Dye-sensitized photoelectrochemical solar cells based on nanocomposite organic–inorganic materials

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Abstract

Dye-sensitized photoelectrochemical solar cells have been constructed by using nanocomposite organic–inorganic sol–gel electrolytes and a titania nanocrystalline film also based on a sol–gel nanocomposite material. Among other advantages connected with nanocomposite electrolytes is the balance between hydrophilic and hydrophobic domains that allows reducing polarity-connected repulsive forces developing between the titania-dye system and the electrolyte. The overall efficiencies of these cells range between 5 and 6% under $100\,mW/cm^2$ illumination (equivalent to 1 sun at AM1.5).
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1. Introduction

Dye-sensitized photoelectrochemical solar cells (DSSC) are considered the best so far low cost alternative to amorphous silicon photovoltaic cells. The components of a DSSC have more or less been standardized and they are a TiO_2 nanocrystalline film deposited on a SnO_2:F transparent conductive electrode (negative electrode), a ruthenium bipyridyl derivative adsorbed and chemically anchored on TiO_2 nanocrystallites, an electrolyte bearing the $I_3{}^-/I^-$ redox couple and a platinized SnO_2:F electrode (positive electrode) [1]. A large volume of the recent works on DSSCs is devoted to the study of the physicochemical state of the electrolyte. This is dictated by some concern that has been expressed as to the long term sealing problems as well as stability and durability of liquid electrolytes [2–8]. Most researchers have chosen to introduce gelifiers into the electrolyte, thus making the so-called quasi-solid state DSSCs [2–4]. Even though, introduction of gelifiers seems to decrease the solvent leakage problem, still cells must be additionally sealed [9] and this represents an extra cost on cell fabrication. We have chosen a different approach to deal with the same question [7,8,10,11]. We make DSSCs with electrolyte supported in a nanocomposite organic–inorganic gel, where the inorganic subphase consists of silica synthesized by the sol–gel procedure [7,8,10,11]. The advantages of the sol–gel electrolytes are numerous: (1) cells containing a sol–gel electrolyte are practically solid devices made of solid components; (2) sol–gel silica is an adhesive material that holds the two electrodes together. This makes cell fabrication very easy. It suffices to place a drop of the sol on the top of the SnO_2:F–TiO_2-dye electrode and press the Pt–SnO_2:F electrode by hand on the top. The drop spreads over the opposing surfaces of the electrodes and binds them together through –O–Si–O– bonds. (3) Since at the initial stage the sol is fluid, it penetrates into the titania nanoporous structure and ensures electrical conduct between titania nanocrystallites and the electrolyte; (4) the nanocomposite material that spreads between the two electrodes prevents short-circuit at the same time acquiring optimal minimal thickness, as the two electrodes are pressed together, thus providing optimal operation conditions and high efficiency at low fabrication cost. What makes electrolyte function in such a gel is that it is "dissolved" in the organic subphase. The latter is usually and mainly composed of poly (ethylene oxide), a well-known ionic conductor, and of an appropriate organic solvent. Solvent mixture with the organic subphase is made at a molecular or supramolecular level so that it is maintained within the structure by strong attractive interactions without any chance of leakage. In addition, even at

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large organic loading, silica network is so robust that the whole structure of the material is practically solid. As reported in previous publications [7,8], cells made of sol–gel nanocomposite electrolytes are efficient and durable. Model cells are functioning for years with overall conversion efficiency ranging between 5 and 6%. In the present work we describe some construction protocols of such cells and present some additional advantages associated with the employment of sol–gel nanocomposite electrolytes. We believe that these data establish these materials as the best choice for solid DSSC.
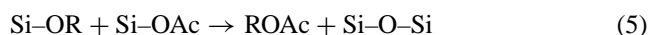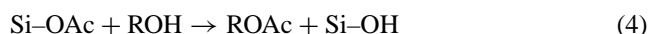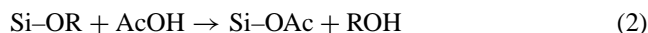
2. Experimental

All reagents were from Aldrich except *cis*-bis(isothiocyanato)bis(2, 2′-bipyridyl - 4, 4′-dicarboxylato)-ruthenium(II) [RuL$_2$(NCS)$_2$] which was provided by Solaronix SA (Switzerland). SnO$_2$:F transparent conductive electrodes (8 Ω/□) were purchased from Hartford Glass Co., USA.

