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Dye sensitised solar cells with nickel oxide photocathodes prepared via scalable microwave sintering

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Abstract

Photoactive NiO electrodes for cathodic dye-sensitised solar cells (*p*-DSCs) have been prepared with thicknesses ranging between 0.4–3.0 μm by spray-depositing pre-formed NiO nanoparticles on fluorine-doped tin oxide (FTO) coated glass substrates. The larger thicknesses were obtained in sequential sintering steps using a conventional furnace (CS) and a newly developed rapid discharge sintering (RDS) method. The latter procedure is employed for the first time for the preparation of *p*-DSCs. In particular, RDS represents a scalable procedure that is based on microwave-assisted plasma formation that allows the production in series of mesoporous NiO electrodes with large surface areas for *p*-type cell photocathodes. RDS possesses the unique feature of transmitting heat from the bulk of the system towards its outer interfaces with controlled confinement of the heating zone. The use of RDS results in a drastic reduction of processing times with respect to other deposition methods that involve heating/calcination steps with associated reduced costs in terms of energy. P1-dye sensitized NiO electrodes obtained via the RDS procedure have been tested in DSC devices and their performances have been analysed and compared with those of cathodic DSCs derived from CS-deposited samples. The largest conversion efficiencies (0.12 %) and incident photon-to-current conversion efficiencies, *IPCEs*, (50 %) were obtained with sintered NiO electrodes having thicknesses of $\sim 1.5\text{--}2.0\ \mu\text{m}$. In all the devices, the photogenerated holes in NiO lived significantly longer ($\tau_h \sim 1\ \text{s}$) than has previously been reported for P1-sensitized NiO

photocathodes. In addition, P1-sensitised sintered electrodes give rise to relatively high photovoltages (up to 135 mV) when the triiodide-iodide redox couple is used.

Keywords: Dye-sensitized solar cells; nickel oxide; nanoparticles; microwave plasma sintering; organic dye; light harvesting; photoelectrochemistry

Introduction

For the last two decades the interest in the development of efficient dye-sensitised solar cells (DSCs) has been growing fast and, with the increasing awareness of the importance of reducing CO₂ emissions, the subject has become more relevant than ever before. So far, investigations have been carried out mostly on the optimisation of *n*-type devices based on TiO₂, [1] and DSCs based on photoactive cathodes (*p*-DSC) were reported for the first time only in 1999 by He *et al.* [2] The aim of the research on *p*-DSCs is to couple dye-sensitised photocathodes with state-of-the-art dye-sensitized photoanodes [1] in tandem cells [3] in order to achieve higher efficiencies with respect to DSCs that use one photoactive electrode alone. However, at present, the efficiency of tandem DSCs is limited by the low efficiency of the photocathode (the maximum reported efficiency is 0.4 %), [3d] and substantial improvements in both photocurrent and photovoltage are still required to exploit the potential of tandem devices. Recently, there has been a renascent interest towards photoactive cathodes for DSCs based on NiO, because relatively high incident photon-to-current conversion efficiencies (*IPCE*) could be achieved, [3d;4] and open circuit voltage (*V_{OC}*) increased. [3c;5] Much of this improvement stemmed from the introduction of new dyes specifically designed for NiO, which exhibit efficient photo-induced charge separation and slower charge recombination at the NiO/dye interface. [3d;6] In addition, thicker NiO cathodes with larger surface area have been prepared to increase the dye loading and, consequently, light harvesting efficiency. [4a;7] The study of new redox couples that replace the system I₃⁻/I⁻ was also undertaken for improving the photovoltage in *p*-DSCs. [3c;8] The most challenging target is to replace the semiconductor with one displaying a lower valence band edge in order to increase the maximum achievable photovoltage. Compared to the range of *n*-type semiconductors that are available, [1b] relatively few *p*-type semiconductors exist with appropriate valence band edge potential with respect to the redox potential of DSCs shuttles. [8] Those which do include metal oxides like NiO, [9] CuO, [10], Cr₂O₃ [11] and, more recently, CuGaO₂. [12] Despite of these efforts in the search for stable, transparent, *p*-type substrates with mesoporous morphology, NiO remains the most suitable material as photocathode for *p*-DSCs. TiO₂ films generally show higher photocurrents than NiO electrodes by virtue of their larger thickness (*l* ~ 8-10 μm for TiO₂ in *n*-DSCs compared

