Design, Fabrication and Modification of Metal Oxide Semiconductor for Improving Conversion Efficiency of Excitonic Solar Cells

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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 (MOSSs), 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.

Key words: Metal oxide semiconductors, dye sensitized solar cell, quantum dot sensitized solar cells, perovskites solar cells, inverted organic photovoltaics.

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; SnO₂, tin dioxide; TEM, transmission electron microscopy; TiO₂, titanium dioxide; UV-vis, ultraviolet and visible light; V_{oc} , open voltage; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; ZnO, zinc oxide.

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 an 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 $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbX}_3$ 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, **Figure 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.

Table 1. Structural and electronic characteristics of TiO₂, ZnO and SnO₂. [56]

MOSs	Crystal structure	Band gap / eV	Conduction Band Minimum / eV	Electron Effective Mass	Static Dielectric Constant	Electron Mobility /cm ² V ⁻¹ s ⁻¹	Electron Diffusion Coefficient (nanoporous film) / cm ² s ⁻¹
TiO ₂	Rutile, Anatase	3.0-3.2	-4.41	9	86, 170	0.1-4	4.3×10 ⁻⁴
ZnO	Wurtzite	3.2-3.4	-4.36	0.26	9.26, 8.2	130-200	1.1×10 ⁻⁴
SnO ₂	Rutile	3.6-3.8	-4.88	0.275	14, 9	200-250	7.3×10 ⁻⁵

Figure 1. Evolution of the number of publications for ‘dye sensitized solar cell’ with ‘TiO₂’, ‘ZnO’ and ‘SnO₂’, respectively. Source: ISI Web of Science, Thomson Reuters.

2. Dye sensitized solar cells (DSCs)

DSCs are in essence a photoelectron-chemical system as shown in **Figure 2** [63]. Nanostructured MOS films are the framework of DSC photoanodes, which serve dual functions as the support for sensitizer loading and transporter of photo-excited electrons from sensitizer to external circuit[58]. Usually, a layer of MOS with the thickness 10 to 20 μm is prepared on a glass substrate coated with a transparent conductive film. The other electrode, the so-called counter electrode, is a glass or silicon substrate coated with a platinum film. As a conductive medium, the liquid electrolyte with I^-/I_3^- redox couples is filled in the gaps of MOS and the space between the photoanode and counter electrode. The work process of DSC is [63] : the light irradiating from the photoanode side is captured by the dye molecules that are adsorbed on the oxide, leading to the generation of

photoexcited electrons in the dye molecules; the photogenerated electrons then transfer into the oxide, diffuse in the oxide, and are finally collected by the transparent conductive film on the glass substrate, which is connected to external circuit; the photooxidized dye molecules are reduced by electrons provided by I^-/I_3^- redox couples in the electrolyte. Those photogenerated electrons at the photoanode travel through the external circuit, reach the platinum-coated counter electrode and, finally, gain access to the electrolyte, reducing I^-/I_3^- redox couples and enabling the electrolyte to be regenerated. In DSCs, the structure of photoanodes has important effect on the light harvesting and photoexcited electrons transport. Not only does the nanostructured MOS offer large surface area to adsorb a large amount of dyes for light harvesting, but also collects the electrons from dyes and transfers them to electrodes. MOS nanoparticles film is first used in DSCs due to its large surface area for loading dyes. But it is not an ideal structure in regard to the electron transport [12, 64]. The first non-ideality results from the lack of a macroscopic electrostatic potential gradient in the film due to the fact that the film is permeated with a concentrated electrolyte [12]. The mesoporous films are very much different compared to their compact analogues because (i) the inherent conductivity of the film is very low, (ii) the small size of the individual colloidal particles does not support a built-in electrical field, and (iii) the oxide particles and the electrolyte-containing pores form interpenetrating networks whose phase boundaries produce a junction of huge contact area [65]. Therefore, the electron transport in the nanoparticle film is dominated by a process of diffusion instead of drift. The drift is a common way in p-n junction solar cells for carrier separation in the presence of an electric field. The second non-ideality comes from the fact that the electron transport in a nanoparticle film undergoes a trapping and detrapping process as shown in **Figure 3**. Numerous grain boundaries, interface defects and connections existing in the nanoparticle film also increase the surface charge recombination, and retard effective charge injection and charge transport, which result in a loss of PCE. So many efforts have been made on the synthesis of a variety of nanostructured MOS photoanodes in the forms of wires, tubes, spheres, rods, sheets, belts, flowers and trees for the efficient DSC devices[66-73].

