A layer-by-layer assembled graphene/zinc sulfide/polypyrrole thin-film electrode via electrophoretic deposition for solar cells

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Abstract

An organic–inorganic photo voltaic electrode consisting of graphene nanosheets, zinc sulfide nanoparticles (ZnS) and polypyrrole nanotubes (PPy) was fabricated on indium tin oxide (ITO) glass using layer-by-layer electrophoretic deposition. The morphology and structure of the as-fabricated electrode were confirmed by X-ray diffraction, high resolution transmission electron microscopy, energy dispersive X-ray analysis, Fourier transform infrared spectroscopy and Raman spectroscopy. The photovoltaic properties of the ZnS, ZnS/PPy (ZP) and graphene/ZnS/PPy (GZP) ternary composite films modified on ITO electrodes were investigated for their solar cell performance. Both transient photocurrent and current–voltage curve measurements illustrated that the photocurrent and the power conversion efficiency of the GZP ternary composite film were significantly enhanced compared to the ZnS and ZP films. Based on these results, PPy nanotubes are an excellent sensitizer and hole acceptor. ZnS nanoparticles act as a bridge and graphene nanosheets are an excellent conductive collector and transporter, which means that, altogether, this combination of materials can significantly increase the photovoltaic efficiency.

Keywords:
Zinc sulfide
Polypyrrole nanotubes
Graphene
Solar cells
Photovoltaic response
Electrophoretic deposition

1. Introduction

The shortage of fossil fuels and the rapid growth of environmental pollution have initiated the need for clean and renewable energy for the sustainability of our society. Solar energy, as the cleanest and least limited energy source, is considered to be an alternative to conventional fossil fuels [1–6], but the vast majority of commercial solar cell modules are based on crystalline silicon due to its high efficiency of approximately 24% [7]. However, this high efficiency is offset by the high cost of commercial solar cell modules [8]. In recent years, to overcome this barrier, many efforts have been focused on developing photovoltaic devices that are inexpensive and non-toxic and that have high stability and high efficiency. Organic–inorganic hybrids, which are used in nanostructured solar cells, are materials that combine electroactive organic molecules and inorganic semiconductors to produce a class of solar cell materials that exhibit high power efficiency in solar energy conversion. A large number of various semiconductors have been investigated for organic–inorganic hybrid solar cells [9,10], especially titanium dioxide (TiO2) nanoparticles, which have been extensively utilized due to their high power conversion efficiency [11].

ZnS is another promising semiconductor, but it has been less explored.

ZnS is an n-type semiconductor with a wide band gap, which is widely utilized in lasers [12], photodetectors [13], light-emitting diodes [14], among others. ZnS is a favorable candidate as a working electrode to substitute for other semiconductors in solar cell devices. For instance, the conduction bands (CB) of both TiO2 and ZnS are approximately the same, while ZnS has a higher electron mobility (approx. two orders of magnitude) [15], which could be favorable for the collection of photoinduced electrons. Modification of the working electrode with semiconductor nanoparticles leads to a higher efficiency for solar cell devices. Over the last few decades, several methods have been used to improve the efficiency of semiconductor working electrodes: (a) improvement of light harvesting or coating a scattering layer on the surface of semiconductor working electrodes to reduce the loss of the photon energy; [16,17] (b) increase of the overpotential that leads to improvement of the electron injection rate; [18] (c) decrease of the possibility of photoinduced charge carrier recombination, which extends the electrode lifetime; [15] (d) change in the redox couple Fermi level to increase the dye regeneration rate; [19] and (e) modification of the chemical composition of the semiconductor working electrode by doping: loading a second semiconductor into the composite or loading polymers, especially conductive polymers, including polyaniline; polythiophene, poly(p-phenylene vinylene); and polypyrrole (PPy) [20–22].

