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Application of a novel microwave plasma treatment for the sintering of nickel oxide coatings for use in dye-sensitized solar cells

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Abstract

In this study the use of microwave plasma sintering of nickel oxide (NiO_x) particles for use as *p*-type photoelectrode coatings in dye-sensitized solar cells (DSSCs) is investigated. NiO_x was chosen as the photocathode for this application due to its stability, wide band gap and *p*-type

nature. For high light conversion efficiency DSSCs require a mesoporous structure exhibiting a high surface area. This can be achieved by sintering particles of NiO_x onto a conductive substrate. In this study the use of both 2.45 GHz microwave plasma and conventional furnace sintering were compared for the sintering of the NiO_x particles. Coatings 1 to 2.5 μm thick were obtained from the sintered particles (mean particle size of 50 nm) on 3 mm thick fluorine-doped tin oxide (FTO) coated glass substrates. Both the furnace and microwave plasma sintering treatments were carried out at ~450 °C over a 5 minute period. Dye sensitization was carried out using Erythrosin B and the UV-vis absorption spectra of the NiO_x coatings were compared. A 44% increase in the level of dye adsorption was obtained for the microwave plasma sintered samples as compared to that obtained through furnace treatments. While the photovoltaic performance of the DSSC fabricated using the microwave plasma treated NiO_x coatings exhibited a tenfold increase in the conversion efficiency in comparison to the furnace treated samples. This enhanced performance was associated with the difference in the mesoporous structure of the sintered NiO_x coatings.

Keywords: Dye-sensitized solar cells; Nickel oxide; Nanoparticles; Microwave plasma sintering; Dye sensitization

PACS codes: 84.60.Jt; 68.47.Gh; 81.07.Wx; 52.50.Sw; 68.43.-h

1. Introduction

Dye-sensitized solar cells (DSSCs) show considerable potential as a relatively low cost alternative to silicon based solar cells. These cells were developed by Grätzel and co-workers in 1991 [1] and there is currently a considerable focus on enhancing their light conversion efficiency and stability [2-8]. In the case of conventional DSSCs, dye sensitization involves solely the semiconductor anode made of *n*-type TiO₂ nanoparticles [1-8]. The counter electrode

is generally a metallic cathode with no photoelectrochemical activity [1-8]. To date the highest conversion efficiency obtained of 11% [9], is less than the best silicon based thin-film cells [10]. A method of further enhancing the light conversion efficiency as suggested by He et al. is to substitute the cathode with a dye-sensitized photoactive *p*-type metal oxide. This tandem dye-sensitized solar cell design utilizes more of the solar spectrum [11]. The efficiency, however of *p*-type metal oxides is still very low, which limits their effectiveness in tandem DSSCs [12]. Amongst the potential reasons highlighted for the poor conversion efficiency of the cathode within tandem DSSC, the more critical are the inefficient light absorption capability, poor charge injection efficiency and charge transport rate, along with inner resistance [13, 14]. One method of improving this efficiency would be the preparation of *p*-type metal electrodes with a surface exhibiting high porosity without sacrificing the mechanical stability of the resulting coatings. This surface morphology ensures higher light absorption by the monolayer of adsorbed dye, while keeping an intimate contact between the *p*-type material and the dye molecules. This in turn reduces the inner resistance and hence improving the charge injection efficiency.

The focus of this research is on nickel oxide (NiO_x) coatings, which has a considerable potential for use as a cathode in tandem cells [11]. This is due to their *p*-type nature [15], excellent chemical stability, in addition to well defined optical and electrical properties [16]. Moreover, NiO_x is considered as a model semiconductor substrate due to its wide band-gap energy range from 3.6 to 4.0 eV depending on the amount of Ni(III) sites [15]. NiO_x films have been fabricated by various techniques which include spin coating, dipping, electrochemical deposition [17], magnetron sputtering [18-20] and sol-gel [21-25]. With the exception of electrochemical techniques, the other deposition methods require subsequent thermal treatments in order to enhance the density of the coatings [21-26], to obtain crystalline structure in the as deposited

