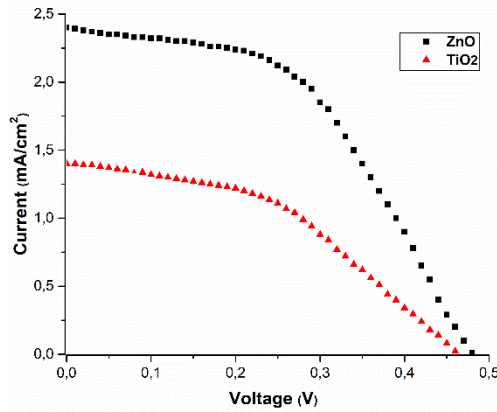


Fig. 4 – J-V curves of ZnO and TiO₂ cells sensitized with C343

As shown in Table 1, ZnO cell yielded higher values of both the short circuit current and the open circuit voltage than TiO₂ cell. The fill factor of the two types of cells is not much different from each other. The conversion efficiency of ZnO solar cell ($\eta = 0.56\%$) is 100% higher than that of TiO₂ cell ($\eta = 0.28\%$) which is basically due to the highest short-current density $J_{sc} = 2.40$ mA for ZnO cell, but $J_{sc} = 1.40$ mA for TiO₂ cell.

Fig. 5 shows dark current curves of ZnO and TiO₂ cells. It can be observed that TiO₂ cell has higher dark current than ZnO cell, indicating more efficient electron recombination with accepting ions in the electrolyte, then lower current density produced by TiO₂ cell [18-23].

However, EIS measurements allow us to better understand the electronic processes in the cell.

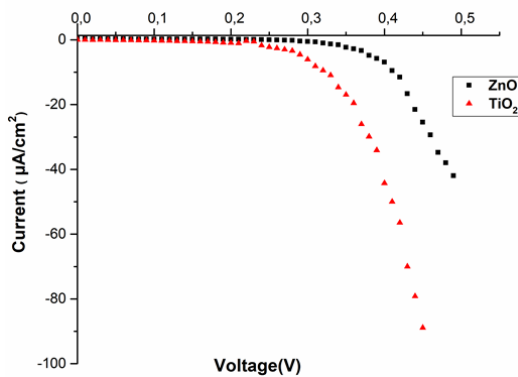


Fig. 5 – Dark current characteristics of ZnO and TiO₂ cells sensitized with C343

3.5 EIS Analysis

The EIS analysis was used to investigate the interfacial electron transport properties of the photo-anode/electrolyte in DSSCs such as charge-transfer resistance (R_{ct}) related to electron recombination with electrolyte and electron lifetime (τ_n) of photo-injected electrons within photo-anode. The Nyquist plots of the impedance spectra are shown in Fig. 6.

In general, the impedance spectra of DSSCs show three semicircles corresponding to the charge transfer processes at the electrolyte/counter electrode in the high-frequency region, the electron diffusion in the photo-

anode and electron transfer at the photo-anode/electrolyte interface in the middle-frequency region, and Nernst diffusion within the electrolyte in the low-frequency region [24, 25]. The charge-transfer resistance (R_{ct}) can be determined from the central semi-circle diameter [26].

The electron lifetime (τ_n) is given by the relation $\tau_n = (2\pi f)^{-1}$, where f is the frequency at which the low frequency peak appears in the Bode plot (Fig. 7) [27].

EIS measurement results of the two types of DSSCs are shown in Table 2.

