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Engineering processes at the interface of p-semiconductor for enhancing the open circuit voltage in p-type dye-sensitized solar cells

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Abstract

To prevent the interfacial charge recombination between injected holes in the valence band and the redox mediator in the electrolyte in p-type dye sensitized solar cells (p-DSSC) the passivation of the recombination sites by organic insulator chenodeoxycholic acid (CDCA) layer is critically investigated in this study. Rather than classical coating of the semiconductor's surface by simultaneous co-adsorption of CDCA during the dyeing step, two other methods were investigated. The first consists in dissolving CDCA in the electrolyte, while the second consists in spin coating an ethanol solution of CDCA onto the already dyed photocathode. In

this study different sensitizers, electrolytes and p-SCs, (NiO, $CuGaO_2$) were explored. Analysis of the current/voltage curves and electrochemical impedance spectroscopy provides evidence that the role of the CDCA layer is to create a physical barrier to prevent the approach of the redox mediator from the NiO surface and consequently raise the Voc. The important finding of this study is the demonstration that the Voc in p-DSSC is heavily limited by interfacial charge recombination and that higher Voc values much above 100 mV and as high as 500 mV can be attained with conventional materials (NiO) if this deleterious side reaction can be suppressed or diminished.

Introduction

During the past decade, p-type dye-sensitized solar cells (p-DSSCs) have been steadily attracting scientific interest owing to their great potential for photovoltaic and solar fuel production.[1] In these devices the power conversion efficiency (PCE) is today much lower (2.5%)[2] than that of conventional Grätzel cells (13-14%).[3] The critical factors limiting PCE in the p-DSSCs are now clearly identified.[4] Two of the most important and challenging factors to overcome is the charge recombination reactions and the shallow valence band potential of NiO, which both restrict the maximum achievable open circuit voltage (Voc). Formally, the maximum Voc is governed by the difference between the electrolyte redox potential and the quasi-Fermi potential of the p-type semiconductor (p-SC). However, Voc is also a kinetic parameter highly dependent of the charge recombination (CR) processes because it is controlled by the concentration of the injected charges in the semiconductor.[5] Accordingly, there are basically three strategies for increasing the Voc in p-DSSCs. The first one involves the replacement of the classical iodide/triiodide redox couple by another redox mediator exhibiting a more cathodic reduction potential.[2, 6] The second consists in the replacement of the commonly used NiO p-SC, by another one with more positive VB potential.[7] It has previously

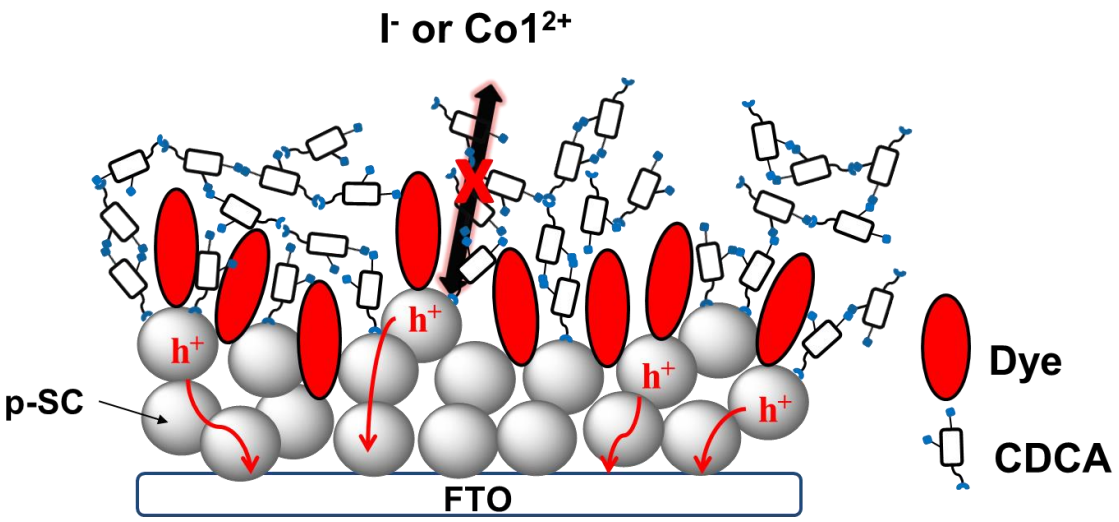
been shown that both approaches are successful. For examples, delafossite materials[8] show higher Voc than NiO-based DSSCs and an impressive Voc of 700 mV was recently achieved using a cobalt or iron complexes as redox mediators having a quite cathodic reduction potential.[2, 6] However, the new p-SCs have hardly outcompeted NiO-based DSSCs[9] and the use of new redox mediators with a more cathodic redox potential will not open the door to an increase of the built-in voltage in tandem dye sensitized solar cells. The third strategy consists in reducing the CR losses as the concentration of the injected charges impacts the Fermi level of the SC. Studies employing blocking layer to improve the Voc in p-DSSCs have been very limited to date.[10] In conventional TiO_2 based DSSCs, chenodeoxycholic acid (CDCA) is often used as a co-adsorbent to break up the π–π aggregates between organic sensitizers and to create a physical barrier on the SC to reduce the recombination between the electrons in TiO_2 and triiodide.[11] It was previously suggested that NiO surface states mediate charge recombination with the electrolyte in much higher extent than n-SCs do and are therefore responsible for major losses by interfacial charge recombination.[4c] Accordingly, passivating them should be a promising strategy to improve the photovoltage in p-DSSCs. The co-adsorption of a fatty carboxylic acid along the sensitizer during the chemisorption step is the classical strategy to achieve such an objective. However, the co-adsorbent is then in competition with the sensitizer to cover the SC surface and when a large ratio of co-adsorbent/sensitizer is used, the surface coverage is dominated by the co-adsorbent. Conversely, when the concentration of the co-adsorbent relative to that of the sensitizer is diminished, the passivation of the surface of the SC is less efficient. Consequently, this approach has not solved in a significant extent the interfacial charge recombination in p-DSSCs. For example, when the sensitizer is chemisorbed on NiO in presence of CDCA, the Voc has remained in the usual range (around 100 mV for iodide/triiodide electrolyte and around 350 mV with polypyridine cobalt complexes).[12] The deposition of an insulating overlayer of Al_2O_3 on NiO proved to be more effective, but the enhancement was limited to tenths of mV.[10] Our strategy to diminish the interfacial charge

recombination with the holes in the valence band is based on the fabrication of an insulating organic layer to make a barrier preventing the approach of the redox mediator to the SC surface. When CDCA and dye molecules are introduced at the same time in the dyeing bath, both compete for free space at the semi-conductor's surface.[13] However, performing the dye chemisorption first and then introducing CDCA, would allow to conveniently passivate "left over sites" during dye chemisorption without threatening the light harvesting efficiency. This could be achieved by dissolving CDCA in the electrolyte bathing the photo-electrode. Such strategy was previously applied with success,[1a, 14] but was, however, seldom employed afterwards despite its advantages. It was inferred that efficient complementary protection of defect sites on TiO_2 photo-anodes by bulky CDCA molecules could occur through the setting up of a dynamic equilibrium between surface adsorbed and solution phase CDCA molecules.[1a, 14] Large improvements in Voc and/or Jsc were observed when rather bulky molecules (cobalt[14] or iron[1a] complexes) were used as redox mediators. To the best of our knowledge, there is only one report of such approach with p-DSSC. Bach and co-workers observed much improved photovoltaic efficiencies for a p-DSSC based on efficient PMI-6T-TPA dye[15] and trisacetylacetonato iron as a redox mediator, when 10 mM CDCA was present in the electrolyte.[2]

