



# Improving photovoltaic performance of titanium oxide thin films by integration of iron doping and dye sensitization



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## ARTICLE INFO

### Article history:

Received 4 November 2013

Accepted in revised form 25 January 2014

Available online 2 February 2014

### Keywords:

Thin films

Sol–gel coating

Iron

Titania

Dye-sensitized solar cells

## ABSTRACT

Iron-titania thin films derived by sol–gel coating were investigated as anode elements in dye-sensitized solar cells. The Fe-doped titania films were shown more hydrophilic and exhibited a higher dye uptake than the undoped (titania) film. The Fe addition induced chemical shifts of Ti and O atoms as revealed by X-ray photoelectron spectroscopy and caused a positive shift in the flat-band potential of titanium oxide (at low Fe/Ti ratios). The Fe-doped titania electrodes at low Fe concentrations produced higher photocurrents than the undoped (titania) electrode under ultraviolet illumination. Electrochemical impedance and pulsed photocurrent analyses suggest that Fe dopants serve as shallow trap states for charge transition to increase charge collection efficiency. The dye addition improved photocurrent and voltage for the oxide electrodes, because the Fe doping modifies surface and electronic structures to enhance dye adsorption and tune conduction band position for accelerating injection of excited electrons. Mechanistic aspects about the Fe-mediated electron transport and transfer from dye sensitization to promote photovoltaic efficiency are discussed.

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## 1. Introduction

Semiconducting metal oxides have been extensively exploited as anode elements in dye-sensitized solar cells (DSSCs), because they possess featured active sites to adsorb dye molecules and provide adequate conduction paths for electron transfer and transport. Currently, research into various approaches for modifying oxide semiconductors to improve photovoltaic performance still has been drawing great attention. For example, the TiO<sub>2</sub> film is surface-treated via hydroxylation to enhance dye adsorption [1], tailored for pore structures to favor electrolyte diffusion [2], or surface-modified by oxide species to increase hydrophilicity [3]. The proton intercalation in TiO<sub>2</sub> particles is known to form shallow trapping states for accelerating charge carrier transport within the oxide [4]. These examples suggest that functionalized oxides might be a promising class of photovoltaic materials because of the opportunity to adjust the variations in surface reactivity and electrical conductivity. Moreover, several research groups develop mesoporous or hierarchically structured titania films by sol–gel process with the use of co-polymers as structure-directing agents and demonstrate the porous structures effective for photovoltaic applications in solar cells [5–7].

Recent studies that have appeared about doping metal cations into semiconducting oxides present many interesting results of improving photovoltaic performance. Among these examples, special attention is focused on how metal dopants influence the surface and electronic

structures of the oxide hosts. Doping La [8], Nb [9] or Ta [10] cations into TiO<sub>2</sub> is reported to be effective to increase dye uptake. Modification of TiO<sub>2</sub> films by WO<sub>3</sub> species is a way to reduce surface states for electron-trapping [11]. Addition of W or Ta species into TiO<sub>2</sub> electrode causes a positive shift in the flat-band potential of TiO<sub>2</sub>, thus favoring electron transfer from dye into the oxide electrode [10,12]. For Zn–TiO<sub>2</sub> anodes in solar cells, the Zn doping can enhance charge carrier separation and promote electron transport by diminishing empty trap states where electron localization occurs [13,14]. In spite of so many excellent findings, efforts are still expected in the in-depth understanding of exploring various metal dopants for tailoring photovoltaic materials.

Iron cations in titanium oxide possess two oxidation states (Fe<sup>2+</sup>/Fe<sup>3+</sup>) to adjust chemical and electrical properties [15,16]. These redox iron sites have been known by serving as photoactive trap states to enhance electron–hole separation for increasing photocatalytic activity [17,18] and photocurrent yield [19]. To our knowledge, the potential of Fe-doped titania nanostructures as anode elements in dye-sensitized solar cells has not been fully explored by either theory or experiment. The present study aimed to characterize the surface states of the Fe-doped titania films and evaluate their photovoltaic properties and electrochemical impedance analysis when they are assembled into N719 dye-sensitized solar cells. The Fe-doped titania films were shown more hydrophilic and adsorptive to N719 dye than the undoped (titania) film. The Fe addition induced chemical shifts of Ti and O atoms and caused a shift in the flat-band potential of TiO<sub>2</sub>. In what follows, we report interesting results about Fe doping and dye sensitization to enhance photovoltaic efficiency and explain how they influence photovoltaic conversion under UV illumination.

