

# Metalloporphyrin Doped Zinc Oxide Films For Flexible ZnO-based Dye-sensitized Solar Cell Application

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## Abstract

**In this investigation, we are reporting for the first time Nickel (II)Tetraphenylporphyrin (NiTTP) doped ZnO-based flexible dye-sensitized solar cell. When the ratio of NiTTP/ZnO in the doping layer is optimized to 0.7%, the light-to-electric conversion efficiency of the DSC reaches to 2.7%, which is about 42% higher compare to the DSC without NiTTP doping.**

## 1. Introduction

DSCs have provoked intensive interest and become one of the hotspots, since the prototype of a low-cost, high efficient TiO<sub>2</sub>-based DSC was reported by Grätzel in 1991 [1]. However, much attentions have also been devoted to Zinc oxide (ZnO)-based DSCs owing to their higher electron mobility, longer carrier lifetime, and similar electronic band structure compared to TiO<sub>2</sub> [2]. Flexible and lightweight plastic-substrate DSCs are getting considerable interest due to their potentials for renewable and mobile power sources for portable electronic devices [3]. Conversion efficiency more than 5% have been reported for flexible ZnO-base DSC [4] though it is considerably lower than cells prepared by glass substrate. Boardening the absorption range is one of the effective method for enhancing the efficiency for DSC. Therefore, many metal complexes dyes have been synthesized and used for DSCs. However, those dyes (N-719, N-749, YD2-o-C8) only absorb visible light in the wavelength rage of 400-600 nm. Doping of metal oxide photoanode with organic or inorganic materials has been considered as a favorable way to improve the photovoltaic properties of DSC. To improve the photo-current density and power conversion efficiency many several investigations have been done by enhancing the charge collection efficiency, charge transport, and suppressing the recombination [5].

In this work, we have used a p-type doping of nickel porphyrine (NiTTP) for ZnO photoanode of a N719 dye sensitized DSC. The level of doping has been optimized for the cells and characterized by a scanning electron microscopy (SEM), solar simulator, X-ray diffraction (XRD), UV-vis absorption sepectroscopy, and electrochemical impedance spectroscopy (EIS).

## 2. Materials and Methods

NiTTP doped ZnO photoanodes have been prepared by

blade coating method. The blade coating paste was consist of 0.35 g ZnO nanoparticle (< 100 nm, Sigma Aldrich) and 2 ml ethanol (99.5%) along with various percentage of NiTTP as a dopant material. The paste was coated onto the indium tin oxide (ITO) coated polyethylene naphthalate (PEN) substrates. All the samples were dried at 100 °C using a hot-plate for 10 min and compressed (Mini TEST Press-10) with 130 MPa compression at 60 °C for 1 min. The prepared photoanodes were immersed into an ethanol solution of the 0.5 mM N719 dye (Ruthenium-535 bis TBA, Solaronix) for 1 h. Finally, the DSC was fabricated by using a Pt-coated glass as a counter electrode, and by inserting a polymer film (Himilan, 50 μm) between the electrodes. The electrolyte (Iodolyte AN 50, Solaronix) was inserted into the space between two electrodes by capillary action using a glass tube injector. A solar simulator (100 mW · cm<sup>-2</sup>, AM 1.5 illumination) with the area of 0.16 cm<sup>2</sup> restricted by a still mask, was used to record photocurrent-voltage (I-V), and dark current measurement. The surface morphology was observed by SEM (JSM-6510). X-ray diffraction (XRD), UV-vis absorption sepectroscopy, and electrochemical impedance spectroscopy (EIS) has also been investigated for the cells.

## 3. Results and Discussions

Fig. 1 shows the surface morphology of the ZnO photoanode for a) without doping, b) 0.7% doping, c) 3% doping, and d) enlarged view of NiTTP aggregates. NiTTP particles are

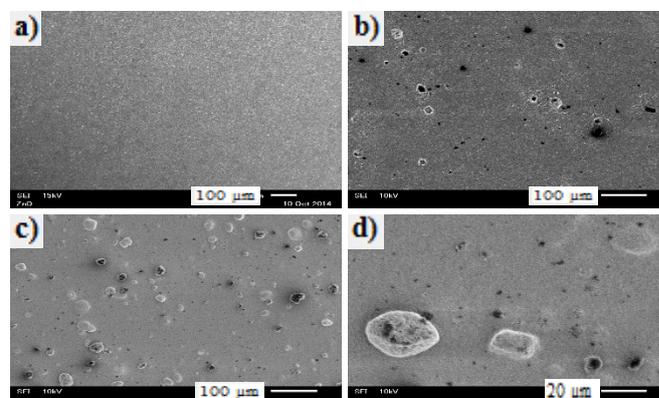


Fig. 1 SEM image of ZnO photoanode for a) without doping, b) 0.7 % doping, c) 3 % doping, d) enlarged view of NiTTP aggregates.