PPy is a p-type organic semiconductor that has a broad absorption spectrum, from the ultraviolet to the visible light region, and a high molar extinction coefficient [23], which makes it a suitable candidate for use in solar cells. It has high mobility, high stability, high conductivity and easy one-step deposition. Polypyrrole can be accumulated on the surface of a solid substrate by simple electropolymerization of pyrrole monomer in an electrolytic cell containing suitable supporting electrolytes [24]. Polypyrrole nanotubes (PPy) are formed by rolling up polypyrrole nanofilaments into a stable nanotube structure [25], with high surface area [26,27]. The polypyrrole surface has a high affinity for various molecules due to its polar nature, which is useful for the immobilization of orga...
for a class of organic–inorganic solid materials with improved light harvesting properties. Higher absorption of incident radiation causes increased migration of the photoinduced electrons from the PPy layer to the ZnS layer, which eventually leads to the generation of higher photocurrents. However, a number of problems remain. For instance, the wide band gap of ZnS leads to low conductance and poor contact with the electrode [24]. Moreover, the efficient dissociation of strongly bound excitons into free photoinduced charge carriers and the subsequent charge collection and transfer are crucial factors for the increase of energy conversion efficiencies. To avoid these problems for improved efficiency, we provide an electron accepting medium for the p–n junction of the PPy–ZnS layer to effectively retard the photo-excited electron–hole recombination and to tailor the charge transport pathway.

Graphene, a flat monolayer of sp²-bonded carbon atoms that are tightly packed into a two-dimensional honeycomb lattice, has attracted tremendous attention due to its excellent properties, such as high crystallinity [25], superior electrical conductivity [26] and high surface area [27]. It also illustrates great promise for the fabrication of solar cell devices [28]. Although graphene has poor photoelectric properties, the formation of heterojunction nanostructures can expand, improve, or alter the properties and applications of pristine graphene [29]. Among the various properties of graphene, its high conductivity makes it a great material to accept photoinduced charge carriers and promote the electron transfer rate of the semiconductor conduction band by trapping photogenerated electrons, thus improving the efficiency of solar cell devices [28]. Many approaches, such as chemical vapor deposition, arc discharge, solar radiation and chemical conversion in liquid-phase, have been developed to prepare graphene [30–33]. Up to now, there has been no report of the fabrication of graphene–PPy composites with ZnS nanoparticles or investigation of the effects of graphene in a photovoltaic device. Herein, we fabricated a photo-sensitized inorganic–organic layer-by-layer structured electrode consisting of a PPy–ZnS composite and graphene deposited by electrophoretic deposition (EPD). EPD allows for the precise control of the several deposited layers without organic binders or additives, and more importantly, EPD leads to good electrical contact between the composite film and conductive substrate. The present study reports the example of enhancing the photovoltaic response of a p–n junction PPy–ZnS-modified indium tin oxide (ITO) electrode with the incorporation of graphene.

2. Experimental methods

2.1. Chemical reagents

All chemicals were purchased from Merck Co., were of analytical purity and were used without further purification. Double distilled water was utilized for all experimental procedures. All experiments were carried out at atmospheric air pressure.

2.2. Synthesis of ZnS nanoparticles

In a typical process, 20 ml of 0.008 M thiourea was added drop-wise into 20 ml of 0.005 M zinc chloride (ZnCl₂) with vigorous stirring for 45 min. The mixture was transferred into a 60 ml Teflon-lined container and autoclaved at 140 °C for 10 h in a hydrothermal reaction. The washing process was then repeated with ethanol and distilled water 3 times before drying the nanoparticles at 60 °C for 12 h.

2.3. Synthesis of PPy nanotubes

PPy nanotubes were prepared by following the method reported by An et al. [34]. 2 mmol of methyl orange and 20 mmol of FeCl₃ were dissolved in 500 ml of distilled water, followed by the addition of 0.84 ml pyrrole monomer with stirring for 24 h. The as-prepared sample was filtered and washed with distilled water several times, and then dried at 50 °C for 12 h.

