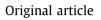
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# Enhanced efficiency of flexible organic polymer solar cells by incorporation of titanium dioxide nanoparticles



Manal A. Awad <sup>a,\*</sup>, Awatif A. Hindi <sup>b</sup>, Khalid M.O. Ortashi <sup>c</sup>, Meznah M. Alanazi <sup>b,\*</sup>, Albandari W. Alrowaily <sup>b</sup>, Taghreed Bahlool <sup>b</sup>, Fatma Aouaini <sup>b</sup>

<sup>a</sup> King Abdullah Institute for Nanotechnology, King Saud University, Riyadh 11451, Saudi Arabia

<sup>b</sup> Department of Physics, College of Science, Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia

<sup>c</sup> Department of Chemical Engineering, King Saud University, Riyadh, Saudi Arabia

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# ABSTRACT

Solar power has quickly become one of the most effective forms of renewable energy today as it provides a clean solution to the growing demand for energy. Most solar panels in the market are rigid as they are made up of metals; therefore, organic polymers provide a flexible alternative. Nanotechnology provides the synthesis of nanoparticles by simple approaches suitable for applications in various fields. Nanoparticles of titanium dioxide (TiO2) were synthesized and characterized in this paper (NPs), which were further incorporated in the construction of a novel, organic polymer solar panel (OPSC) that is flexible and portable; it is made from thylakoid (chloroplast) extract of chard (B. vulgaris subsp. cicla) combined with polystyrene polymer matrix. Insertion of TiO<sub>2</sub> NPs in the OPSC improved the current generation compared to the reference devices (OPSC) without TiO<sub>2</sub> NPs. Therefore possible uses for the constructed solar panel were suggested. The prepared films were tested for the current generation. Under illumination, the solar panels generated a current of  $-140 \mu$ Ap, and  $-213 \mu$ Ap without and within TiO2 NPs, respectively. This study opens windows for manufacturing flexible, efficient, and stable organic polymer solar panels.

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# 1. Introduction

New technologies are being pushed forward by the increasing need for resources and the availability of renewable energy that uses photovoltaic energy conversion. Recently, polymer solar panels have become attractive and gained much interest as sustainable solar energy converters because they are cheap, light in weight, and have potential applications in vast areas of flexible devices (Jin et al., 2021; Riede et al., 2021; Liu et al., 2021). The present method for constructing polymer solar cell systems is based on

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the bulk heterojunction structure idea, where the polymer donor is the electron-rich active ingredient. At the same time, an electron-poor fullerene is an acceptor (Song et al., 2010). However, in addition to the merits of classical polymers, organic solar cells (OSCs) have the distinction of being non-toxic raw materials (Hou et al., 2008; Yang et al., 2021).

Inserting an inorganic buffer layer between the electrode and active layer is one of the methods for improving the efficiency of power conversion and the lifetime of OSCs. Such a buffer layer could lead to modifications in the interface of organic/electrode and changes in the interface's chemical nature (Turak, 2013; Zhou et al., 2013; Wang et al., 2021). Moreover, it could prevent electrode atoms, oxygen, and water from penetrating the device's active layer (Williams et al., 2013). Various inorganic and n-type inorganic salts and semiconductors have been used as buffer layers to improve the efficiency of power conversion and the OSC lifetime. These materials include LiF, CsCO3, and ZnO (Turak, 2013; Yang et al., 2010; Hau et al., 2008).

Oxides of transition metals have attractive semiconductor properties as they offer optically and electronically excellent charge transporters. They can be tuned by introducing dopants in various

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<sup>\*</sup> Corresponding authors.

*E-mail addresses*: mawad@ksu.edu.sa (M.A. Awad), AAHindi@pnu.edu.sa (A.A. Hindi), ortashi9@ksu.edu.sa (K.M.O. Ortashi), mmalenazy@pnu.edu.sa (M.M. Alanazi), awalrowaily@pnu.edu.sa (A.W. Alrowaily), Tmbahlool@pnu.edu.sa (T. Bahlool), fasaidi@pnu.edu.sa (F. Aouaini).

ways to generate nanostructures or modify their surfaces. Thus, these metal oxides serve different roles in a 'hybrid' inorganic/or-ganic photovoltaic device (Gershon, 2011).

