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Study on Dye-sensitized Solar Cells based on ZnO Nanorods and Graphene Enhanced P3HT as HTM

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Abstract

A quasi solid state dye-sensitized solar cells (DSSC) is fabricated using 1-propyl-3methylimidazolium iodide and Poly (3-Hexail Thiophene) P3HT, and P3HT-loading graphene (G) as the composite electrolyte. The electrolyte without added iodine is sandwiched between ZnO NW photo electrode both pristine and graphene enhanced P3HT (G-P3HT, 5% wt graphene) were used in solid state dye as Hole transport material draw a lot of attention due to easy fabrication, using P3HT-Graphene (P3HTI-graphene) nanocomposites were synthesized on FTO glass by solution process and employed as HTM to replace the conventionally used expensive Pt electrode, The solar cells based on vertical ZnO nanowire arrays by utilizing a mixture paste of LiI, PMII and solid iodine as electrolyte. The initial results showed the power conversion efficiency of 2.1%. The cells with pristine and G-P3HT showed different performance. The power conversion efficiency was improved from 0.16 to 2.1 mA for G-P3HT solar cells. It exhibited increased power conversion efficiency from 0.87 to 2.1%.

Keywords: Nanocomposite; graphene; organic elecronics; metal oxide semiconductor; solid state dye- sensitive solar cells.

دراسة وتصنيع الخلايا الشمسية الصبغية باستخدام شبه موصل ذو الترتيب الاعمدة النانوية و الخلائط البوليمرية من البولي هكسايل ثايوفين المحسن بالكرافين كخلائط وتستخدم كمواد ناقلة للفجوات

سامر مهدي عبد المحسن فؤاد نمر عجيل شاكر عبد الحسين السعيدي
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الخلاصة

تم تصنيع خلايا شمسية متحسسات صبغية من مواد ذات محاليل الكتروليتية شبه صلبة القوام من ١-بروبايل-٣ مثليمودوزول ايودين وبولي ٣-هكسايل ثايوفين النقي وبولي ٣ هكسايل ثايوفين كخلائط متعددة النسب مع الكرافين واستخدمت الخلائط كمحلول الكتروليتي شبه صلب ذات خلائط مختلفة النسب .تم دراسة وتصنيع خلايا شمسية بوجوداليود وباستخدام نسب مختلفة من اليود في تركيبة المحلول الالكتروليتي شبه الصلب ودراسة تاثير اليود على كفائة الخلية الشمسية حيث وجد ان افضل تركيز ٠.١ M والذي يقابل اعلى كفاءة من بين جميع نسب اليود بالاضافة الى ذالك تم دراسة تاثير الكرافين على المادة الناقلة للفجوات المتمثلة بالبوليمر الموصل العضوي بولي ٣-هكسايل ثايوفين حيث وجد ان هنالك تحسن كبير وواضح بزيادة الكفائة للخلية الشمسية من% ٠.١٦ الى ٢.١%

الكلمات المفتاحية: خلائط بوليمرية نانوية ،كرافين، الالكترونيات العضوية ، التراكيب النانويةلاكاسيد المعادن الشبه موصلة، الخلايا الشمسية الصبغية ذات القوام الشبه صلب .

