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To cite this article: Andrew Nattestad et al 2008 Nanotechnology 19 295304

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Nanotechnology 19 (2008) 295304 (9pp)

Dye-sensitized nickel(II)oxide photocathodes for tandem solar cell applications

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Received 4 April 2008, in final form 16 May 2008 Published 10 June 2008 Online at stacks.iop.org/Nano/19/295304

Abstract

To date, nickel(II) oxide (NiO) is one of the few p-type semiconductors that has successfully been used for the construction of dye-sensitized photocathodes as well as tandem dye-sensitized solar cells. In this study we present a novel fabrication method for the preparation of mesoporous NiO films based on preformed NiO nanopowders. Critical properties such as pore-size distribution, crystallinity, and internal surface area of the resulting NiO films were controlled through the sintering process and optimized for their application as dye-sensitized photocathodes, resulting in a significantly increased photovoltaic performance, compared to earlier studies. A series of different sensitizers and electrolytes was scrutinized for their application in dye-sensitized NiO photocathodes. Despite its limited absorption range the dye coumarin 343 clearly outperforms other sensitizers used in this study. Values for short-circuit current densities of 2.13 mA cm⁻² and overall energy conversion efficiencies of 0.033% under simulated sunlight (AM1.5, 1000 W m⁻²) are the highest values reported in literature so far.

S Supplementary data are available from stacks.iop.org/Nano/19/295304

1. Introduction

Dye-sensitized solar cells (DSSCs) can be produced at low cost from cheap starting materials, providing high solar to electric energy conversion efficiency [1]. Over the past decade, however, the efficiency improvements seen for DSSCs have been rather marginal, suggesting that more radical concepts might be required to achieve conversion efficiencies well beyond 11% [2]. Concepts originally developed and successfully applied in the area of conventional photovoltaics, such as those of multi-junction or tandem solar cells, may hold the key for the development of a new generation of high-efficiency DSSCs.

Several tandem cell concepts comprising DSSC technology have been described previously [3–9]. While some of these devices require the stacking of pre-assembled DSSCs, an alternate concept, originally reported by He *et al* [6], combines dyesensitized photoanodes and photocathodes in a single sandwich cell structure. From a commercialization perspective this concept appears attractive, as it requires only marginal extra manufacturing costs when compared to a single-junction DSSC.

The tandem DSSC suggested by He *et al* represents a simple series connection of a dye-sensitized photoanode with a dye-sensitized photocathode. The series connection implies that the maximum voltage will be increased, theoretically to the sum of the maximum voltage of the two component electrodes. The overall photocurrent that passes through the device is, however, limited by the least efficient electrode. At present the choice of (dye-sensitized) photocathodes that could be combined with high-performance photoanodes is very limited. The few examples reported in the literature suffer from very poor device performance compared to the conventional TiO_2 systems [6, 10–14]. As a result, tandem devices based on these photocathodes generally show much lower photovoltaic performances than conventional, single-junction, DSSCs.

High-performance photocathodes are of course required for realization of high-efficiency tandem dye-sensitized solar

Table 1. Summary of production conditions for NiO nanoparticle films from the literature.						
First author	Time (min)	Temp (°C)	Precursor	Comments		
He [6, 11] Boschloo [10] & Morandeira [12]	60 15	500 300–320	Ni(acetate) NiCl ₂ .6H ₂ O	Via Ni(OH) ₂ sol–gel Via Ni(OH) ₂ sol–gel		
Vera [14]	30	250	$Ni(NO_3)_2 \cdot 6H_2O$	$10 \times dip coat$		

cells. This work focuses on dye-sensitized NiO photocathodes as one of the few systems studied to date. Our initial focus is to gain control over the morphology of the NiO nanoparticle semiconductor film to evaluate its impact on the final device performance. In the second section of this research we explore the influence of different sensitizers and electrolyte compositions.