sputtered coatings [26] and to remove the binder in the case of sol-gel deposited coatings [21-25]. Typically sintering conditions of 300-450 °C for 30 to 60 minutes are reported [21-25]. There have also been a large number of reports in the literature on the interaction between microwave radiation and materials [27, 28]. The ability of microwaves to penetrate the surface of the work piece enables rapid volumetric heating in microwave processing, reducing the need for external heat sources [27]. Advantages of non-plasma microwave processing over furnace treatment are reported to include finer grain sizes, rounded porosity and higher ductility and toughness [29]. Increased shrinkage rates and decreased grain sizes can be achieved with microwave plasma treatments compared with furnace sintering [30-32]. With these advantages and significantly reduced cycle times, microwave-assisted plasma sintering offers an economic route for the production and reduced energy consumption per process. In this study, the use of microwave plasma as a sintering technology for the NiO_x particles is investigated for the first time. The microwave plasma treatment technique is called Rapid Discharge Sintering (RDS) and it involves the immersion of the samples in microwave plasma formed under reduced pressure conditions. In this study a comparison is made between the RDS sintered NiO_x coatings and those obtained using conventional furnace sintering. In addition to a comparison of their physical properties, the performance of the sintered coatings in dye-sensitized solar cells was also evaluated.

The objective of this study is to prepare *p*-type NiO_x coatings to be used as a photocathode in tandem DSSCs application. The challenge is to develop coatings exhibiting mesoporous properties with enhanced interconnectivity between particles and the FTO/NiO_x interface to reduce the inner resistance. The mesoporous structure of the *p*-type electrode also favors dye adsorption and charge injection from the sensitizer to the photocathode with resulting increase of

the light-to-photocurrent conversion efficiency. In this study in addition to comparing the influence of sintering process technology on the performance of the NiO_x coatings, a second object is to evaluate how the duration of RDS sintering treatment influences coating performance.

2. Experimental

2.1. Sample preparation and deposition of NiO_x coatings

The NiO_x particulate layer was deposited onto fluorine doped tin oxide (FTO) glass (3 mm thick) supplied by Mansolar. The glass substrates (2 × 2cm) were ultrasonically cleaned in propanol followed by acetone, each for 5 minutes prior to the application of the NiO_x particulate layer. The NiO_x nanoparticles (~50 nm) were suspended in methanol (20 mg/ml) and the particulate layer NiO_x is deposited by spraying using a similar technique to that described previously [33]. The microwave-assisted plasma sintering process known as rapid discharge sintering was carried out using a circumferential antenna plasma (CAP) microwave system described in detail elsewhere [34]. The plasma was formed at a pressure of 5 mbar in an argon and oxygen (10:1) atmosphere. Input powers of 2.4 kW were supplied from a Mugge microwave power supply operating at a frequency of 2.45 GHz. The initial study with microwave plasma sintering evaluated the influence of sintering time over a 1 to 10 minute period. Substrate temperatures were measured using a LASCON QP003 two-colour pyrometer from Dr Mergenthaler GmbH & Co. The furnace treatments were carried out in air using a Carbolite Furnace (RHF 1200). For both the furnace and microwave plasma sintering systems three NiO_x samples were treated simultaneously at temperatures of ~450 °C, for a treatment time of 5 minutes.

2.2. Characterization equipment

The NiO_x film thickness was measured by step height measurement using a WYKO NT1100 optical profilometer in vertical scanning interferometry (VSI) mode. For the cross sectional investigations, the coatings were mounted on stubs using double-sided carbon tape, and sputter coated with platinum, using a Emitech K575X sputter coating unit, to prevent surface charging by the electron beam. Samples were then examined using a FEI Quanta 3D FEG DualBeam (FEI Ltd, Hillsboro, USA). X-ray Diffraction (XRD) measurements were carried out using a Siemens D500 diffractometer operating at 40 kV and 30 mA with Cu K α radiation in normal diffraction mode at 0.2°/min scan rate in the 2 θ range of 40-50°.