2.4. Preparation of graphene nanosheet

Micron-sized graphite powder (1–2 μm, Aldrich) was utilized as the initial precursor for the synthesis of graphene oxide (GO) by a modified Hummers method [35]. In a typical reduction procedure from GO to graphene, 30 mg of GO powder was dispersed with 60 ml of distilled water with the aid of ultrasonication to form a black-brown GO aqueous colloidal suspension. Then, 50 μl of hydrazine hydrate solution (Aldrich, 80 wt.% in water) was added to the GO solution in a 100 ml flask. After being vigorously stirred for 10 min, the mixture was heated at 160 °C with a microwave irradiation power of 150 W for 5 min using a microwave system (AX1100 VR Steamwave, 27 l, 900 W) cooled to room temperature, forming a black graphene aqueous dispersion. Subsequently, graphene powder was prepared by centrifugation of graphene dispersion.

2.5. Modification and EPD of graphene-modified ITO electrode

To obtain a homogeneous suspension (0.05 mg l⁻¹), 2 mg of Mg(NO₃)₂ and 2 mg of graphene were dispersed in 40 ml of isopropyl alcohol under ultrasonication for 15 min. Before EPD, the suspension was adjusted to pH 3 with a NaOH solution. A pair of ITO glass substrates, with an area of 12 mm × 20 mm, was immersed in a 5% HF solution for a few minutes to remove the native oxide layer followed by washing in acetone and distilled water and then was vertically immersed into the suspension. The linear distance between the two electrodes was kept at 10 mm. The DC power supply and deposition time were set at 30 V and 10 min during EPD to form the Mg-modified graphene film.

2.6. The layer-by-layer deposition of graphene/ZnS/PPy (GZP)-, pure ZnS- and ZnS/PPy (ZP)-modified ITO electrodes by EPD

The experimental set-up for the layer-by-layer deposition of the GZP ternary composite followed by EPD was reported by Mehrali et al. [36]. The electrolyte solution was prepared by adding 30 mg of ZnS and 8 mg of poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) nanotubes to 40 ml isopropyl alcohol separately and then ultrasonicing for 20 min. Both electrolytes were adjusted to pH 3 with dilute HCl. EPD was carried out in a conventional two-electrode cell at a constant voltage of 60 V for 5 min. A clean ITO glass substrate was the positive electrode (anode), while a fresh graphene film-coated ITO was the counter electrode (cathode). The linear distance between the two electrodes was approximately 10 mm. The suspensions were pumped through the deposition cell by peristaltic pumps. Peristaltic tubing was used for the circulation system, and the diameter of the tubing was 6 mm. The maximum and minimum feed rates were 4.30 and 0.14 ml s⁻¹. The freshly coated film was kept to dry at 50 °C in a vacuum oven to remove all of the solvent from the EPD. The preparation of the pure ZnS- and ZnS/PPy (ZP)-modified ITO electrodes by EPD is the same as for the GZP ternary composite film mentioned earlier. The electrolyte solution contained 30 mg of ZnS and 8 mg of PPy dispersed in 40 ml of isopropyl alcohol.

2.7. Device and photoelectrochemical measurements

All working electrodes were prepared by EPD. The organic–inorganic solar cell devices were assembled by layer-by-layer composite working electrodes that consisted of graphene, ZnS, ZP and GZP photoanode-modified ITO films and a Pt foil as a counter electrode, which was filled with the electrolyte in a 50 μm thick spacer. The 1:1 liquid electrolyte consisted of 0.5 M KI, 0.05 M I₂, 0.6 M tetraethylammonium iodide and 0.5 M 4-tert-butylypyridine in acetonitrile. A PLS-SXE150 halogen lamp (Beijing perfectlight Technology Corp., China) was utilized as an illumination source. The light intensity at the photoanodes was 10 mW/cm², the area illuminated of photoanodes was 0.5 cm² and the distance
between the working electrode and the lamp was approximately 40 cm. The photocurrent was recorded continuously during the on and off period of the lamp. The photocurrent transient measurements and current-voltage (I–V) curves of the films were performed using a potentiostat/galvanostat (Autolab PGSTAT30) from Ecochemie (Netherlands).

