

Research Article

Effect of Organic Binders of TiO₂ Pastes in the Photoanodes of Cost-Effective Dye Sensitized Solar Cells Fabrication

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Introduction

In recent years, dye-sensitized solar cells (DSSCs) have showed enormous potential over the conventional silicon solar cells as inexpensive solar cells due to the surpassing power conversion efficiency (~13%) and their ease of fabrication. Also, the low-cost of fabrication of DSSCs has made them very attractive to the researches related to the device performance enhancement and on integrating the DSSCs in to domestic products [1-3]. Usually, DSSCs are made by the sandwich of mesoscopic TiO₂ film anode, an electrolyte and a metal (platinum) coated cathode. Among these components, the techniques used for TiO₂ film deposition on transparent conducting oxide (TCO) are critical to the fabrication of highly efficient DSSCs, together with the mesoscopic TiO₂ film typically coated by a monolayer of high molar extinction co-efficient dye molecules to extend the visible light absorption of anode [4]. Moreover, for the fabrication of high performance DSSC, coating of nano-sized highly porous TiO₂ film on TCO plays a significant role. Consequently, TiO₂ nanoparticles used for the fabrication of DSSCs expected to have a particle diameter of about 20 – 25 nm, which makes the long wavelengths of visible light to penetrate the TiO₂ film easily. And to improve the light scattering, an additional layer of particle diameter around 400nm is introduced on top of the smaller size nanoparticles layer. Generally, TiO₂ nanomaterials exist in rutile, brookite and anatase crystalline phases. The most utilized phase of TiO₂ in DSSC application is anatase phase. Brookite phase exists only in ore form and due to smaller surface area, lower fermi level and larger crystallite size rutile phase is not favorable to the DSSC applications. Therefore, the maximum efficiency achieved in DSSC fabricated with the thin film of anatase TiO₂ nanoparticles which are mostly synthesized

Abstract

A simple method of preparation of screen printable TiO₂ paste from commercial anatase TiO₂ nanopowder using two different organic binders i.e. polyvinylpyrrolidone and ethyl cellulose was tested, to study the effect of organic binders on their TiO₂ films used as photoanodes in dye sensitized solar cells. In this study, TiO₂ films made from the TiO₂ paste with ethyl cellulose binder showed an improved power conversion efficiency of 4.47% over the TiO₂ paste with polyvinylpyrrolidone binder producing power conversion efficiency of 3.59%, in their respective DSSC photoanodes. Also, the electrochemical impedance studies revealed a better charge transfer dynamics with reduced recombination processes for the DSSC photoanode made from TiO₂ paste with ethyl cellulose binder. These results show a superior photovoltaic performance for the TiO₂ paste with ethyl cellulose binder made by the simple method introduced in this work, which can open up options for the large-scale production of TiO₂ pastes useful to the manufacturing of cost-effective DSSCs.

Keywords: Dye-sensitized solar cells; TiO₂ nanopowder; TiO₂ pastes; Organic binders; Photovoltaic performance

via hydrothermal method. And for the above mentioned reasons, anatase phase TiO₂ film preparation adoptable to the screen printing technique for printing the uniform thickness TiO₂ layer on top of fluorine doped tin oxide (FTO) coated glass has been widely preferred.

For the industrial scale manufacturing of inexpensive DSSC, screen printing of TiO₂ layer on top of FTO or polymer surface is one of the widely used technologies. The applications of TiO₂ paste also covers areas including gas sensors, Gamma – radiation sensors, corrosion resistance, and microwave absorption and so on [5-7]. Since titanium dioxide is nontoxic and eco-friendly, it has also found a wide variety of applications in health care products, cosmetics and paints. The main factor which influences the screen printing is the characteristics and quality of TiO₂ paste. The preparation of TiO₂ paste with controllable nanoparticles size via hydrothermal method takes minimum of 28 hrs to complete and follows a lengthy procedure. A lengthy procedure of TiO₂ paste making may not fit industrially due to the economic constraints and the slow processes. So, to achieve an easy TiO₂ paste preparation with comparable efficiency as that of nanoparticles, several methods are tried using commercially available nanopowder (P25, Degussa) [8].

