

LOW TEMPERATURE TiO₂ SYNTHESIS STRATEGIES FOR FLEXIBLE DYE-SENSITIZED SOLAR CELLS ON CONDUCTIVE POLYMER SUBSTRATES

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Abstract: The idea of creating flexible dye-sensitized solar cells (DSSCs) using plastic substrates instead of traditional glass substrates has recently emerged as a significant topic in the field of photovoltaics. One of the primary challenges in creating these DSSCs using plastic substrates is generating TiO₂ nanoparticles at low temperatures. This article reviews a variety of low-temperature sintering methods, such as chemical sintering, hydrothermal treatment, microwave irradiation, and compression techniques, for fabricating TiO₂ films on conductive plastic substrates below 150°C. Strategies for producing TiO₂ pastes without organic surfactants as binders are also discussed. The DSSC structure and mechanism of operation, as well as the roles of its three main components, are included. The article concludes by reviewing the current advancements in large-scale flexible DSSC module fabrication and their endurance. The significant benefit of using flexible substrates for cost-effective and mass-produced photovoltaics that fulfill diverse application requirements is highlighted. The results of various manufacturing techniques showed comparable efficiency for DSSCs fabricated using flexible substrates and those made on glass substrates.

Keywords: flexible substrate, dye-sensitized solar cell, low-temperature sintering, TiO₂, conductive polymer substrate.

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 fragility, 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 numerous 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 TiO₂ films on conductive plastic substrates using low-temperature sintering below 150 °C (Fan *et al.*, 2010). Pichot *et al.* (2000) sintered TiO₂ 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 low-temperature fabrication of TiO₂ 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 TiO₂ paste for flexible substrate

Preparation of suitable TiO₂ 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 TiO₂ nanoparticles are required to be well dispersed in the paste. Wante *et al.* (2020b) prepared TiO₂ paste by synthesizing TiO₂ powder with ethanol and de-ionized water for TiO₂ 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 TiO₂ powder so that the TiO₂ particles were well dispersed in the paste. Yamaguchi *et al.* (2007) prepared TiO₂ paste, which composed of a mixture of TiO₂ 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 TiO₂ nanoparticles and organic-free TiO₂-sol individually in organic-free solution. They mixed the pure anatase TiO₂ with the newly developed TiO₂-sol binder, they prepared mechanically robust and well-interconnected TiO₂ 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_2 slurry (Weerasinghe *et al.*, 2013).

Methods of deposition of TiO_2 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_2 films via high-temperature sintering for the use of flexible working electrodes. Kumar *et al.* (2019) reported a TiO_2 films prepared by spreading binder free TiO_2 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_2 film. Yoo *et al.* (2015) reported a completely TCO-free and flexible dye sensitized 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-temperature annealed TiO_2 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 (I^-/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 (I^-/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_2) 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_2 . The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO_2 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^*):



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.

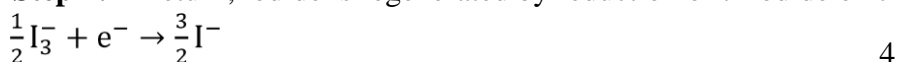


Electrons are then transported to the current collector of the anode via diffusion processes.

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



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



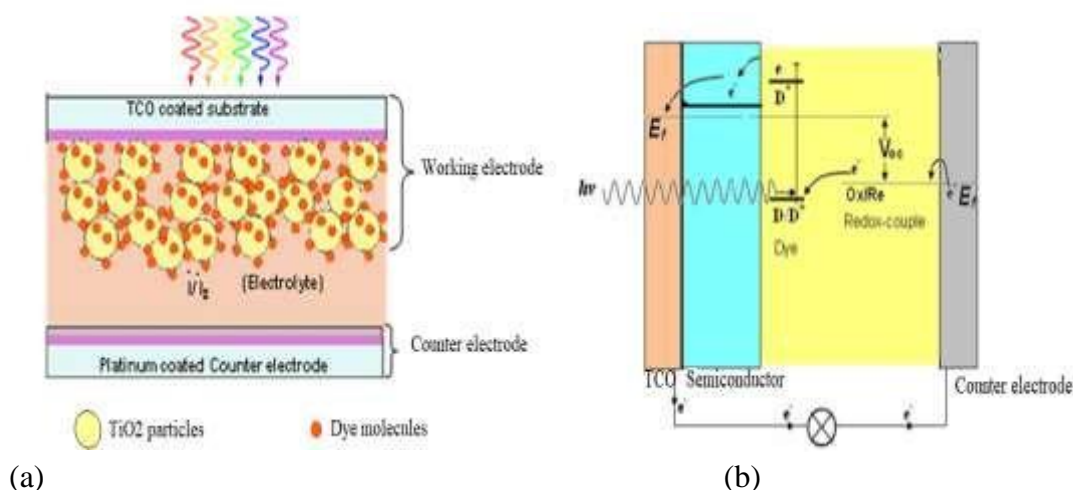


Figure 2: Schematic diagram of the (a) structure and (b) mechanism of DSSC (Weerasinghe *et al.*, 2013).