The binary metal oxide titanium dioxide (TiO2) is one of the Earth's most common elements. It often exists in the rutile and anatase phases and is known as a photocatalyst that is chemically stable and non-toxic (Radzuan et al., 2017; Xu, 2019). Photosensitizers comprise compounds that can absorb light in a photochemical reaction and transfer energy to the reactant (Ahmad et al., 2021). TiO<sub>2</sub> can also act as a photosensitizer (Glass et al., 2018). However, photocatalysis is the most attractive property of TiO<sub>2</sub> nanoparticles (TiO<sub>2</sub> NPS) reported applications. But, the cosensitization of TiO<sub>2</sub> NPs was proposed for improving the photovoltaic performance of solar panels by increasing the wavelength of harvested light; they can harvest unlimited energy of visible light and UV parts of the sunlight (Balasingam et al., 2013; Luo et al., 2019).

As a semiconductor,  $TiO_2$  has been used in polymer solar cells as a buffer layer in previous studies (Yoon et al., 2008; Lee et al., 2007; Cho et al., 2021).  $TiO_2$  can also serve as an efficient electron transporter, optical spacer, hole-blocking layer, and scavenging and shielding layer, improving polymer solar cell devices' power conversion efficiency and blocking oxygen and moisture from penetrating the active layer (Zhong et al., 2019).

In the present study, we report a framework for developing a facile method to construct organic polymer solar panels by incorporating chloroplasts extracted from chard (*B. vulgaris* subsp. *cicla*) which is a green leafy vegetable that has very rich thylakoids and the synthesis and characterization of  $TiO_2$  NPs, which were inserted in OPSC. The performance of the constructed organic polymer solar panel to generate current was then determined.

#### 2. Materials and methods

#### 2.1. Synthesis of titanium dioxide nanoparticles (TiO<sub>2</sub> NPs)

Titanium dioxide nanoparticles were synthesized by mixing titanium (IV) isopropoxide (TTIP) and distilled water at a ratio of 2:1 under continuous stirring for 5 h at room temperature until a milky paste solution was formed. The answer was heating at 80 °C for 2 h in a hot plate. The paste was dried at 60 °C in the oven, pulverized, and then calcinated in a muffle furnace at 400 °C. The resulting white powder contained  $TiO_2$  nanoparticles.

#### 2.2. Characterization of titanium dioxide nanoparticles (TiO<sub>2</sub> NPs)

Several techniques were used to characterize the powder sample, as follows:

X-ray diffraction (XRD) analysis. This was accomplished utilizing a 40 KV, 40 MA, nickel-filtered Cu radiation (k = 1.54056) X-ray diffractometer manufactured by Bruker (Company, City, Country).

Dynamic light scattering(DLS). Particle size distribution of produced TiO2 NPs was analyzed using dynamic light scattering. This was achieved by completely dissolving the pulverized TiO2 NPs in distilled water. Then, ultrasonication (Bransonic-M3800-E, 50 – 60 Hz, 130 W., Mexico) was applied to ensure that the NPs were uniformly distributed in the solution; in this solution, particle size distribution was determined using Malvern Instruments (Zetasizer Nano Series HT laser, UK).

Transmission electron microscope (TEM). The size, shape, and distribution of the produced TiO2 NPs were analyzed by TEM (JEOL (JEM 1400 Plus, USA).

Energy-dispersive spectrometer (EDS). To identify the composition of the synthesized TiO<sub>2</sub> NPs, an X-ray Energy Dispersive Spectrometer (EDS) was as used as described previously (Awad and Hendi, 2021) JEM-2100F, JEOL Ltd., USA)

#### 2.3. Extraction of chloroplast thylakoids

A green extract of *B. vulgaris* subsp. *cicla* was made in the same way it had been reported earlier, and it proved to be an effective thylakoid stabilizer (CT) for making chloroplasts(Deshmukh and Deshmukh, (July. 2015)). This was accomplished by washing and mixing half a conventional-sized bag of *B. vulgaris* subsp. *cicla* leaves in around 200 mL of water for 3 to 5 min and then centrifugation at 6,000 rpm for 15 s to get rid of crude cell debris and nuclei, dense organelles. Then, the supernatant was centrifuged for 20 min. After centrifuging the pellet for 20 min, it was reassembled in water.

