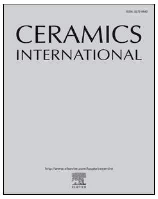
Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Niobium and iron co-doped titania nanobelts for improving charge collection in dye-sensitized TiO_2 solar cells

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ARTICLE INFO

Keywords:
Dye-sensitized solar cells
Nanobelts
Doped titania
Composite anode

ABSTRACT

Niobium (Nb) and iron (Fe) co-doped titanium oxide nanobelts were prepared in a one-pot alkaline hydrothermal process followed by calcination treatment, and evaluated in TiO_2 nanoparticle-based composite anodes for dye-sensitized solar cells. Addition of Nb and Fe species caused an increase in donor density and trap-mediated charge transition, as characterized by electrochemical and photoluminescence analyses. Under illumination with simulated solar light, the co-doped single-crystalline nanobelts promoted photocurrent yield and open-circuit voltage, because they facilitate electronic conduction and chemical capacitance in the composite anodes. This improved photovoltaic performance is associated with the enhanced charge collection efficiency, mechanistically attributed to rapid electron transport and prolonged electron lifetime via shallow trapping sites. Results demonstrate that the Nb and Fe co-doped titania nanobelts are effective to provide longer electron diffusion lengths and favor charge accumulation during cell operation.

1. Introduction

Fine particles of titanium oxide have been widely exploited as anode materials in dye-sensitized solar cells (DSSCs), because they possess high surface area for dye adsorption and adequate chemical stability to electrolyte solution. From a practical point of view, however, anomalous electron diffusion and trap-limited transport through these oxide particles may cause a major concern of low photocurrent yield [1]. In recent years, considerable progress has been made in the realization of semiconducting oxides about doping metal cations to tune electronic and band-gap structures. For example, the Cr doping in titania particles is found to generate charge donors and enhance electronic conductivity [2], and metal dopants such as Ce and Sn species in titania particles can cause a shift in flat-band potential so as to influence election injection rates from dye sensitizer into oxide electrode [3,4]. Furthermore, great advances have been made in the approach of co-doping two different kinds of metal cations into titania matrices. The Zn and Mg co-doped titania particles facilitate electron transport for increasing photocurrent in solar cells [5]. The Mg and La co-doped titania particles possess surface trap states for reducing recombination loss to achieve a higher photovoltaic efficiency [6]. These findings uncover the basis that the doping method has great potential to functionalize anode materials for solar cells.

One-dimensional (1D) metal oxide nanostructures have received great interest in many fields from photocatalysis [7] to photovoltaics [8] and optoelectronics [9], because they offer directional pathways for charge carrier diffusion. For dye-sensitized solar cells, special attention is focused on how these 1D nanostructures enhance power conversion efficiency. As reported about TiO_2 1D/TiO_2 NP composite DSSCs, the TiO_2 nanofibers enhance energy-harvesting yield by light scattering to generate more photoelectrons [10], and the TiO_2 nanobelts favor electron transfer and transport to increase photocurrent [11]. Several authors address that W-doped TiO_2 nanowires facilitate electron diffusion and impede charge recombination to achieve a higher photovoltaic efficiency for dye-sensitized solar cells [12]. Till date, we believe that this class of extrinsic (doped) semiconducting oxide 1D nanostructures still has great potential to be explored as photovoltaic materials by either experiment or theory.

In the present study, niobium (Nb) and iron (Fe) co-doped titania nanobelts (NBs) were prepared via hydrothermal reaction followed by calcination treatment, and utilized by mixing with TiO_2 nanoparticles (NPs) for fabrication of NB/NP composite anodes in N719 dye-sensitized solar cells. Considering that TiO_2 (P25) nanoparticles are frequently used as anode materials in DSSCs, we attempted to introduce the co-doped and undoped nanobelts as additives in order to promote electron diffusion in the NB/NP composite anodes. Both Nb and Fe species were selected as the dopants in order to tailor electronic donor states for this work, since they are known to influence electron

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https://doi.org/10.1016/j.ceramint.2018.07.005
Received 28 February 2018; Received in revised form 8 June 2018; Accepted 1 July 2018
0272-8842/

Please cite this article as: Wang, C.-T., Ceramics International (2018), https://doi.org/10.1016/j.ceramint.2018.07.005

Table 1
Characterizations of pure TiO_2 and Nb and Fe co-doped titania nanobelts.