Figure 2. Structure and operating mechanism of a DSC. Reprinted from reference [63].

Figure 3. Schematic illustrations of electron transport in a nanoparticle film suffering a trapping/detrapping process

To increase the electron mobility and reduce grain boundaries and interfaces, one-dimensional (1D) nanostructures, such as nanotube arrays and single-crystalline nanowire arrays, have been studied as photoanodes for DSCs[66]. However, DSCs based on 1D structures have not reached high conversion efficiency as expected due to the much small surface area for dye adsorption[74]. The 3D hierarchical nanostructures can offer larger surface areas for dye adsorption while simultaneously enhancing light scattering for efficient photon harvesting, and thereby, improving PCE[70, 74-76]. The aggregate structure consisting of primary nanocrystallites can provide both large specific surface area and light scattering effect so as to enhance the performance of DSCs [8, 12, 24, 76-79]. In addition, the diffusion of electrolyte in the aggregate structure is faster than that in nanoparticle film, which boosts the charge transport. Our previous works [12, 24, 77, 79-82] showed that the photoanodes with

the hierarchical aggregates structure are promising for the highly efficiency DSCs. Our recent works have been continuing to improve the fabrication and design of the hierarchical structure of MOSs for increasing the PCE of DSCs.

2.1 TiO₂ hierarchical structures for DSCs

In the last few decades, many methods have been used to synthesize TiO₂ nanostructures, such as sol-gel processing [83], hydrothermal[84], solvothermal[85] and template growth [86] approaches. The hydrothermal and solvothermal methods have been frequently used for the reason that they are readily capable of obtaining the desired size and structure of TiO₂ nanocrystals by controlling the temperature and duration of the reaction, and the type and concentration of the reactants, as well as the solvent and additives used. However, defects in the resultant nanocrystals like complex and time-consuming process have been pointed out in the hydrothermal and solvothermal methods. The high cost and low productivity of the hydrothermal and solvothermal methods are also considered as a big hindrance for their applications in DSCs. There is a growing need to develop a fast and high productivity synthesis method to obtain TiO₂ nanocrystals for the application in DSCs. Compared with hydrothermal and solvothermal methods, the microwave assisted synthesis offers rapid processing speed, homogeneous heating and simple control of processing conditions, and thus has attracted much attention in the last few years [87]. Recently, microwave assisted synthesis was employed to fabricate hierarchically structured TiO₂ nanocrystallite aggregates, which are shown in **Figure 4**[88]. Hierarchically structured TiO₂ nanocrystallite aggregates with a size of ~500 nm in diameter consisted of ~10 nm nanocrystallites were synthesized by microwave assisted method at 150°C in a short time (~10 minutes) using ethanol and TiCl₄ as the solvent and titanium precursor, respectively. The rapid heating rate and superheating / “hot spots” of the reaction system under microwave irradiation resulted in huge supersaturation leading to a high density of nuclei instantly so as to form a great deal of uniformly sized small particles/nanocrystals, which were subsequently assembled to uniformly sized aggregates. The TiO₂ aggregates showed much better light scattering property, larger specific surface area and higher dye-loading than those of the commercial P25 TiO₂ nanoparticles. In comparison with P25, the short current density (J_{sc}) and dye-loading of DSC based the as-synthesized TiO₂ aggregates increased by 33% and 62%, respectively. As a result, the PCE of the DSC was up to 7.64%.

Figure 4. (a) SEM images of as-synthesized TiO_2 aggregates, (b) schematic illustration of TiO_2 aggregates formation process, (c) schematic illustration of the effect of the aggregates for the light scattering and (d) Diffuse reflection spectra curves of P25 nanoparticles TiO_2 film and TiO_2 aggregates film. Reprinted from reference [87].