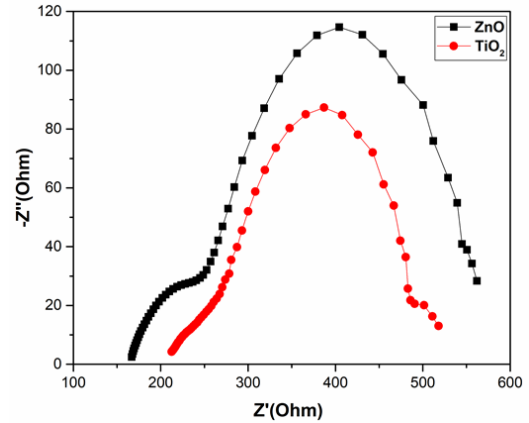


Fig. 6 – Nyquist plots of DSSCs

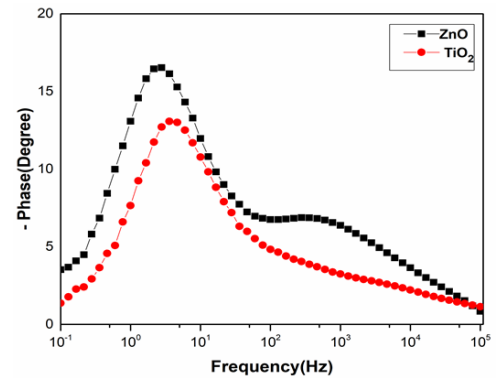


Fig. 7 – Bode plots of DSSCs

Table 2 – EIS parameters of ZnO and TiO₂ cells sensitized with C343

DSSC	τ_n (ms)	R_{ct} (Ω)
ZnO	57.22	287.75
TiO ₂	44.30	204.59

The electron recombination resistance R_{ct} in ZnO cell is larger than in TiO₂ cell which indicates that the back electron recombination at the ZnO photo-anode/electrolyte interface is slower and more abundant electron interfacial recombination occurs in case of TiO₂. Correlatively, the longer lifetime (τ_n) in ZnO cell means an effectively suppressed electron-hole recombination.

Larger R_{ct} and longer lifetime (τ_n) results of ZnO cell are partly responsible for their higher current density and increase in V_{oc} , then exhibit better photovoltaic performance compared to TiO₂ cell. These results are in agreement with the dark current curves.

The above results indicate the more dye molecules loading and slower back electron recombination are responsible for the highest photovoltaic performance in ZnO cell compared to TiO₂ cell. As seen in UV-Vis spectra, ZnO/C343 photo-anode has higher absorption in the visible range. This confirms that more incident light is harvested and more dye molecules are adsorbed in ZnO cell compared to TiO₂ cell, then produces larger photocurrent. Moreover, ZnO/C343 photo-anode with high dye adsorption can reduce the surface contact of ZnO with the electrolyte, thus the interfacial recombination can be reduced. On the other hand, EIS results reveal the lowered recombination of injected electrons with accepting ions in the electrolyte (larger R_{ct} and τ_n) in ZnO cell, and the higher recombination losses for TiO₂ cell are partly responsible for its lower performance. As a result, the conversion efficiency of low cost ZnO cell sensitized with Coumarin C343 is 100 % higher than that of low cost TiO₂ cell sensitized with Coumarin C343.

4. CONCLUSIONS

Two types of low cost DSSCs were fabricated using ZnO and TiO₂ porous films, organic dye Coumarin C343,

carbon counter electrode and iodide electrolyte. These films were deposited by the same simple technique (doctor Blade) and have approximately equally sized nanoparticles which were revealed by SEM and XRD characterizations. The photovoltaic performance of ZnO and TiO₂ solar cells sensitized with C343 was compared and investigated. It was found that ZnO cell gives better photovoltaic performance than TiO₂ cell.

UV-Vis spectra, dark current characteristics and EIS measurements explain the different photovoltaic behavior of ZnO and TiO₂ cells. The absorption spectra of the photo-anodes reveal that ZnO/C343 photo-anode has better absorption range, this indicates higher dye loading. Also, lower dark current, larger R_{ct} and longer lifetime (τ_n) results of ZnO cells indicate that the back electron recombination is slower than in TiO₂ cells.

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Порівняння продуктивності недорогих сонячних елементів TiO₂ та ZnO, сенсibilізованих за допомогою кумарину C343

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Були виготовлені та порівняні сенсibilізовані барвниками сонячні елементи (DSSCs) на основі наночастинок TiO_2 та ZnO з використанням недорогого органічного барвника Кумарину 343 (C343), вуглецевого протиелектрода та йодистого електроліту. Два типи тонких плівок наносились на прозорі провідні оксидні підкладки за методикою Blade. Морфологічні та структурні властивості цих тонких плівок вивчали за допомогою SEM та XRD. Вимірювання струму та напруги проводили для дослідження фотоелектричної ефективності DSSCs. Порівняльне дослідження продуктивності показує, що комірка з $\text{ZnO}/\text{C343}$ як фотоанодом дає більшу густину струму короткого замикання (J_{sc}) та напругу холостого ходу (V_{oc}), що призводить до вищої ефективності перетворення енергії, ніж комірка з $\text{TiO}_2/\text{C343}$ як фотоанодом. Дослідження ультрафіолетової і видимої та електрохімічної імпедансної спектроскопії виявили кращу продуктивність елементу ZnO за рахунок більшого поглинання світла та повільнішої рекомбінації електронів порівняно з сонячним елементом TiO_2 .

Ключові слова: DSSCs, ZnO , TiO_2 , Кумарин 343.