Coordination Chemistry Reviews 320–321 (2016) 193–215

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Design, fabrication and modification of metal oxide semiconductor for improving conversion efficiency of excitonic solar cells

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Contents

Abbreviations: 1D, one-dimensional; 2D, two-dimensional; 3D, three-dimensional; ABL, anode buffer layer; AFM, atomic force microscopy; ALD, atomic layer deposition; CBD, chemical bath deposition; CBL, cathode buffer layer; DSC, dye-sensitized solar cell; EDS, X-ray energy dispersive spectroscopy; EDX, energy dispersive X-ray; EIS, electrochemical impedance spectroscopy; ESC, excitonic solar cells; FESEM, field emission scanning electron microscopy; FF, fill factor; FTIR, Fourier transform infrared spectroscopy; FTO, F-doped tin oxide; HRTEM, high resolution transmission microscope; HTM, hole transport material; IPCE, incident photon-to-current conversion efficiency; ITO, indium tin oxide; J_{sc}, current density; MEG, multiple exciton generation; LUMO, lowest unoccupied molecular orbital; MOS, metal oxide semiconductor; OPV, organic photovoltaic; P3HT, poly(3-hexylthiophène); pcAFM, photoconductive atomic force microscopy; PCBM, [6,6]-phenyl-C61-butyric acid methyl ester; PCE, power conversion efficiency; PEDOT, poly(3,4-ethylenedioxythiophene); PL, photoluminescence spectra; PSC, perovskites solar cell; QD, quantum dot; QDSC, quantum dot-sensitized solar cell; SAED, selected area electron diffraction; SEM, scanning electron microscope; SKPM, scanning Kelvin probe force microscopy; SILAR, successive ionic layer absorption and reaction; SnO_2, tin dioxide; TEM, transmission electron microscopy; TiO_2, titanium dioxide; UV–vis, ultraviolet and visible light; V_{oc}, open voltage; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; ZnO, zinc oxide.

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http://dx.doi.org/10.1016/j.ccr.2016.02.016
0010-8545/

ARTICLE INFO

Article history:
Received 3 November 2015
Received in revised form 15 February 2016
Accepted 20 February 2016
Available online 11 March 2016

Keywords:
Metal oxide semiconductors
Dye sensitized solar cell
Quantum dot sensitized solar cells
Perovskites solar cells
Inverted organic photovoltaics

ABSTRACT

Excitonic solar cells (ESCs) including dye-sensitized solar cells (DSCs), quantum dot-sensitized solar cells (QDSCs), perovskites solar cells (PSCs) and inverted organic photovoltaics (OPVs), are built upon metal oxide semiconductors (MOSs), which have attracted considerable attention recently and showed a promising development for the next generation solar cells. The development of nanotechnology has created various MOS nanostructures to open up new perspectives for their exploitation, significantly improving the performances of ESCs. One of the outstanding advantages is that the nanostructured mesoporous MOSs offer large specific surface area for loading a large amount of active materials (dyes, quantum dots or perovskites) so as to capture a sufficient fraction of photons as well as to facilitate efficient charge transfer. This review focuses on the recent work on the design, fabrication and surface modification of nanostructured MOSs to improve the performance of ESCs. The key issues for the improvement of efficiency, such as enhancing light harvesting and reducing surface charge recombination, are discussed in this paper.

1. Introduction

Transition metal oxides, particularly those wide bandgap metal oxide semiconductors (MOSs), such as titanium dioxide (TiO_2), zinc oxide (ZnO) and tin dioxide (SnO_2) have found wide applications in sustainable clean energy, including solar cells, solar fuel, photo catalysis and energy storage devices due to their natural abundance, chemical inertness, and excellent photoelectric and electrochemical properties [1–7]. In the past decades, the development of nanotechnology has created various MOS nanostructures to open up new perspectives for their exploitation, significantly improving the performances of end-user devices including lithium, sodium and magnesium ion batteries and supercapacitors [8–10], especially in the next generation solar cells [11–13]. As the traditional photovoltaics, the p–n junction crystalline silicon (c-Si) solar cells suffer from high cost of manufacturing and installation and long energy payback time [14,15]. There is an imperative demand for the development of low cost and high performance solar cells to allow sustainable energy sources to replace fossil fuels [14,16]. As a cost effective alternative to silicon based photovoltaics, excitonic solar cells (ESCs) including dye-sensitized solar cells (DSCs), quantum dot-sensitized solar cells (QDSCs), perovskites solar cells (PSCs) and inverted polymer solar cells or inverted organic photovoltaics (OPVs), based upon nanostructured MOSs have attracted considerable attention recently and showed a promising development for the next generation solar cells [17–23]. MOS plays a very important role in ESCs either as electron transporting layer while blocking hole transport (known as cathode buffer layer) or as hole transporting layer while blocking the electron transport (anode buffer layer) [13].

