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A solid-state dye-sensitized solar cell based on a novel ionic liquid gel and ZnO nanoparticles on a flexible polymer substrate

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Abstract

This paper describes a new strategy to make a full solid-state, flexible, dye-sensitized solar cell (DSSC) based on novel ionic liquid gel, organic dye, ZnO nanoparticles and carbon nanotube (CNT) thin film stamped onto a polyethylene terephthalate (PET) substrate. The CNTs serve both as the charge collector and as scaffolds for the growth of ZnO nanoparticles, where the black dye molecules are anchored. It opens up the possibility of developing a continuous roll to roll processing for THE mass production of DSSCs.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The conversion efficiency of dye-sensitized solar cells (DSSCs) has currently been improved to above 11% [1]. DSSCs with high conversion efficiency and low cost have been proposed as an alternative to silicon based photovoltaics [2, 3]. However, due to the encapsulation problem posed by the use of the liquid electrolyte in conventional liquid electrolyte based DSSCs, solvent leakage and evaporation are two main challenges; therefore, much work is being done to make an all solid-state DSSC [4]. In addition, the use of solvent-free electrolytes in the DSSC is expected to offer stable performance for the device.

Plastic and solid-state DSSCs incorporating single-walled nanotubes (SWNTs) and imidazolium iodide derivative have been fabricated [5]. The introduction of carbon nanotubes (CNTs) can improve solar cell performance through reduction of the series resistance. TiO₂ coated CNTs were recently used in DSSCs [6]. Compared with a conventional TiO₂ cell, a TiO₂-coated CNT (0.1 wt%) cell gives an increase in short

circuit current density (J_{SC}), resulting in ~50% increase in conversion efficiency. When employing SWNTs as conducting scaffolds in a TiO₂ based DSSC, the photoconversion efficiency can be boosted by a factor of 2 [7]. TiO₂ nanoparticles were dispersed on SWNT films to improve the photoinduced charge separation and transport of carriers to the collecting electrode surface. An alternative material to TiO₂ used in DSSCs is ZnO [8]. ZnO has a similar band gap (3.2 eV) and band edge position to TiO₂ [9], with similar or smaller crystallite sizes than that of typical TiO₂. ZnO nanowires have been used in DSSCs [10]. Nanoparticle films enable large internal surface area for the attachment of dye molecules and provide percolation pathways for electrons. In this paper, we report a novel methodology to fabricate a flexible solid-state DSSC based on ZnO nanoparticles and a new type of ionic liquid gel.

2. Experimental details

The best dye sensitizer reported so far is the tris(isothiocyanato)-ruthenium(II)-2, 2';6', 2''-terpyridine-4,4', 4''-tricarboxylic acid,

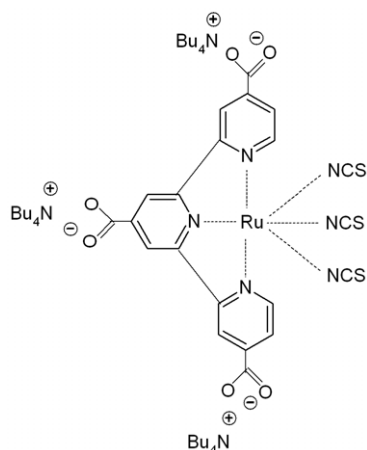


Figure 1. The chemical structure of the black dye.

tris-tetrabutylammonium salt (the so-called black dye) with visible absorption extending to near-IR region up to 920 nm [1]. The chemical structure of the black dye is shown in figure 1. A solution of 0.5 mM black dye dissolved in ethanol is used in this work. The SWNT-PET electrode containing ZnO is immersed in the dye solution for 24 h.

A novel ionic liquid was synthesized by grafting polyvinyl alcohol (PVA) with ionic liquid 1-butyl-3-vinylimidazolium bromide (VIC₄Br) under the irradiation of a ⁶⁰Co- γ source.

2.1. Synthesis of 1-butyl-3-vinylimidazolium bromide (VIC₄Br)

A mixture consisting of 5 g 1-vinylimidazole (60.9 mmol), 9.43 g butyl bromide (68.9 mmol), 3 ml acetonitrile and 2 ml chloroform was heated at 40 °C for 96 h. The obtained product was precipitated in diethyl ether. Further purification consisted in dissolution in chloroform and precipitation in ethyl acetate, and the residual solvent was evaporated under vacuum.