Notwithstanding the meticulous analysis of Salvatori and co-workers on n-DSSC[14] a detailed analysis of the impact of CDCA within the electrolyte for p-DSSC is missing. More importantly, some parameters require deeper exploration. Indeed, little is known about the effect of CDCA concentration in the electrolyte, the influence of the nature of the redox mediator, of the dye and of the p type semi-conductor itself. We propose in this work to explore the scope and the versatility of this strategy by analyzing the performances of p-DSSCs using two different dyes, **P1** and **DPP-NDI**, two different electrolytes (iodide/triiodide and Co1) and two different p-SCs, namely NiO and $CuGaO_2$ doped with Mg ($CuGaO_2$/Mg) (Figure 1). In addition, we have explored another technique to depose CDCA on the photocathode consisting

of a spin coating solution of the latter. This strategy gives good photovoltaic performances and appears particularly well-suited when CDCA is poorly, let alone insoluble, in the solvent of the electrolyte.

The two important findings of this study are firstly the demonstration that the Voc in NiO and $CuGaO_2$ based p-DSSC is heavily limited by interfacial charge recombination with the electrolyte and the p-SC surface and secondly that higher Voc values much above 100 mV such as 630 mV can be attained in p-DSSC if this deleterious side reaction can be suppressed or diminished. This crucial parameter is extremely important, not only for p-DSSC but also for the photoproduction of hydrogen where the role of the interface SC/electrolyte is often underestimated.[1b, 16]



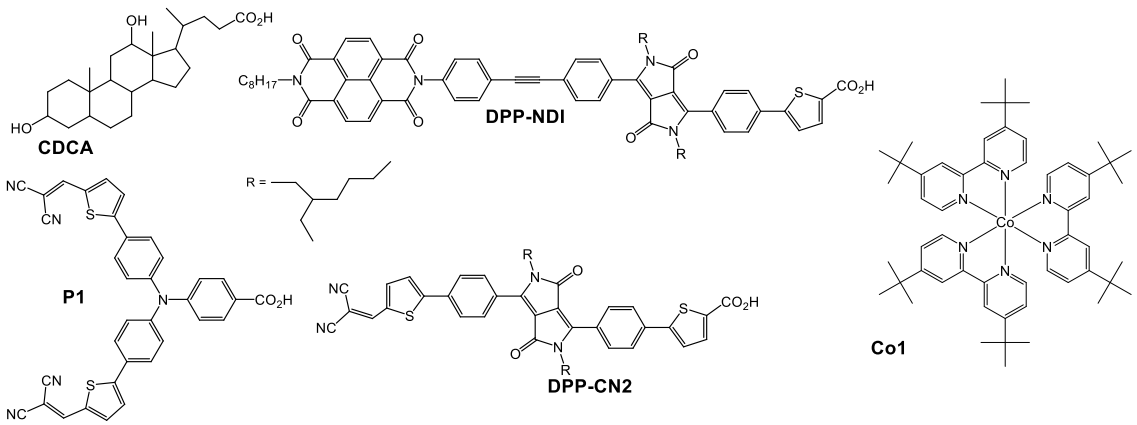


Figure 1. Schematic illustration of a portion of the p-DSSC and the structures of the dyes **P1** and **DPP-NDI** and those of the redox mediator **Co1** used in this study.

Results

First, two different photosensitizers were used in this work: the classical push pull dye **P1**, which is among the most studied and best performing sensitizer in p-DSSC,[17] and the dyad **DPP-NDI**, displaying a long-lived interfacial charge separation state enabling to use a slow electron redox shuttle (Figure 1).[12, 18] The paper is organized as follow: first, we have investigated the effects of the introduction of CDCA into iodide based electrolyte with the dye **P1** and then with **DPP-NDI** sensitizer on NiO based DSSCs. The photovoltaic results are rationalized by electrochemical impedance spectroscopy measurements. Second, we present the results with the cobalt based electrolyte and the **DPP-NDI** dye along with the electrochemical impedance spectroscopy study of the NiO based solar cells. In this case, because CDCA is only slightly soluble in propylene carbonate, it was deposited on the photocathode by the spin coating from an ethanol solution. Third, we have elucidated by atomic force microscopy (AFM) the organization of the spin coated CDCA layer on NiO electrode. Fourth, the valence band potential of NiO in different environments was rationalized with impedance electrochemical

and Kelvin probe measurements. Fifth, the impact of spin coated layer of CDCA was studied on $CuGaO_2$/Mg based p-DSSC with the cobalt electrolyte and the **DPP-NDI** dye. Finally, aging tests of the cells were conducted to compare the deposition method of CDCA (in the electrolyte or by spin coating) on the temporal evolution of the photovoltaic performances.

1) Iodine based electrolytes

Previous works have been done to optimize the electrolytes compositions, which strongly depend on the structure of the dyes. For **P1** and **DPP-NDI** the optimal iodine based electrolyte compositions are respectively 0.1 M I_2 and 1 M LiI in acetonitrile (electrolyte "A")[17a, 17b] and 0.03 M I_2, 0.1M guanidinium thiocyanate, 0.6 M 1,2-dimethyl-3-butylimidazolium iodide and 0.5 M 4-*tert*-butylpyridine in acetonitrile (electrolyte "B").[12] Importantly, a nominal concentration of 10 mM CDCA has been used in previous works.[1a, 2, 14] Thus, when CDCA is dissolved in the electrolyte, we have first focused on the influence of CDCA concentration on the overall PCE of p-DSSC. Various quantities of CDCA were added to these conventional electrolytes. CDCA concentrations of 10, 25, 50 and 100 mM could be solubilized in iodine based electrolytes A and B. Electrolytes became significantly turbid with higher concentrations of CDCA, and were not considered as viable for the study. Importantly, the well-known poor solubility of CDCA in acetonitrile was overcome in presence of all the additives present in the electrolytes.

