MÜHENDİSLİK BİLİMLERİ ve ARAŞTIRMALARI DERGİSİ

ENGINEERING SCIENCES AND RESEARCHES

SPDA:AG NANOTEL AĞ ELEKTROTLU ORGANİK GÜNEŞ HÜCRESİ

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ÖZET

Bu çalışmada, organik güneş pilleri için yüksek saydamlık ve düşük dirence sahip olması beklenen Sülfonatlı poli (difenilamin): Ag nanotel ağ saydam iletken elektrot hazırlanmıştır. Sülfonatlı poli (difenilamin): Ag nanotel ağ saydam iletken elektrotun yüzey direnci 10Ωcm^{-2} ve optik geçirgenliği % 88'dir. Elektrot organik güneş hücresinde kullanıldığında güneş hücresinin verimi %2,7 elde edilmiştir. Hazırlanan Sülfonatlı poli (difenilamin): Ag nanowire ağ elektrotu, gelecek vaat eden bir elektrot olarak organik elektronik cihazlarda kullanım için Indiyum kalay oksit malzemeye alternatiftir ve esnek elektronik uygulamalarda da kullanılabilir.

Anahtar Kelimeler: *Saydam İletken Elektrot, Organik Güneş Hücresi, Ag Nanotel*

ORGANIC SOLAR CELL WITH SPDA: AG NANOWIRE NETWORK

ABSTRACT

In this study, Sulfonated poly (diphenylamine): Ag nanowire network transparent conductive electrode was prepared that is expected to have high transparency and low resistance for organic solar cells. The resistance value was 10 Ωsq^{-1} and the optical permeability value was 88% with Sulfonated poly (diphenylamine): Ag nanowire network electrode. By using the electrode in organic solar cell, the solar cell efficiency was obtained 2.7%. The prepared Sulfonated poly (diphenylamine): Ag nanowire network electrode is an alternative to Indium tin oxide for use in organic electronic devices as a promising electrode and can also be used in flexible electronic applications.

Keywords: *Transparent Conductive Electrode, Organic Solar Cell, Ag Nanowire*

1. INTRODUCTION

Studies on the preparation of metal NWs have increased in recent years especially for the development of flexible substrates. Metal NWs can be obtained from solution. Among the possible metallic nanostructures, Ag NWs are the most preferred because of their optical, electrical and mechanical properties. Furthermore, the synthesis of Ag NWs is much easier than the long preparation processes of other NWs currently being developed.

2. SILVER NANOWIRE BASED TRANSPARENT CONDUCTIVE ELECTRODE

There are several experimental ways to produce Ag nanostructures that can be produced in different shapes and forms: hydrothermal method, microwave assisted process, electrochemical technique, molding technique and uv-irradiation technique [1-3]. The need for nanostructures to develop high-performance transparent conductive materials is increasing. Therefore, it is imperative that the random or evenly ordered NW layers are obtained by easy, reliable and cost-effective preparation techniques. NW networks, spray coating [4-6], dry printing [7,8], dipping [9,10], electrical field assisted sequencing [10,11], printer [12], electrochemical [13], dropping [14-16], rotary coating [17,18] or rod coating [19]. All these techniques are compatible with low temperature processes (below 200 °C) and do not require vacuum equipment. Electrodes from such solution processes have been shown to be applicable in organic electronics such as organic solar cells [14,15,17,18,20]. The coatings obtained by spraying method are more homogeneous and have a more uniform morphology. One of the most important points to focus on for device applications is surface smoothness and contact strength between nanowires. The first one could be solved by lamination [16], line changing [15], wet chemical methods [21] and sandwiching the metal web between two metal oxide layers [22]. The contact resistance problem was prevented by selective curing by plasmonic welding [23].

