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Semi-Transparent Dye-Sensitized Solar Panels for Energy Autonomous Greenhouses

A. Mourtzikou, D. Sygkridou, T. Georgakopoulos, G. Katsagounos, E. Stathatos

Abstract**—**Over 60% highly transparent quasi-solid-state dye-sensitized solar cells (DSSCs) with dimension of 50x50 cm^2 were fabricated via inkjet printing process using nanocomposite inks as raw materials and tested under outdoor illumination conditions. The cells were electrically characterized, and their possible application to the shell of greenhouses was also examined. The panel design was in Z-interconnection, where the working electrode was inkjet printed on one conductive glass and the counter electrode on a second glass in a sandwich configuration. Silver current collective fingers were printed on the glasses to make the internal electrical connections. In that case, the adjacent cells were connected in series via silver fingers and finally insulated using a UV curing resin to protect them from the corrosive (I^-/I_3^-) redox couple of the electrolyte.

Keywords**—**Dye-sensitized solar panels, inkjet printing, quasi-solid-state electrolyte, semi-transparency, scale up.

I. Introduction

THIN film solar cell technology is a very important development in the field of photovoltaic technology, being considered as "second generation photovoltaics". Third-generation approaches to photovoltaics aim to achieve high-efficiency with low cost devices but still use thin-film, second-generation deposition methods. The latter class of solar cells is based either on nanocrystalline inorganic oxides or on organic materials with developed conductive properties (or in combination), e.g. polymeric membranes. The aforementioned materials, which are relatively low cost and easy to manufacture, can be used on flexible substrates to be easily molded and adapted to different household, architectural and decorative applications [1], [2]. The unprecedented progress made in recent years in the preparation and characterization of these new photonic materials has greatly expanded the opportunities for growth of these kinds of solar cells such as dye sensitized or perovskite solar cells [3].

Unlike the ominous predictions, these photovoltaic cells showed remarkably high laboratory-scale yields that are fully competitive with those of conventional cells. In fact, financial reports predict that the technology of classical solid-state photovoltaics (e.g. crystalline silicon) will soon be replaced by systems based on either thin film technology or "pure" photoelectrochemical devices, where a liquid electrolyte replaces conductive phase that is conventionally in contact with the inorganic semiconductor. A particular category of this family of devices is DSSC, or otherwise sensitized electrochemical cells [4]. In this category of photovoltaics, the processes of absorption and electron transfer are separated by a combination of a sensitizer acting as an absorption material with a nanocrystalline large energy band gap semiconductor. The major advantages of these cells compared to the rest technologies is the environmentally friendly fabrication procedures, the low cost and the unique perspective of manufacturing transparent cells that can be integrated as photovoltaic windows at building facades and greenhouses operating by front-face light incidence, but also by diffuse light and even by back face light incidence [5], [6]. In particular, the basic aim in greenhouses is to generate energy by the application of DSSC panels on the shell of the construction to enable at the same time the crop photosynthesis, while minimizing the energy-operating cost to near zero [7]. However, the goal and the motivation to go from the laboratory scale to large area dye sensitized solar devices, which would also lead to their mass production, is to reach a satisfactory efficiency. In case that overall performance is the first priority for the possible commercialization of this technology, then it has to be over 5% to the panel in order to cover energy expectations. Alternatively, if the energy produced during a year is comparable to that obtained from conventional silicon-based photovoltaics then DSSCs could cover the proposed business plans for their possible application in glass facades so as this technology could aim its commercialization. In particular, the measured energy produced during a day or alternatively the energy produced per year is comparable to the energy produced by the other solar cells' technologies, then it could cover the expectations for a possible investment to this technology. Over the past years, research groups have attempted manufacturing large area dye-sensitized solar modules, trying to overcome the difficulties that they come across which will lead to the fabrication of an optimized device [8], [9].

