



An insight into titania nanopowders modifying with manganese ions: A promising route for highly efficient and stable photoelectrochemical solar cells



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ABSTRACT

In this study, we firstly report the synthesis of pure and manganese (Mn) doped titania nanopowders by solution-based chemical process followed by ball-milling and ultra-sonication processes and their usage as photoanode material in dye-sensitized solar cells (DSSCs). Besides examining the properties of physical and charge transfer dynamics, we also made a detailed cost analysis to compare with commercial P25 nanopowders. By incorporating Mn^{4+} ions into titania matrix, we have also succeeded not only in lower price but also in significantly enhancing the dye loading capability by increasing specific surface area and the retarding the recombination of electron-hole pairs by forming the discrete interstitial states within the band gap as well as accelerating electron transfer by tailoring in energy gap, leading to better photovoltaic performance. Such that, the cell assembled with 0.4 mol% Mn doped TiO_2 yields an efficiency of 7.33%, which is $\sim 17\%$ and $\sim 65\%$ higher than the value obtained for P25 and pure titania-based photoanode, respectively, and shows a fast, stable, and completely reversible photocurrent response accompanying each switch-on/off event. Furthermore, the photoinduced electron transfer (PET) measurements indicate an efficient interfacial charge transfer for 0.4 mol%Mn doped titania ($k_{ET} = 0.99 \times 10^8 \text{ s}^{-1}$) compared to the both synthesized pure TiO_2 ($0.74 \times 10^8 \text{ s}^{-1}$) and commercial P25 ($0.94 \times 10^8 \text{ s}^{-1}$) photoanodes. This work renders the possibility of synthesizing low-cost and easy-preparation Mn-doped titania nanopowders and describes an innovative approach to further boost the efficiency of green technologies such as solar-driven water splitting, photoelectrochemical and perovskite solar cells applications.

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1. Introduction

In recent years, a considerable research effort has been directed towards the dye sensitized solar cells (DSSCs) owing to their low cost, ease of device fabrication, and relatively high efficiency (Ates Sonmezoglu et al., 2016; Akin et al., 2016, 2017; Ozel et al., 2016; Tas et al., 2017). The main components affecting the performance of DSSCs are mesoporous photoanode film as a charge collector, dye as a sensitizer, redox based electrolyte, and counter electrode (Akin et al., 2016; Sonmezoglu et al., 2012, 2014; Tas et al., 2016). Among these components, photoanode plays a predominant role in boosting the efficiency because it controls the

dye loading ability, charge transfer mechanism, and recombination kinetics (Ates Sonmezoglu et al., 2016).

Titanium dioxide (TiO_2) is frequently adapted as an adequate photoanode material in DSSCs due to its low cost, long-term thermodynamic stability, and photostability (Sonmezoglu et al., 2014; Tian et al., 2014; Sönmezoğlu et al., 2012a,b; Akin and Sönmezoğlu, 2012; Yildiz et al., 2016). However, the nature of TiO_2 commonly leads to low electrochemical activity, poor absorption properties, low dye loading, and high recombination rate. To modify these intrinsic properties of host TiO_2 and further improve the photoanode's efficiency with the aim of maximizing the dye- TiO_2 interface area and light absorption, extensive attempts have been employed by the scientists (Ates Sonmezoglu et al., 2016; Akin et al., 2016; Sonmezoglu et al., 2014). One of the most promising approaches to significantly improve the electronic properties and yield of the photoanode materials is doping with transition metal ions which increase the lifetime of electrons with the inhibition of charge

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recombination as well as change the opto-electronic response of TiO₂ surface (Duan et al., 2012; Zhang et al., 2011a, 2011b; Wang and Teng, 2009; Lu et al., 2010; Niu et al., 2016). Besides, the insertion of transition metal ions into TiO₂ increases the constitution of a wide range of new energy states close to the conduction band arising from its partially filled d-orbitals. All these features make transition metal ions suitable dopants to tune the conduction band structure of TiO₂. Among the various transition metal ions, manganese (Mn) as 3d transition metal ion seems to be a promising candidate for improving the photoresponse of TiO₂ because of (i) having similar ionic radius with Ti ions, (ii) enable significant optical absorption in the visible region by reducing the energy gap, (iii) enhance the surface area by changing the growth rate of TiO₂ particles, and (iv) improve the charge transport mechanism by tailoring the electronic structure (Roose et al., 2015; Shalan and Rashad, 2013; Lu et al., 2012; Shao, 2009). As well known, (i) the ionic radius of a dopant may not differ much from the host ion to prevent lattice distortion, (ii) the decrement in energy gap results in a fast electron transportation from dye to TiO₂, (iii) the increased surface area accommodates more dye molecules, leading to higher light absorption and (J_{sc}), and (iv) the increase in shallow trap states (new energy levels) can lead to enhanced electron mobility, leading to an improved J_{sc} . Mn-doped titania was recently implemented in the case of photocatalytic and hydrogen evolution (Liu et al., 2013; Devi et al., 2009; Lee and Aikens, 2014). As described in above reports, Mn ions act as electron trap centers in doped material for photoexcited electrons thus provide the advantage of retarding charge recombination dynamics and result in an improved performance of the devices. Although Mn-doped metal oxides were found to be better materials for conversion of solar energy, the effect of Mn ions on the excited-state dynamics and charge transfer mechanisms is, surprisingly, not reported in literature.

