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Enhanced open-circuit voltage of p-type DSC with highly crystalline NiO nanoparticles[†]

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Highly crystalline NiO nanoparticles synthesized through a facile thermolysis route were used as photocathode materials in p-type dye-sensitized solar cells resulting in open-circuit voltages exceeding 300 mV with an iodide/triiodide mediator.

A number of tandem configurations for dye-sensitized solar cells (DSCs) have recently been described with the aim to boost the efficiencies of DSCs beyond their current limits. One of these approaches involves the combination of a dyesensitized photoanode (n-DSC) and photocathode (p-DSC) in a simple two-electrode sandwich configuration (pn-DSC). This concept has first been described by Lindquist and co-workers and represents the only two-terminal tandem DSC configuration known to date.¹ Here, a conventional photoanode, typically consisting of a dye-sensitized mesoporous n-type TiO₂ electrode is combined with a dye-sensitized mesoporous p-type semiconductor electrode, composed of e.g., p-type NiO. Photoexcitation of the sensitizer on the p-DSC results in hole-injection into the valence band of the p-type semiconductor. The photoreduced dye is then regenerated by a conventional iodide/triiodide electrolyte. The series connection of both dye-sensitized junctions implies that the photocurrent and energy conversion efficiency of the tandem device will be limited by the weaker of the two photoelectrodes. Until recently p-DSCs produced very limited photocurrent densities and open-circuit voltages of typically <1 mA cm⁻² and <150 mV.²⁻⁷ Consequently, the poor photovoltaic performances generally observed for p-DSCs represented a major impediment for the realization of highly efficient pn-DSCs.

Recently the development of novel sensitizers for mesoporous p-type NiO electrodes has led to strong improvements in the performance of dye-sensitized photocathodes.^{8–13} In a recent paper we could show that absorbed photon to charge carrier conversion efficiencies of up to 96% can be observed in p-DSCs based on a novel generation of donor–acceptor dyes.¹²

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Open-circuit voltages of up to 218 mV under full sun illumination were recorded, in conjunction with conventional iodide/ triiodide based electrolytes.

The maximum photovoltage produced by the photocathode strongly influences the theoretical efficiency gain that can be afforded by a tandem configuration. A straightforward strategy towards the development of more efficient photocathodes involves the replacement of NiO with alternative p-type semiconductor materials with lower conduction band edges.¹⁴ However, the choice of potential wide-bandgap p-type materials with suitable band edge positions is very limited.

While the open-circuit potential is ultimately dependent on the valence band edge position, the quality of the NiO used to produce the mesoporous p-type films also strongly affects the performance of p-DSCs. Here we show that the maximum open-circuit potential of NiO-based p-DSCs can be significantly improved to beyond 300 mV when highly crystalline NiO materials synthesized *via* a novel synthetic route are used for the construction of p-DSCs. This provides a new upper limit for the theoretical efficiency limitation of NiO-based tandem pn-DSCs. Especially when combined with a low-bandgap NIR p-DSC sensitizers, this $V_{\rm oc}$ improvement will be vital for the development of highly efficient NiO p-DSCs based on low-bandgap NIR sensitizers.

Highly crystalline NiO nanoparticles were synthesized through a high temperature thermolysis. Typically, nickel oxalate and sodium chloride were ground into fine powders before thermolysis at 950 °C for 2 hours. The thermolysis in molten salt media provides a facile and efficient synthesis technique to prepare nickel oxide nanoparticles in a large quantity. X-Ray diffraction pattern (XRD) in Fig. 1(a) reveals the overall crystal structure and phase purity of the products. All sharp peaks match well with cubic rock salt structured NiO and indicate high crystallinity of the particles.

The nickel oxide nanoparticles were analyzed by a fieldemission scanning electron microscopy (FESEM). In Fig. 1(b), the as-synthesized NiO nanoparticles exhibit regular octahedral shape with particle size range of 20–200 nm. The inset selected area electron diffraction (SAED) rings well accord with XRD patterns on the cubic NiO. An individual octahedral NiO particle with smooth surfaces and straight arris is clearly identified in Fig. 1(c), similar to the model cubic structure with eight enclosed {111} facets, as shown in Fig. 1(d).