2.8. Characterization

The phase and crystallite size of the ZnS nanoparticles were characterized using an automated X-ray powder diffractometer (XRD, PANalytical’s Empyrean) with monochromated CuKα radiation (λ = 1.54056 Å). The particle size and the structural characterization of the as-synthesized product were performed using high-resolution transmission electron microscopy (HRTEM, FEI–Tecnai) and high-resolution field-emission scanning electron microscopy (FESEM, Hitachi SU8000). The samples were ultrasonicated in distilled water before the HRTEM and FE-SEM characterization. Energy dispersive X-ray analysis (EDAX), using an EDAX-System (Hitachi SU8000) instrument that was attached to the FE-SEM instrument, was employed to investigate the elemental composition of the samples. The UV–Visible absorption spectrum was recorded using a UV–VIS–NIR spectrophotometer (Hitachi, U-3500). The Fourier transform infrared (FTIR) analysis was performed on a Perkin Elmer System 2000 series spectrophotometer (USA) between 4000 and 400 cm⁻¹. The Raman spectroscopy was performed using a Renishaw Invia Raman Microscope using (λ = 514 nm) laser excitation.

3. Results and discussion

3.1. Crystalline structures

Fig. 1a shows the X-ray diffractograms of graphene oxide (GO), graphene, pure PPy and pure ZnS. The XRD pattern of both GO and graphene show only one peak, centered at 10.6° and 25.63°, respectively. The XRD pattern of GO shows an intense and sharp diffraction peak at 2θ = 10.6°, attributed to the (001) lattice plane, corresponding to a d-spacing of 0.83 nm. This is consistent with the lamellar structure of GO. For comparison, the diffractogram of graphene shows the disappearance of this strong peak and the appearance of a very broad (002) peak at 2θ = 25.63°, corresponding to a d-spacing of 0.33 nm, which indicates the reduction of GO. Moreover, a broad peak of amorphous PPy appears at 26°, which may be integrated with ZnS in the GZP ternary composite. In the diffractogram of the pure ZnS nanoparticles, the peaks at 2θ values of 29.063°, 47.835° and 56.403° can be indexed to the (111), (220) and (311) lattice planes of cubic sphalerite ZnS (JCPDS card no. 00-003-0579), respectively, with the lattice constant a = b = 5.40 Å. On the other hand, the XRD pattern of the as-prepared GZP ternary composite-modified ITO electrode illustrates an additional peak at 25.63°, attributed to the (002) plane of the hexagonal graphite structure, suggesting that the graphene is incorporated into the composite as seen in Fig. 1b.

3.2. Morphology and chemical composition

Fig. 2 shows the FESEM images of the as-synthesized graphene nanosheets and GZP ternary composite emitter after 5 min of deposition onto a modified ITO electrode. As seen in Fig. 2a, a uniform spread of graphene nanosheet was obtained across the substrate. The high magnification FESEM shows that the nanosheets are randomly stacked and oriented relative to one another, with a number of nanosheets protruding above others, while some nanosheets are almost perpendicular to the substrate, as shown in the inset of Fig. 2a. Moreover, each nanosheet remained thin after the EPD, and the distribution of the nanosheets is largely homogeneous with no particular aggregation observed in specific areas. Fig. 2b shows a lower magnification FESEM image of the GZP ternary composite-modified ITO electrode. PPy was spread homogeneously on the graphene surface. Higher magnification of the FESEM image clearly revealed that the PPy nanotubes and the ZnS nanoparticles are well distributed on the graphene surface and the ZnS nanoparticles create an interface of separation between the graphene and the PPy, as shown in Fig. 2c. The observed length and diameter of the PPy nanotubes in the GZP ternary composite are approximately 1–1.5 µm and 60–80 nm, respectively, as illustrated in the inset of Fig. 2c. Moreover, Fig. 2d clearly shows that the layer-by-layer formation of the GZP ternary composite onto the ITO surface had occurred during the EPD.

