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A novel and large area suitable water-based ink for the deposition of cobalt sulfide films for solar energy conversion with iodine-free electrolytes

Mirko Congiu [a,*], Alessandro Lanuti [b,1], Aldo di Carlo [b,1], Carlos F.O. Graeff [a,c]

[a] UNESP–Univ. Estadual Paulista, POSMAT-Programa de Pós-Graduação em Ciência e Tecnologia de Materiais, Av. Eng. Luiz Edmundo Carrijo Coube 14-01, Bauru, SP 17033-360, Brazil

[b] CHOSE—Centre for Hybrid and Organic Solar Energy, Department of Electronic Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy

[c] Department of Physics, Faculty of Sciences-UNESP, Bauru, SP, Brazil

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Abstract

A novel, cheap, reliable water based precursor ink has been used for the large scale production of amorphous cobalt sulfide (CoS) on fluorine doped tin oxide (FTO). The method uses a metal–organic complex of Co(II) and thioglycolic acid (TGA), it is cheap and easy to prepare. The electrodes prepared using our method have been applied in the oxidation/reduction using different redox couples dissolved in liquid electrolytes containing: I^-/I_3^-; ferrocene/ferrocenium; bipyridine $[Co(bpy)_3]^{2+/3+}$ complexes and sodium polysulfide. The composition, morphology and the efficiency of the CoS electrodes have been investigated. The CoS films show a good adherence to the substrate, good transparency and an excellent electrocatalytic efficiency with all of the different redox electrolytes. The electrodes have been used in DSSC devices using the organic dye D5 with efficiencies up to 6.8%.

Keywords: Iodine-free; Electrolytes; DSSC; Cobalt sulfide

1. Introduction

Dye sensitized solar cell (DSSC) (O'regan and Grätzel, 1991) is a very interesting technology due the facility of production, good efficiencies up to 13% (Mathew et al., 2014) and low costs. A typical DSSC consists of a dye, responsible for the light absorption, anchored to a wide band-gap semiconductor, such as TiO_2. The photocurrent is generated by the injection of electrons into the conduction band of the n-type TiO_2. After the charge injection, the dye is regenerated by a redox couple, dissolved in a liquid electrolyte. The redox couple is finally regenerated on the surface of the counter electrode, ensuring the continuous functioning of the device. The I^-/I_3^- redox couple is generally used, in DSSCs electrolytes, despite the problems related to the long-term stability (Lee et al., 2010; Yanagida et al., 2009) and the partial absorption of visible light (Hamann, 2012). Iodine-free liquid electrolytes based on cobalt (II)/(III) organic complexes (shuttles) have been applied with efficiencies up to 12.3%, in DSSC sensitized with a porphyrin organic dye (Yella et al., 2011). Another interesting

* Corresponding author.
E-mail address: mirko.congiu@fc.unesp.br (M. Congiu).
[1] Fax: +39 06 96038029.

