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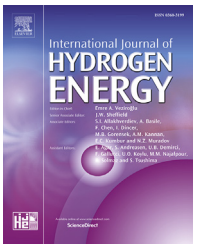

Active and robust novel bilayer photoanode architectures for hydrogen generation via direct non-electric bias induced photo-electrochemical water splitting

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ABSTRACT

Photo-electrochemical (PEC) water splitting is a promising and environmentally benign approach for generation of hydrogen using solar energy with minimum greenhouse gas emissions. The development of semiconductor materials for photoanode with superior optoelectronic properties combined with excellent photoelectrochemical activity and stability is vital for the realization of viable commercial development of PEC water splitting systems. Herein, we report for the very first time, the study of nanoscale bilayer architecture of WO_3 and Nb and N co-doped SnO_2 nanotubes (NTs), wherein WO_3 NTs are coated with $(Sn_{0.95}Nb_{0.05})O_2$:N-600 (annealed in NH_3 at 600 °C) layer of different thicknesses, as a potential semiconductor photoanode material for PEC water splitting. An excellent long term photoelectrochemical stability under illumination in the acidic electrolyte solution combined with a solar-to-hydrogen efficiency (STH) of ~3.83% (under zero applied potential) is obtained for the bilayer NTs, which is the highest STH obtained thus far, to the best of our knowledge compared to the other well studied semiconductor materials, such as TiO_2, ZnO and Fe_2O_3. These promising results demonstrate the excellent potential of bilayer NTs as a viable and promising photoanode in PEC water splitting.

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Introduction

Identification of a sustainable and an economically viable energy supply is the principle and a primary research challenge facing the entire world and the global population today [1–4]. Over the years, the anthropogenic overconsumption of carbonaceous fuels has caused deleterious effects on the environment due to excessive emission of well-known greenhouse gases which are the main drivers contributing to the global climatic change leading to the gradual rise in the earth's temperatures particularly, in the polar ice caps [3–6]. Consequently, the efficient use of energy, transitioning from fossil energy sources into renewable and clean (low carbon footprint) energy sources is of paramount importance to achieve a sustainable energy supply. This will be highly critical in developing a harmonious and energy efficient as well as an energy sufficient modern society meeting the colossal future global demands of an energy intensive technological savvy society with an energy infrastructure that is largely environment-friendly with minimum greenhouse gas emissions [3,4,7–14]. Identification and implementation of these non-carbonaceous energy sources thus, should be efficient, safe, economically producible, and easy to handle with the ability to transport/distribute in a cost-effective manner. In line with the above grave demands, hydrogen has been long considered as a promising clean and non-carbonaceous energy source due to its high energy density (120 MJ/kg for H_2 that is much higher than 44.4 MJ/kg for Gasoline) [15–23]. However, the concomitant progress towards realizing commercialization of hydrogen as a fuel has been largely thwarted due to significant challenges which include economic production, storage and cost-effective distribution of hydrogen [24–27].

Hydrogen production from photoelectrochemical (PEC) splitting of water has received special interest mainly due to the use of non-carbonaceous and environmentally benign implementation of water as a fuel. The absence of greenhouse gas production combined with the lack of any toxic/corrosive byproduct generation in the electrochemical water splitting process makes it an even more attractive approach [25,26]. The utilization of solar energy in driving the water splitting reaction is indeed an attractive option and has gained special interest in recent years, since the sun delivers a massive average energy of 120,000 TW per year to the surface of the Earth [25,28]. Fujishima and Honda's pioneering work on PEC water splitting using n-type TiO_2 semiconductor has clearly demonstrated that PEC water splitting is indeed the foremost technology among the many promising approaches for hydrogen production in an environmentally benign manner [25,29].

The progress of PEC water splitting approach towards commercialization is nevertheless, stymied due to lack of availability of the desired semiconductor materials exhibiting superior light absorption properties, excellent photo-electrochemical activity and stability [25,26]. Materials such as TiO_2, ZnO and α-Fe_2O_3 are widely studied for photoanode applications in PEC water splitting, mainly due to their low cost and ease of availability [21,30–35]. The wide band gap of TiO_2 (~3.2 eV) despite its demonstrated promise, has primarily limited its use as a photoanode for commercialization of PEC water splitting cells [36–40]. α-Fe_2O_3 on the other hand, faces the major problem related to very short minority carrier (hole) diffusion lengths of the photo-generated carriers, low electron mobility and high recombination rates of the photo-generated carriers [41,42]. In the case of ZnO, inferior light absorption due to the wide band gap (~3.2 eV) and additionally, poor long term stability in aqueous electrolyte solutions are key issues limiting the widespread implementation of ZnO [35,43–45]. On the grounds of different challenges faced by the well-studied semiconductor materials so far as mentioned above, it is clear that identification and development of novel semiconductor materials exhibiting superior optoelectronic properties, excellent photo-electrochemcial activity and stability is of paramount importance to realize economic development and consequent commercialization of PEC cells for water splitting.

Amongst the many materials considered to date, SnO_2 is a promising candidate semiconductor material widely explored in dye sensitized solar cells (DSSCs) due to its good electron mobility (~100–200 $cm^2\ V^{-1}\ s^{-1}$ for SnO_2 *vs* ~10^{-1} $cm^2\ V^{-1}\ s^{-1}$ for TiO_2) and in addition, it exhibits excellent corrosion resistance in acidic electrolyte solutions [46–49]. However, the wide band gap of SnO_2 (~3.5 eV) offers poor light absorption properties leading to poor photo-electrochemical activity [50]. Systematic band gap engineering was carried out using Nb and N as potential co-dopants for SnO_2 enabling its use for photoanode applications in PEC water splitting and the beneficial results were reported by us earlier [49]. Nb, which is widely used for improving the electrical conductivity of SnO_2 in transparent and conductive oxide thin films (TCO) [51–54], was therefore used as a dopant due to its intrinsic availability of abundant electronic states and more importantly, minor influence on the SnO_2 lattice structure, due to the lower ionic radii of Nb^{4+} (69 pm) than Sn^{4+} (71 pm) affording good solubility in the solid state [49,55,56].

Nitrogen was also used as a dopant for SnO_2 to achieve hybridization of the substitutional N 2p states with O 2p states and thus, shifting the valence band (i.e., highest occupied molecular orbital, HOMO) upwards, without affecting the conduction band (i.e., lowest unoccupied molecular orbital, LUMO), thereby, reducing the band gap [49,57–61]. Thus, the electronic states of Nb and N simultaneously introduced in the band gap of SnO_2 contributed to significantly reducing the band gap of SnO_2 from ~3.5 eV to ~1.99 eV for $(Sn_{0.95}Nb_{0.05})O_2$:N-600 nanotubes (NTs) (annealed in NH_3 at 600 °C), resulting in superior light absorption properties as reported by us [49]. These experimental aspects were also ably aided and complemented by the results of theoretical first principles calculations, as reported earlier by us [49]. Nb and N co-doping in SnO_2 as discussed in our earlier report offered 4-orders of magnitude improved carrier density resulting in improved number of carriers available for reaction at the cathode and photoanode [49]. The superior optoelectronic properties of $(Sn_{0.95}Nb_{0.05})O_2$:N-600 NTs offered improved photo-electrochemical activity with the negative onset potential of (−0.14 V *vs* RHE) and the highest applied bias photon-to-current efficiency (ABPE) of ~4.1% (at applied potential of ~0.75 V *vs* RHE), which is higher than that obtained using the

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