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Facile one-pot controlled synthesis of Sn and C codoped single crystal TiO_2 nanowire arrays for highly efficient photoelectrochemical water splitting

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ABSTRACT

Here we report a (Sn, C) cation–anion codoped single crystal TiO_2 nanowire (NW) arrays as a highly efficient solar water splitting photoelectrode, able to be fabricated using a facile one pot hydrothermal synthesis method. The synergetic effects of codoping on the photoelectrochemical activity of the photoanode were investigated and compared to undoped and monodoped photoelectrodes. The (Sn, C) codoped TiO_2 NW photoanode generated the highest saturated photocurrent density i.e. 2.8 mA/cm^2 at 1.23 V vs RHE while yielding a maximum solar energy conversion efficiency of 1.32% at a potential of 0.55 V vs RHE – representing 60%, 94%, and 100% efficiency improvements compared to undoped, Sn doped, and C doped TiO_2 NW respectively at same potential. This improvement is attributed to the synergetic effects of Sn and C codopants to lower recombination and enhance life time of photogenerated charge-separated carriers on the surface states that lead to efficient hole transfer at the photoelectrode/electrolyte interface. In addition, an increased charge carrier density and conductivity (as evidenced from electrochemical impedance spectroscopy) and the enhanced incorporation of dopants in the codoped system, compared to monodoped system as quantified by XPS, highlights the importance of codoping. The nanomaterial was characterized by XRD, TEM, SEM and Raman UV–vis measurements. This study will guide improvements in the efficiency of TiO_2 for PEC water splitting using optimized codopant pairs.

1. Introduction

The increasing demand for sustainable, carbon-free energy production is driving the development of solar energy conversion and storage technologies. Photoelectrochemical (PEC) water splitting, that captures solar energy and stores it in the chemical bond of H_2 that can be used in several applications, is a promising way to address energy and environmental issues. Many semiconductor metal oxides have been examined to develop photoelectrodes that can harvest sunlight effectively and catalyze the photoelectrolysis of water into molecular hydrogen and oxygen. Different methods have been employed to improve the efficiency of semiconductor materials for photoelectrochemical water splitting. Some of these include anchoring a non-noble metal [1] or noble metal [2] water oxidation catalyst, activating wide band gap semiconductors in the visible light region by ion implantation and doping [3,4]. Heterogeneous metal oxide semiconductor photocatalysts, such as TiO_2, WO_3, Fe_2O_3, and ZnO, are inherently photoactive and can perform water splitting, while retaining excellent chemical stability in aqueous solution. The solar-to-hydrogen (STH) conversion efficiencies for these materials are still rather low, compared to theoretically expected values, because of their intrinsic limitations. For TiO_2 and ZnO for instance, their relatively large band-gap (>3.0 eV) limits visible light absorption and thereby STH conversion efficiency. In comparison, α-Fe_2O_3 is a semiconductor metal oxide with an indirect band-gap of 2.1 eV, which is encouraging for visible light absorption. Yet, its efficiency has been harshly restricted by its intrinsic material properties such as its short excited state lifetime

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(∼10 ps), short hole diffusion distance (2–4 nm) and low-lying conduction band (∼0.3 V below the water reduction potential) [5–7]. TiO_2 is the best known photocatalyst for overall water splitting into H_2 and O_2 – unlike WO_3 and α-Fe_2O_3, which are used only for water oxidation, due to their low lying conduction band positions.

In this regard, TiO_2 has been one of the most investigated photoanode materials since the first report of solar driven PEC energy conversion [8] and has remained as one of the most promising candidates due to its high photocatalytic activity, appropriate band edge positions for overall water splitting, strong optical absorption, chemical stability, photo-corrosion resistance, non-toxicity, and low cost [9–14]. TiO_2 materials with highly reactive crystal facets e.g. (1 1 1) and (0 0 1) surfaces [15,16] have been synthesized for photocatalytic water splitting and organic dye degradation. Much research has been devoted to addressing the large band gap of TiO_2 (3.0 eV for rutile) by coupling it with small band gap semiconductors [17]. Cation and/or anion doping (or alloying) [18,19], post growth hydrogen annealing [20], or by surface sensitization with organic dyes to improve the photocatalytic efficiency. Due to high intrinsic trap densities in TiO_2, it has a high charge carrier recombination rate, which is worsened by monodoping with cations or anions [13]. Heterostructuring the TiO_2 by codoping with two or more dopants is reported to achieve significant synergistic effects compared to their single ion doped or undoped TiO_2 counterparts, due to the strong interaction between these codopants within the TiO_2 matrix that alters the charge carrier transfer-recombination dynamics [21]. Codoping results in a much better effect on band gap narrowing due to strong interactions between the dopant metal and non-metal ions resulting in strong hybridization that gives rise to a fully occupied band above the top of the valence band edge and an empty band below the bottom of the conduction band [22]. Much theoretical work suggests that codoping TiO_2 improves light absorption, material quality, and the solubility limit of dopants [23–26]. A one-dimensional TiO_2 NW [27] structure has received much attention for PEC water splitting due to its large surface area, fast charge transport, and short diffusion distance for the photogenerated carriers [28,29]. Tin doping of TiO_2 [30,31] is essential as SnO_2 and TiO_2 have a low lattice mismatch that gives good structural compatibility and material stability. The incorporation of Sn or SnO_2 into TiO_2 by doping [31–33], to form core-shell structures [34], and heterostructure composites [30,35] has been shown to enhance photocatalytic activity. Doping TiO_2 with carbon is considered to be a promising way to improve the photocatalytic properties of TiO_2 photoanode for water splitting [36,37] and for pollutant decomposition [38]. Theoretically, compared to other N-cation codoped systems, C-cation systems exhibit greater band gap narrowing due to deeper C acceptor energy levels and much stronger interactions between C and the cations [22].

