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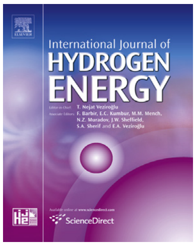

Effect of Ti- or Si-doping on nanostructure and photo-electro-chemical activity of electro-spun iron oxide fibres

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ARTICLE INFO

Article history:
Received 22 February 2017
Received in revised form
28 March 2017
Accepted 29 March 2017
Available online xxx

Keywords:
Hematite
Electro-spinning
Silicon-doping
Titanium-doping
Photo-anodes

ABSTRACT

Pure and titanium- or silicon-doped iron oxide fibres are synthesised by electro-spinning over conductive fluorine doped tin oxide (FTO)/glass substrates, and the effect of the type of dopant on the morphology of the fibres and the crystalline phase of the oxide is investigated by means of several complementary characterisation techniques. Results show that in the absence of dopant, highly porous fibres, consisting of interconnected polycrystalline hematite grains, are obtained. Doping with titanium does not influence the crystalline phase of the oxide, but the better packed structure of the fibres causes them to detach from the support. Silicon-doping results in a different phase of the host oxide (maghemite) and good adhesion of the fibres to the FTO/glass support. Very preliminary tests to evaluate the photo-electrochemical activity of the samples demonstrate that the photocurrent measured with Si-doped maghemite fibres is 53% higher with respect to that obtained with pure hematite fibres, as an effect of the nearly threefold increase in the donor concentration brought about by doping. This, in turn, improves the charge transfer at the interface, leading to a higher charge injection from the electrode to the electrolyte and, thus, to a greater photo-oxidation efficiency.

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http://dx.doi.org/10.1016/j.ijhydene.2017.03.204
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Introduction

The increasing energy demand associated to the growth of the world population and the enhancement of living standards and the need of limiting effects on climate changes call for developing clean energy sources. Solar energy conversion for hydrogen (H_2) production via photo-induced water splitting (WS) represents one of the most promising approaches.

TiO_2 has been the pioneering semiconductor for the photocatalysis of water [1,2]. It is environmentally friendly, easily available, cheap and stable, but absorbing in the near UV region it can use only an exiguous fraction (5%) of the solar light.

Its favourable properties (2.1–2.2 eV optical band gap, valence band edge lower than the water oxidation potential, chemical stability in oxidative environment), low cost and non-toxicity make of hematite (α-Fe_2O_3) one of the most attractive alternative photo-anode semiconductors [3–5]. However, poor conductivity, short diffusion length and high charge recombination rate mainly limit the photoelectrochemical (PEC) activity of α-Fe_2O_3 [3,4,6–8].

It is well known that grain boundaries, acting as electron–hole trap sites [6], constitute a serious problem in polycrystalline films. Therefore, on one hand, a winning strategy to reduce or eliminate the limitations of iron oxide toward efficient solar WS may be acting on the morphology. One-dimensional nanostructures, such as nanowires or nanofibres, can have fewer grain boundaries [6]. Besides, minimising the length scale through which the minority carriers must diffuse and, hence, reducing the probability of recombination losses, one-dimensional nanostructures may contribute to increase the efficiency of hematite [6]. On the other hand, their conductive properties can be significantly enhanced by the addition of a sufficient amount of aliovalent impurities in the lattice that, acting as electronic substitutional dopants, lead to (Mg^{2+}- or Cu^{2+}-doped) *p*-type or (Zr^{4+}-, Ti^{4+}, or Sn^{4+}-doped) *n*-type hematite, thus improving its photocurrent [4,9–13].

Thanks to its simplicity, cheapness, versatility and scalability, the electro-spinning (ES) represents a very commercially competitive technique for the preparation of one-dimensional high surface area materials [14]. It has been successfully utilised for the synthesis of pure [15], doped [16] and composite [17] TiO_2-based photo-catalysts for hydrogen generation by splitting of water. Dispersions of the sintered TiO_2 fibres produced via ES have been employed to obtain photo-anodes for WS in the form of homogenous films on FTO/glass substrates by the use of doctor-blade, or sol–gel dip coating, or by combining the two techniques [18].

