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## Tailoring of boron-doped MnTe semiconductorsensitized TiO<sub>2</sub> photoelectrodes as near-infrared solar cell devices



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#### ABSTRACT

We studied the photovoltaic performance of a new tailoring of boron-doped MnTe semiconductor-sensitized solar cells (B-doped MnTe SSCs). The B-doped MnTe semiconductor was grown on TiO<sub>2</sub> using two-stages of the successive ionic layer adsorption and reaction (SILAR) technique as a photoelectrode. The phase of the boron-doped MnTe and MnTe2 semiconductor as sensitizers were characterized with  $\sim$ 20–50 nm in diameter. The B-doped MnTe(5) exhibited the best efficiency of 0.04%, compared to that of the undoped sample of 0.006%. In addition, the band gaps of 1.30 and 1.26 eV were determined for the undoped and B-doped MnTe NPs, respectively. The change in the band gap after boron doping was performed due to crystal quality improvement and the larger size of the MnTe NPs, leading to a broader absorption of the sensitizer and a noticeable improvement in the photovoltaic performance. This kind of semiconductor and synthesis procedure can be applied for further improvement in a higher efficiency and more stability in SSCs.

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#### 1. Introduction

Currently, narrow band gap semiconductor sensitizers commonly used in SSCs such as CdS [1], CdSe [2], PbS [3], ZnSe [4] and CdTe [5] are a promising candidate for the next generation of solar cells

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and are considered as good sensitizers due to their tunable absorption effected from the quantum size effect [6,7], their high extinction coefficient and also their ability to generate multi-excition through impact ionization [8,9]. However, while the theoretical efficiency produced by SSCs can be up to 44% [10], but the highest efficiency into date is  $\sim 5-6\%$  [11-13] and they absorb incident light only in the visible region. Alternatively, a tailoring of narrow band gap chalcogenide semiconductors as sensitizers to absorb the incident light in the near-infrared region with low toxicity are available with optical and photovoltaic properties and have recently been published such as SnS with band-gap values of ~1.4 eV [14] or SbS<sub>3</sub>, which can be used as a potential novel photosensitizer in TiO<sub>2</sub> mesoscopic with a liquid electrolyte and its band gap of 1.7-1.8 eV [12,13]. In these sense, the synthesis of a new tailored semiconductor as a sensitizer is of interest. The study of polycrystalline MnTe thin film using various techniques had been undertaken by many groups. Investigation of the electrical and optical properties has revealed good performance of such material [15–17], but there are no published reports on MnTe semiconductor nanoparticles as a sensitizer for SSCs to date. Thus, this study demonstrated a new semiconductor sensitizer for photovoltaic performance based on the use of II-VI compounds alloyed with chalcogenide manganese telluride (MnTe), which is a p-type semiconductor and has a very high density of impurity charge carriers [18] for favoring charge transport in a device. Furthermore, it has a narrow optical direct band gap of 1.3 eV [19], which is close to optimum for photo-conversion [20] and the bulk band gap of SnS ( $E_g \sim 1.3-1.4$  eV) [14,21-23]. It can be a very high optical absorption material.

Doping with active transition metal elements has demonstrated many advantages and exhibited remarkable optical and photovoltaic performances, which improves the electronic and photophysical properties of semiconductor nanoparticles. For instance, Huang et al. [24] fabricated Cu-doped PbS/ CdS co-sensitized mesoporous TiO2 and their cell showed a power conversion efficiency of 2.01% with a remarkable superior current density up to 21 mA/cm<sup>2</sup>, Santra and Kamat [11] reported the first demonstrated strategy of transition metal-Mn<sup>2+</sup> doping in single CdS and double-layered CdS/CdSe on a mesoporous TiO<sub>2</sub> photoanode. The efficiencies of both devices were improved after Mn<sup>2+</sup> doping by 2.53 and 5.42% with photocurrent densities of 7.2 and 20.7 mA/cm<sup>2</sup>, respectively. However, the study of Chen et al. [25] noted that doping with metal elements was impaired by their thermal instability which induced more carrier recombinations in the cells; meanwhile, doping with nonmetal elements instead of metal elements has been introduced to improve the photocatalytic efficiency and reduce thermal instability in the cell which leads to suppression of the carrier recombination and modify semiconductor crystallization. Many groups have expressed interested in synthesizing a nonmetaldoped semiconductor as a sensitizer for solar cell applications. For example, Hao et al. [26] fabricated a multilayered-phosphorus-doped silicon semiconductor on a SiO<sub>2</sub> matrix to investigate its electrical properties and optical emission. Luke et al. [27] synthesized a nitrogen-doped CdSe semiconductorsensitized nanocrystalline TiO<sub>2</sub> film as a photoelectrode, which yielded a power conversion efficiency of 0.84% and noted that combining nitrogen doping with the semiconductor sensitizer on TiO<sub>2</sub> thin films is an effective and promising procedure to enhance the photoresponse in the near-UV and visible region. Furthermore, Liu et al. [28] successfully synthesized carbon quantum-dot-doped CdS microspheres (C/CdS). The C/CdS exhibited a crucial role in enhancing the photoelectrochemical activity, efficient charge separation and transportation in the composites and in addition, a higher and more stable photocurrent density was generated in the cell.

According to the study of Grey et al. [29], semiconductor–metal oxide material incorporated with boron (B<sup>3+</sup>) as a nonmetal element assigning as a dopant with p–p transition that could improve the photocatalytic activity and act as photogenerated electron traps to facilitate the charge separation and also play an important role in the suppression of the recombination between photogenerated electrons and holes in the electrolyte region, but there has been little study of boron doping in semiconductor sensitizing until now. In our previous work, we reported on optimal condition of the MnTe(7)-coated boron-doped TiO<sub>2</sub> with the highest power conversion efficiency of 0.033%, compared to that of undoped sample, the yielded power conversion efficiency reduced by 103%. It can be noted that boron-doped metal oxide film improves the power conversion efficiency and play the remarkable role to improve the photocatalytic activity [30]. Herein, this work effort to prepare undoped and boron-doped MnTe (B-doped MnTe) semiconductor-sensitized TiO<sub>2</sub> photoelectrodes by the successive ionic layer adsorption and reaction (SILAR) technique. The as-prepared photoelectrodes were

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