In this study, we report on the basic fabrication steps of making a photovoltaic panel of DSSC technology consisting of individual long stripes of solar cells connected internally in a series. In particular, we examine the case of all inkjet printed DSSC in large scale panels of the size 50x50 cm^2 as the standard size for their application in greenhouses. Both electrodes, photoanode and counter electrode were fabricated

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through inkjet printing ensuring uniformity of the films while the silver collecting grid was also printed on the conductive glass for an efficient current collection. The panel was outdoor electrically characterized and the parameters were monitored through I-V characteristic curves. Finally, preliminary studies to the application of this technology as novel glass facades in greenhouses are also presented.

II. Materials and Methodology

A. Materials

Commercially available lithium iodide, iodine, 1-methyl-3-propylimidazolium iodide, tert-butyl pyridine, guanidine thiocyanate, chloroplatinic acid hexahydrate (H_2PtCl_6), poly(propylene glycol)bis(2-aminopropyl) ether 230, 3-isocyanatopropyltriethoxysilane and all solvents were purchased from Sigma-Aldrich and used as received: 3-*Cis*-di(isothiocyanato) - bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium), D719 was purchased from Everlight (Taiwan). SnO_2:F transparent conductive electrodes (FTO, TEC^{TM} A10) 10 Ohm/square were purchased from Pilkington NSG Group. UV-cured resin ThreeBond was used to isolate the silver grids inkjet printed on FTO glasses using Cabot silver ink. Commercial ultra-pure titanium butoxide (TTBU, 97%, Aldrich), Triton X-100 (polyethylene glycol p-tert-octylphenyl ether) surfactant (99.8%, Fisher Scientific), glacial acetic acid (AcOH, Aldrich) were used to make precursor TiO_2 sols.

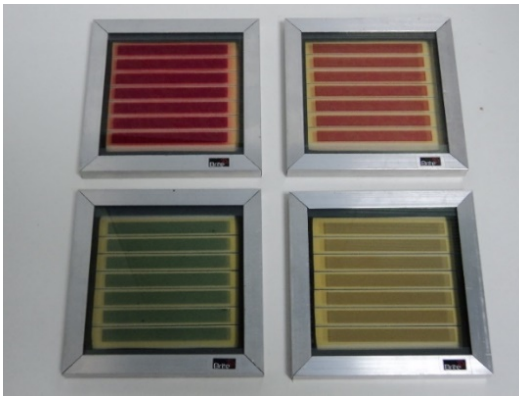


Fig. 1 Inkjet printed dye molecules with different color on TiO_2 photoelectrodes

B. Preparation of TiO_2 nanostructured Photoanodes Sensitized with Dye and of Platinum Counter Electrode

TiO_2 transparent thin films were fabricated via the sol-gel method following a previously reported procedure [10]. Briefly, for 5.4 ml solution, 0.72 g of Triton X-100 was mixed with 4 ml of ethanol, followed by addition of 0.4 ml of glacial acetic acid and 0.37 ml of titanium butoxide under vigorous stirring. After a few minutes stirring, the solution was deposited on the FTO glasses with inkjet printing (Dimatix, Materials Printer DMP-5000). The films were heated up to 500 ^oC for 15 minutes using 40^oC/min heating ramp rate. This procedure, of sequential printing and sintering steps, was repeated several times until the TiO_2 thickness was approximately 3 μm. Since most of the active materials of DSSC can be deposited by printing, it would be advantageous from the point-of-view of manufacturing if also the dye could be simply printed on the TiO_2 films. This process, which took only three minutes at shortest in comparison with conventional methods of electrode soaking in dye's solution for at least 20 hours, may prove that a similar performance can be achieved with fast sensitization as with the traditional sensitization technique. Finally, on the TiO_2 films, D719 dye in ethanol/ acetonitrile (1/1 v/v) solution of (the dye concentration was 4 10^{-2} M) was inkjet printed in order to sensitize the TiO_2 electrode in the visible. The dye was adsorbed within 3 minutes after the deposition. Excessive dye molecules that were not adsorbed on the TiO_2 surface were removed by rinsing the electrode with acetonitrile.

Several dye molecules could be printed on TiO_2 surface using inkjet printing method giving a different aesthetic result to the solar panels as presented in Fig.1. The platinized FTO glasses were made by inkjet printing of a H_2PtCl_6 solution (5 mg/1ml of n-propanol) followed by heating at 500^{o}C for 10 minutes.