In this study, a commonly available TiO₂ nanopowder (Sigma Aldrich, USA) is converted into paste in lesser time when compared to the hydrothermal method. A faster and easier procedure makes the industrial manufacturing of DSSC more easy and rapid, without compromising the performance and quality. So, we have prepared the TiO₂ pastes by following a simple method with different binders and tested their photovoltaic performances, and also studied the influence of dispersion agent with the best performing paste made

from commercially available TiO_2 powder. The paste preparation doesn't involve any sophisticated equipments and the overall paste preparation has been completed in less than 6 hours. In contrast, the paste preparation using laboratory made nanoparticles requires trained hands and well equipped machineries. Moreover, the commercially available TiO_2 nanopowder based paste provides almost similar performance throughout and high reliability regardless of number of batches of the TiO_2 paste prepared.

Experimental

Materials

Commercial TiO_2 nanopowder (Anatase) was procured from Sigma-Aldrich, USA. Ethyl cellulose powder (18-22 cps) was purchased from Loba Chemie, India. Polyvinylpyrrolidone was purchased from Himedia, India. Fluorine doped tin oxide (FTO) glass slides (12-14 ohm/sq) were purchased from Dyesol Corporation, Australia. Commercial N719 dye (4-tertbutylpyridine, cis di(thiocyanato)-N, N'-bis (2,2' bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxylate) ruthenium (II) were procured from Dyesol Corporation, Australia. Adhesive film (Surllyn, Meltronix 1170-25PF) was purchased from Solaronix, Switzerland.

Preparation of screen-printable TiO_2 pastes

Different type of TiO_2 pastes were prepared using commercially available TiO_2 nanopowder by varying different organic binder concentrations. Then their TiO_2 films adhesion and performance were tested. Based on the literature, the widely known two organic binders ethyl cellulose, and polyvinyl pyrrolidone were selected for this study and compared with the TiO_2 paste made without binder.

Preparation of TiO_2 paste without binder: In the beginning, anatase TiO_2 powder was mixed with few drops of DI water and ethanol thoroughly. Then, the mixture was crushed in an agate mortar until it converts as viscous state [9] by following the detailed procedure given below:

TiO_2 powder was taken in a crucible and heated at 400°C for 30 minutes to remove the absorbed moisture and impurities. 2mL ethanol was then added to 1 gram TiO_2 powder drop wise in an agate mortar followed by constant grinding, until the mixture turns in to a smooth white viscous paste. This mixture was then ultrasonicated for an hour and kept for magnetic stirring up to 12 hours at a speed of 300 rpm to obtain a homogenous, viscous paste. This paste was then used for TiO_2 doctor blading/screen printing on substrates.

Polyvinyl pyrrolidone as binder: TiO_2 powder was taken in a crucible and heated up to 400°C for 30 minutes to remove the absorbed moisture and organic impurities. Then the powder was mixed with polyvinylpyrrolidone (PVP) in different concentrations. Polyvinylpyrrolidone (PVP), also commonly called polyvidone or povidone, is a water-soluble binder extracted from the monomer N-vinylpyrrolidone. Therefore, at the outset TiO_2 films were made using TiO_2 paste with different concentrations of poly(vinylpyrrolidone) as a binder to understand the effect of PVP. Then, Triton X-100, acetic acid and ethanol were used in different stages of the TiO_2 paste preparation. The amount of each chemical used for making the TiO_2 paste with different PVP concentrations was followed as per the literature procedure [10]. TiO_2 powder mixed with PVP in different proportions was crushed using 2mL of ethanol