It was also found that the electron diffusion in the TiO_2 aggregate network was enhanced through the addition of TiO_2 nanoparticles with preferential filling at the necks between adjacent TiO_2 aggregates, which resulted in strengthening the connections, while retaining the porous structure of the TiO_2 network as shown in **Figure 5**. [89] The fortified necks was found to reduce the transport resistance (R_t) by allowing facile transfer of electrons from one aggregate to another, while the scattering effect of the TiO_2 aggregate network got weakened with adding the TiO_2 nanoparticles as a result of reduction of the light scattering centers such as the necks and gaps between the aggregates. However, due to the increase in surface area as the TiO_2 nanoparticles were added, the diminished light scattering effect of the aggregate network was compensated and even the highest performance was achieved when the 10% TiO_2 nanoparticle was added into the TiO_2 aggregate film, suggesting that widening necks between sub-micrometer sized light scatters such as an aggregate would be a good strategy in achieving further improvement of PCE of dye sensitized solar cells through the improved charge transport property.

Figure 5. Schematics illustrating (a) electron diffusion in aggregates and through necks between aggregates, (b) low possibility of electron transfer from one aggregate to adjacent one due to poor neck, (c) high possibility of electron transfer as a result of widened neck compared to the diameter of the aggregate and (d) the widened neck between two aggregates achieved by filling with the added nanoparticles, (e) J–V curves of the DSCs with the photoanodes composed of TiO₂ aggregate and mixture of the aggregates and nanoparticles (Mix10 and Mix20). Reprinted from reference [88].

Figure 6. Schematic illustration of the paste formation process based on (a) Ti-155, Ti-155, and Ti-105 samples and the ones based on (c) Ti-85 sample, as well as HR-SEM pictures of photoanode films based on (k) Ti-105 and (l) Ti-85 samples. Reprinted from reference [89].

However, dye molecules and electrolyte are difficult to penetrate into the interior pores of the aggregates, which is not helpful for the improvement of enhanced photon capture and efficient transport of the photoexcited electron. The inverted aggregate hierarchical structure would have both high dye adsorption and strong light scattering. Our recent work reported a strategy for the synthesis of hierarchically structured three-dimensionally ordered macroporous (HS-3DOM) TiO₂ with controlled macropore sizes (ca. 85–155 nm) by using well-ordered polymethyl methacrylate with different diameters as well as two kinds of photoanode films based on hierarchically structured porous TiO₂ filled with nanoparticles have been demonstrated as shown in **Figure 6** [90]. DSCs based on a special TiO₂ photoanode with a macropore size of 105 nm exhibited a current density of 20.6 mA/cm² and a high PCE of 9.7%. The hierarchically structured porous TiO₂ layer has much large surface area to load dyes and high diffused reflectance and scattering to harvest photons, which is the main reason for high photo-generated current density. The results showed the electron lifetime was prolonged and charge recombination was reduced. This may be due to the special geometry architecture of the photoelectrodes. Therefore, this high PCE is ascribed to the special morphology of the TiO₂ photoanode with high dye adsorption due to its ordered and

open structures, and also its light scattering and charge collection efficiency.

