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Electrochemical Synthesis of a Polypyrrole/TiO_2 Nanocomposite as a Novel High Efficiency Solar Cell

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Abstract
In this research study Polypyrrole nanoparticles were synthesized on the copper surface using the amperometry technique, and their morphology, particle size, and thermal properties were investigated. Titanium dioxide particles were added to the texture of polypyrrole nanoparticles as the filler in order to increase electron transfer in the active layer of the solar cell. Polypyrrole nanoparticles were electrochemically synthesized in the shortest time possible with an ideal morphology and a particle size of less than 40 nm using a new multi-step amperometry technique. The results of EDAX analysis confirmed the existence of titanium particles in the texture of polypyrrole. The crystal size was determined through XRD analysis. SEM images confirmed the uniform and spherical appearance of polypyrrole nanoparticles with spongy and porous structures. Based on the results, the increase in the efficiency of the prepared solar cell based on polypyrrole/TiO_2 nanocomposite coated on the copper surface (compared to common polymeric solar cells) was 39.7%. Application of copper as the conductive metal surface improves the electrical conductivity .

Keywords
Polypyrrole Nanoparticle; Titanium Dioxide; Solar Cell; Energy Conversion Efficiency.

1. INTRODUCTION

Energy has always been among the most challenging issues in the world. Regarding the recent technological advances and the increasing need of plants and industrial centers for energy, availability of cheap and unlimited resources seems to be necessary. For many years, fossil fuels such as oil, coal, and natural gas have been considered as the main sources of energy. Sunlight is the predominant renewable source of energy in the world and genesis and survival of living organisms depend on solar energy. The energy stored in all fossil fuel reserves on the planet is equal to that of only 4 days of sunshine on the earth.

Conversion of sunlight into electricity was first introduced by Edmund Bequerel in 1839 after the discovery of photovoltaic (PV) effect[1]. However, the first commercial application of solar cells was proposed 100 years later, with the invention of Silicon-based crystalline cells by researchers at Bell Labs in 1954[2]. The first Silicon cell had an efficiency of about 4%. Since then, researchers have sought to produce and commercialize solar cells with higher efficiencies and lower manufacturing costs[3]. Development of nanostructured products has brought new insight into the material science. Due to the unique size of nanomaterials and their characteristics, quantum laws have become of great importance. When the size or dimensions of a matter steadily changes from very large to very small dimensions, its features do not initially change. Then, small changes start to occur when it reaches a size below 100 nanometers, where molecular bonds break and London forces can result in the movement, arrangement and displacement of atoms. Generally, a group of materials that are less than 100 nm in size are called nanomaterials. An important characteristic of nanomaterials is their high surface/volume value, which is defined as the number of surface border atoms divided by the total number of atoms. This unique property of nanomaterials has made them good candidates for application in solar cells and panels[4]. In general, the extensive use of nanomaterials can open new ways into the world of solar energy or renewable sources of energy. As mentioned earlier, due to the increasing energy demand, finitude of fossil fuels and environmental problems caused by pollutants, utilization of clean energy sources (especially solar power) has attracted a great deal of interest. Currently, more than 80% of commercially available solar cells are made of crystalline silicon. However, despite the higher efficiency of these cells compared to other solar cells, their production is very expensive. The aim of the present research was to study the electrochemical synthesis of a nanocomposite of Polypyrrole

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(PPy) and TiO_2 on the copper surface and its application as the active layer in solar cells. PPy/TiO_2 nanocomposite enhances the efficiency of solar cells[5-15]. Pyrrole-TiO_2 bounded systems are used to find the best tailored composite for photo degradation of environmental pollutants and solar water splitting[13]. In this study, PPy/TiO_2 nanocomposites were successfully prepared through a simple chemical method and based on the results, they were stable for practical applications[14].

2. EXPERIMENTAL

2.1. Materials

To synthesize polypyrrole nanoparticles, pyrrole, oxalic acid (which was used as the electrolyte) and titanium dioxide powder were all purchased from Merck Co. (Germany). We used a copper electrode with a spherical surface and an area of 0.5 cm^2 as the working electrode.