As early as 1991, MOS TiO_2 with porous nanostructure was successfully used in DSCs to get high power conversion efficiency (PCE) of greater than 7%, which was a significant breakthrough for the next generation solar cells with low cost [22]. DSC is a category of photovoltaic device based on a photo-electrochemical system in which a porous MOS film with dye molecules adsorbed on the surface serving as the working electrode for light harvesting and the generation of photoexcited electrons [24]. Many efforts have been focused on improving light absorption of sensitizers [25–28]. In 2014, a recorded PCE of 13% of DSC has been obtained by using a molecularly engineered porphyrin dye coded SM315 and the cobalt (II/III) redox electrolyte [29]. In comparison with c-Si solar cells, PCE of DSCs still is much low. One of the effective approaches is to developing new sensitizers for absorbing photons in the full sunlight spectra. Narrow-band-gap semiconductor quantum dots (QDs) with wide light absorption region, such as CdS [30,31], CdSe [23,32], PbS [33] and InAs [34] have been investigated as photo-sensitizers instead of organic dyes to form QDSCs that have attracted a lot of attention particularly due to: (1) adjustable band gap through design and control the size of QD, (2) good chemical stability (3) much efficient light absorption (a high extinction coefficient) and (4) multiple exciton generation (MEG) promising a power conversion efficiency theoretically up to 40% in a single junction solar cell [35–37]. Practically efficiencies in the range of 6% for CdSe [38,39] and 8% for CdSeTe [40–42] QDSCs have already been achieved; the PCE of QDSCs remains lower than that of DSCs, due likely to large surface charge recombination, attributable to the surface imperfection of QDs and the less ideal contact between QDs and MOS scaffold [43]. In 2009, Miyasaka group reported the solar cells with DSC structure using organic–inorganic hybrid perovskite $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$ as visible-light sensitizers instead of organic dyes [44]. This attempt led to PCE of 3.8%. Although, the PCE was low, the attempt provided a new approach for the next generation solar cells [45]. In 2011, Park's group reported a 6.5% efficient $CH_3NH_3PbI_3$ PSC [46], though this work did not attract much attention due to the liquid electrolyte used in the devices. In 2012, an all solid ESC using perovskite with a PCE greater than 10% was obtained by Snaith's group, which had attracted worldwide attention [47]. In 2015, PSCs based on the MOS TiO_2 assembled with $CH_3NH_3PbX_3$ achieved PCE of greater than 20% [48]. In recent years, OPVs have attracted extensive investigation as one of ESCs, mainly due to their inherent advantages of being low-cost, and compatible with flexible substrate and solution-based roll-to-roll processing technique [17–21,49]. Compared with the organic photovoltaics with a traditional structure, which typically have a configuration ITO/PEDOT/P3HT:PCBM/MOS/Al, inverted OPVs with the configuration ITO/MOS/PCBM:P3HT/PEDOT/Ag avoid the contact of ITO with PEDOT (which degrades the conductivity of ITO glass) and allow the use of high work function metal (e.g., Ag) as top electrode, and can therefore significantly enhance the stability of polymer solar cells [13].

Among various MOSs, TiO_2, ZnO and SnO_2 have been studied widely in ESCs, due to their matching band structure, excellent physical properties and high electronic mobility [50–55]. Table 1 shows structural and electronic characteristics of TiO_2, ZnO and SnO_2 [56]. It can be seen that TiO_2, ZnO and SnO_2 have similar band structure and physical properties. In the past decades, more and more efforts have been focused on the application of TiO_2, ZnO and SnO_2 in ESCs. For example, Fig. 1 displays the evolution of the number of publications for 'dye sensitized solar cell'. In addition to research works, many excellent review and perspective articles have covered the fundamentals and technical approaches for the design, fabrication, and characterization of MOSs for ESCs [11,51,54,57–62]. In this review, we would focus mainly on the recent work on the MOS structure and their interface for improving the efficiency of ESCs, such as enhancing light harvesting and reducing surface charge recombination.