2.2 ZnO hierarchical structures for DSCs

ZnO is known to have band structure and physical properties similar to that of TiO_2 , but a higher electron mobility than that of TiO_2 [24, 77, 79]. In addition, ZnO with a hexagonal crystal structure possesses facets with different surface energy and, thus, can easily form anisotropic structures, such as nanorods, nanowires and nanoflowers, which enables it to exhibit unique electronic and optical properties [82, 91]. ZnO nanostructured photoelectrodes for DSCs have been investigated over the last several years [73, 74, 92, 93]. For ZnO based DSCs, the ZnO films with hierarchical structure have exhibited much better performance in DSCs than that of nanoparticles and 1-D structure, due to the larger specific surface area for dye-adsorption, effective light scattering within the photoanode, and more pores for the penetration of electrolyte into the photoanode films [76]. As early as 2008, we had prepared ZnO aggregates spheres made up of nanocrystallites for DSCs [79]. With increased dye-adsorption and light-scattering capabilities by the primary nanoparticles and secondary colloids, 5.4% of PCE was obtained, which is one highest PCE of ZnO based DSCs at that time. Recently, we develop a novel interface precipitation method to synthesize hierarchically structured ZnO nanocrystallite aggregates as shown in **Figure 7** [76]. The conventional homogeneous precipitation process in aqueous solution is an efficient way to synthesize ZnO nanoparticles at low temperature. In this process, ethanol and water were used as solvents to first separately dissolve NaOH and zinc acetate dihydrate under stirring, respectively. The reaction occurred in the interface of the different solvents with a slow rate, which was easier to form a porous hierarchical structure. In comparison with ZnO nanoparticles synthesized by conventional homogeneous precipitation method, such hierarchical structure has larger specific surface area, more efficient dye-loading and effective light scattering within the photoelectrode; all result in an increased photocurrent. Furthermore, electrochemical impedance spectroscopy study revealed that reduced charge recombination in ZnO nanocrystallite aggregates resulted in enhanced V_{oc} . As a result, a PCE of 5.07% with commercially available dye N719 had been obtained without applying anti-reflection coating and chemical treatment, which was more than 200% of the PCE achieved in ZnO nanoparticles synthesized by homogeneous precipitation method in aqueous solution.

Figure 7. (a) schematic diagram of ZnO formation process using interface precipitation, (b) SEM image of ZnO aggregates, (c) diffuse reflectance of ZnO film prepared by different precipitation process and (d) J-V curves of DSCs based on the different ZnO photoanodes. Reprinted from reference [75]

A porous ZnO aggregates of nanocrystallites were thought to be helpful to retain their high surface area. However, their PCEs are still lower than that of TiO₂ based DSCs, due likely to the poor chemical stability for dye solution and lots of surface defects for high charge recombination. A lot of research results showed that the charge recombination could be reduced by applying a core-shell configuration [94, 95]. Such a core-shell configuration is expected to suppress the charge recombination by forming an energy barrier to prevent the electrons in the conduction band of the semiconductor from transferring to the oxidized dyes and ions in the electrolyte, leading to increased open circuit voltage and short current density[94-96]. It was also reported[92] that the shell (TiO₂) has a more negative conduction band edge than that of the core oxide (ZnO) or it creates a dipole at the core – shell interface that shifts the band edge of the core upward in energy, which suppresses recombination and increases the open voltage and fill factor. Many novel core/shell structures, for example, ZnO/TiO₂, ZnO/Al₂O₃, ZnO/ZrO₂ and ZnO/MgO photoelectrodes, have been used in DSCs for this purpose [92, 94-97]. In an earlier study, atomic layer deposition (ALD) method was utilized to deposit ultrathin TiO₂ layer on the porous structure of ZnO aggregates and, the resultant devices demonstrated much enhanced PCE of ZnO DSC with photoelectrodes made of submicrometer-sized aggregates of ZnO nanocrystallites as shown in **Figure 8** [95]. The ZnO core/TiO₂ shell

structure increases the open-circuit voltage, without impairing the photocurrent density and results in an increased PCE from 5.2% to 6.3%.

Figure 8. Schematics illustrating ALD TiO_2 thin layer on the surface of ZnO nanocrystallites, inset shows SEM image ZnO aggregate coated by TiO_2 thin layer. Reprinted from reference [94]

ALD is rather time consuming and not cost effective [98]. Recently, a facile solution method was applied to modify the surface of ZnO aggregate photoanodes for DSCs as shown in **Figure 9** [99]. During the modification process, the surface of the ZnO will be dissolved through a chemical reaction in an aqueous solution of $(\text{NH}_4)_2\text{TiF}_6$ and H_3BO_3 , while the deposition of TiO_2 nanocrystallites takes place sequentially and concurrently. This method can be considered as an in-situ alternative deposition method. As the chemical reaction on the surface of photoanode material is always easy to take place at an area with high surface energy, so TiO_2 is more likely to deposit on the defect region of ZnO surface, which reduces the surface defects while further increases the surface stability [100]. The IPCE of the TiO_2 -modified film with a 3 min treatment exhibits a highest maximum to 60%, whereas the film with a 20 min treatment shows a lowest maximum as shown in Figure 9 (c). The trend observed with IPCE matches with that of the J_{sc} , and the integrated current from the spectra correlates closely with the photovoltaic data. Figure 9 (d) displays the whole process of the photon-electric conversion in solar cells. Initially, the photons are captured by the dyes to realize the harvesting of light. Then, the electrons generated by dye will inject into photoanode. The energy difference between the lowest unoccupied molecular orbital (LUMO) of the dye and the conduction band of TiO_2 provides driving force for charge injection. Therefore, the surface modification process introduces a thin layer of TiO_2 nanoparticles on the surface of ZnO aggregates can reduce the charge recombination and increase the charge collection, at the same time, open the inner pores through in-situ selective etching of ZnO at pore apertures. As a result, the PCE of DSC was increased from 4.81% to 6.27%, after

