

## ENHANCEMENT IN NANOCRYSTALLINE TiO<sub>2</sub> SOLAR CELLS SENSITIZED WITH ZnPc BY NANOPARTICLES

LUNG-CHIEN CHEN\*, CHUNG-CHIEH WANG, BO-SHIANG TSENG

*Department of Electro-optical Engineering, National Taipei University of Technology, 1, sec.3, Chung-Hsiao E. Rd., Taipei 106, Taiwan, Republic of China*

This work discusses a ZnPc composite in dye-sensitized solar cells (DSSCs). The enhanced performance of solar cells is due to the role of gold nanoparticles (GNPs), ZnSe quantum dots (QDs), and carbon nanotubes (CNTs) to increase the energy conversion efficiency. Both charge separation effect by GNPs and driving force effect by ZnSe QDs can improve the efficiency of cells, and obtained similar energy conversion efficiency results. CNTs-doped TiO<sub>2</sub> DSSCs exhibited poorer properties than others due to the nonradiative decay. GNPs- and ZnSe QDs-doped TiO<sub>2</sub> DSSCs sensitized with ZnPc demonstrated the energy conversion efficiency results to be 0.70 and 0.67 %, respectively.

(Received August 12, 2009; accepted September 20, 2009)

**Keywords:** ZnPc ; TiO<sub>2</sub> solar cells ; nanoparticles ; ZnSe quantum dots

### 1. Introduction

Recently, dye-sensitized solar cells (DSSCs) are the most ambitious targets in the utilization of solar energy field. [1-5] The DSSC with high efficiency is formed by a combination of organic and inorganic components that could be produced at a low cost. The DSSCs are photoelectrochemical solar cells based on the photosensitization of nanocrystalline TiO<sub>2</sub> semiconductor electrodes by dyes. The key feature of this solar cell is the use of nanocrystalline TiO<sub>2</sub> films that have an extremely large surface-to-volume ratio. [6] However, there are limiting factors are the quantity of dye absorption and charge recombination between TiO<sub>2</sub> electrode and electrolyte.

Gold (Au) nanoparticles (GNPs) have been attracting a lot of attention due to their particular optical and electronic properties. Enhanced charge separation effect in chlorophyll solar cell and application for anode buffer layer of the solar cell to increase the photocurrent and power conversion efficiency were reported. [7,8] On the other hand, because of the quantum size effect, the band gap of semiconductor quantum dots (QDs) can be changed by controlling the size of QDs and, therefore, it can used the optical properties to adjust the range of solar photon absorption. QDs have also been several potentially properties that are attractive for applications as an alternative sensitizer for DSSC. Appropriate combinations of TiO<sub>2</sub> films with semiconductor QDs have been investigated, such as CdS [9-12], CdSe [13-15], PbS [16], InP [6], and InAs QDs [17]. QDs are also used to improve the performance of conventional silicon solar cells [18]. In this work, we elucidate the influence of the Au nanoparticles, ZnSe QDs, and carbon nanotubes on the performance improvement of the solar cells based on zinc phthalocyanine (ZnPc) sensitized TiO<sub>2</sub> nanocrystalline films. The photovoltaic properties of the devices were studied by spectral response and illuminated current density-voltage (*J-V*) measurements.

## 2. Experiment

The solution consisting of 1 g  $\text{TiO}_2$  nanocrystalline powder (diameter about 25 nm), 1 ml tritonX-100, acetic acid, and deionized water were mixture with nanoparticles as colloidal solution, and the colloidal solution were daubed uniformly onto indium tin oxide (ITO) conductive glass to form an about 8  $\mu\text{m}$ -thick film. The nanoparticles were selected from Au nanoparticles, ZnSe QDs, or carbon nanotubes. All particle size is about 5 nm. The  $\text{TiO}_2$  films with nanoparticles were annealed at 120  $^\circ\text{C}$  for 10 min. After that, ZnPc sensitizer was prepared. A tetrahydrofuran solution (50 ml) incorporated with ZnPc (0.5 g), PMMA (0.2 g), and  $\text{I}_2$  (0.2 g) was deposited on the  $\text{TiO}_2$  films with nanoparticles by spin coating to form an  $\text{I}_2$ -doped ZnPc film with a thickness of about 3  $\mu\text{m}$ .

