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Review: Low Temperature Sintering of TiO_2 for Dye Sensitized Solar Cells (DSSCs) Fabrication on Flexible Substrates

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ABSTRACT: *This article discusses the most recent developments in the manufacture of flexible dye-sensitized solar cells (DSSCs), with a focus on the use of flexible plastic substrates instead of rigid glass substrates. The temperature restriction of the substrate in generating TiO_2 nanoparticles is a key problem for creating DSSCs on plastic substrates. Ball-milling, acid/water treatments, chemical vapor deposition, and electrophoretic deposition, as well as chemical and mechanical film processing methods such as chemical sintering, hydrothermal treatment, microwave irradiation, and various compression techniques, are all discussed here. It also includes research on novel flexible counter electrode manufacturing processes and recently produced new materials that are particularly beneficial for flexible DSSCs. Finally, the progress and possibilities of large-scale flexible DSSC module fabrication, as well as their endurance, are reviewed.*

KEYWORDS*:* review, low temperature sintering, TiO2, dye Sensitized solar cells (DSSCs), fabrication, flexible substrates

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_2 films on conductive plastic substrates using low-temperature sintering below 150 ^oC (Fan *et al.*, 2010). Pichot *et al.* (2000) sintered TiO_2 colloidal at lower temperature of 100 ^oC 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/cm^2, 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 TiO_2 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_2 paste for flexible substrate

Preparation of suitable TiO_2 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_2 nanoparticles are required to be well dispersed in the paste. Wante *et al.* (2020b) prepared TiO_2 paste by synthesizing TiO_2 powder with ethanol and de-ionized water for TiO_2 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_2 powder so that the TiO_2 particles were well dispersed in the paste. Yamaguchi *et al.* (2007) prepared TiO_2 paste, which composed of a mixture of TiO_2 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_2 nanoparticles and organic-free TiO2-sol individually in organic-free solution. They mixed the pure anatase TiO_2 with the newly developed TiO_2-sol binder, they prepared mechanically robust and well-interconnected TiO_2 films via UV-irradiation at low-temperature for applications in plastic dye-sensitized solar cells (p-DSSCs).

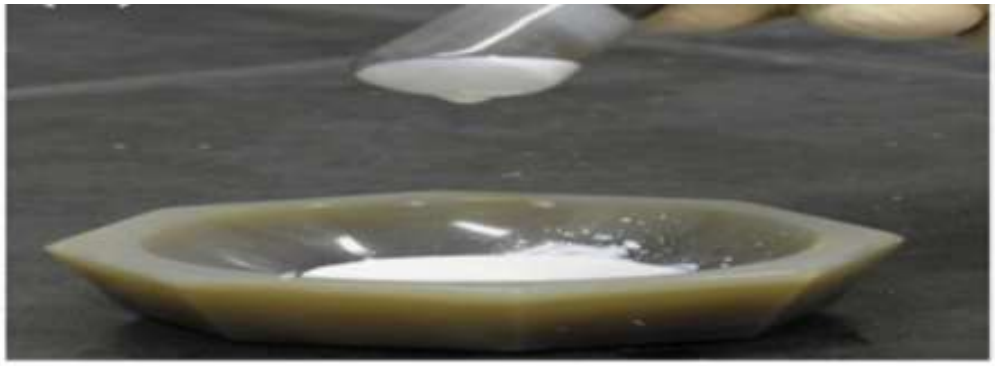


Figure 1: Image for an ethanol based TiO_2 slurry (Weerasinghe *et al.*, 2013).

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 TiO2 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*):

$$S+h\nu \rightarrow S^* \qquad 1$$

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.

$$S^* \rightarrow S^+ + e^- \qquad 2$$

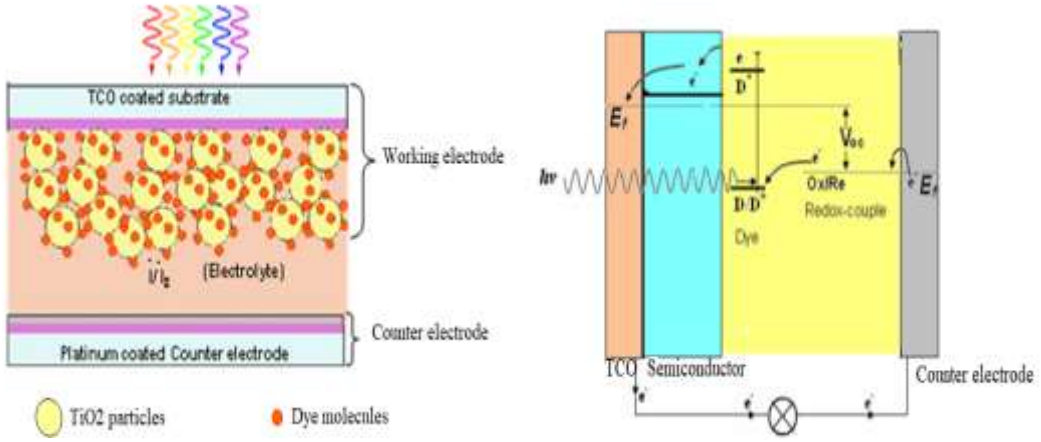
Electrons are then transported to the current collector of the anode via diffusion processes.