For **P1** based p-DSSC, a very fast dye desorption took place after infiltration of CDCA containing electrolyte A within the cell cavity, even at the lowest CDCA concentration. This was expectable taking into account that **P1** is significantly soluble in acetonitrile. If the concentration of CDCA equals 10 mM, and assuming the p-DSSC cavity contains 2 µL of electrolyte, the number of CDCA molecules are still one order of magnitude more numerous than those of **P1** adsorbed molecules. In presence of a competitor adsorbent, the thermodynamic

equilibrium driving the association of **P1** with NiO is strongly displaced in favor of **P1**'s solubilization, assuming the association constant is the same for both species (a safe assumption since both **P1** and **DPP-NDI** bear only one anchor of the same nature).[19] In conclusion, these experiments showed that if the dye is soluble in the electrolyte (such as **P1** dye) therefore solubilizing CDCA in the electrolyte is highly compromised owing to rapid dye leaching by competitive adsorption by CDCA on NiO surface.

DPP-NDI, on the other hand, is insoluble in acetonitrile; therefore photocathodes kept their light harvesting efficiency in presence of CDCA regardless the concentration of the latter. The photovoltaic performances obtained for the different CDCA concentrations are gathered in Table 1. All results correspond to the average of at least two different cells, where the figures of merit varied less than 5%. Chosen current/voltage curves under AM 1.5 irradiation can be consulted in the supplementary information materials (Figure S1).

Table 1. Photovoltaic parameters of the cells recorded under AM1.5 simulated irradiation. Conditions: **DPP-NDI** as a photosensitizer, iodine based electrolyte (B) with increasing concentrations of CDCA, noted $B_{[CDCA]\,/\,mM}$.

Electrolyte	B_0	B_{10}	B_{25}	B_{50}	B_{100}
Jsc	2.55	2.68	2.48	2.41	2.31
Voc	163	175	189	198	207
ff	29.1	30.6	29.7	28.4	27.8
PCE	0.12	0.14	0.14	0.14	0.13

These experiments show that Jsc is only marginally affected by the presence of CDCA in the electrolyte B. A slight decrease of the latter is, however, monitored when the concentration of CDCA is rather high (100 mM). This is likely due to the significant increase of the electrolyte

viscosity when large amounts of CDCA are added to the latter. This is incidentally corroborated by the concomitant subtle decrease of the fill factor. Incident Photon to Current Efficiency (IPCE) measurements (Figure S2) were carried out on p-DSSCs elaborated with and without CDCA in the electrolyte. They are all similar in agreement with the small variations of Jsc (Table 1).

Basically, IPCE is the product of the charge collection efficiency (η_{coll}), the hole injection efficiency (η_{inj}) and the light harvesting efficiency (η_{LHE}) according to the equation:

$$IPCE = \eta_{coll} \times \eta_{inj} \times \eta_{LHE}$$

As can be observed on Figure S2, the photoaction spectra for both conditions are virtually identical, proving the presence of CDCA in the electrolyte has little or no influence on η_{coll}, η_{inj}, η_{LHE}. On the other hand, Voc steadily increases with the concentration of CDCA, from 163 mV to more than 200 mV when the concentration reaches 0.1 M, leading to a rise of the photoconversion efficiency (PCE) (Table 1). Such increase of the output potential can be due to two factors. First, a shift of the valence band towards more positive potential could account for the improved Voc. Kelvin probe and Mott Schottky measurements, indeed, have shown that the strong concentration of CDCA induces a little upward movement of the valence band potential by *circa* 100 mV (see below). Analysis of the current/voltage curves recorded in the dark also reveals that, as expected, leakage currents decrease when the concentration of CDCA rises (Figure S3). Therefore, counter-productive charge recombination seems efficiently blocked by the presence of CDCA molecules in the electrolyte, probably chemisorbing on left naked sites after dyeing.

Electrochemical impedance spectroscopy (EIS) is a powerful tool to study the various electron transfers taking place at the vicinity of an interface, considering the latter to be electronically equivalent to a resistance and capacitance wired in parallel. Within this frame, p and n type dye sensitized solar cells are commonly modelled by the so called “transmission line”.[4c, 20] In

particular, one can extract from EIS data the charge transfer resistance at the level of the photo-electrode, namely the "ease" with which charges flow through the interfaces dye|semiconductor|electrolyte: the higher the interfacial charge transfer resistance, the lower the leakage currents. The Nyquist plots recorded in the dark for p-DSSC without (B_0, circles) and with 50 mM CDCA in the electrolyte (B_{50}, squares) are given in Figure 2. In both cases, two semi-circles can be clearly observed: the high frequency one is commonly assigned to the interface electrolyte|counter electrode, while the larger middle frequency one is characteristic of the interface electrolyte|photocathode. One can clearly see on Figure 2 that the latter loop is larger for the B_{50} based device, meaning that the B_{50}|photocathode interface is more resistive than the B_0|photocathode interface. After fitting the experimental data, recombination resistance values R_{Rec} = 200.0 and 242 Ω were respectively obtained for B_0 and B_{50} based devices. This was naturally assigned to the efficient passivation of the naked NiO surface by CDCA molecules. Under AM1.5 simulated solar light, the interfacial resistance accordingly decreases because of the activation of two additional recombination channels upon light soaking: first, dye regeneration following hole injection leads to the accumulation of the reduced form of redox mediators, here I^-, which can readily react with holes in the valence band. Second, a charge recombination may occur between photo-reduced dye and holes in the valence band. If the latter is less likely due to the dyad structure of **PMI-NDI**, the former however necessarily takes place and entails the premature annihilation of the charge separated state before charge collection in the external circuit. This translates into a blatant decrease of the interfacial resistance.[4c] The same trend than in the dark is nevertheless monitored with R_{Rec} = 32 Ω and 42 Ω for p-DSSC filled with B_0 or B_{50} respectively.

The monitored increase of the PCE for a DSSC using an iodine based electrolyte contrasts with previous works, where n-DSSC in similar conditions were unaffected by the presence of CDCA.[14] However, charge recombination on TiO_2 electrodes is far less pronounced than on NiO,[4a] the latter having proven to be an efficient catalyst for I^- to I_3^- oxidation. Additionally,

it is worth mentioning that when the dyeing step was traditionally performed in presence of CDCA, no improvement of Jsc nor Voc was monitored, indicating that aggregation of dye molecules on NiO is not a significant problem in this case.

All these results prove that the superficial sites, where charge recombination between the electrolyte and the holes in NiO are favored, are efficiently protected by an additional layer of CDCA when it is present in decent concentration in the electrolyte (c > 25 mM). In addition, the optimal concentration of CDCA in iodine based electrolyte is between 10 and 25 mM with DPP-NDI dye (Table 1).