Finally, the electrolyte was formed by mixing uniformly 20 ml propylene carbonate, 0.254 g iodine ( $\text{I}_2$ ), and 1.66 g KI. The electrolyte ( $\sim 0.03$  ml) was dropped into the film and combining with another ITO conductive glass with carbon coating to complete  $\text{TiO}_2$  solar cell. Fig. 1 shows the cross section of the completed structure. The  $J$ - $V$  characteristics were measured using a Keithley 2420 programmable source. A solar simulator (Oriel class B, AM 1.5, 100  $\text{mW}/\text{cm}^2$ ) was used as the light source.

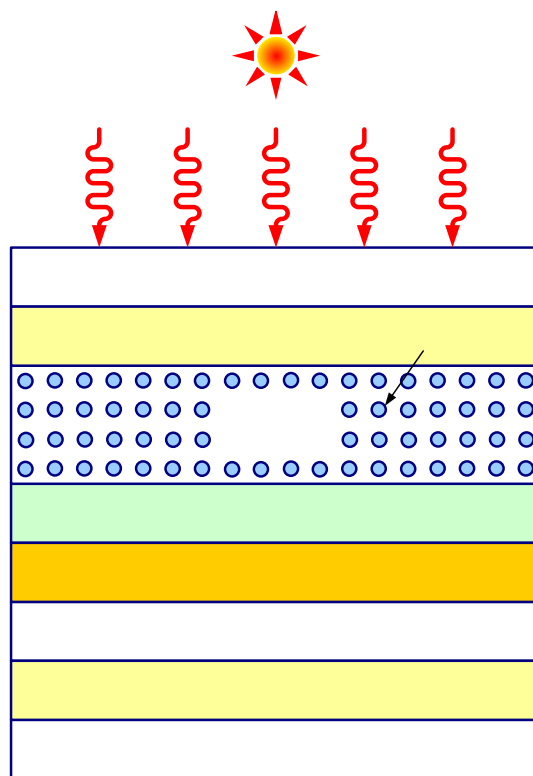


Fig. 1. Schematic cross section of the completed structure.

## 3. Results and discussion

Fig. 2(a) shows the energy level diagram and mechanism of photocurrent generation in GNPs-doped  $\text{TiO}_2$  DSSCs. The CB and VB are the conduction band and valence band, respectively. The LUMO and HOMO are the lowest unoccupied molecular orbit and highest occupied molecular orbit, respectively. The brief operating process as follows: Dye ZnPc was excited by incident light, and electrons transit from HOMO to LUMO. Electrons inject into GNPs, and raise the Fermi level ( $E_F$ ) to more close the CB of  $\text{TiO}_2$ , such that a quick shuttling of electrons from Au to  $\text{TiO}_2$  takes place. The electronics transferred to  $\text{TiO}_2$  particles were collected at the back contact

to generate a photocurrent. The dye ZnPc captures back the electrons from the electrolyte by reduce. The electrolyte can regenerate by oxidation. Similarly, figure 2(b) shows the energy level diagram and mechanism of photocurrent generation in ZnSe QDs-doped TiO<sub>2</sub> DSSCs. The brief operating process as follows: Dye ZnPc was excited by incident light with lower energy, and electrons transit from HOMO to LUMO. At the same time, ZnSe QDs was excited by incident light with higher energy, and electrons transit from VB to CB. ZnSe QDs have a large driving force such that the electronics transferred to TiO<sub>2</sub> particles were collected at the back contact to generate a photocurrent. [6].

