



Electrophoretically self-assembled mixed metal oxide-TiO₂ nano-composite film structures for photoelectrochemical energy conversion: Probing of charge recombination and electron transport resistances



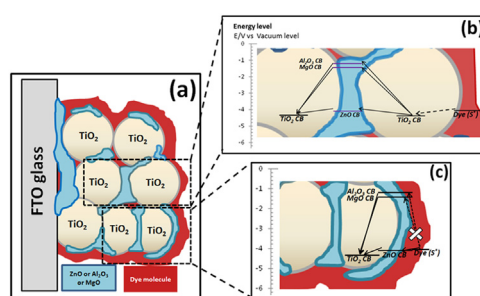
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HIGHLIGHTS

- EPD construction of nanotitania/metal oxide composite films for DSSC application.
- In-situ metal oxide nanocoating of TiO₂ provides charge recombination resistance.
- TiO₂-Al₂O₃ nanocomposite film exhibits highest charge recombination resistance.
- TiO₂-ZnO film exhibits least electron transport resistance and highest efficiency.
- Optimization of electronic properties of metal oxide with photovoltaic performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 19 December 2012

Received in revised form

11 April 2013

Accepted 12 April 2013

Available online 16 May 2013

Keywords:

Electrophoretic deposition

Dye sensitized solar cell

Nanocomposite film

Electron transport

Charge recombination

Electrochemical impedance spectroscopy

ABSTRACT

Nanotitania/metal oxide composite films are prepared via the coupling of low DC voltage Electrophoretic Deposition (EPD) of P25 TiO₂ nanoparticles with simultaneous electrolytic deposition of hydrous metal oxides, namely ZnO, MgO and Al₂O₃. The nanocomposite films are built into dye-sensitized solar cell photoanodes and their interfacial charge recombination and electronic resistances are investigated. The nano hydrous oxides were found to co-deposit (1–3 wt%) uniformly within the TiO₂ film (forming island-like nanodeposits) significantly increasing film adhesion. Analysis via Electrochemical Impedance Spectroscopy and Open Circuit Voltage Decay techniques found, among the three composite films, the TiO₂-Al₂O₃ electrode to exhibit the highest charge recombination resistance at the TiO₂/electrolyte interface (R_{rec}) and as consequence an increase in V_{oc} . However, its conversion efficiency (4.14%) was the lowest because it suffered from very high electron transport resistance (R_t) in the TiO₂ network. By comparison, the TiO₂-MgO film resulted in 5.40% efficiency and the TiO₂-ZnO film in 5.85% efficiency—both exhibiting significantly lower R_t resistance. The obtained results point to the need for simultaneous optimization of the nanocomposite TiO₂/metal oxide film structure in terms of high interfacial charge recombination resistance and low overall electron transport resistance.

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1. Introduction

The dye-sensitized solar cell (DSSC) is a unique photoelectrochemical energy conversion device, which since its first

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introduction in 1991 [1] has attracted tremendous R&D attention. The DSSC is typically composed of a mesoporous nanocrystalline TiO_2 film covered by a monolayer of dye molecules, electrolyte, and counter electrode. The structure of TiO_2 photoanode provides a large surface area that enables abundant dye loading on the surface to maximize the amount of photogenerated charge. In addition to efficient light harvesting, a large electron diffusion length in TiO_2 photoanode is necessary to obtain good collection efficiency. It is noted that unhindered charge transport in the TiO_2 network accompanied by minimized interfacial charge recombination can lead to the large diffusion length.

There have been intensive studies on a range of fabrication procedures to modify the TiO_2 photoelectrode by incorporating different composite films in order to enhance the cell conversion efficiency. Some studies constructed the composite photoanode based on a mixture of nanoparticles with different size, shape such as, nanotube and nanowire, which resulted in enhanced conversion efficiency due to the facile electron transport as well as light scattering [2–4]. Moreover, different metal oxides have been investigated as scattering layer on top of the transparent TiO_2 film such as ZrO_2 [5] and Al_2O_3 [6]. Another approach in fabrication of composite photoanodes is the coating of the transparent TiO_2 film with a thin layer of another metal oxide (a type of core–shell configuration applied to the whole film as opposed the individual particles). This approach has been reported to enhance the cell performance of DSSCs by retarding interfacial recombination. As overcoat materials, different metal oxides with higher conduction band (CB) edges, e.g., MgO , ZnO , Nb_2O_5 , Al_2O_3 , SiO_2 , and ZrO_2 , are selected in order to minimize the back transfer of photoinjected electrons through the TiO_2 /dye/electrolyte interface and, hence, improve the V_{oc} and subsequently cell efficiency [7–17]. Furthermore, overcoating with different metal hydroxides such as $\text{Mg}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, and $\text{La}(\text{OH})_3$ prepared by electrodeposition has also been reported [18,19]. It is worth noting that different metal hydroxides with more negative CB compared to that of TiO_2 (–4.21 eV vs. vacuum scale [20]) were also applied as a blocking TiO_2 layer at the FTO/ TiO_2 interface in order to decrease electron leakage from the substrate to electrolyte [21–23].