to 1-2 μm for NiO in *p*-DSCs) and, consequently, greater dye loading.[13] In the present work we report a new scalable method of preparation of nanoporous NiO electrodes for *p*-DSCs by spraying films of NiO nanoparticles (diameter ~ 50 nm) onto fluorine-doped tin oxide(FTO)/glass substrates and sintered them using a technique based on microwave assisted plasma sintering.[14] This is a faster sintering procedure when compared to conventional furnace sintering (CS), and this is why it is also known as rapid discharge sintering (RDS) technique. RDS performs sintering of thick NiO films ($l \sim 3$ μm)[3c] with good mechanical stability, and strong adhesion on various types of substrates.[14d] The electrodes of sintered NiO were characterised with a range of surface and electrochemical techniques. The NiO films obtained were sensitised with the organic dye **P1** which has previously shown to produce high *IPCE* in combination with NiO.[4] Sealed devices containing the photoactive P1-sensitized NiO electrodes, prepared using the two different techniques, were assembled with a platinised FTO anode and infiltrated with an acetonitrile solution of triiodide-iodide. The *J-V* characteristics of these *p*-DSCs were measured and the photoelectrochemical behaviour was determined. Samples prepared by the CS techniques are called **1**, and those by RDS are **2**. The samples were prepared with three different thicknesses: samples **1a-c** and **2a-c**. The results obtained are compared with those previously reported for *p*-DSCs based on NiO photocathodes prepared with wet, non-scalable methods that require the utilization of NiO precursors and do not make use of preformed NiO nanoparticles.[4a;5;7b;15] To our knowledge this is the first report on nanoporous NiO photocathodes prepared with a scalable method for *p*-DSCs purposes.

Experimental Section

NiO layer deposition

The fluorine-doped tin oxide (FTO) coated glass (supplied by Solaronix with a sheet resistance ~ 15 Ω/sq and glass thickness 3 mm) were cut to an area of 2×2 cm^2 and cleaned in ultrasonic bath for 5 minutes in propanol and then acetone. NiO nanoparaticles films were then deposited by spraying a slurry made of NiO nanoparticles (obtained from Sigma-Aldrich with diameter of *ca.* 50 nm, as confirmed from SEM pictures recorded for films prior to sintering) in 2-propanol (20 mg/mL) onto the FTO substrates according to the procedure reported by Halme *et al.* for the deposition of TiO_2 layers.[16] Layer thickness layer could be varied through the number of spraying passes: for samples **a** (thickness 0.4 μm) a single pass was applied, whereas samples **b** (thickness 1.5-2.0 μm) and samples **c** (thickness 2.5-3.0 μm) required 3 and 5 passes, respectively. ~~Samples **b** and **c** were sintered with a single thermal treatment after the completion of the number of spraying passes.~~

NiO thin film sintering

After spray deposition, a sintering step was carried out to optimise the electrical connectivity between the NiO particles in the sprayed layer, and to achieve a higher level of adhesion between the NiO film and the FTO substrate. The sintering was carried out using two different approaches: **1** in a conventional muffle furnace (CS method), and **2** using microwave assisted plasma sintering technique (RDS method).[14d] Three samples of each type were made to compare the reproducibility of the electrochemical results and the DSCs performance (*vide infra*).

In the CS method three NiO films (type **1**) were heated in air in a Carbolite Furnace (RHF 1200) at the rate of 15 °C/min until the maximum temperature of 450 °C was reached then and sintered for 5 minutes. After this a cooling ramp of 15 °C/min was applied.

RDS (type **2**) was carried out using a circumferential antenna plasma (CAP) microwave system described in detail elsewhere.[17] Input powers of 2.4 kW were supplied from a Mugge microwave power supply operating at a frequency of 2.45 GHz. The microwaves were guided to the plasma chamber via a coaxial tunable waveguide, which had a radial expansion and was directed towards a ring-shaped quartz window. The microwaves passed through the window with uniform amplitude and phase distribution, and possessed a rotational symmetry of propagation. Plasma was formed in a gaseous mixture of argon and oxygen with partial pressures ratio 10:1 at the total pressure of 5 mbar. The composition of the gas mixture and the total pressure were selected in order to achieve the required treatment temperature of 450 °C during the RDS process. The dwell time of the samples in the plasma chamber during the RDS treatments was 5 minutes. During sintering the temperature of the substrates was continuously monitored with a LASCON QP003 two-colour pyrometer from Dr Mergenthaler GmbH & Co. Three spray-deposited NiO samples were simultaneously treated with plasma by rotating them inside a 5 cm diameter plasma sphere located at the centre of the CAP chamber.

