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Research paper

Interconnected ZrO_2 doped ZnO/TiO_2 network photoanode for dye-sensitized solar cells

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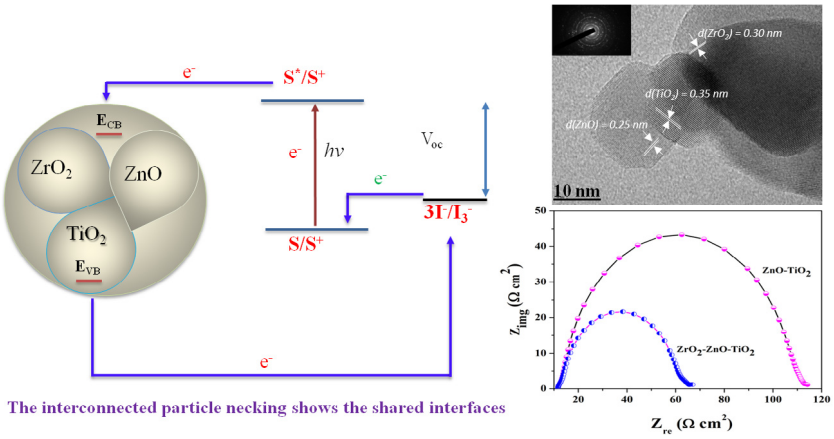
HIGHLIGHTS

- ZrO_2 surface passivated ZnO/TiO_2 photoanode is investigated for DSSC.
- ZrO_2 prevents charge recombination and improves open circuit voltage.
- Open circuit voltage is enhanced due to composite/electrolyte band edge shift.
- IPCE measurements reveal higher photons absorption and superior photocurrent.
- Longer electron life time and higher efficiency for ZrO_2 based photoanode.

GRAPHICAL ABSTRACT



The interconnected particle necking shows the shared interfaces

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ABSTRACT

In this study, ZrO_2 surface modified ZnO/TiO_2 composite film is adapted as photoanode in dye sensitized solar cells (DSSCs) and compared with un-passivated ZnO/TiO_2 DSSC performance. The performance is investigated by dark and photocurrent density–voltage (*J–V)* characteristics, quantum efficiency and electrochemical impedance spectroscopy. The *J–V* characteristics shows that DSSCs with ZrO_2 surface passivation produces significantly high open-circuit voltage of 0.87 V, short-circuit current density of 13.6 mA cm^{-2}, fill factor of 0.65 and a power conversion efficiency of ∼6.97% under simulated AM1.5 solar irradiation. The higher onset potential in the dark, larger open-circuit potential under illumination, and an enhancement in power conversion efficiency strongly suggests an efficient suppression of back electron transfer from the conduction band of the hetero-phase junctions to the oxidized species in the electrolyte as established by dark and illuminated *J–V* characteristics. Thus, the oxidized dye molecules are readily regenerated by a redox couple dissolved in an electrolyte, allowing more photon excitation by dye molecules. The electrochemical impedance data extracts further provide additional evidence of the enhancement in photocurrent and lower charge carrier resistances observed in ZrO_2/ZnO/TiO_2/dye

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photoelectrode. With the ZrO_2 surface modification, main loss mechanism in the device is suppressed and backward recombination reaction is minimized.

1. Introduction

Affordable and more easily processed solar cells together with long term stable efficiency are the holy grails of renewable energy research. As such, dye sensitized solar cells (DSSCs) have attracted intense academic and technological interest because of its low fabrication cost as opposed to *p-n* junction silicon solar cells (Toivola et al., 2009). It is the only photovoltaic device that converts light energy into electrical energy using organic dyes stained metal oxide semiconductors. DSSCs have several advantages over silicon-based photovoltaics counterparts. It offers the high power conversion efficiency under low-light (i.e. cloudy skies) and artificial light conditions (Grätzel, 2005; Somasundaran et al., 2011).

In 1991, Gratzel group successfully developed DSSC based on novel electrode architecture in the form of a mesoporous TiO_2 film. The nature of the mesoporous TiO_2 network provides large specific surface area that improves dye chemisorption and light harvesting efficiency of incident photons to electrons (Grätzel, 2001; Pai et al., 2014; Docampo et al., 2014). Since the breakthrough, different TiO_2 morphologies in the form of spheres (Veerappan et al., 2014), nanowires (Lee et al., 2012), nanorods (Wang et al., 2012a) and nanotubes (Chen et al., 2009) have been widely employed in a typical device architecture. With these morphologies, different energy conversion efficiencies were observed. Through the planar nanocrystalline TiO_2 structure and ruthenium (II) based dyes, a record high power conversion efficiency of 12.3% (Yella et al., 2011) was achieved for devices prepared under high vacuum processes. Recently, high power conversion efficiency of 13% is reported by employing newly engineered porphyrin SM315 dye, (Mathew et al., 2014). However, it is still short of *p-n* junction derived solar efficiency of 25% (Green et al., 2011).