In the present work, given that the majority of previous works have focused on the core–shell (overcoat) composite structure, we have decided to fabricate and study the photovoltaic behavior of an alternative self-assembled co-deposited mixed metal oxide film. We call this film geometry, hybrid or mixed composite structure. There are a few previous studies with which the new mixed composite structure can be related. Thus Chou et al. [24] reported the fabrication of a TiO_2 /NiO mixed composite film by mixing the Ni powder with TiO_2 particles, and depositing it on FTO-glass substrate via the spin coating process; the cell employing the composite structure yielded a better conversion efficiency ($\eta \sim 3.80\%$) than that of the conventional TiO_2 film-based DSSC (3.27%). This improvement was attributed to the blocking effect of the NiO particles. Moreover, Niu et al. [25] demonstrated that mixed TiO_2 – SiO_2 composite electrode led to pronounced increase in η from $\sim 5.8\%$ (bare TiO_2) to $\sim 8.4\%$. This increase was explained in terms of the favorable effect SiO_2 particles had on the dispersion of TiO_2 , as well as on its role as blocking layer against charge recombination. However, Chappel et al. [26] claimed that the core–shell film structure is preferable as they argued the metal oxide (usually with more negative CB compared to TiO_2 ; distributed in the entire film of the mixed structure) will act as energy barriers to photoinjected electrons diffusing toward the current collector. However, this loss in charge transport depends on how far the CB position of the second metal oxide is located compared to TiO_2 . In addition, in the core–shell (overcoat) film structure, dye molecules are adsorbed directly onto the co-deposited shell and

not TiO_2 . As a result, not only the amount of dye loading can be affected depending on shell's surface properties (IEP-iso electric point) [15], but also owing to the higher CB edge of the shell oxide, electron injection into TiO_2 can be hindered in agreement to [10,19,27]. This issue motivated us to investigate the photovoltaic properties of a hybrid/mixed metal oxide nanodeposit configuration that allows for effective interfacial charge recombination resistance without compromising photoelectron generation and injection achieved by direct dye loading on uncoated areas of TiO_2 surface.

Recently, we showed a significant improvement in overall cell efficiency using a nanocomposite TiO_2 – ZnO electrode structure as compared to TiO_2 alone [28]. Therefore, we decided to expand our study by considering $\text{Mg}(\text{NO}_3)_2$ and AlCl_3 in addition to $\text{Zn}(\text{NO}_3)_2$ as charging agents, prepare three mixed (TiO_2 – MO_x) composite films, probe their charge recombination and electron transport properties and relate ultimately film structure to device performance. To this end self-assembled composite electrode films are constructed via our recently developed aqueous suspension-based EPD method [29] and after characterization they are analyzed by electrochemical impedance spectroscopy (EIS), incident photon current conversion efficiency (IPCE) and open circuit voltage decay (OCVD) techniques.

2. Experimental

2.1. Aqueous suspension preparation and EPD procedure

An aqueous suspension was prepared as optimized in our previous work [29]. The suspension consisted of 5% v/v de-ionized water–isopropanol and 5 g L^{-1} of TiO_2 powder (AEROXIDE® TiO_2 P25, Evonic). In addition, 10^{-3} M of 3 different salts namely, $\text{Zn}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, and AlCl_3 were added act as charging and binder (upon electrolytic deposition) agents. The suspension was first mixed for 75 min with a magnetic stirrer and after for 15 min with an ultrasonic stirrer prior to EPD. The zeta potential and suspension conductivity were measured with a Malvern Zetasizer Nano ZS (Malvern Instruments) and an Oakton conductivity meter, respectively. In order to perform EPD, constant current density (0.1 – 0.3 mA cm^{-2}) was applied between a stainless steel sheet (anode) and a fluorine-doped tin-oxide conducting glass substrate (FTO-Glass, 7 Ω cm^{-2} , Nippon Sheet Glass, Japan). This current density range was used in order to minimize water decomposition by applying low voltage (~ 2.2 – 4.2 V) between two electrodes [29]. The deposition area of the electrode was 5 cm^2 . The distance between the two electrodes was 2 cm. The deposition was performed for different times over the range of 5–15 min using a Keithley 2400 Source Meter as a power supply. After deposition, the mixed composite films were dried at room temperature and subjected to annealing at 450 °C in air for 30 min [30].

2.2. Characterization of mixed nano-composite films

The thickness and roughness of the three composite films (no separate scattering layer was applied) were measured using the Dektak 3030 surface profiler system (Veeco Instruments Inc., U.S.A.). The morphology of the TiO_2 films was characterized by a cold-FEG-SEM Hitachi SU-8000. Energy-dispersive X-ray spectroscopy (Oxford, SU-8000 Hitachi) was also employed to determine the chemical species of the composite substrates. High resolution Transmission Electron Microscopy (HR-TEM) images were obtained using a Philips CM-200 microscope operating at 200 kV. X-ray diffraction (XRD) analysis was performed using a Bruker D8 diffractometer equipped with a GADDS 2D detector and Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm) at a scan rate of 5°/min. X-ray

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