Thermal and more generally environmental stability is critical to the application of nanostructures to devices. Placing nanostructures between oxide materials to achieve stability is highly promising. Essentially, this method was used to prevent degradation of Ag NWs [22,24,25]. Ramasamy et al. [25] have shown that Ti nanocapsulated Ag NWs can withstand thermally up to 750 ° C. Chung [17] and Kim [22] reduced joint strength and surface roughness with similar layered structure. Semiconductor ZnO is a very attractive material for transparent electrodes due to its wide bandwidth, optical properties, non-toxicity and low cost. However, the electrical resistance of ZnO films is too high to apply to optoelectronic devices. Compared to inorganic materials, there are some advantages of organic materials such as low cost preparation, mechanical flexibility, and the ability to adjust the optical properties and energy levels as desired. From a fabrication point of view, they can be coated onto flexible substrates and by low-cost solution-processing techniques such as roll-to-roll and printer techniques that allow large area coatings. Therefore, organic materials are promising candidates for

transparent electrodes to be used in large area and flexible base applications. Polystyrene sulfonic acid doped poly (3,4-ethyleneedioxythiophene) (PEDOT: PSS) is the most widely used organic based material in transparent electrode applications. In general, however, PEDOT: PSS cannot be used alone as an electrode in organic electronics due to its limited electrical properties (typical PEDOT: PSS resistance 10^4-10^5 Ωsq^{-1}) [26]. In recent years, PEDOT: PSS resistance has been reduced to 40-50 Ωsq^{-1} by treatment with acids such as H_2SO_4, and the permeability value has reached about 90% [27, 28]. However, there is still a significant difference between the resistance of ITO (~ 10 Ωsq^{-1}, 85% permeability) and PEDOT: PSS, and PEDOT: PSS electrodes need to be further developed to meet the requirements of organic electronics. Therefore, the permeability and conductivity values of multilayer transparent films consisting of metal layers sandwiched between the PEDOT: PSS layers have been optimized to achieve high permeability and conductivity values by optimizing the thickness of the PEDOT: PSS layer and the metal layers [29-31]. Previous studies have shown that the permeability of a metal layer can be increased by introducing a metal layer between two organic layers having suitable refractive indices. In order to increase the permeability and conductivity of the multilayer transparent film in an organic-metal-organic structure, optimization of the thicknesses of the organic and metal layers is required. Depending on the type of organic electrode, an appropriate electrode / organic interface can be expected in organic solar cells, where the interface potential barrier and active layer morphology can be more appropriately controlled and have a better charge collection efficiency.

Xiaoyang Guo et al. [32], poly (N-vinylcarbazole) PVK/Ag thin film/PVK and PVK/Ag thin film/PEDOT: PSS (Ag thin film used in this study, not Ag NW network) structure between organic films produced electrodes sandwiched metal sheet. These electrodes showed high electrical conductivity and optical permeability; The resistance of this electrode, which is especially composed of multiple layers, was optimized to 10 Ωsq^{-1} and its permeability was 85% optimized. These developments have triggered the search for alternative materials for PEDOT: PSS. Several other organic dielectric materials such as self-doping PSSA-g-PANI copolymer whose conductivity and acidity can be adjusted by changing the molar ratio of poly (styrene sulfonic acid) (PSSA) and polyaniline (PANI) are also being investigated. In photovoltaics using optimized PSSA-g-PANI films, thermal stability and yield were improved compared to PEDOT: PSS based devices. Although conductive polymers such as PANI or polypyrrole (PPY) have poor physical and mechanical properties, these problems can be overcome by methods such as copolymerization, monomer modification and blending with other polymers. Li et. al, PEDOT: sulfonated poly (diphenylamine) (SPDA) instead of PSS, it was applied to polymer photovoltaic devices as a hole transport layer. The addition of the skeletal structure of the conjugated polymer prevents the isolation of heterogeneous electricity induced in the PSS group. However, the acidic and water-loving nature of conductive polymers can cause degradation problems seen in PEDOT: PSS [33-39]. In the literature, it is the first time that we have reported the preparation and

characterization of Sulfonated poly (diphenylamine): Ag nanowire network transparent conductive electrode for organic solar cells.