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Fig. 1 (a) XRD pattern and (b) SEM observation of NiO nanoparticles with SAED pattern (inset). (c) SEM image of a single NiO particle and (d) schematic illustration of an octahedral NiO crystal. (e) HRTEM image of NiO particle and corresponding SAED spot. (f) SEM images of cross sectional view of NiO film.

In Fig. 1(e), a high resolution transmission electron microscopy (HRTEM) image reveals a lattice spacing of 0.21 nm which can be indexed to the lattice fringe of d_{200} of cubic NiO. Furthermore, the HRTEM image clearly identified lattice fringes and smooth surface (without any amorphous shell). The clarity of diffraction spots in the inset and the corresponding SAED pattern confirm the high crystallinity and defect free native of the as-synthesized NiO nanoparticle.

Nickel(II) oxide is generally known as a non-stoichiometric compound (Ni_{1-x}O with 0.003 < x < 0.17) with color varying from gray to black,^{15,16} however, in our experiments, the octahedral NiO nanoparticles synthesized *via* thermolysis are light green in color, which suggests that the as-synthesized NiO is close to 1 : 1 stoichiometry with less nickel vacancies and holes. Energy-dispersive X-ray spectroscopy (EDS) confirmed that the NiO sample contains nickel and oxygen with a molecular ratio of 1 : 1, with no trace of sodium or chlorine (Fig. S1, ESI[†]).

It has been reported that nanoparticles with less surface defects can reduce the probability of recombination between injected electrons (or holes) and the electrolytes, improving DSC performance.¹⁷ The high crystalline stoichiometrical NiO nanoparticles from the above preparation might be able to reduce the recombination due to its less surface defects.

A finely dispersed colloidal solution was generated by ball-milling the NiO nanoparticles. The paste for screen printing was made by evaporating a fine mixture of the NiO colloidal solution, ethyl cellulose and terpinol. The films were sintered at 500 °C for 1 h before soaking them in the dye solution. These films were also examined by FESEM. Fig. 1(f) is a cross-sectional view of the NiO film. The compact underlayer can be clearly identified being approximately 100 nm thickness.

The chemical structure of dye 3 is shown in Fig. 2(a). Fig. 2(b) shows the photocurrent-density *vs.* voltage behavior of the NiO DSCs without and with compact underlayer measured at 100 mW m⁻² under AM 1.5 irradiation.



Fig. 2 (a) Chemical structure of dye 3 and (b) photocurrent density–voltage curve of dye-sensitized NiO photocathodes with and without underlayer.

The p-type DSC with highly crystalline NiO nanoparticles and no adhesion layer exhibited a markedly enhanced open-circuit voltage ($V_{\rm oc}$) of 350 mV, using I^-/I_3^- which is comparable with the recently reported NiO DSC using Co^{II}/Co^{III}.¹¹ The current density ($J_{\rm sc}$) value is however quite low, only 0.04 mA cm⁻². Since the NiO nanoparticles were obtained at 950 °C, these particles have considerable stability at lower temperature such as the sintering temperature of 500 °C. Contacts between these highly crystalline NiO nanoparticles and between the NiO film and FTO glass formed at 500 °C are therefore very weak.

To improve contact, the FTO glass was pretreated by dip-coating in a nickel acetate ethanolic solution (0.05 M) 5 times before screen printing NiO paste. During the sintering process, the underlayer of nickel acetate thermally decomposes by the following reaction:

$$Ni(CH_3COO)_2 + 4O_2 \rightarrow NiO + 4CO_2 + 3H_2O$$

This will form a compact NiO blocking layer between NiO film and FTO glass. The improvement was confirmed by enhanced p-type NiO DSC performance.

