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ORIGINAL RESEARCH PAPER

ENHANCING THE EFFICIENCY OF AZO-BASED DYE SENSITIZED SOLAR CELLS BY SURFACE TREATMENTS

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Abstract: We studied the conductive glass and/or the semiconductor surface treatments with aluminum ions as a technique to enhance the characteristics of dye sensitized solar cells (DSSCs) based on Al-doped ZnO. The aluminum ions were deposited on the surfaces using aluminum isopropoxide as precursor, by an easy and efficient method. We measured the characteristics of the dye sensitized solar cells based on pre- and/or post-treated electrodes. Our study showed a clear enhancement of cells efficiencies for the DSSCs based on Al(III) pre-treated electrodes (*i.e.* a percentage increase of almost 18 %) and also a smaller improvement in the efficiencies of DSSCs based on Al(III) post-treated photoelectrodes (*i.e.* a percentage increase of almost 10 %), giving a overall enhance of about 21 % reported to the untreated photoelectrode based DSSC.

Keywords: *Al-doped ZnO, aluminum isopropoxide, Al_2O_3, blocking layer, semiconductor treatment, dye sensitized solar cell*

INTRODUCTION

Since Grätzel and O'Reagan published in Nature (1991) their famous article [1], the dye sensitized solar cells (DSSCs) proved to be a convenient source of energy and constitute a potential solution to the current energy crisis. A conventional DSSC comprises a sensitizing dye-adsorbed mesoporous TiO_2 electrode put in contact with a liquid electrolyte containing I^-/I_3^- redox couple [2]. Therefore, the heart of a DSSC is a mesoporous oxide layer composed of nanometer-sized particles, sintered together to allow for the electronic conduction to take place. The material of choice has been TiO_2 (anatase), but other alternative wide band gap oxides (ZnO, Nb_2O_5, SnO_2) have also been investigated [3, 4]. Despite the efficiencies of ZnO-based DSSCs are inferior to those of TiO_2-based, ZnO has some advantages which make it a serious alternative for TiO_2 [5]. ZnO thin films are n-type semiconductors with intrinsic defects, such as interstitial zinc atoms and oxygen vacancies; its electrical conductivity can be increased by doping with 13-group elements, such as aluminum. The Al-doping of ZnO (Al-doped ZnO, AZO) enhances the electrical conductivity of ZnO thin films and transparency to the visible range of sunlight, *i.e.* minimized optical and electrical loss [6, 7]. The AZO films have potential applications in solar cells, solid-state display devices, optical coatings, heaters, defrosters, chemical sensors, etc. [8 - 10].
The aluminum oxide (Al_2O_3), an isolator, may be involved in DSSCs constitution as blocking layer and/or as energy barrier layer, like some other metal oxides [4]. A blocking layer between conductive transparent electrode and porous semiconductor film in the dye-sensitized solar cell prevents the short-circuit [11]. The nanoporous electrode may introduce the charge recombination, which mainly occurs at the electrode/electrolyte interface, thus a recombination barrier layer is an important for a proper operation of DSSCs [12]. Several methods (*e.g.* spray pyrolysis, atomic layer deposition [4], reactive magnetron sputtering technique [13], etc.) are used for the deposition of metal oxide layer. However, an easily available method for the preparation of a blocking layer and/or a recombination barrier layer is important to make DSSCs a commercially competitive technology [12].
In our study, we proposed the use of Al_2O_3 both as blocking layer and/or recombination barrier layer. The layers were prepared by a facile and efficient method, which was previously used for cosensitization of DSSCs [14].

MATERIALS AND METHODS

Manufacture of DSSCs

The semiconductor films were obtained by doctor-blading method, using an AZO nanopowder. The AZO films were deposited directly on FTO conducting glass (AZO **1**, AZO **2**), or on FTO conducting glass immersed in aluminum isopropoxide solution (AZO **3**, AZO **4**; also labeled pre-treated plates). The photoanodes were used without further treatment (AZO **1**, AZO **3**), or after a second immersion in aluminum isopropoxide solution (AZO **2**, AZO **4**; also labeled post-treated plates).
All reagents were purchased from commercial sources and used as received.