2.3. *Dye sensitization, UV-vis measurements and IV-characteristics*

NiO_x coatings were sensitized with 0.3 mM Erythrosin B (ERY) dye [11, 17, 22], in a 99.8 % ethanol solution for 24 h. The dye adsorption was investigated in transmission mode using an AnalytikJena *Specord* 210 UV-vis spectrophotometer in the wavelength range of 350-700 nm. The photovoltaic performance (I-V characteristic) of dye sensitized NiO_x coatings were analyzed in two electrode configuration using 870 W m⁻² AM 1.5 solar simulator and platinum coated FTO was used as a counter electrode. The *p*-type behavior of ERY-sensitized NiO_x coatings was observed using a custom made photoelectrochemical cell in three-electrode configuration: Working electrode was ERY-NiO_x on FTO; counter electrode was platinum, and a standard calomel electrode (SCE) was utilized as the reference electrode. The Electrolyte was 0.5 M LiI and 0.05 M I₂ in Propylene Carbonate (from Sigma-Aldrich).

3. Results and discussion

Loosely adherent NiO_x particulate layers were prepared from the metal oxide / methanol slurry using the spray technique. The layer thickness was maintained between 1-2 μ m. The initial study with the RDS technique evaluated the influence of sintering time over a 1 to 10 minute period,

on coating performance. Using the Scherrer equation [35] to examine the XRD data, an increase in crystallite size from 6.5 to 19.0 nm was observed on increasing the sintering time from 1 to 10 minutes (Fig. 1a). Only a small decrease in the NiO_x particulate layers coating thickness was observed after sintering.

In order to sensitize *p*-type NiO_x coatings, the oxide was treated with ERY dye. The UV-vis absorption spectra of the samples prepared under different sintering times showed a gradual decrease (Fig. 1b) of the amount of adsorbed dye for the coatings with the smaller crystallite size to those with the largest crystallites. In order to prepare *p*-type DSSCs, the ERY sensitized NiO_x electrodes were squeezed together with platinum coated FTO using binder clips. The electrolyte was filled uniformly into the interelectrode space by capillary forces. To optimize the NiO_x coatings preparation, the open current photovoltage (V_{OC}), the short circuit photocurrent density (J_{SC}) and overall photocurrent efficiency (η), were measured as a function of sintering time. Fig. 2a details the I-V characteristics of the ERY sensitized NiO_x coatings sintered at different times (thickness: 1-2 μ m). Though dye adsorption levels were higher for the 1 minute sintered coatings, the 5 minutes sintered sample (RDS5) exhibited the highest efficiency. These sintering conditions facilitate a high level of dye diffusion, while maintaining interconnectivity between individual oxide grains and FTO/NiO_x interface. Thus the mesoporous sintered metal oxide structure facilitates efficient charge injection from the ERY dye. A subsequent study with 2.5 μ m thick NiO_x coatings also demonstrated a similar trend. The *p*-type behavior of ERY- sensitized NiO_x coatings (RDS5) was investigated as shown in Fig. 2b, the curves in dark and under UV illumination demonstrated cathodic photocurrents of ERY-sensitized NiO_x coatings with an onset of photocurrent at approximately +120 mV vs (standard calomel electrode) SCE reference [11]. In order to compare the performance of RDS technique with conventional furnace treatments, the

NiO_x coatings were also sintered at 450 °C for 5 minutes in a box furnace. The properties of the furnace sintered coatings were then compared with those obtained using the RDS technique. XRD examination of the sintered NiO_x coatings demonstrated a significantly smaller crystallite size of 6.5 nm for the microwave plasma sintered samples, as compared to the 14 nm obtained after the furnace treatment (Fig. 3a). Thus the smaller grain size along with more homogeneous heating / sintering is achieved using the RDS technique thus helping to maintain the mesoporous structure of the NiO_x nanoparticles. A cross section of the coatings obtained by FIB/SEM from the two sintering techniques is given in Fig. 4. It is clear from these images that the RDS sintered coating exhibits a higher level of bonding at the interface between the NiO_x coating and FTO layer. A possible explanation for this is that the RDS treatment involves volumetric heating, which provides more effective heating inside the metal oxide coating matrix than obtained with the conductive heating obtained using the furnace. Indeed the latter treatment may give rise to selective heating of the outer surface of a coating to produce a heat affected zone [36]. From Fig. 4 it is clear that the RDS sintered oxide yields a much rougher surface morphology, which would also assist dye adsorption (Fig. 3b).