Synthesis of ureasil PPO-230 has been repeatedly described in previous publications [12]. *N*-[3-(Triethoxy-λ^4-silyl)propyl]-1*H*-benzimidazole-1-carboxamide (ICS-BIM) was synthesized by mixing isocyanatopropyltriethoxysilane and benzimidazole in anhydrous tetrahydrofurane and refluxing for 8 h. The product was isolated by vacuum distillation. Synthesis of 3-[2-(2-methoxyethoxy)ethyl]-1-methyl-1*H*-imidazol-3-ium iodide (MEOII) was carried out by the following steps. First, 1-iodo-2-(2-methoxyethoxy)-ethane was prepared from 2-(2-methoxyethoxy)ethanol via tosyl ester [13]: 34.75 g of tosyl chloride was added to 10.22 g of KOH in diethyl ether. To this mixture 25.5 g of 2-(2-methoxyethoxy)ethanol was added drop wise. The mixture was then refluxed for 1 day. Suspension was filtered and ether was removed by vacuum distillation. 1-Iodo-2-(2-methoxyethoxy)ethane was obtained via simple exchange with NaI. Finally, this iodo derivate and 1-methylimidazole were dissolved in 1,1,1-trichloroethane and refluxed for 5 h. The solvent was decanted and ionic liquid was washed twice with ether and dried by vacuum distillation.

Materials deposition and cell construction is explained in Section 3. *I–V* curves have been recorded by connecting the cell to an external variable resistor and by measuring the current flowing through the resistor and the corresponding voltage across the resistor. Cell dimension for these measurements was 1 cm^2. Illumination was done by an Oriel 450 W xenon lamp. Control of intensity of incident light was obtained with superposed multiple wire grids. Illumination intensity was 100 mW/cm^2, which corresponds to 1 sun at AM1.5. Outdoors experiments using natural sunlight (performed in Patras, Greece) gave similar results with simulated light of equivalent intensity. UV–vis absorption measurements were made with a Cary 1E spectrophotometer. The equilibrium contact angle was measured by the sessile drop method and by using a stereoscope and computer image analysis.

3. Results and discussion

DSSCs cannot function without a sufficiently expanded organic subphase [8]. This is due to two reasons: (1) ionic conductivity is made possible only through the organic subphase; (2) the organic subphase penetrates into the titania nanoporous structure and ensures electrical conduct with an optimal number of nanocrystallites. It has been found that among the most efficient protocols for organic subphase composition is a mixture of polyether-chain-bearing non-ionic surfactants, like Triton X-100 [11], with an appropriate solvent. Another possibility is to use polyether chains covalently connected to silica mixed with some solvent. A large number of solvents have been tested as well as several sol–gel nanocomposites. Very good results have been obtained with a combination of ureasil with sulfolane [8]. Ureasils are precursors of sol–gel nanocomposites and they are composed of a short poly(ethylene oxide) chain end-capped through urea bridges with triethoxysilane groups (Fig. 1). Optimal results have been obtained with ureasils bearing a short polyether chain of only three ether groups (PPO230). Polymerization occurs by hydrolysis or organic acid solvolysis through the following possible reaction routes [12] (one alkoxide group is shown for reasons of simplicity):

