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## ENHANCING PHOTOVOLTAICS: TIO2 ON CONDUCTIVE POLYMERS FOR DSSCS

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#### **Article Info**

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#### **Abstract**

Solar energy presents significant potential as a clean and renewable source of electricity. In recent years, there has been a growing interest in the development of low-cost solar cells based on molecular materials and semiconductor nanostructures. While silicon solar cells currently dominate the commercial market, their energy-intensive production methods and high manufacturing costs have spurred the exploration of alternative technologies such as dye-sensitized solar cells (DSSCs) and organic solar cells (OSCs).

To achieve widespread adoption of next-generation photovoltaics, the focus has shifted towards creating versatile and cost-effective devices. One promising approach involves replacing traditional glass substrates with flexible plastic substrates and eliminating costly transparent conducting oxides (TCO), thereby paving the way for extremely low-cost photovoltaics with diverse applications. Conductive polymer substrates, including ITO-coated polyethylene terephthalate (PET), polyester, and polyethylene naphthalate (PEN), have emerged as leading candidates for flexible substrates.

Developing techniques for the preparation of TiO2 films on conductive plastic substrates at low temperatures (below 150 oC) has been a key research area. Several methods have been explored, such as sintering TiO2 colloidal at 100 oC on flexible substrates without the use of organic surfactants as binders, leading to promising results with open-circuit voltage, short-circuit current density, fill factor, and overall power conversion efficiency of 647 mV, 2.05 mA/cm2, 69%, and 1.22%, respectively, under 1 sun illumination.

Another noteworthy approach involves the low-temperature fabrication of TiO2 electrodes for flexible dye-sensitized solar cells using an electrospray process. Varying the electrode thickness resulted in power conversion efficiencies of 2.93%, 3.80%, 5.02%, 4.90%, 4.84%, 4.53%, and 4.26% for thicknesses of 3, 6, 9, 12, 15, 18, and 21  $\mu$ m, respectively.

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These advancements in low-cost, flexible photovoltaic technologies hold great promise for realizing efficient, lightweight, and portable solar cells that can be integrated into a wide range of applications. The continuous efforts to innovate and optimize these devices bring us closer to a sustainable energy future.

#### INTRODUCTION

Solar or photovoltaic (PV) cells, for example, offer a variety of strategic benefits in terms of their capacity to directly transform plentiful solar energy into electricity in a clean, quiet, and dependable manner, necessitating the development of sophisticated renewable energy technologies. There has been a rising interest in the production of low-cost solar cells based on molecular materials and semiconductor nanostructures during the last two decades (Weerasinghe et al., 2013). Solar cells made of silicon now dominate the commercial market, however their production methods are energy demanding and need high vacuum conditions, resulting in high manufacturing costs (Wante et al., 2020b). Dye-sensitized solar cells (DSSCs) and organic solar cells (OSCs) have shown their potential as low-cost alternatives to silicon solar cells in this area. Furthermore, fabricating DSSCs on a rigid clear conducting oxides glass substrate has certain drawbacks in terms of fragibility, weight, and stiffness, prohibiting roll-to-roll mass manufacturing and integration of DSSCs in a variety of portable devices (Yoo et al., 2015). Polymer based DSSCs have shown the potential to be used for roll to roll processes due to its numerious advantages such as flexibility and light weight.

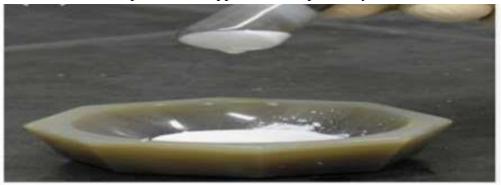
It is critical to create versatile and cost-effective devices in order to commercialize and widely apply next-generation photovoltaics. Given this, replacing traditional glass substrates with flexible plastic substrates and eliminating costly transparent conducting oxides (TCO) provides a plausible method for achieving extremely low-cost photovoltaics with a potentially broad use (Yoo et al., 2015).

Most of the flexible substrates are conductive polymer substrates, such as ITO coated polyethylene terephthalate (PET), polyester and polyethylene naphthalate (PEN) (Yamaguchi et al., 2007)As a result, several attempts have been undertaken to develop preparation techniques for TiO<sub>2</sub> films on conductive plastic substrates using lowtemperature sintering below 150 °C (Fan et al., 2010). Pichot et al. (2000) sintered TiO<sub>2</sub> colloidal at lower temperature of 100 °C on a flexible substrate without the use of any organic surfactant as binder under 1 sun illumination, yielding an open-circuit voltage of 647 mV, a short-circuit current density of 2.05 mA/cm², and a fill factor of 69%, and an overall power conversion efficiency of 1.22%. Lee et al. (2012) also reported a lowtemperature fabrication of TiO<sub>2</sub> electrodes for flexible dye-sensitized solar cells using an electrospray process at different thicknesses of 3, 6, 9, 12, 15, 18, and 21 μm which yielded power conversion efficiencies of 2.93, 3.80, 5.02, 4.90, 4.84, 4.53 and 4.26 % respectively.

