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Low cost fabrication of tandem dye-sensitized solar cells

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The overall objective of this research was to deposit metal oxide semiconductor in order to construct dye-sensitized solar cell (DSSC) for converting solar energy into electric energy. It is well known that, TiO_2 is the most common constituent of conventional dye-sensitized solar cell, whereas platinum counter electrode was replaced by *p*-type semiconductor (in this study, NiO) in order to construct tandem dye-sensitized solar cell. The main focus of this research was to prepare NiO electrodes with high surface area in order to increase its photo-conversion efficiency since *p*-type electrode is the limiting factor which was not allowing exploring the potential of tandem cell. In this technique, both NiO and TiO_2 nanoparticles were sprayed onto the conductive glass substrates to prepare loosely adhered particulate coatings. After performing furnace sintering, both NiO and TiO_2 coatings were sensitized with suitable dyes and joined together in order to prepare tandem dye-sensitized solar cells (DSSCs).

Keywords: Dye-sensitized solar cells, TiO_2, *p*-type semiconductor, NiO, sintering

INTRODUCTION

The total power utilized by the world is estimated to be approximately 15 terawatts in one year [1], only 1.6 terawatts of which are produced from renewable energy resources including nuclear fission [2-4]. It is predicted that the fossil fuels, the main ingredient to our energy recipe, may finish in few hundred years (Fig. 1). The diminution of fuel and the global warming, for which the burning of fossil fuels is a major issue, is pushing humanity towards renewable energy resources. The sun is potentially the chief resource of renewable energy as the total power from sunlight striking the earth is a massive of 101,000 terawatts and experts have estimated that if we could harness one hour of that sunlight, it is possible to meet one year energy demands of the world's population.

Bell Laboratories' pioneering work on photovoltaic cells in 1954 [6] helped to carry out solar to electric energy conversion. All three 1st, 2nd and 3rd generations of solar cells are presented in Fig. 2. DSSCs have low efficiencies when compared with other thin film solar cells; however, they offer many advantages over their competitors. They are fabricated through the use of low cost material [7], can be produced more economically and at a lower cost [8]. More importantly, DSSCs can be used in building integrated photovoltaics (BIPV) because of their availability in different color and transparency grades. Lastly, there is a significant DSSCs market for products which require low power input such as consumer electronics [9, 10].

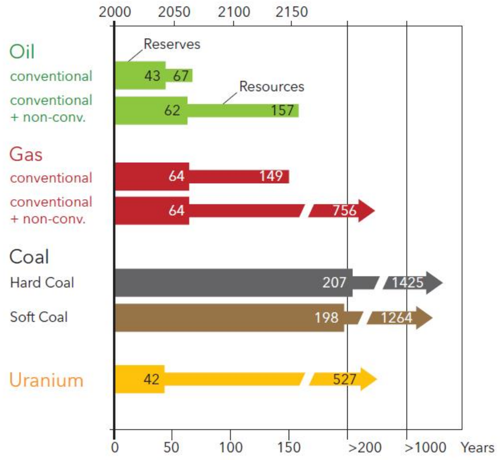
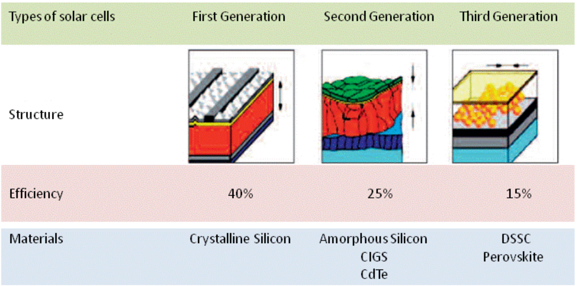


Fig. 1. Range of conventional fuels in years [5]



Types of solar cells	First Generation	Second Generation	Third Generation
Structure			
Efficiency	40%	25%	15%
Materials	Crystalline Silicon	Amorphous Silicon CIGS CdTe	DSSC Perovskite

Fig. 2. Basic structure and current efficiencies of 1st, 2nd and 3rd Gen solar cells

The dye-sensitization process started with the invention of photography back in the 19th century [11]. However, the main credit of converting