surface modification of ZnO aggregates.

Figure 9. (a, b) SEM images of submicrometer-sized aggregates of ZnO nanocrystallites in different magnifications, (c) Incident photon-to-current conversion efficiency (IPCE) spectra of ZnO-based DSCs with different solution treatment times; (d) photoelectric conversion process in solar cells. Reprinted from reference [98].

2.3 SnO₂ hierarchical structures for DSCs

Figure 10. SEM images of (a), (b) SnO₂ (hydrothermal) nanostructure and HRTEM images, inset, SEM images of (c), (d) SnO₂ (microwave) nanostructure and HRTEM images, inset. The scale bars in SEM images of (a), (c) represent 200 nm. The scale bars in SEM images of (b), (d) represent 100 nm. The scale bars in HRTEM figures represent 1 nm. Reprinted from reference [114].

SnO₂ is an important n-type wide-bandgap semiconductor with wide applications in transparent conductive films, gas sensors, lithium-ion batteries, and solar cells [53, 101-105]. SnO₂ as a possible alternative of TiO₂ photoanode in DSCs with various morphologies, such as nanoparticles [106, 107], nanofibers [108], nanowires [109], nanotubes [110] and hollow nanospheres [111-114], have been successfully synthesized and characterized. For example, Cheng et al. [115] reported the synthesis of single-crystalline SnO₂ nanorods with small size (15–20 nm in length and 2.5–5 nm in diameter) by hydrothermal treatment of TiCl₄. Wu et al. [116] prepared 3D hierarchical SnO₂ nanostructures composed of 2D nanosheets. TiO₂-coated multilayered SnO₂ hollow microspheres had achieved 5.65% of PCE [117]. Among various techniques used for SnO₂ synthesis, hydrothermal growth is one of the most common methods, which can form desired size and morphology by manipulating reactant ratio and reaction parameters [118]. Our recent work reported a microwave assisted synthesis of assembled SnO₂ nanosheets and their characterization and application as photoanodes in DSCs as shown in **Figure 10** [119]. The assembled SnO₂ nanosheets photoanode, with large specific surface area, effective light-scattering and an easy path for electron transport with long lifetime, demonstrated appreciably increased

short-circuit photocurrent density, reduced charge recombination and consequently high PCE. However, the limitations of SnO_2 based DSCs are the relatively weak adsorption of the dyes with acidic anchoring groups, and the recombination of conduction band electrons with the oxidized dye [53]. In future, a lot of efforts should be focused on the surface and electronic modification of hierarchical SnO_2 photoanodes to improve the PCE of DSCs.

3. Quantum dot sensitized solar cells (QDSCs)

QDSCs can be regarded as a derivative of DSCs, which use narrow-band-gap semiconductor quantum dots (QDs) photo-sensitizer instead of organic dyes in DSCs. **Figure 11** shows the QDSC structure consists of a MOS photoanode, QDs (sensitizer), polysulfide electrolyte and counter electrode[64]. When the photons are harvested by QDs, the electron-hole pairs will be excited and then are rapidly separated into electrons and holes at interface between the MOS and QDs. The electrons are transferred by MOS, at same time, the holes are released by redox couples in the liquid electrolyte[37, 120]. The principles for choosing QDs and MOS photoanodes to construct QDSCs are: (1) narrow and direct band gap QDs are preferred due to their high optical absorption, (2) MOS and QDs should have perfect matching in energy levels so that charges transport efficiently in the solar cells[8]. **Table 2** shows the energy band parameters of QDs, which are usually chosen to fabricate QDSCs. Similar to DSCs, we can know that nanostructured MOS plays a key role in designing QDSCs. The difference between them is that the size of QDs is much larger than that of organic dye. The distribution and adsorbing capacity of QDs in MOS substrate are important issues for the performance of QDSCs. In this section, we will introduce and discuss our recent works on the fabrication of QDs, design and surface modification of TiO_2 and ZnO MOSs to improve the performance of QDSCs.