2.2. Methods

Before starting the experiments, the surface of copper electrode was carefully polished using a 1500 sandpaper, decreased in a 1:1 mixture of acetone/ethanol, washed with double distilled water and dried at room temperature [12]. All solutions utilized in this study were prepared using double distilled water and all experiments were conducted at ambient temperature and pressure. A potentiostat and a three-electrode electrochemical cell were used for coating tests and synthesis of polypyrrole nanoparticles. In addition, platinum and calomel electrodes were used as the auxiliary and reference electrodes, respectively. Coated polypyrrole nanoparticles were synthesized on the copper surface through chronoamperometry in an aqueous solution of oxalic acid containing pyrrole monomer at a concentration of 0.1 M (T_{RUN}=100 s, $T_{Interval}$=0.01 mv/s, E_{dc}=1 V) using an Emstst 1 compact potentiostat (PalmSens, Poland).

3. RESULTS AND DISCUSSION

3.1. Synthesis of polypyrrole

Since the oxidation potential ranges of copper and polypyrrole are close to each other, copper may oxidize before polypyrrole oxidation and therefore, a polypyrrole film can grow on the surface while copper oxide is being formed, resulting in a heterogeneous and less adhesive polymer. Therefore, before starting the synthesis process, it was necessary to first conduct a passivation process using the oxalate factor and cyclic voltammetry technique so as to prevent the early oxidation of copper. In this stage, four full passivity cycles were conducted using a 0.1 M aqueous solution of oxalic acid and the cyclic voltammetry technique at a potential range of -1 to +1 V and a scanning rate of 0.020 mV/s (as shown in Fig.1).

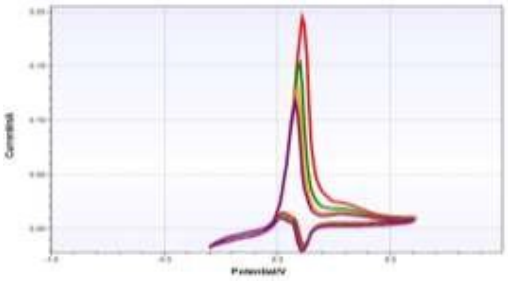

Fig. 1. The cyclic voltammetry behavior of copper in a 0.1 M oxalic acid solution at a scanning speed of 0.020 mV/s (oxidation-passivation of copper).

The passivity mechanism involves the formation of insoluble compounds such as copper oxide (of types I and II) and copper oxalate on the metal surface. However, a passive layer of copper oxalate (I) with a very low solubility product is often formed.

$2Cu + H_2O \Leftrightarrow Cu_2O + 2H^+ + 2e^-$, $E = 0.166$ V

$Cu + H_2O \Leftrightarrow CuO + 2H^+ + 2e^-$, $E = 0.267$ V

$Cu^{+2} + C_2O_4^{-2} \Leftrightarrow CuC_2O_4$, $K_{sp} = 2.87 \times 10^{-8}$

The participation rate of copper oxides in the passive layer was small, as the synthesis solution was acidic and these compounds exhibit little stabilities in environments with pH levels below 7. A sharp anodic peak was observed at +113 mV, being related to the oxidation-passivation process on the copper surface. In addition, a cathodic (reductive) peak was observed at +0.13 mV, as a result of the reduction of copper oxides (I and II). After copper surface passivation, polypyrrole nanoparticles were synthesized on the copper surface through the amperometry technique (as illustrated in Fig. 2).

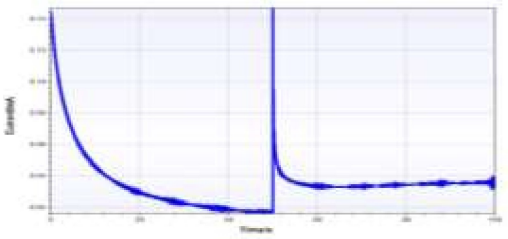

Fig. 2. Multi-step amperometry curve in a 0.1 M oxalic acid solution and a 0.1 M polypyrrole solution.

This method, in which the coating process is carried out in two stages, is called the multi-step amperometry technique. E_{dc} levels were set to 1 and 2 V in the first and second steps, respectively, while T_{RUN} was 50 s in both steps. The two steps were performed continuously and there was no

delay between them[5]. After synthesis of polypyrrole nanoparticles and coating them on the copper surface, they were immersed in a 0.01 M titanium dioxide solution for 24 hours so as to allow titanium particles locate in the spongy texture of the polypyrrole nanoparticles[6,7].