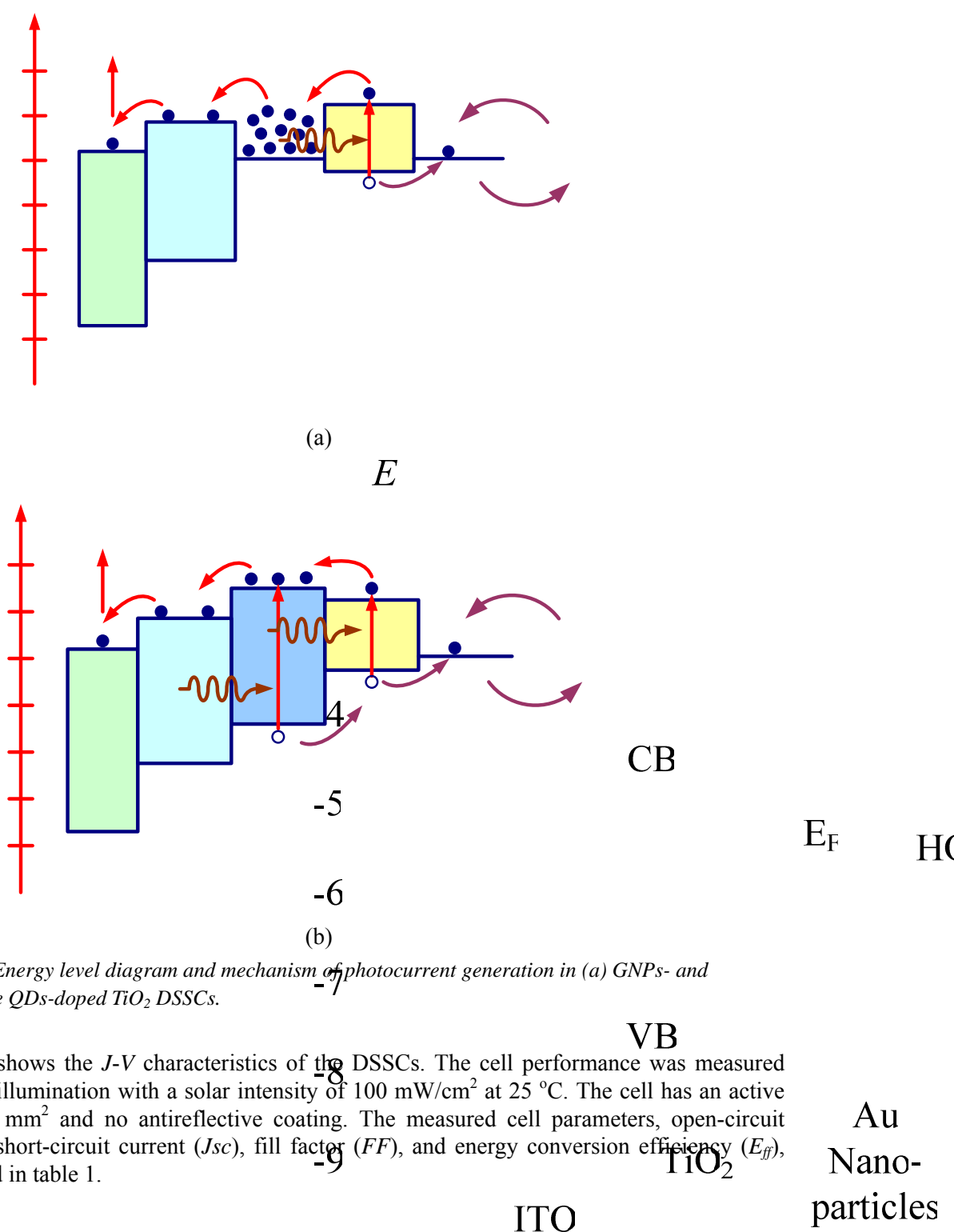


Fig. 2. Energy level diagram and mechanism of photocurrent generation in (a) GNPs- and (b) ZnSe QDs-doped TiO<sub>2</sub> DSSCs.

Fig. 3 shows the  $J$ - $V$  characteristics of the DSSCs. The cell performance was measured under AM 1.5 illumination with a solar intensity of 100 mW/cm<sup>2</sup> at 25 °C. The cell has an active area of 3 × 3 mm<sup>2</sup> and no antireflective coating. The measured cell parameters, open-circuit voltage ( $V_{oc}$ ), short-circuit current ( $J_{sc}$ ), fill factor ( $FF$ ), and energy conversion efficiency ( $E_{ff}$ ), are summarized in table 1.

Table 1. One-sun illuminated cell parameters of three different nanoparticles doped TiO<sub>2</sub> DSSCs measured at 25 °C.

Nanoparticles	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	E <sub>ff</sub> (%)	Improvement
Undoped	0.21	3.37	0.311	0.22	---
GNPs	0.35	5.79	0.345	0.70	218%
ZnSe QDs	0.48	4.83	0.289	0.67	205%
CNTs	0.27	5.03	0.361	0.49	123%

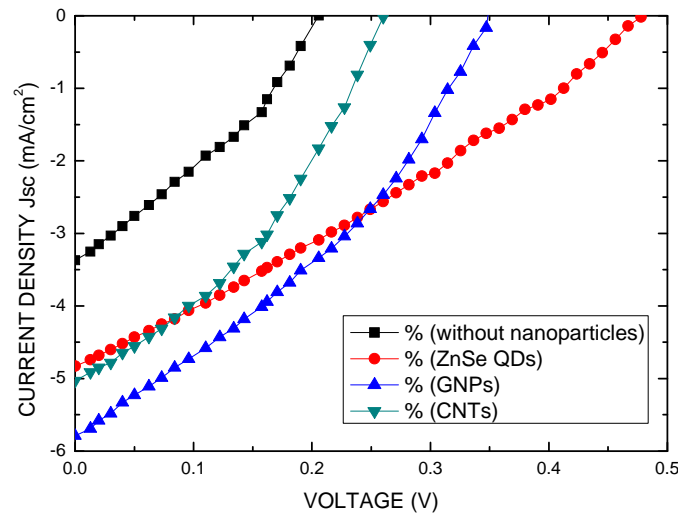


Fig. 3. J-V characteristics of solar cells.