Figure 11. Schematic illustration of the structure of QDSC and photo-induced charge-transfer processes.

Reprinted from reference [64]

Table 2. Energy band parameters of some most commonly used QDs for QDSCs[121, 122] .

Semiconductors	Band gap (eV)	Conduction band minimum (eV)	Valence band maximum (eV)
Ag ₂ S	0.92	-4.5	-5.42
CdS	2.40	-3.98	-6.38
CdSe	1.74	-4.10	-5.84
CuInS ₂	1.50	-4.06	-5.56
Cu ₂ S	1.10	-4.44	-5.54
PbS	0.37	-4.74	-5.11
PbSe	0.27	-4.93	-5.20
Sb ₂ S ₃	1.72	-4.72	-6.44
SnS ₂	2.10	-4.44	-6.54
SnS	1.01	-4.66	-5.67

3.1 Fabrication of QDs for QDSCs

QDs are usually deposited onto mesoporous MOS films to form QDSCs electrodes via two approaches: (a) adsorption of pre-synthesized quantum dots, and (b) in-situ growth directly from the precursor solutions. The introduction of rapid injection of precursors into the reaction solvent at a certain temperature, called hot-injection synthesis, have been used to prepare colloid QDs since 1993 [123, 124]. This method has attracted much attention for QDSCs due to the advantages in using pre-synthesized monodispersed QDs of high crystallinity, with expectation to obtain overall control over the QD size, size distribution, and surface passivation. Recent years have witnessed the development of the post-synthesis assembly to fabricate high efficiency QDSCs, which generally involves three approaches: direct adsorption, electrophoretic deposition and linker-assisted deposition [125]. By exploiting this approach, CdSe_xTe_{1-x} QDSCs with greater than 8% of PCE was obtained in 2015 [42]. In-situ growth of QDs within the mesoporous MOS scaffolds, including chemical bath deposition (CBD)[126] and successive ionic layer absorption and reaction (SILAR)[36, 127], has shown highly photoelectric conversion efficiency when being adopted to assemble QDSCs[128]. The CBD is a relatively simple method to deposit QDs and nanoparticles films, which possesses many advantages, such as stable yields, robust adherence, uniform and good reproducibility. The growth of QDs strongly depends on the growth conditions, such as the duration of deposition, composition and temperature of the solution, and characteristics of the mesoporous films. The SILAR method is based on successive reactions on the surface oxides. Each reaction is followed by rinsing, which enables a heterogeneous reaction between the solid phase and the solvated ions in the solution. So a thin film can be grown layer by layer. In-situ growth method is regarded as a convenient, reproducible and cost-effective way to

QDSCs. In addition, QDs can be adsorbed on the surface of MOS, which is helpful for injecting and transfer of photoexcited electron. We deposited CdS and CdSe QDs onto the mesoporous TiO_2 film using SILAR and CBD, respectively, to form CdS/CdSe co-sensitized QD[37]. **Figure 12** shows the schematic illustration of the formation process of CdS/CdSe QDs co-sensitized solar cells. The PCE of QDSC was up to 4.62%.

Figure 12. Sketch of the formation of CdS/CdSe QDs on the mesoporous TiO_2 film and J-V curve of QDSCs. Reprinted from reference [37].

Figure 13. (a) J-V curve of CdMnSe QDSC, inset is the CBD process of CdMnSe QD; (b) external quantum efficiency (EQE) spectra curves of QDSCs. Reprinted from reference [38].