The sensitizers considered for use with a NiO electrode must fulfil a number of basic requirements. They must have a highest occupied molecular orbital (HOMO) level far enough below the valence band edge of NiO (-5.0 eV AVS (versus absolute vacuum scale) [6]) and a lowest unoccupied molecular orbital (LUMO) far enough above the redox potential of the iodide–triiodide system (-4.85 eV AVS [15]) to offer sufficient driving forces for hole injection into the valence band as well as converting triiodide to iodide. Ideally sensitizers should absorb across a broad range of the spectrum, such that the greatest number of photons can be harvested to do work; they should also be stable over a long period of time. A further requirement for a viable dye is that it needs to have a high charge injection efficiency into the semiconductor.

In this work we present a novel fabrication method for the preparation of mesoporous NiO films based on preformed NiO nanopowders as components for dye-sensitized photocathodes. Critical properties such as pore-size distribution, crystallinity, and internal surface area of the resulting NiO films were controlled through the sintering process and optimized for their application as dye-sensitized photocathodes. The films are deposited directly from slurries of NiO nanoparticles in water and then exposed to a sintering step to produce mechanically stable nanostructured films, analogously to the process used to form nanostructured TiO₂ electrodes [16].

Nanostructured NiO films have found application in electrochromic devices [17-24], gas sensors [25, 26], supercapacitors [27, 28], and solar cells [6, 10–14]. The fabrication methods reported so far for these NiO electrodes involve the deposition of a thin film of a precursor such as nickel nitrate or nickel chloride, followed by in situ hydrolysis of these nickel(II) salts. The films are then converted into nanostructured NiO in a subsequent heattreatment step. Table 1 summarizes the processing conditions described for the formation of NiO films by other authors. The sintering conditions varied greatly, with either a short time at low temperature (30 min; 250 °C) or a long time at high temperature (60 min; 500 °C) being reported. Our work shows that the sintering conditions have a dramatic effect on the film morphology, and subsequently on the photovoltaic performance of the devices they are incorporated into. Therefore the use of preformed NiO nanoparticles as in this work, instead of a nickel(II) precursor, allows greater flexibility to optimize the sintering process with respect to the film formation, independent of the reaction conditions which are usually dictated by the chemical conversion of the precursors to NiO. This allows us to tailor the sintering step to optimize the nanostructure of our NiO film. To the best of our knowledge, there has been no work published looking at systematic optimization of nanoporous NiO films from preformed powders for use in a dye-sensitized photocathodic device. In this paper we report such a systematic study of the preparation of NiO photocathodes.

2. Experimental details

2.1. Chemicals used

Nanosized NiO powder was used as received from Inframat (nominal particle size: 20 nm, 73.22 wt% Ni). Acetylacetone and cresol red were acquired from British Drug Houses (BDH). Cis-bis(isothiocyanato)bis(2, 2'-bipyridyl-4, 4'-dicarboxylato)ruthenium(II) bis-tetrabutylammonium (N719) dye was ob-Hexachloroplatinic acid (H₂PtCl₆), tained from DyeSol. propylene carbonate ferrocene, erythrosin B sodium salt (also known as erythrosin J), Triton X 100, lithium iodide, iodine, coumarin 343, and eosin B were acquired from Sigma-Aldrich. Isopropanol and ethanol were purchased from Merck. Coumarin 540, rhodamine 101 and rhodamine 110 were obtained from Exciton. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was purchased from G Frederick Smith Chemicals (GFS). The TBAPF₆ was purified by dissolving in acetone, with potassium hexafluorophosphate added to precipitate iodide impurities. The solution was filtered and then evaporated to dryness, followed by recrystallization from ethanol. All other chemicals were used without further purification.

