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## A High-Performance Solid-State Dye-Sensitized Photoelectrochemical Cell Employing a Nanocomposite Gel Electrolyte Made by the Sol-Gel Route\*\*

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Grätzel's discovery that ruthenium bipyridyl derivatives can efficiently sensitize titanium dioxide nanocrystalline films by visible light and the subsequent construction of the dye-sensitized photoelectrochemical cell (DSPEC)<sup>[1,2]</sup> instigated a great deal of research in several laboratories worldwide.<sup>[3–12]</sup> A standard configuration for a DSPEC consists of two optically transparent electrodes facing each other and supporting between them a thin multilayer of active components. A nanocrystalline n-type semiconductor, usually TiO<sub>2</sub>, is deposited on the negative electrode followed by chemical attachment of a dye sensitizer. On the positive electrode a thin semi-transparent or opaque (reflecting) Pt film is deposited, which acts catalytically to enhance cell efficiency. The two electrodes are brought in close proximity with the help of micrometer-thick spacers. The gap is filled with a liquid electrolyte containing a redox couple, usually I<sub>3</sub><sup>-</sup>/I<sup>-</sup> in a solvent mixture of propylene and ethylene carbonate. The electrolyte provides internal electrical contact between the two electrodes and, mainly, provides the potential barrier necessary for photovoltaic conversion. The barrier exists because of the difference between the Fermi level of the semiconductor and the redox potential of the redox couple. Every time a photon is absorbed by the dye sensitizer, the excited electron is injected into the conduction band (CB) of the nanoparticle that the dye is attached to, thanks to a convenient combination be-

tween the LUMO level of the dye and the CB edge of the semiconductor. This electron is led through the TiO<sub>2</sub> nanoparticle network, the negative electrode, and the external load to the positive electrode, where it is neutralized by holes internally carried by the electrolyte. The direction in which the electron resulting from photon absorption moves is, of course, dictated by the potential barrier set at the semiconductor/electrolyte interface. Meanwhile, the hole created in the dye by photon absorption is scavenged by the electrolyte and carried to the positive electrode. Thus the components of the cell are continuously regenerated and the cell function is guaranteed.

The overall efficiency of such a cell is around 10 % when I<sub>3</sub><sup>-</sup>/I<sup>-</sup> is employed as the redox couple and *cis*-di(thiocyanato)-*N,N*-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid)-ruthenium(II) dihydrate [RuL<sub>2</sub>(NCS)<sub>2</sub>] as the dye-sensitizer.<sup>[2]</sup> This efficiency is equivalent to that of photovoltaic cells (PCs) made of amorphous silicon. This fact makes DSPECs very competitive versus silicon PCs for several reasons: 1) DSPECs are constructed under, practically, ambient conditions by a soft chemistry route, therefore, at low cost. 2) DSPECs are semi-transparent and they can be tailor-cut to provide sufficient transparency. Therefore, they can be used as "photovoltaic windows", which silicon PCs cannot. 3) DSPECs make a greater use of diffuse light than silicon PCs, thus increasing their efficiency. Any ray of light at any angle of incidence can in principle be absorbed by DSPECs, which does not hold for silicon PCs.

However, the liquid electrolyte present in DSPECs creates both short- and long-term sealing problems that weigh on final cost. For this reason, there has been a recent effort, made by several laboratories, to replace the liquid electrolyte by a solid thin film conductor. A few major research "schools" have treated this question. Thus, in some cases the electrolyte has been replaced by a hole-transporting organic material<sup>[9–11,13]</sup> while in another case a p-type semiconductor has been deposited on the TiO<sub>2</sub>-dye-sensitizer film.<sup>[4,14,15]</sup> Several researchers have replaced the liquid electrolyte by a solid thin-film organic polymer incorporating the redox couple.<sup>[6–8,16]</sup> We have followed a similar route but we have used the sol-gel process and SiO<sub>2</sub> as a gelling agent. In our first efforts, we produced a solid electrolyte by introducing I<sub>3</sub><sup>-</sup>/I<sup>-</sup> (I<sub>2</sub> and KI) into a matrix made by the sol-gel process by utilizing tetramethoxysilane (TMOS) and poly(ethylene glycol)-200. The mixture of these two materials provides a solid gel known as a class I nanocomposite material.<sup>[17]</sup> Employment of this gel in DSPECs using [RuL<sub>2</sub>(NCS)<sub>2</sub>] gave an overall photovoltaic efficiency of only 1.2 %.<sup>[3]</sup> This rather low efficiency comes from the fact that slow evaporation of volatile components entrapped in the gel during the sol-gel process leads to agglomeration and electric contact failure. We have subsequently found a successful solution to this problem by replacing class I by so-called class II nanocomposite materials,<sup>[17]</sup> that is, by using organically modified sol-gel precursors where the polyether chains and the silica chains are covalently bound. The final product, after sol-gel transformation, is composed of covalently linked SiO<sub>2</sub> and