Nanobelt	Atomic ratio (nominal)		Crystallite size	XPS $Ti2p_{3/2}$	Donor density	Flat-band potential
ID	Nb/Ti	Fe/Ti	by XRD (nm)	(eV)	(cm^{-3})	(V) vs. Ag/AgCl
TiO_2			10.7 ± 2.6	458.20	3.66×10^{20}	− 0.629
5Nb5FeTi	0.0005	0.0005	10.9 ± 0.5	458.14	4.37×10^{20}	− 0.627
10Nb5FeTi	0.0010	0.0005	9.5 ± 0.9	458.16	3.72×10^{20}	− 0.587

population and trap distribution in various titania-based anode materials (e.g., Nb-TiO_2 particles [13], Fe-TiO_2 nanobelts [14] and Fe-TiO_2 nanorods [15]). We characterized their structural and electronic properties by spectroscopic and electrochemical methods, and further elucidated why the co-doped nanobelts are effective in improving charge collection in the NB/NP composite DSSCs. Results are quite encouraging, as the work will show below.

2. Experimental

2.1. Preparation of nanobelts

Niobium (Nb) and iron (Fe) co-doped titania nanobelts were synthesized by a one-pot alkaline hydrothermal method. The following procedure is an example of the 10Nb5FeTi nanobelts (i.e., nominal atomic ratio Nb/Fe/Ti = 0.0010/0.0005/1, Table 1). As the Ti-precursor, TiO_2 powders (4 g, Degussa P25) were dispersed in a 10 N NaOH aqueous solution (200 ml), and then niobium pentachloride (13.6 mg, $NbCl_5$, 99.95%, Sigma-Aldrich) and iron nitrate nonahydrate (10.1 mg, $Fe(NO_3)_3{\cdot}9H_2O$, 98%, Strem) were added to dissolve in the alkaline solution. The precursor suspension was poured into a Teflon liner placed inside a 316 stainless steel autoclave. After sealed, the reactor was heated from ambient to 110 °C, kept at 110 °C for 2 h, then heated to 180 °C and kept at 180 °C for 24 h to ensure hydrothermal reaction. The collected precipitate (sodium titanate) was washed with de-ionized water to remove salt species, then dispersed in a 0.1 N HCl aqueous solution for 24 h (to exchange Na^+ with H^+) and finally washed with de-ionized water till solution pH = 7. The obtained product (hydrogen titanate) was dried at ambient and then calcined in air at 500 °C for 1 h.

2.2. Materials characterizations

The oxide nanobelt powders were characterized for morphology by field emission scanning electron microscope (FESEM, JEOL, JSM-6700F) and high resolution transmission electron microscope (HRTEM, JEOL, JEM-2100F). They were examined for crystal structure by X-ray diffractometer (XRD, Regaku, Miniflex II) equipped with Ni-filtered CuKα radiation (15 mA, 30 kV and $\lambda = 1.5405$ Å), and for element state by X-ray photoelectron spectrometer (XPS, ULVAC-PHI, Quantera SXM) with an AlKα radiation source (1486.6 eV). Their electronic structures were analyzed by electron paramagnetic resonance spectrometer (EPR, Bruker, EMX-10) operating at the X band frequency and by photoluminescence spectrophotometer (PL, Perkin Elmer, LS-55) with 300 nm light excitation.