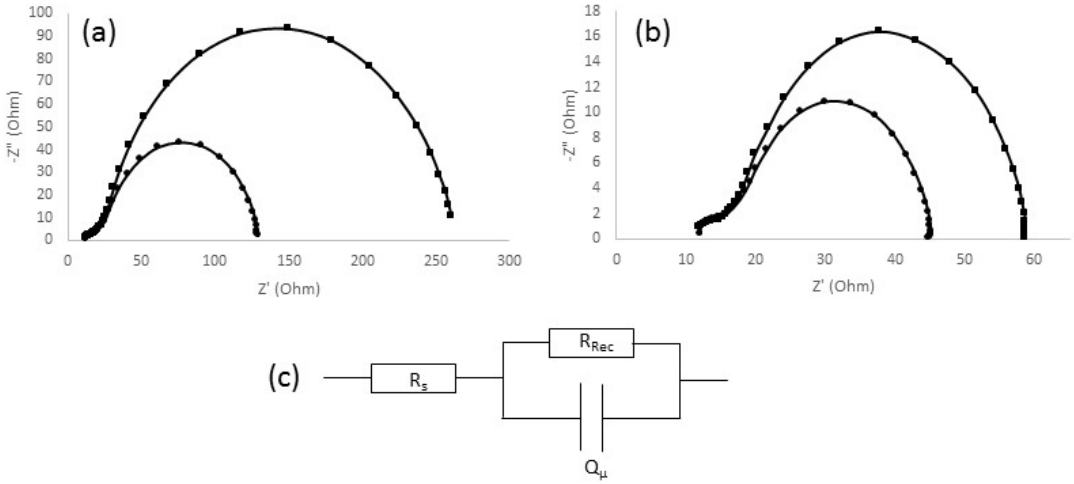


Figure 2. Nyquist plots for p-DSSC based on **DPP-NDI**|NiO photocathodes in the dark (a) and under AM 1.5 simulated solar light (b), for electrolytes containing no CDCA (B_0,dots) and 50 mM CDCA (B_{50},squares) and (c) equivalent circuit used to fit the impedance data.

2) Cobalt based electrolyte

Iodine based electrolytes are known to favor interfacial charge recombination on NiO surface, and the development of alternative redox mediators proved to be a successful option. Among others, the redox couple **Co1**$^{3+}$/**Co1**$^{2+}$ where **Co1** is cobalt tris(4,4'-diterbutyl-2,2'-bipyridine) perchlorate (Figure 1) was successfully used in p-DSSCs as redox mediator in presence of 0.1 M lithium perchlorate in propylene carbonate.[12, 21] Importantly, cobalt formulated electrolytes are compatible with TiO_2 conventional photoanodes,[3a, 22] suggesting their uses into tandem dye sensitized solar cells.[21c] The high steric bulk of the six terbutyl groups and the high to low spin transition taking place during the shift from +III to +II redox states contribute to limit interfacial charge recombination by respectively preventing deleterious interactions with the semi-conducting material and slowing down the kinetics of outer sphere electron transfer.[21a] In return, the use of **Co1** based electrolytes necessitates a long-lived charge separation state (NiO(h^+)|Dye$^-$) in order to allow the sluggish Dye$^-$ oxidation (regeneration step) to occur before the recombination. This is precisely the case with dyad **DPP-NDI**, because the primary photo-induced hole injection is followed by a fast electron transfer from the DPP to NDI moiety, shifting the electron farther away from NiO's surface and slowing down by several orders of magnitude the kinetics of charge recombination (μs time scale).[12, 18] In these conditions, the interfacial charge recombination (i.e. between holes in NiO and the **Co1**$^{2+}$ ions in the electrolyte) is the main deleterious process, dominating the geminate charge recombination (i.e. between holes in NiO and reduced adsorbed dye). We, therefore, endeavored to dissolve CDCA in **Co1** based electrolyte with a view to further limiting the charge recombination processes. CDCA is, however, only very moderately soluble in this medium since only a low concentration of 2.5 mM could be obtained without saturating the electrolyte, and no significant reproducible impact on the performances of the devices could be monitored in the same conditions.

In the light of the above results, the beneficial impact of CDCA on the performances of NiO p-DSSC is, however, unquestionable and highly desirable even with a bulky redox mediator such as **Co1** is used. We, therefore, endeavoured to deposit chenodeoxycholic acid by spin coating

an ethanol solution of the latter on already dyed photocathodes, before assembling them with the counter-electrode and filling the cell with the electrolyte. This method was successfully used to infiltrate hole transporting materials within the porous network of photo-electrodes for the elaboration of solid state devices.[23] Importantly, this method is all the more efficient for thinner electrodes, which is precisely our case (δ = 1.2 µm). Bearing this in mind, we spin coated ethanol solutions of CDCA on NiO|**DPP-NDI** photocathodes, with different concentrations ([CDCA] = 10^{-4}, 10^{-3}, 10^{-2}, $5x10^{-2}$ and 10^{-1} M) and assessed then the performances of the resulting photovoltaic cells. First, we observed that the amount of dyes on NiO surface was negligibly decreased upon this treatment as confirmed by the desorption experiments made on the dyed NiO film (Figure S4). p-DSSC were assembled immediately after treatment and measured under AM1.5 simulated solar light (Table 2). A sample of current/voltage curves is given in Figures S5 and S6 and the photoaction spectra in Figure S7. First of all, the use of **DPP-NDI** with plain **Co1** based electrolyte unsurprisingly affords a much higher Voc (327 mV) than with iodine based electrolytes because of decreased interfacial charge recombination, as previously published.[12, 21c] Spin coating 10^{-4} M or 10^{-3} M CDCA solutions virtually changed nothing concerning the different photovoltaic parameters (Table 2). However, a steady increase of the Voc can be observed when more concentrated CDCA solutions were spin coated on the photocathode. For instance, a more than 100 mV gain in Voc is experienced for 5.10^{-2} M, which compensates a slight but noticeable decrease of the short circuit current density (Table 2). At higher concentration of CDCA, a very high Voc of 543 mV was obtained, but the short circuit current decreases, probably because of the more difficult diffusion of the large cobalt redox mediator across the thick layer of CDCA, thus curbing dye re-oxidation and redox mediator regeneration at the counter electrode. This hypothesis is corroborated by the concomitant decrease of the fill factor and AFM images of the electrodes (see below).

Table 2. Photovoltaic parameters of the p-DSSCs recorded under AM1.5 simulated irradiation using either NiO or $CuGaO_2$/Mg cathode. Conditions: **DPP-NDI** as a photosensitizer, ethanolic solution of CDCA spin coated on the photocathode and cobalt based electrolyte subsequently introduced by vacuum back filling.

p-SC	NiO						$CuGaO_2$/Mg	
$[CDCA]_{spin}$	0	10^{-4}	10^{-3}	10^{-2}	5.10^{-2}	10^{-1}	0	10^{-1}
Jsc	1.46	1.47	1.52	1.48	1.36	1.11	0.82	0.56
Voc	327	348	379	396	438	543	529	630
ff	28.9	28.6	29	27.5	25.4	24.0	37.6	32.7
PCE	0.14	0.15	0.17	0.17	0.15	0.14	0.16	0.12

All in all, a large increase of the Voc is experienced when CDCA is spin coated on NiO photocathodes and this is largely due to a spectacular decrease of the interfacial charge recombination, as evidenced by the strongly decreased dark current (Figure S5) and EIS measurements in the dark, at potentials close to Voc (Table 3). In Figure 3 are given the Nyquist plots of p-DSSC with and without treatment by spin coated CDCA in the dark. In each case, treated cells display a much larger R_{CT} than untreated cells, proving that the large steric bulk of **Co1** is apparently not sufficient to efficiently prevent charge recombination with holes in NiO's valence band. Indeed, R_{Rec} steadily increases from 1465 to 7640 Ω when the concentration of CDCA in the spin coating solutions increases (Table 3).