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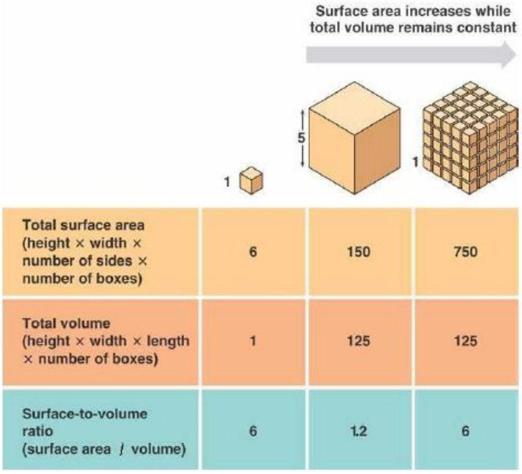
photons into an electric current should be given to Tributsch who reported his results with a chlorophyll sensitized zinc oxide (ZnO) electrode [12]. The use of nanoporous metal oxide (TiO_2) electrodes with a roughness factor of ca. 1000 introduced by O'Regan and Grätzel in 1991 [7] transformed the materials from bulk to nano which reduced the size of the material and lead to an increase in surface area [13] (Fig. 3). Because of the higher surface area of TiO_2 nanoparicles resulting in dramatic increase in the light harvesting efficiency, solar cells with an efficiency of 7 % were obtained.



Total surface area (height × width × number of sides × number of boxes)	6	150	750
Total volume (height × width × length × number of boxes)	1	125	125
Surface-to-volume ratio (surface area / volume)	6	1.2	6

Fig. 3. A cartoon showing the variations in surface-to-volume ratio of bulk vs. nano (adapted from [13]).

With the recent invention of perovskite sensitized solar cells, the efficiencies have gone beyond 11 to 15 % [14-17], which is less than other generations of solar cells [18]. This reduction of efficiency in DSSCs is primarily due to the inefficiency of the dye to absorb all the light from the solar spectrum from visible to near IR region. A method of more effective utilization of the solar spectrum was suggested by He *et al*. [19] in which they substituted the cathode of a conventional DSSC [which is generally a platinum coated fluorine doped tin oxide (FTO) displaying no photoelectrochemical activity] with a dye-sensitized photoactive *p*-type metal oxide, and hence turned the simple cathode into photocathode. By combining this photocathode with a photoanode of a conventional DSSC, a tandem cell is constructed. By using this cell, more visible energy of the solar field could be utilized with the two dyes to complement a wide absorption range. The theoretical upper limit of the efficiency of a cell with two photoactive electrodes is estimated to surpass by 13 % the 32 % theoretical conversion efficiency of the conventional DSSC with one photo-active electrode [19].

In this work, the main requirement was to choose a *p*-type semiconductor surface having high dye adsorption capability. Nickel oxide (NiO) was chosen for these applications in this study, due to its *p*-type nature [20] and remarkable chemical immovability, in addition to good optical and electrical properties [21]. Additionally, NiO wide band-gap energy range from 3.6 to 4.0 eV makes it suitable for tandem solar cell application [20]. NiO coatings have been prepared by spray pyrolysis [22, 23], plasma enhanced chemical vapor deposition [24, 25], pulsed laser deposition [26, 27], electrodeposition [28], chemical bath deposition [22, 29], sol gel [19, 30-34], sputtering [35, 36] and hydrothermal synthesis [28, 37]. Most of the methods involved sintering in order to enhance the packing density of the coatings, to get crystalline structure in the as deposited sputtered coatings [38] and to get rid of the binder in the case of sol-gel prepared coatings. Mostly, heating at 350-550 °C for 30 to 60 min was used [31, 39-41] in conventional furnace treatments.

The purpose of this work was to prepare *n*-type TiO_2 and *p*-type NiO coatings for employing them as electrodes in tandem DSSCs (Fig. 4). The main objective was to prepare coatings displaying meso-structure with improved interconnectivity between the particles and the substrate/electrode interface in order to reduce inherent resistance in the metal oxide structure. The type of structure of the electrode is of extreme importance to obtain the required dye adsorption and charge injection from the dye to the cathode which will eventually enhance the light-to-photocurrent conversion efficiency.

