

ENHANCEMENT IN NANOCRYSTALLINE TiO₂ SOLAR CELLS SENSITIZED WITH ZnPc BY NANOPARTICLES

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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 TiO₂ DSSCs exhibited poorer properties than others due to the nonradiative decay. GNPs- and ZnSe QDs-doped TiO₂ DSSCs sensitized with ZnPc demonstrated the energy conversion efficiency results to be 0.70 and 0.67 %, respectively.

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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 TiO₂ semiconductor electrodes by dyes. The key feature of this solar cell is the use of nanocrystalline TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ 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 μm-thick film. The nanoparticles were selected from Au nanoparticles, ZnSe QDs, or carbon nanotubes. All particle size is about 5 nm. The TiO₂ films with nanoparticles were annealed at 120 °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 I₂ (0.2 g) was deposited on the TiO₂ films with nanoparticles by spin coating to form an I₂-doped ZnPc film with a thickness of about 3 μm.

Finally, the electrolyte was formed by mixing uniformly 20 ml propylene carbonate, 0.254 g iodine (I₂), and 1.66 g KI. The electrolyte (~ 0.03 ml) was dropped into the film and combining with another ITO conductive glass with carbon coating to complete TiO₂ 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 mW/cm²) was used as the light source.

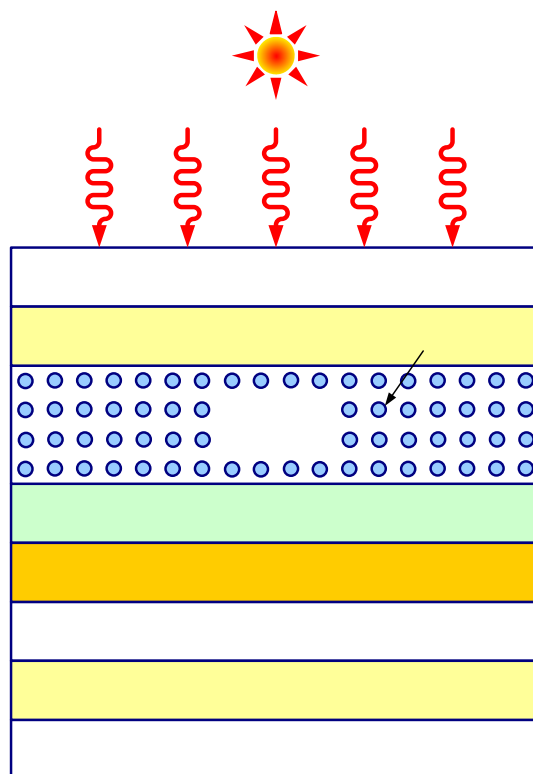


Fig. 1. Schematic cross section of the completed structure.

3. Results and discussion

Fig. 2(a) shows the energy level diagram and mechanism of photocurrent generation in GNPs-doped TiO₂ 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 TiO₂, such that a quick shuttling of electrons from Au to TiO₂ takes place. The electronics transferred to TiO₂ 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 TiO₂ 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 TiO₂ particles were collected at the back contact to generate a photocurrent. [6].