¹H NMR (300 MHz, CDCl₃), (ppm, from TMS): 0.99 (3H, t, CH₃), 1.40(2H, m, CH₂), 1.96(2H, t, CH₂), 4.45(2H, t, CH₂), 5.40(1H, m, CH₂), 6.00(1H, d, CH), 7.50(1H, m, CH), 8.04(1H, s, CH), 10.83(1H, s, CH).

2.2. Synthesis of PVA-g-VIC₄Br

Polyvinyl alcohol 124 (PVA-124) was purchased from SinoPharm Chemical Reagent Co., Ltd. 5 ml PVA-124 aqueous solution (7 g PVA-124 in 100 ml water) and 2.30 g (0.01 mol) 1-butyl-3-vinylimidazolium bromide was added to 20 ml distilled water. The mixed solution was irradiated in a ⁶⁰Co- γ source whose total dose was 10 KGy. The molar ratio of the vinyl alcohol repeat unit in the PVA backbone to imidazolium unit in PVA-g-VIC₄Br was estimated to be ca 4:5. The chemical structure of PVA-g-VIC₄Br is represented in figure 2. Details of the preparation and characterization for the immobilization of ionic liquid with such polymers and/or polyelectrolytes have been reported before [11]. This type of ionic liquid (PVA-g-VIC₄Br) is easily processed and can be dried to the solid state in 5 min.

A residue of trace water may be kept by the PVA group grafted in the backbone of the imidazole ionic liquid. This is, however, supposed to improve the performance of the DSSC by increasing the ionic conductance and the energy difference between the redox potentials of I₃⁻/I⁻ and the Fermi level, as reported by Mikoshiba *et al* [12].

2.3. Synthesis of CNT on PET

Single walled carbon nanotube (SWNT) thin films were prepared using the vacuum filtration method described by Wu *et al* [13]. Briefly, surfactant aided (1 wt% sodium dodecyl sulfate) aqueous dispersions of SWNTs (Nanocyl Inc., purified and COOH functionalized) at a concentration of 2 mg l⁻¹ were prepared through sonication for 1 h. Filtration (through 220 nm pore size Millipore mixed cellulose ester membranes with a diameter of 25 mm) of a volume of 30 ml allowed the deposition of SWNT films. The ester membrane with SWNT thin film was then transferred onto polyethylene terephthalate (PET) substrates, compressively loaded and heated to 80 °C by a hot plate and etched in consecutive acetone and isopropanol baths, leaving behind SWNT thin films on the substrates. The SWNT thin film with a sheet resistance of 250 Ω/\square and 65% transparency was then used as a scaffold to deposit ZnO nanoparticles.

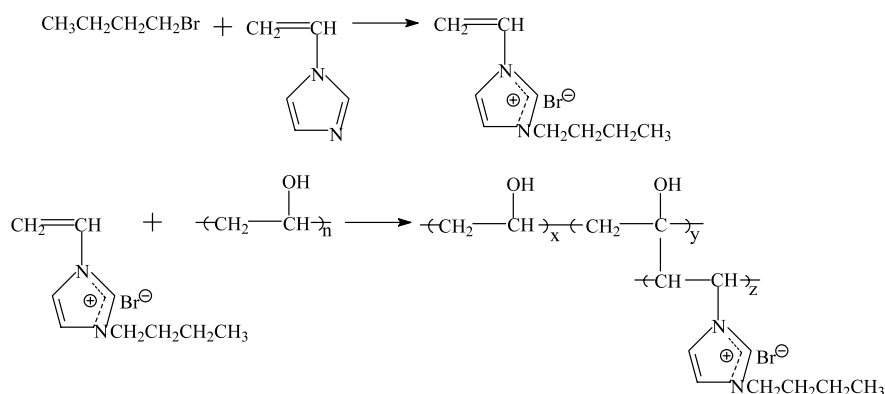


Figure 2. Structure and synthesis procedure of PVA-g-VIC₄Br.