Finally, the photovoltaic performances of both RDS and furnace sintered coatings were measured as detailed in Table 1. A tenfold increase of conversion efficiency was observed for the RDS sintered NiO_x coatings (for both 1-2 μm thick and 2.5 μm) as compared to the furnace sintered sample. This Table also includes some recent literature reports for ERY sensitized NiO_x. These measurements were also obtained under the same test methodology. 1-2 μm thick furnace sintered and RDS sintered coatings reported here are broadly similar in efficiency to the values reported in the literature while 2.5 μm thick NiO_x coatings obtained with the RDS treatment exhibit significantly higher performance may be due to higher level of dye adsorption.

Conclusion

The use of microwave plasma (RDS) sintering is compared with conventional furnace treatment in order to prepare NiO_x photocathodes for dye-sensitized solar cells application. The optimized sintering time was evaluated in terms of conversion efficiency for the RDS technique. The NiO_x coatings produced with RDS exhibited superior adhesion to FTO substrates compared with that obtained using furnace treatments. The 44 % increase in the quantity of adsorbed dye in the case of the RDS treated coatings significantly contributed to the tenfold increase in light-to-current conversion efficiency, compared with that obtained with the furnace sintered coatings. This enhanced performance of the microwave plasma sintered NiO_x coatings is associated with their smaller grain size after sintering, higher surface roughness and enhanced level of interconnectivity between grains in the mesoporous metal oxide structure.

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Table 1. Photovoltaic performance of *p*-type photocathodes prepared by RDS and furnace (compared with reported values in literature). Light source was AM 1.5 solar simulator ($I:870 \text{ W m}^{-2}$). Electrolyte: 0.5 M LiI and 0.05 M I_2 in propylene carbonate.

This study / Reported data (NiO thickness)	Sintering time (min)	V_{oc} (mV)	I_{sc} (mAcm^{-2})	FF	Efficiency
Rapid Discharge Sintered (RDS) (~2.5 μm thick)	5	120.00	1.05	36	0.0450
Furnace sintered (~2.5 μm thick)	5	84.00	0.22	25	0.0050
Furnace sintered (~2.5 μm thick)	30	35.29	0.21	26	0.0023
Rapid Discharge Sintered (RDS) (~1-2 μm thick)	5	72.14	0.53	28	0.0118
Conventionally Sintered (CS) (~1-2 μm thick)	5	50.30	0.24	28	0.0037
<i>He et al. [11]</i> (~1 μm thick)	60	83.00	0.20	27	0.0070
<i>Nattestad et al. [22]</i> (~1.6 μm thick)	20	120.00	0.36	26	0.0110

Figures captions

Fig. 1a XRD spectra of 1 to 10 minute rapid discharge sintered NiO_x coatings (1-2 μm). The crystallite size information was calculated using the Scherrer equation.

Fig. 1b UV-vis absorbance spectroscopy of 1-2 μm thick dye sensitized NiO_x coatings (sintered 1 to 10 minutes).

Fig. 2a Photovoltaic performance of ERY sensitized NiO_x coatings (1-2 μm thick) using the light from AM 1.5 solar simulator ($I : 870 \text{ W m}^{-2}$). Electrolyte: 0.5 M LiI and 0.05 M I₂ in propylene carbonate.

Fig. 2b Current density vs applied potential curves for 5 minute, 2.5 μm thick RDS sintered NiO_x coatings sensitized with ERY.

Fig. 3a XRD spectra of 2.5 μm thick NiO_x coatings sintered for 5 minutes using furnace and the RDS technique. The crystallite size was calculated using the Scherrer equation.

Fig. 3b UV-vis absorbance spectra of 2.5 μm thick ERY sensitized-NiO_x coatings sintered for 5 minutes using the furnace and the RDS technique.