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted worldwide attention because of their low fabrication costs, promising light harvesting to energy conversion efficiency and environmental friendliness but it has shifted recently from base on liquid electrolytes to quasi solid-state dye ,because of the problems such as hermetic sealing of the cells, evaporation of liquids at high temperatures, permeation of water and oxygen molecules into the electrolyte especially due to the corrosive nature of iodine. Replacing the liquid of electrolyte with a solid or quasi solid electrolyte is to solve these problems. The high-energy conversion efficiency of dye-sensitized solar cells are accomplished through the use of highly porous semiconductor films coated with dye sensitizer as the working electrode [1]. O'Regan developed these dye-sensitized solar cells consist of three main components: working electrode, electrolyte and a counter electrode. The working electrode is usually TiO2 coated with dye to absorb light and generate exitons. The electrolyte is a mixture of I-/I3- for transferring electrons from counter electrode to excited dyes. The counter electrode is coated with a catalyst film to promote electron transfer to the electrolyte through the reduction of tri-iodide I3- [2]. They have the highest catalytic activity with the I3. However, due to their high cost, alternative materials are intensively studied such as carbon black [3] carbon nanotube [4] and conductive polymers [5]. Conducting polymers are promising candidates for DSSC or for solid-state dye sensitive solar cells counter electrodes because of their unique properties, including low cost, good conductivity, remarkable stability and good catalytic activity for I3- reduction [6]. Many conductive polymers (poly pyrrole, polyaniline, poly(3,4-ethylenedioxythiophene), polythiophene) were investigated as materials for DSSC counter electrodes. P3HT is one of the most studied polymers because of its high conductivity and good topographic properties [7]. It is widely used in various applications such as super capacitors [8], field emission [9], sensors [10], dye-sensitized solar cells and Bulk hetrojunction solar cells. Deibel et al (2010) constructed P3HT films by dissolving 10 mg /1ml in chloroform and then affixed this polymer material to conductive glass, where it was used as hole transport materials. This study obtained high DSSC efficiency ~7.73%. This high solar cell performance is most likely due to an increase in counter electrode interfacial area. Serap Gunes [9] and Deibel et al (2010) used P3HT film as hole transport Materials on the top TiO2-dye conductive glass by spin coater deposition and used this as counter electrodes of a quasi solid-state DSSC. They obtained promising results with the highest efficiency ~0.3 %. Direct polymer deposition on conductive glass should favor strong polymer bonding to conductive surfaces. This will facilitate electron transport from the conductive glass to polymer and improve DSSC performance where it so called solid-state dye sensitive solar cells. In this present work, we report the preparation of nanocomposite materials of P3HT-G films by spin coater, with and without graphene. The performance of P3HT-graphene and pristine P3HT based on ZnO nanorods as a photo anode deposited on the top of FTO glass. The influence upon solar cell performance was analyzed by I-V characteristic under light and dark. The polymer structure was characterized by scanning electron microscopy (SEM).

2. Experimental Details

A- Materials:

1- P3HT mix 5% wt graphene films

A Fluoride-doped TiN Oxide (FTO, sheet resistance 16Ω/sq) glass was used as the conducting substrate for both working and counter electrodes. P3HT use (Aldrich) 10 mg and 5% wt loading graphene dissolve them in 1 ml chloroform then using a bath stirrer for 30 min to dispersing graphene with P3HT. Then, using spin coater 600 for 40 sec to get very uniform thin films on FTO glass were used as the counter electrode and the TiO_2 and, ZnO nanorods as working electrode, respectively.

2- ZnO nanorods

The most widely used fabrication methods to obtain ZnO nanorods by electrochemical method. ZnO nanorods on FTO glass substrates [11] are typically prepared by two steps, first step prepare ZnO thin film by electrochemical method using 0.05 M Zinc nitrate dissolve in (50:50) ethanol :DI water for 5 min applied voltage -2.5 volt using FTO glass as working electrode and Au wire as reference and counter electrode second step using zinc nitrate 0.01 M and hexamethaial amine 0.01 M dissolve with 100 ml water for at least 60 min then washed by DI water and dry it by polling with nitrogen gas to be ready for use.

3- Synthesis of graphene, P3HT, and P3HT-graphene Composites.

The graphene were purchased from cheap tube as nanoplates, and the surface area equal 500 cm^2/g semimetal. The P3HT-graphene nanocomposite was prepared with 5% wt graphene by the weight of polymer.

B- Solar cell fabrication:

N719 ethanol solution was dipped on the as-prepared FTO glass/ZnO NW and dried naturally. Then, a mixture electrolyte (0.6 M 1-methyl-3 propoylimidazolium iodide (PMII) + 0.1 M LiI + 2g I) was dipped onto the surfaces of both FTO/ZnO NW/N719 and FTO/P3HT-graphene. The final devices were made by sandwiching the FTO glass/ZnO NW/N719/PMII and P3HT-graphene/FTO glasses as shown in Figure 7

C- Structural analyses:

Figure 1 shows the SEM images of ZnO nanorods, ZnO thin film and AZO films. The top view and cross section of as-grown ZnO Nanorods shows the hexagonal structure of individual nanowires vertically aligned on the substrate. The average diameter of the nanorods is 200-300 nm with a density of 20 nanorods per μm^2.