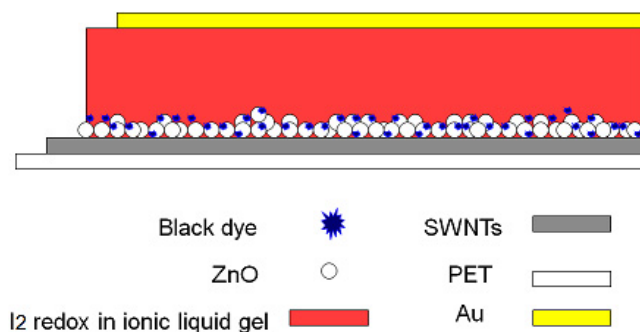


Figure 3. The structure of the solid-state DSSC.

2.4. Preparation of ZnO nanoparticles

The preparation of ZnO nanoparticles followed the procedure described by Vietmeyer *et al* [14]. 0.02 M $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was first sonicated in ethanol solution at 0°C and then $\text{LiOH} \cdot \text{H}_2\text{O}$ powder was added and mixed in the solution (the $\text{LiOH} \cdot \text{H}_2\text{O}$ amount added will be up to 0.02 M in the ethanol mixture). The mixture was continuously sonicated for 30 min at 0°C .

A stable and transparent ZnO suspension was made by this method. The PET stamped with CNTs was then immersed in the obtained suspension to let the ZnO nanoparticles precipitate on the CNTs.

The structure of the solid-state DSSC is shown schematically in figure 3.

3. Results and discussion

Substrates based on organic polymers offer flexibility and can be used in roll to roll printing techniques for mass production of organic electronics. Conventional DSSCs are based on rigid substrates such as glasses coated with FTO to stand the high temperature for annealing the TiO_2 nanoparticles. Not all organic polymers can withstand the annealing temperature while keeping the property of optical transparency. In this study, ZnO nanoparticles were deposited at low temperature on the transparent PET substrate stamped with CNTs. After deposition, the substrate (PET/SWNT/ZnO) was annealed at around 100°C for 10 min. The morphology of the synthesized materials was investigated by scanning electron microscopy (SEM: JEOL 6340F, operated at 5 kV). Figure 4 shows the

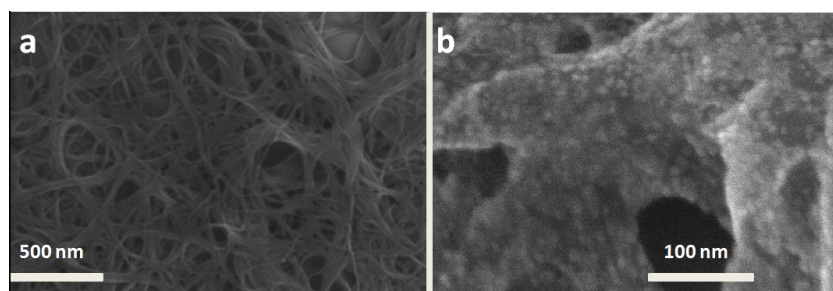


Figure 4. SEM images of (a) stamped single-walled carbon nanotubes and (b) ZnO nanoparticles on the single-walled carbon nanotubes.