TEM imaging was utilized for a detailed observation of the morphology of the samples. A more careful and close-up view reveals the presence of tiny ZnS nanoparticles, which are highly dispersed on the graphene surface, as illustrated in Fig. 3a. The graphene nanosheets can also function as conductive bands for the interconnection between the various ZnS nanoparticles and the transfer of photo-generated charge carriers for enhancement of the photocurrent effect. The high-magnification TEM image in Fig. 3b clearly reveals that the average particle size of ZnS is approximately 5 nm. Moreover, the lattice fringes of 0.27 nm correspond to the (220) crystal planes of the sphalerite ZnS crystal structure, which was confirmed by high-magnification HR-TEM analysis, as shown in the inset of Fig. 3b. However, in the TEM image in Fig. 3c, the GZP is evidently different, and fewer black dots are observed due to the PPy coating on the surface of graphene-ZnS layer-by-layer-modified ITO electrode. The inset of Fig. 3c clearly reveals that, in the case of GZP, the ZnS nanoparticles act as a connecting bridge between the graphene and the PPy to form homogeneous PPy on the graphene surface. Furthermore, the EDAX of the GZP composite-modified ITO electrode confirms the presence of Zn, S, C, O and N in the GZP composite where the atomic Zn:S ratio is approximately 1:1.06 and is consistent with the stoichiometric ratio of the ZnS nanoparticles, as shown in Fig. 3d.

To assess the reduction of GO and the formation of the composite, FTIR spectra of GO, graphene, PPy and the GZP ternary composite are shown in Fig. 4a. The FTIR spectrum for GO shows the presence of various oxygen-containing groups; the carbonyl C=O stretching vibration at 1731 cm⁻¹, the aromatic stretching vibration of sp² hybridized
Fig. 2. (a) FESEM image of graphene on an ITO substrate (the inset is a high-magnification FESEM image of graphene); (b) low-magnification FESEM image of the GZP ternary composite; (c) high-magnification FESEM image of GZP (the inset clearly shows the formation of PPy nanotubes); (d) FESEM image of the GZP ternary composite on an ITO electrode.

Fig. 3. (a and b) TEM images of ZnS deposited on a graphene-modified ITO electrode (the inset a is high-resolution transmission electron microscopy (HRTEM) image of ZnS); (c) TEM image of the GZP ternary composite (the inset clearly shows the bridge formation between graphene and PPy by ZnS); (d) EDAX spectrum of the GZP ternary composite.
C–C bond at 1625 cm\(^{-1}\), the OH bending vibration of C–OH at 1424 cm\(^{-1}\), the C–OH stretching at 1218 cm\(^{-1}\) and, finally, the epoxy C–O stretching vibration at 1051 cm\(^{-1}\). However, after chemical reduction, the characteristic peaks of oxygen functional groups were significantly reduced or disappeared. For graphene, the remaining peaks at 1574 cm\(^{-1}\) is assigned to the aromatic C–C bond [37]. The characteristic PyPy peaks are located at 1562 and 1472 cm\(^{-1}\) due to the stretching vibrations of the pyrrole rings (C–C and C–N), indicating the presence of a large conjugation. The peaks at 1215 and 941 cm\(^{-1}\) indicate the doping state of the polypyrrole. Furthermore, the peaks at 1329 and 1052 cm\(^{-1}\) are attributed to C–N stretching vibrations and C–H deformation vibrations, respectively [37]. Due to the low amount of graphene mixed with PyPy, the FTIR spectra for GZP present similar peaks to those of the pure PyPy. However, the peak of GZP centered at approximately 908 cm\(^{-1}\) can be assigned to the dipolaron state of PyPy [38], which is due to the antisymmetric and symmetric ring-stretching modes. Therefore, the FTIR results indicate the presence of PyPy in the GZP composite.