3. PREPARATION AND CHARACTERIZATION OF THE ORGANIC SOLAR CELL WITH SPDA:AG NANOWIRE NETWORK ELECTRODE

Ag NWs were synthesized by the polyol method [40]. 247.5 mg (0.45 M) of polyvinyl prolidone (PVP), placed in a 250 ml three-necked flask, was dissolved in 10 ml ethylene glycol (EG) on a magnetic stirrer. 7 mg of sodium chloride (NaCl) was added and stirring was continued. The temperature was raised very slowly to 160 °C. 102 mg (0.12 M) of $AgNO_3$ solution prepared with 5 ml EG was added dropwise via syringe. The reaction mixture was stirred at the same temperature for 30 min. For purification, Ag NWs were centrifuged twice with 15:1 ratio of acetone at 7000 rpm for 15 min. The same centrifugation process was repeated with ethanol.

Water-soluble sulfonated SPDPA was synthesized according to the procedure in Figure 1 [35]. First, poly (diphenylamine) (PDPA) was prepared by chemical oxidation method. Diphenylamine (3.4 g, 0.04 mol), 2M H_2SO_4 solution (300 mL) and acetone (200 mL) were placed in a 1L flask. After stirring vigorously with a magnetic stirrer, cooling to 5 ° C, a solution of ammonium peroxydisulfate (APS) (4.5 g, 0.04 mol) in 30 mL 2M H_2SO_4 was added dropwise. It was found that DPA polymerization took place when the solution turned green. The reaction mixture was stirred continuously for 16 hours. The green crude prepare was filtered off and washed with a large amount of deionized water until the precipitate became colorless. PDPA with H_2SO_4 was then added with 1 N aqueous ammonia solution for 24 hours. The PDPA became transparent after filtration and washing. In addition, PDPA was dispersed in acetone and centrifuged at 5000 rpm for 15 minutes. The precipitate was washed several times with acetone to remove impurities. Gray neutralized PDPA powder was dried in vacuum at room temperature for 24 hours. Neutralized PDPA (0.5 g) dissolved in 40 mL of fuming sulfonic acid was sulfonated with stirring at 5 °C for 1 hour. The solution was added to 500 mL of acetone at 10 °C to give a green precipitate. The green precipitate was washed with acetone and centrifuged and dried in vacuum. Then, SPDA deionized aqueous solution was dialyzed with semipermeable membrane to remove excess acid and purified. Finally, it was dried in vacuum.

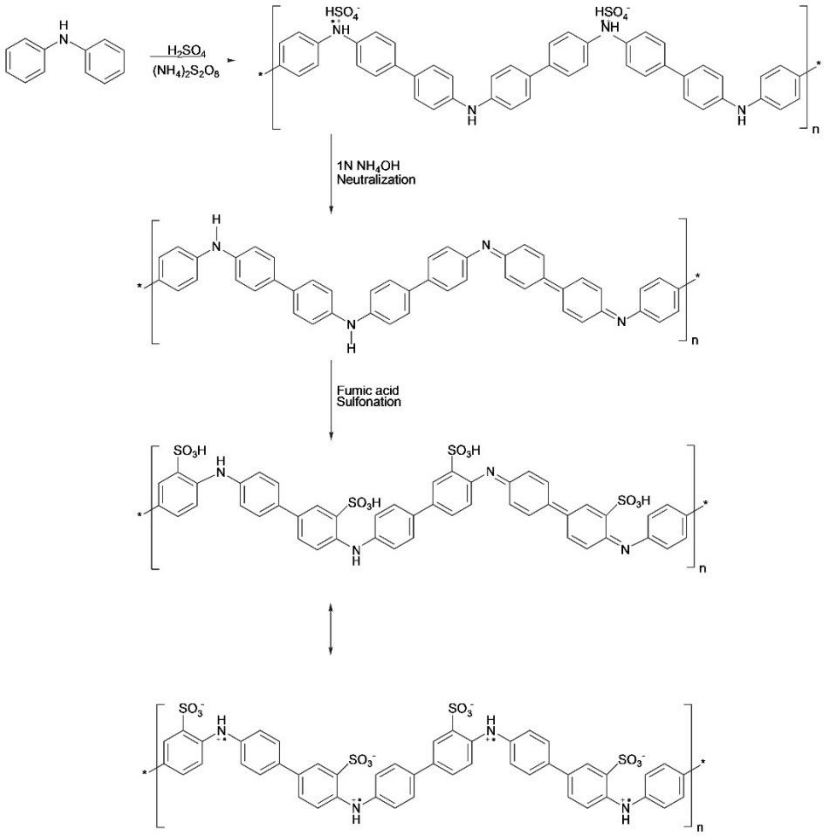
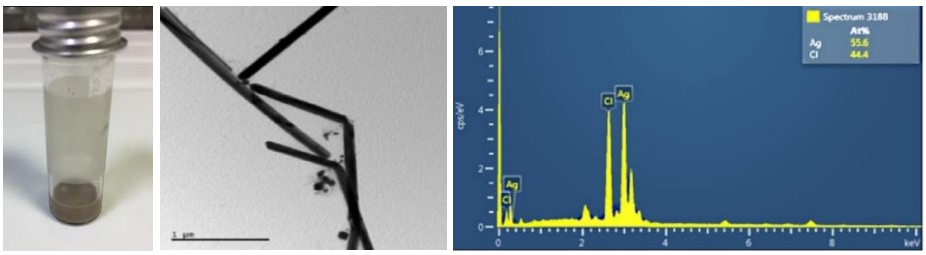


