



Two dimensional graphitic-phase C_3N_4 as multifunctional protecting layer for enhanced short-circuit photocurrent in ZnO based dye-sensitized solar cells

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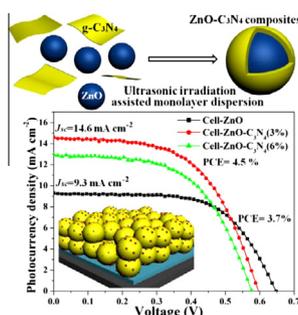
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HIGHLIGHTS

- g- C_3N_4 was decorated on ZnO nanoparticles *via* an ultrasonic irradiation assisted monolayer dispersion.
- The g- C_3N_4 expands the absorption spectrum of ZnO photoanode to visible region.
- The stepwise energy gradient at the interface improves the injection efficiency.
- Large stride J_{sc} and PCE enhancements ($\sim 57\%$ and $\sim 20\%$) were demonstrated on Cell-ZnO- C_3N_4 .

GRAPHICAL ABSTRACT

Two dimensional g- C_3N_4 was, for the first time, adopted in a solar energy conversion device and the DSSC with ZnO- C_3N_4 composite demonstrates a $\sim 57\%$ J_{sc} enhancement compared with that derives from pure ZnO.



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ABSTRACT

Two dimensional graphitic-phase C_3N_4 (g- C_3N_4) was successfully coated as multifunctional protecting layer on ZnO nanoparticles *via* ultrasonic irradiation assisted monolayer dispersion. The as-prepared composites were applied as photoanode materials in dye-sensitized solar cells. Based on the optical and electrochemical measurements, the g- C_3N_4 stretches the absorption spectrum of the ZnO based photoanodes to visible region and enhances the harvesting of low energy photons. Moreover, the g- C_3N_4 with compatible band structure builds a stepwise energy gradient at the ZnO/ C_3N_4 /dye interface, which improves the injection efficiency of photo-generated electrons and leads to $\sim 57\%$ enhancement in the short-circuit photocurrent of Cell-ZnO- C_3N_4 (3%). Therefore, a high power conversion efficiency of 4.5% was demonstrated, indicating $\sim 20\%$ improvement compared with the pure ZnO based device (3.7%).

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been intensively studied for decades because of their low cost, high efficiency and facile preparation process [1–3]. Photoanode is one of the key

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components in the configuration and nano-sized TiO_2 is the most commonly used photoanode materials. Due to the similar electron band structure, excellent bulk electron mobility and the richest family of nanostructures, ZnO is also regarded as promising candidate for the photoanode in DSSC [4–6]. Although many researchers have been devoted to prepare various ZnO structures for DSSC application, the highest power conversion efficiency (PCE) of ZnO-based devices merely reaches to $\sim 7.5\%$, which is far less than the TiO_2 based DSSCs with PCE of $\sim 13\%$ [7–10]. In addition, the ZnO nanoparticles are vulnerable in the ruthenium based dyes, because the acid function groups in the dye molecules can detach Zn^{2+} from the host lattice to form Zn^{2+} -dye agglomerations. The agglomerations on the ZnO surface not only result in low electron injection efficiency but also trigger massive charge recombination opportunities [11–13]. Therefore, surface modification with protecting layers such as SiO_2 , Al_2O_3 or TiO_2 were widely adopted to enhance the stability of ZnO and suppress the charge recombination [14–17]. In these researches, the additional coating layers function as physical passivating layer to minimize the direct contact between ZnO and the dye molecules, which could significantly improve the fill factor (FF) and open circuit voltage (V_{oc}) of the devices. However, the introduced semiconducting or insulating layers could not directly improve the harvesting efficiency of the incident light and usually bring forth injection problem of the photo-generated electrons. Therefore, these strategies seldom increases the short circuit current (J_{sc}) of the devices.

Recently, two-dimensional crystals with thicknesses in atom scale attracted extensive attentions because of their excellent electronic, optical, and biocompatible properties [18–20]. Metal-free graphitic-phase C_3N_4 ($g\text{-C}_3\text{N}_4$) possesses graphite-like structure with layer distance of ~ 0.33 nm and band gap of ~ 2.69 eV [21]. Heretofore, $g\text{-C}_3\text{N}_4$ with different topological structures and $g\text{-C}_3\text{N}_4$ based heterogeneous materials have been applied in various fields [22]. The foremost research interests are focused on the photo-degradation for environmental remediation [23–31] and water splitting for H_2 fuel [32–34]. In addition, the potential application of $g\text{-C}_3\text{N}_4$ were also expanded to many territories such as adsorption [35], fuel cell [36], sensors [37], bio-imaging [38], and Li ion batteries [39]. However, so far as we know, $g\text{-C}_3\text{N}_4$ has been seldom studied to explore its potential application in solar energy conversion devices [40].