Fig. 4 FIB/SEM cross section images of NiO_x coatings obtained after 5 minute sintering using (a) the furnace and (b) the RDS technique. Both coating thicknesses were approximately 2.5 μm.

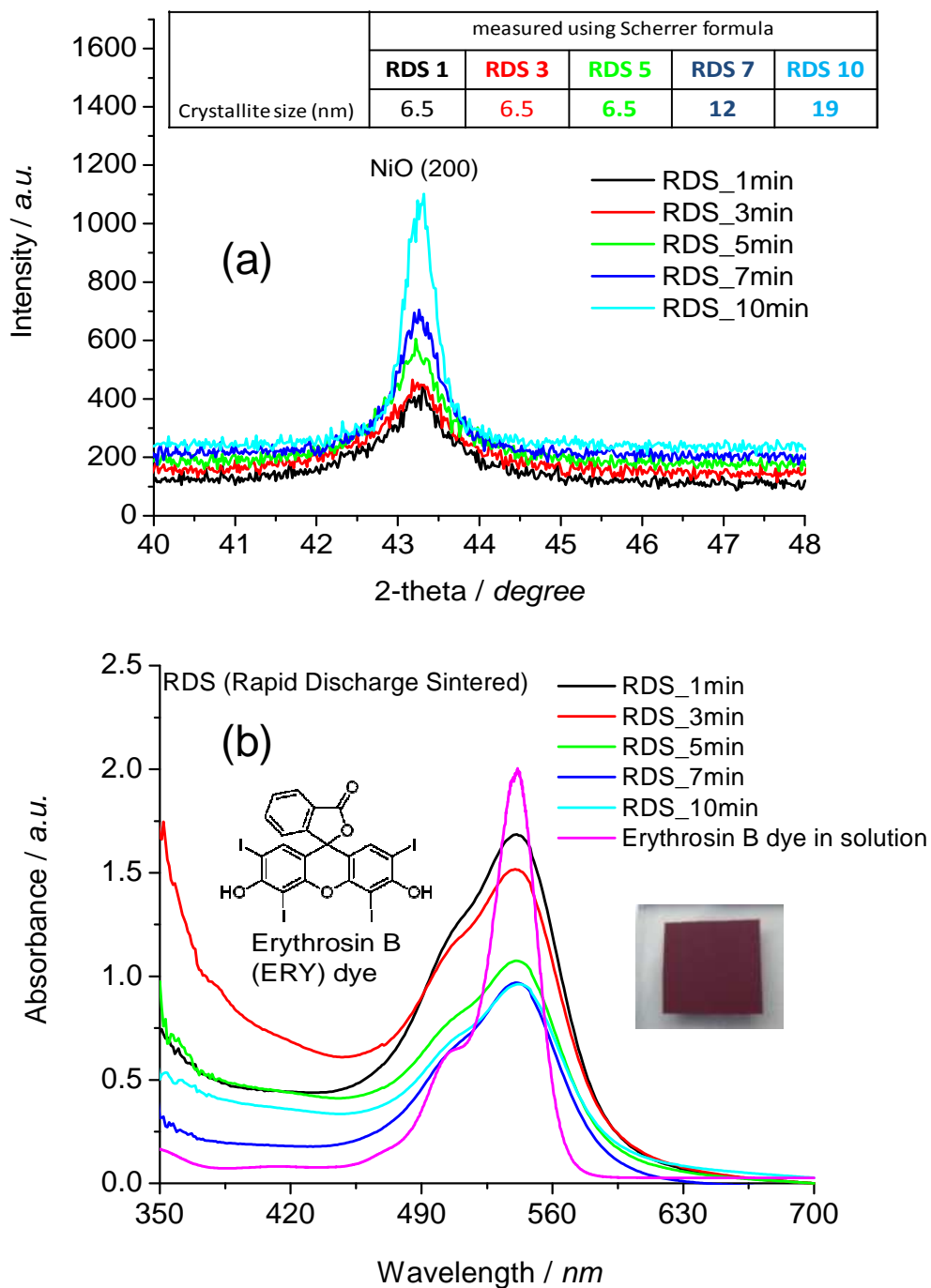


Fig. 1