#### 2.3.1. Fabrication and construction of the solar panel

The polymer matrix solar panel was fabricated and constructed as previously described (Deshmukh and Deshmukh, 2015; De Rossi et al., 2015). To create the flexible solar panel, 4 g of polystyrene (PS) was dissolved in 30 to 60 mL of toluene with vigorous stirring at 60 °C to generate a first solution. Then 30 to 50 mg of CT was added to the mixture and stirred until it was uniform (Fig. 1). The solar panels' ability to generate electricity was measured using a microvolt digital multimeter (Keithley 177  $\hat{A}\mu V$  DMM) after being exposed to light from a 12-volt bulb (producing a mean intensity of 700 lx) (Awad and Hendi, 2021).

## 3. Results and discussion

The phase formation and crystallinity of TiO2 NPs may be determined using the X-ray diffraction (XRD) method. Fig. 2 depicts the XRD pattern of TiO2 NPs. Using diffraction angles, the sample showed a high degree of crystallinity (2 theta) of 25.61° (101), 37.88° (004), 47.85° (200), 54.64° (105) (211), 62.76°(204), 69.39° (116) and 75.77° (215), This demonstrates that the titanium is highly crystalline and contains anatase phase. The obtained raw data were evident with the standard JCPDS card (COD 2300113). The pure and crystalline nature of the manufactured nanoparticles may be deduced from the strong peaks produced by diffraction (Kalaiarasi and Jose, 2017). It is well-known that the anatase phase is the most dynamic for photocatalysis (Mohammadizadeh et al., 2015). Moreover, anatase phase layers are typical super hydrophilic surfaces (Mariquit et al., 2015). Due to its more significant photocatalysis activity, anatase recorded the highest application score in the industry as the commercial form that is mainly used (Hasan et al., 2021).

The dynamic light scattering (DLS) method was used to analyze the particle size distribution of the produced TiO2 NPs. Fig. 3 represents the DLS plot. TiO<sub>2</sub> NPs synthesis is indicated by the maximum intensity recorded for 130.5 nm average particle size. Mono-dispersed TiO2 NPs also show good dispersion and longterm stability with a PDI of 0.472. TiO2 NP aggregation was calculated using PDI values between 0 and 1 (Awad et al., 2021). This further justified the size distribution of the synthesized TiO<sub>2</sub> NPs as determined by the TEM study.

To identify the composition of the synthesized  $TiO_2$  NPs, an Xray Energy Dispersive Spectrometer (EDS) was used. The EDX spectrum is shown in Fig. 4. The peaks of titanium (Ti) and oxygen (O) indicate the purities of the prepared  $TiO_2$  NPs: oxygen and titanium in the sample are 34.08% and 65.92%.

The size, morphology, and distribution of synthesized TiO<sub>2</sub> NPs were determined by the transmission electron microscope (TEM).

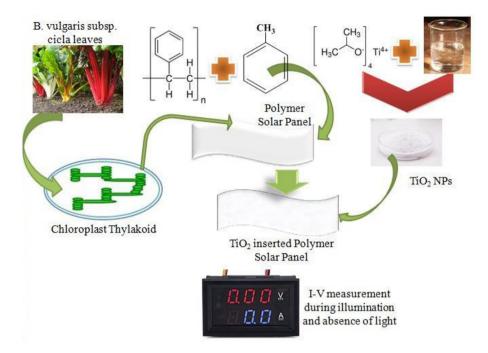


Fig. 1. Schematic diagram showing all steps involved in synthesizing TiO-NPs, fabrication, and construction of the solar panels.

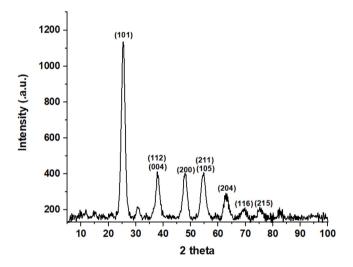
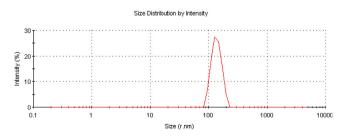


Fig. 2. X-ray diffraction (XRD) patterns of crystalline titanium dioxide nanoparticles ( $TiO_2$  NPs).