In this work, ZnO- C_3N_4 composites were prepared by an ultrasonic irradiation assisted monolayer dispersion and the effects of $g\text{-C}_3\text{N}_4$ coating layer on the performances of ZnO-based DSSCs were interpreted (Scheme 1). It was found that the $g\text{-C}_3\text{N}_4$ could expand the absorption spectra of ZnO based photoanodes to visible

region and enhance the harvest of low energy photons. Moreover, the compatible band structure of $g\text{-C}_3\text{N}_4$ builds a stepwise energy gradient at the ZnO/ C_3N_4 /dye interface, which improves the injection efficiency of photo-generated electrons and finally leads to $\sim 57\%$ J_{sc} enhancement. Therefore, a higher PCE of 4.5% was demonstrated, indicating $\sim 20\%$ improvement compared with the pure ZnO based device.

2. Materials and methods

2.1. Materials preparation

2.1.1. Graphitic-phase C_3N_4

The $g\text{-C}_3\text{N}_4$ nano-sheet is prepared through an ultrasonic assisted liquid phase exfoliation. The bulk C_3N_4 was prepared by heating melamine at 550°C for 2 h in N_2 atmosphere. 0.1 g of the yellowish product are grounded and ultrasonicated in 100 mL distilled water for 1 h and centrifuged for 15 min at 4000 rpm to remove the unexfoliated $g\text{-C}_3\text{N}_4$ and obtain the light yellow suspension for later use.

2.1.2. ZnO nanoparticles

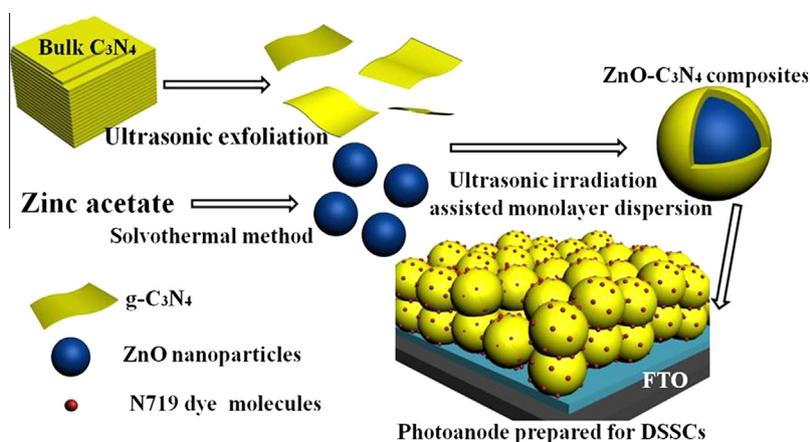
The ZnO nanoparticles were prepared by decomposing $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ in a solvothermal method. Briefly, 0.3 g $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was dispersed into 40 mL absolute ethanol. After stirring for 1 h, the suspension was transferred into 50 mL Teflon-lined autoclave and heated at 180°C for 4 h. The white powder were rinsed with distilled water and absolute ethanol, and finally dried in vacuum for later use.

2.1.3. ZnO- C_3N_4 hybrid materials

The ZnO- C_3N_4 hybrid materials were prepared by monolayer dispersion method proposed by Zhu et al. and received a slight modification [41]. Typically, 0.2 g of ZnO nanoparticles were dispersed into appropriate volume of $g\text{-C}_3\text{N}_4$ suspension and the mixtures were placed in ultrasonic bath for 30 min and then stirred to volatilize the water for about 2 days. The products were dried in vacuum for 3 h at 100°C . The loading amount of the $g\text{-C}_3\text{N}_4$ was controlled by the volume of the $g\text{-C}_3\text{N}_4$ suspension. In addition, ZnO loaded with 3 wt.% and 6 wt.% $g\text{-C}_3\text{N}_4$ are named as ZnO- C_3N_4 (3%) and ZnO- C_3N_4 (6%).

2.2. Preparation of the photoanodes

Hydroxypropyl cellulose was added into diethylene glycol with a concentration of ~ 10 wt.% under magnetite stirring to yield



Scheme 1. Schematic illustration of the ultrasonic irradiation assisted monolayer dispersion to prepare the ZnO- C_3N_4 composites and their application as multifunctional protecting layer on the photoanode for DSSCs.

