

A viable surface passivation approach to improve efficiency in cobalt based dye sensitized solar cells



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ARTICLE INFO

Article history:

Received 14 March 2014

Accepted 3 June 2014

Available online 12 June 2014

Keywords:

DSSC

Cobalt mediators

Surface passivation

Dark current

Silanization

ABSTRACT

A successful general strategy for improving the electron collection efficiency in Dye Sensitized Solar Cells based on common Ru(II) complexes like Z907 and kinetically fast redox mediators based on the $[\text{Co}(\text{bpy})_3]^{3+/2+}$ couples was investigated.

The post-treatment of the dyed photoanode with commercially available tri-alkoxy silanes was effective in screening the TiO_2 surface by electron recapture involving Co(III), but, interestingly, silanes endowed with relatively short propyl chains like aminopropyl-triethoxysilane (APTS) and trimethylammoniumpropyl-trimethoxysilane (TMAS) bearing a cationic charge, proved to be more effective than longer and more sterically hindered C16 chains in suppressing the dark current. In the best cases (TMAS and APTS), the siloxane treatment resulted in overall improvements of the cell efficiency of the order of respectively 600% and 500% by comparison with the untreated photoanode based on the Z907 Ru(II) Dye. This approach may represent a viable procedure for improving the electron collection efficiency in cobalt mediated DSSCs even without the use of highly sterically hindered dyes specifically designed to work in conjunction with kinetically fast metal based mediators.

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1. Introduction

With the increasing world demand of renewable energy sources with minimal environmental impact, the exploitation of solar energy becomes a priority in the global race for sustainable energy. After the first publication of Graetzel and O'Regan at 1991 [1], dye-sensitized solar cells (DSSCs) were recognized to hold great potential for a relatively cheap and easy-to-scale approach to direct solar-to-electrical power conversion. Furthermore, their transparency, versatile design and wide color palette offers unique structural and architectural possibilities in the emerging field of building integration [2,3], for example through the realization of photovoltaic windows and façades.

The Iodide/Iodine redox couple is the most common choice for high performing electrolytes in liquid based DSSCs, although polypyridine Cobalt complexes are emerging as one of the most interesting and promising class of alternative redox mediators [4–7] which have scored absolute record efficiencies when used in

conjunction to custom tailored dyes based on push pull structures employed in optimized cell configurations. One of the key elements for reaching high efficiency with cobalt based mediators is to employ unsubstituted kinetically fast redox couples, like the simple $[\text{Co}(\text{bpy})_3]^{2+}$ complex, displaying both a relatively fast dye regeneration, good exchange currents at the catalytic counter electrodes and a reasonably efficient mass transport, at least in low viscosity electrolytes. One of the main drawbacks of fast Co(III)/(II) couples is their ability to recapture photoinjected electrons, which are mostly trapped in the TiO_2 surface states, yielding high recombination (dark) current. This drawback can be almost entirely eliminated by using bulky dyes having enough steric hindrance and assembling on the titania surface in such a way to screen completely the surface from Co(III). Very successful examples of this approach have been provided first by Hagfeldt, with the D35 [8] dye, by Graetzel with the Y123 [9], YD2-O-C8 [10] and SM315 [11] and by Koumura and Bach with the MK2 [12,13] sensitizers. Nevertheless, there is a limited choice of these types of highly engineered dyes, which are usually obtained through costly multistep synthetic routes, resulting in high cost, limited color palette and limited availability of these sensitizers. Thus, it would be interesting for both fundamental and applicative reasons to devise general

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strategies for surface passivation, which can be applied to the widest numbers of already available dyes, including the existing ample variety of well known Ru(II) complexes, without requiring further chemical modification of the dyes themselves. Usually, with ruthenium(II) sensitizers [5,6,14–17], only limited performances have been achieved with cobalt electrolytes. The only notable example of a sterically hindered cyclometalated Ru(II) dye exhibiting comparable efficiencies (8.6%) under 1 sun illumination with both cobalt ($[\text{Co}(\text{phen})_3^{3+/2+}]$) and I^-/I_3^- redox mediators, in the presence of chenodeoxycholic acid (CDCA), has been recently described by the Graetzel's group [18].

Besides achieving TiO_2 surface passivation by adopting either sterically hindered sensitizers or bulky redox mediators, the use of surface post treatments based on molecular co-adsorbates can be a simple, reproducible and convenient route to protect exposed surface sites, left uncovered by the dye, from which recombination with the oxidized electrolyte would predominantly occur.

Functionalization of hydrophilic inorganic surfaces with silanes is a well known procedure that yields very robust coupling between organic and inorganic materials [19–21]. Despite the large amount of literature about new sensitizers, alternative electrolytes and cathodic materials, the employment of silane functionalization as a photoanode passivation tool has not been deeply investigated [22–24]. Some recently published results, concerning a family of multi-branched push pull organic sensitizers, demonstrate that it is possible to improve charge collection efficiency in cobalt based DSSCs by co-adsorbing long chain alkyl-siloxanes as surface passivating agents [25].

Here we extend and confirm the previous observation, showing that it is possible to achieve an even larger improvement in power conversion efficiency by the careful choice of short chain siloxanes like aminopropyl-triethoxysilane (APTS) and trimethylammoniumpropyl-trimethoxysilane (TMAS) chloride featuring a positively charged end, which should help in screening the TiO_2 surface from Co^{3+} species by both steric and electrostatic repulsion. A rather common Ru(II) complex $[\text{Ru}(\text{H}_2\text{DCB})(\text{dnbpy})(\text{NCS})_2]$ (Z907) was used as a dye model for such comparative study, which includes molecular modeling, DC and AC photoelectrochemical investigations.