Recently, the method of using doping metal ions into QDs is thought an effective way to improve the performance of QDSCs. Some results, such as Hg^{2+} into PbS [129], Mn^{2+} into CdS [130] and Mn^{2+} into CdSe [38], showed the increase of photo-electric properties of the solar cells. By using doping Mn^{2+} into CdSe , we have successfully prepared a high efficiency of 6.33% $\text{Cd}_{0.8}\text{Mn}_{0.2}\text{Se}$ quantum dot solar cell using CBD method as shown in **Figure 13**[38]. The Mn^{2+} ions doped into QDs can increase the light harvesting to produce more excitons. In addition, Mn^{2+} dopant also raises the conduction band of CdSe , accelerates the electron injection

kinetics and reduces the charge recombination to improve the charge transfer and collection. The increase of the efficiencies of light-harvesting, charge-transfer and charge-collection results in the improvement of the quantum efficiency of the solar cells.

Figure 14. (a) HRTEM image showing the arrangement of ZnSe/CdS/CdSe QDs around a TiO₂ crystallite and (b) Nyquist curves of the different layered QD-sensitized solar cell measured in the dark at -0.6 V bias. (c) Relative band positions of TiO₂, ZnSe, CdS, and CdSe in bulk and (d) ideal stepwise structure of band edges for the efficient transport of excited electrons and holes in a TiO₂/ZnSe/CdS/CdSe photoelectrode. Reprinted from reference [126].

Inserting a layer of non-sensitized QDs on the surface of MOS photoanodes not only helps to grow the subsequent sensitized QDs, but also suppresses the back charge recombination between the electrons in oxide and the holes in electrolyte. Recently, we prepared a multi-layered semiconductor (ZnSe/CdS/CdSe) QDs on the surface of TiO₂ mesoporous films as shown in **Figure 14** [131]. The multi-layered QDs-sensitized solar cells showed a larger short circuit currents and higher efficiency than those of single-layered QDs sensitized solar cells due to a complementary effect in light harvesting. **Figure 14** (b) shows the recombination resistance is also increased by a seeding layer of ZnSe, which leads the reduction of the charge recombination and the prolonging of the electron lifetime. The possible reason is that the cascade structure of multi-layered semiconductor is advantageous to the electron injection and hole recovery of QDs. The band edges and relative Fermi levels positions of TiO₂, ZnSe,

CdS, and CdSe in the bulk are schematically shown in **Figure 14c**. When TiO₂, ZnSe, CdS and CdSe are connected together, the difference in energy levels induces electron flow from the higher level (ZnSe) to the other lower levels. Therefore, the Fermi level of ZnSe would shift down with respect to the location of Fermi level in TiO₂, and the conduction band edges of CdS and CdSe are elevated. Such electron transfer is known as the Fermi level alignment. The photoexcited electrons would transfer from the higher conduction band to the lower band with the help of a driving force. Therefore, the resulting conduction band edges for the ZnSe/CdS/CdSe device are inferred to have a stepwise structure, as shown in **Figure 14d**. The layer of ZnSe also acts as a blocking layer to shield the TiO₂ core from the outer CdS/CdSe QDs and electrolyte, and provides a physical separation of the injected electrons in TiO₂ from the positively charged QDs and the electrolyte, thus retarding the interfacial recombination to obtain a high efficiency. As a result, the PCE was increase from 2.26% for QDSC without ZnSe to 4.94% for QDSC with multi-layered QDs. So researchers may concentrate on designing more multi-layered QDs for QDSCs.

3.2 TiO₂ hierarchical structures for QDSCs

Figure 15. SEM image of TiO₂ beads aggregates (a) 0 mL, (b) 0.5 mL, (c) 1 mL and (d) 2 mL ammonia solution; (e) TEM and (f) HRTEM images of the ultramicrotomed sample of the calcined mesoporous TiO₂ beads without ammonia treatment during the solvothermal process. The inset of (f) shows the SAED pattern of TiO₂ beads. (g) UV-Vis spectra of CdS/CdSe QDs co-sensitized TiO₂ beads aggregates films, and (h) J- V curves for CdS/CdSe QDs co-sensitized solar cells using the photoanodes prepared by TiO₂ beads aggregates. The beads prepared with the addition of 0, 0.5, 1 and 2 mL ammonia to a mixture of 12 mL ethanol and 6 mL deionized water during the solvothermal treatment are denoted as beads A, B, C and D, respectively. Reprinted from reference [127].

