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# A swift dye uptake procedure for dye sensitized solar cells

**Md. K. Nazeeruddin,* R. Splivallo, P. Liska, P. Comte and M. Grätzel***
*Laboratory for Photonics and Interfaces, Institute of Molecular and Biological Chemistry, School of basic Sciences, Swiss Federal Institute of Technology, CH - 1015 Lausanne, Switzerland.*
*E-mail: MdKhaja.Nazeeruddin@epfl.ch*

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**Solar cells based on swift self-assembled sensitizer bis(tetrabutylammonium)-*cis*-di(thiocyanato)-*N*,*N*′-bis(4-carboxylato-4′-carboxylic acid-2,2′-bipyridine)ruthenium(II) (N719) on double layers of 12 + 4 μm thick nanocrystalline $TiO_2$ films exhibit the incident monochromatic photon-to-current conversion efficiency (IPCE) 90% and show a short circuit current density of 17 mA $cm^{-2}$, 750 mV open circuit potential and 0.72 fill factor yielding power conversion efficiencies over 9.18% under AM 1.5 sun. For the first time highest power conversion efficiencies are obtained for dye sensitized solar cells using a swift self-assembled procedure.**

Dye sensitized solar cells are currently attracting widespread academic and commercial interest for the conversion of sunlight into electricity because of its low cost and high efficiency.[1–9] The added advantages of these cells are the availability and non-toxicity of the main component *i.e.*, titanium dioxide, which is used in paints, cosmetics and health care products. So far, the best performing charge transfer sensitizer employed for such an application is the *cis*-dithiocyanato bis(4,4′-dicarboxylic acid-2,2′-bipyridine)ruthenium(II) complex referred to as (N3).[10] The general procedure applied for dye absorption onto the $TiO_2$ working electrode is dipping it into dye solutions for 15–20 hours. However, such long dipping conditions are not economic for industrial production of dye-sensitized solar cells. Therefore, the dye coating time has to be reduced in order to produce solar cells on-line on an industrial scale. Towards this goal, we have developed a procedure that takes less than 10 minutes to anchor the dye onto nanocrysatlline $TiO_2$ electrodes. This study reports a rapid dipping procedure and its effectiveness for producing highly efficient solar cells.

$TiO_2$ anatase nanoparticles of 16 nm were prepared by hydrolysis of titanium(IV)isopropoxide as described before.[11] The nanocrystalline $TiO_2$ thin films of 12 μm thick were deposited onto transparent conducting glass by screen printing. These films were dried at 150 °C for 20 minutes and then a 4 μm thick layer of 400 nm $TiO_2$ particles (400 nm particles were obtained from CCI, Japan) was deposited again using a screen printing method. The double layered films were sintered at 500 °C for 20 minutes, and were then further treated with $TiCl_4$ as described before.[11] Finally the electrodes were heated at 520 °C for 20 minutes and allowed to cool to 50 °C before dipping into the dye solution.

Details of the sensitizer bis(tetrabutylammonium)-*cis*-di-(thiocyanato)-*N*,*N*′-bis(4-carboxylato-4′-carboxylic acid-2,2′-bipyridine)ruthenium(II) (719) are available from our previous studies.[12] Solutions of $2 \times 10^{-2}$ M were prepared by mixing 25 mg of N719 in 1 ml of desired solvent. However, in acetonitrile the solubility of N719 is low, therefore 25 mg of the N719 dye and 20 μl of tetrabutylammonium hydroxide 30-Hydrate solution were dissolved in 980 μl of acetonitrile (the concentration of the dye and ammonium hydroxide is $2 \times 10^{-2}$ M and 2.5 $\times 10^{-2}$ M, respectively). The heated $TiO_2$ electrodes were dipped into the $2 \times 10^{-2}$ M dye solution for 10 minutes. Alternatively, a measured volume of the concentrated solution was pipetted (10 μl for 0.5 $cm^2$ $TiO_2$ area) onto the surface of the $TiO_2$ electrode and the dye solution left for 10 minutes. The dye-coated electrodes were rinsed quickly with acetonitrile and used as such for photovoltaic measurements. The dye uptake procedure is fast and the difference in the photovoltaic performance of cells dipped for between 3–20 minutes is within experimental error.

The platinum coated counter electrode was prepared using NSG 10 conducting glass with chemically deposited platinum from 0.05 M hexachloroplatinic acid. The dye coated $TiO_2$ film and the platinum coated counter electrode were put together with a thin transparent film of polymer gasket frame (DuPont, *Bynel*). The sandwiched electrodes were tightly held and then heat was applied around the polymer frame to seal the two electrodes. A thin layer of electrolyte was introduced into the inter electrode space from the counter electrode side through a pre-drilled hole. The drilled hole was sealed with a microscope cover slide and *Bynel* to avoid leakage of the electrolyte solution. The electrolyte composition was 0.6 M M-methyl-*N*-butyl imdiazolium iodide, 0.05 M iodine, 0.05 M LiI and 0.5 M *tert*-butylpyridine in a 50 : 50 (v/v) mixture of valeronitirile and acetonitrile. Photovoltaic data were measured using a 450 W xenon light source that was focused to give 1000 W $m^{-2}$, the equivalent of one sun at AM 1.5, at the surface of the test cell.

