

CHAPTER 7

SnO₂ dye-sensitized solar cells

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Contents

7.1 Introduction	205
7.1.1 Tin oxide	208
7.2 Various SnO ₂ nanostructures employed as photoanodes in dye-sensitized solar cells	208
7.2.1 Pure SnO ₂ nanostructures based on nanoparticles in dye-sensitized solar cells	208
7.2.2 Characterization of synthesized nanostructures	209
7.2.3 Dye-sensitized solar cells fabrication and testing	214
7.3 Photoanode based on SnO ₂ one-dimensional nanostructures	228
7.3.1 Porous and multiparous tin oxide nanofiber	229
7.3.2 Characterization of porous and multiporous nanofibers	229
7.4 Dye-sensitized solar cells fabrication and testing	240
7.4.1 Morphology and thickness of the electrodes	240
7.4.2 Light scattering properties of the dye-anchored electrodes	241
7.4.3 Photovoltaics characteristics of tin oxide nanostructures	244
7.4.4 Charge transport properties of dye-sensitized solar cells	245
7.5 Photoanode based on SnO ₂ composite or hybrid	249
7.5.1 Characterization of composite nanostructures	250
7.5.2 Dye-sensitized solar cells fabrication and testing	260
7.6 Doped photoanode	268
7.7 Three-dimensional SnO ₂ nanostructures	270
7.8 Photoanodes based on SnO ₂ core—shell	270
7.9 Outlook and future recommendations	277
References	278

7.1 Introduction

It has been previously shown that TiO₂ is the most employed photoanode material in dye-sensitized solar cells (DSSCs). Despite the high surface area of TiO₂, it is characterized by slow electron diffusion

($\sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and lower μ_e ($< 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), consequently resulting in high charge recombination at the $\text{TiO}_2/\text{electrolyte}$ interface [1]. ZnO is another widely employed photoanode material that has similar band gap ($\sim 3.2 \text{ eV}$) to TiO_2 while providing higher μ_e than the latter. However, it is chemically unstable with the successful Ru commercial dyes due to the fact that the carboxylic group present in the dye dissolves the ZnO and creates a $\text{Zn}^{2+}/\text{dye}$ aggregate, which consequently affects the electron injection to the metal oxide semiconductor (MOS) [2,3]. Furthermore, SnO_2 has a lower Conduction band (CB) edge (more positively located, i.e., $\sim 300\text{--}500 \text{ eV}$) [4–6] than TiO_2 (Fig. 7.1B) as it is made of lower energy orbitals (*s* orbitals) [7]. The lower CB position enables electron injection from the low-lying Lowest unoccupied molecular orbitals (LUMO) sensitizer, such as perylene dyes [9] and PbS quantum dots [10]. The incorporation of such sensitizers may lead to the utilization of the near-infrared part of the solar spectrum. Although SnO_2 is one of the earliest materials that showed the photovoltaic effect in the 1980s [11,12], its intrinsic lower CB ($\sim 300 \text{ eV}$ lower than TiO_2) results in routinely achieving a low $V_{\text{OC}} \sim 500 \text{ mV}$ (V_{OC} for $\text{TiO}_2 \sim 800 \text{ mV}$) despite the high $J_{\text{SC}} \geq 15 \text{ mA cm}^{-2}$. Inspired from the high μ_e of SnO_2 , a number of researchers have attempted doping various transition metals to uplift its Fermi energy level; for example, Zn-doped SnO_2 resulted in a $V_{\text{OC}} \sim 780 \text{ mV}$ [13]. Various semiconductor divalent metal oxides, such as Cd, Ni, Cu, and Pb are doped in SnO_2 to improve its performance in DSSCs [14]. Such dopants enhanced the surface area, the dye loading, raised its flat-band potentials, and eventually enhanced the η compared to a pure SnO_2 -based DSSCs. Despite these advancements, η of SnO_2 -based DSSCs remains lower than that of the state-of-the-art TiO_2 .

Another issue with SnO_2 is its low iso-electric point (IEP) ($\text{pH} \sim 4\text{--}5$) compared to that of TiO_2 ($\text{pH} \sim 6\text{--}7$) and ZnO ($\text{pH} \sim 9$) [15], which makes weak bonding with the carboxylic groups upon dye anchoring, and consequently yielding low photocurrent in DSSCs. Toward this end, a number of SnO_2 morphologies other than nanoparticles (NPs), such as nanotubes (NTs), core–shell structures, and composite nanostructures are employed in DSSCs. These structures provide two advantages: (1) provide larger surface area for dye loading and (2) a directed transport path for electron diffusion. Such developments have brought SnO_2 to deliver η as high as $\sim 4\%$ in its pure form and 7.6% in hybrid photoanodes [16].