Figure 1. Synthesis procedure of sulfonated poly (diphenyl amine) (SPDA) polymer [35].

Substrate glasses were cleaned with detergent water, purified water, acetone and isopropanol in ultrasonic bath and dried with nitrogen gas and finally cleaning process was kept in ozone for 5 min. SPDA: Ag NW (1: 0.8) was coated by spin coating for 5 s at 3000 rpm and 10 s at 4000 rpm, then annealed at 120^0C for 10 minutes. Thickness of the film was determined using P-6 model profiler by considering the step heights of the device. The instrument has an accuracy from nanometer scale to micrometer scale. Electrical measurements were made with a 4-probe measuring station and a 4200-SCS parameter analyzer (Keithley Instruments). The 4-probe measuring station is structured with 2mm spacing between the needles. The diameter of the needles used is 0.3 mm. Sheet resistance was calculated using the ready-made method on 4200-SCS. Organic solar cell was prepared on SPDA: Ag NW electrode. P3HT: PCBM active materials were used. P3HT: PCBM was prepared with 20 mg/ml dichlorbenzene, mixed at a ratio of 1:8. The solution was coated on the electrode by rotary coating at 500 rpm for 40 s. Subsequently, 10 nm thick Ca thin film and 100 nm thick Al thin film were coated by evaporation on P3HT: PCBM thin film, respectively. The prepared electrode was tested with P3HT: PCBM active layer under solar simulator. Organic solar cell characterization was performed under the light intensity AM1.5G 1000W/m^2 with Oriel Lot Brand Solar Simulator.

4. RESULTS

Ag NWs were synthesized by polyol method. The image of Ag NWs dissolved in ethanol, TEM image and EDX analysis of Ag NWs are given in Figure 2.



(a) (b) (c)

Figure 2. (a) The image of Ag NWs dissolved in ethanol, (b) TEM image of Ag NWs, (c) EDX analysis of Ag NWs.

Ag NWs were successfully prepared (Figure 2a), showing two characteristic absorption peaks in the UV-vis absorption spectrum at 350 nm and 380-483 nm range, as given in Figure 2b. The peak at 350 nm shows the out-of-plane quadrupole resonance, while the large peak at 380 nm shows the sub-planar dipole resonance of the Ag NWs. It is also thought that the peak in the 380-483 nm region is due to the combination of electromagnetic waves between aggregation and neighboring NWs.