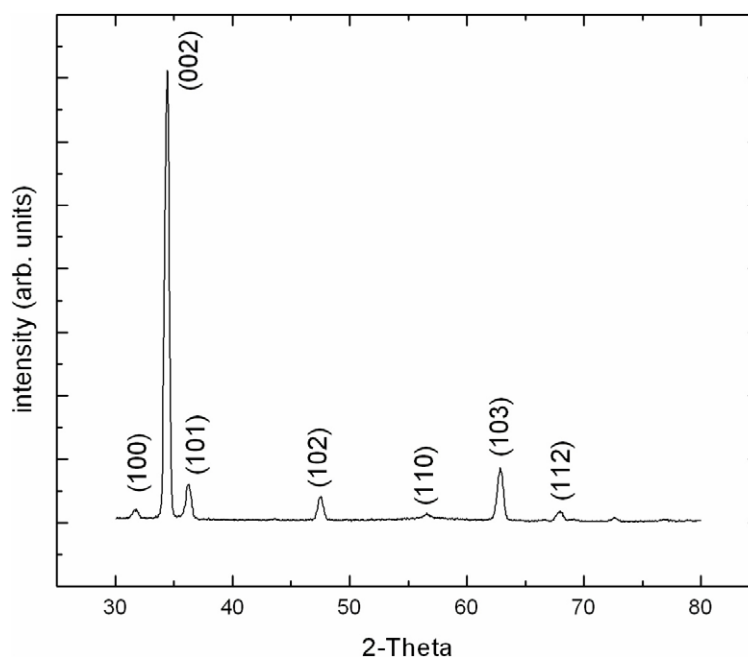


Figure 5. XRD pattern of the deposited ZnO nanoparticles.

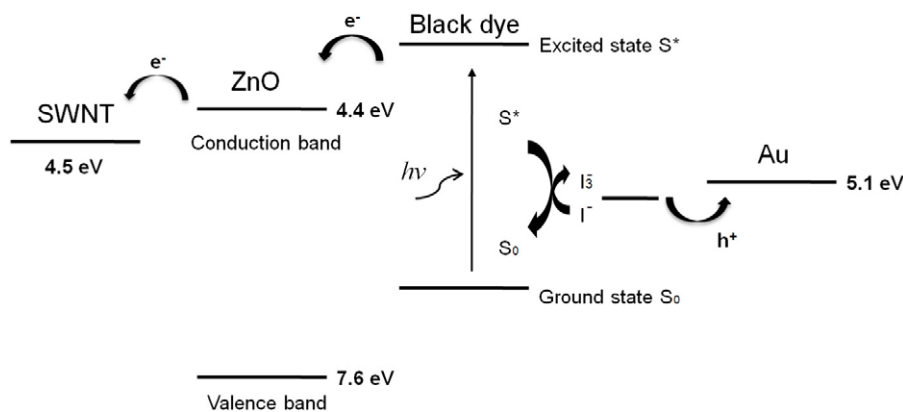


Figure 6. Energy diagram of the DSSC.

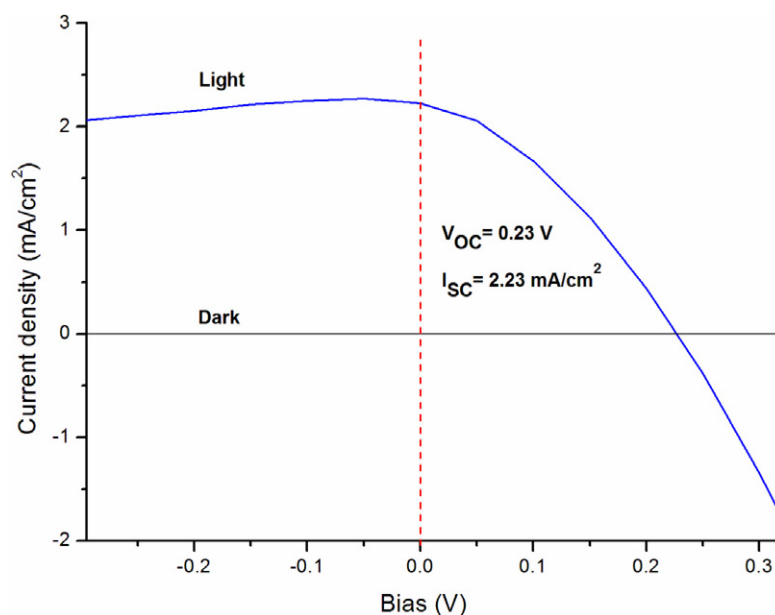


Figure 7. Photocurrent density–voltage characteristics of the DSSCs with the solid electrolyte based on ionic liquid containing 0.1 M LiI, 0.05 M I_2 and 1 wt% of PEO.

SEM images of (a) CNTs stamped on PET and (b) CNTs deposited with ZnO nanoparticles. It can be seen that ZnO nanoparticles with diameters of ~ 5 nm were evenly deposited on the bundles of the CNT matrix.