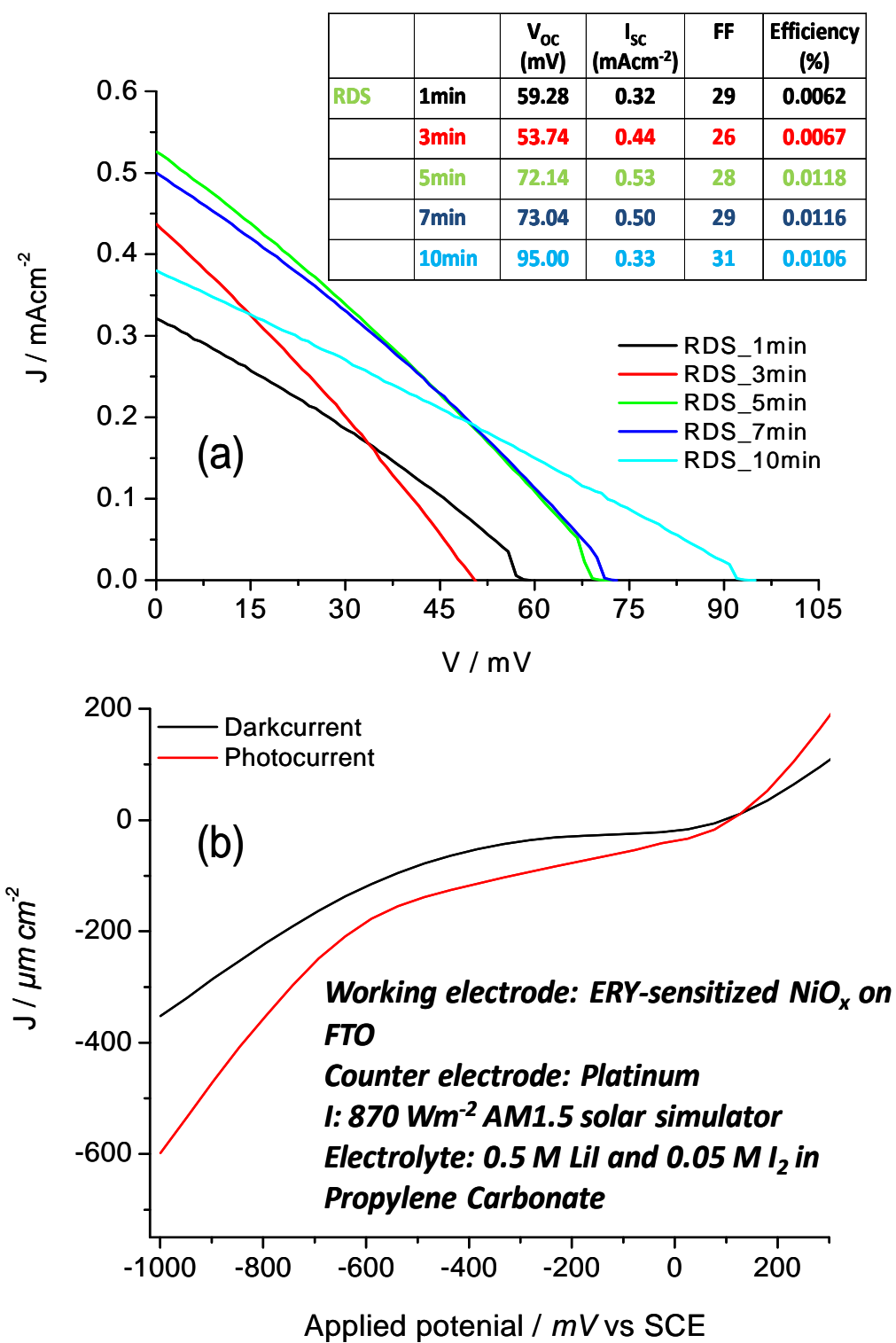


Fig. 2

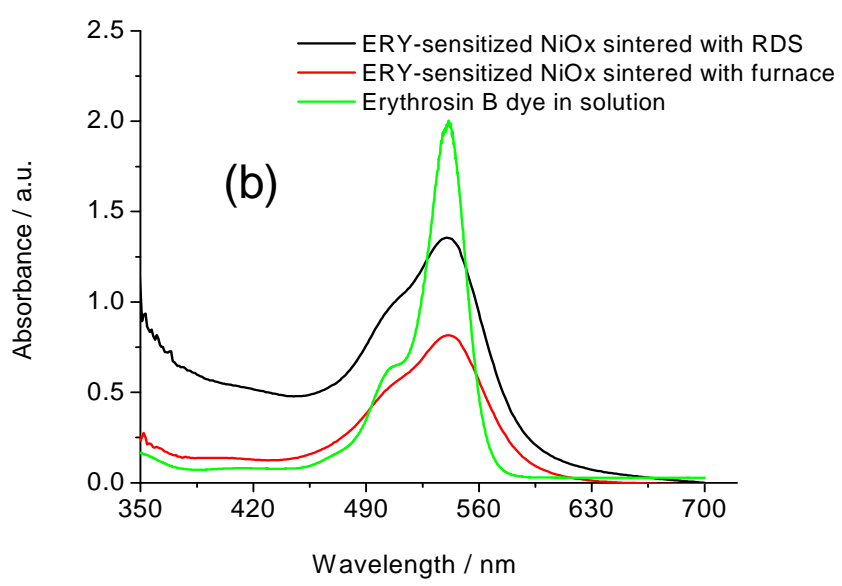
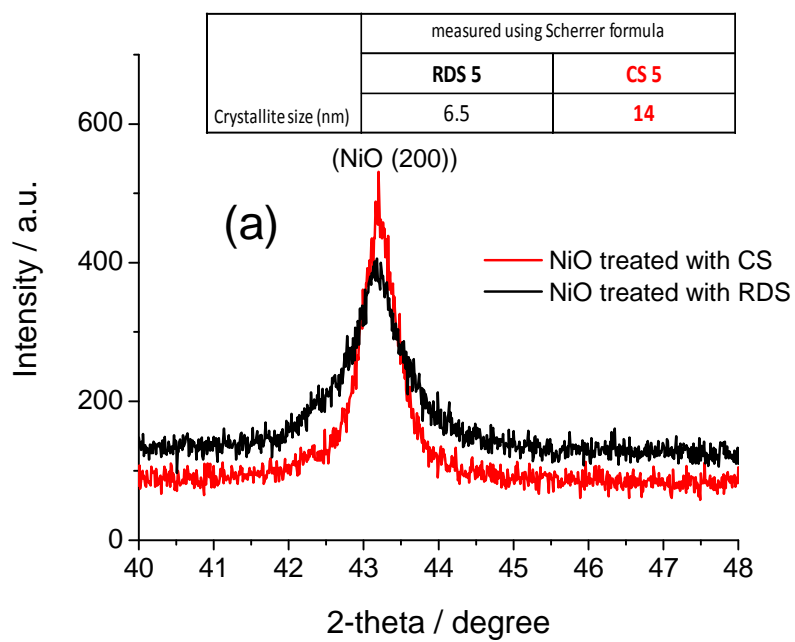