In this study, we implicitly want to focus the attention on synthesizing titania with non-vacuum chemical method to decrease the product cost. For this purpose, high-quality Mn⁴⁺ ions-doped titania (Mn:TiO₂) nanopowders at different concentrations (0.2, 0.4, 0.6, 0.8, and 1.0 mol%) were firstly synthesized by proposed chemical methods alternative to commercial P25 and utilized as photoanode material in DSSCs. This novel perspective provides a feasible way to alternate commercial P25, such that, this approach not only reduces the production cost of the cell but also indicates a significant enhancement of charge transfer kinetics by the presence of an impurity energy level which led to increase in the driving force of electron injection. ~17% increase in PCE compared to commercial P25 based cell has been achieved at 0.4 mol% Mn doping concentration. This increment in photovoltaic performance was mainly ascribed to the improved interfacial charge transfer and/or retarded charge recombination process as further evaluated by decay and electrochemical measurements.

2. Experimental details

2.1. Synthesis and growth of pure and Mn:TiO₂ nanopowders

All chemicals were purchased from Sigma-Aldrich and used without further purification. The pure and Mn:TiO₂ nanopowders were synthesized using a chemical method with follow-up ball-milling and ultra-sonication processes. Briefly, 4.8 ml of titanium (IV) isopropoxide (TTIP) was dissolved in ethanol/deionized water (1/24, v/v) and stirred on a magnetic stirrer for 1 h. After this step, 0.96 ml of hydrochloric acid (HCl) was slowly added into the solution and it was subjected to stirring to form homogenous TiO₂ sol. At the end of 48 h, the obtained solution was centrifuged and washed three times with deionized water for degradation of

contamination in the sol and then the product was dried in an oven for 12 h at 50 °C. The obtained precipitate was diluted in ethanol and subjected into a ball milling system using 10 mm balls at 500 rpm for 6 h (Retsch PM 100). After ball milling, the solution was transferred to an ultrasonic homogenizer (Sonics Vibra-Cell) for further homogenization and particle size reduction. The homogenization was carried out for 2 h (30-s sonication followed by a 20-s rest on) at 30% amplitude. Finally, the solution was dried by a rotary evaporator (IKA RV 10) for dehydration and to remove the excess ethanol. To obtain Mn:TiO₂ nanopowders, above procedure was applied in the same sequence by adding Mn source with 0.2, 0.4, 0.6, 0.8, and 1.0 mol% during the dissolution step. The optical digital images of the obtained nanopowders, before and after the size reduction steps, can be seen in Fig. S1(a and b). To prepare the films, certain amounts of terpineol and ethyl cellulose were dissolved in ethanol as a binder mixture, and, few drops of this binder were added into the P25, pure, and Mn:TiO₂ nanopowders. These pastes were printed on ultrasonically cleaned fluorine-doped tin oxide (FTO) substrates by doctor blade technique. Then, all films were annealed in muffle furnace at 150 °C for 5 min, 250 °C for 5 min, 400 °C for 15 min, and 500 °C for 45 min, sequentially. The thickness of the obtained TiO₂ anodes were measured from the cross-sectional SEM images as ~15 μm (not shown here). Therefore, the effect of thickness on photovoltaic performance can be ignored.

2.2. Assembly of cells

All films were immersed in a 5 mM of N-719 dye and sensitized for 18 h under dark conditions. To prepare the triiodide/iodide (I⁻/I₃⁻) redox electrolyte, 0.01 M iodine, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.1 M 4-tert-butylpyridine, and 0.1 M lithium iodide hydrate were prepared in 3-methoxypropionitrile solvent, separately. Then, the prepared solutions were mixed and subjected to magnetic stirrer for 2 h. The preparation of platinum (Pt) counter electrode as well as the assembly of corresponding devices were carried out according to our previous reports (Tas et al., 2017). The active area of the device is approximately 0.36 cm².

2.3. Characterizations and equipments

The crystal structures of the nanopowders were investigated using Bruker D8 Advanced X-ray diffraction (XRD) system at the 20° ≤ 2θ ≤ 70° boundary values. The Raman spectra of these powders were recorded with Renishaw inVia spectrometer using a 532 nm diode-pumped solid state laser. The absorption measurements were carried out with Shimadzu 3600 UV-vis-NIR spectrophotometer. To analyze the loading amount of the dye on electrodes, dye was desorbed from electrode surface into sodium hydroxide (NaOH) solution in water/ethanol (1.0 mM, 50:50, v/v). The spectrophotometer was employed to measure the dye concentration of the desorbed dye solution. The photoluminescence (PL) spectra of the films were recorded using a PTI Quanta Master 30 PC spectrofluorophotometer with a Xe lamp as the excitation source. X-ray photoelectron spectroscopy (XPS) measurements were performed to provide the surface chemistry data using Thermo Scientific K-Alpha spectrometer. The specific surface area was determined from the linear portion of Brunauer-Emmett-Teller (BET) equation by Quantachrome-Quadrasorb Evo 4 Gas Sorption Surface Area and Pore Size Analyzer. The crystal lattice and morphology of the samples were investigated by high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-2100F) and field-emission scanning electron microscopy (FESEM, JEOL, JSM-6700F), respectively. The time-resolved fluorescence lifetime measurements were recorded using a PCI-Board system

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