NiO film characterization

The NiO film thickness (l) was measured by step height measurement using a WYKO NT1100 optical profilometer in the vertical scanning interferometry (VSI) mode.

For the cross sectional investigations and morphological analysis, the NiO electrodes were mounted on stubs using double-sided carbon tape, and sputter-coated with platinum using an Emitech K575X sputtering unit. The metallization of NiO coatings prevented surface charging by the electron beam. Samples morphology was then examined using a FEI Quanta 3D FEG Dual Beam (FEI Ltd, Hillsboro, USA).

The XPS data were taken with a Kratos AXIS 165 XPS spectrometer. XPS spectra were collected in the normal mode with X-rays excitation along the direction normal to surface for testing the binding energy range 0-1400 eV. The curve fitting was carried out on Ni_{2p} and O_{1s} core level peaks to determine and survey the chemical composition of NiO coatings. Casa XPS software was used to analyze the data.

Electrochemical characterization of NiO coatings

Electrochemical investigations were carried out using a CH Instruments (Austin, Texas, USA) potentiostat (604C) and a three-electrode cell configuration: the NiO coatings and their dye-sensitised version on fluorine doped-tin oxide (FTO) substrate were used as working electrodes; the counter electrode was a platinum disk (diameter: 2 mm, from CH Instruments); the reference electrode was the Ag/AgCl redox couple in water. The electrolyte composition was 0.2M KCl, 0.01 M KH₂PO₄ and 0.01M K₂HPO₄ in water.[15e] For cyclic voltammetry experiments a scan rate of 40 mV s⁻¹ was used. Cyclic voltammetry was carried out with an electrochemical workstation (Mod. 604C) from CH Instruments (Austin, Texas, USA).

Cathodic DSC preparation and characterization

Sintered NiO films were cut, washed with ethanol and dried at 250 °C for 10 mins and allowed to cool to 100 °C. Subsequently, the films were immersed in the sensitizer solution (0.2 mM **P1** in acetonitrile) for 16 hrs. The transmittance spectra of the sensitized films were recorded using a Varian Cary 5000 spectrophotometer fitted with an integrating sphere. The sensitised films were sealed face-to-face with a platinised FTO counter electrode in a sandwich configuration using 30 µm thick pre-cut Surlyn® thermoplastic frame (6 × 6 mm interior) as separator. The device was filled with the electrolyte 0.1M I₂, 1.0M LiI in acetonitrile through a pre-drilled hole in the counter electrode using reduced pressure. The hole was finally sealed with Surlyn® and a glass cover-slide. For *J-V* and *IPCE* measurements the films were masked using a 4 × 4 mm opaque frame and in all cases the cells were illuminated from the NiO working electrode side. *J-V* characteristic curves were measured with a Newport solar simulator (model 91160) giving light with AM1.5G spectral distribution. The spectrum of the incident light was calibrated using a reference cell (Fraunhofer ISE) certified to an intensity 100 mW cm⁻². *IPCE* spectra were recorded using a computer controlled setup consisting of a xenon light source (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110), and a potentiostat (EG&G PAR 273). Hole lifetime and transport times measurements were performed using a white LED (Luxeon Star, power: 1W) as

light source. Voltage and current traces were recorded with a 16-bit resolution digital acquisition board (National Instruments) in combination with a current amplifier (Stanford Research Systems SR570), and a custom made system using electromagnetic switches. *IPCE* was determined according to the experimental procedure reported in ref.[18](#). Transport times and lifetimes were determined by monitoring photocurrent and photovoltage transients at different light intensities upon application of a small square wave modulation to the base light intensity. The photocurrent and photovoltaic responses were fitted using first-order kinetics to obtain time constants.[\[18b\]](#)

Results and discussion

NiO electrodes characterization

The NiO electrodes were prepared as shown in Table 1. The thicknesses are given with an uncertainty of 0.5 μm because of the non-uniformity of the film height as observed with the optical profilometer. The thickness slightly decreased in passing from the centre to the side of the NiO electrode irrespective of the sintering method.