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poly(alkylene oxide) networks, well mixed on the nanoscale. The link, in our case, is a urea bridge (ureasils).<sup>[18]</sup> These new precursors gave stable gels and high-efficiency DSPECs, the highest ever published with solid DSPECs.

We constructed DSPECs by the following procedure. We used low surface resistance indium tin oxide (ITO) glasses ( $<10 \Omega/\square$ ) and we deposited  $\text{TiO}_2$  mesoporous films on them by the reverse-micellar route.<sup>[3]</sup> Briefly, a reverse micellar solution containing 0.2 M Triton X-100 and 0.4 M water was prepared in cyclohexane. To this solution we added 0.2 M titanium isopropoxide under stirring. After a few minutes, an organic/inorganic nanocomposite film can be deposited on the ITO glass by dipping or spinning while a mesoporous anatase film can be obtained by slow heating up to  $450^\circ\text{C}$ . The procedure can be repeated several times in order to make films of about  $1.5 \mu\text{m}$  thickness. These films are transparent. The advantage of the present method is that it provides nanoparticles with sizes controlled in a narrow size range. Our experience with these systems has taught us that this is a very important parameter to take into account. Nanoparticles of different sizes correspond to different energy levels that create energy barriers inside the semiconductor film acting at the expense of conductivity and cell efficiency. For this reason we opted for the reverse-micellar route to make our titania films. The dye-sensitizer was attached on the titania film simply by dipping the hot films in an ethanolic solution of the dye and leaving to interact overnight.<sup>[3]</sup> Finally, the gel containing the redox couple ( $\text{I}_3^-/\text{I}^-$ ) and the platinized electrode were applied as described in the experimental section. The electrolyte gel was synthesized by the sol-gel route using various ureasil precursors. Optimal results were obtained with a precursor composed of a poly(propylene oxide) chain end-capped with triethoxysilane groups, henceforth abbreviated as PP-4000, the chemical structure of which is shown as **1** ( $n \sim 68$ ).

Gelation of this material was first attempted using acidified water, i.e., by a common and typical sol-gel procedure. However, in the course of time we have realized that HCl hydrolysis and gelation is so rapid with these materials that entrapment of solvent in the cell leads to poor cell performance. We then found that a gelation process based on catalysis by acetic acid (AcOH) gives a much improved quality of the final product. The data presented below have not been published before by us or any other researchers working with similar systems.

Temporal attenuated total reflection (ATR) IR measurements were performed to follow the sol-gel transition of PP-4000, catalyzed with either HCl or AcOH. Results revealed a much faster hydrolysis rate for the samples catalyzed with HCl. This was demonstrated by the absence of the SiOEt

group band<sup>[19]</sup> at  $954 \text{ cm}^{-1}$  less than 1 h after the addition of the HCl. The hydrolyzed ureasil gelled quickly and as a result EtOH was entrapped in the gels and could evaporate only very slowly. In contrast, EtOH evaporated much faster from gels catalyzed with AcOH due to the slower “hydrolysis” rate in this case. ATR spectra (Fig. 1) revealed that even 7 h after the addition of AcOH, the SiOEt stretching shoulder band at  $956 \text{ cm}^{-1}$  was still visible, while the EtOH bands ( $1050$  and