The same trend was observed under light soaking, revealing the efficiency of the CDCA spin coating treatment to drastically curb the extent of charge recombination between the redox mediator and the photoelectrode. Interestingly, devices treated with the 0.1 M CDCA solution show a higher charge transfer resistance under irradiation than untreated devices in the dark. In addition, a two folds increase of the hole lifetime (τ_{h+}) was be measured when the concentration of CDCA is raised (Table 3)

Table 3. Impedance parameters in the dark (R_{Rec}) and under AM 1.5 irradiation (R_{CT} and τ_{h+})) at Voc. Before measurement, all devices were light soaked until Voc was stable.

	In dark	Under AM1.5 irradiation	
$[CDCA]_{spin\text{-}coating}$	R_{Rec} (Ohm)	R_{Rec} (ohm)	τ_{h+} (s)
No CDCA	1465	523	0.272
10^{-2} M	2209	755	0.271
$5x10^{-2}$ M	2895	818	0.274
10^{-1} M	7640	1552	0.519

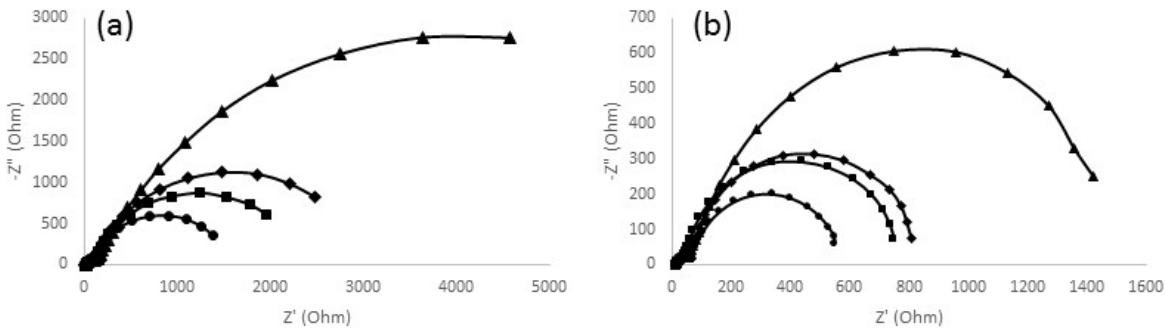


Figure 3. Nyquist plots for p-DSSC based on **DPP-NDI**|NiO photocathodes treated by spin casting a solution of 10^{-2} M (squares), $5x10^{-2}$ M (diamonds), 10^{-1} M (triangles) CDCA in ethanol and plain untreated cells (dots) in the dark (a) and under AM 1.5 simulated solar light in open circuit conditions (b). Electrolyte is **Co1**$^{3+}$/**Co1**$^{2+}$/$LiClO_4$ 0.1M / 0.1 M / 0.1 M in propylene carbonate.

3) Atomic Force Microscopy (AFM) imaging

The surface of the NiO film was investigated by AFM to elucidate the organization of the CDCA molecules after spin coating. Figure 4 illustrates the image of the NiO surface recorded

in different environments. In these series of experiments, we have also prepared a NiO film on which a spin-coated layer of CDCA was deposited and then washed with methanol to eliminate the excess of non chemisborbed compounds. Clearly, the images of the bare NiO films directly prepared after screen printing, or simply coated with a monolayer of **DPP-NDI**, or coated with **DPP-NDI**, spin coated with CDCA solution and then washed by ethanol are all very similar to one another and reveal a cavernous surface with a high roughness (Figures 4A-C and S8). This is not unexpected as the size of the dye is small relative to the pore diameter of the mesoporous NiO network (20 ±5 nm). It also indicates that the washing of the CDCA layer by methanol completely removes the non-chemisorbed CDCA molecules leaving most probably only those which could bind to NiO surface with carboxylic group on naked NiO surface. Indeed, the washed photocathodes were also used to fabricate p-DSSCs. The Voc of the p-DSSCs mounted after washing the spin-coating CDCA layer was a bit higher than those without treatment by CDCA (Voc passes from 358 mV to 374 mV after spin-coated CDCA and then washing), but far from that recorded without washing (Voc= 536 mV). This underscores that the protection of NiO surface is very different when CDCA layer was washed after spin coating than when it is left. Conversely, the image of the NiO surface covered with the spin-coated CDCA layer over the monolayer of **DPP-NDI** displays a very different morphology since the porous texture of the NiO film has disappeared (Figure 4 D-E and S8). Spherical vesicles of amphiphilic CDCA with a diameter around 200 nm can be seen over a relatively smooth layer of CDCA, which nevertheless contains holes of various sizes and depths. By XPS, the NiO surface is not any more detectable indicating that the thickness of CDCA layer is over 10 nm (Figure S9). The depth of the holes are non-homogenous between 200 and 800 nm and their diameter might allow the penetration of the redox mediator within the structure.

Summarily, these AFM images show that the accessibility of the NiO surface is completely different after spin coating of the CDCA solution as it is covered with a thick layer of CDCA. However, the CDCA layer contains many cavities which most certainly enable the redox

mediator to communicate with the dyes and permit it to collect the electrons located on the reduced sensitizers after hole injection.