$$Si–OR + H_2O \rightarrow Si–OH + ROH \tag{1}$$

$$Si–OR + AcOH \rightarrow Si–OAc + ROH \tag{2}$$

$$ROH + AcOH \rightarrow ROAc + H_2O \tag{3}$$

$$Si–OAc + ROH \rightarrow ROAc + Si–OH \tag{4}$$

$$Si–OR + Si–OAc \rightarrow ROAc + Si–O–Si \tag{5}$$

where R is a short aliphatic group (ethyl or isopropyl, in our case). The highly reactive Si–OH, created by hydrolysis reaction 1 can polymerize (Si–O–Si) and lead to gelation while some limited polymerization can be also obtained through reaction 5. In any case, gelation is mainly obtained through the hydrolysis route [12]. The sol is exposed to ambient conditions so that hydrolysis can be obtained even in the absence of added water, either by ambient humidity or by water produced through the esterification reaction (3). Sulfolane, or any other solvent as well as potassium iodide salt and iodine are added to the original sol. Optimal concentration conditions have been studied and reported in previous works [7,8,11]. In a typical preparation, 4 g of a solution containing 30 wt.% PPO230 and 70 wt.% sulfolane were mixed with 0.7 g of glacial acetic acid as well as with of KI and I$_2$ at concentrations 0.5 and 0.05 M, respectively, under vigorous stirring. The waiting time before sol application was approximately 24 h. The sol then was a viscous fluid but solidified fast after application due to further exposure to ambient humidity. Sulfolane, also known as tetramethylene sulfone (Fig. 1), is a high dielectric constant (43.16) [14] non-protic solvent, it has a high boiling point (285 °C) and it is a good solvent for both KI and I$_2$. Its strong electron
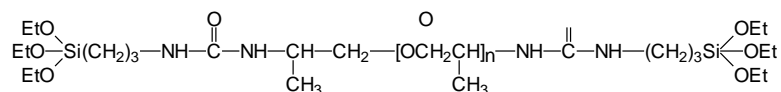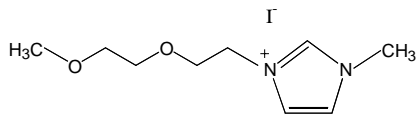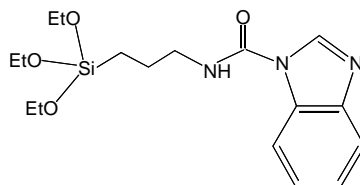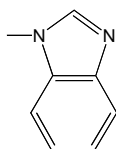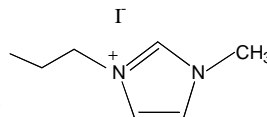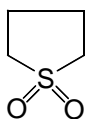
PPO 230(n ~ 3)

MEOII

ICS-BIM

NMBI

MPII

Sulfolane

Fig. 1. Chemical structure of the main reagents used.

donating properties make this solvent favor triodide formation [15], $I_3{}^-$, which is the main ionic conductivity vehicle through the cathodic dark reaction $I_3{}^- + 2e^- \rightarrow 3I^-$ on the counter electrode [8].

The titania nanocrystalline films used in this work have also been deposited through sol–gel nanocomposite materials. Sols were prepared by mixing acetic acid, titanium isopropoxide and the surfactant Triton X-100 at various proportions. Gelation is obtained by the same reaction routes ((1)–(5)) presented above. In an optimal preparation protocol, 3 g of EtOH were mixed with 0.7 g Triton X-100. Then 0.61 ml AcOH and 0.36 ml titanium isopropoxide [Ti(OiPr)$_4$] were mixed in this order under vigorous stirring and at ambient conditions. After 5 min of stirring (sol–gel procedure in the presence of titanium isopropoxide is a very fast process), the sol was deposited on the SnO_2:F electrode and titania nanocrystallites could be obtained by calcination at 550 °C. The obtained films were transparent and relatively thin (~2 μm) but they have high active surface area and excellent nanocrystallinity [16,17]. Indeed, BET nitrogen measurements performed on films gave an area of about 115 m^2/g, which is unique for such high calcination temperature. Films gave a well-defined X-ray diffractogram revealing particles of size of about 11 nm and composition

of 35% rutile–65% anatase. These films had a very high adsorption capacity for *cis*-bis (isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) [RuL$_2$(NSC)$_2$], the dye-sensitizer employed in this work. This is seen by the absorption spectrum of Fig. 2. Absorbance at maximum over passed 80%. Cells made by the simple as above procedure, produced the *I–V* curve of Fig. 3 and gave [8] an overall efficiency of 5.3%.

These results promote nanocomposite gels as choice materials for synthesizing both electrolyte supports and TiO$_2$ nanocrystalline films for application with DSSCs. The nanocomposite nature of the gels and the coexistence of hydrophilic–hydrophobic domains within their structure offer them additional advantages, as it will be seen by the following results. A lot of research dealing with DSSCs is recently also devoted to the study of molten iodide salts, for example, alkylimidazolium iodide salts as alternative fluid materials to substitute alkaline iodide solutions [6,11,18,19]. Molten salts offer several advantages for solving stability problems, such as low solubility of alkaline iodides and subsequent crystallization and precipitation [11]. Alkylimidazolium iodide molten salts are usually accompanied by 1-methylbenzimidazole (NMBI) [11,19] a substance that offers higher open-circuit voltage V_{oc} and improved
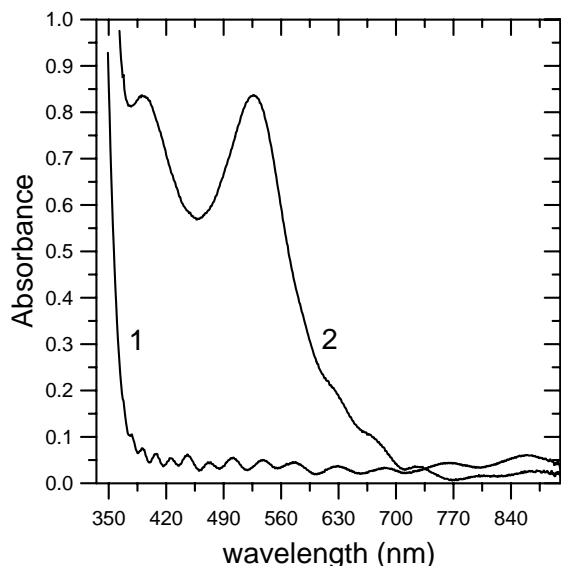
Fig. 2. Absorption spectrum of the titania film without (1) and with adsorbed $RuL_2(NSC)_2$ (2).