transparent paste for later use. The as-prepared paste was added into the ZnO–C₃N₄ (3%) and ZnO–C₃N₄ (6%) with appropriate ratio and stirred to obtain homogenous slurries. Doctor-blade method was adopted to deposit the slurries onto fluorine-doped tin oxide (FTO) glass substrate (TEC-8, LOF). After dried in air, the photoanodes were heated to 450 °C with a rate of 5 °C min⁻¹ and maintained for 30 min. The film thicknesses were all controlled at ~12 μm. After cooled to 80 °C, the films were sensitized in a solution of cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) bis-tetrabutylammonium (N719, Solaronix SA, Switzerland) in ethanol (3×10^{-4} M) for 1 h. The dyed films were then sandwiched together with platinized FTO counter electrodes and electrolyte was then injected into the cell from the edges by capillarity. The content of the electrolyte is 0.05 M LiI, 0.05 M I₂, 0.5 M 4-terbutylpyridine and 0.6 M 1-propyl-3-methylimidazolium iodide (PMII) in 3-methoxypropionitrile.

2.3. Materials characterizations

The morphologies and structures of the products were characterized by field-emission scanning electron microscopy (FESEM, HITACHI, S4800), X-ray powder diffraction (XRD, Rigaku D/max-2500 diffractometer with Cu K α radiation, $\lambda = 0.1542$ nm, 40 kV, 100 mA), transmission electron microscopy (TEM, FEI Tecnai F30), and Brunauer–Emmett–Teller (BET, Micrometrics ASAP 2010). The high-angle annular dark field scanning transmission electron microscopy (STEM-HAADF) was employed using the same TEM instrument, which is equipped with a scanning unit and a HAADF detector from Fischione (model 3000). Additionally, the compositional analysis of the microstructures was performed with the energy dispersive X-ray spectroscopy (EDS, EDAX Inc.) attachment on the Tecnai F30 during the TEM measurements.

2.4. Photovoltage measurements

Photocurrent–voltage (*I*–*V*) measurements were performed on a Keithley 4200 semiconductor characterization system using simulated AM 1.5 sunlight with an output power of 100 mW cm⁻²

produced by a solar simulator (Newport 69911). Incident monochromatic photo-to-electron conversion efficiency (IPCE) was recorded on a Keithley 2000 sourcemeter under the irradiation of a 150 W tungsten lamp with 1/4 m monochromator (Spectral Product DK240). The optical diffuse-reflection spectra were measured by spectrophotometer (HITACHI U-4100). Mott–Schottky spectra were obtained with Frequency Response Detector (FRD 100) and Potentiostat/Galvanostat Model 283 System (Princeton Applied Research). The potential was systematically varied between 1.00 and –1.00 V with the frequency of 1000 Hz by choosing Mott–Schottky technique template.

3. Results and discussion

The SEM image displayed in Fig. 1a shows the as-prepared ZnO nanoparticles have prism-like shapes and the particle size is about 20–50 nm. The TEM image in Fig. 1b shows well-defined lattice fringes and the interplanar spacing could be measured as ~0.26 nm, which corresponds to the (0001) plane. After coated with ~3% (wt) g-C₃N₄, many wrinkle-like patterns appear on each ZnO nanoparticle, which is obviously different from the clear surface condition of pure ZnO, indicating the homogenous coverage of g-C₃N₄ (Fig. 1c). As it is described in Zhu et al.'s pioneer work, the uniform coverage derives from monolayer dispersion of sheet-like g-C₃N₄ on the surface of ZnO nanoparticles and the driving force is the minimization of surface free energy [41]. As depicted in Fig. 1d, the HRTEM image taken from one of the nanoparticles clearly reveals the (0001) and (01 $\bar{1}$ 0) lattice planes of wurtzite structured ZnO with interplanar spacing of ~0.26 and ~0.28 nm, which could be further confirmed by the inset FFT dot patterns. In addition, very thin amorphous-like layer could be observed, which is distinctly different from the clear surface of pure ZnO, indicating g-C₃N₄ layer was coated on the ZnO surface. The thickness could be roughly measured as ~0.39 nm, suggesting the g-C₃N₄ layer was approximately coated with monolayer patterns. High-angle annular dark field scanning transmission electron microscopy (STEM-HAADF) was employed to compositionally analysis the composite (Fig. 1e). The energy dispersive X-ray spectrum shows the