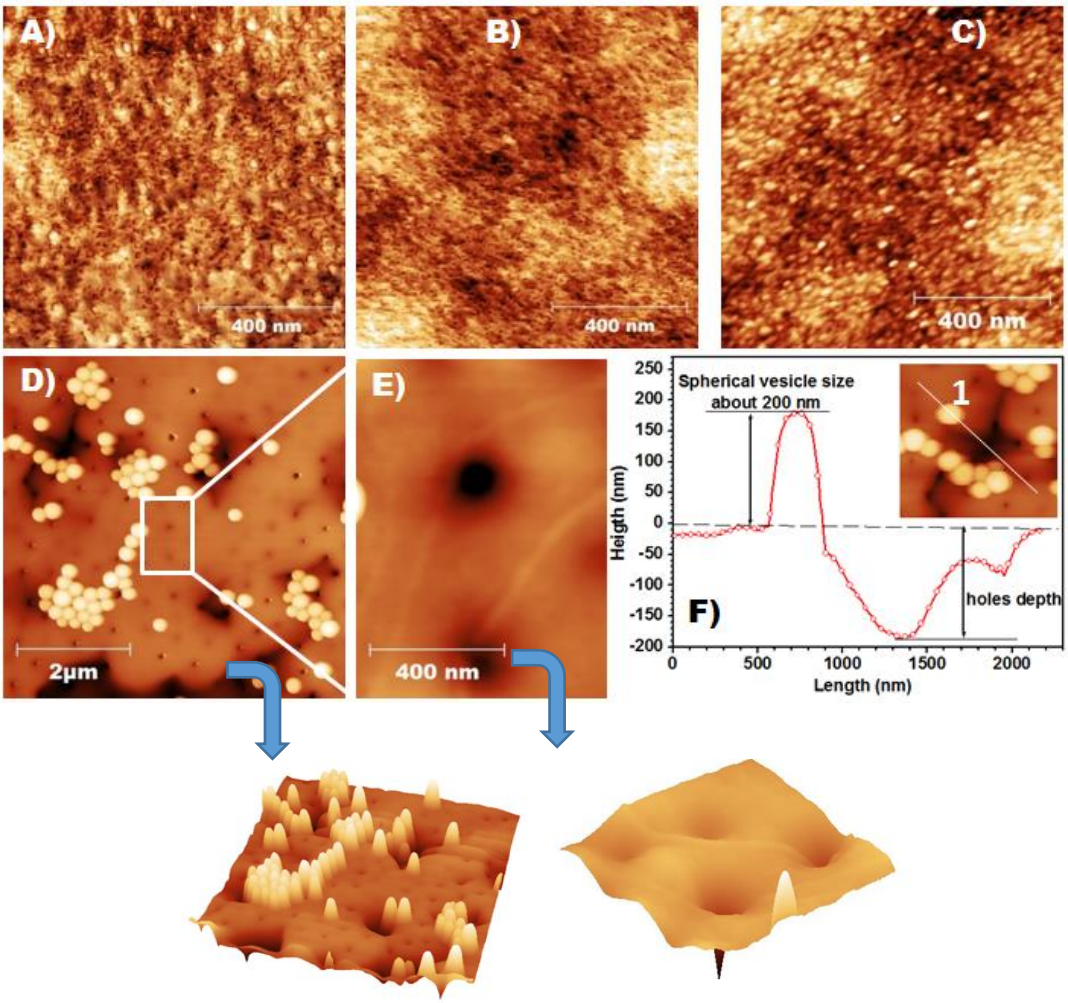


Figure 4. AFM images of the NiO surface recorded in different conditions. (a) Bare NiO (b) DPP-NDI coated NiO, (c) DPP-NDI coated NiO then CDCA spin coated and washed with ethanol (d) and (e) DPP-NDI coated NiO then CDCA spin coated and dried. A depth profile was presented in (f) to represent the depth of the holes and the size of the spherical vesicles.

4) Kelvin probe measurements

The Kelvin probe method is a surface-potential detection technique that enables the determination of the change of the work function of inorganic materials after adsorption of molecules on its surface including dyes on mesoporous metal oxides.[24] It is based on the compensation, with an applied voltage, of the potential offset arising from the workfunction difference between two materials. A freshly cut sample of highly oriented pyrolytic graphite (HOPG) was used as reference material and its workfunction was set to 4.6 eV relative to vacuum. The measurements were made on a bare NiO mesoporous electrode, a NiO mesoporous electrode coated with a spin coated layer of CDCA, a NiO mesoporous electrode coated with the **DPP-NDI** dye and the NiO mesoporous electrode coated with **DPP-NDI** dye on which a CDCA layer was spin coated. The measured work function of NiO in each condition is illustrated on a diagram shown in Figure 5.

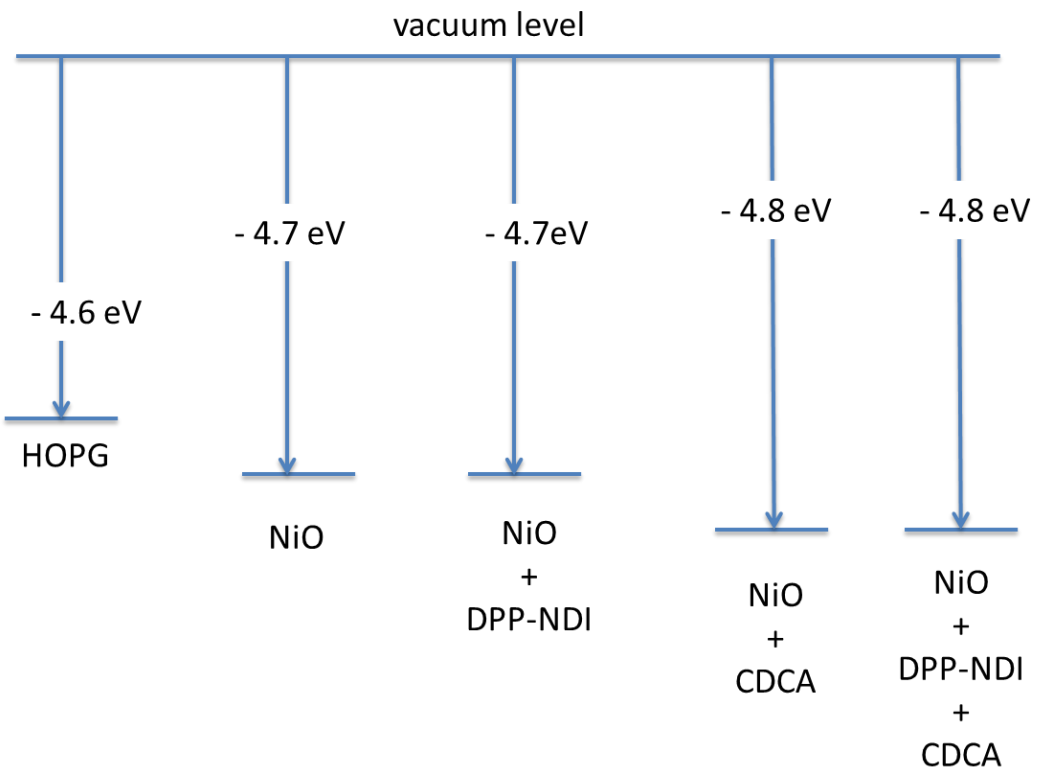


Figure 5. Diagram of the workfunction of the NiO electrode coated in different conditions as determined by Kelvin probe measurements.

The work function of NiO is measured at -4.7 eV relative to the vacuum level, which is a bit below the previously reported value (-5.0 eV), but it is admitted that work function depends a lot on the preparation method of the semiconductor. The deposition of a spin coated layer of CDCA induces a *circa* 100 meV positive shift of the work function of NiO as it was also demonstrated by ESI below. The valence band shift measured by Mott-Schottky experiments for NiO/**DPP-NDI** was not observed with Kelvin probe measurements, probably because the variation is too small and falls within the experimental measurement uncertainty, but the mixture **DPP-NDI** with the spin coated layer of CDCA leads to the expected upward movement of the workfunction of NiO by 100 meV.