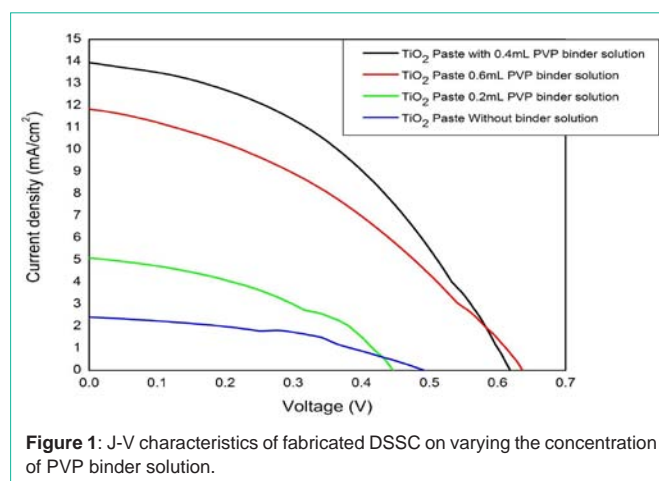


Figure 1: J-V characteristics of fabricated DSSC on varying the concentration of PVP binder solution.

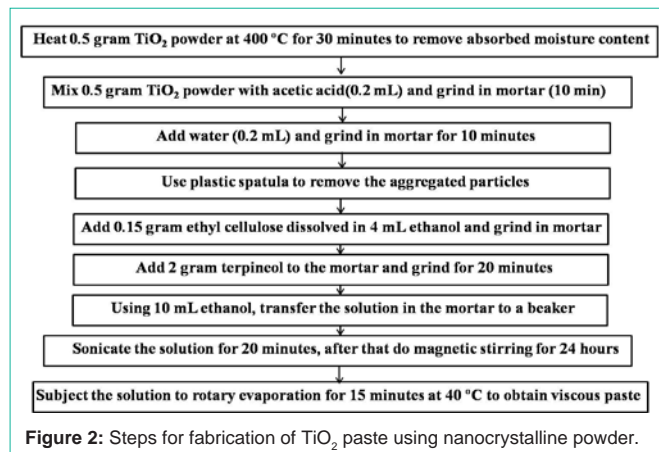
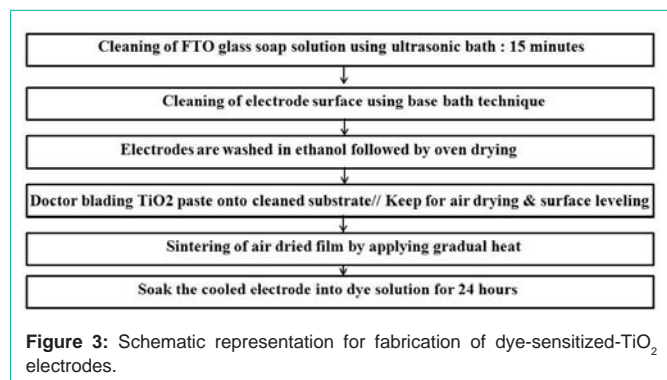


Figure 2: Steps for fabrication of TiO_2 paste using nanocrystalline powder.

in an agate mortar for 20min to avoid aggregation. After that, 0.2mL of acetic acid was added. Triton X-100 was used as a dispersing agent; subsequently ethanol was used to dilute the mixture. After thorough mixing, the mixture was concentrated by heating on the hotplate to obtain a viscous paste [10,11].

As shown in the Figure 1 the photovoltaic properties of TiO_2 films in DSSC photoanode are usually influenced by the methods of TiO_2 paste made. PVP was used as a binder to regulate the viscosity of the paste, inhibit the aggregation of TiO_2 nanopowder and improve the mechanical stability and continuity of the sintered film. An optimal paste composition, suitable for superior dye adsorption to improve the DSSC performance was obtained. Even though PVP enables good adhesion of paste on the FTO, the dye absorption was found to be poor, because the film was forming non-porous surfaces in several places after the sintering.