This contribution deals with the synthesis, characterisation and testing, as photo-anodes for PEC WS, of highly-porous fibrous webs deposited, via ES, over conductive FTO/glass substrates. The fabrication of integrated active material/FTO support photo-anodes is not new, and several reports are available in literature [5,19–21]. The hydrothermal method [5,19] appears to be the preferred approach for the preparation of the integrated photo-anodes, even if also different routes, e.g. atmospheric pressure chemical vapour deposition [20], are followed. Very recently, the production of photo-anodes consisting of pure hematite fibrous mats over FTO/glass plates has been reported [21]. The mats have been prepared by electro-spinning a solution containing iron nitrate and polyvinyl alcohol.

In this work, a solution containing polyacrylonitrile and iron acetate, added with tetraethyl orthosilicate or titanium isopropoxide, is used to produce FTO-supported electro-spun webs consisting of both pure and doped iron oxide fibres. The integrated fibrous webs/FTO glass photoanodes are synthesized by ES followed by heat treatment. After sintering, the electro-spun active materials are characterised in order to investigate how presence and type of the dopant influence nanostructure and crystalline phase of the oxide. Preliminary results on the PEC performances of the FTO-supported electro-spun webs in WS are presented and the perspectives for their improvement are briefly discussed.

Experimental

Sample preparation

Table 1 reports the composition of the spinnable solution utilised for the preparation of the pure and doped iron oxide fibres. Polyacrylonitrile (PAN, $(C_3H_3N)_n$, purity: 99.9%, average molecular weight: 150,000 g/mol) and *N*,*N*-dimethylformamide (DMF, purity: 99.8%) acted as polymer and solvent, respectively. Iron (II) acetate ($FeAc_2$, $Fe(C_2H_3O_2)_2$), tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), titanium (IV) isopropoxide (TIPO, $Ti(OCH(CH_3)_2)_4$) were utilised as precursors. All reactants were supplied by Sigma–Aldrich and used as received.

The experimental procedure followed for the sample preparation is schematically described in Fig. 1. The spinnable solution was first prepared by dissolving PAN in DMF and stirring until a clear solution was obtained. Then, precursor(s) was (were) added, and the solution was kept under magnetic stirring for 4 h. Si-doped and Ti-doped samples were prepared using quantities of the proper precursors giving a fixed [Fe]/[Si] or [Fe]/[Ti] atomic ratio, and keeping constant the total metal load of the solution (2.5 wt%).

The as-prepared homogenous solutions were electro-spun using a CH-01 Electro-spinner 2.0 (Linari Engineering s.r.l.). The apparatus consists of a syringe equipped with a stainless steel needle, a grounded collector, and a high voltage power supply. During the spinning process, the collector is continuously translated along direction perpendicular to the syringe axis. The spinnable solution, fed at a constant rate by means of a pump that moves the syringe piston, is ejected under the high voltage applied between the syringe nozzle and the collector. For further technical details on the spinning set-up, see Ref. [14]. In the present case, a 20 mL syringe, equipped with a 40 mm long 0.8 mm gauge stainless steel needle, was utilised. Solution was fed at a volumetric rate of 1.41 mL/h. A 15 kV voltage over an 11 cm collection distance was applied. The spinning process was carried out in an open-air environment (relative air humidity: 40%) at 20 ± 1 °C temperature.

Before their use, the conductive fluorine-doped SnO_2/glass plates were cleaned by sonication in isopropanol for 10 min, then rinsed with distilled water and ethanol and finally dried under an air flow. Prior to spinning, the (2 cm × 1 cm) FTO/glass substrates were partly masked to have electrical contact

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