With a compact underlayer, the NiO DSC shows a dramatic increase on the current density (J_{sc}) to 1.32 mA cm⁻² with a slight drop in the open-circuit voltage (V_{oc}) to 305 mV. As a result, the photovoltaic-conversion efficiency (η) is significantly increased to 0.14% under full sunlight illumination. Incident photon-to-current efficiency (IPCE) spectra of the NiO DSC are shown in Fig. S3 (ESI[†]). Photovoltaic performance characteristics of the p-type NiO DSCs with and without underlayer are listed in Table S1 (ESI[†]).

It could be conjectured that the sensitized underlayer could add substantially to the photocurrent (from 0.4 mA cm⁻² to 1.26 mA cm^{-2}) due to additional surface area for dye loading. UV-vis absorption spectroscopy was used to determine the absorption difference of dyed NiO films between with and without underlayer (Fig. S4, ESI†). The small variation in absorption suggests that the underlayer has negligible effect on dye loading. The dramatic increase of current density is more likely due to the improved contact between the NiO film and FTO glass. This was also confirmed by the following electrochemical impedance spectroscopy measurements.

Compared with commercial NiO nanoparticles, the highly crystalline octahedral NiO nanoparticles exhibited a significantly increased open-circuit voltage (V_{oc}) by about 85 mV.¹² The high voltages presented by the octahedral NiO nanoparticles are probably due to the decreased recombination paths owing to the low surface defect concentration of the high crystalline particles. The current density (J_{sc}) is majorly limited by lower surface area of the NiO nanoparticle (10.288 m² g⁻¹) due to broad size range from 20 to 200 nm.

In order to investigate charge transport and recombination in the p-type NiO DSCs, electrochemical impedance spectroscopy (EIS) measurements were carried out as a function of frequency measured at 1 sun with an applied potential bias of V_{oc} (Fig. S5, ESI†). From the Bode phase plots in Fig. S5(a), the electron lifetime with the NiO DSC using underlayer is 20 ms, a fourfold increase compared to the non-underlayer NiO DSC (5 ms). In Fig. S5(b) and (c), the central arcs are attributed to the impedance based on charge-transfer processes occurring at the dye-sensitized NiO/dye/redox (I⁻/I₃⁻) interface. The radius of the intermediate-frequency semicircle in the Nyquist plot decreased with using underlayer, which indicates the improved electron (hole) generation and transport. This result is also in good agreement with the trend of the overall cell efficiency.

The stability of DSCs performance, including photochemical, chemical, and physical stability of the DSCs, is another important issue. Aging tests were performed to scrutinize the photo stability of the p-type photocathode system employing the highly crystalline NiO nanoparticles along with dye 3. Fig. 3 presents the photo-voltaic data of the p-type DSC during aging at roomtemperature in the dark. The performance was remarkably stable over this period, with only a 0.09 mA cm⁻² decay in J_{sc} , which was compensated by an increase of 15 mV in V_{oc} (320 mV).



Fig. 3 Variations of V_{oc} , J_{sc} and efficiency (η) as a function of the life-time of the NiO photocathode.

Hence, the initial photovoltaic efficiency was retained even after a continuous 127 days aging test under above conditions.

A maximum open-circuit voltage (V_{oc}) of 320 mV and a solar to electric conversion efficiency (η) of 0.14% had been found during the stability testing. The reason of the increase on the open-circuit photovoltage is probably due to the slow diffusion of the electrolyte into inner pores of the NiO films and the accompanied rearrangement of the adsorbed dye.

In summary, we demonstrated a facile thermolysis process for producing large quantities of octahedral NiO nanoparticles with high crystallinity. The highly crystalline NiO yielded an open-circuit photovoltage (V_{oc}) of 350 mV in a NiO, $I^-/I_3^$ p-DSC system. A compact NiO underlayer was formed and employed to improve charge transfer in p-type NiO DSCs. A solar to electric conversion efficiency (η) of 0.14% was achieved. Further size selection of NiO nanoparticles is likely to allow device improvement. Additionally, the p-type NiO based devices have also shown excellent stability during a long-term testing.

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