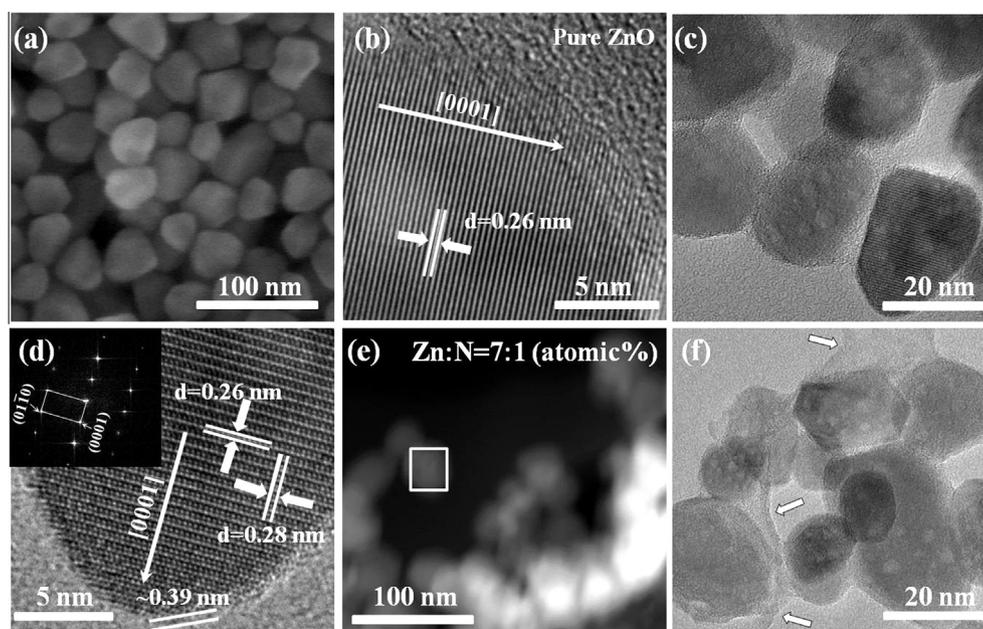


Fig. 1. (a) The SEM and (b) TEM images of as-prepared ZnO particles, (c and d) TEM images of the ZnO particles coated with 3% g-C₃N₄, the inset is Fast Fourier transform (FFT) patterns of the lattice fringes, (e) Zn/N atom ratio measured by energy dispersion analysis in the STEM-HAADF mode and (f) TEM image of the ZnO particles coated with 6% g-C₃N₄.

ratio between Zn and N in an individual particle (marked in white square) is 7/1, indicating the dosage of g-C₃N₄ in ZnO is ~3.88% (wt) which is in accord with our experimental dosage. Fig. 1f shows the TEM image of ZnO–C₃N₄ (6%). In addition to the g-C₃N₄ coated on ZnO nanoparticles, individual sheet-like patterns could be also observed (denoted by the arrows), implying excessive g-C₃N₄ was added for the surface modification.

The crystallographic structures of the samples are confirmed by the X-ray diffraction (XRD) and displayed in Fig. 2. The ZnO nanoparticle is highly crystallized and of pure wurtzite phase. In addition, no obvious characteristic diffractions peaks belonging to g-C₃N₄ is detected in the ZnO–C₃N₄ composites (3% and 6%), indicating the g-C₃N₄ is uniformly coated on the ZnO nanoparticles. As described in previous work, the composite with 6% g-C₃N₄ dosage usually exhibits a weak g-C₃N₄ peak. In our case, the ultrasonic irradiation could better disperse the g-C₃N₄ monolayer on ZnO nanoparticles, which diminishes the characteristic diffraction peak of g-C₃N₄. The samples are further investigated by Fourier Transform Infrared (FT-IR) spectra (Fig. 3). For g-C₃N₄, the peaks centered at 1243, 1324, 1415, 1421, 1564, and 1645 cm⁻¹ dominate the spectrum, corresponding to the typical stretching mode of CN heterocycles. Additionally, the characteristic breathing mode of s-triazine ring is observed at 807 cm⁻¹. [41,42] As for ZnO–C₃N₄ composites, the main characteristic peaks belonging to g-C₃N₄ are suppressed, indicating the bond strengths of intrinsic C–N bonds are weakened. Moreover, new prominent signals at 1156 cm⁻¹ corresponding to the C–O bonding are observed, which indicates that new bonding models are formed between the C and O atoms respectively from g-C₃N₄ and ZnO. The FT-IR analysis demonstrates that a conjugated system was built between g-C₃N₄ and ZnO, which may be of great significance for the charge migration in the hybrid material.

Pure ZnO and ZnO with different g-C₃N₄ dosages (3% and 6%) were respectively deposited on FTO substrate as photoanodes for DSSC application. The photovoltaic performances of the as-prepared DSSCs were tested under one sun illumination with a power density of 100 mW cm⁻². Fig. 4 shows the typical *I*–*V* curves of the DSSCs and the detailed photovoltage characteristics are listed in Table 1. Cell-ZnO shows *J*_{sc} of 9.3 mA cm⁻², *V*_{oc} of 646 mV and *FF* of 61.6%, which gives a *PCE* of 3.7%. Although the *FF* and *V*_{oc} of Cell-ZnO–C₃N₄ (3%) are decreased, it demonstrates a much higher *J*_{sc} of 14.6 mA cm⁻², indicating ~57% enhancement compared with Cell-ZnO, which leads to a higher *PCE* of 4.5%.