### Synthesis of TiO<sub>2</sub> paste for flexible substrate

Preparation of suitable TiO<sub>2</sub> pastes to produce high quality mechanically stable films without organic binders is one of the challenges when fabricating DSSCs on plastic substrates. In order to prevent film cracks due to large agglomerates, the TiO<sub>2</sub> nanoparticles are required to be well dispersed in the paste. Wante et al. (2020b) prepared TiO<sub>2</sub> paste by synthesizing TiO<sub>2</sub> powder with ethanol and de-ionized water for TiO<sub>2</sub> layer deposition without the use of any organic surfactant as binders. They stirred the mixture for 10 mins for proper dilution of the compound and the TiO<sub>2</sub> powder so that the TiO<sub>2</sub> particles were well dispersed in the paste. Yamaguchi et al. (2007) prepared TiO<sub>2</sub> paste, which composed of a mixture of TiO<sub>2</sub> powder and ethanol at a concentration of 20 wt% and deposited on a flexible PEN which yielded a reasonable PCE. Fu et al. (2015) synthesized pure anatase TiO<sub>2</sub> nanoparticles and organic-free TiO<sub>2</sub>-sol individually in organic-free solution. They mixed the pure anatase TiO<sub>2</sub> with the newly

developed TiO<sub>2</sub>-sol binder, they prepared mechanically robust and wellinterconnected TiO<sub>2</sub> films via UV-irradiation at low-temperature for applications in plastic dye-sensitized solar cells (p-DSSCs).



**Figure 1**: Image for an ethanol based TiO<sub>2</sub> slurry (Weerasinghe et al., 2013).

## Methods of deposition of TiO2 paste on flexible substrate

In order to fabricate flexible DSSC, several techniques have to be employed to enable low temperature synthesis of layers. Chao et al. (2013) proposed a pressurization transfer technique which can let TiO<sub>2</sub> films via high-temperature sintering for the use of flexible working electrodes. Kumar et al. (2019) reported a TiO<sub>2</sub> films prepared by spreading binder free TiO<sub>2</sub> paste on flexible ITO/PEN substrates (Peccells, Japan) by the doctor blade method using Scotch tape as a mask to delineate the active area of the TiO<sub>2</sub> film. Yoo et al. (2015) reported a completely TCO-free and flexible dyesensitized solar cell (DSSC) fabricated on a plastic substrate using a unique transfer method and back-contact architecture. By adopting unique transfer techniques, the working and counter electrodes were fabricated by transferring high-temperatureannealed TiO<sub>2</sub> and Pt/carbon films, respectively, onto flexible plastic substrates without any exfoliation.

## **Structure and Principle of Operation of DSSC**

#### Structure of DSSC

Three major components mainly consist of the structure of a dye sensitized solar cell, namely: the working electrode which is usually a dye molecule coated nanocrystalline porous  $TiO_2$  film deposited on a transparent conductive oxide (TCO) coated substrate; the counter electrode which is often a platinum-coated TCO deposited substrate and an electrolyte containing usually an iodide-triiodide ions ( $\Gamma/I_3^-$ ) redox couple (Weerasinghe et al., 2013). Each of the components in the DSSC contributes an important role that affects the energy conversion efficiency. DSSC is a device for the conversion of visible light into electricity, based on photosensitization produced by the dyes on the wide band-gap mesoporous metal oxide semiconductors. This sensitization is due to the dye absorption of a part of the visible light spectrum. The sensitized dye works by absorbing the sunlight which then converts it into electrical energy (Zulkifili et al., 2015).

## Principle of operation of DSSC

The operational principle of the DSSC is based on the absorption of photons and excitation of the dye, followed by fast electron injection into the conduction band (CB) of the  $TiO_2$  surface. Figure 2(b) shows the operational principle of the DSSC. When DSSC is exposed to the photon, dye molecules that are mounted on the surface of semiconductor photoanode layer will absorb the incoming photon. The photoexcitation of the dye will cause an injection of electrons into semiconductor photoanode layer. The injected electrons will disperse through the semiconductor photoanode structure and emits through the working electrode, external load and proceed to the counter electrode. Next, electrolyte that contains iodide–tri-iodide ( $\Gamma/I_3$ ) will act as the mediator to fetch the

electrons which arrived at the counter electrode and regenerate the oxidized electrons in the dye molecules. The cycle will continue repeatedly with the presence of photon in the environment (Jamalullail et al., 2018).

In recently years, titanium dioxide (TiO<sub>2</sub>) has attracted much attention from researchers across the globe due to its potential applications in energy generation and environmental protection and has been largely applied in DSSC due to its nanocrystalline mesoporous nature that translates to high surface area for dye absorption (Saadoun et al., 2000). The absorbed dye molecules can be excited by the solar energy to generate electron-hole pairs that are subsequently separated and transported within the lattice of TiO<sub>2</sub>. The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO<sub>2</sub> are important parameters in determining the efficiency of the cell (Zulkifili et al., 2015).