The synthesized Sulfonated poly (diphenyl amine) (SPDA) polymer is soluble in water and DMSO. Figure 3 shows the 1H-NMR spectra of the sulfonated poly (diphenyl amine) (SPDA) polymer in d-DMSO.

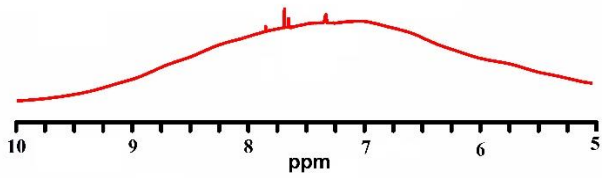


Figure 3. 1H-NMR spectrum of the SPDA polymer in d-DMSO

Thickness of the prepared SPDA: Ag NW electrode were determined 15 nm using profiler. UV-Vis spectrum of the prepared SPDA: Ag NW electrode with different thickness was given in Figure 4.

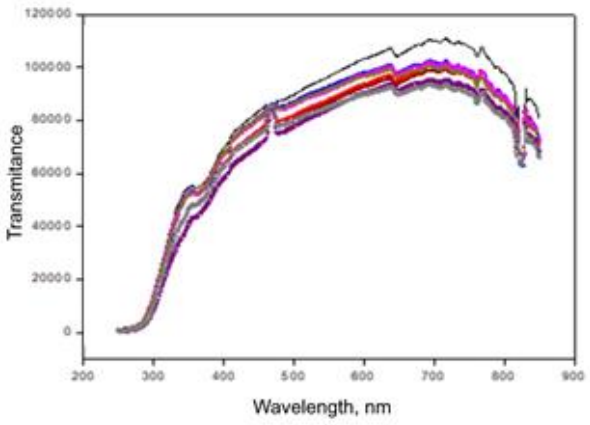


Figure 4. UV-Vis spectrum of the prepared SPDA: Ag NW electrode with different thickness.

The prepared SPDA: Ag NW electrode was tested with P3HT: PCBM active layer under solar simulator (Figure 5). Organic solar cell characterization was performed under the light intensity AM1.5G 1000W/m^2 with Oriel Lot Brand Solar Simulator.

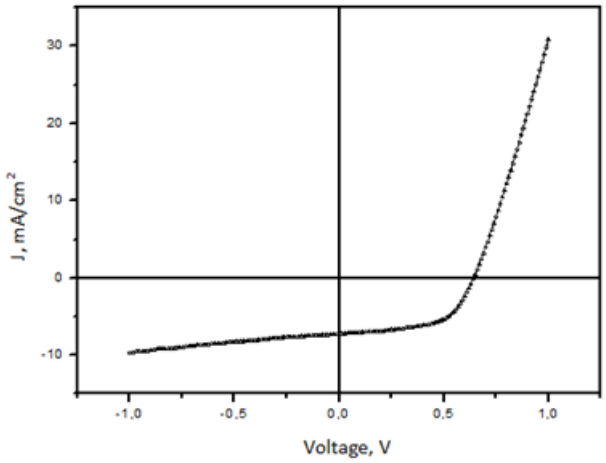


Figure 5. J-V characteristic of SPDA: Ag NW electrode/P3HT: PCBM/Ca/Al solar cell.

According to the Figure 5, organic solar cells prepared SPDA: Ag NW electrode was found to work. Open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), and FF value of the cell were obtained as 0.64, 7.25, and 0.57, respectively. The efficiency of the cell was obtained as 2.7 %. Ag NWs and SPDA polymer were successfully synthesized and SPDA: Ag NW electrode preparation was successfully performed. The resistance value was 10 Ωsq^{-1} and the optical permeability value was 88% with Sulfonated poly (diphenylamine): Ag nanowire network electrode. By using the electrode in P3HT: PCBM active layer organic solar cell, the solar cell efficiency was obtained 2.7%. The prepared SPDA: Ag NW electrode is an alternative to ITO for use in organic electronic devices as a promising electrode and can also be used in flexible electronic applications.

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