Ethyl cellulose as binder: The commercial TiO_2 powder was taken in a crucible and heated up to 400°C for 30 minutes to remove the absorbed moisture and organic impurities. Figure 2 shows the scheme for the preparation of TiO_2 paste by following a modified procedure obtained from the literature [8]. Then the preheated nanopowder was added with 0.2mL glacial acetic acid and 0.2mL DI water. This mixture was grinded well in an agate mortar. The dispersion of TiO_2 nanopowder into the dilute acetic acid was controlled by mortar grinding. This assisted in reducing the mean particle size by increasing



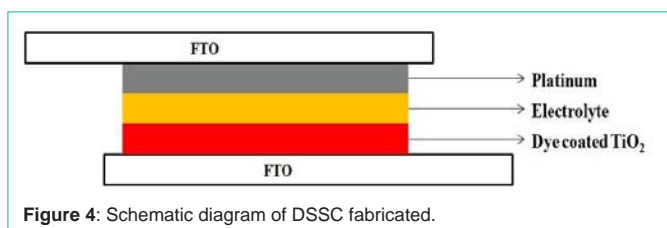
the dispersion time. Transparency of the coated film also improved on increasing the grinding time. Powder which stuck inside the mortar was removed using a plastic spatula, to obtain a smooth homogenous paste. A well dispersed TiO₂ particles in homogenous paste were then transferred using ethanol (or any appropriate solvent) to a round bottom flask. This solution was then subjected to ultrasonication about 15 minutes for homogenous mixing of particles. Followed by sonication, the obtained homogenous white liquid was subjected to magnetic stirring for 2 hours at a speed of 300rpm. Then rotary evaporation of homogenous white liquid for 15 minutes at 40°C produced a viscous paste. The viscous paste was again ultrasonicated for another 15 minutes to get a fine homogenous paste. This prepared paste was protected from moisture before coating on the substrates.

Fabrication of porous-TiO₂ electrodes

To avoid surface contamination by ions or iron oxides, which will be formed during the sintering of TiO₂ film causing enhanced charge recombination in photocells, plastic spatulas and glass rods was used. This charge recombination will reduce the photo current (JSC) and the efficiency of DSSCs. Prior washing with acidic solution can remove the iron contamination and hence a 0.1M HCl was used to remove the iron contamination.

As shown in Figure 3, FTO glass used as a current collector, therefore clean FTO was doctor-bladed with TiO₂ paste to prepare the anode. The TiO₂ nanopowder based paste was coated on top of the FTO to produce the TiO₂ thin film. This film was air dried to reduce the surface irregularity. This process is known as leveling, and the leveling time must be observed visually, which depends on the viscosity of the paste applied. The air dried and leveled film was then gradually heated in a muffle furnace at 325°C for 5 min, 375°C for 5 min, 450°C for 15 min and 500°C for 15 min. Then the film was allowed to cool down naturally to a temperature of 70°C. This electrode was then immersed into a 0.5 mM N-719 dye solution and kept for 24 hours for the dye loading.

Preparation of counter electrodes



To prepare the platinum counter electrode, the conducting glass was subjected to all the pre-cleaning procedures. The residual contaminations including the iron contamination were cleaned from the FTO surface by heating it in the oven, H₂PtCl₆ solution was drop casted on its surface. After air-drying, the drop casted film was heat treated for 400°C for 15 minutes [4].

Electrolyte

The iodine/tri-iodide electrolyte solution was prepared by adding 0.5M I₂, 0.1M LiI, and 0.5M of 4-tert-butylpyridine in acetonitrile. This solution mixture was then kept for magnetic stirring for 24 hours for the uniform mixing.

DSSC fabrication

Figure 4 shows the schematic diagram of DSSC. The dye coated TiO₂ electrode and platinum counter electrode were assembled into a sandwich type cell. In between the working electrode and the cathode, a Surlyn® spacer film was kept. Then a drop of iodine/tri-iodide electrolyte solution was added in between the electrodes.