#### The mechanism of DSSC

The mechanism of DSSC is basically on the processes of photoelectrochemical system, which include photoexcitation, electron injection, oxidation, and reduction, as follows (Lai et al., 2017):

**Step 1**: The dye molecule is initially in its ground state (S).

When light irradiates the working electrode, the dye molecules absorb photons and change from the ground state (S) to the excited state  $(S^*)$ :

$$S+hv \rightarrow S^*$$

The excited dye molecule has higher energy content now and overcomes the band gap of the semiconductor.

**Step 2:** The excited dye molecule (S\*) is oxidized (as shown in equation 2) and an electron is injected into the conduction band of the semiconductor. Electrons can now move freely as the semiconductor is conductive at this energy level.

$$S^* \to S^+ + e^-$$

Electrons are then transported to the current collector of the anode via diffusion processes.

**Step 3:** The oxidized dye molecule  $(S^+)$  is again regenerated by electron donation from the iodide in the electrolyte.

$$S^{+} + \frac{3}{2}I^{-} \rightarrow S\frac{1}{2}I_{3}^{-}$$

Step 4: In return, iodide is regenerated by reduction of triiodide on the cathode, as shown in equation (4).

$$\frac{1}{2}I_3^- + e^- \to \frac{3}{2}I^-$$
 4

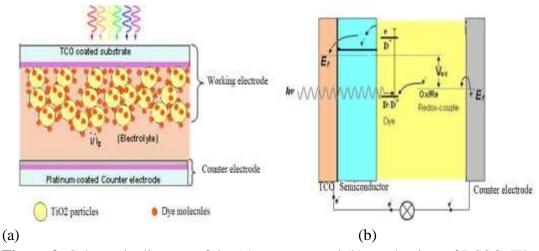
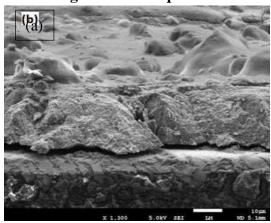
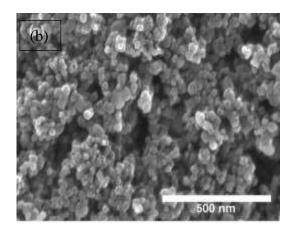


Figure 2: Schematic diagram of the (a) structure and (b) mechanism of DSSC (Weerasinghe et al., 2013).

## **SEM Images of flexible photoelectrode**

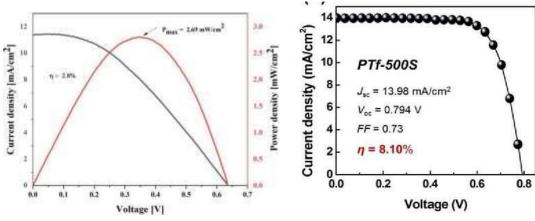




**Figure 3**: (a) Cross-sectional view of SEM images of TiO<sub>2</sub> coated on ITO at 1300 magnification and 10 μm scale (Wante et al., 2020a) (b) Scanning electron microscopy image of film deposited from suspension of TiO<sub>2</sub> (Kim et al., 2005).

Figure 3 shows SEM images of films deposited from the suspensions of TiO<sub>2</sub> nanoparticles. Figure 3(a) presents the cross-sectional view of FE-SEM image of TiO<sub>2</sub> P25 based film prepared using doctored blade method at an annealing temperature of 200°C. The cross-sectional view shows clearly the evidence of a second phase interfacial layer between TiO<sub>2</sub> and ITO layer. Figure 3(b) shows an electron micrograph demonstrating the formation of porous TiO<sub>2</sub> film, having high surface area. Both the SEM images also reveal that the TiO<sub>2</sub> film is uniform and crack-free on the surface.

#### 5. J-V Characteristics



**Figure 4:** (a) J-V and power density curves for 100 nm ITO coating at 10  $\mu$ m thickness of TiO<sub>2</sub> and power density variation with voltage for 100 nm TiO<sub>2</sub> (Wante et al., 2020a). (b) J–V curve obtained under an illuminated state (light intensity: 100 mW/cm<sup>2</sup>, AM 1.5G filter, active area: 0.425 cm<sup>2</sup>, TiO<sub>2</sub> film thickness: 14.25  $\mu$ m) (Yoo et al., 2015).

From Figure 4(a), Wante et al. (2020a) reported a power conversion efficiency of 2.8% using a flexible PEI polymer as a substrate and used doctor blade technique for the deposition of TiO<sub>2</sub> paste. This result is higher compared with the results obtained by Ndeze et al. (2021) that uses transparent conductive oxide glass substrate. From Figure 4(b), Yoo et al. (2015) fabricated a completely transparent conducting oxide-free and flexible dysensitized solar cells fabricated on plastic substrates which yielded a current density of 13.98 mA/cm<sup>2</sup>, an open circuit voltage of 0.794 V and power conversion efficiency (PCE) of 8.10%.

### **CONCLUSION**

DSSCs fabrication using flexible substrate produced comparable efficiency to DSSCs fabricated on a transparent conducting oxide glass substrate. We concluded that DSSCs fabrication using flexible substrate should be encourage due to its advantages such as roll to roll mass production and it does not require any organic surfactant when preparing the TiO<sub>2</sub> paste thereby using low temperature sintering of TiO<sub>2</sub>.

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