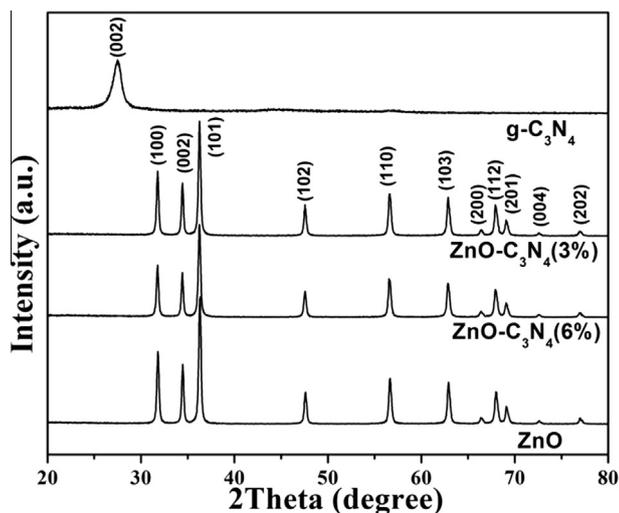


Fig. 2. The XRD patterns of the as-prepared g-C₃N₄, ZnO–C₃N₄ (3%), ZnO–C₃N₄ (6%) and ZnO nanoparticle.

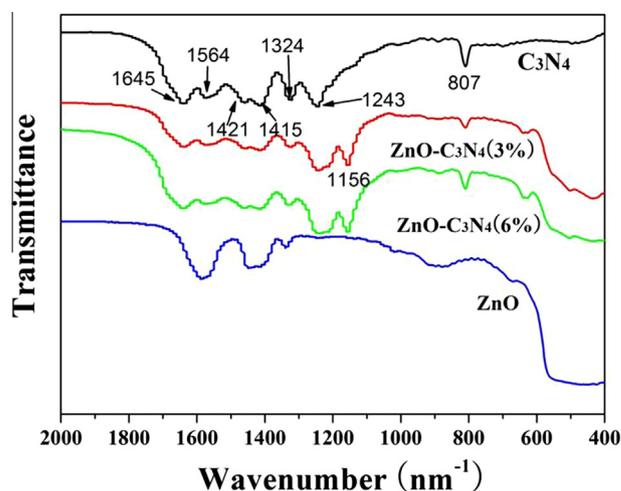


Fig. 3. FT-IR spectra of the as-prepared g-C₃N₄, ZnO–C₃N₄ (3%), ZnO–C₃N₄ (6%) and ZnO nanoparticle.

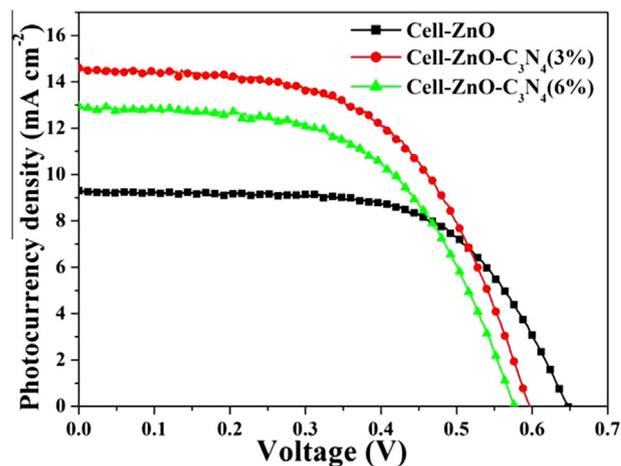


Fig. 4. The current–voltage characteristics measured under one sun (100 mW cm⁻²) of the as-prepared DSSCs.

Table 1

The photovoltaic characteristics for DSSCs based on the pure ZnO, ZnO–C₃N₄ (3%) and ZnO–C₃N₄ (6%).

| Cells | <i>J</i> _{sc} (mA cm ⁻²) | <i>V</i> _{oc} (mV) | <i>FF</i> (%) | <i>PCE</i> (%) | Dye absorb. (mol cm ⁻²) |
|--|--|--------------------------------|------------------|-------------------|--|
| ZnO | 9.3 | 646 | 61.6 | 3.7 | 2.5 × 10 ⁻⁷ |
| ZnO–C ₃ N ₄ (3%) | 14.6 | 596 | 51.7 | 4.5 | 2.4 × 10 ⁻⁷ |
| ZnO–C ₃ N ₄ (6%) | 12.9 | 576 | 48.4 | 3.6 | 2.2 × 10 ⁻⁷ |

Thanks to the g-C₃N₄ coating layer, the *J*_{sc} of Cell-ZnO–C₃N₄ (6%) is also improved. Nevertheless, the greatly reduced *FF* and *V*_{oc} result in a lower *PCE* of 3.6%. It is obvious that the higher *PCE* of Cell-ZnO–C₃N₄ (3%) derives from the substantially improved *J*_{sc}.