C. Quasi-Solid Electrolyte Preparation

In the construction of the solar cells, a quasi-solid-state electrolyte was used. This was chosen as a promising approach to DSSC technology as it combines the high ionic conductivity of liquids while it reduces the risk of leaks and minimizes sealing problems in the cells. To the construction of the solar cells a quasi-solid-state electrolyte was finally used. For the gel electrolyte applied to the DSSCs, we used a hybrid organic-inorganic material ICS-PPG230 which was prepared according to a procedure described in previous publications [11], [12]. The gel electrolyte was synthesized by the following procedure: 0.7 grams of the functionalized alkoxide precursor ICS-PPG230 were dissolved in 2.4 grams of sulfolane under vigorous stirring. Then, 0.6 ml AcOH were added followed by 0.3 M 1-methyl-3-propylimidazolium iodide, 0.1 M LiI and 0.05 M I_2 in a final molar ratio of AcOH:LiI:MPImI:I_2 = 2.5:0.1:0.3:0.05. Finally, 0.5 M of *tert*-butyl pyridine was added to the above mixture and 0.00445 g guanidine thiocyanate. For the application of the electrolyte, the two electrodes were merged using also a sealant and finally stuck together isolating each solar stripe by the other. After a few minutes of stirring, a quantity of the obtained sol before it gelled, was placed on the top of the titania electrode with adsorbed dye molecules from holes exist to the slightly platinized FTO counter electrode was merged on the top. The two electrodes tightly stuck together also by Si-O-Si bonds developed by the presence of the hybrid material.

D. Fabrication of DSSC

Large area modules with total size 50x50 cm^2 were fabricated after merging the two photoelectrodes and UV cured the photosensitive resin as a sealant. The electrolyte was inserted between the individual solar stripes when it was still in liquid phase. Then, the electrolyte was finally converted to a gel in an hour due to the inorganic polymerization-

condensation of the triethoxylane groups present at both edges of the hybrid ICS-PPG230 material that co-exists in the electrolyte. A visual appearance of the panel can be seen in Fig. 2. It is obvious that the panel is highly transparent due to the specific fabrication process using inkjet printing technology for materials deposition. As it was previously mentioned, the DSSC panel was fabricated using a sandwich Z-interconnection where the working electrode is deposited on one glass and the counter electrode on the second glass. The interconnection appears in Fig. 3. In particular, the silver paste was printed on the glasses to make the internal electrical connections and serially connect the adjacent cells.

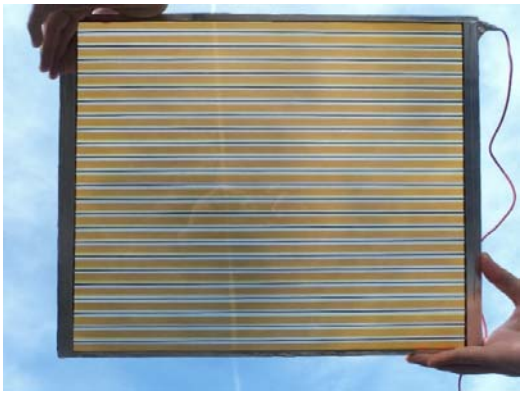


Fig. 2 A highly transparent 50x50 cm^2 DSSC module with 21 serially connected individual solar stripes

After the deposition of the silver fingers, the glasses were sintered at 400 °C for 10 minutes before the application of the dye and the electrolyte. A UV curing resin was used to insulate the silver wires to avoid their corrosion from the electrolyte.

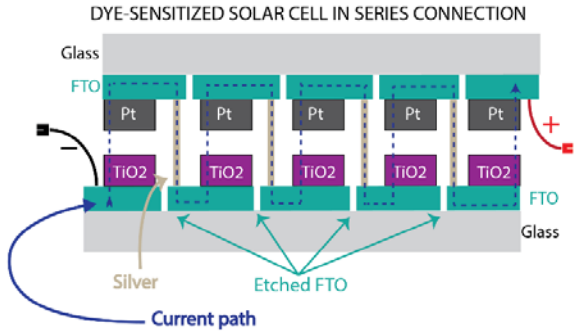


Fig. 3 The interconnection is followed among individual solar cells in 50x50 cm^2 DSSC panel