Blocking layer. The conductive glass substrate, consisting in soda lime glass sheet of 2.2 mm thickness covered with a conductive layer of fluorine-doped tin oxide (SnO_2:F) (FTO) with a 15 Ω/square resistivity (Solaronix) was ultrasonically cleaned for 15 min in acetone, ethanol and deionized water, respectively, to remove any traces of impurities. Al_2O_3 layers were prepared by immersing the glass plates in a 15 mM solution of aluminum isopropoxide (Al(O-*i*-Pr)$_3$, Sigma-Aldrich) in 2-propanol (Sigma-Aldrich), for 15 min, followed by drying in air [14].
Semiconductor film. ZnO doped with 6 % Al nanopowder (AZO, Sigma Aldrich, 1 g) was dispersed in a solution containing acetic acid (Sigma-Aldrich, 0.25 mL), ethanol (Sigma-Aldrich, 16.75 mL) and deionized water (8 mL). The nanocrystalline AZO paste thus obtained was coated on FTO conducting glass sheets by doctor-blading technique. The coated films were initially dried at 90 ^oC for 30 min and then heated at 450 ^oC for 10 min in air [15].
The semiconductor films (AZO **2**, AZO **4**) were treated with aluminum isopropoxide using the same procedure as for blocking layers [14].
Semiconductor sensitization. The AZO plates were immersed in a 0.3 mM solution of N-719 dye (di-tetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II), Sigma-Aldrich) in anhydrous ethanol and heated for 2 h at 80 ^oC. The non-adsorbed dye was washed away with anhydrous ethanol until the rinse liquid was colorless and then the plates were dried at 80 ^oC for 30 min [16].
Counter electrode. Platinum counter electrodes were prepared by spreading a few drops of 5 mM $H_2[PtCl_6]\cdot 6H_2O$ solution in 2-propanol on the FTO glass, followed by drying at 100 ºC for 10 min and then at 385 ºC for 30 min [17].
DSSC assembling. DSSCs were assembled following the procedure described in the literature [18], the catalyst-coated counter electrode being placed on the top, so that the conductive side of the counter electrode faced the AZO film. The iodide electrolyte solution (50 mM of tri-iodide in Tetraglyme, Iodolyte TG-50 from Solaronix) was placed at the edges of the plates. The liquid was drawn into the space between the electrodes by capillary action. Two binder clips were used to hold the electrodes together.

Measurements

The electro-optical parameters of DSSCs, the short circuit current (I_{SC}), the open circuit voltage (V_{OC}), the fill factor (*FF*), and the photovoltaic conversion efficiency (η) were measured under AM 1.5 G standard conditions (1000 $W\cdot m^{-2}$) at 25 ^oC, using a homemade class A small area solar simulator [19]. The cell surface was exposed to light through a circular slit of 10 mm diameter, resulting in a useful area of about 0.785 cm^2. The current and voltage values were measured using two digital bench multimeters (Mastech MS8050) and a decadic resistance box. All measurements were made at intervals of 45 s, allowing for each reading to stabilize. The equivalent shunt and series resistances, needed for identifying the loss mechanisms of the cells, were calculated using the curve slopes at the Y and X intercepts respectively.
We compared the performance of AZO-based DSSCs to the standard DSSCs prepared with TiO_2 nanopowders and N-719 dye, using the photoanodes pre- and post-treated with $TiCl_4$, which lead to a solar energy conversion efficiency of 2.26 %, in the same experimental conditions [20].

RESULTS AND DISCUSSION

The aluminum oxide (alumina) can be synthesized both by hydrolysis and thermal decomposition of aluminum isopropoxide. Particularly, the hydrolysis of aluminum isopropoxide is a facile route for synthesis of mesoporous alumina at room temperature [21]. We used the aluminum isopropoxide as precursor for Al_2O_3 in order to obtain thin layers deposited on the conductive glass and/or on the semiconductor layer. Thus, we obtained four types of DSSCs, based on photoanodes treated or not with aluminum isopropoxide (Table 1).

Table 1. *Schematic procedure for the manufacture of AZO-based DSSCs*

	Conductive glass/FTO	**Pre-treated plates**	**Semiconductor layer (AZO)**	**Post-treated plates**
AZO **1**	x	-	x	-
AZO **2**	x	-	x	x
AZO **3**	x	x	x	-
AZO **4**	x	x	x	x

The typical values resulting from the electro-optical measurements performed on DSSCs fabricated with AZO as semiconductors and N-719 pigment are displayed in detail in Table 2 and illustrated as I–V curves in Figure 1.