2.3. DSSC fabrication and evaluation

The oxide nanobelts (NBs) were mixed with TiO_2 nanoparticles (NPs, Degussa P25) (mass ratio NB/NP = 1/9), ethanol, acetic acid, terpineol and ethyl cellulose to form slurry paste. The paste is coated by a screen-printing method on FTO glass substrates to fabricate NB/NP composite electrodes (active pixel area 0.5 cm × 0.5 cm) followed by 500 °C calcination in air. The coated substrates were immersed in a N719 dye solution (e.g., 3×10^{-4} M in anhydrous ethanol) for 24 h at room temperature inside a dark chamber. Next, the dye-adsorbed substrates were rinsed with ethanol liquid and then dried at 50 °C. The N719 dye loading was estimated from the N719 concentration of a dye-leaching solution, collected after the dye-loaded substrate was soaked in a 0.1 N $NaOH_{(aq)}$ solution for 2 h. The electrolyte solution is composed of 0.5 M lithium iodide (LiI, 99.9%, Aldrich), 0.05 M iodine (I_2, 99.99%, Sigma-Aldrich), 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII, 99.95%, UniRegion Bio-Tech) and 0.5 M 4-tert-Butylpyridine (4-TBP, $C_9H_{13}N$, 96%, Aldrich) in acetonitrile (99.5%, J.T. Baker).

The fabricated NB/NP N719 DSSCs (with Pt counter electrode) were evaluated under simulated 1 Sun AM1.5 illumination (100 mW/cm^2, 400–1000 nm), and their current, potential and impedance were recorded with a programmed potentiostat (AutoLab, Model PGSTAT302). Measurements by intensity-modulated photocurrent spectroscopy (IMPS) and voltage spectroscopy (IMVS) were obtained under 530 nm LED illumination (14.3 mW/cm^2).

3. Results and discussion

3.1. Structural and electronic properties of nanobelts

Fig. 1 shows XRD patterns for the Nb and Fe co-doped titania (5Nb5FeTi and 10Nb5FeTi) and pure (undoped) TiO_2 nanobelt powders calcined at 500 °C. These diffraction peaks were indexed to the monoclinic TiO_2(B) structure (JCPDS 74-01940), as similarly reported for TiO_2 nanofibers prepared in a hydrothermal process [16]. Evidently, the Nb and Fe addition caused a decrease in the intensity of the XRD peaks and a shift of the peak positions toward higher angles (see magnified peaks (110) and (020)). Further analysis reveals dopant-induced lattice distortion according to inter-planar *d*-spacing narrowing (e.g., measured $d_{(110)} = 3.57$ Å for TiO_2, and 3.53 Å for 10Nb5FeTi) and also crystallite size shrinkage (ca. 10.7 nm for TiO_2 vs. 9.5 nm for 10Nb5FeTi, Table 1). Therefore, both Nb^{5+} (radius = 0.64 Å) and Fe^{3+} (0.55 Å) dopants have been introduced to substitute for the Ti^{4+} (0.61 Å) host ions in TiO_6 lattices. By charge compensation mechanism,

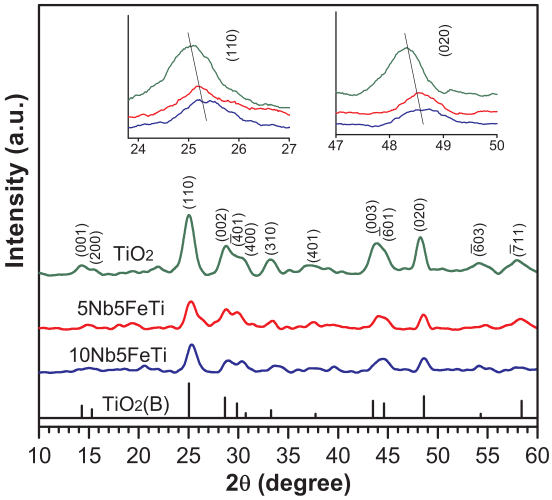

Fig. 1. XRD patterns of Nb and Fe co-doped titania and TiO_2 nanobelts calcined at 500 °C.