2. Materials and methods

2.1. Materials

Chemicals and solvents were Sigma Aldrich products and were used as received, except trimethylammoniumpropyl-trimethoxysilane (50% solution in methanol) that was purchased by ABCR-Gelest. Z907 dye and TiO_2 colloidal paste (DSC 18NRT) were purchased from Dyesol.

Platinized FTO counter electrodes were prepared by screen-printing of a conductive colloidal platinum paste Chimet (Pt-10-004F-05, batch 5738) and were annealed at 400°C for 10 min in air immediately before use.

$[\text{Co}(\text{bpy})_3]^{3+/2+}$ complexes were prepared according to literature procedures [26].

2.2. Solar cell fabrication

We will use the terms Z907, DCA, C16, TMAS and APTS to indicate DSSCs assembled with pure Z907 dye, Z907/20 mM Deoxycholic acid, hexadecyl-(triethoxy)silane, trimethylammoniumpropyl-trimethoxysilane and aminopropyl-trimethoxysilane respectively.

Mesoporous titania films (ca. $6\ \mu\text{m}$ thick) were prepared by blading a commercial colloidal TiO_2 paste on FTO electrodes, which were left to dry under a gentle warm air stream before sintering at

450°C for 30 min. The resulting transparent films were immersed in a 0.4 M TiCl_4 solution for 12 h, rinsed with water and fired at 450°C for 30 min. Finally, the photoanodes were dipped for 24 h in a 0.1 mM solution of Z907 in ethanol, or in solution of 0.1 mM Z907 and 20 mM DCA in ethanol. The silane post treatment of the Z907 photoanodes consisted in the immersion of the dyed photoanodes in a 0.1% v/v solution of the appropriate alkoxy-silane in toluene, for 1 h at $55/60^\circ\text{C}$; the electrodes were rinsed with toluene several times and dried under air before use.

The blocking underlayer was obtained by either immersing the well cleaned FTO in 0.2 M TiCl_4 at 70°C for 30 min, or, equivalently by carrying out the reaction at room temperature overnight. The resulting slides were rinsed with deionized water and fired at 450°C for 30 min. The porous TiO_2 layer was cast on the compact underlayer as described above.

Solar cells were equipped with transparent screen printed platinum counter electrodes and assembled in open configuration by holding the two electrodes together with metallic clamps and by using a $25\ \mu\text{m}$ thick Surlyn frame as sealer. The active cell area was $0.25\ \text{cm}^2$.

Electrolyte formulation used for the DSSCs characterization were based on $[\text{Co}(\text{bpy})_3]^{3+/2+}$: 0.18 M $\text{Co}(\text{II})/0.028\ \text{M}\ \text{Co}(\text{III})/0.1\ \text{M}\ \text{Li}(\text{CF}_3\text{SO}_3)$ in acetonitrile. In some cases 0.2 M 4-Tert-butyl-pyridine (TBP) was added to previous formulation.

2.3. Solar cell characterization

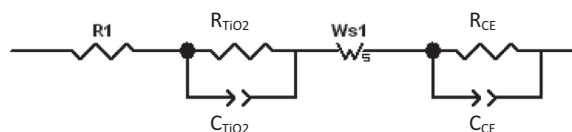
Current–voltage measurements were performed with an Autolab PGSTAT 302/N potentiostat equipped with a FRA2 frequency response analyzer at a scan rate of $20\ \text{mV}\ \text{s}^{-1}$. Cell performances were evaluated under AM 1.5 illumination (ABET sun simulator). Electrochemical Impedance Spectroscopy (EIS) potentiostatic measurements in DSSCs were performed at open-circuit potential (V_{oc}) by applying a sinusoidal perturbation of the amplitude of 10 mV in the 10^2 – 10^{-2} Hz frequency range. The simplified electric equivalent of the cell at V_{oc} is represented in Scheme 1 where the parallel elements modeling the TiO_2 /electrolyte and the counter electrode (CE)/electrolyte interfaces are reported.

The non ideal capacitances of the interfaces are described by constant phase elements (CPE). W_s is the short Warburg element describing electrolyte diffusion in a thin layer cell.

Absorption spectra on TiO_2 thin films were collected with a JASCO V 570 UV–Vis spectrophotometer. IPCE spectra were collected with a custom built apparatus comprising an Applied Photophysics Monochromator, a 175 W Xe source (Luxtel) and various optical elements. Short circuit photocurrents were measured with an Agilent 34401 A multimeter while incident irradiance was provided by a calibrated silicon photodiode (Centronic OSD 100 7Q).

2.4. Computational modeling

Computational studies were carried out by using Gaussian 09 C02 revision for windows. The geometry of a TiO_2 surface slab (101) ($\text{Ti}_{64}\text{O}_{128}$) was optimized at the Molecular Mechanics-Universal force Field (MM-UFF) level with charge embedding. Ground state equilibrium geometries of Z907, TMAS and $[\text{Co}(\text{bpy})_3]^{3+}$ were optimized at the DFT-B3LYP level with a LANL2DZ basis set for the



Scheme 1. Electrical circuit model used to fit experimental EIS data at open circuit.

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