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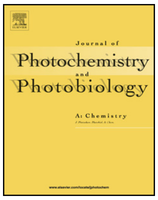

TiO_2/graphene nanocomposite layers for improving the performances of dye-sensitized solar cells using a cobalt redox shuttle

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ABSTRACT

Progresses in dye-sensitized solar cells (DSSCs) have revealed limitations due to I^-/I_3^- redox shuttle and the necessity of its replacement. Cobalt-complexe redox species are the most promising alternatives for the application. In the present work, we have optimized the preparation of solar cells based on a Co-complex redox shuttle and Z907 Ru-complex dye. The system has been studied using pristine TiO_2 and TiO_2_single-layered graphene composite mesoporous layers for the electron transport. Our results on TiO_2_graphene are promising since these cells, with the cobalt redox electrolyte, yielded to a power conversion efficiency close to that of a TiO_2 photoelectrode combined with the iodine electrolyte. Using the nanocomposite layers permitted a significant increase in the photoelectrode specific surface area, dye loading and then cell short circuit current (J_{sc}). Moreover, the use of $[Co(phen)_3]^{2+/3+}$ improved the cell V_{oc} due to a higher standard redox potential. However a limitation was found due to a shift of the TiO_2 conduction band towards lower energy. Impedance spectroscopy study of the systems revealed a higher recombination rate for the Cobalt electrolyte and that the photoelectrode conductivity was slightly increased by adding graphene. It is shown that, even if improved in the presence of graphene, the charge collection efficiency was lower for the cobalt electrolyte compared to the iodide one. Globaly graphene improved the DSSC performance mainly due to the enlargement of the photoelectrode specific surface area and then of the dye loading.

1. Introduction

Solar light, as an abundant and renewable source of energy, is the most promising candidate to replace fossil resources. Consequently, the development of researches on photovoltaic devices which convert the solar energy into electricity is of utmost importance. Dye-Sensitized Solar Cells (DSSCs) are photovoltaic systems that have attracted great attention due to a cost-effective and simple fabrication [1–7]. They are based on an oxide semiconductor layer combined to organic or organo-metallic dyes, an electrolyte containing a redox couple and a counter-electrode [1–12]. Compared to silicon solar cells, DSSCs can generate electrical power with a high efficiency from weak indoor light and is less dependent on the angle of incident light. Since the pioneering work by O'Regan and Grätzel published in 1991, I^-/I_3^- redox couple has been used as the main redox shuttle in electrolyte for DSSCs [1]. Progresses in DSSC research have revealed that I^-/I_3^-redox shuttle should be replaced due to corrosive properties towards metals including Ag, Au and Cu, that makes the material selection for DSSC module very limited. Other disadvantages include light absorption in the 350–450 nm wavelength region and a low redox potential value which restricts the open circuit voltage in the DSSCs [13–15].

Cobalt (II)/(III) complex redox couples have emerged as the major candidates to replace I^-/I_3^- and have been used in recent record efficiency DSSCs [13–15]. They have promising properties such as low absorbance in the 350–450 nm wavelength region and low-corrosive properties. Moreover, by changing the ligands or by adding certain groups to ligands, the shuttle can be fitted to the dye ground state potential to favor the dye regeneration with a minimal overpotential loss [13,15–17]. On the other hand, cobalt (II)/(III) complexes have a bulky structure that hinders mass transport through the photoelectrode and the rapid recombination of electron in TiO_2 conduction band to the cobalt (III) species has been reported [7,13,18,19]. Some efforts have been made to overcome the limitation of cobalt-based DSSCs. The utilization of thin and more porous photoelectrodes is required to facilitate mass transport of cobalt redox species [11,14,18]. In some studies, the TiO_2 surface was covered by a thin alumina layer to passivate it. Alumina was reported to inhibit the recombination of electrons by

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acting as a barrier between electrons in the conduction band and the redox mediator [20]. Employing dyes that contain long alkyl chain or bulky alkoxy groups can also restrain the charge recombination at the TiO_2/electrolyte interface [14,18,21,22]. One of the best cobalt-based DSSC developed until now employed a donor-pi-bridged-acceptor (D-π-A) porphyrin dye endowing with alkoxy group as sensitizers for cobalt based DSSC, and reached more than 12% of efficiency [6].

Graphene is a real two-dimensional material that can be prepared with a single atomic layer thickness which is characterized by a very high electronic conductivity, transparency and thermal stability [23,24]. For the DSSC application, it has been reported that the addition of graphene into the TiO_2 layer can increase the short circuit current (J_{sc}) [25–33]. The beneficial effect of graphene has been assigned to: (i) an increase in the photoelectrode surface area that improves their dye loading [27,32,33], (ii) a role as a structuring agent that builds larger pores in the photoelectrode thus finally facilitating the diffusion of the redox shuttles [29]. (iii) The work function of graphene (−4.4 −4.5 eV) is localized below the conduction band of TiO_2 (−4.2 eV) that could favour the charge extraction from TiO_2 [27,32]. (iv) Graphene increases the conductivity of the photoelectrode layer [33] then yields a faster transport of the charges to the front contact [27]. In our previous report we have shown that the addition of an optimized concentration of 1.2 wt.% of graphene to TiO_2 photoelectrode can significantly increase the layer conductivity [33]. This result encouraged us to couple cobalt redox shuttles to TiO_2/graphene photoelectrodes. The enhancement of electron transport in photoelectrode due to the addition of graphene is promising to limit the recombination of electron at the photoelectrode and electrolyte interface which is a problem in cobalt-based DSSC.