J-V Measurements

Photocurrent-photovoltage (J-V) measurements of DSSCs were obtained by using an AM 1.5 solar simulator (Newport corporation, USA) equipped with xenon light irradiation of 1000 W/m² at ambient conditions. With a Keithley model 2400 digital source meter, I-V curves were obtained by applying an external bias to the cell, and the generated photocurrent was also measured. According to equations (1) and (2), fill factor and efficiency were calculated.

$$\text{Fill Factor} = \frac{J_{\max} \times V_{\max}}{J_{sc} \times V_{oc}} \quad (1)$$

$$\text{Efficiency (\%)} = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100 \quad (2)$$

J_{sc} and V_{oc} are the short circuit current density (mA cm⁻²) and open circuit voltage (V) respectively. P_{in} is the power of incident light. Where, J_{max} and V_{max} are the current density, voltage at the point of maximum power output in the J-V curves, respectively.

Results and Discussions

The films prepared without water and acetic acid found to have large cracks and peeling-up from the FTO glass. This indicates for the TiO₂ paste preparations acetic acid and water are necessary to obtain more homogeneity in the paste. Also, the film structures after sintering, due to the presence of water and/or acetic acid is improved many times as confirmed by the optical images [not shown]. To make strong bonding between the TiO₂ nanoparticles and the FTO surface, the presence of hydroxides (-OH) groups can play a vital role. The hydroxide groups can ensure the increased chemical bonding of each other by the dehydration while sintering at high temperature. Moreover, by adding DI water, paste provides more hydroxide groups on the surfaces and helps in reducing the inter-particle aggregations. If the particles are aggregated, it can cause more shrinkage in the film upon high temperature sintering, which reduces bonding between the TiO₂ particles and the FTO surface. By adding acetic acid, the rate of aggregation of particles is inhibited, due to its adsorption on the surface of TiO₂ [12].

Furthermore, Figure 1 shows the J-V performance variations of different DSSCs fabricated using TiO₂ pastes made with various PVP binder concentrations. When compared to the paste without binder,

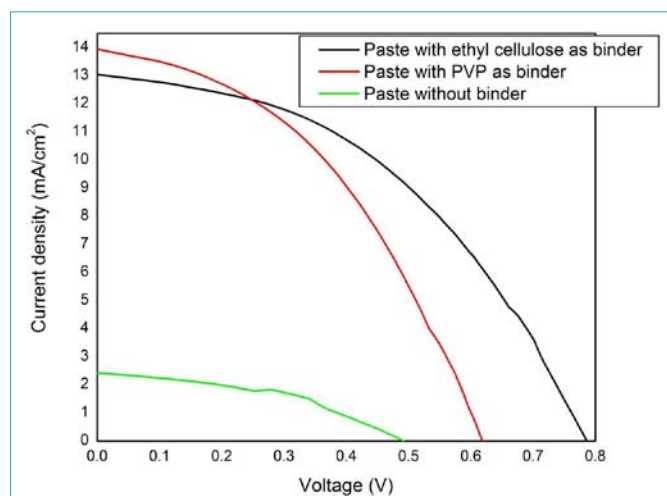


Figure 5: Comparison of J-V characteristics of the DSSCs fabricated with two different pastes.

TiO₂ photoanodes fabricated from the TiO₂ paste with PVP binder showed an improved FF and current density. However by increasing the quantity of PVP in binder solution, it was found that the efficiency was decreasing. Even though, the adhesion of TiO₂ particles to the FTO was improved, on sintering, it was observed that the porous structures of the film was reduced considerably, which resulted to the poor dye adsorption and hence the poor efficiency. Due to this problem, ethyl cellulose was introduced as the binder and dye adsorption issue was resolved. This resulted in an improved power conversion efficiency of 4.47% when compared to the efficiency 3.59% that of TiO₂ paste with PVP binder as shown in the Figure 5 and in Table 1. And also, better dye adsorption resulted in good solar cell stability and an increased fill factor.