In addition to TiO_2 nanocrystals, various nanostructured metal-oxides such as ZnO (Shintaro Ueno and Fujihara, 2011), SnO_2 (Duan et al., 2015), $SrTiO_3$ (Hod et al., 2010), Fe_2O_3 (Shang et al., 2015), WO_3 (Yong et al., 2013), and binary oxides including ZnO/TiO_2 (Liu et al., 2012), ZrO_2/TiO_2 (Wang et al., 2012b), SnO_2/TiO_2 (Mohan et al., 2012), ZnO/SnO_2 (Milan et al., 2015), $SrTiO_3/TiO_2$ (Jose et al., 2009) have been actively investigated as photoelectrodes in DSSCs. In binary metal oxides, the band edge offset facilitate strong driving force for efficient charge transport and collection (Hussein et al., 2013). However, despite considerable efforts made, the overall efficiency obtained with binary system was inferior to the nanoparticle TiO_2 based films (Law et al., 2006; Chen et al., 2013).

The power conversion efficiency is the performance indicator of the DSSCs. It reflects the device ability in the light harvesting, charge separating and transferring processes. The performance largely hindered by the non-sufficient utilization of the low-energy photons (i.e. near red and near-infrared light) and difficulties in effectively extracting photo-generated electrons due to competing and spontaneous back-electron transfer reactions.

In the DSSC sandwich configuration and working mechanism, inherently complex and competitive interfacial elements exist, namely TiO_2/electrolyte, dye/electrolyte and Fluorine-doped tin oxide (FTO)/electrolyte, where physical interactions occur and carriers in separate phases meet each other. Thus, there are series of recombination reaction rates that compete with the forward reactions. The photo-generation, and subsequent charge separation and recombination occur exclusively at hetero-interfaces (Gu et al., 2017; Gao et al., 2017). The proximity of electrons and holes, and the lack of potential barrier between them lead to charge carrier's annihilation. Quite naturally, the device performance strongly depend on interfacial physical and photo–electrochemical interactions (Annamalai et al., 2011). Thus, major energy losses via recombination are almost entirely an interfacial process as opposed to bulk process in p–n junction solar cells (Gregg et al., 2001).

Energy losses associatively occur at TiO_2/electrolyte interface (Tang et al., 2013) or FTO/electrolyte interface (Ofir et al., 2008). Thermodynamically spontaneous back charge reaction between the conduction band electrons and oxidative species present in the electrolyte reduces photocurrent available to the load. Likewise, back-electron transfer reactions occur at the contact of an electrolyte with an FTO surface by a permeation mechanism, causes an electrical leakage in the device, leading to loss of the photocurrent (Smiglak et al., 2014). Specifically, dark current originates from physical contact of electrolyte with a bare conductive FTO surface due to the porous nature of the TiO_2 structure (Yu et al., 2009). Minimizing the dark current at TiO_2/electrolyte interface, will improve in an open circuit potential. Therefore, retarding the spontaneous recapture of injected electrons by oxidative species at the photoanode/electrolyte interface or blocking the current leakage at FTO/electrolyte interface is critical to extract maximum power conversion.

To address these problems, numerous approaches have been proposed to minimize the recombination losses at the interfaces. Particularly, device architectures that include metal oxide overcoats to create barrier layers with more negative conduction band potential (Palomares et al., 2003) and organic framework as additives to suppress potential-dependent dark current (Katz et al., 2012), thereby leading to reduction in current–voltage hysteresis, an increase in the open-circuit potential and the power conversion efficiency of the solar cell.

In this study, the arrangement of the photoanode constituting conjoined and ZrO_2 surface passivated ZnO/TiO_2 compact layer was investigated in DSSCs to address the aforementioned problems. The device performance was discussed in relation with the spatial photoinduced charge separation, blocking back electron transfer in the photoanode and bandgap off-set. Herein, we report improvements in solar energy conversion efficiency and high open circuit potential attributed to improved reduced current–voltage hysteresis, enhanced photon absorption and light-harvesting efficiency, effective charge transport and separation, and suppressed dark current by employing hetero-phase photoanode in the form of ZrO_2 surface passivated ZnO/TiO_2 compact layer. The recombination losses were greatly minimized as confirmed by impedance analysis and dark current measurements. The photocurrent density–voltage characteristics, incident photon-to-current efficiency *(IPCE)* and electrochemical impedance spectroscopy methods have been employed to understand the surface passivation effect of the photoanode and obtain evidence responsible for the improved open circuit potential, reduced recombination and DSSC performance. A comparative study of DSSCs performance based on ZnO/TiO_2 and ZrO_2 surface passivated ZnO/TiO_2 compact layer nanostructured electrodes is presented.

2. Experimental

2.1. Synthesis of ZrO_2 surface passivated ZnO/TiO_2 nanostructure

The ZrO_2 surface passivated ZnO/TiO_2 nanostructure was synthesized according to the previously reported method (Hussein