The absorption spectra of the N719 dye in solution show two broad visible bands at 535 and 398 nm due to metal-to-ligand charge-transfer (MLCT) origin. The 312 nm band in the UV is due to intra-ligand ($\pi$–$\pi^*$) charge transfer transitions. It is interesting to note that the position of the maximum low energy MLCT band of N719 in solution and anchored onto the $TiO_2$ nanocrystalline electrodes is very similar. This is because in solution there are two protons on carboxylic acid groups that are *trans* to the $NCS^-$ ligands, which upon adsorption release and bind to $Ti^{4+}$. The $Ti^{4+}$ behaves as an electron withdrawing moiety like a proton, which lowers the energy of the $\pi^*$ orbital of the ligand resulting in no change in the position of MLCT absorption bands. The ATR-FTIR data of the N719 complex adsorbed on $TiO_2$ films show that the dye anchors onto the $TiO_2$ surface using two of its four carboxylate groups in a bidentate chelation or bridging coordination mode.[13,14] The quantity of the anchored dye on a given geometric electrode area was determined spectrophotometrically by de-sorption into pH 7 buffer solution, which is $(1.5 \pm 0.1)\ 10^{-7}$ moles $cm^{-2}$, consistent with mono-layer molecular packing of the sensitizer on the surface.

The photocurrent action spectra obtained with a sandwich cell under illumination by simulated AM 1.5 solar light is shown in Fig. 1. The photocurrent action spectra of the N719 dye show broad features covering a large part of the visible spectrum. The incident monochromatic photon-to-current conversion efficiency (IPCE) is plotted as a function of excitation wavelength showing a plateau region at 90%. From the overlap integral of this curve with the standard global AM 1.5 solar emission spectrum one measures a short circuit photocucrrent densitiy of 17.1 mA $cm^{-2}$. In agreement with this measurement under standard global AM 1.5 solar conditions the cell gave a photo-current density of 17 mA $cm^{-2}$, 750 mV open circuit potential and 0.72 fill factor yielding 9.18% efficiency. In these measurements, no anti-reflection layer was used, which would

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**Table 1** Performance characteristics of photovoltaic cells based on nanocrystalline $TiO_2$ films sensitized by N719 and N3 dye in acetonitrile and *N*,*N*-dimethylformamiide.

| Dye | Number of protons | Concentration/M | Solvent | $I_{sc}$/mA cm$^{-2}$ | *Voc*/mV | Fill factor | Efficiency at 1 sun (η %) |
|---|---|---|---|---|---|---|---|
| N719 | ≤1 | $2 \times 10^{-2}$ | $CH_3CN$ | 17 ± 0.5 | 750 ± 20 | 0.72 | 9.18 |
| N719 | 2 | $2 \times 10^{-2}$ | DMF | 17.4 ± 0.5 | 708 ± 20 | 0.70 | 8.62 |
| N3 | 4 | $9 \times 10^{-3}$ | DMF | 18 ± 0.5 | 623 ± 20 | 0.69 | 7.73 |
| N3 | 4 | $2 \times 10^{-3}$ | DMF | 17.9 ± 0.5 | 627 ± 20 | 0.68 | 7.63 |

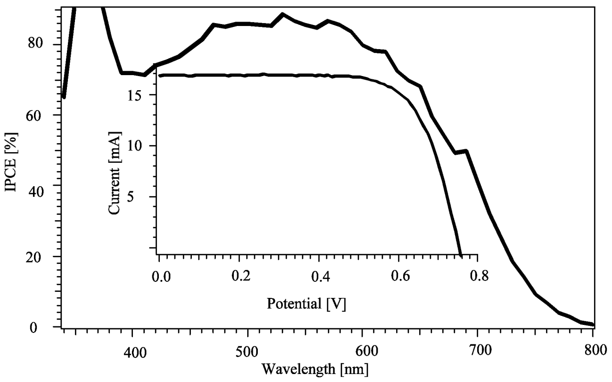

**Fig. 1** Photocurrent action spectrum obtained with the N719 dye attached to nanocrystalline $TiO_2$ films. The incident photon to current conversion efficiency is plotted as a function of the wavelength of the exciting light. The insert shows photocurrent density and voltage characteristics of nanocrystalline $TiO_2$ cell sensitized with N719 dye measured under AM 1.5 sun. The electrolyte composition was 0.6M M-methyl-*N*-butyl imdiazolium iodide, 0.05 M iodine, 0.05 M LiI and 0.5 M *tert*-butylpyridine in a 50 : 50 (v/v) mixture of valeronitirile and acetonitrile.

enhance the efficiency yield another 5%. The current–voltage characteristics of a sandwich-type cell with N719 and N3 dyes are included in Table 1 (see also insert in Fig. 1). The short circuit photocucrrent densitiy in N3 dye is slightly higher than in N719 dye. However, the photovoltage of the cell containing N719 dye is 150 mV higher than the N3 dye. The difference in the opencircuit potential is due to a negative shift of the Fermi level that increases the gap between the redox couple iodide–triiodide and the Fermi level caused by less protons in N719 compared to the N3 dye.

The important effect asserted by the 4 µm thick 400 nm particles layer is evident in the red region. The incident monochromatic photon-to-current conversion efficiency at 700 nm is twice as high for the $TiO_2$ film containing a scattering layer as compared to the 12 µm thick $TiO_2$ film without a scattering layer. The influence of dye deposition solvent on current and voltage was investigated in acetonitrile, *N*,*N*-dimethylformamiide, *N*-methyl-2-pyrrolidone, dimethylimidazolidone, tetramethyl urea, γ-butyrolactone and 3-methyl-2-oxazolidinone. The optimum performance of the dye sensitized solar cell was observed with acetonitrile and DMF as the dye deposition solvents. The rapid deposition method of concentrated solution is potentially an important finding, which can be used for fabricating dye-sensitized solar cells online at room temperature by screen-printing or inkjet printing.

In conclusion for the first time we have successfully employed a swift self-assembling deposition procedure that yields 9.18% efficiency and opens the way to fabricate nanocrystalline photovoltaic cells online.

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