The *J*_{sc} variation is complicated and the affecting factors are rather multiple-folded. Generally, the *J*_{sc} is determined by the light harvesting efficiency of the photoanode, the injection and collection efficiencies of the photoelectrons [43,44]. UV–vis absorption spectra of the photoanodes before and after dye loading are presented in Fig. 5a and b. Without dye loading, the ZnO film shows clear absorption onset at ~380 nm which corresponds to the intrinsic band edge absorption of ZnO. Due to the incorporation

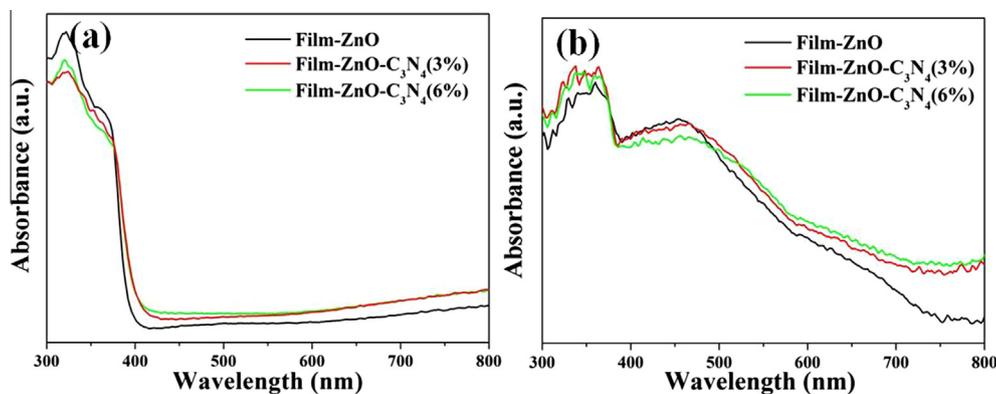


Fig. 5. The UV-vis absorption spectra of the photoanode films (a) before and (b) after dye loading.

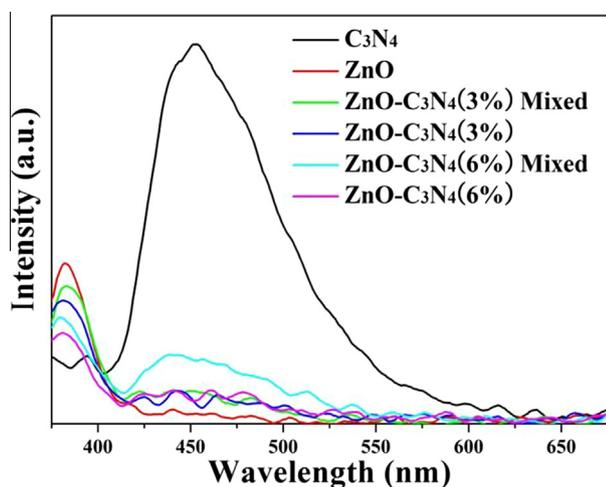
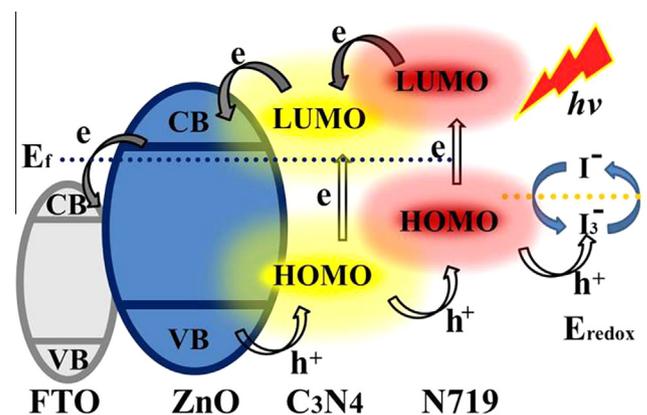


Fig. 6. Photoluminescence spectra of the g-C₃N₄, ZnO and the composites prepared through monolayer dispersion and directly mixed ZnO and g-C₃N₄.