As shown in Fig. 3, GNPs- and ZnSe QDs-doped TiO<sub>2</sub> DSSCs sensitized with ZnPc exhibited the following static parameters:  $V_{oc}$  of 0.35 V and  $J_{sc}$  of 5.79 mA/cm<sup>2</sup>, and  $V_{oc}$  of 0.48 V and  $J_{sc}$  of 4.83 mA/cm<sup>2</sup>, respectively. As is well known, the fill factor ( $FF$ ) can be described by [19]

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}} \quad (1)$$

where  $J_m$  is the maximum output current, and  $V_m$  is the maximum output voltage. Therefore, the value of  $FF$  results equal to 0.345 and 0.289, respectively. Similarly, the energy conversion efficiency ( $E_{ff}$ ) defined by [19]

$$E_{ff} = \frac{J_m V_m}{P_{inc}} \quad (2)$$

with  $P_{inc}$  the incident power,  $E_{ff}$  results to be 0.70 and 0.67 %, respectively.

Further, as shown in Fig. 3, the DSSCs with CNTs-doped nanostructured TiO<sub>2</sub> film exhibited poorer properties than others due to the nonradiative decay by the one-dimensionality of the band structures and the tube end states [20].

Fig. 4 shows the incident photon to current conversion efficiency (IPCE) spectra of GNPs- and ZnSe QDs-doped TiO<sub>2</sub> DSSCs. The IPCE at different wavelengths was determined from the

short circuit photocurrents monitored at different excitation wavelength ( $\lambda$ ) using the expression

$$\text{IPCE} = \frac{1240 \times J_{sc}}{\lambda \times P_{inc}} \times 100\% \quad (3)$$

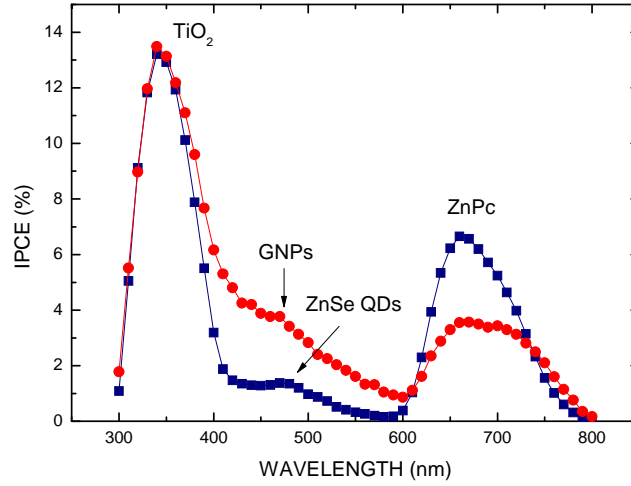


Fig. 4. The incident photon to current conversion efficiency spectra of GNP- and ZnSe QDs-doped TiO<sub>2</sub> DSSCs.

All cells show photocurrent responses in contrast with TiO<sub>2</sub> film ( $E_g = 3.2$  eV) that responds only in the UV region ( $<400$  nm). A maximum IPCE value of around 13.5% was observed for all cells. The absorption band in red region (600 – 780 nm) is interpreted as ZnPc absorption with an IPCE value of around 4 - 7%. The absorption peak around 470 nm and 480 nm correspond to plasmon band of GNPs and bandgap of ZnSe QDs, respectively. [21,22] It is clear that addition of GNPs and ZnSe QDs to the nanocrystalline TiO<sub>2</sub> solar cells increase the photon absorption. Therefore, both of charge separation effect by GNPs and driving force effect by ZnSe QDs can improve the energy conversion efficiency of cells. The absorption spectrum correspond to the GNPs have higher photocurrent than the ZnSe QDs in 400 – 600 nm region, but lower in red region, therefore obtained similar energy conversion results.