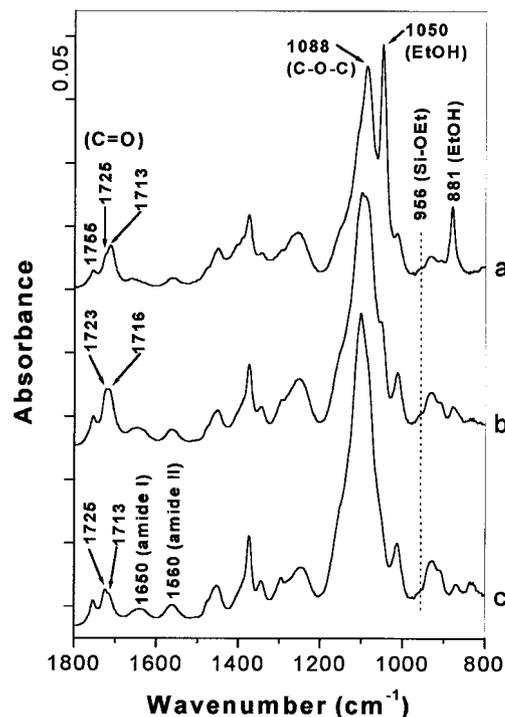
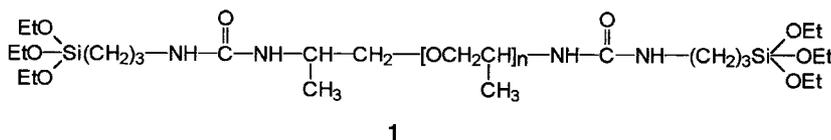


Fig. 1. IR ATR spectra of PP-4000 catalyzed with AcOH in the spectral range  $1800\text{--}800 \text{ cm}^{-1}$ : a) 1 h, b) 2 h, and c) 7 h after AcOH addition.

$881 \text{ cm}^{-1}$ ) rapidly declined. The temporal ATR spectra also confirmed the two-step reaction mechanism as was proposed by Pope and Mackenzie<sup>[20]</sup> for the acetic acid “hydrolysis” of tetraethoxysilane (TEOS). AcOH attacks alkoxy groups on silicon ( $\text{C}_2\text{H}_5\text{OSi}-$ ), forming a silica ester ( $\text{CH}_3\text{COOSi}-$ ) in the first step. During the second step the silica ester reacts with ethanol, producing ethyl acetate ( $\text{CH}_3\text{COOC}_2\text{H}_5$ ) and SiOH groups. The gradual formation of the silica ester in the first step of hydrolysis of ureasil was proved by the appearance of the band located between the C=O stretching of the AcOH cyclic dimer ( $1713 \text{ cm}^{-1}$ ) and the C=O stretching mode of the monomer ( $1755 \text{ cm}^{-1}$ ) in the corresponding ATR spectra (Fig. 1). This intermediate band at  $1725 \text{ cm}^{-1}$  is attributed to the silica ester carbonyl groups<sup>[21,22]</sup> and becomes stronger with the time of gelation relative to the  $1713 \text{ cm}^{-1}$  band. However, all the C=O stretching bands became weaker with the time of gelation as the second step of hydrolysis proceeded. In 24 h,  $\text{CH}_3\text{COOSi}-$  groups are consumed and in their place SiOH groups are formed together

**PP-4000 ( $n \sim 68$ )**



er with the free esters that continuously evaporate during gelation. We then believe that this slow gelation process in the absence of water produces a compact and uniform gel without any entrapment of liquid, which would finally reduce the quality of the gel.

Cell performance has been tested by illumination with a tungsten-halogen lamp, satisfactorily simulating the solar radiation spectrum on the surface of the earth. The cell was illuminated through the ITO glass, both the intensity of the incident light and its wavelength being controlled. The active cell area was 0.5 cm<sup>2</sup>. The efficiency of the photoelectrochemical conversion of the absorbed photons can be judged by measuring the so-called IPCE% value, which is given by<sup>[2,23]</sup>

$$\text{IPCE}\% = \frac{1240 \times I(\mu\text{A}/\text{cm}^2)}{\lambda(\text{nm}) \times P_{\text{inc}}(\text{W}/\text{m}^2)} \quad (1)$$

where  $P_{\text{inc}}$  is the incident light power at the wavelength  $\lambda$  and  $I$  the produced photocurrent. IPCE% thus gives, as a percentage, the number of electrons produced with respect to the number of photons absorbed. Figure 2 reveals that the maximum efficiency recorded for the present system was ~75 %.