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## 2. Experimental

### 2.1. Colloid and film preparation

The Fe–TiO<sub>2</sub> film samples investigated in this work are listed in Table 1. These oxide films were prepared by sol–gel and spin-coating techniques. Considering the Fe/Ti = 0.01 film as an example, a typical procedure was described below. Titanium(IV) tetra-isopropoxide (2.93 g, TTIP, Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>, 97%, Aldrich) was dissolved in a liquid mixture (21 g) of 1-butanol (99.9%, Tedia) and ethanol (99.9%, J.T. Baker) (mass ratio = 1.5:1) followed by addition of acetylacetone (0.60 g, AcAc, 99.5%, Fluka). The formed solution was kept under stirring for 30 min at 27 ± 2 °C, which allows chelating reaction of acetylacetone with TTIP molecules. Iron(III) nitrate nonahydrate (0.04 g, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 98%, Strem) was used as the Fe precursor, and its complete dissolution in ethanol (3 g) was ensured. The two precursor solutions were mixed under agitation and then slowly added with deionized water (0.36 g) for hydrolysis at 27 ± 2 °C (molar ratio TTIP:AcAc:H<sub>2</sub>O = 1:0.6:2) to avoid rapid TiO<sub>2</sub> precipitation. After agitation for another 1 h, a clear yellow sol was obtained and then stored in the dark for 72 h before use.

The resultant Fe–TiO<sub>2</sub> colloid solution was deposited by spin coating to form thin film (coating area 1.0 cm × 1.0 cm) on a fluorine-doped tin oxide (FTO) conductive glass substrate (Pilkington, 6–8 Ω cm<sup>-2</sup>, Haze 5%). Prior to the coating, the glass substrate was cleaned sequentially with detergent, acetone and then de-ionized water. Each spin-coating cycle was done in two stages, respectively at 800 rpm for 10 s and then 2000 rpm for 20 s, and drying followed at ambient for 5 min and then at 125 °C for 15 min to evaporate liquid. After three coating cycles were completed, the Fe–TiO<sub>2</sub>/FTO glass substrate was heated from ambient temperature to 500 °C at a rate of 5 °C/min and annealed at 500 °C for 1 h in air inside an oven, and then stored for characterizations and evaluation.

### 2.2. Material characterizations

The Fe–TiO<sub>2</sub> film samples were characterized for morphology on a field emission scanning electron microscope (FESEM, JEOL, Model JSM-6700F) and for wettability analysis on a contact angle measurement system acquiring images by a CCD camera. X-ray photoelectron spectroscopy (ULVAC-PHI, Model Quantera SXM) with an Al-K $\alpha$  radiation source (1486.6 eV) was used to examine the chemical states of Ti and O elements. The binding energy scale was precisely calibrated by taking the adventitious C 1s peak at 284.5 eV as a reference. The sample used in the XPS analysis was prepared in a form of thick film, by dripping sol solution on FTO glass substrate followed by drying at ambient for 5 min and at 125 °C for 5 min. This deposition process was repeated iteratively for about 20 times, and the final film substrate was calcined in air at 500 °C for 1 h.