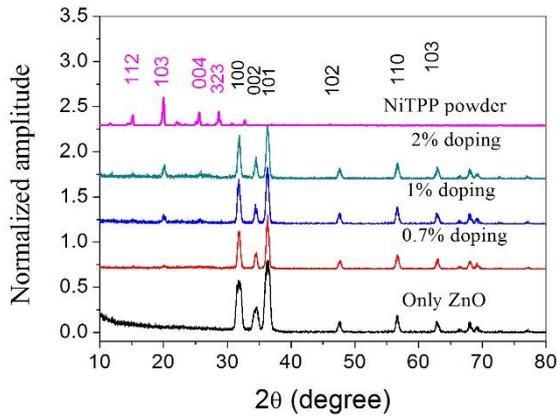


Fig. 2 XRD of NiTPP powder and different percentage of NiTPP doped ZnO photoanode.

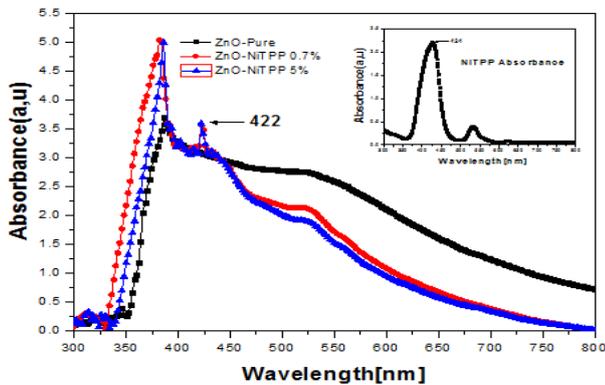


Fig. 3 UV-absorbance curve for photoelectrodes prepared by ZnO only, 0.7% and 5% NiTPP doped ZnO cells.

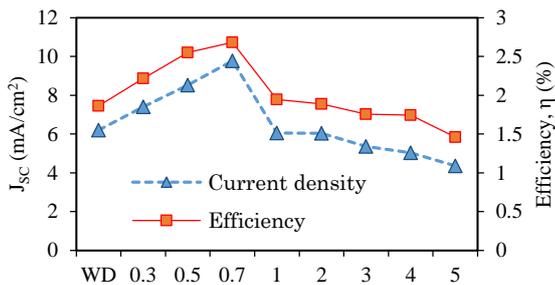


Fig. 3 Current density and Efficiency of the cells prepared by different percentage of NiTPP doping.

visible on the photo- anode surface. By increasing the doping percentage, more NiTPP particles are visible (Fig. 1 c). However, the NiTPP particles are seem to form aggregates. Fig. 1 d shows the NiTPP agreeegate of a size of more than 20  $\mu\text{m}$ . The X-ray diffraction (XRD) pattern of NiTPP powder (purple color) and different percentage of NiTPP doped ZnO photoanode are shown in Fig. 2. The diffraction peaks of NiTPP powder are indicated by purple numbers and for NiTPP doped

ZnO photoanode are indicated by black numbers. The crystallite size is estimated with Scherrer equation from the full width at half-maximum of the strongest ZnO diffraction (101). The crystallite size of the without doped ZnO cell is found about 15 nm and after doping it becomes 25 nm. From figure we find only the (103) diffraction peak for the cell doped by 0.7% NiTPP. By increasing the doping concentration some other peaks like (112), (004), and (323) are also visible.

The effect of NiTPP doping with ZnO nanoparticle on the optical absorbance has been investigated by UV-absorbance spectroscopy analysis measured in the range of 300 to 800 nm, shown in Fig. 3. At inset the typical absorbance spectra of the NiTPP is presented. From the figure it is clearly evident that after the doping of NiTPP one new peak appears at the wavelength of 420 nm which is in the similar position found for the original NiTPP absorption spectra. It represents the positive shift of conduction band, and as a result increment of open circuit voltage ( $V_{OC}$ ) for the doped cells confirmed by photovoltaic parameters.

Photovoltaic performance of the cells as an effect of NiTPP doping is shown in Fig. 4.  $V_{OC}$  has been increased from 0.56 to 0.61 V by increasing the amount of NiTPP doping from 0 to 5%. Current density ( $J_{sc}$ ), and power conversion efficiency is increased up to 0.07% doping and decreased after doping at a higher percentage. The fill factor has not changed considerably for this investigation. Without doping the efficiency ( $\eta$ ) of the cell is 1.88%. However, at 0.3% NiTPP doping it reaches to 2.21% and at an optimum doping level of 0.7% it reaches to 2.68%. By further increment in doping level up to 5% the  $\eta$  reduces to 1.46% though the  $V_{OC}$  has been improved to 0.61 V. The reason for decreasing photovoltaic performance is might be due to the aggregation formed by the NiTPP particle at higher doping concentration as shown in Fig. 1.

#### 4. Conclusions

In conclusion, we have introduced NiTPP as a successful dopant for ZnO-based flexible DSC. The photovoltaic performance has been improved substantially by increasing the amount of doping to 0.7%. The power conversion efficiency has been improved about 40% by 0.7% NiTPP doping. Shift in the optical absorption spectra confirms that the NiTPP doping gives rise to new absorption peaks also slightly increase the absorption spectra by left shift in the band edge region.

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