Table 1. *Samples numbering, layers thickness specification and outline of the deposition conditions.*

Deposition method and sintering technique	Samples	Thickness / μm
Spray deposition of NiO nanoparticles on FTO and sintering in conventional furnace (CS, Samples 1)	Sample 1a	0.40
	Sample 1b	1.5-2.0
	Sample 1c	2.5-3.0
Spray deposition of NiO nanoparticles on FTO and sintering via rapid discharge sintering (RDS, Samples 2)	Sample 2a	0.40
	Sample 2b	1.5-2.0
	Sample 2c	2.5-3.0

The maximum sintering temperature ($T_{\text{MAX}} = 450\text{ }^{\circ}\text{C}$), and the dwelling time (5 mins) at T_{MAX} for the completion of NiO coatings sintering are the same in both CS and RDS procedures. However, the heating/cooling time was considerably longer for the CS procedure (see Figure S1 in the Supplementary Information), and, more importantly, the direction of the heat flow during the sintering process. In the muffle furnace the heating element causes heat to flow from the exterior towards the bulk of the sample. Conversely, the RDS procedure has the unique feature of heating a sample from its bulk to its borders (inside-out heat flow) as a consequence of the presence of

plasma which confines the volume where microwave radiation is absorbed and heating takes place.[14]

The morphology of the NiO samples was investigated using SEM (Figure 1). There was a reduced grain growth and the surfaces, for the RDS samples **2**, were less even than those of CS samples **1**. The increased growth of NiO grains in samples **1** is ascribed to the slower cooling rate (15 °C/min - see Experimental Section) employed in the CS procedure. Longer cooling times lead to the actual prolongation of the sintering process which can occur also at temperature values slightly different from T_{MAX} . In contrast, in the RDS procedure the heating, which is based on a rapidly switchable microwave radiation, requires only 5 min of cooling time subsequent to the plasma treatment. This represents the minimum period necessary to prevent thermal shocks that would cause coating cracks or the breakage of the FTO/glass substrates.

Figure 1. SEM images showing the surface morphology of (left) sample **1b** and (right) sample **2b**.

The mesoporous features of the differently sintered NiO coatings were also examined using a FIB/SEM cross-sectional view of the films (Figure 2). From these images it is clear that RDS sintered electrodes **2** present larger voids than CS electrodes **1** through the whole thickness of the film. As a consequence of that, samples **2** have a more open morphology and exhibit a higher porosity than samples **1**. This difference can be explained in terms of the different heating dynamics in the RDS and CS procedures. As already outlined, RDS treatment involves the volumetric heating of the sample, and it is chosen for providing a homogeneous release of heat inside a small matrix like micron-sized NiO electrodes. In the CS procedure, the furnace operates

by means of a conductive mode of heating and the outer surface of the NiO electrodes represents the primarily selected heat-affected zone.[19]

Figure 2. Dual beam Focused Ion Beam–Scanning Electron Microscope (FIB–SEM) images showing the cross sections of (left) NiO electrode **1b**, and (right) NiO electrode **2b**.

The surfaces of samples **1** and **2** have been also characterized with X-ray photoelectron spectroscopy (XPS) to analyse their chemical composition and the surface morphology [5] (Figure 3). A larger extent of crystallinity in the type **2** samples is expected from the better resolved shoulders associated with the main signals of Ni 2p_{3/2} [shoulder at 856 eV, Figure 3(a)] and O 1s [shoulder at 531.5 eV, Figure 3(b)] in the XPS spectra of RDS.[20] The type **1** samples generally display broader peaks in their XPS spectra which indicates a lower degree of crystallinity.[20] Differences in the number of electronic defects, e.g. Ni³⁺ sites, and structural defects like O²⁻ vacancies, on the surface of NiO cannot be ruled out as possible origins of the variations observed in the XPS spectra of CS and RDS samples.[21]

Figure 3. XPS spectra of (a) Ni 2p, and (b) O 1s of NiO electrodes deposited onto FTO/glass substrates with RDS (red profiles) and CS (black profiles) techniques. BE: binding energy. Intensities are normalized with respect to the maxima.

Electrochemical properties of sintered NiO electrodes

The cyclic voltammograms of the nanoporous NiO coatings (Figure 2) prepared with the two different sintering procedures present the characteristic profiles of compact[22] and nanostructured sol-gel films[15e] with two broad reversible oxidation peaks in aqueous electrolyte (Figure 4). The

direct comparison of the cyclic voltammograms of NiO samples **1** and **2** having the same thickness is provided in the Supplementary Information (Figure SI4).