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redox couple is the ferrocene/ferrocenium (Fc/Fc^+) proposed, for DSSC sensitized with organic and natural dyes (Daeneke et al., 2011; Sönmezoğlu et al., 2012). Other advantages of both Fc/Fc^+ and $[Co(bpy)_3]^{2+/3+}$ shuttles are the low molar extinction coefficients in the visible region and the mono-electronic redox reaction, different from than of the I^-/I_3^- that involves two electrons and the formation of highly reactive radical species (Boschloo and Hagfeldt, 2009). The counter electrode (CE) is a fundamental part of a dye solar cell. In a typical DSSC the CE consists of a thin transparent layer of platinum nanoparticles deposited on the FTO by sputtering, electrodeposition or screen-printing (SP) (Khelashvili et al., 2006; Lan et al., 2010). The technique for Pt counter electrodes preparation is screen printing of a paste based on hexachloroplatinic acid (HCPT), a chemical precursor of Pt. This relatively simple process has led to its widespread use. In fact, HCPT is soluble in ethanol and water, solvents that are commonly used for the preparation of SP pastes. The same precursor can be used in other deposition techniques such as spin coating (Lan et al., 2010) and electrodeposition (Fu et al., 2012). However platinum is a scarce and expensive element and thus its application increases the costs of DSSC. Several different materials have been proposed to replace Pt such as multi-walled carbon nanotubes (AbdulAlmohsin et al., 2012; Ahn et al., 2014; Anwar et al., 2013), graphene (Wang and Hu, 2012), carbon-based nano materials (Ahmad et al., 2014) and transition metal sulfides such as Ni_2S_3 and CoS (Lin et al., 2011; Yang et al., 2014). Cobalt sulfide in particularly, has been demonstrated in numerous studies to be more efficient than platinum in the catalytic reduction of triiodide (I_3^-) to iodine (I^-) in DSSC electrolytes (Congiu et al., 2015; Wang et al., 2009). Among those counter electrodes with high catalytic efficiency, CoS has shown a reasonably good chemical stability with the I^-/I^{3-} redox couple. In functioning DSSCs devices a 30 day study was conducted by (Lin et al., 2011) showing good stability in all cell parameters. In our previous research on CoS counter electrodes we have investigated the effect of electrochemical stress on the electrocatalytic activity of dummy cells (Congiu et al., 2015). Another advantage of CoS is that it can also be used in quantum-dot sensitized solar cells (QDSSC) (Faber et al., 2013). It is important to remember that platinum counter electrodes are unsuitable for QDSSCs uses due the surface poisoning caused by sulfur polysulfide electrolytes normally used in these type of solar cells (Ke et al., 2014; Meng et al., 2014). Despite the great advantages and reduced costs, cobalt sulfide counter electrode is not as commonly used as Pt, and remains excluded from industrial production. In fact there is still no commercial product based on this material. Among the reasons why, are the preparation methods proposed so far in the literature for CoS CE. One of the most common technique for the deposition of CoS is electrodeposition (ED). This technique produces excellent CEs, however it requires the use of highly toxic precursors such as thiourea (Lin et al., 2011; Wang et al., 2009; Yang et al., 2014). Recently chemical vapor deposition (CVD) has been used to prepare efficient CoS CEs (Mgabi et al., 2014). However both CVD and ED are not ideal for large area electrodes nor for large scale production. It is important to remember that modern industrial production of DSSC is based on SP and other printing techniques. An interesting review work on solar cells counter electrodes materials, was recently published by Yun et al. (2014). In this review work, the authors, highlighted the importance of printing and in-situ growth process as the requirements for future research in the field of Pt-free counter electrodes. Previously, we proposed a new single precursor route for the deposition of efficient and cheap CoS CEs (Congiu et al., 2015) using an ink based on cobalt diethyldithiocarbamate ($CoDTC_2$) as chemical precursor. However this ink could only be prepared using organic solvents, which are not ideal for large-scale production. In this paper we propose a new single precursor-based method suitable for the large area and large scale production of efficient CoS CEs for DSSC and QDSSC. The method is based on a water soluble chemical precursor that is cheap and easy to prepare. We have tested these CoS CEs with different redox couples, such as Fc/Fc^+ (Daeneke et al., 2011; Sönmezoğlu et al., 2012) and $[Co(bpy)_3]^{2+/3+}$ electrolytes as well as a polysulfide electrolyte suitable for QDSSC.

2. Materials and methods

Sulfur (S); sodium sulfide nonahydrate; cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$); thioglycolic acid (TGA); ferrocene ($Fe(C_5H_5)_2$); $NOBF_4$, ferrocenium tetrafluoroborate ($Fe(C_5H_5)_2BF_4$); propylene carbonate (PEC); chenodeoxycolic acid (CHENO); absolute ethanol (EtOH); acetonitrile (ACN) and fluorine doped tin oxide coated glass slides (FTO $\sim 7\Omega/\square$) were purchased from Sigma–Aldrich. Titanium dioxide ($TiO_2 \sim 20$ nm nanoparticles) transparent screen-printing paste; Platisol T\SP paste and high stability I^-/I_3^- electrolyte BV12 (HSE) were purchased from Dyers, Italy and Solaronix. The organic dye 3-(5-(4-(diphenylamino)styryl)thiophen-2-yl)-2-cyanoacrylic acid (D5) was purchased from Dyenamo, Sweden. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed on a Netzsch Thermische Analyse-STA 409 equipment, under nitrogen atmosphere. X-ray diffraction patterns (XRD) were collected on powder samples with a DMAX Ultima (Rigaku International Corporation, Tokyo, Japan), operating at 40 kV and 2 mA. Scans were performed from 5° to 80° with a step size of 0.02° with a scan speed of 2 °/min. Scanning electron microscopy and energy dispersive X-ray spectroscopy (EDS) were performed using a Zeiss EVO LS15SEM microscope. Electrochemical impedance spectroscopy (EIS) spectra were collected on bisymmetric devices at 0 V and on complete DSSC devices at V_{oc} applying a sinusoidal modulation with a 10 mV amplitude with a