In the present paper, we investigate the performances, properties and functioning of DSSCs based on the pure TiO_2 and TiO_2/graphene, and we compare the use of electrolytes containing I^-/I_3^- and $[Co(Phen)_3]^{2+/3+}$ redox couples. The photoelectrodes were sensitized by the Z907 ruthenium-complex dye which contains two long C9 alkyl chains on one of the bipyridine ligand (Schematic S1, Supplementary Material) and is then suitable for the two studied redox couples. The cells were in-depth investigated using the impedance spectroscopy (IS) technique which has proven to be a powerful mean to extract the key cell functioning parameters and to understand the electron dynamics in the photoelectrodes [4,34].

2. Material and methods

2.1. Film preparation

A viscous paste was created using the TiO_2 particles mixed or not with single-layered graphene oxide sheets (SLG) purchased from CheapTubes [35–37]. 1 g of TiO_2 nanoparticles prepared according to Ref. [38]. was mixed with 4.06 g of terpineol and 5 mL of ethanol under vigorous agitation. In the case of composite layers, 1.2% (wt) amount of single-layered graphene oxide were added into the mixture [33]. 281 mg of ethyl cellulose (EC) powder (5–15 mPa s) and 219 mg of EC (30–50mPa s) were dissolved in 4.5 mL of ethanol. The two solutions were then mixed and sonicated several times using an ultrasonic horn. Afterwards, ethanol was removed in a rotary-evaporator at a temperature of 58 °C in order to create a viscous paste [38].

FTO glass substrates (TEC15, Pilkington) were cleaned-up with soap and rinsed with distilled water. Then, they were treated in an ultrasonic bath in acetone for 5 min and in ethanol for 5 min. The substrates were dried and placed in a 450 °C furnace for 30 min. After cooling down, they were immersed in a 40 mmol L^{-1} aqueous solution of $TiCl_4$ at 70 °C for 30 min and rinsed with water and ethanol, before to be heated for 30 min at 500 °C (This step was done twice) [38]. A layer of TiO_2/SLG paste was coated on the conducting glass substrates by the doctor blading technique, relaxed and dried at 125 °C for 5 min. The step was repeated several times in order to achieve the accurate film thickness. The films were then annealed at 500 °C for 15 min. They were subsequently treated in a 40 mmol L^{-1} $TiCl_4$ solution at 70 °C for 30 min and annealed again at 500 °C. The related TiO_2/graphene composite porous layers are hereafter denoted TiO_2_SLG.

The BET specific surface area of the films was determined from the adsorption isotherms of Kr at the boiling point of liquid nitrogen (approx. 77 K) using a Micromeritics ASAP 2010 apparatus [39,40]. The film porosity (p) was estimated by mass and thickness measurements equal to 0.62. The optical film properties (total transmission and total reflection) were recorded with a Carry 5000 UV-VIS-NIR spectrophotometer equipped with an integrating sphere.

2.2. Synthesis of cobalt (II) complexes

$[Co(bpy)_3](PF_6)_2$ and $[Co(phen)_3](PF_6)_2$ were synthesized by adding drop-by-drop a molar excess of ligand ethanolic solution to an ethanolic solution of cobalt (II) chloride hexahydrate under heating at 70 °C and vigorous stirring. The initially blue solution became red. Heating and stirring were maintained during 1 h and then the mixture was cooled to room temperature. The complex was subsequently precipitated by addition of a saturated aqueous solution of NH_4PF_6. Small orange crystals appeared. They were filtered and washed with diethyl ether [41]. NMR spectroscopy measurement. More details are given in the Supplementary Material, section A. The synthesized products were identified by 1H NMR spectroscopy measurement.

2.3. Solar cell preparation and characterizations

The TiO_2 and composite layers were immersed upon cooling in a 0.3 mmol L^{-1} Z907 dye solution in a mixture of acetonitrile and *tert*-butanol (1:1) and kept in the dark at room temperature for 24 h. For the counter-electrode preparation, FTO glass substrates were cleaned by ultrasound in acetone and ethanol for 5 min each. Then, they were treated in a furnace for 30 min at 450 °C to remove organic contaminants. The Pt catalyst was deposited by spreading a H_2PtCl_6 solution (6 mg in 1 mL ethanol) on the FTO glass and heating at 400 °C for 20 min. This step was repeated once. The two electrodes were sealed with a 50 μm hotmelt spacer (Surlyn, DuPont) and the internal space was filled with the electrolyte through a hole made in the counter electrode, which was subsequently sealed with Surlyn and an aluminum foil. Two different electrolytes were tested. The I-El electrolyte consisted of 0.6 mol L^{-1} 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 mol L^{-1} LiI, 0.05 mol L^{-1} I_2, and 0.2 mol L^{-1} 4-tertbutylpyridine in a mixture of acetonitrile and valeronitrile (85/15 volume ratio). The Co-El electrolyte with the Co^{2+}/Co^{3+} redox couple consisted of 0.11 mol L^{-1} $[Co(Phen)_3](PF_6)_2$, 0.022 M of $NOBF_4$ (used as an oxidant to obtain $[Co(phen)_3]^{3+}$), 0.1 mol L^{-1} $LiClO_4$ and 0.2 mol L^{-1} 4-tertbutylpyridine (TBP) in acetonitrile. The dye loading of the photoelectrode was determined by spectrophotometry, after complete dye desorption from a sensitized layer of TiO_2 into 4 mL of 10 mM tetrabutyl ammonium hydroxide (TBAOH) in ethanol [42]. The electrochemical potential difference measured between the latter and the former electrolyte was 270 mV.

The I–V curves were recorded by a Keithley 2400 digital sourcemeter, using a 0.01 V s^{-1} voltage sweep rate. The solar cells were illuminated with a solar simulator (Abet Technology Sun 2000) filtered to mimic AM 1.5 G conditions. The illuminated