**Fig. 3.** Particle size distribution curve of synthesized titanium dioxide nanoparticles using dynamic light scattering (DLS) technique.

TEM images of the prepared  $TiO_2$  samples were well uniform and dispersible, as shown in Fig. 5. Red arrows point to TEM bright field images of  $TiO_2$  NPs in the anatase phase. These findings agree with

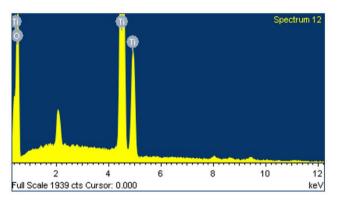


Fig. 4. X-ray energy dispersive spectrometry (EDS) pattern of synthesized TiO<sub>2</sub> NPs.

the XRD results of other investigators (Thamaphat et al., 2008; Hossain et al., 2021).

The panels were constructed on a transparent sheet (template) made of a polymer matrix with incorporated thylakoids with and without synthesized  $TiO_2$  NPs. After drying, the polymers were removed from the templates; the result was portable and flexible films. Then, the films were tested for the current generation. Under illumination, the solar panels without  $TiO_2$  NPs generated a current of  $-140 \mu$ Ap. Moreover, the solar panel, which contained TiO2 NPs, was subjected to testing of current generation under illumination after exposure to the light. A current of  $-213 \mu$ Ap was generated, thus also exhibiting a noticeable rise in the present age with the presence of NPs. The output current obtained is in microampere ( $\mu$ Ap). Prospects research can cover further investigations and measurements that could be performed, such as shelf life, thermal stability, conductive stability, and study of solar panel efficiency.

The theoretical base for this experiment lies on the natural phenomenon that occurs in the natural light-harvesting system resulting in electron excitement, i.e., a photosystem embedded in the thylakoid that is accepted finally by nicotinamide adenine dinucleotide phosphate (NADP) out of the thylakoid membrane. To use this phenomenon, an artificial electron acceptor was used here

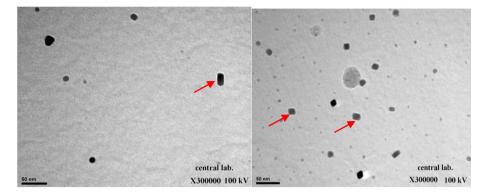


Fig. 5. Transmission electron microscope (TEM) image of synthesized anatase titanium dioxide nanoparticles (TiO<sub>2</sub> NPs).

to replace the NADP. This way, the electron that flows through Electron Transport Chains (ETC) will be accepted by this conducting polymer leading to completing the electrical circuit, thus generating electrical energy (Koli and Sharma, 2021; Shen et al., 2021). Many studies have been discussed. The leading critical technologies for further improvement of PSC of "flexible-ultrathin" organic SC have been addressed in many studies, and techniques for improving the mechanical robustness, thermal efficiency, and overall stability of flexible OPSCs were discussed. Also, other researches were the target of current achievements in the field of flexible OPSCs, stressing the principles and concepts behind the leading technologies and elaborating on future challenges in this discipline (Fukuda et al., 2020; Pagliaro et al., 2008; Liu et al., 2021).

The advantages of this solar panel are that it can be easily constructed and disposed of after being used. Besides its flexibility and portability, it is cost-effective. Such solar panels can easily be used everywhere in the future.

The constructed solar panel in the present study represents a small module in a primary stage. The current output measured in the microampere was successfully improved by incorporating  $TiO_2$  NPs as semiconductors in the light-harvesting system. This solar panel can be a portable charger for small devices like watches and mobile phones.

#### 4. Conclusion

The present study outlined a simple and successful method for synthesis and further physical/chemical characterization of  $TiO_2$  NPs. XRD spectrum proves that the synthesized  $TiO_2$  nanoparticles are pure crystalline anatase phase. Furthermore, the successful construction of a solar panel using a biological system as a principal component was achieved by the incorporation of the synthesized  $TiO_2$  NPs. The produced solar panel can be easily constructed, maintained, and disposed of; it is portable, flexible, and cheap, thus suitable for daily use.

#### **Author contribution**

All co-authors have contributed to this work and are aware of this submission.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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