E. Characterization Techniques

The investigation of TiO_2 films is very important for the overall performance of the solar panel as highly porous nanocrystalline films of the semiconductor are necessary to absorb high amounts of organic (dye) sensitizer and also maintain a high level of transparency of the panel. Therefore, the structural properties of the TiO_2 films were investigated through nitrogen sorption-desorption analysis using Micromeritics Tristar 3000, and the surface area, porosity, and pore size distribution were derived by differentiating them according to BET method. The Ultraviolet-Visible/NIR absorption diffuse reflectance spectra of the perovskite films were obtained in a range of 300 nm to 850 nm using Jasco V-770 spectrophotometer equipped with a 60 mm integrating sphere embedding a PbS Detector (ISN-923). For the I-V curves, the cells were subjected to outdoor solar irradiation. The light intensity was almost constant at 975 W/m^2 (high Intensity) and 210 W/m^2 (low Intensity) during the experiments and measured with a Newport power meter (Model 843-R) and corrected using a reference cell and meter consisting of a monocrystalline silicon (Newport 91150V). Finally, the I-V plots were recorded by connecting the device to a Keithley Source Meter (model 2601A) which was controlled by Keithley computer software (LabTracer). The cells' total area was 50 cm x 50 cm. Three panels were tested under the same conditions in order to avoid any misleading estimation of their efficiency and the mean values are finally presented. Cell performance parameters, including short-circuit current (I_{SC}), open circuit voltage (V_{OC}), maximum power (P_{max}), fill factor (FF) and overall cell conversion efficiency, were measured and calculated from each I-V characteristic curve.

II. Results and Discussion

A. Photoanode Characterization

The measurement for the porosity of the TiO_2 film was carried out on powder which resulted by scratching thick films made on glass microscope slides and grinding the obtained flakes to break all agglomerations. The sample was degassed for 2 h at 100°C before N_2 sorption analysis. The sorption-desorption curve is presented in Fig. 4. The particle surface area and pore structure of the TiO_2 powder are summarized in Table I and compared with standard Degussa P25 powder usually referred to the preparation of DSSC modules by other groups.

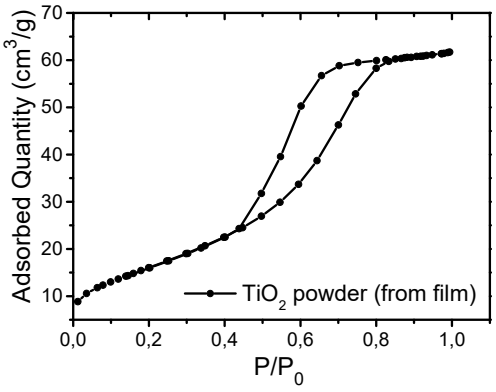
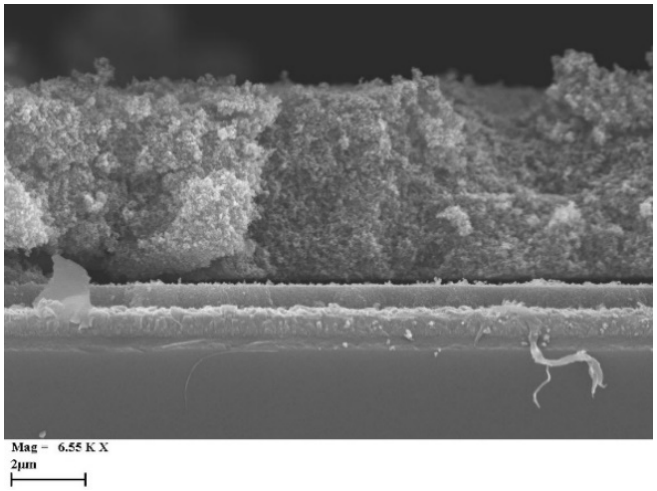