Fig. 3. I–V curve for a DSSC made by employing a nanocomposite electrolyte containing ureasil PPO230 and sulfolane.

fill factors. Such substances have been tested in sol–gel nanocomposite electrolytes [11]. We have synthesized derivatives of imidazolium salt and benzylimidazole, i.e., 3-[2-(2-methoxyethoxy)ethyl]-1-methyl-1H-imidazol-3-ium iodide (MEOII) and N-[3-(triethoxy-λ^4-silyl)propyl]-1H-benzimidazole-1-carboxamide (ICS-BIM), giving the structures shown in Fig. 1. Thus MEOII bears a methoxyethoxy group while ICS-BIM contains a benzimidazole group bound through a urea bridge with a triethoxysilane group. 1-Methyl-3-propylimidazolium iodide (MPII) [11] and NMBI have also been tested for comparison. Cells made by employing three characteristic electrolyte compositions but the same electrode structure gave the data listed in Table 1. Electrolyte #1 is a liquid electrolyte where the additive NMBI and iodine are dissolved in MEOII, the source of I^-. Its efficiency was substantially lower than that of electrolytes #2 and #3, even though, the latter are gels, due to sol–gel polymerization of ICS-BIM, particularly, electrolyte #3 where an additional gelifier, tetramethoxysilane (TMOS) has been added. This is rather surprising since gels are expected to give lower currents due to lower conductivity, owing to lower fluidity. The increase of the efficiency with higher open circuit voltage V_{oc} and higher short circuit current density J_{sc} is due to a rather intriguing phenomenon. Fig. 4 shows contact angle (CA) measurements of drops of water and various electrolytes on the surface of the titania nanocrystalline film

after dye ($RuL_2(NSC)_2$) adsorption. Water on titania film in the absence of the dye gives CA equal to zero (not shown) since the surface of these films is very hydrophilic. When, however, the dye was adsorbed, the surface became very hydrophobic giving water CA = 55.0°. Alkylimidazolium iodide molten salts, for example, MPII, gave an even higher contact angle CA = 59.3°. The presently synthesized MEOII gave a smaller value of CA but it was still high: CA = 47.2°. Both MPII and MEOII are amphiphilic in nature, however, it seems that in interacting with the titania/dye surface, repulsive forces prevail. On the contrary, when the sol leading to nanocomposite electrolyte was placed on the titania-dye surface a dramatic drop of the value of the contact angle was detected: CA = 25.4°, making interaction between the two materials more efficient. Obviously the accommodation of the organic subphase within the nanocomposite material, the harmony of coexistence of hydrophobic and hydrophilic domains and the development of –O–Si–O– bonds offer additional advantage to these materials. Previous works attempt to give a solution to the problem of polarity-connected repulsive forces by introducing amphiphilic additives [20]. Nanocomposite materials offer solutions by themselves.

Finally, it must be stressed that nanocomposite electrolytes are not only good to employ with DSSCs but they are equally good with other systems, for example, electrochromic cells [21].