#### 4. Conclusion

In this work, we develop ZnPc composites dye-sensitized solar cells under AM 1.5 illumination condition. The enhanced performance of solar cells is due to the charge separation effect or driving force to increase the energy conversion efficiency. GNP- and ZnSe QDs-doped TiO<sub>2</sub> DSSCs sensitized with ZnPc demonstrated the following static parameters:  $V_{oc}$  of 0.35 V and  $J_{sc}$  of 5.79 mA/cm<sup>2</sup>, and  $V_{oc}$  of 0.48 V and  $J_{sc}$  of 4.83 mA/cm<sup>2</sup>, respectively, and the value of  $FF$  results equal to 0.345 and 0.289, respectively. The energy conversion efficiency results to be 0.70 and 0.67 %, respectively. Therefore, the energy conversion efficiency was improved by approximately 218 and 205 %, respectively. Therefore, both of charge separation effect by GNPs and driving force effect by ZnSe QDs can improve the efficiency of cells, and obtained similar energy conversion efficiency results.

### Acknowledgement

Financial support of this work was provided by the National Science Council of the Republic of China under Contract No. NSC 97-2215-E-027-022.

### References

- [1] B. O' Regan, M. Grätzel, *Nature* **353**, 737 (1991).
- [2] A. Hagfeldt, M. Grätzel, *Acc. Chem. Res.* **33**, 269 (2000).
- [3] M. Grätzel, *Inorg. Chem.* **44** (2005) 6841.
- [4] K. N. Mohammad, D. A. Filippo, F. Simona, S. Annabella, V. Guido, L. Paul, I. Seigo, T. Bessho, M. Grätzel, *J. Am. Chem. Soc.* **127**, 16853 (2005).
- [5] J. Bisquert, D. Cahen, G. Hodes, S. Rühle, A. Zaban, *J. Phys. Chem. B* **108**, 8106 (2004).
- [6] A. Zaban, O. I. Micić, B. A. Gregg, A. J. Nozik, *Langmuir* **14**, 3153 (1998).
- [7] S. Barazzouk, S. Hotchandani, *J. Appl. Phys.* **96**, 7744 (2004).
- [8] S. W. Tong, C. F. Zhang, C. Y. Jiang, G. Liu, Q. D. Ling, E. T. Kang, D. S. H. Chan, C. Zhu, *Chem. Phys. Lett.* **453**, 73 (2008).
- [9] Y. Tachibana, K. Umekita, Y. Otsuka, S. Kuwabata, *J. Phys. D: Appl. Phys.* **41**, 102002 (2008).
- [10] S. C. Lin, Y. L. Lee, C. H. Chang, Y. J. Shen, Y. M. Yang, *Appl. Phys. Lett.* **90**, 143517 (2007).
- [11] C. H. Chang, Y. L. Lee, *Appl. Phys. Lett.* **91**, 053503 (2007).
- [12] Y. Tachibana, H. Y. Akiyama, Y. Ohtsuka, T. Torimoto, S. Kuwabata, *Chem. Lett.* **36**, 88 (2007).
- [13] Q. Shen, J. Kobayashi, L. J. Diguna, T. Toyoda, *J. Appl. Phys.* **103**, 084304 (2008).
- [14] L. J. Diguna, Q. Shen, J. Kobayashi, T. Toyoda, *Appl. Phys. Lett.* **91**, 023116 (2007).
- [15] I. Robel, V. Subramanian, M. Kuno, P. V. Kamat, *J. Am. Chem. Soc.* **128**, 2385 (2006).
- [16] R. Plass, S. Pelet, J. Krueger, M. Grätzel, *J. Phys. Chem. B* **106**, 7578 (2002).
- [17] P. Yu, K. Zhu, A. G. Norman, S. Ferrere, A. J. Frank, A. J. Nozik, *J. Phys. Chem. B* **110**, 25451 (2006).
- [18] E. C. Cho, S. Park, X. Hao, D. Song, G. Conibeer, S. C. Park, M. A. Green, *Nanotech.* **19**, 245201 (2008).
- [19] S. M. Sze, *Physics of Semiconductor Devices*, 2<sup>nd</sup> ed. (John Wiley & Sons, New York, 1981).
- [20] J. Guo, C. Yang, Z. M. Li, M. Bai, H. J. Liu, G. D. Li, E. G. Wang, C. T. Chan, Z. K. Tang, W. K. Ge, X. Xiao, *Phys. Rev. Lett.* **93**, 017402 (2004).
- [21] Y. C. Nah, S. S. Kim, J. H. Park, D. Y. Kim, *Electrochem. Solid-State Lett.* **10**, J12 (2007).
- [22] H. Y. Lin, C. L. Cheng, Y. Y. Chou, L. L. Huang, Y. F. Chen, *Optics Exp.* **14**, 2372 (2006).