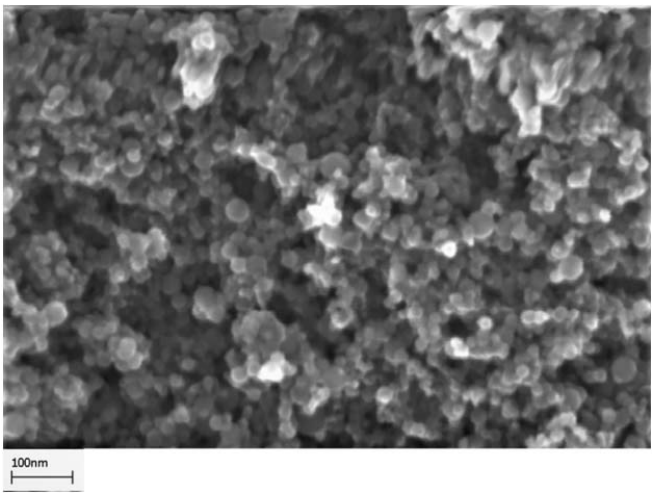
Fig. 4 Sorption-desorption isotherm of TiO_2 powder

The hysteresis loop in Fig. 4 appears at low relative pressure ($0.4 < P/P_0 < 0.8$) which is attributed to smaller mesoporosity of the material. The sample's Brunauer, Emmett and Teller (BET) specific surface area was high while the

Barrett, Joyner and Halenda (BJH) pore volume was relatively low. Moreover, the TiO_2 sample had a small mean pore diameter. In addition, based on the SEM cross section image (Fig. 5 (a)), the film was thin, highly homogeneous and the desirable thickness of ~5 μm was achieved in order to be semi-transparent. Besides, the film is consisted of small nanoparticles of spherical shape with an average diameter of ~15-20 nm. The particles appear in a dense agglomerated form. However, the average diameter of the particles was very small in size and with narrow distribution around mean diameter which could cover the basic requirement for large amount of dye's adsorption in the film. The specific evidence is directly in line with porosimetry results of Fig. 4 where it was proved the high porosity of the TiO_2 films.



(a)



(b)

Fig. 5 (a) Cross section of the TiO_2 film with an average thickness of 5 μm and (b) image of the surface of the film consisted of nanoparticles with average size 15-20 nm

B. Optical Characterization of the Solar Panel

The solar panel was optically examined in order to meet the standards of greenhouses for maximum solar light intensity to enter to them and does not obstruct the plans to photosynthesize. This means that the dye's sensitizer absorption spectrum in the cell should not overlap the absorption in the area of 430-480 nm; 600-750 nm of the chlorophyll which wavelengths are fundamental for the growth of the plants. Indeed, the absorption spectrum of the solar panel is presented in Fig. 6 where it is proved that it is highly transparent in the area of longer wavelengths namely 600-700 nm. Furthermore, the CIE L*a*b* color parameters of the panel are L = 54, a = 17, b = 22. The temperature coefficients of the solar glass are also measured and there are $\alpha = +1.38$ %/°C and $\beta = -0.112$ %/°C.

TABLE I
STRUCTURAL PROPERTIES OF TiO_2 POWDER

Sample	Porosity (%)	S_{BET} (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)	Pore width (nm)
TiO_2 powder (film)	26.6	60.5	4.5	0.10	6.4
TiO_2 (P25)	48.7	56.0	8.6	0.25	17.5

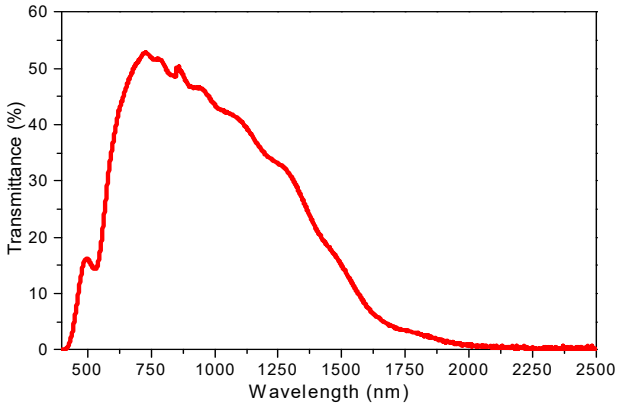


Fig. 6 Transmittance (%) of the solar panel measured in the whole region of the solar light