The current waves are generated by the reversible transformations of Ni(II) into Ni(III) (Eqs. 1, 2 and 3) and, possibly, Ni(III) into Ni(IV) (Eq.4), and are associated with a succession of the solid-state electrochemical reactions as shown below:[23]

and

or, alternatively, by the succession of the processes:[15e;22b]

and

depending on the actual extent of hydration of the sintered nickel oxide layers upon contact with the aqueous electrolyte.[22]

The total charge exchanged reversibly by the different NiO electrodes during the oxidation processes I and II has been calculated by time-integrating the current density profiles of Figure 3. The corresponding electrochemical parameters for the different samples have been listed in Table 2 and the data obtained from the analysis of the cyclic voltammograms are shown in Figure 4. For the evaluation of Q'_{exc} we have used an averaged thickness value in case of samples **b** and **c** (see Experimental Section). The proportionality between the current density exchanged by the oxide and its thickness reveals the mesoporous nature of the two types of sintered NiO electrodes. This is a direct consequence of that fact that thicker nanoporous samples have a larger electroactive surface area.[1a] Moreover, it indicates that both CS and RDS methods generate an effective electrical contact between metal oxide nanoparticles, and between the FTO substrate and oxide layer during sintering process.

Figure 4. Cyclic voltammograms of (top) CS (1), and (bottom) RDS (2) NiO electrodes with three different thicknesses. Scan rate: 40 mV s^{-1} ; counter electrode: Pt; electrolyte composition: 0.2 M KCl , $0.01 \text{ M KH}_2\text{PO}_4$ and $0.01 \text{ M K}_2\text{HPO}_4$ in water solvent. Arrows indicate the direction of potential scan.

Table 2. Electrochemical parameters for the NiO samples studied. Symbols definition: $E_p(I)$ = oxidation potential of peak I (Figure 4); $J_p(I)$ = current density of oxidation peak I; $E_p(II)$ = oxidation potential of peak II (Figure 4); $J_p(II)$ = current density of oxidation peak II; Q_{exc} = total charge exchanged in redox processes I and II per geometrical surface unit; Q'_{exc} = charge exchanged in redox processes I and II per film volume unit. $E_p(I)$ and $E_p(II)$ are referred to the redox couple Ag/AgCl.

Sample	$E_p(I)$ / V	$J_p(I)$ / A cm ⁻²	$E_p(II)$ / V	$J_p(II)$ / A cm ⁻²	Q_{exc} / mC cm ⁻²	Q'_{exc} / C cm ⁻³
1a	0.465	$2.46 \cdot 10^{-4}$	0.857	$3.48 \cdot 10^{-4}$	5.2	130
1b	0.424	$6.27 \cdot 10^{-4}$	0.830	$9.28 \cdot 10^{-4}$	14.4	96
1c	0.567	$1.3 \cdot 10^{-3}$	0.968	$1.8 \cdot 10^{-3}$	29.1	120
2a	0.487	$2.85 \cdot 10^{-4}$	0.873	$4.04 \cdot 10^{-4}$	6.3	160
2b	0.397	$6.27 \cdot 10^{-4}$	0.816	$1.0 \cdot 10^{-3}$	15.5	100
2c	0.548	$1.8 \cdot 10^{-3}$	0.945	$2.3 \cdot 10^{-3}$	40.6	160

The parameters listed in Table 2 refer to bare NiO samples **1** and **2** with different thicknesses **a-c**. Since NiO oxidation is localised at the surface of the oxide film being being $J_p(I)$ and $J_p(II)$ linearly dependent on the scan rate for both samples **1** and **2**[15e] (see Electronic Supplementary Information, Figures SI2 and SI3), it is reasonable to assume that the amount of charge exchanged by the coatings is directly correlated with the surface area of the oxide samples within the examined range of thicknesses $0.4 \leq l \leq 3.0 \mu\text{m}$. [7] CS electrodes **1** display lower values of Q_{exc} and Q'_{exc} with respect to RDS electrodes having the same thickness (Table 2) as a consequence of the larger voids and higher porosity of the latter films (Figure 2). Within the same type of samples the volume density Q'_{exc} of the total charge exchanged by the NiO electrode presents the lowest value for the intermediate thickness **b**, whereas thicknesses **a** and **c** have considerably larger and comparable values of Q'_{exc} (Table 2). A possible explanation for such an anomalous trend could be because the thicker electrodes **b** and **c**, i.e. the samples obtained through multiple spraying passes, are not uniform (see Experimental Section). The area of the sample considered for the calculation of the average thickness of electrodes **b** and **c** is based on the scan of a small portion of the samples. For electrodes **b** with intermediate thickness the variability of the height over the total geometrical area of the electrode may be more pronounced than for samples **c**. As a consequence of that, the evaluation of the average thickness could have been less well defined for electrodes **b** than for the thickest layers **c**.