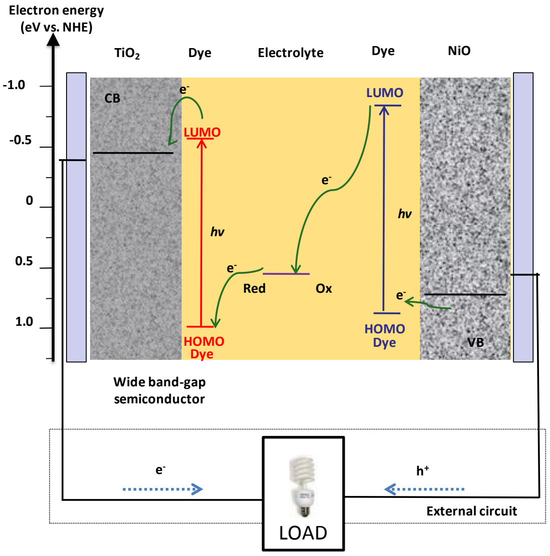


Fig. 4 A schematic showing the working of tandem DSSC

EXPERIMENTAL

NiO coating depositions

The TiO_2 and NiO particulate layers were prepared onto fluorine doped tin oxide (FTO) glass substrates (12 Ω/sq, 3 mm thick) supplied by Solaronix.

The glass substrates (2 × 2 cm) were ultrasonically cleaned in methanol followed by acetone, each for 5 minutes prior to the application of the particulate layers. 50 nm NiO nanoparticles (99.8 %) and 100 nm TiO_2 nanoparticles (99.8 %) supplied by Sigma-Aldrich, were mixed in 2-propanol (20 mg/ml) to make suspension and the particulate layers of TiO_2/NiO were deposited by to-and-fro nebulized spraying [42]. The heat treatments were carried out in air using a Carbolite Furnace (RHF 1200). TiO_2 or NiO samples were treated at temperatures of ~450 ºC, for a time of 60 min for TiO_2 and 5 and 30 min for NiO coatings.

Characterizations

The thickness of NiO coatings was measured using step height with WYKO NT1100 optical profilometer in vertical scanning interferometry (VSI) mode. For the morphological analysis and cross sectional investigations, the samples were inspected using a FEI Quanta 3D FEG DaulBeam system (FEI Ltd, Hillsboro, USA). X-ray diffraction (XRD) investigations were performed using a Siemens D500 diffractometer operating at 40 kV and 30 mA with Cu Kα radiation in normal diffraction mode at 0.2°/min scan rate in the 2θ range of 40-50°. NiO coatings were sensitized using 0.3 mM Erythrosin B (ERY) dye [19, 39], in a 99.8 % ethanol solution for 1 whole day. The dye adsorption was measured in transmission mode using an Analytik Jena *Specord* 210 UV-vis spectrophotometer. The wavelength range was 350-700 nm. In order to construct *p*-type DSSCs, the sensitized coatings were sealed face-to-face in a sandwich configuration with a platinum coated FTO counter electrode using 30 μm thick pre-cut Surlyn® thermoplastic frames (6 × 6 mm interior). The device was filled with 0.5M I_2, 0.05M LiI in propylene carbonate electrolyte from a pre-drilled hole made through the counter electrode under reduced pressure. The hole was sealed with Surlyn® and a glass cover-slide. For *J-V* measurements the coatings were masked using a 4 × 4 mm opaque frame and in all cases the cells were illuminated from the NiO working electrode side. The photovoltaic performance (*J-V* characteristics) was measured using a solar simulator AM1.5G, at an intensity of 87 mW cm^{-2}. The electrochemical investigations were performed with a three-electrode configuration: NiO coatings and dye sensitized NiO coatings were the working electrodes, whereas two Li rods (Sigma-Aldrich) were utilized as reference and counter electrodes, respectively. Electrolyte was 0.5 M $LiClO_4$ in anhydrous propylene carbonate (Fisher). The potential values were referred to the Li^+/Li couple. Cells were prepared in an argon atmosphere inside a glove-box from Innovative Technology (Newbury Port, Massachusetts, USA). In this glove-box the oxygen content was maintained below 10 ppm and water content below 5 ppm. Cyclic voltammetries were calculated using an electrochemical analyzer (model 604C) from CH Instruments (Austin, Texas, USA).