Table 2. *Typical values of the short circuit current (I_{sc}), open circuit voltage (V), fill factor (FF), and photovoltaic conversion efficiency (η), determined for AZO-based DSSCs sensitized with N-719 pigment*

Substrate	I_{sc} **[mA·cm^{-2}]**	V **[mV]**	***FF***	η **[%]**
AZO **1**	3.055	486.4	0.439	0.653
AZO **2**	3.178	488.0	0.432	0.670
AZO **3**	3.336	489.1	0.439	0.716
AZO **4**	3.635	488.0	0.445	0.790

As an overall remark, the efficiencies of DSSCs based on Al^{3+} treated photoanodes are higher than those of untreated AZO-based DSSC (Table 2). The better efficiencies rely on the increase of short-circuit current density, whereas the values for fill factor and open circuit voltage remain almost constant.

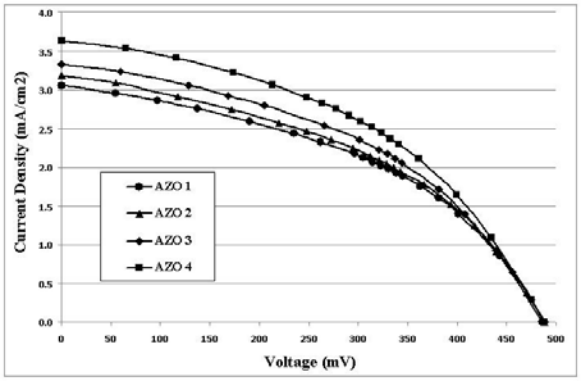

Figure 1. *Current–voltage curves for AZO-based DSSCs*

The I-V curves (Figure 1) reveal a relatively high equivalent series resistance given by the slope of the curve when the current density approaches zero.
Altghough both pre- and post-treatments are increasing the DSSCs efficiency, the more effective seems to be the pre-treatment (an efficiency growth of 10 %, respective 18 %), which may be due the preventing of short-circuits. The increase of efficiency after post-treatment (3 %, respective 10 %) may be assigned to the reduction of the interfacial recombination by insulating oxide layer [22].
Table 3 presents two more parameters used in the characterisation of the solar cells, *i.e.* the series resistance (R_{series}) and the shunt resistance (R_{shunt}, which describes the unwanted short circuit between the front and back surface contacts of a solar cell) [23].

Table 3. *The series resistance (R_{series}) and the shunt resistance (R_{shunt}) for AZO-based DSSCs*

DSSC	R_{series} (Ω)	R_{shunt} (Ω)
AZO **1**	65.57	732.2
AZO **2**	61.18	744.5
AZO **3**	62.22	762.8
AZO **4**	55.55	811.5

The introduction of the intermediate oxide layers decreased the series resistance, R_{series} and increased the shunt resistance, R_{shunt}, probably due to charge diffusion to FTO and dye regeneration, wich are desirable processes in the DSSCs [24]. Another desirable proces is the favoring of charge injection from dye into AZO semiconductor, which may explain the increase of the I_{sc} for the devices with post-treated Al_2O_3 layers. Hagfeldt *et al.* have studied the treatment of titania with low quantities of Al(III) ions and assumed that treatment affects the solar cell in different ways (the potential of the conduction band is shifted, the electron lifetime is increased, the electron transport is slower when aluminum ions are present between interconnected semiconductor particles), having as consequence the improvement of DSSC efficiency [22]. A similar explanation may be conclusive for AZO-based DSSCs post-treated with Al(III).

CONCLUSIONS

We increased the eficiency of AZO-based DSSCs by treatment with Al^{3+}, using aluminum isopropoxide as precursor. The obtained Al_2O_3 was used both as blocking layer and/or recombination barrier layer, and the DSSCs efficiency had an overall increase of 21 % (pre- and post-treated photoanode compared with untreated photoanode). The most important improvement of DSSC efficiency was due to the deposition of Al_2O_3 on the surface of conductive glass, which probably prevented the short-circuits in solar cells.

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