SEM Images of flexible photoelectrode

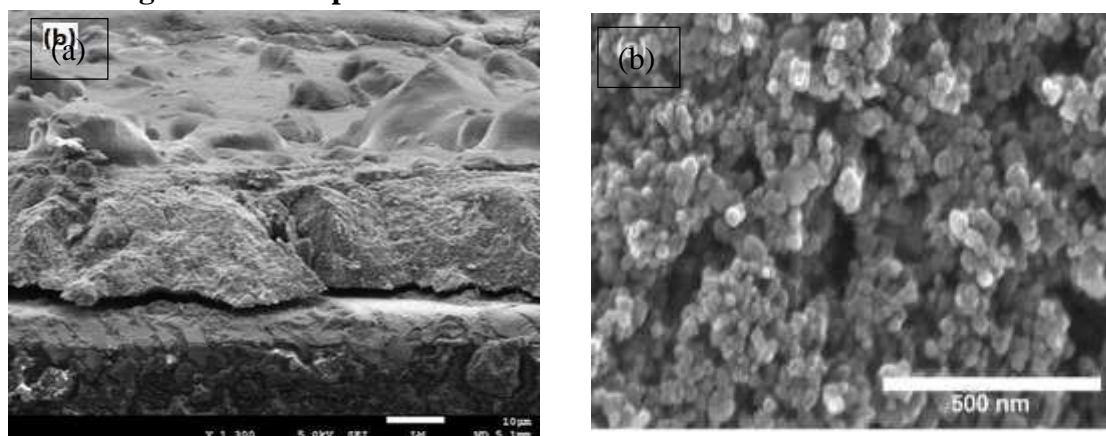


Figure 3: (a) Cross-sectional view of SEM images of TiO₂ coated on ITO at 1300 magnification and 10 μm scale (Wante *et al.*, 2020a) (b) Scanning electron microscopy image of film deposited from suspension of TiO₂ (Kim *et al.*, 2005).

Figure 3 shows SEM images of films deposited from the suspensions of TiO₂ nanoparticles. Figure 3(a) presents the cross-sectional view of FE-SEM image of TiO₂ P25 based film prepared using doctor blade method at an annealing temperature of 200°C. The cross-sectional view shows clearly the evidence of a second phase interfacial layer between TiO₂ and ITO layer. Figure 3(b) shows an electron micrograph demonstrating the formation of porous TiO₂ film, having high surface area. Both the SEM images also reveal that the TiO₂ film is uniform and crack-free on the surface.

5. J-V Characteristics

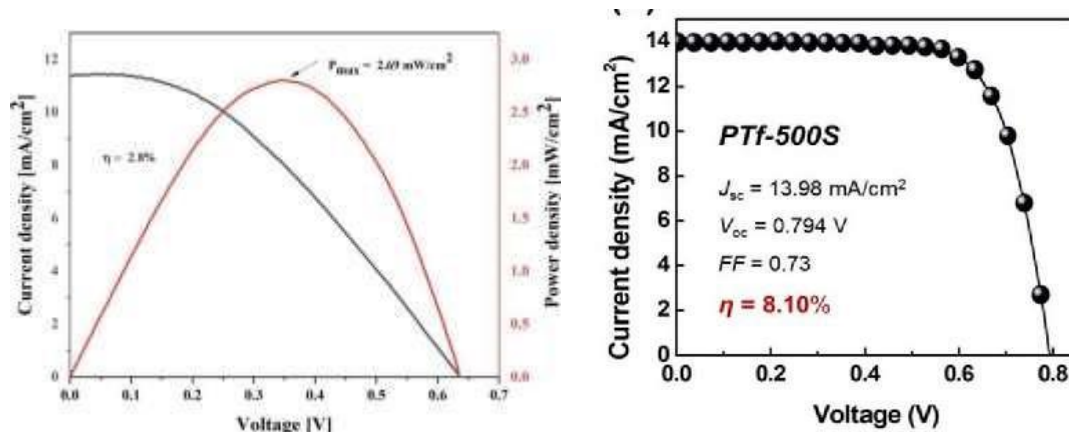


Figure 4: (a) J-V and power density curves for 100 nm ITO coating at 10 μm thickness of TiO_2 and power density variation with voltage for 100 nm TiO_2 (Wante *et al.*, 2020a). (b) J-V curve obtained under an illuminated state (light intensity: 100 mW/cm^2 , AM 1.5G filter, active area: 0.425 cm^2 , TiO_2 film thickness: 14.25 μm) (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_2 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 dye-sensitized solar cells fabricated on plastic substrates which yielded a current density of 13.98 mA/cm^2 , 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_2 paste thereby using low temperature sintering of TiO_2 .

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