ZnO nanoparticles were further characterized by the x-ray diffraction (XRD) method, as shown in figure 5. The XRD pattern indicated the crystalline nature of the ZnO nanoparticles with a major (002) peak.

0.1 M LiI and 0.05 M I_2 were first dissolved in this ionic liquid. Polymeric or gel materials incorporating triiodine/iodide redox couple have been introduced to substitute liquid electrolytes with solid or quasi-solid-state materials [15]. However, the main limiting factors in a DSSC based on ionic liquids compared with a conventional liquid electrolyte based DSSC are higher recombination rates and lower injection of charge [16]. Many attempts to reduce the viscosity of ionic liquids for improvement of their conductivity have not yet been successful [17, 18]. Ionic conductance was recently reported to be improved by mixing poly(ethylene

oxide) (PEO) into the ionic liquid electrolyte matrix [19, 20]. It was also shown that the increase of the PEO molecular weight in the ionic liquid oligomers results in faster dye regeneration and lower charge transfer resistance of I_3^-/I^- reduction, leading to the improvement of DSSC performance [13]. Here, 1 wt% of PEO was quickly suspended homogeneously in the ionic liquid electrolyte containing I_3^-/I^- redox species and PVA-g-VIC₄Br with the help of ultrasonics. The mixture will still be in a liquid form until exposed to air. It was then drop cast on the working electrode, which comprises dye, ZnO and stamped SWNTs on PET. Following the solidification of the electrolyte, a 100 nm thick Au top electrode was thermally evaporated at a vacuum level of 10^{-6} mbar with an evaporation rate of 0.5 nm s^{-1} .

The energy diagram of the DSSC is shown in figure 6. The incident light excites the black dye to donate electrons to the LUMO of ZnO and then to the SWNT matrix. The work function of SWNTs varies from 4.5 to 5 eV depending on the intrinsic properties (metallic or semiconducting) of

the tubes [21]. The SWNTs act as the contacting channels that transfer the electrons to the negative electrodes. In the meantime, holes are collected at the counter Au electrode. The I_3^-/I^- redox species regenerate the black dye in the solid ionic liquid electrolyte. The conductance of the stamped CNTs is similar to that of the ITO used in conventional DSSCs. We reduced the fabrication processes by combining the charge collecting materials (stamped CNTs) with the ZnO nanoparticles.

Photoelectrochemical measurements were conducted under ambient conditions. An Oriel 450 W xenon arc lamp with an AM 1.5 filter was used as an excitation source and the solar simulator was calibrated before use. An HP 4140B semiconductor analyser was used to measure the current–voltage characteristics. Photocurrent density measurement was carried out by applying a bias from -0.3 to 0.3 V under light illumination intensity of 100 mW cm^{-2} (AM 1.5 G) at 25°C . Figure 7 shows the photocurrent density–voltage curves of the DSSC. It shows the short circuit current density $J_{\text{SC}} = 2.23 \text{ mA cm}^{-2}$ and open circuit voltage $V_{\text{OC}} = 0.23 \text{ V}$.

However, the light to electricity conversion efficiency of a DSSC using ionic liquids is still lower than of those using organic solvents, because the high viscosity of the ionic liquids may retard the physical diffusion of I_3^- and I^- . Even though the efficiency and V_{OC} are low, a promising photocurrent density (J_{SC}) has been produced using such novel ionic liquid gel, organic dye, ZnO nanoparticles and a thin film of CNTs stamped on a flexible PET substrate.

4. Conclusions

This paper describes a novel strategy to make a full solid-state flexible DSSC based on ionic liquid. A novel ionic liquid gel synthesized by ^{60}Co - γ ray irradiation was applied to dissolve the triiodine/iodide redox couple. SWNTs stamped on the flexible PET substrate served both as the charge collector and as scaffolds for the growth of ZnO nanoparticles, where the black dye molecules are anchored. A promising photocurrent is observed from this device. The production of TiO_2 nanoparticles always requires a high annealing temperature, which limits the use of polymers as substrates. The

low-temperature production of ZnO nanoparticles guarantees the fabrication of such DSSCs on optical transparent polymers. The proof of this concept is very important for developing a continuous roll to roll process for the mass production of flexible and lightweight DSSCs.

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