The advantages of TiO_2, e.g. its high photocatalytic activity, well-positioned band edges, strong optical absorption, chemical stability, photo corrosion resistance, non-toxicity, and its low cost need to be balanced against its limited photon-to-hydrogen efficiency. This results from its large band gap and the rapid recombination of photogenerated electrons and holes as a result of the high intrinsic trap density. We believe a metal/nonmetal codoped TiO_2 photoanode material treated with hydrogen can result in an enhanced PEC performance for water splitting.

Only few reports feature TiO_2 codoped with cations and anions, prepared by sol–gel [39] and hydrolysis precipitation methods [40], for photocatalytic activity with degradation of organic dyes. As yet, no report has demonstrated experimental work applying codoped TiO_2 NW to PEC water splitting – except for one that used sequential ex situ flame doping at 1100 °C [41].

In this study we fabricated a single crystal TiO_2 NW array photoanode codoped with Sn and C in a facile one pot hydrothermal synthesis method and investigated its PEC solar water splitting performance. Our material generated a saturated photocurrent density greater than the best current literature values under standard conditions [31,41]. The Sn only doped, C only doped and undoped TiO_2 NW arrays were also synthesized under the same reaction conditions for photoactivity comparisons with the codoped TiO_2 NW. All the samples were annealed in air at 450 °C for 2 h to increase crystallinity and further annealed in reducing gas (50% H_2 + 50% Ar) for an additional 60 min at 450 °C. A complete material characterization and PEC water splitting performance were performed. The amounts of Sn and C dopants were controlled by the concentrations of $SnCl_4$ and the glucose precursor reactant mixtures respectively. The pristine TiO_2 NW photoanode generated a saturated photocurrent density of 2.25 mA/cm^2 at 1.23 V vs RHE which is in agreement with literature values [20]. A maximum solar-to-fuel (STH) efficiency of 1.32% was achieved for the (Sn, C) codoped TiO_2 NW, which represents 60%, 94%, and 100% efficiency improvements compared to undoped, Sn doped, and C doped TiO_2 NW respectively at the same potential.

2. Experimental

2.1. Materials and synthesis

Titanium (IV) n-butoxide (99%), tin (IV) chloride (99%, anhydrous), alpha-D (+)-glucose (99+%, anhydrous) all from ACROS ORGANICS and HCl (37%) were used for the photoelectrode synthesis. Fluorine-doped tin oxide (FTO, 15 Ω) coated glass substrate was cleaned prior to use by sonicating with a 1:1:1 mixture of deionized water, acetone and 2-propanol prior to oven drying. Pristine TiO_2, Sn-doped, C-doped and (Sn, C)-codoped TiO_2 NW arrays were grown on FTO using a previously reported hydrothermal method [27]. In a typical synthesis, 15 ml of deionized water and 13 ml of concentrated hydrochloric acid were mixed in a 100 ml Teflon-bomb containing FTO substrate with conducting side facing up. Ti $(OBu)_4$ solution (250 μl) was added into this mixture. Selected amounts (0–1.44 ml) of $SnCl_4$ (0.1 M) and glucose (0–4.4 mg) as carbon dopant precursors were added into same reaction solution. The Teflon bomb containing all these components was sealed in a stainless steel autoclave. The mixture was kept in an oven at 150 °C for 12 h after which the material grown on FTO was rinsed in deionized water. Next, the sample was annealed at 450 °C for 2 h in a furnace followed by treating it under 50% H_2 + Ar gas in a tube furnace at 450 °C for 1 h.

2.2. Characterization

X-ray diffraction measurements were performed on a D2 phaser XRD-300W diffractometer equipped with a Cu Kα source operating at 30 kV and 10 mA. Scans were made from 20–80° 2θ at a rate of 3° per minute. A dual-beam focused ion beam (FIB, FEI Quanta 3D FEG) equipped with scanning electron microscope (SEM) mode operated at an accelerating voltage of 30 kV was used to capture FIB images. For TEM sample preparation, thinning of the specimen was achieved through the process of sputtering with gallium ions using FIB technology. UV–vis diffused reflectance spectra of the samples were obtained using a JASCO (ISV-469) V 560 UV–Vis spectrometer. Micro-Raman spectroscopy was used to characterize the phase and defects using a 532 nm green laser. The TEM images and Energy-dispersive X-ray (EDX) mapping images were collected on a Philips/FEI Tecnai 20G2 S-Twin TEM apparatus. X-ray photoelectron spectra (XPS) (PHI, 1600S) were recorded at the National Synchrotron Radiation Research Centre (NSRRC), Taiwan with 24A XPS beam line station.