of g-C₃N₄, Film-ZnO-C₃N₄ (3%) shows evident red shift and the absorbance was also enhanced in the range of 400–800 nm, which suggests that the band gaps of these composites are reduced [45]. Compared with Film-ZnO-C₃N₄ (3%), no obvious band shift is detected in Film-ZnO-C₃N₄ (6%). Moreover, the absorbance in the region of 400–600 nm is slightly enhanced as increasing the g-C₃N₄ dosage. After loaded with N719 dyes, Film-ZnO-C₃N₄ (3%) shows similar absorbance in the range of 400–600 nm corresponding to the intrinsic absorption of N719, which indicates the low g-C₃N₄ dosage won't affect the dye loading amount (Table 1). Moreover, the Film-ZnO-C₃N₄ (3%) shows higher absorbance in the range from 500 to 800 nm, implying more visible light could be trapped in the photoanode as g-C₃N₄ was introduced. However, as increasing the g-C₃N₄ dosage, the absorbance in the range of 550–800 nm is further promoted for Film-ZnO-C₃N₄ (6%). However, the absorbance in the range of 400–550 nm is greatly reduced, which proves the dye loading amount is reduced (Table 1). In order to interpret the differences in the dye loading amount of the photoanodes, the surface area of the composites were measured as 39.1 and 40.3 m² g⁻¹ for ZnO-C₃N₄ (3%) and ZnO-C₃N₄ (6%) respectively, which are marginally increased from that of pure ZnO (38.6 m² g⁻¹). However, the dye loading amount of the photoanodes are slightly reduced as increasing the dosage of g-C₃N₄ (Table 1). Therefore, it could be concluded that the introduced g-C₃N₄ didn't help to increase the dye loading amount of the



Scheme 2. Illustration of the stepwise energy levels built at the ZnO/C₃N₄/dye interface.

photoanodes but increase the light harvesting at the longer wavelength range (500–800 nm), which finally leads to the J_{sc} enhancement.

In addition, the band gap of g-C₃N₄ is 2.69 eV, and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) potentials of g-C₃N₄ are -1.12 and 1.57 eV, respectively [21]. Therefore, when coated on the ZnO surface, a stepwise band alignment could be built, which facilitates the photoelectron injection and the hole scavenging of the redox couples. The band alignment between ZnO and g-C₃N₄ could be verified by the photoluminescence (PL) spectra [25,27,31]. The PL curves of pristine g-C₃N₄, ZnO, and composites including ZnO-C₃N₄ (3%), ZnO-C₃N₄ (6%), ZnO-C₃N₄ (3%, mixed) and ZnO-C₃N₄ (6%, mixed) are shown in Fig. 6. The emission peak of pristine g-C₃N₄ appears at ~450 nm (denoted as Vis-peaks), which is attributed to the band edge emission of g-C₃N₄. While, the peaks centered at ~380 nm (denoted as UV-peaks) represent the near-band-edge recombination of ZnO. Compared with the sample directly mixed with 3% g-C₃N₄, the UV-peak intensity of ZnO-C₃N₄ (3%) is further suppressed, indicating the charge transfer between ZnO and g-C₃N₄ is promoted. Similarly, with same g-C₃N₄ dosage level, ZnO-C₃N₄ (6%) shows much lower Vis-peak than ZnO-C₃N₄ (6%, mixed). The quenching of both the UV- and visible-emissions demonstrate the effective separation of photogenerated electrons and holes at the ZnO/C₃N₄ interface [46]. As displayed in Scheme 2, an energy gradient could be built at the ZnO/C₃N₄/dye interface due to the band alignment, which enhances migration of the charge carriers and the injection efficiency of photogenerated electrons.

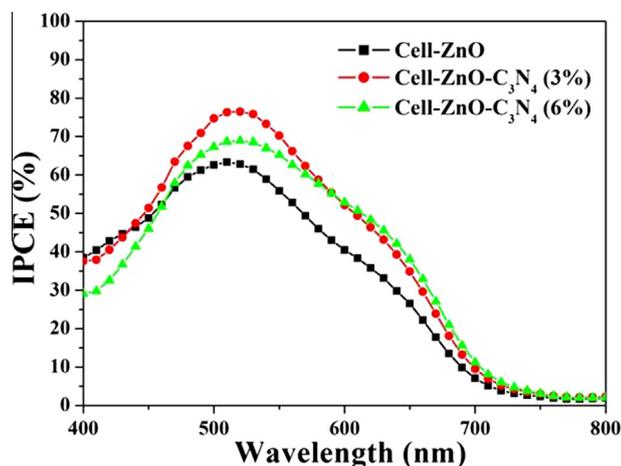


Fig. 7. Incident photon to current efficiency (IPCE) spectra of the as-prepared DSSCs.