The sensitisation of NiO electrodes with P1 dye [4a,b;6a] does not introduce any additional redox process in the examined range of potential as verified by the comparison of the voltammograms of P1-sensitised NiO and its bare version (Figure 5).

Figure 5. Cyclic voltammograms of NiO (sample **2b**) in the P1-sensitised version (red profile), and as a bare electrode (black profile). Scan rate: 40 mV s^{-1} . NiO electrode thickness: $1.5\text{-}2.0 \text{ }\mu\text{m}$. NiO film has been deposited onto a FTO/glass substrate via the RDS procedure. Electrolyte as in Figure 4. Arrows indicate the direction of potential scan.

This finding (not shown) is common for all NiO coatings obtained with both RDS and CS sintering procedures. The different shapes of the voltammograms and the shifts of the oxidation peaks are ascribed to the different extent of protonation of the NiO surface in passing from the bare to the sensitised state. The nature of the redox processes occurring in P1-sensitised NiO is the same as in case of bare NiO coatings and involve always NiO as the actual electroactive species (Figure 4). These regard the conversion of Ni^{2+} to Ni^{3+} (peaks I and II), and eventually to Ni^{4+} (peak II), with occurrence of protons exchange between the surface of NiO and the electrolyte (Eqs. 1-4).[\[15e;22a\]](#) This consideration implies that the actual chemical composition of oxide surface is better described as a mixture of nickel oxide and nickel hydroxide.[\[15e;22b\]](#) Since sensitizer anchoring implies the replacement of the surface protons of the oxide with the carboxylic group of P1 [\[25\]](#), the extent of NiO surface protonation is altered slightly. This affects the electrochemical behaviour of the sensitized oxide as observed (Figure 5).

Photoelectrochemical performance of *p*-DSCs based on sintered NiO samples

The P1-sensitized NiO electrodes were assembled in *p*-DSCs with the I_3^-/I^- redox shuttle in acetonitrile, and a platinised counter electrode.[3c;4a,b] The dark *J*-*V* characteristic curves of P1-sensitized CS samples **1** and **2** were recorded for the three different thicknesses (Figure 6). The dark current density of the *p*-DSCs increased with the thickness of P1-sensitized NiO films and followed the same trend of the current density of bare NiO electrodes in aqueous electrolyte (Figure 4).

Therefore, ~~sensitization, sensitization of mesoporous of mesoporous~~ NiO coating with P1 does not create a blocking layer ~~and the~~ and the P1 sensitized nanostructures retain their electrochemical reactivity as in the bare state.

The *J*-*V* characteristic curves obtained under illumination are shown in Figure 7 and the parameters obtained from these profiles have been listed in Table 3. The direct comparison of the characteristic curves obtained under illumination of NiO samples **1** and **2** having the same thickness is available in the Supplementary Information (Figures SI5 and SI6).

Figure 6. Dark *J*-*V* curves for *p*-DSCs assembled with NiO samples **1** (dotted line) and **2** (full line) with different thicknesses **a-c**.

Figure 7. *J-V curves under illumination for p-DSCs assembled with NiO samples 1 (dotted curves), and 2 (full line) with different thicknesses a-c.*

Table 3. *Solar cell parameters for p-DSCs with PI-sensitised NiO as photoactive electrode. V_{OC} : open circuit voltage; J_{SC} : short-circuit current density; FF: fill factor; η : overall efficiency. Electrolyte: 1.0M LiI, 0.1M I_2 in acetonitrile. Data recorded under irradiation with AM 1.5 (intensity: 100 mW cm^{-2}).*

SAMPLE	V_{OC} / V	$J_{SC} / \text{mA cm}^{-2}$	FF	$\eta / \%$
1a	0.133	1.67	0.318	0.072
1b	0.135	2.15	0.333	0.098
1c	0.128	2.42	0.352	0.110
2a	0.126	2.56	0.325	0.105
2b	0.125	2.84	0.337	0.121
2c	0.103	3.12	0.326	0.101

On the basis of the data presented in Table 3 the behaviour of the various samples can be compared and the potential of the application of the CS and RDS deposition methods evaluated. The p-DSCs assembled with the thinnest NiO samples **a** and **b** ($0.4 \leq l \leq 2.0 \text{ }\mu\text{m}$) give the larger open circuit potential V_{OC} and higher overall efficiencies η with respect to the corresponding thicker electrodes **c** ($2.5 \leq l \leq 3.0 \text{ }\mu\text{m}$). The overall efficiency increases in going from **a** to **b** whereas the short circuit photocurrent J_{SC} always increases with thickness over the whole examined range $0.4 \leq l \leq 3.0 \text{ }\mu\text{m}$.