Raman spectroscopy is a useful tool to investigate significant structural changes from GO to the GZP composite. Fig. 4b shows the Raman spectra for graphite, GO, graphene, PyPy and the GZP layer-by-layer ternary composite-modified ITO electrode. In all of the Raman spectra of graphite, GO and graphene, two dominant peaks for the D and G band, are observed. The D band is attributed to the disorder of graphene, resulting from the breathing mode of \(A_{1g}\) symmetry, which is caused by phonon phonon near the K zone boundary, whereas the G band is attributed to the ordered \(E_{2g}\) phonon mode of sp\(^2\)-bonded carbon atoms [39]. The intensity ratio of the D band to G band \((I_D/I_G)\) is related to the density of defects in the graphene based-composites which is used to measure the quality of graphitization or defective disorders in crystalline graphite. As shown in Fig. 4b, the two typical peaks of GO can be found at 1361 and 1604 cm\(^{-1}\), corresponding to the D and G bands, respectively.

Compared to graphite, the \((I_D/I_G)\) of GO is significantly increased from 0.28 to 0.86, which is due to the increase of the disordered structure in the graphene during the oxidation process. With the reduction of GO, the D and G bands of the graphene were shifted to lower wavenumbers of 1352 and 1583 cm\(^{-1}\), respectively, compared to GO. However, the major evidence is the degree of disorder in graphene compared to GO, which can be observed from the intensity ratio of the D and G bands \((I_D/I_G)\). As seen in Fig. 4b, the ratio for graphene has increased from 0.86 to 1.04 compared to GO, implying that the chemical reduction has created a large amount of sp\(^2\) bonds and structural defects in the graphene lattice. In the spectrum of pure PyPy, two broad peaks are observed at 1577 and 1336 cm\(^{-1}\), attributed to the C=C backbone stretching and the ring stretching mode of PyPy, respectively, and the intensity ratio \(I_D/I_G\) is 0.62. However, compared to those of GO, graphene and PyPy, the intensity ratio \(I_D/I_G\) decreases to 0.56 for GZP due to the integration of C–C in-plane deformation and the C=C backbone stretching of PyPy. It may ameliorate the disordered structure of graphene [40], leading to the better electronic properties of GZP.

3.3. UV–Vis absorption spectra

Fig. 5 illustrates the UV–Vis spectra of the pure ZnS, ZP secondary composite and the GZP ternary composite-modified ITO electrodes. As seen in Fig. 5, the deposition of ZnS onto ITO causes an obvious absorption below 380 nm, which is due to the band edge of ZnS. Compared to pure ZnS, the absorption spectra of ZP and the GZP-modified ITO electrode illustrates more absorption in the visible region and is gradually increased in the wavelength range between 400 nm and 700 nm. This result indicates that the presence of PyPy and graphene could improve the light conversion efficiency for the ZnS nanoparticle-modified ITO electrode. However, the remarkable absorption peak of the PyPy and graphene was not observed in the spectra because both absorption peaks are overlapped with the absorption edge of ZnS.

3.4. Photoelectrochemical performance

A schematic of the solar cell device fabricated with the GZP layer-by-layer ternary composite-modified ITO electrode is illustrated in Fig. 6. To investigate the photoelectrochemical conversion efficiency of the solar cell devices, the current–voltage (I–V) curves of the devices fabricated with graphene-, pure ZnS-, ZP- and GZP-modified ITO electrodes were performed in the dark and under 10 mW cm\(^{-2}\) light illumination at room temperature, as illustrated in Fig. 7(a–d). It can be seen in Fig. 7a that the graphene nanosheets exhibit good conductance and approximately ideal ohmic contacts with the electrodes, especially under positive bias, but exhibits poor light response, where almost no obvious response can be detected under illumination. The pure ZnS nanoparticle-modified ITO electrode illustrates a typical I–V curve originating from the junction of the n-type semiconductor and metal as seen in Fig. 7b. The pure ZnS-modified ITO electrode shows a large light response, where the current density increases by more than two-fold under illumination. Moreover,
the I–V curves of the pure ZnS nanoparticles show a large insulating response in the dark with a resistance of $3.23 \times 10^3 \ \Omega \ \text{cm}^2$, a power conversion efficiency of 0.18% and a fill factor of 0.28. Compared to that of the pure ZnS, the photocurrent response in the current–voltage curves of the solar cell device fabricated from the ZnS/PPy composite-modified ITO electrode created a lower resistance of $2.81 \times 10^3 \ \Omega \ \text{cm}^2$, a power conversion efficiency of 0.27% and a fill factor of 0.17. The results also suggest that the pure ZnS in the composite was not directly excited by the light. However, compared with the GZP, these were significantly lower conductance and poor contact with the electrode. The I–V curves of the GZP ternary composite-modified ITO electrode shows a minimum resistance of $1.35 \times 10^3 \ \Omega \ \text{cm}^2$, a maximum power conversion efficiency of 0.92% and a fill factor of 0.23 compared to the pure ZnS and ZP composite-modified ITO electrode, as shown in Fig. 7d. For comparison, Table 1 summarizes the photoelectrochemical parameters for all electrodes.