3.2. Particles size and morphology

To determine the morphology and size of particles, we used scanning electron microscopy (SEM), which allows imaging with a magnification of 10 to 500,000 times and a resolution of less than 1 to 20 nm (depending on the sample type) [8]. Fig. 3 depicts SEM images of polypyrrole nanoparticles synthesized on copper surface. These images confirm the uniform and spherical appearance of polypyrrole nanoparticles with spongy and porous structures. The presence of some larger particles in the micrographs is due to the density or overlapping of some smaller particles during the preparation stage. The average size of particles was in the nanometer scale (100 nm), with a minimum size of less than 34 nm. Such size of polypyrrole nanoparticles in association with their spongy and porous structure make them ideal for application as the active layer in solar cells.

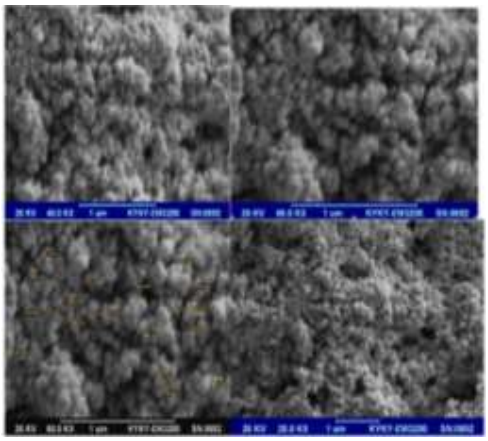

Fig. 3. SEM images of polypyrrole nanoparticles synthesized on copper with three different magnifications (20000X, 40000X, and 60000X).

3.3. Crystalline structure and phase purity

X-ray diffraction, which is a method for assessing the structure of crystalline materials, was discovered by Von Laue in 1912 and later used by William Henry Bragg and William Lawrence Bragg for studying crystals. X-rays with wavelengths in the range of 0.5 to 2.5 Å are usually used for diffraction. This method is based on the wave nature of X-ray. The nuclei of atoms in a crystal lattice are in a short distance (about a few angstroms) from each other. X-ray reflection of these successive sheets results in the constructive or destructive interference of the X waves. In the case of constructive interference, the distance between crystalline sheets and also the size and type of unit cell can be obtained using the Bragg's formula [9]. In Fig. 4, the crystalline structure and phase purity have been demonstrated via the XRD model. Peaks of the polypyrrole/titanium dioxide nanocomposite in the scattering angles are related to diffraction sheets.

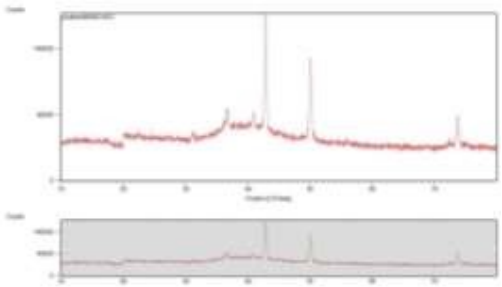

Fig. 4. XRD pattern of the prepared PPy/TiO_2 nanocomposite.

Based on Expert software and its database, the synthesized nanoparticles had been crystallized in the monoclinic system. No impurity peak was observed in the XRD pattern, which showed a good consistency with the reference material. The broadness of lines in the XRD pattern was indicative of very small-sized nanoparticles. In addition, according to the outputs of Expert software, the crystallization rate of nanoparticles was above 80%, which can certainly increase the surface to volume ratio. The crystallite size was calculated to be 40.76 nm, based on the Debye-Scherrer formulation.

3.4. Elemental analysis of PPy/TiO_2 nanocomposite synthesized on the copper surface

Energy dispersive X-ray spectroscopy (EDS or EDX) is an analytical method for analyzing the structural or chemical properties of a sample, based on the interaction between an X-ray excitation source and the sample. The descriptive capabilities of this method are generally based on the principle that each element has a unique atomic structure and therefore exhibits a set of unique peaks in its X-ray spectrum. To stimulate the X-ray emission of a sample, a high-energy beam of charged particles such as electrons or protons or a set of X-rays is focused on the sample. Each atom inside the sample at rest includes the ground state or unstimulated electrons at a discrete level of energy or electron layers attached to the core. The applied ray may stimulate an electron in an inner shell and make it slough, while creating an electron hole in the former location of the electron. Then, a higher-

energy electron from an outer layer fills the hole. As a result, the energy difference between the high- and low-energy layers is released in the form of an X-ray. The number and energy of X-rays emitted from a sample can be measured using an energy dispersive spectrometer. Since X-ray energy represents the energy difference between two layers and the atomic structure of the corresponding element, it can be used to determine the elemental composition of sample [10]. The results of EDX analysis for PPy/TiO_2 nanocomposite (shown in Fig. 5) confirmed the presence of carbon and oxygen with high concentrations and titanium with a lower concentration. It is notable that a high peak intensity is indicative of the high concentration of the corresponding element in the sample.