In summary, the photocurrent increase observed in going from samples **b** (1.5-2.0 μm) to **c** (2.5-3.0 μm) is offset by a decrease of the open circuit photovoltage (Table 3). These findings are explained considering that the increase of film thickness increases the surface area of the film. Since more dye can be absorbed, higher photocurrents are observed. In addition to that, thicker films expose a larger surface to the electrolyte and, consequently, give more recombination with the redox shuttle. Recombination scales linearly with the thickness of mesoporous films whereas light absorption and photo-injection do not follow an analogous trend. The greater recombination in the thickest samples **c** lowers the Fermi level of illuminated P1-sensitized NiO and lower photovoltages are found for **c** compared to **a** and **b** (Table 3). Further information can be obtained from the transmission spectra of the samples before and after sensitization as shown in Figure 8 for NiO electrodes **1a-c**. The predominant contribution to the absorption of visible light comes from the NiO material itself. For example, at a film thickness of 0.40 μm (sample **a**) 48% of the light is absorbed by the film itself, and adsorption of P1 only decreases the transmittance by a further 28% at the peak maximum (Figure 8 and Table 4). Since the spectrum is practically saturated for sensitised films with 1.5-2.0 μm thickness (sample **b**), sensitization brings a little gain in optical density on increasing the film thickness to 2.5-3.0 μm (sample **c**). Because of that, further increase of the film thickness of sintered samples **1** and **2** does not significantly improve the overall light harvesting efficiency, LHE, defined as $1-10^{-A}$, A being the absorbance of the sample (Table 4). It was noted that the photocurrent density, measured at 100 mW cm^{-2} , increased for thickest **2c** compared to **2b** (Table 4), whereas *IPCE*, which is measured at a lower light intensity,[**3c;18a**] decreased over the visible spectrum with the thickness of sample **2** going from 1.5-2.0 to 2.5-3.0 μm (Table 4). This is not the case for samples **1** (Table 4). The observed behaviour of **2** implies that for these samples higher light intensity, i.e. the condition of a larger number of photons impinging the electrode per time unit during current-voltage measurements, overcomes the shortening of photo-holes lifetime induced by the increase of the thickness in the nanoporous electrode (*vide infra*). P1-sensitised electrodes **1** and **2** display among the largest values of conversion efficiencies ever reported [**4;6b;26**] being *IPCE* in the order of 40-50 % within the spectral interval 400-600 nm (see Supplementary Information, Figure SI8). To our knowledge solely double layered NiO samples prepared from colloids gave a better result with sensitizer P1 being *IPCE* comprised in the range 45-60 % within the spectral range of dye maximum absorption.[**4a;6a**]

When comparing samples **1** and **2**, data show that for the thickness range $0.4 \leq l \leq 2.0 \mu\text{m}$ CS coatings produce larger V_{OC} values but lower η values than their type **2** analogues, whereas RDS coatings **2** always display the largest photocurrents (Table 3). The latter observation on

photocurrent is consistent with the trends the dark current observed for types **1** and **2** electrodes in both bare and sensitised states (Figures 6 and SI4).

Figure 8. Transmission spectra of unsensitized and sensitized NiO samples **1 a-c**.

Table 4. Transmittance at 475 nm (T_{475} / %), for NiO electrodes **1a-c** and **2a-c**. Light harvesting efficiency at 475 nm (LHE_{475}), and LHE_{475} increment in going from the bare to the sensitized state (ΔLHE_{475}) for the two differently deposited samples **a**.
 $IPCE_{470nm}$: incident photon-to-current conversion efficiency at 470 nm.

SAMPLES	T_{475} / %	LHE_{475}	ΔLHE_{475}	$IPCE_{470nm}$ / %
1a / P1-sensitized 1a	47.8 / 19.3	0.522 / 0.807	0.285	26.5
1b / P1-sensitized 1b	17.6 / 1.6	-	-	48.3
1c / P1-sensitized 1c	4.6 / 0.8	-	-	50.0
2a / P1-sensitized 2a	59.6 / 16.1	0.404 / 0.839	0.435	36.8
2b / P1-sensitized 2b	20.0 / 3.7	-	-	48.0
2c / P1-sensitized 2c	2.7 / 1.1	-	-	44.0

The comparison of the optical spectra of bare NiO films reveals that RDS samples **2** are generally more transparent and less scattering than CS samples **1** within the thickness range $0.4 \leq l \leq 2.0 \mu m$ (see Supplementary Information, Figure SI7) by virtue of the lower density of electrodes **2** vs electrodes **1** (Figures 1 and 2). Since the grain size of NiO particles in sample **2** appears to be

smaller (Figures 1 and 2), this enables a larger loading of sensitizer per unit area and explains why RDS samples **2** have more contribution to light harvesting from the dye than CS samples **1** (Table 4).