The enhanced efficiency of the ZP composite-modified ITO electrode compared with the pure ZnS could be attributed to two factors: the sensitization mechanism in the hybrid nanostructures and the light absorption. ZnS is a semiconductor with a suitable band gap and band position, as shown in Fig. 6. The sensitization mechanism of PPy for ZnS nanoparticles could be explained based on their semiconducting properties, which have suitable energy band positions that match the energy bands of ZnS, and a suitable band gap of 2.2 eV, which matches the solar spectrum, as shown in Fig. 6. From the electronic structures of ZnS and PPy, a p–n junction is formed in the composite structure (the inset of Fig. 3c). It is inferred that the formation of the p–n junction results in the diffusion of electrons from the ZnS nanoparticles to the PPy nanotubes due to the large interface layer. Therefore, a lower current in the dark could be ascribed to the decrease in the charge carriers in the ZnS nanoparticles. However, during visible light irradiation, the quick migration of the photoexcited electrons from the CB of PPy nanotubes to the CB of ZnS nanoparticles leads to the generation of photocurrent, which results in the sensitization of PPy on ZnS. The second reason for the efficiency enhancement of the ZP secondary composite is due to the extended light absorption range. As shown in Fig. 5, compared to the bare ZnS, the light absorbed by the ZP composite is greatly increased from a wavelength range between 400 and 700 nm. This finding
conductance and poor contact with the electrode, while the graphene–ZP ternary composite is related to the role of graphene. As mentioned above, the second reason for the light conversion efficiency enhancement of the ZP ternary composite-modified ITO electrode could be explained by the following processes: (a) the band gap migration from the valence band (VB) to the CB of PPy under illumination, (b) electron transfer from the CB of PPy to the CB of ZnS, (c) electron transfer from the CB of ZnS to graphene, (d) electron transfer from graphene to the ITO electrode and (e) hole transfer to PPy. Indeed, the photo-excited electrons can be extracted and transferred to graphene, which retards the fast charge pair recombination. Moreover, graphene nanosheets play the role of an efficient electron shuttle between the ZnS and the ITO electrode due to its high conductance compared with ZnS nanoparticles.