2.2. NiO film/photocathode preparation

Porous p-type films were produced by the doctor blade technique, using a slurry made by grinding 2 g of NiO with 10 μ l acetylacetone, 25 μ l triton X 100, and distilled water. The slurry was ground with a pestle for 10 min with 12 ml water, added in small aliquots, in order to break up larger agglomerates. The slurry was then sonicated for 30 min, and centrifuged for 20 s at 4000 rpm (equivalent to a relative g-force of 1500 cm revs² min⁻²) to remove large agglomerates. Films were produced on 2 mm thick conductive glass (F:SnO₂ coated, purchased from Libbey Owens Ford). The film thickness was determined with a Veeco Dektak 6M stylus profilometer to be 1.6 \pm 0.1 μ m. Thicker films were initially manufactured; however, these tended to suffer from poor mechanical properties. The centrifugation step improved



Figure 1. Scanning electron microscopy (SEM) images of NiO films made from (a) non-centrifuged slurry (b) centrifuged (4000 rpm for 20 s) slurry, both sintered for 10 min at 550 °C; the film thickness was $1.6 \pm 0.1 \,\mu$ m for both samples.

the film property dramatically (see figure 1). Smooth crackfree films of up to $1.6 \pm 0.1 \ \mu$ m thickness could be readily formed from the centrifuged slurry, while the non-treated slurry produced cracked films with poor mechanical stability.

2.3. Cell construction

Catalytic counter electrodes were produced by thermal decomposition of H_2PtCl_6 . A single drop of H_2PtCl_6 in isopropanol (0.05 M) was placed on the conductive side of a piece of F:SnO₂ glass. This was then allowed to dry and placed on a hot plate at 380 °C for 10 min in air. NiO electrodes were sintered in air, in a preheated furnace, at temperatures ranging from 350 to 650 °C, for times between 5 and 200 min. After sintering, the electrodes were allowed to cool to 110 °C, before being immersed in an ethanolic dye solution for 24 h (unsintered electrodes were heated to 110 °C prior to dying). All organic dye solutions (coumarin 343, coumarin 540, Cresol Red, eosin B, erythrosin J, rhodamine 101, and rhodamine 110) were used at 0.1 mM, and N719 at 0.3 mM. A series of films was left undyed. These were immersed in ethanol overnight for comparative purposes.

Photoelectrodes were sandwiched together with the platinized counter electrodes, and sealed with a 25 μ m Surlyn (DuPont) gasket. The cells were then filled with an electrolytic solution by a vacuum backfilling method. The electrolytes consisted of propylene carbonate containing various concentrations of iodine and lithium iodide.

2.4. Photovoltaic testing

Solar cells were tested using simulated sunlight (AM1.5, 1000 W m⁻²) provided by an Oriel solar simulator with an AM1.5 filter. Current–voltage characteristics were measured using a Keithley 2400 source metre. Cells were biased from +300 to -500 mV, with 10 mV steps and a 250 ms settling time (time delay between application of the potential and the actual current measurement). It was found that this comparatively long settling time was required to avoid measurement artefacts due to the capacitive nature of the NiO electrode.

The photovoltaic data presented are based on sample sizes of five individual solar cells for each data point. Errors and error bars shown in tables and graphs respectively show the standard deviations for each device series.

2.5. Other characterization

Dye loading was analysed with the aid of a Cary 5000 photospectrometer, measuring the optical absorption of NiO films before and after dying (with coumarin 343). All films were sintered at $550 \,^{\circ}$ C for 10 min if not otherwise specified.

The oxidation potentials of the dyes were measured by means of a three-electrode electrochemical cell set-up using a glassy carbon working electrode, a Pt counter electrode and a Ag/AgNO₃ reference electrode (calibrated against ferrocene) in 0.5 mM dye, 0.1 M TBAPF₆ acetonitrile solutions. These oxidation potentials were used to estimate the position of the highest occupied molecular orbital (HOMO), using a correction factor described in the literature previously [29]. The energy levels of the lowest unoccupied molecular orbital (LUMO) was estimated based on this HOMO position and the optical band gap of the dye, measured by UV–vis analysis of the dye dissolved (0.1 mM) in ethanol.

A Brunauer, Emmett, and Teller (BET) analysis was conducted using nitrogen desorption at 77 K on Micrometrics TRiSTAR 3000 equipment, for a series of powders (collected from prepared films). These powders were also used for xray diffraction (XRD) analysis (Phillips powder diffractometer with a 1° divergence slit, 0.2° receiving slit and carbon monochromator), where they were examined under Cu K α radiation from 25° to 60° at 0.02° increments. SEM images were obtained on a Phillips XL30 FESEM microscope operating at 5 keV.