3. Results and Discussion

In this section, we showed characterization of graphene, P3HT and the P3HT-graphene composites, as follows:

1- Optical Properties of Materials

The optical absorption spectrum of the poly (3HT) film was displayed from 200 nm to 1000 nm in Figure 2. The absorption range is from 450 nm to 650 nm. It should be noted that the strong Terrestrial solar photons flux between 400 nm to 800 nm should be considered to be a primary factor influencing the photo induced carrier mechanism of a solar cell. The presence of P3HT in the solution is characterized by the absorption band between 350 to 600 nm, with a peak at 450 nm. It can be seen that the P3HT-graphene composite has almost the same absorption range and peak as that of the pure P3HT solution in the wavelength range from 350 to 600 nm, except that the absorption peak of the P3HT-graphene composite is slightly broadened, and absorbs more strongly below 400nm and above 550 nm. This should be caused by the absorption of graphene in the composite film. The absorption spectrum of the P3HT solution shows no significant change upon adding 5% wt of graphene. This implies that in the P3HT-graphene composite, no significant ground-state interactions take place between the two materials, and hence, no charge transfer occurs in the ground state, which is consistent with the literature [12]. Figure 3 displays the optical absorption spectra of ZnO NW on FTO, N719 in solution, and ZnO NW modified with N719 were measured and shown in Figure 3. The modified ZnO NW. The N719 in solution has a strong 2 absorption peaks are 423 nm, 515 nm and a number of small peaks in the visible range, which is similar to that reported in the literature [13]. The ZnO NW modified exhibits a strong increase in absorption around 515 nm, which is attributed to the additional absorption of the N719 coating. Figure 4 presents the X-Ray diffraction (XRD) spectra of N719 on ZnO NW (black curve), and N719 on ITO glass (red), ITO glass (yellow) the peak at the centered at 2 theta ~31.110 and 36.130 are from ITO glass, and the strong peaks 2 theta ~34.2 0 is from the ZnO NW surface. XRD results explain that the final crystalline structure does not effect after modified by

N719 and aggregation of N719 to ZnO NW surface introduce no change in crystalline structure of ZnO NW.

2- Current density-Voltage Characteristic

Based on P3HT and P3HT mix 5% wt graphene for ZnO nanorod modified N719 as a working electrode explained in the figure 5 where the pristine P3HT, P3HT-G as HTM, as seen from the figures of I-V characteristic that P3HT-graphene better performance than pristine P3HT, due to graphene used to enrichment of P3HT and that will help decrease the internal resistivity. Furthermore, the performance of solar cells at 0.1 M Iodine represent best PCE as we see from the Table 1,and Figure 6 the best efficiencies for the optimum condition which are 0.1 M Iodine and P3HT-Graphene with ZnO nanorods modified N719 represent most efficient solid-state dye sensitive solar cells. Figures 4 , 5,and 6 display I-V characteristic of the photovoltaic devices.

4. Conclusions

Recently, graphene, a single layer hexagonal lattice of carbon nanotube atoms, has recently emerged with conductive polymer for improving properties because graphene possesses a range of unusual properties therefore the efficiency increase for both designs when loading 5% wt graphene with P3HT as counter electrode (HTM), Table 1 shown increasing in efficiency and the efficiency for ZnO nanorod, as a working electrodes The better performance of solar cells with 0.1 M iodine as a solid electrolyte and P3HT-Graphene as HTM in solid-state dye sensitive solar cells less performance than pristine P3HT because P3HT-graphene provide an intrinsic energy barrier which effectively suppresses charges recombination and increases the electron life time. In addition the Iodine has high electrons provider to less electron lifetime.

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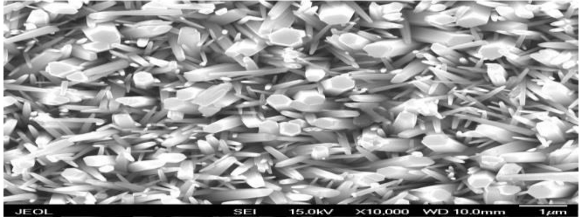

Figure 1: SEM images of ZnO nanorods.