RESULTS AND DISCUSSION

As shown in Fig. 5, loosely adherent TiO_2 and NiO particulate layers were deposited onto FTO glass substrates, from a metal oxide / 2-propanol slurry using spraying. The coating thickness was maintained at ~2.5 μm by controlling the number of spraying cycles.

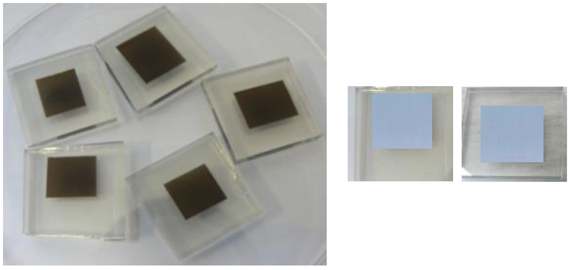


Fig. 5. Approx. 2.5 μm thick NiO (Black) and TiO_2 (White) coatings (1 x 1) cm deposited onto (2 x 2) cm FTO glass substrates using spraying technique.

Thickness was measured using optical profilometry with the help of step height measurements (Fig. 6). In order to enhance the packing density of loosely adhered particles deposited, the conventional furnace treatments of NiO coatings were carried out at 450 °C for 5 min in a box furnace (as described earlier). Heating and cooling rate of 10 °C/min were applied.

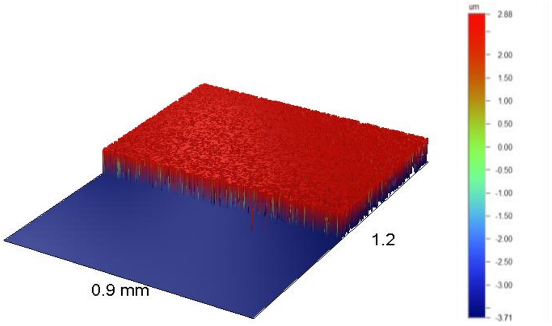


Fig. 6. Approx. 2.5 μm thick NiO coating layer measured via step height measurement using an optical profilometer.

There were already many reported results on TiO_2 based DSSC, thus prior to constructing a tandem DSSC by joining dye-sensitized TiO_2 and NiO electrodes, a comprehensive performance evaluation of NiO *p*-type DSSC was carried out, that included the examination of crystal structure, morphology and dye adsorption properties. The preferred orientation of NiO coatings was found to be (200) with crystallite size of 14 nm using Scherrer equation (*Vide supra*). Enhanced packing density with good interaction between particles and appropriate contact of the particles with the substrates was found on evaluating the morphology/cross sectional investigations of the coatings (Fig. 7). Similar dye absorption was found to correspond to the requirement to construct dye-sensitized solar cells.

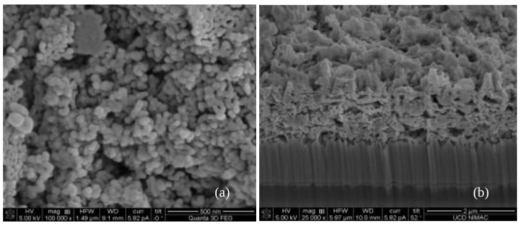


Fig. 7. (a) SEM image of a NiO coating (b) FIB/SEM cross section images of a NiO coating

Finally, *p*-type DSSC were constructed by attaching the sensitized NiO electrodes with platinum counter electrodes and inserting electrolyte between them and their photovoltaic performances were analyzed (Table 1). For 5 min sintering time the results were similar to the reported; however when we increased the sintering time from 5 min to 60 minutes the efficiency, voltage and current density of the solar cells started to decrease. This could be due to convective type of heating that blocks the sensitizer to penetrate into the nanoparticles. Table 1 also includes a literature report for ERY sensitized NiO. These measurements were obtained under the same test methodology as used in this work and quite similar results were obtained for the case of our sprayed/sintered NiO coatings.