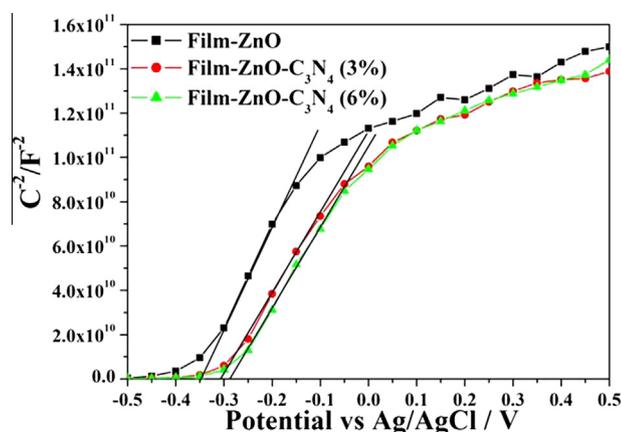


Fig. 8. Mott-Schottky spectra of the photoanode films without N719 sensitization.

Fig. 7 shows the incident photon to current efficiency (IPCE) spectra in function of wavelength, which directly reflects the J_{sc} variation. Cell-ZnO- C_3N_4 (3%) shows much higher IPCE value than Cell-ZnO, especially in the range of 550–800 nm. In addition, the IPCE in the range of 600–700 nm is enhanced for Cell-ZnO- C_3N_4 (6%) because more g- C_3N_4 is decorated on the photoanode. However, the IPCE in the range of 400–500 nm is decreased, which matches well with the optical and dye uptake measurements.

It should be noticed that, for Cell-ZnO- C_3N_4 (3%), the $\sim 57\%$ J_{sc} augment only leads to $\sim 20\%$ enhancement in PCE, which obviously derives from the reduced FF and V_{oc} compared with Cell-ZnO. As indicated in previous literature, the low FF mainly results from the increased series resistance of the cell [15]. Considering the g- C_3N_4 was wrapped on each ZnO nanoparticle, the additional coating layer inevitably increases the series resistance of photoanode. Moreover, the V_{oc} of the devices could be expressed according to Eq. (1), [47]

$$V_{oc} = \frac{E_{cb}}{q} + \frac{kT}{q} \ln \left(\frac{n}{N_{cb}} \right) - \frac{E_{redox}}{q} \quad (1)$$

where E_{cb} is the conduction band edge, E_{redox} is the energy level of redox couples in the electrolyte, k_bT is the thermal energy, n_c is the free electrons density in the conduction band and N_c is the effective density of conduction band states. The sum of first two items in Eq. (1) is the quasi Fermi energy level (E_f) of the photoanode. Therefore, the V_{oc} is determined by the voltage gradient between

the E_f and the E_{redox} [48]. Moreover, E_f is greatly affected by the variation of E_{cb} . As shown in Fig. 5a, the red shift of absorption curve indicates the band gap of the ZnO- C_3N_4 composites are reduced, which is usually associated with the downward shift of E_{cb} . Thermodynamically, the lower E_{cb} will lead to a lower E_f position and reduce the V_{oc} of DSSC. In addition, the Mott-Schottky analysis on the flat potential is a powerful method to directly indicate the E_f shift [49,50]. As shown in Fig. 8, the ZnO- C_3N_4 curves are shifted to positive potential range compared with that of pure ZnO, suggesting the g- C_3N_4 decoration leads to a downward E_f shift of the photoanode. Considering the E_{redox} usually remains unchanged, the V_{oc} of corresponding ZnO- C_3N_4 based DSSCs are decreased accordingly.

4. Conclusions

Two dimensional g- C_3N_4 was incorporated as multifunctional protecting layer on ZnO nanoparticles via a monolayer dispersion method. The as-prepared ZnO- C_3N_4 (3%) composite shows enhanced photovoltaic performances than pure ZnO when used in DSSCs. Based on the optical and electrochemical investigations, the enhancement could be ascribed to the following reasons: (1) the g- C_3N_4 reduces the band gap of the composite, which expands the absorption spectrum and enhances the light harvesting of the photoanode, (2) the compatible band structure of g- C_3N_4 builds stepwise energy gradient at ZnO/ C_3N_4 /dye interface, which improves the injection efficiency of photo-generated electrons, (3) the g- C_3N_4 may also function as a physical barrier layer to avoid the direct contact between the ZnO and the acid dye molecules to alleviate the corrosion of ZnO surface. In addition, the Achilles' Heel is that the g- C_3N_4 layer increases the series resistance and decreases the E_f of the photoanode, which results in lower FF and V_{oc} . Nevertheless, due to great J_{sc} enhancement ($\sim 57\%$), Cell-ZnO- C_3N_4 (3%) demonstrates higher PCE of 4.5%, indicating $\sim 20\%$ improvement compared with Cell-ZnO. Based on the intrinsic qualities such as suitable band structure, ultrathin thickness, chemical and photo-stability, environmental benign and low cost, g- C_3N_4 may be further applied as sensitizers, conducting materials or interfacial layers in other solar energy conversion devices.

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