From Table 1, it is evident that, on improving the dye adsorption i.e., for the paste with ethyl cellulose binder the open circuit voltage improved significantly. The main reason behind the improved efficiency was due to the increase in the open circuit voltage and fill factor. Furthermore, electrochemical impedance spectroscopy (EIS) was performed to analyze the charge transfer dynamics in DSSC fabricated using TiO₂ photoanodes made from paste with different binders. Figure 6 shows the Nyquist plot obtained under dark condition for the DSSC fabricated using TiO₂ pastes made with PVP and ethyl cellulose as a binder. The internal impedance components of DSSC usually contain three semi-circles that are attributed to the low-frequency, mid-frequency and high-frequency regions.

These semicircles are related to charge transfer at cathode-electrolyte interface which is denoted as R₁, charge transfer at TiO₂/dye/redox electrolyte interface in the middle frequency range denoted as R₂ and charge transport within the electrolyte including Nernstian

Table 1: Table on J-V characteristics performance of DSSC made with various paste.

Type of paste	J _{sc} (mA cm ⁻²)	V _{oc} (V)	Fill factor	Efficiency (%)
Without binder	1.25	0.33	0.41	0.50
Paste with PVP as binder	14.04	0.61	0.42	3.59
Paste with ethyl cellulose as binder	13.00	0.78	0.44	4.47

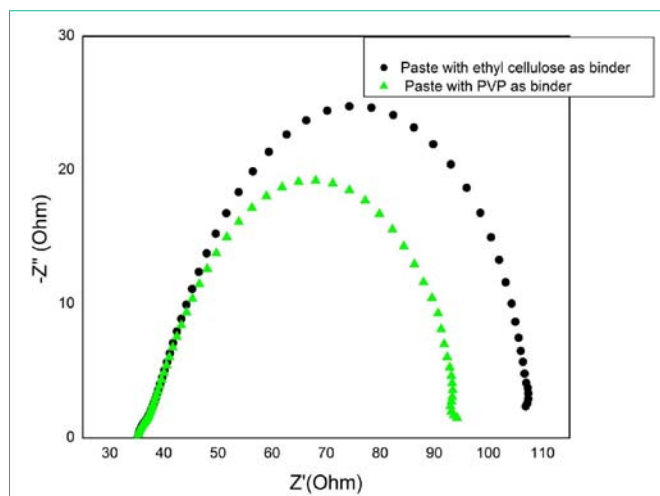


Figure 6: Nyquist plot of the DSSCs fabricated with two different pastes.

diffusion process usually observed in the low-frequency range, which is R₃. R₃ is the component which is the magnitude of origin to the start point of the first semi circle, which is the sheet resistance of the cell including the resistance of the conducting glass. The high resistance at the middle frequency range accounts the reduced charge recombination processes and an increased electron transport within the TiO₂ layer. The high charge transfer resistance (R₂) obtained for the DSSC fabricated using TiO₂ paste with ethyl cellulose binder indicates the superior charge transfer at the TiO₂-electrolyte interface which can produce a high photovoltaic performance in the DSSC when compared to the TiO₂ paste with PVP binder [4].

Conclusion

In summary, we prepared TiO₂ pastes with two different organic binders and compared their DSSC photoanodes' J-V characteristics and impedance results. TiO₂ paste made with ethyl cellulose binder showed better open circuit voltage and fill factor compared that of TiO₂ paste made with PVP binder, due to the better TiO₂ film formation with increased porous structures in the photoanode. Furthermore, EIS results showed a high charge transfer resistance (R₂) obtained for the DSSC fabricated using TiO₂ paste with ethyl cellulose binder due to the reduced recombination processes. These results suggests a superior DSSC photovoltaic performance for the TiO₂ nanopowder based paste made with ethyl cellulose binder which opened up options for TiO₂ pastes industrial scale production useful for the manufacture of cost-effective DSSCs. Also, the additional scattering layer and TiCl₄ treatment to these TiO₂ paste based photoanodes can increase the performance of their DSSCs further. By using this TiO₂ nanopowder based paste, sustainably efficient TiO₂ anodes can be made for the large scale DSSC production.

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