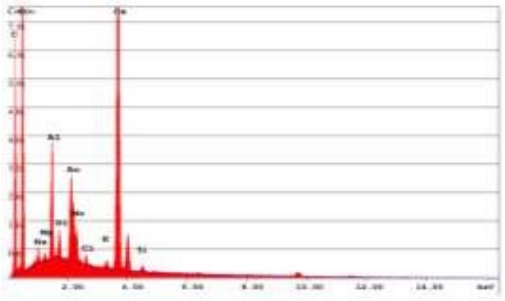

Fig. 5. EDX spectrum of the prepared PPy/TiO_2 nanocomposite.

3.5. Efficiency of the prepared solar cell based on PPy/TiO_2 nanocomposite synthesized on the copper surface

The three main parameters defining the characteristics of a solar cell include the short circuit current (I_{SC}), the open circuit voltage (V_{OC}), and the maximum power point (I_{MP} and V_{MP}). Another important parameter in solar cell characteristics is the Fill Factor (FF) (Fig. 6.) which actually indicates how much the characteristic curve can fill the rectangle defined by I_{SC} and V_{OC}. This parameter represents the semiconductor quality and measures cell capability to collect carriers generated by light, as the following:

$$FF = \frac{Vmp\ Imp}{IscVoc}$$

With a slight simplification, the following equation can be obtained:

$$IscVoc.FF = ImpVmp = p_{max}$$

It is evident that FF value is always less than 1 and may vary in different cases. The closer this value is to 1, the better the performance of the solar cell. FF level of high quality cells may be even greater than 0.85, while this feature is about 0.68 for common parts [11].

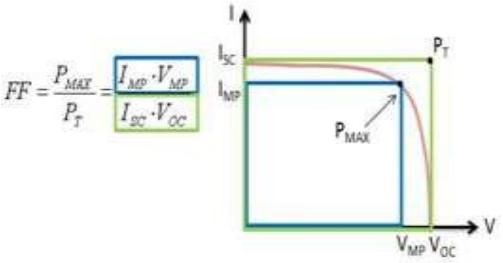

Fig. 6. Characteristics of a solar cell and FF.

3.6. Solar cell efficiency

The best power conversion efficiency (PCE) in photovoltaic power conversion for a solar cell, which is usually shown with η, is defined as below:

$$\eta = \frac{JmpVmp}{PIN}$$

Here, J_{MP} and V_{MP} denote the density of maximum power flow and the maximum power voltage, respectively. In addition, P_{IN} represents the power of emitted photons. This equation is based on the assumption that the area of photovoltaic cells in which photons are collected is equal to the area where the flow is generated. In the case of cells in which light is collected in an area larger than the flow generation area, the efficiency is obtained using the following equation:

$$\eta = \frac{AS}{AC}\frac{JmpVmp}{PIN}$$

Where A_S and A_C represent the flow generation and photon collection areas, respectively. In addition to the power conversion efficiency, another efficiency is also defined for a solar cell, which is called the quantum efficiency (QE). This efficiency is equal to the ratio of the number of carriers of the collected charges by the solar cell to the number of photons emitted to the cell surface with a specific energy. As a result, QE is related to the solar cell response to different wavelengths of the solar spectrum. If all photons of a certain wavelength are absorbed and all minority carriers created could be collected, then QE at that wavelength is equal to 1. Quantum efficiency is zero for photons with energies below the band gap energy. Calculation of quantum efficiency is a method for part analysis by experts and is not simply and directly related to power conversion efficiency. For example, for a cell with a PCE of 15%, QE may be more than 90%.

3.7. The efficiency of solar energy conversion into electricity (η) by PPy/TiO_2 nanocomposite synthesized on the copper surface as the active layer in solar cell

To obtain the efficiency and maximum power of PPy/TiO_2 nanocomposite as the active layer in a

solar cell, the flow-voltage curve was used. The following circuit was developed to perform analysis: A potentiometer was connected to the solar cell (Table 1). First of all, the open circuit voltage at the maximum state was obtained under direct sunlight. Then, the resistance level was changed and the flow rate was measured. According to Fig. 7, the point where the voltage starts to decrease is the point at which the maximum power is obtained.

Table 1. Parameters obtained from a solar cell under direct sunlight.