Table 1
Efficiency data of DSSC at various electrolyte compositions

Electrolyte composition	V_{oc} (V)	J_{sc} (mA/cm²)	ff	η (%)
(1) MEOII + NMBI (0.5 M) + I_2 (0.5 M)	0.76	10.02	0.68	4.8
(2) 1 ml ICS-BIM + 2 ml sulfolane + 0.7 ml AcOH + 0.6 M MEOII + 0.06 M I_2	0.78	12.60	0.69	6.0
(3) 1 ml ICS-BIM + 0.15 ml TMOS + 2 ml sulfolane 0.7 + ml AcOH + 0.6 M MEOII + 0.06 M I_2	0.79	10.92	0.68	5.4

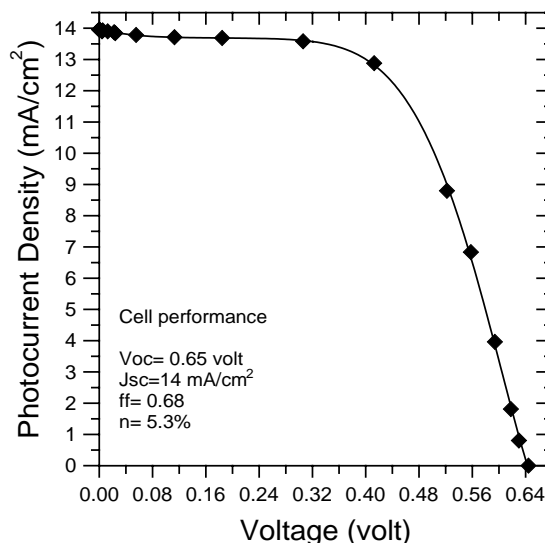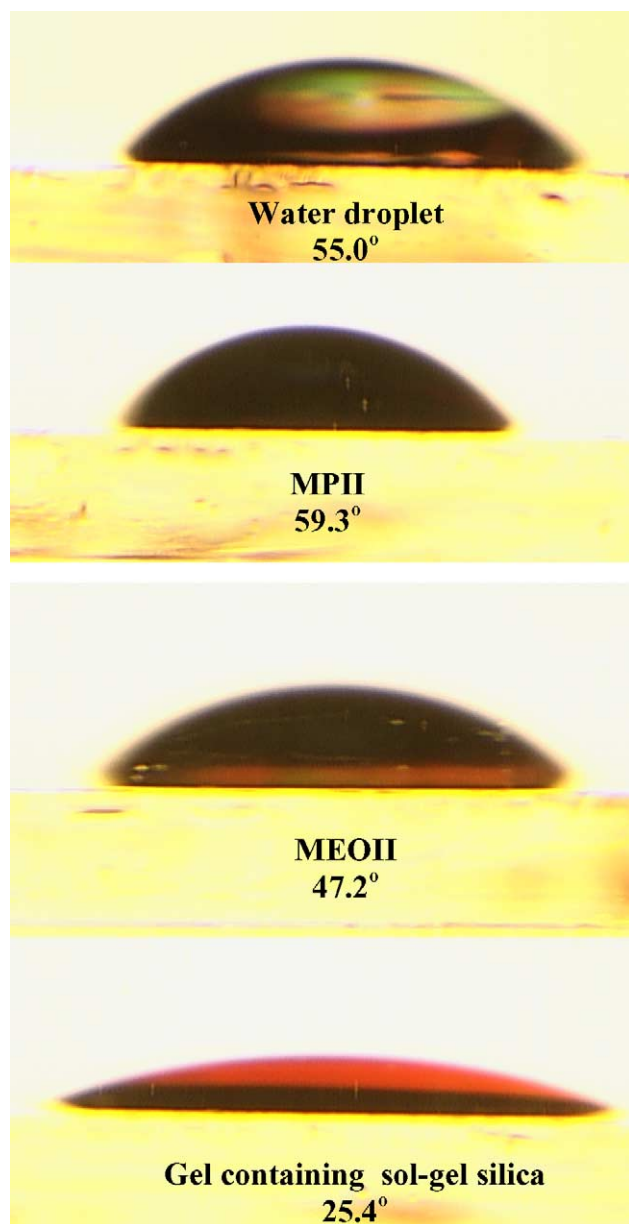V_{oc} = open circuit voltage; J_{sc} = short circuit current density; ff = fill factor

Fig. 4. Contact angles of various fluids on the TiO_2^- $RuL_2(NSC)_2$ surface.

4. Conclusion

Nanocomposite organic–inorganic gel electrolytes made by the sol–gel method incorporating the redox couple I_3^-/I^- have been successfully employed with dye-sensitized solar cells providing an overall efficiency that ranges between 5 and 6%. The contact angle between the semiconductor-dye-sensitizer electrode and the electrolyte is very small when nanocomposite materials are used. The nanocomposite organic–inorganic materials provide a balance between hydrophilic and hydrophobic domains and allow reduction of polarity-connected repulsive forces thus offering higher cell efficiency.

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