### 2.3. Cell fabrication and evaluation

The Fe–TiO<sub>2</sub>/FTO glass substrate was assembled as the anode in a sandwich-type solar cell with Pt counter electrode, and the sensitizer

was N719 dye (Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II), C<sub>58</sub>H<sub>86</sub>N<sub>8</sub>O<sub>8</sub>RuS<sub>2</sub>, molecular weight 1188.55 g mol<sup>-1</sup>, Sigma-Aldrich). Dye uptake was carried out by soaking the Fe–TiO<sub>2</sub>/FTO substrate in a N719 dye solution (3 × 10<sup>-4</sup> M in anhydrous ethanol) for 24 h at ambient temperature inside a dark chamber, followed by rinsing with ethanol and drying at 50 °C. The amount of dye adsorbed was determined with UV–Vis spectrophotometer (Varian, Model Cary 50) to quantify the N719 concentration of a dye-leaching solution, obtained by soaking the dye-loaded substrate in a 0.1 M NaOH<sub>(aq)</sub> solution for 2 h. The electrolyte solution is composed of 0.5 M LiI and 0.05 M I<sub>2</sub> in acetonitrile (AN) and, prior to use, treated by sonification for 15 min to remove dissolved oxygen.

The N719 dye-adsorbed Fe–TiO<sub>2</sub> electrodes (active pixel area is 1 cm × 1 cm) were investigated under monochromatic 365 nm illumination to obtain photocurrent, voltage and electrochemical impedance measurements, recorded with a computer-controlled potentiostat (AutoLab, Model PGSTAT302). Three curve–voltage curves were recorded for each sample, and their average value was obtained (error between measurements within 1%). A monochromator (PTI, Model 102) equipped with a 150 W xenon lamp was used as the light source to irradiate photovoltaic cells. The illumination was performed at monochromatic light 365 nm (intensity 2.0 mW/cm<sup>2</sup>) from the front side of the N719/Fe–TiO<sub>2</sub> electrode (working area 1 cm<sup>2</sup>) at normal incidence.

## 3. Results and discussion

### 3.1. Hydrophilic nature and dye uptake

Fig. 1 presents the SEM images and contact angle measurements of the undoped and Fe-doped (Fe/Ti = 0.0005) titania films coated on FTO glass substrates and calcined at 500 °C. Both film samples were shown quite flat and compact in texture (photos a–b), and primary particles were sized about 17–21 nm. The Fe-doped titania films at various Fe concentrations (Fe/Ti = 0.0003 to 0.01) for this work (Table 1) were measured about 207 to 213 nm in thickness. In the wettability analysis, the Fe-doped (titania) film (Fe/Ti = 0.0005) had a smaller contact angle for water droplets than the undoped (titania) sample (i.e., 64.5° vs. 74.5°). The increase in hydrophilicity after Fe addition is attributed likely to the formation of Fe–OH and Ti–OH groups on surface, resulted from H<sub>2</sub>O dissociation over Fe-induced oxygen vacancy sites adjacent to a Ti–O structure or over Lewis acid Fe sites [20] and Ti sites [16]. Results about water dissociation over oxygen vacancy sites to produce hydroxyl groups have been reported in literature [21,22]. Also possibly, the difference in the wetting behavior after Fe addition may be related to a deviation in the porous structure of the oxide film (e.g., capillary attraction).

Fig. 2 shows N719 dye uptake and contact angle measurements as a function of Fe concentration (Fe/Ti atomic ratio). The amount of dye adsorbed increases monotonically with increasing the Fe content in film. Compared with the undoped (titania) sample, the Fe-doped (titania) films are more hydrophilic so as to favor access of N719 dye species (in ethanol) to the film surface for reaction with hydroxyl groups (Ti–OH and Fe–OH). It is known that N719 dye species can be anchored to the TiO<sub>2</sub> particle surface via chemisorption through bidentate chelating or bidentate bridging coordination between the carboxylate moieties of

**Table 1**  
Time constants and collection efficiency estimated from EIS analysis.

Fe/Ti ratio (nominal)	N719/Fe–TiO <sub>2</sub>			Fe–TiO <sub>2</sub> (Ref. [19])		
	$\tau_n$ (ms)	$\tau_t$ (ms)	$\eta_{cc}$ (%)	$\tau_n$ (ms)	$\tau_t$ (ms)	$\eta_{cc}$ (%)
0	94	35	63.2	94	65	31.1
0.0005	75	22	70.8	60	27	54.5
0.002	147	65	55.5	360	295	18.1
0.01	117	67	43.2	230	210	8.4

$\tau_n$ : electron lifetime;  $\tau_t$ : transport time;  $\eta_{cc}$ : charge collection efficiency.

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