The electrochemical properties of bare NiO coatings and dye-sensitized NiO coatings, were examined in order to evaluate their redox properties [43]. From the integration of the anodic currents observed in the cyclic voltammetries the sintered coatings were 3.96 mCcm^{-2}. The NiO oxidation was found to be fully reversible. The integration of the anodic current associated with the oxidation of ERY-sensitized NiO coatings gave a 0.58 mC cm^{-2} anodic charge. However, the anodic charges exchanged by the sensitized coatings were generally lower than those exchanged by the unsensitized coatings (0.58 *vs.*3.96 mCcm^{-2} for NiO coatings). This reduction in the charge could be due to a passivation effect of the ERY film in the process of NiO oxidation. In addition, no change in the electrochemical process of oxidation was observed for sensitized NiO coatings when compared with the bare NiO coatings, since ERY did not introduce additional redox processes in the potential window considered here.

A preliminary study was carried out to investigate the performance of NiO coatings in a tandem DSSC configuration. Erythrosin B (ERY) dye [19, 39] was used for sensitizing the NiO electrode to work as a photocathode [19], whereas N719 dye [19, 44, 45] was used to sensitize TiO_2 to work as a photoanode in the tandem DSSC configuration. An 80 mV increase in the open current photovoltage was observed for tandem DSSC when compared with a single photoactive electrode. This value was in close agreement with the reported value (83 mV) in the literature [19]. This preliminary study demonstrated that NiO coatings can be utilized in tandem DSSC configurations. A more detailed investigation is needed in order to optimize properties such as thickness, morphology and open pore structure of the NiO coatings for their use in tandem DSSCs.

Table 1: Photovoltaic performance of *p*-type DSSCs prepared by spraying furnace sintering treatments (compared with reported values in literature).

This study / Reported data	Sintering time (min)	V_{OC} (mV)	J_{SC} (mAcm^{-2})	FF	Efficiency (η)
In house sprayed and sintered	5	84.00	0.22	25	0.0050
In house sprayed and sintered	30	35.29	0.21	26	0.0023
In house sprayed and sintered	60	25.29	0.20	20	0.0018
He et al. [19] (~1 μm thick)	60	83.00	0.20	27	0.0070

CONCLUSION

In this work, the use of spraying and sintering was investigated for preparing TiO_2 and NiO photoelectrodes for tandem dye-sensitized solar cells. Prior to demonstrate the work of the tandem cell, a standalone *p*-type NiO cell was prepared and its photovoltaic and electrochemical performance was evaluated. The properties of NiO coatings such as crystal structure, morphology and dye adsorption behavior were also investigated in order to relate their performance in solar cells. In this work, tandem DSSC was constructed, however, the potential of NiO in tandem DSSC needs future studies.

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ЕВТИНА ИЗРАБОТКА НА ТАНДЕМНИ ЦВЕТНО-ЧУВСТВИТЕЛНИ СЛЪНЧЕВИ БАТЕРИИ

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(Резюме)

Общата цел на това проучване е да се отложи полупроводник от метален оксид, за да се изградят цветно-чувствителни слънчеви батерии (DSSC) за преобразуване на слънчевата енергия в електрическа енергия. Добре известно е, че TO_2 е най-честата съставка на конвенционалните цветно-чувствителни слънчеви батерии, докато платиновия противоелектрод е заменен от *p*-тип полупроводник (в това изследване, NiO), за да се изгради тандемна цветно-чувствителна слънчева батерия. Основната цел на това проучване е да се подготвят NiO електроди с голяма повърхност, за да се повиши тяхната ефективност при фото-преобразуване, тъй като *p*-тип електрода е ограничаващият фактор, което не позволява разкриването на потенциала на тандемната клетка. В тази техника, покрития от наночастици от NiO и TiO_2 се напръскват върху проводимите стъклени субстрати за получаване на свободно прилепнали покрития от частици. След извършване на синтероване в пещ, NiO и TiO_2 покрития са сенсибилизирани с подходящи бои и се свързват, за да се подготвят тандемни цветно-чувствителни слънчеви батерии (DSSCs).