3. Results and discussion

Nanostructured NiO electrodes were prepared from a commercial NiO powder. The films were produced smooth and crack-free and typically 1.6 μ m thick. These electrodes were exposed to different sintering conditions and subsequently analysed according to their morphologies and photovoltaic properties.

Specific surface areas and pore-size distributions of unsintered as well as sintered films were analysed using the BET method; see table 2 and figure 3. Samples made from unsintered films showed a very high surface area of $122 \text{ m}^2 \text{ g}^{-1}$, confirming the nanoparticulate nature of the NiO starting material used in this study. A 10 min sintering step at 550 °C reduced the specific surface area of the film to less



Figure 2. Pore volume distribution for powders collected from NiO films sintered for various times.

Table 2. BET surface area and porosity data for NiO films sintered for various times.

Sample	Surface area (m ² g ^{-1})	Porosity (%)
Unsintered film 10 min at 550 °C 200 min at 550 °C	$\begin{array}{c} 122.1 \pm 1.2 \\ 56.0 \pm 0.3 \\ 12.4 \pm 0.1 \end{array}$	59.0 51.2 39.9

than half the original value. The pore volume versus pore diameter plot (figure 2) reveals that most of the surface area loss is due to the disappearance of pores with a diameter below 6 nm. Dye-absorption studies, conducted with films sintered for different times, reveal that the drastic reduction in surface area during the first 10 min of sintering also results in an equivalent reduction in the number of adsorbed dye molecules per film volume (see figure 5). This suggests that pores with a diameter less than 6 nm are still accessible to dye adsorption. It remains questionable whether the remaining free volume in such narrow pores, after dye adsorption, is large enough to allow for the unrestricted diffusion of I_3^- ions to the dye (required for fast regeneration of the photoreduced dye) and Iions away from the surface. Barbe et al showed that electrolyte penetration into pores of 4 nm diameter or less in TiO₂ systems is restricted when N719 dye is used [16]. Sintering for 200 min resulted in further significant reduction in surface area as well as the almost complete annihilation of pores with a diameter less than 25 nm.

The total volume of pores with diameters over 6 nm increases slightly after a 10 min sintering step at 550 °C. Sintering for longer times at 550 °C leads to a general reduction of pore volume. Figure 2 includes the pore-size distribution of a NiO film that has been sintered for 200 min at 550 °C. The film shows a greatly reduced surface area and porosity. The remaining pores feature diameters of about 25–50 nm and are therefore easily accessible to the dye, as well as the electrolyte. The surface area analysis suggests that sintering at 550 °C rapidly reduces the photovoltaically active internal surface area, which leads to reduced light harvesting efficiencies.

XRD was carried out (figure 3) on the same samples used in the BET analysis, and showed a dramatic increase in crystal size with sintering, evidenced by peak sharpening. The



Figure 3. XRD spectra of NiO films sintered for different times. The peaks visible at 37.25° and 43.28° correspond to the (111) and (200) crystallographic planes, respectively (other peaks are beyond the scanned range). The XRD results also show the absence of Ni metal (45.502° and 53.045°).

Scherrer equation gives particle sizes increasing from 14 nm (unsintered) to 22 nm (after 10 min at 550 °C) and finally nearly 45 nm for particles sintered for 200 min at 550 °C. This correlates with the decrease in small pores, as smaller crystals and amorphous material are eradicated during extended heat treatment, with diffusion allowing the grain growth, driven by a decrease in surface energy.

Sintered nanostructured NiO electrodes were sensitized with a number of different dyes and assembled to photocathodic devices. The observed effects of sintering conditions on the morphology of NiO nanostructures was expected to have a strong influence on the photovoltaic device performance. Both time and temperature were varied in order to obtain optimal sintering conditions.