The hole lifetimes (τ_h) of both samples **1** and **2** were dependent on film thickness (Figure 9). The comparison of samples **1** and **2** evidences that CS samples **1** display longest hole lifetimes in the order of 0.5 - 1 s (samples **c**, Figure 10), in accordance with the observed trend of V_{OC} (Table 3). In fact, the smaller surface area of **1** with respect to **2** (Figures 2, 4 and 6) brings about a slowest charge recombination in NiO **1**. The τ_h value for the thickest CS sample **1c** is very high and similar to that of the thinnest CS sample **1a** (Figure 9) in contrast with what one would expect if the trend of the open circuit photovoltage is considered (Table 3). This finding is consistent with the idea that in case of CS sample **1c** a fraction of the total surface is actually photoactivated (and eventually in contact with the electrolyte) under the condition of open circuit. When τ_h values of sintered samples **1** and **2** are compared with those reported for the best performing *p*-DSCs based on sol-gel NiO photocathodes sensitized with P1, we find that the NiO electrodes prepared with RDS and CS methods have longer hole lifetimes at the same value of open circuit photopotential when the redox couple triiodide-iodide is used (see Supplementary Information, Figure SI9).^[4a;6c;26] This implies that the rate of charge transfer between the electrolyte and our NiO samples is generally slower with respect to the mesoporous NiO samples obtained via wet methods.^[3,4] The slope of τ_h vs V_{OC} is less steep in comparison to NiO electrodes with comparable thickness prepared using sol-gel techniques (Supplementary Information, Figure SI9).^[4a;5;6c;7;10;26] This is associated with the suppression of charge recombination in sintered samples. A possible cause of this effect is the structural order present in sintered NiO samples (Figure 3), which derives from the narrow distribution of the diameter in the starting nanoparticles and the low dispersion of the grains size in the resulting sintered films (Figure 1).

Figure 9. Hole lifetimes (τ_h) as a function of open circuit potential (V_{oc}) for *p*-DSCs prepared with NiO samples **1** in three different thicknesses **a-c**.

Figure 10. Hole lifetimes (τ_h) as a function of the open circuit potential (V_{oc}) for *p*-DSCs prepared with NiO samples **1-2** with thickness **c**.

Conclusions

We have demonstrated that NiO electrodes obtained via sintering of preformed NiO nanoparticles can be proficiently used as photoactive electrodes for cathodic *p*-DSCs. The deposition procedures considered are conventional sintering and microwave plasma assisted sintering, both of them representing scalable procedures. In particular, RDS possesses the important feature of transmitting heat from the bulk of the system towards its outer interfaces (outgoing heating mode) within a

confined volume. This has proved to be advantageous for the preparation of nanoporous NiO electrodes having large voids through the entire thickness of the film. As a consequence of that, the efficient sensitization of the RDS samples could be achieved with positive consequences on the light harvesting properties, dark-/photo-current densities and photo-carrier lifetimes. In operational terms the adoption of RDS reduces drastically the processing times with respect to all the other coating methods traditionally used for the preparation of DSCs electrodes. Overall efficiencies as high as 0.12 % and *IPCEs* of about 50% were obtained with P1-sensitized RDS samples having thickness 1.5-2.0 μm . The conversion efficiencies of the *p*-DSCs based on sintered NiO films sensitized with P1 are among the largest ever reported for photoactive NiO cathodes. In all *p*-DCS devices reported, the photogenerated holes lived significantly longer ($\tau_h \sim 1$ s) than has previously been found for P1-sensitized NiO photocathodes in analogous photocell configurations. These important results derive from the suppression of charge recombination and combine with the determination of relatively high photovoltages (up to 135 mV) when the triiodide-iodide redox couple is used. Improvements of the performances of the *p*-DSC derived from RDS NiO samples are expected due to the wide margins of optimisation of the microwave sintering technique. This will enable further gains of efficiency and photocurrent densities when mesoporous NiO samples with larger thickness (up to 7-8 μm) will have to be considered

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