V_{OC}(V)	I_{SC}(A)	P_{MAX}	V_{MP}(V)	I_{mp}(A)	FF	η
0.6	.116	3.6%	0.58 V	0.62	56.7	39.7

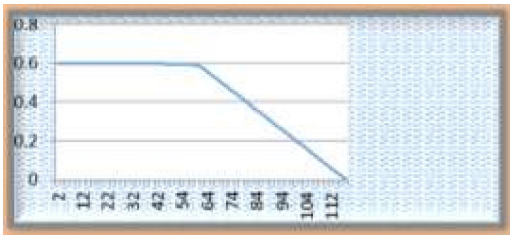

Fig. 7. The V-I curve for PPy/TiO_2 nanocomposite under direct sunlight and different resistance levels.

The solar cell efficiency was obtained through calculating the maximum power and Fill factor (FF). The maximum voltage under direct sunlight was obtained as 0.6 V and the maximum flow was calculated to be about 116 mV. These two values along with voltage and flow values were used at the point corresponding to the maximum power so as to determine the efficiency. Table 1 shows the results obtained for the solar cell based on PPy/TiO_2 nanocomposite coated on the copper surface (1 x 1 cm^2). Finally, the efficiency of such nanocomposite as the active layer in solar cell was obtained to be about 39.7%, which was very ideal. Fig.7. shows that in addition to the ideal properties of the studied nanocomposite, utilization of copper as the conductive metal surface can enhance the electrical conductivity and result in a considerable flow from the collision of the produced photons, though it may also increase the production costs of polymer solar cells.

4. CONCLUSION

One of the very valuable events in the field of energy and particularly solar cells is the application of nanomaterials in the manufacture of solar cells and equipments. The aim of the present project was to reduce the production costs and improve the power conversion efficiency of solar cells, using cheap organic (polypyrrole nanoparticles) and mineral (TiO_2) materials as flow creating layers in solar cells. First of all, using a new multi-step amperometry technique, polypyrrole nanoparticles were electrochemically synthesized in the shortest time possible with an ideal morphology and a particle size of less than 40 nm (according to SEM data). To improve the structure of polypyrrole nanoparticles synthesized on the copper surface, TiO_2 particles were used, as both polypyrrole and TiO_2 are among the best fillers and exhibit high conductivities. The presence of titanium particles in the polymer coating layer was confirmed by EDX data. Based on XRD results, not only the existence of the PPy/TiO_2 phase was confirmed, but also the size of crystal structure was determined to be about 40 nm, which is very suitable for application in solar cells. Finally, using the open circuit voltage and the flow resulting from the prepared nanocomposite in a solar cell, its power conversion efficiency was calculated to be about 39.7%.

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سنتز الکتروشیمیایی نانو کامپوزیت پلی پیرول/دی اکسید تیتانیم به عنوان یک سل خورشیدی با ظرفیت بالا

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چکیده

در تحقیق حاضر، نانوذرات پلی پیرول بر روی سطح مس با بکار بردن روش آمپرومتری سنتز شده‌اند. خواص سطحی و اندازه ذرات و خصوصیات دمایی آن مورد بررسی قرار گرفتند. ذرات دی اکسید تیتانیم به عنوان پرکننده برای افزایش انتقال الکترون در لایه فعال سل خورشیدی به نانوذرات پلی پیرول اضافه شدند. نانوذرات پلی پیرول به روش الکتروشیمیایی در کمترین زمان ممکن با ایده‌آل‌ترین مورفولوژی و اندازه ذرات کمتر از ۴۰ نانومتر به روش امپرومتری چند مرحله‌ایی سنتز شدند. نتایج آنالیز EDAX حضور ذرات دی اکسید تیتانیم در ساختار پلی پیرول را اثبات کرد. سایز کریستال‌ها توسط XRD مشخص شدند. تصاویر SEM حضور ذرات کروی نانو پلی پیرول را مشخص کرد. براساس نتایج بدست آمده، ظرفیت سل خورشیدی تهیه‌شده بر پایه نانوکامپوزیت پلی پیرول/دی اکسید تیتانیم ۳۹,۷ درصد می‌باشد. کاربرد مس به عنوان سطح فلزی رسانا، خاصیت هدایت الکتریکی و شارش جریان بهتر فوتون‌ها را بهبود می‌بخشد.

واژه‌های کلیدی

نانو ذرات پلی پیرول؛ تیتانیوم دی اکسید؛ سلول خورشیدی؛ بازده تبدیل انرژی.