De Jesus *et al* have previously shown hydroxy group losses occurring in the production of NiO from precursors at high temperatures [30]. This temperature range can be seen to correlate with changes in photovoltaic results (figure 4), as well as our thermal gravimetric analysis (TGA) results (provided in the supplementary information (available at stacks.iop.org/Nano/19/295304)).

Sintering at 550 °C was shown to result in a reduction of internal surface area. This is accompanied by a decrease in dye adsorption and hence overall light harvesting efficiency of the device. Figure 5 plots the photocurrent of DSSCs made from sensitized NiO films against the sintering time (temperature 550 °C) and relates this to the accompanied reduction in dye adsorption (given by absorption characteristics) for the sensitized film. A logarithmic correlation between the dye adsorption and short-circuit current for films sintered for 5-200 min can be observed. While unsintered films feature more than twice the dye absorption of any sintered film studied here, their photocurrents are comparable to those of films sintered for 15-20 min. It can be postulated that this discrepancy is due to electron injection or charge transport issues rather than light harvesting. Several factors affect the magnitude of photocurrent in DSSCs: (1) the light harvesting efficiency, (2) the charge injection efficiency, and (3) the charge collection



Figure 4. Photovoltaic performance of coumarin 343 sensitized NiO photocathodes under simulated AM1.5 light (1000 W m⁻²) as a function of sintering temperature: (a) short-circuit current density, (b) open-circuit voltage, (c) fill factor, and (d) overall efficiency of cells made using films sintered at various temperatures for 10 min. All devices used an electrolyte of 0.5 M LiI and 0.5 M I₂ in propylene carbonate.

efficiency. Unsintered films feature a reduced photocurrent, indicative of either a reduced charge injection and/or charge collection efficiency that overcompensates their stronger light harvesting efficiency.

Sintering, and the accompanied establishment of interparticle necking, is known to strongly affect the charge collection efficiency in nanostructured TiO₂ films [16]; devices made with unsintered films generally show significantly reduced photocurrents compared to those with sintered films. Reduced charge collection efficiency is therefore a likely reason for the observed reduction in photocurrent despite the higher light harvesting (higher dye loading) of unsintered NiO films. Another reason could be the degree of surface area contained in small pores in unsintered films, as described in figure 2. The additional dye adsorption seen in the unsintered films compared to those sintered for even only a short period of time is almost exclusively due to the much greater number of pores smaller than 6 nm (see figure 2). Insufficient accessibility or mobility of I^-/I_3^- within these small pores would result in slow regeneration of photoreduced dye molecules, and subsequently in increased recombination (electron transfer from the photoreduced dye back to the valence band of the NiO), which also leads to a reduction in charge collection efficiency. At the same time it is remarkable that unsintered films yield photocurrents that are comparable to those of sintered films, showing that NiO electrodes may also be prepared by low-temperature techniques, compatible with plastic substrates.



Figure 5. (Diamonds) normalized absorption of dyed films (at 400 nm) and (squares) short-circuit current density of devices of films sintered for various times.

Figure 4 shows the photovoltaic performance of a series of dye-sensitized DSSCs that feature NiO electrodes sintered at different temperatures. The sintering time was kept constant at 10 min, with the most efficient devices assembled from films sintered at 550 °C. The short-circuit current peaks for films sintered at 500 °C, while the open-circuit voltage more than



Figure 6. (a) Short-circuit current density, (b) open-circuit voltage, (c) fill factor, and (d) overall efficiency of devices made using films sintered for various times at $550 \,^{\circ}$ C. All devices use C343 as a sensitizer and an electrolyte of 0.5 M LiI and 0.5 M I₂ in propylene carbonate.

Table 3. Photovoltaic performance of devices constructed with NiO films sensitized by various dyes. All tested with 0.5 M LiI and 0.05 M I_2 in propylene carbonate as an electrolyte solution. All NiO electrodes were sintered for 20 min at 500 °C.