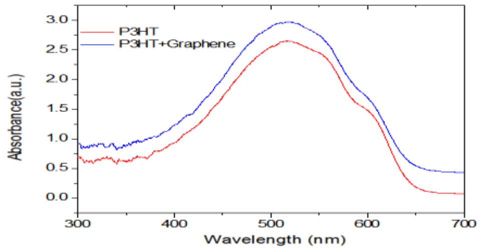

Figure 2: The optical absorption spectrum of the poly (3HT 5% wt) in the UV-visible-NIR range.

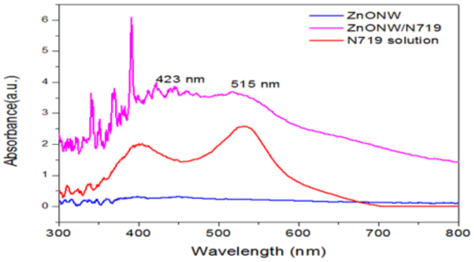

Figure 3: The Optical Absorption spectrum of ZnO NW, ZnO NW/N719, and N719 solution.

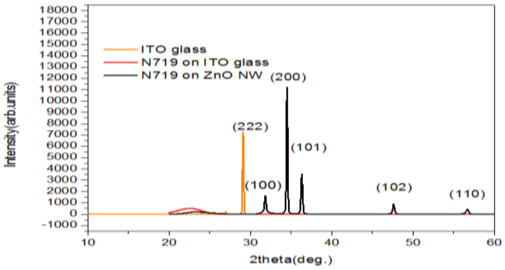

Figure 4: XRD spectrum of pristine N719 (red curve), N719 on ZnO NW arrays (black curve), and ITO (yellow).

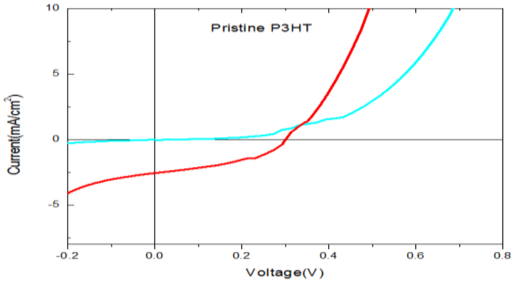

Figure 5: Current density vs. voltage measured on P3HT/ZnO nanowire arrays solid state dye for Pristine.

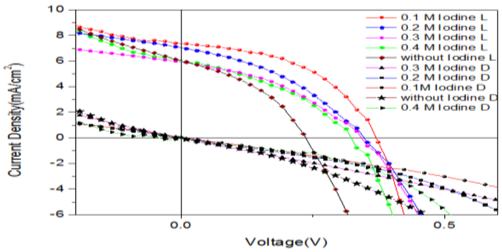

Figure 6: Current density vs. voltage measured on G-P3HT/ZnO nanowire arrays solid state dye with different loading of Iodine.

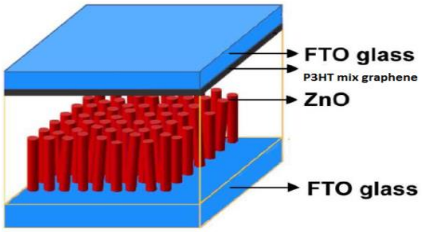

Figure 7: Schematic diagrams of the new-structure ZnO nanorod DSSC fabricate.

Table 1: I-V values for solid-state dye sensitive solar cells.

Dye Sensitive solar Cell	V_{oc}	I_{sc}	FF	Efficiency
Pristine P3HT	0.3	1.77	0.58	0.311
Nanocomposite P3HT-G for 0.1 M of Iodine	0.37	7.4	0.45	1.25
P3HT-G for 0.2 M Iodine	0.347	7.03	0.36	0.9
P3HT-G for 0.3 M Iodine	0.341	5.95	0.379	0.77
P3HT-G for 0.4 M Iodine	0.322	6.03	0.378	0.73
P3HT-G without Iodine	0.236	6	0.374	0.53

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