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

$$S^+ + \frac{3}{2}I^- \rightarrow S\frac{1}{2}I_3^- \qquad 3$$

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

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



(a) (b)

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

SEM Images of flexible photoelectrode

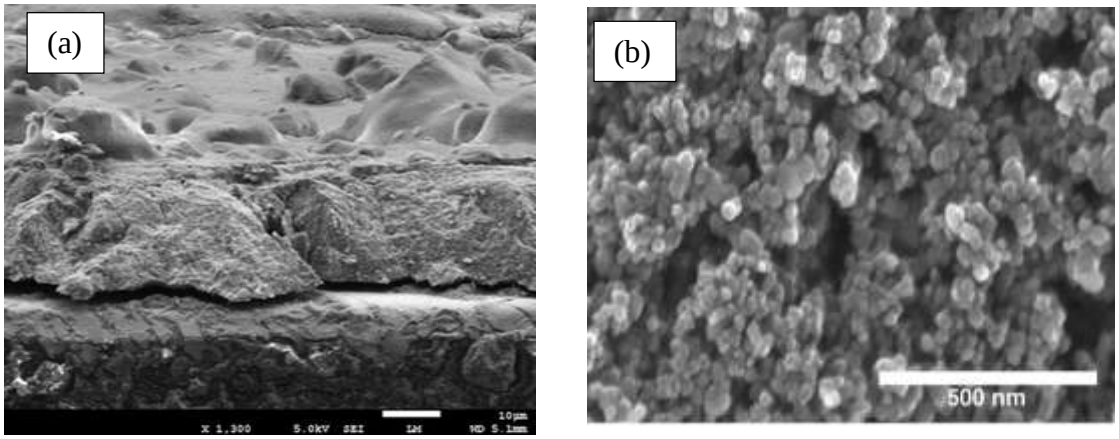


Figure 3: (a) Cross-sectional view of SEM images of TiO_2 coated on ITO at 1300 magnification and 10 µm scale (Wante *et al.*, 2020a) (b) Scanning electron microscopy image of film deposited from suspension of TiO_2 (Kim *et al.*, 2005).

Figure 3 shows SEM images of films deposited from the suspensions of TiO_2 nanoparticles. Figure 3(a) presents the cross-sectional view of FE-SEM image of TiO_2 P25 based film prepared using doctored blade method at an annealing temperature of 200ºC. The cross-sectional view shows clearly the evidence of a second phase interfacial layer between TiO_2 and ITO layer. Figure 3(b)shows an electron micrograph demonstrating the formation of porous TiO_2 film, having high surface area. Both the SEM images also reveal that the TiO_2 film is uniform and crack-free on the surface.

5. J-V Characteristics

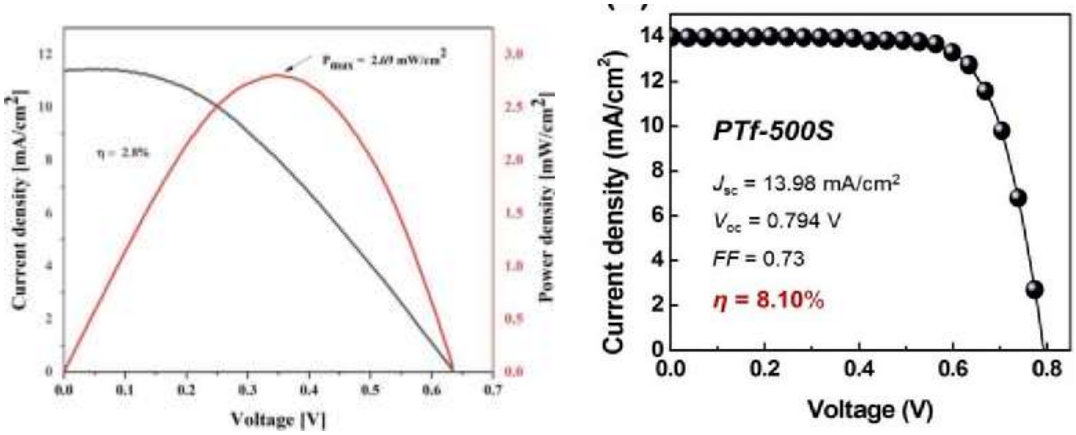


Figure 4: (a) J-V and power density curves for 100 nm ITO coating at 10 µm thickness of TiO_2 and power density variation with voltage for 100 nm TiO_2 (Wante *et al.*, 2020a). (b) J–V curve obtained under an illuminated state (light intensity: 100 mW/cm^2, AM 1.5G filter, active area: 0.425 cm^2 , TiO_2 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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