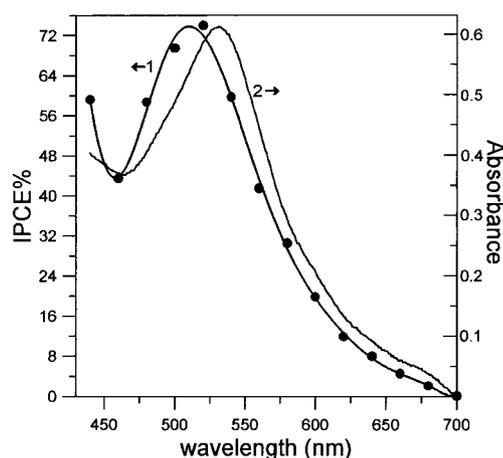


Fig. 2. IPCE% (1) and absorbance (2) curves of the cell.

This value is underestimated since it is measured under the assumption that all incident photons are absorbed, which is not true. If we take into account the maximum absorbance of the titania/dye film, which is 0.62 and corresponds to 76 % absorbance, it is obvious that the photoelectrochemical efficiency of our cell is practically 100 %. The IPCE% and the absorption spectrum do not strictly overlap but they are very close, indicating that the photoelectrochemical conversion is achieved through photosensitization, i.e., that photons are absorbed by the dye and the excited electrons are transferred to the conduction band of the semiconductor.

Figure 3 shows the current–voltage relationship of the cell. These data were obtained with the following procedure: a variable resistor was connected in parallel with the cell and current and voltage were measured at different resistance values. Figure 3 shows that the open-circuit voltage, produced at an illumination intensity of 90 mW/cm<sup>2</sup>, was 0.62 V, while the

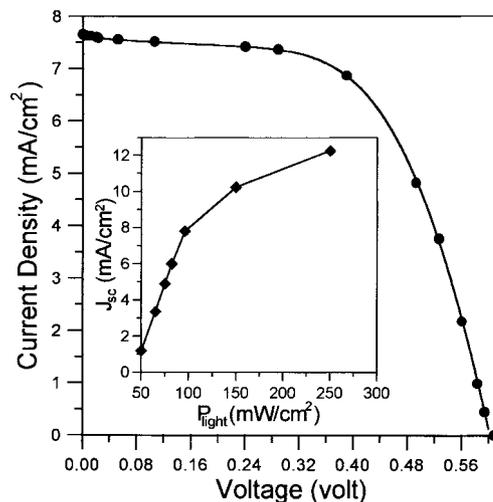


Fig. 3.  $I$ - $V$  curve. The evolution of short-circuit current with incident light intensity is inset.

short-circuit current density was 7.8 mA/cm<sup>2</sup>. The overall efficiency of the cell is given by the ratio of the produced power to the incident power, which is usually calculated from the data of the diagram of Figure 3 according to<sup>[23,24]</sup>

$$\eta\% = \frac{I_{\text{sc}} V_{\text{oc}} ff}{P_{\text{inc}}} 100 \quad (2)$$

where  $I_{\text{sc}}$  is the short-circuit current (7.8 mA in our case),  $V_{\text{oc}}$  is the open circuit voltage of the cell (0.62 V in our case) and  $ff$  is the so-called fill factor, which was calculated from the above diagram for the maximum product  $IV$  divided by the product  $I_{\text{sc}} V_{\text{oc}}$  (0.71 in our case). Thus the overall efficiency of the cell was ~4 %, i.e., a satisfactory value, considering that the maximum DSPEC efficiency recorded so far (with a liquid-electrolyte cell, where the charge mobility is higher) is 10 %.<sup>[2]</sup> The performance of the above cell was also satisfactory with respect to the level of illumination. Thus, in the inset of Figure 3, we see a continuous increase of current with light intensity up to air mass (AM) 1.5 (96 mW/cm<sup>2</sup>, i.e., 1 sun). At higher intensities, the cell approaches saturation, but this is not a problem.

In conclusion, we have constructed a solid-state DSPEC by using a nanocomposite ureasil gel as an electrolyte support. The application of the gel in a thin sandwich configuration is made through the sol–gel method. The quality of the gel electrolyte is guaranteed simply through acetic acid catalysis in the absence of water. The overall cell efficiency was 4 %, which is higher than in any other solid-state device recorded so far.