C. Solar Panel's Performance

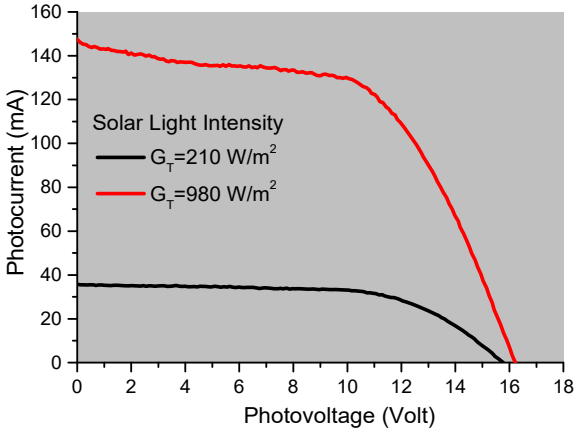


Fig. 7 Photocurrent-Photovoltage characteristic curves of DSSC at two different solar light intensities

Fig. 7 presents the photocurrent - photovoltage (I-V) characteristic curves of the solar panel measured outdoor

under two different light intensities. The electrical parameters of the cell measured and calculated from both curves are summarized in Table II.

It can be seen that the short circuit current density values are dependent to the solar light intensity, which is expected, but the open circuit voltage values are not seriously affected by the light. Variations were mainly noticed at the fill factor values calculated and as a result, also to the overall efficiency. The decrease to the FF with light intensity is due to the total internal in series resistance of the cell (R_s) which does not allow the large number of carriers created to avoid internal recombination. High transparency and serial connection have demonstrated that the module I-V characteristics were almost independent from the light direction, i.e. front or back illumination providing similar performances. It can be seen that there are no serious differences among the efficiencies obtained from the DSSC panel with total effective area 844 cm^2 either illuminated from the front or the back side.

TABLE II
ELECTRICAL CHARACTERISTICS OF DSSC PANEL IN VARIABLE SOLAR INTENSITY

Solar Intensity (Wm^{-2})	I_{sc} (mA)	V_{oc} (V)	FF	n (%)
210	36	15.8	0.63	2.1
975	147	16.2	0.57	1.6

Fig. 8 100 m^2 greenhouse prototype made with DSSC solar panels

D. Application of Solar Panels to Greenhouses

The properties of the solar glass for greenhouse applications have been validated through a greenhouse prototype of 100 m^2 in Greece with hydroponic tomato cultivation. Two experimental units were used: a conventional greenhouse and a smart greenhouse where the shell of the construction was replaced with the solar panels described herein (Fig. 8). The results showed that the greenhouse made with solar panels was an energy autonomous greenhouse, and reduced the energy operating costs up to 25%. In contrast to other photovoltaic panels alternatives, the solar panel has been shown to enable a better crop growth through the full entrance of the light inside the construction. Additionally, the use of DSSC panels was shown to reduce the use of pesticides, as the complete blocking of UV light to the inner side of the greenhouse leads to decreased insect populations and fungal diseases. The ambient conditions sensors were operated by the electricity produced by the solar panels which proves the energy autonomy of the greenhouse by the presence of DSSC panels to its shell.

III. CONCLUSIONS

In the present work, we prepared DSSCs panels at the fixed dimension of 50 cm x 50 cm. The cells were constructed with thin nanocrystalline TiO_2 films made with inkjet process using appropriate sols. We have shown that the serial connection of individual cells with a suitably chosen size to encompass a simple electrode pattern while keeping current losses at minimum values, was demonstrated to be a successful approach. The use of quasi-solid-state electrolytes in such geometry was possible after the two electrodes were merged with a sealant and the electrolyte when it was still liquid was dispensed in the space after making small diameter holes on counter electrode. Stability issues can be addressed by the use of gel electrolytes, which avoid leakage problems and lead to a stable shelf life. The possible application of the technology to the shell of greenhouses, when these are made of glass, is then very promising because the as-presented results showed that the plans' growth was not limited by the presence of the solar cells while these cells could contribute to the energy consumption of the construction.

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