Mott-Schottky measurements were also recorded on the NiO films in the above conditions. They confirmed the valence band movement observed above when CDCA is deposited on NiO (Figure S10). For an unmodified mesoporous NiO film, we found a flat band potential at 0.35 V *vs* SCE in agreement with previously reported data.[7b, 25] When the NiO surface is modified with a monolayer of the dye **DPP-NDI** the flat band potential of NiO shifts to the value of 0.40 V *vs* SCE and with a spin coated layer of CDCA to 0.50 V *vs* SCE. Finally, when the NiO surface was first coated with **DPP-NDI** and then a layer of spin coated CDCA, the flat band potential remains at 0.50 V *vs* SCE.

Collectively these results confirm that NiO valence band potential is bent upward by about 100 mV upon deposition of CDCA layer probably owing to the acidity liberated by the large concentration of the carboxylic acid groups. However, the large concentrations of lithium in the electrolytes (> 0.1 M) certainly overshadow this effect, implying that the effect of CDCA on NiO valence band position is certainly negligible in our conditions.

5) Investigation of another semiconductor

NiO is a p-type semi-conductor exhibiting a low lying valence band (ca. 0.3 V vs. SCE),[26] intrinsically limiting the maximum achievable Voc. One exciting way of increasing the output potential of p-DSSC is thus to replace NiO by another mesoporous semi-conducting material. Among them, copper oxides such as CuO[27] and Cu_2O,[28] binary cobalt oxides with Zn or Ni,[29] and particularly delafossite materials such as $CuMO_2$ with M = Ga,[7, 9a, 30] Cr,[9b, 31] Al[32] and B[33] have showed great potential for implementation in p-DSSC.[8] In particular, the valence band of $CuGaO_2$ is deeper than NiO by 200 mV, which allows to reach higher Voc; in addition to this, doping the latter by magnesium ions increased hole mobility and afforded a much improved specific surface area.[30] For all these reasons, we chose $CuGaO_2$/Mg(1%) to test if the CDCA treatment could be extended to semi-conductors other than NiO. Photocathodes $CuGaO_2$/Mg(1%)|**DPP-NDI** were prepared and a 10^{-1} M CDCA solution was spin-coated on the latter, before assembly with the counter electrode and cobalt electrolyte infiltration, following the exact same protocol than for NiO based p-DSSC.

Interestingly, an already high Voc value of ca. 530 mV was reached for plain p-DSSC devices. However, this value was further increased to 630 mV upon spin-coating a 10^{-1} M CDCA solution onto the photo-electrode (Table 2). This is the highest Voc ever reported in p-DSSC using conventional redox mediator exhibiting redox potential in the range of 0.1 V vs SCE. Again, electrochemical impedance spectroscopy measurements (Figure S11) confirmed the effective passivation of recombination sites by CDCA molecules, with an increased charge transfer resistance both in the dark (10140 Ω vs. 2930 Ω for p-DSSC respectively treated by CDCA and untreated) and under AM 1.5 irradiation (1341 Ω vs. 906 Ω for p-DSSC respectively treated by CDCA and untreated). Similarly to NiO based p-DSSC, excess CDCA in the pores likely account for the decrease of both Jsc and ff. Altogether, the same behavior is observed regardless the semi-conductor, showing that the benefit of the CDCA treatment by spin coating goes beyond NiO-based DSSC and could be certainly generalized to other p-DSSCs.

6) Impact of maturation

In order to assess the impact of the maturation, new batches of p-DSSC have been prepared and their performances were regularly monitored. Cells were kept in the dark at room temperature in the laboratory in between measurements. For p-DSSC assembled with iodine-based electrolyte B_{50} (containing 50 mM CDCA) a slight, but significant, increase of the Voc could be monitored over time (Table 4). However, the latter could not counter-balance the decrease in Jsc yielding an overall lower PCE with time. Since no such behavior was observed for plain devices assembled with electrolyte B_0 and knowing, besides, that the chemisorbed monolayers are involved in a dynamic rearrangement within working DSSCs,[34] we therefore assign the rise of Voc to a progressive re-arrangement of the layer of CDCA on NiO, discouraging interfacial recombination.

When CDCA is spin coated on NiO|**DPP-NDI** photocathodes and the latter are assembled with the cobalt based electrolyte, Voc remains constant while Jsc decreases by about 30% to reach a plateau after two to three days maturation. The low solubility of CDCA in the cobalt electrolyte could prevent the reorganization of the passivating overlayer resulting in a steady increase of Voc. The drop of about 30% in Jsc experienced for both electrolytes in presence of CDCA remains, however, the overall PCE remains relatively constant.

Table 4. Impact of CDCA on the evolution of the metrics of the cells over time. The cells are composed of a NiO film sensitized with the **DPP-NDI** dye.

electrolyte		Jsc	Voc	ff	PCE
Iodine electrolyte B_{50}	Day 0	2.41	198	28.4	0.14

	Day 3	1.76	229	29.5	0.12
cobalt electrolyte + spin coating of 0.1M CDCA on photocathode	Day 0	0.89	530	19.8	0.09
	Day 1	0.62	528	18.9	0.06
	Day 2	0.67	523	19.7	0.068
	Day 3	0.66	532	19.9	0.070

Discussion

The above experiments demonstrate that the presence CDCA either dissolved in the electrolyte or deposited as a spin-coated layer on the photocathode has clearly a strong and beneficial impact on the Voc with both the iodide/triiodide and the cobalt electrolytes as the Voc was increased in both cases. This corresponds to a remarkable improvement with a quite simple methodology, because it led among the highest Voc ever reported in NiO-based DSSCs using conventional redox couples with moderately cathodic Nernst potential (around 0.1 V vs SCE). The main reason behind this Voc enhancement can be understood as a significant reduction of the interfacial charge recombination. With the **DPP-NDI** sensitized NiO films, the Voc was increased by *circa* 40 mV when CDCA is dissolved in the iodine electrolyte (Voc = 207 mV against 163 mV without CDCA) and by *circa* 210 mV with **Co1** electrolyte and when CDCA was spin coated on NiO electrode (Voc = 543 mV against 327 mV without CDCA). These two redox shuttles have similar Nernst potentials (0.09 V vs. SCE for the $\mathbf{Co1}^{3+}/\mathbf{Co1}^{2+}$ couple and 0.1 V vs SCE for I_3^-/I^-), therefore if the band bending induced by the diffusion of protons into the p-SC would be responsible for the higher Voc, there should be only little variations of Voc within these series of electrolytes (A, B or Co1), which is far from being the case. On the other hand, the charge transfer resistance at the electrolyte/NiO interface is importantly increased in the presence of CDCA and therefore can majorly account for the observed Voc enhancement. The higher Voc with the cobalt electrolyte reflects the larger bulkiness of the Co1 complex

relative to iodide anion, which limits the close approach to the p-SC surface in agreement with the larger charge transfer resistance measured with the latter redox mediator.