Dye	$V_{\rm OC}~({\rm mV})$	$I_{\rm SC}~({\rm mA~cm^{-2}})$	Fill factor (%)	Efficiency (%)
Coumarin 343 Eosin B Erythrosin J	98 ± 8 77 ± 8 122 ± 3	$\begin{array}{c} 0.55 \pm 0.14 \\ 0.14 \pm 0.02 \\ 0.36 \pm 0.12 \end{array}$	29 ± 3 29 ± 8 26 ± 6	$\begin{array}{c} 0.016 \pm 0.004 \\ 0.0032 \pm 0.0001 \\ 0.011 \pm 0.001 \end{array}$
N719 Rhodamine 101 Rhodamine 110 Undyed	4 ± 2 69 ± 18 80 ± 5 24 ± 11	$\begin{array}{c} 0.008 \pm 0.004 \\ 0.12 \pm 0.06 \\ 0.15 \pm 0.04 \\ 0.046 \pm 0.05 \end{array}$	0.5 ± 0.8 21 ± 9 25 ± 1 18 ± 4	$\begin{array}{c} 3.6 \times 10^{-7} \pm 6.2 \times 10^{-7} \\ 0.0022 \pm 0.0002 \\ 0.0031 \pm 0.0006 \\ 0.00036 \pm 0.00004 \end{array}$

doubles when the sintering temperature is increased from 500 to 550 °C. This remarkable increase could be due to a change in NiO surface morphology, such as the loss of surface hydroxyl groups, as previously discussed.

The photovoltaic measurements for devices made using films sintered at 550 °C for various times are shown in figure 6. The efficiencies for the devices shown in figure 6(d) are the highest for solar cells assembled from films sintered for 5– 20 min, ranging around 0.03%. The relatively low efficiencies compared to conventional TiO₂ DSSCs are due to reduced photocurrent, photovoltage, and fill factor. As previously mentioned, NiO was used in this study as a model system for p-type DSSCs. The reduced photovoltage can be explained in terms of the small built-in potential between the I^-/I_3^- redox electrolyte and the valence band of the NiO photocathode. This limits the overall efficiencies that can be reached with this system by limiting the maximum photovoltage (around 100 mV compared to around 800 mV for TiO_2 -based DSSCs), as well as the maximum fill factor (around 50%, compared to about 87% TiO_2 -based DSSCs) [31].

Table 3 shows the photovoltaic performance of NiO-based DSSCs, sensitized with a number of different dyes. The highest conversion efficiencies are obtained for coumarin 343, followed by erythrosin J. The short-circuit currents measured for those devices do not follow the light harvesting properties of the sensitizers tested. C343, with an absorption maximum of 442 nm (in ethanol), shows poor light harvesting properties, yet produces the highest short-circuit current. A comparison of photovoltaic performance (table 3) and the molecular orbital energy levels (table 4) of the different dyes does not show any clear trends. Erythrosin J shows the highest open-circuit potential, 122 mV. In each case the HOMO and LUMO of



Figure 7. Energy levels (HOMO and LUMO) of different sensitizers tested on NiO electrodes, using 0.05 M I_2 and 0.5 M LiI in propylene carbonate.

(This figure is in colour only in the electronic version)

Table 4. Photovoltaic data for photocathodic devices made with electrolytes containing different I_2 concentrations (0.5 M LiI was used throughout). Films were dyed with C343 (adsorbed from 0.1 mM solution in ethanol). NiO electrodes were sintered for 20 min at 500 °C.

<i>I</i> ₂ (M)	Measured $V_{\rm OC}$ (mV)	$I_{\rm SC}$ (mA cm ⁻²)	Fill factor (%)	Efficiency (%)
0.05	98 ± 8	0.55 ± 0.14	29 ± 3	$\begin{array}{c} 0.016 \pm 0.004 \\ 0.025 \pm 0.006 \\ 0.024 \pm 0.003 \end{array}$
0.5	65 ± 10	1.15 ± 0.35	32 ± 6	
2	37 ± 2.4	2.13 ± 0.2	28 ± 1.4	

the dye should offer sufficiently large driving forces when compared to the redox couple and the valence band for the forward reactions to occur (figure 7).

