



# 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 photovoltaic 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.

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## 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 (TiO<sub>2</sub>) nanoparticles, which have been extensively utilized due to their high power conversion efficiency [11]. Zinc sulfide (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 TiO<sub>2</sub> 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

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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  $sp^2$ -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 thioacetamide was added drop-wise into 20 ml of 0.005 M zinc chloride ( $ZnCl_2$ ) 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  $FeCl_3$  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  $\mu m$ , 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 mixed with 60 ml of distilled water with the aid of ultrasonication to form a black-brown GO aqueous colloidal suspension. Then, 50  $\mu l$  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 ( $0.05 \text{ mg l}^{-1}$ ), 2 mg of  $Mg(NO_3)_2$  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  $\times$  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 polypyrrole nanotubes to 40 ml isopropyl alcohol separately and then ultrasonicated 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  $\text{ml s}^{-1}$ . 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  $\mu m$  thick spacer. The  $I^-/I_2^-$  liquid electrolyte consisted of 0.5 M KI, 0.05 M  $I_2$ , 0.6 M tetrabutylammonium iodide and 0.5 M 4-tert-butylpyridine 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  $\text{mW/cm}^2$ , the area illuminated of photoanodes was 0.5  $\text{cm}^2$  and the distance

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