An interesting strategy to protect the semi-conductor surface from the approach of the redox mediator was developed by Hanaya and co-workers.[35] It consists to the post treatment of a TiO_2 based photoanode by a battery of various co-adsorbates (mostly alkyl silanes and fatty carboxylic and phosphonic acid derivatives). We have investigated this "alkyl ticket strategy" on NiO with the **P1** and **DPP-NDI** dyes and it turns out that the dyes desorb from NiO surface especially upon treatment with silane derivatives or phosphonic co-adsorbates. However, we have recorded the photovoltaic performances of the solar cells without and with alkyl ticket treatment and it turns out that they were greatly diminished, due to a drastically decreased of the Jsc. For example, with **DPP-NDI** sensitizer (the dye which desorbs the most slowly) and the electrolyte B_0, the Jsc passes from 2.28 mA/cm^2 (without treatment) to 0.94 mA/cm^2 (after alkyl ticket procedure), while the Voc was raised only by 5 mV only after treatment (Voc = 154 mV). In addition, when a carboxylic fatty acid co-adsorbate was used (such as CDCA) as a post-treatment of the photocathode and then rinsed, the photovoltaic performances of the solar cell were not improved (see experiments described below in part 3). Overall, the method reported by Hanaya and co-workers is effective to protect the TiO_2 surface, but it is only compatible with sensitizers bound with very stable anchoring groups such as silane. However, most dyes developed for DSSCs are functionalized with carboxylic acid anchoring groups, making this strategy inapplicable to them and therefore more limited.

Interestingly, it is worthwhile noting that the short circuit current density (Jsc) and the fill factor (ff) were not significantly modified upon these treatments in spite that the impedance measurements show that the interfacial charge recombination was importantly diminished after the deposition of the CDCA monolayer. The Jsc is directly proportional to the light harvesting efficiency (LHE) of the electrode, the hole injection efficiency (ϕ_{inj}) and the charge collection

efficiency ($\phi_{collect}$). The absorbance of the electrode after deposition of the CDCA monolayer was not modified to a significant extent (Figure S4), therefore a decreased of LHE cannot account for the constant Jsc. The injection quantum yield, must not be affected by the presence of CDCA as the hole injection driving force and electronic coupling of the dye with NiO valence band cannot be importantly modified by the presence of CDCA. In the light of the AFM pictures, the most plausible explanation is a reduction of the accessibility of the dyes by the redox mediator. The presence of the CDCA layer creates a thick molecular barrier, which prevents the electrolyte from approaching the NiO surface but also restricts the access to all the dyes. As a consequence, fewer chemisorbed dyes are active for electricity production, but it is compensated by the reduced interfacial charge recombination losses. As a result, the overall photocurrent does not change significantly. As observed from the AFM images, the CDCA layer contains many cavities which provide a path for the redox mediator to reach the reduced sensitizers after hole photoinjection. Furthermore, lateral diffusion of charges within a compact monolayer of sensitizers chemisorbed on a mesoporous semiconductor was previously evidenced by several studies both on TiO_2[36] and NiO.[37] Accordingly, the sensitizers covered by the thick layer of CDCA offer the possibilities to transfer their electrons to the electrolyte *via* this mechanism, which can enhance the charge collection efficiency. The slow diffusion of the redox mediator, particularly the amphiphilic tris(di*tert*butyl bipyridine) cobalt complex, within the layer of CDCA cannot be excluded as a complementary mechanism of electron exchange between the electrolyte and the dyes coated on the NiO surface.

Concerning the fill factor, the negligible impact of the reduced interfacial charge recombination brought by the CDCA layer indicates that the low ff constantly measured in p-DSSCs is not majorly governed by this type of recombination, but must be caused by another factor.[4c] This points to probably the fast geminate charge recombination reaction between the reduced dye and the injected hole as already proposed by Wu[4c] and Bach.[4b]

Conclusion

One of the greatest challenges for the development of efficient p-DSSC is to get rid of counter-productive charge recombination processes taking place between photo-injected holes and 1) photo-reduced chemisorbed dyes (called "geminate" recombination) and 2) the redox mediator molecules dissolved in the electrolyte (interfacial recombination). We took care of the former with the design of dyad-like photosensitizers allowing to dramatically decrease the kinetics of geminate charge recombination. The latter, on the other hand, is likely to occur mainly through naked sites on the mesoporous semi-conducting material. To address this issue, we propose to mend the somehow patchy dye monolayer with an insulating, transparent bulky organic molecule, namely the famous anti-aggregates CDCA according to two strategies. The first method relies on directly dissolving CDCA in the electrolyte as previously reported by Bach and co-workers. We show that this approach is satisfying only when the dye is quite insoluble in the solvent of the electrolyte, otherwise dye leaching quickly occurs. In case CDCA is poorly soluble in the electrolyte, a second method was developed, where a CDCA layer was deposited on the photocathode by spin coating. The first advantage of both methods is that CDCA does not compete with the photosensitizer during chemisorption, thus leaving unaffected the light harvesting efficiency of the electrode. The second and main advantage is that naked sites are efficiently covered by CDCA molecules, as proven by the strong increase of the hole lifetime and the interfacial charge resistance. Interestingly, the output potential increased by 25% when CDCA is dissolved in iodine based electrolyte and an impressive 65% rise was experienced when CDCA was spin coated onto the photocathode, in presence of **Co1** based electrolyte, reaching 540 mV on NiO and 630 mV on $CuGaO_2$/Mg. Very interestingly, this strategy seems to be particularly general as it was applied with success to two other dyes such as **P1** and **DPPNDI** and preliminary experiments also indicate its applicability to other p-SCs than NiO such as $CuGaO_2$/Mg.

Our results have clear implications for future development in p-DSSCs and photoelectrochemical cells because they reveal that interfacial charge recombination is an important source of energy loss and it is possible to boost the usual Voc measured in p-DSSC and to achieve quite significant Voc as high as 500 mV with NiO and using regular dyes and electrolytes if these interfacial charge recombination are suppressed or reduced. Secondly, these results are important findings because they highlight that interfacial charge recombination with the electrolyte is majorly responsible of the low Voc measured in p-DSSCs and therefore minimizing it is fundamental for further improvement of the PCE of these devices. This fact is clearly evidenced by the large Voc enhancement resulting from the electrolyte change when we pass from I_3^-/I^- to cobalt electrolyte **Co1**. A large increase of the Voc from values of about 100 mV (with I_3^-/I^-; E = 0.1 V vs SCE) until more than 500 mV (cobalt complex **Co1**; E = 0.09 V vs SCE) was obtained with the same dye and same p-SC (NiO), while the redox potentials of the two mediators have not changed more than few tens of mV. The successful exploitation of a spin-coated layer of co-adsorbent or other innovative strategies, that enable to passivate the surface of the p-SC, are certain new effective directions for increasing the Voc of p-DSSC even with conventional materials (dyes, p-SCs and electrolytes). We believe that this information can be useful to develop better performing photocathodes for photovoltaic and photoelectrochemical cells.

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Supporting information available: Fabrication of the DSSCs and their J/V characteristics and IPCE spectra, absorption spectra of the NiO films, Mott-Schottky plots and EIS measurements.

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