The photocurrent transient response was performed under visible light irradiation to investigate the photo-electrochemical properties of the various samples. The transient photocurrents of graphene, pure ZnS, ZP and the GZP ternary composite-modified ITO electrode irradiated with visible light are illustrated in Fig. 8. An anodic photocurrent of 0.23 μA cm⁻² was obtained under visible light irradiation for graphene, as seen in Fig. 8. Moreover, an anodic photocurrent of 0.23 μA cm⁻² was obtained for pure ZnS, as seen in Fig. 8, which can be assigned to the ability of the pure ZnS nanoparticles to absorb visible light and generate electron–hole pairs. Compared to pure ZnS nanoparticles, an increase of 240% and 450% in photocurrents of the ZP composite and the GZP ternary composite were observed, respectively. These results clearly illustrate the existence of an easier electron transport mechanism in ZP and GZP composites than in pure ZnS. These photocurrent transients were steady, prompt and reproducible during several on-off cycles of the visible light irradiation as well; no overshoots were observed at the beginning and the end of the flash. The rectangular response illustrates that no grain boundaries exist in the direction of electron diffusion. The grain boundaries create deep traps to slow down the electron transport and may exist at the particulate electrode [44]. This finding also suggests that the excited electrons are collected efficiently in the external circuit. These results show that PPy nanotubes are an excellent sensitiser and hole acceptor, ZnS nanoparticles are a bridge and graphene is excellent conductive collectors and transporters, all of which play important roles in the photocurrent transient response. Based on the comparative analysis between different types of polymer solar cell electrodes shown in Table 2, the present GZP ternary composite electrode is capable of affording favorable open circuit voltage (Voc) and short circuit current (Jsc) for improvement of the power conversion efficiency of solar cell devices.

4. Conclusions

In conclusion, ZnS nanoparticles, with an average size of 5 nm; PPy nanotubes and; graphene nanosheets were grown onto an ITO substrate using EPD for the fabrication of photovoltaic cells. Both current–voltage curves and transient photocurrent results illustrate that (i) a ZnS/PPy secondary composite-modified ITO electrode demonstrated enhanced properties compared to the other electrodes.

Table 1

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<tr>
<th>Sample</th>
<th>Voc (V)</th>
<th>Jsc (mA cm⁻²)</th>
<th>ff</th>
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<td>95</td>
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**Fig. 8.** Photocurrent versus time (1–t) curves of the solar cell device based on graphene, ZnS, ZP secondary composite and GZP ternary composite.

Table 2

<table>
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<th>Type of electrode</th>
<th>Voc (V)</th>
<th>Jsc (mA cm⁻²)</th>
<th>ff</th>
<th>References</th>
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<td>0.47</td>
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<td>0.42</td>
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</tbody>
</table>

**Summary and a comparison of the present work with previous reports in the literature regarding the photoconductive properties of the solar cell devices.**

Table 2

<table>
<thead>
<tr>
<th>Type of electrode</th>
<th>Voc (V)</th>
<th>Jsc (mA cm⁻²)</th>
<th>ff</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO-polypyrrole</td>
<td>0.32</td>
<td>0.44</td>
<td>0.26</td>
<td>[45]</td>
</tr>
<tr>
<td>ZnO-mercurichrome</td>
<td>0.50</td>
<td>3.40</td>
<td>0.49</td>
<td>[46]</td>
</tr>
<tr>
<td>TiO₂-polyaniline</td>
<td>0.56</td>
<td>0.45</td>
<td>0.47</td>
<td>[48]</td>
</tr>
<tr>
<td>TiO₂-polypyrrole</td>
<td>0.49</td>
<td>0.58</td>
<td>0.51</td>
<td>[47]</td>
</tr>
<tr>
<td>SnO₂-polyaniline</td>
<td>0.17</td>
<td>0.03</td>
<td>0.34</td>
<td>[49]</td>
</tr>
<tr>
<td>ZnS-polyaniline</td>
<td>0.56</td>
<td>0.45</td>
<td>0.47</td>
<td>[48]</td>
</tr>
<tr>
<td>Graphene–ZnS–polypyrrole</td>
<td>0.48</td>
<td>0.42</td>
<td>0.23</td>
<td>This work</td>
</tr>
</tbody>
</table>
power conversion efficiency compared to that of a pure ZnS-modified ITO electrode under visible light irradiation due to the occurrence of the photoinduced electron transfer between PPy and ZnS, which increases the efficient dissociation of excited electron–hole pairs; and (ii) a maximum power conversion efficiency of 0.92% and a higher photocurrent response were observed under visible light irradiation with a GZP ternary composite-modified ITO electrode than were observed with ZnS or ZP due to the creation of an interfacial separation between the graphene and the PPy by ZnS nanoparticles, which act as a bridge, and due to enhanced charge transport by graphene.

Acknowledgments

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References