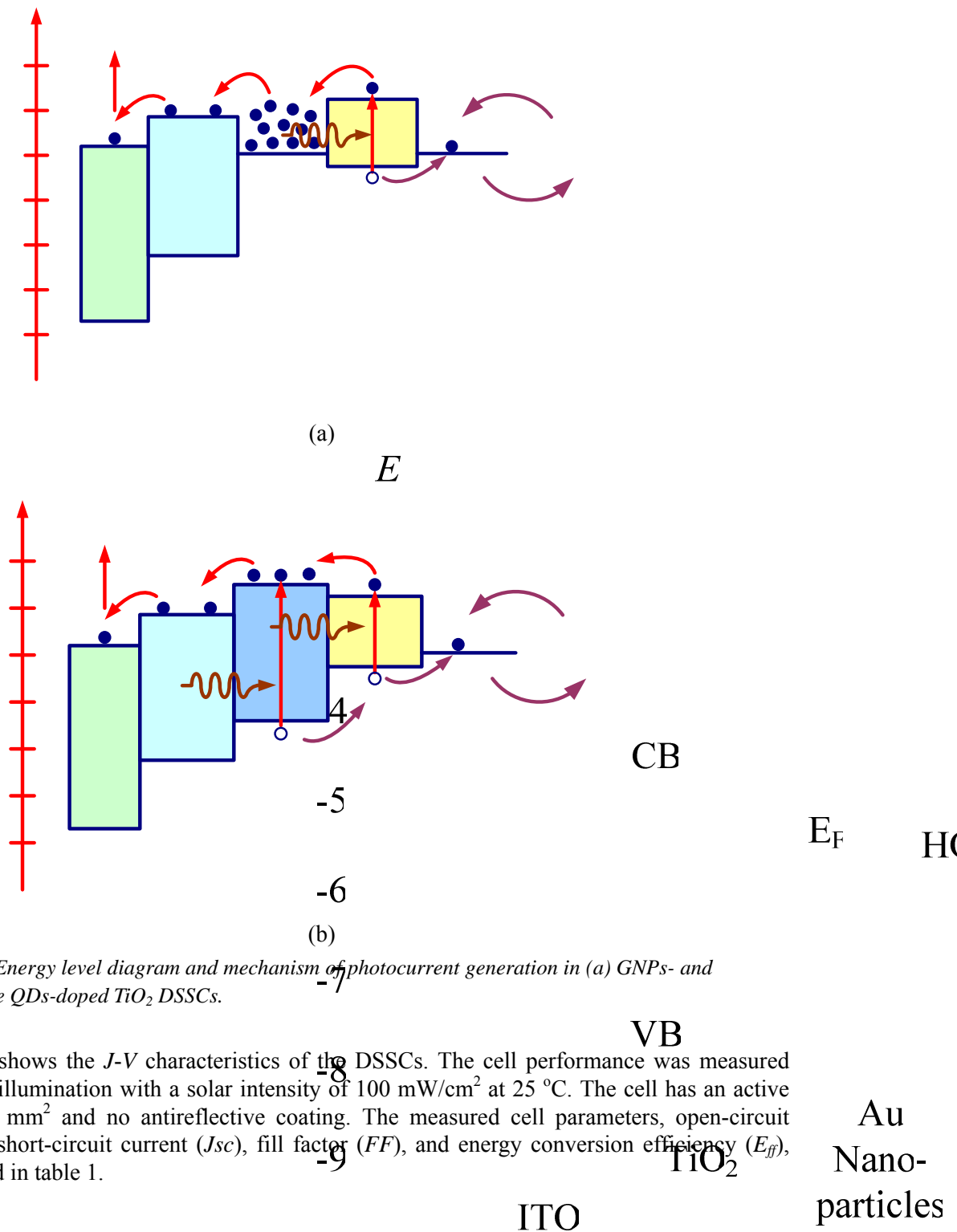


Fig. 2. Energy level diagram and mechanism of photocurrent generation in (a) GNPs- and (b) ZnSe QDs-doped TiO₂ DSSCs.

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/cm² at 25 °C. The cell has an active area of 3 × 3 mm² 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 TiO₂ DSSCs measured at 25 °C.

Nanoparticles	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	E _{ff} (%)	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%

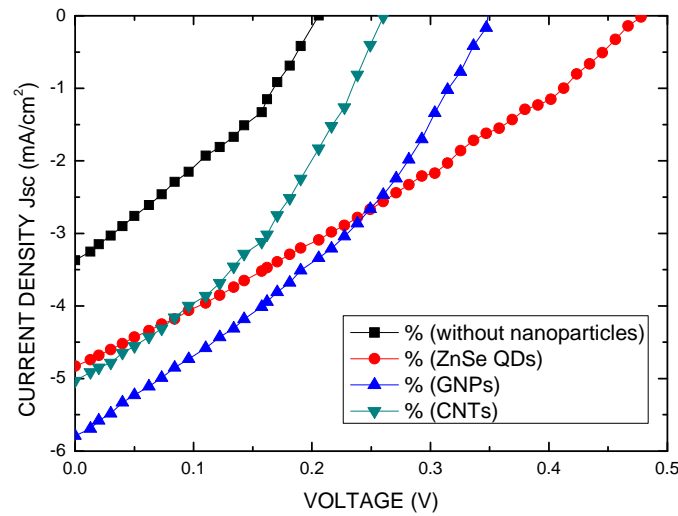


Fig. 3. J-V characteristics of solar cells.

As shown in Fig. 3, GNPs- and ZnSe QDs-doped TiO₂ DSSCs sensitized with ZnPc exhibited the following static parameters: V_{oc} of 0.35 V and J_{sc} of 5.79 mA/cm², and V_{oc} of 0.48 V and J_{sc} of 4.83 mA/cm², 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 TiO₂ 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 TiO₂ DSSCs. The IPCE at different wavelengths was determined from the

short circuit photocurrents monitored at different excitation wavelength (λ) using the expression

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

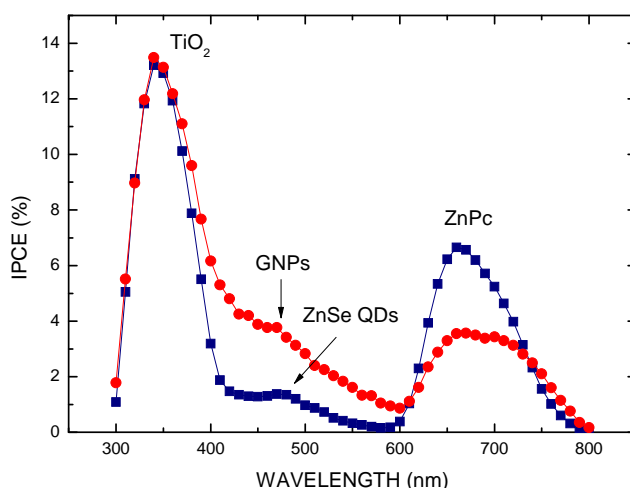


Fig. 4. The incident photon to current conversion efficiency spectra of GNP- and ZnSe QDs-doped TiO₂ DSSCs.

All cells show photocurrent responses in contrast with TiO₂ 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 TiO₂ 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 TiO₂ DSSCs sensitized with ZnPc demonstrated the following static parameters: V_{oc} of 0.35 V and J_{sc} of 5.79 mA/cm², and V_{oc} of 0.48 V and J_{sc} of 4.83 mA/cm², 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.

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