Surprisingly, the ruthenium sensitizer N719, one of the best light harvesting dyes for conventional TiO₂ DSSCs, acts as a *desensitizer* for NiO photocathodes. While non-sensitized NiO electrodes produce a photocurrent of 46 μ A cm⁻², NiO DSSCs sensitized with N719 show photocurrents of only 8 μ A cm⁻². The open-circuit voltage is similarly affected. These desensitized electron injection into the conduction band of NiO or (2) dye-catalysed interfacial charge recombination of holes located in the NiO valence band and iodide present in the electrolyte.

Mechanism (1) can be clearly ruled out on the basis that N719 has one of the least negative LUMO levels of all the

dyes tested (-3.84 eV AVS). This is well below the actual conduction band edge of NiO of -1.4 V [12]. The upper valence band edge of NiO also lies $\sim 500 \text{ mV}$ above the HOMO level of N719 [32].

N719 has, however, been reported to catalyse the oxidation of iodide, through the formation of a stable dye-iodide complex [33]. The dye could thereby act as a catalyst for interfacial charge recombination, where the photocurrent gain due to the sensitizing activity of N719 is overcompensated by the enhancement of charge recombination induced by its presence at the interface. Some experimental support for this mechanism is gained from the comparison of dark-current voltage characteristics that clearly indicate a change in dark current when NiO electrodes are sensitized with N719 (see the supplementary information (available at stacks.iop.org/Nano/19/295304)). The dark and light currents for undyed films, and those sensitized with coumarin 343, show a notably lower series resistance than those using N719. This effect may be explained by the surface blocking effect of N719, as noted by Ito et al [34]. They observed that N719 was responsible for a reduction in charge recombination across the fluorine doped tin oxide coated glass (FTO)-electrolyte interface. The absence of this effect with organic dyes (such as coumarin 343) has been noted by Burke et al [35].

The series resistance increases again as light in shone onto the cell. This may be caused by photo de-doping due to N719 injection of electrons into the NiO (possibly into surface states, or the valence band). There has also recently been work carried out that calculated the location of electron density in the LUMO of N719, showing a substantial shift towards and even into the semiconductor surface [36].

Figure 7 provides data of the HOMO and LUMO levels calculated by the aforementioned method. These correlate well with literature values [6, 12, 32], and show each dye to be suitable for sensitization of NiO in devices where iodide–triiodide is used as a redox couple. In a situation where the dye's HOMO is situated between the energy level of the electrolyte and the upper valence band edge of NiO, hole injection from the excited state of the dye to the valence band of NiO is no longer possible. In this case hole transfer from the semiconductor to the dye becomes energetically favoured in a situation that would result in strong recombination currents. Based on energy band positions reported for NiO in earlier publications [6], this mechanism seems implausible for any of the dyes employed here, including N719.

Table 4 shows the photovoltaic performance of a series of coumarin 343 sensitized NiO solar cells (films sintered for 20 min at 500 °C) assembled with electrolytes containing different iodine concentrations. The lithium iodide concentration was kept constant at 0.5 M, while the iodine concentration was varied from 0.05 to 2.0 M. The open-circuit voltage was found to decrease with increasing iodine concentrations, while short-circuit currents increased dramatically. The highest efficiency was recorded for devices assembled with a 0.5 M iodine electrolyte. When a 2 M iodine electrolyte was used, short-circuit currents of 2.13 mA cm⁻² were measured. This is the highest value reported so far for dye-sensitized NiO solar cells. Further investigations are currently underway to better understand the relationship between the concentrations of components in the electrolyte and the final device performance.

The decreased open-circuit voltage can partially be rationalized in terms of a Nernstian shift in the redox potential of the I^-/I_3^- couple that leads to a reduced built-in potential of the solar cell. The increase in short-circuit current can be explained in terms of an accelerated dye regeneration in the presence of higher concentrations of triiodide ions. However, an alternative charge separation mechanism that involves electron transfer from the excited dye to the triiodide, followed by dye regeneration through electron transfer from the NiO valence band to the dye, cannot be ruled out [12].