Fig. 3

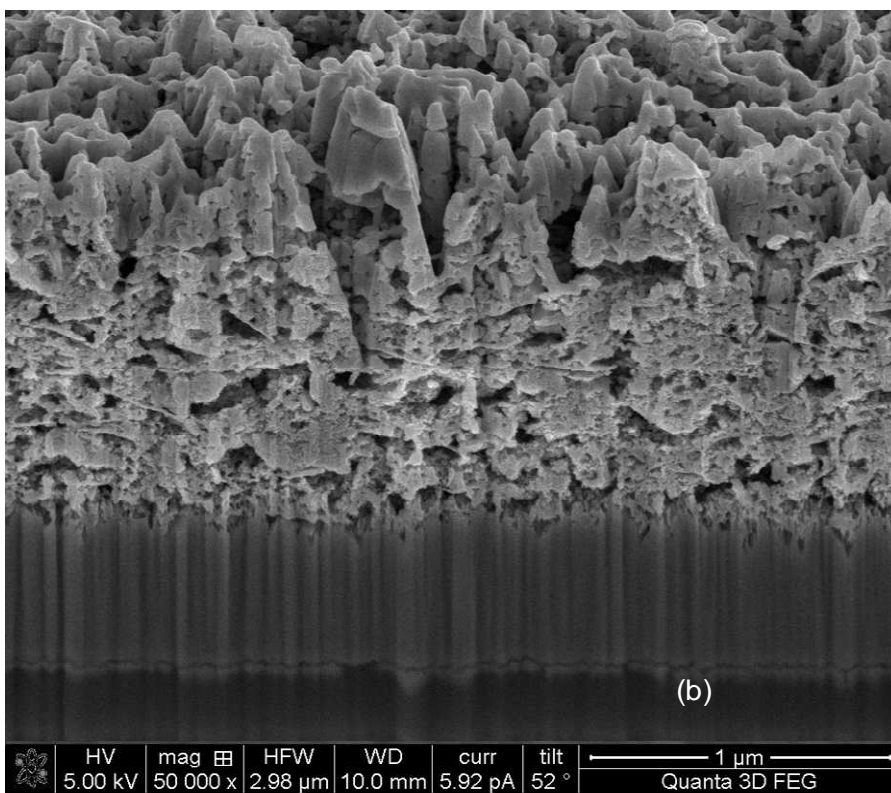
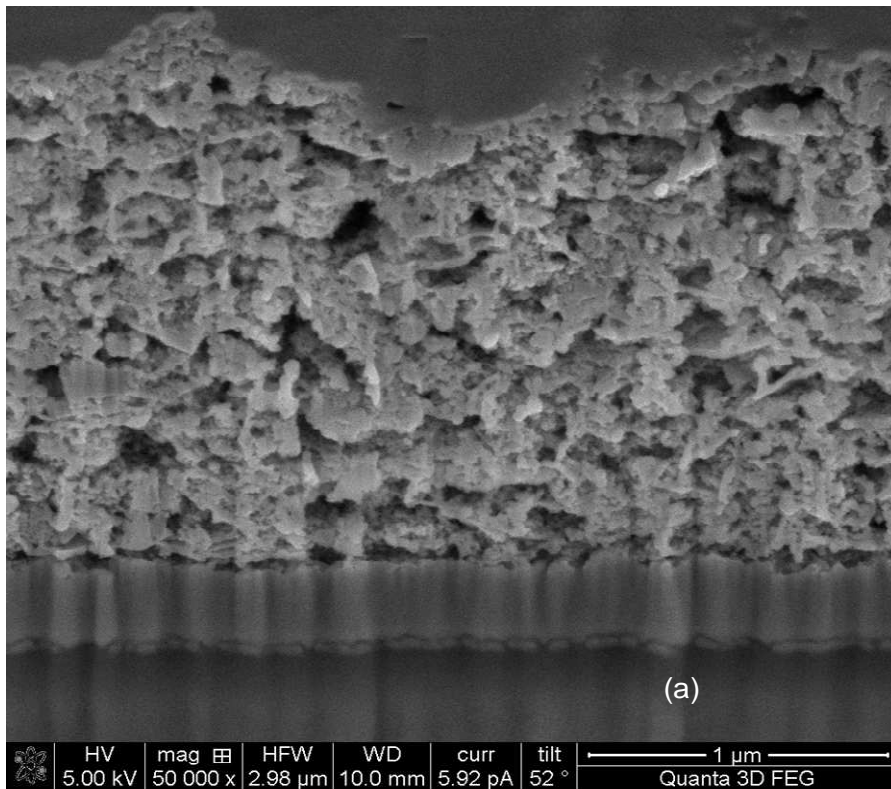


Fig. 4