### Experimental

All chemicals used in the present work were from Aldrich and Merck. *cis*-Di(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) dihydrate [2] [RuL<sub>2</sub>(NCS)<sub>2</sub>] was provided by Solaronix SA (rue de l'Ouriette 129, CH-1170 Aubonne VD, Switzerland). Millipore water was used in all experiments. Optically transparent electrodes were cut from an indium tin oxide (ITO) coated glass (<10 Ω/□) purchased from Pilkington-Flabeg, Germany.

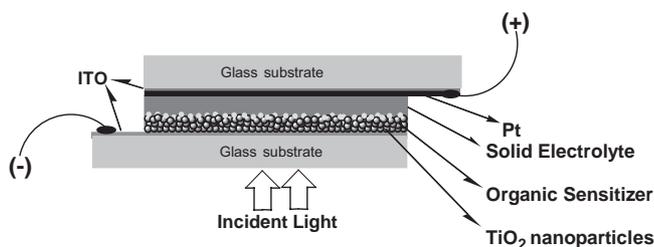


Fig. 4. Schematic cross section of the DSPEC.

ATR IR spectra were measured on a Fourier transform infrared (FTIR) Perkin-Elmer System 2000 spectrometer equipped with a SpectraTech horizontal ATR cell (60° incident angle, Ge ATR crystal).

Titanium dioxide mesoporous films were deposited on ITO glass by the reverse-micellar route and the photosensitizer RuL<sub>2</sub>(NCS)<sub>2</sub> was attached as in [3]. The ureasil precursors were synthesized as in [18]. Synthesis of class II nanocomposite gels using ureasil precursors, their enrichment with the iodine/iodide couple, and their deposition in a DSPEC was carried out as follows: absolute ethanol (2 mL) was mixed with the ureasil precursor (PP-4000, 2 g). KI (0.5 M) and I<sub>2</sub> (0.05 M) were added to the above mixture with stirring at ambient conditions. The mixture was continuously stirred for about 3 h. Then acetic acid (0.35 mL) was added and stirring continued for another 4 h at ambient conditions. At the end of this period, a viscous brown fluid was obtained. A few drops of this solution were applied to the electrode-bearing TiO<sub>2</sub> film with attached dye and we placed the second (platinized) electrode on top, simply by pressing the two electrodes together. Connections were made with silver paste and a copper ribbon as seen schematically in Figure 4.

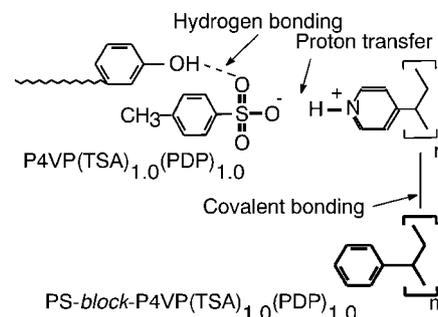
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## Tridirectional Protonic Conductivity in Soft Materials\*\*

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Hierarchical polymeric materials, with *structure-within-structure* morphologies, have attracted interest due to their potential as functional materials.<sup>[1]</sup> For this work, we constructed an assembly of nanoscale protonically conducting “wires” using hierarchical self-organization of polymeric supramolecules. The supramolecules consist of poly(styrene)-*block*-poly(4-vinyl pyridine), PS-*block*-P4VP, where the latter block forms a stoichiometric acid–base complex with toluene sulfonic acid (TSA), which is in turn stoichiometrically hydrogen bonded with 3-*n*-pentadecylphenol (PDP), to form PS-*block*-P4VP(TSA)<sub>1.0</sub>(PDP)<sub>1.0</sub>, Scheme 1. In an effort to achieve “a monodomain”, the local structures are aligned



Scheme 1.

globally by shear flow and the conductivity is enhanced. Protonic transport is macroscopically tridirectional, and largest along the “wires”, both below and above the glass transition point. The nanoscale structures thus allow tuning of the protonic conductivity and anisotropy in soft materials once the structures have been globally aligned.

Electroactive polymers range from conjugated polymers<sup>[2]</sup> to ionic and protonic conducting<sup>[3]</sup> materials. They allow conceptually new applications to be realized with a flexibility of the products, as well as new processing and design opportu-

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