It has also been noted that with increased iodine concentrations the shape of the incident photon to charge carrier efficiency (IPCE) response (not shown here) changes. This may suggest sensitization occurring from the electrolyte, which has recently been reported by Zhu *et al* [9].

Coumarin 343 has also been reported as an efficient sensitizer for TiO₂ photoanodes [37]. The highest short-circuit current value reported for the TiO₂-based DSSC system so far is 4.1 mA cm⁻² [37]. Although this is dramatically lower than currents obtained for other sensitizers on TiO₂, it is not unexpected given the spectral absorbance of the dye. It can be calculated that, at a quantum efficiency of 100%, roughly 5 mA cm⁻² can be obtained from a C343-sensitized system irradiated with AM1.5 (100 mW cm⁻²). Current matching

of photoanodes and photocathodes is an important requisite for the construction of efficient tandem solar cells. In this respect it is quite remarkable that the difference of photoanodic and photocathodic current densities can be reduced to less than a factor of two for the given model system. This should be encouraging for the exploration of more suitable p-type semiconductors, sensitizers, and electrolyte systems towards the realization of dye-sensitized photocathodes for their integration into highly efficient tandem devices.

Several aspects of this model system will impede its future use as an efficient photocathode in tandem dyesensitized solar cells in combination with TiO₂ photanodes. First of all it is based on a coumarin dye with limited light harvesting properties ($\lambda_{max} = 442$ nm in ethanol), compared to conventional ruthenium sensitizers. Secondly, the built-in potential between DSSC photoanodes based on TiO₂ and photocathodes based on NiO is only marginally higher than the open-circuit potential of conventional TiO₂ based DSSCs (using the iodide–triiodide redox couple). Nevertheless, this work shows that there should be no fundamental limitations for the development of novel, efficient dye-sensitized photocathodic systems.

4. Conclusion

In this work we have presented a novel preparation method to fabricate nanostructured NiO electrodes based on a preformed NiO nanopowder. Critical properties such as pore-size distribution, crystallinity, and internal surface area of the resulting films were controlled through the sintering process and optimized for their application as dyesensitized photocathodes. The film preparation conditions were found to strongly influence the nanostructure and photovoltaic performance of dye-sensitized nanostructured NiO photocathodes. Under optimized conditions we found that coumarin 343 is an efficient sensitizer for NiO, generating photocathodic currents of up to 2.13 mA cm⁻² under simulated sunlight conditions. This is more than half the photocurrent that has been obtained with the same sensitizer for conventional dye-sensitized TiO₂ photoanodes, suggesting that there are no fundamental limitations to achieving high photon to electron conversion efficiencies with dye-sensitized NiO (or other p-type material) photocathodic solar cells. Other sensitizers with superior light harvesting properties proved less efficient for the sensitization of photocathodic currents in NiO. The standard sensitizer for TiO_2 photoanodes, N719, even exhibited remarkably strong desensitizing properties when adsorbed onto NiO photocathodes.

Further advances in the area of dye-sensitized tandem solar cells will require the identification of nanostructured p-type semiconductor materials with optimized band positions for their use in conjunction with dye-sensitized TiO_2 photoanodes, as well as novel hole injecting sensitizers that allow the realization of tandem solar cells with increased spectral sensitivities, compared to conventional TiO_2 dye-sensitized solar cells.

Acknowledgments

The authors would like to thank the ARC Centre of Excellence for Electromaterials Science (ACES) and the Victorian Consortium for Organic Solar Cells (ViCOSC) for financial support. They would also like to thank the ARC for supporting Dr Udo Bach with an ARF as well as Monash University for providing support through an MRF programme. Further, they wish to acknowledge the assistance of Mr Fuzhi Huang (University of Melbourne) and Dr Rachel Caruso (University of Melbourne) for assistance with the BET measurements, Mr Rod Mackie (Monash University) for assistance with the XRD measurements, Mr John Ward (CSIRO) and Mr Mark Greaves (CSIRO) for assistance with SEM, and Dr Scott Watkins (CSIRO) and Dr Chris Harris (CSIRO) for assistance with the profilometry measurements.

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