The TiO₂ aggregates film shows a better light scattering property to extend the light pathway for light harvesting, which has been used in DSCs in our previous works. Different from dye, QD is difficult to enter into the interior of the aggregates film due to their large size, which results in the low loading of QDs and poor performance of QDSCs. In order to dissolve this problem, we proposed a two-step fabrication method of TiO₂ aggregates to increase the porosity of the aggregates [132]. The aggregate made of the mesoporous TiO₂ beads has been prepared through a combined precipitation and solvothermal process. **Figure 15** (a-d) shows SEM image of the mesoporous TiO₂ beads aggregates. The aggregates were first synthesized using precipitation and solvothermal process. And then, an optimal amount of ammonia was adopted to etch TiO₂ spheres and achieve the desired porosity of the beads for QDs adsorption. The ammonia etches the precursor aggregate beads to open the pore size of the aggregates. From **Figure 15** (g), the absorbance of the films increases with increase of the addition ammonia, which followed the trend of increased pore size and pore volume but a decreased specific surface area. The properties of QDSCs are almost in accordance with the light absorbance of the aggregates (**Figure 15** (h)). As a result, a PCE of the solar cell up to 4.05% has been achieved for a CdS/CdSe QDSC.

3.3 Nanostructured ZnO for QDSCs

3.3.1 1D nanostructured ZnO for QDSC

It was demonstrated [37] that QDs experienced difficulty penetrating into the inner pores of the nanoparticles films, leading to several issues: (1) the direct exposure of MOS film in electrolyte resulting in a serious degree of recombination between the electrons in the MOS and holes in the electrolyte; (2) less QD loading in the films. Open structures, such as 1 D structure of nanorods, nanowires and nanotubes, can facilitate the distribution of QDs from the surface to the interior of the films and enhance the QD loading. In addition, 1D structured MOS has a higher electron mobility than that of the nanoparticles. For ZnO nanowires, the electron diffusion coefficients (D_n) are 0.05-0.5 cm² s⁻¹, which are several hundred times larger than those of nanoparticle films. The electron diffusion coefficient determines the electron diffusion length as the following equation[12, 64]:

$$L_n = \sqrt{D_n \tau_n}, \quad (1)$$

where L_n is the electron diffusion length, D_n is the electron diffusion coefficient, and τ_n is the electron lifetime. A longer diffusion length is typically associated to the higher charge collection efficiency. For QDSCs, such open structures of 1D MOS can also facilitate the permeation of QDs from the surface to the interior of the films. 1D nanostructure offers a straightforward path for the electrons and shorten their transport time inside MOS, and then reduces the charge recombination probability. So the 1D nanostructure array is considered the most promising candidate materials for QDSCs owing to its effective electron transport, which helps to collect photogenerated electrons [133]. However, QDSCs based on 1D structure have not reached a high conversion efficiency as expected due to the limited surface area for QDs adsorption. Introducing a surface profile modification for 1D MOS can be thought as an effective way to increase QD loading. Recently, we designed a facile surface modification process for ZnO nanowire arrays as shown in **Figure 16** [134]. The ZnO nanowire arrays were fabricated by growing on seeded indium-doped tin oxide (ITO) substrate without using a template or high temperature conditions. After surface modification, the edges of the ZnO nanowires become “rough”, which helps to harvest QDs as shown in **Figure 16** (d). The surface modification method not only formed a barrier layer on the surface of the ZnO nanowire, which suppresses charge recombination by preventing the electrons in the ZnO conduction band from transferring to the oxidized ions in the electrolyte, but also modified the surface characteristics of the ZnO nanowire so as to harvest a greater amount of QDs and increase the short current density of the QDSC. PCE of QDSC was increased from 1.54% to 3.14% by surface modification.

Figure 16. (a) Schematic illustration of the fabrication process of ZnO NR array photoelectrode for QDSC, (b) SEM images of ZnO NR array, (c) SEM image of modified ZnO nanorod array, (d) TEM image of ZnO nanorod coated by QDs. Reprinted from reference [129]

3.3.2 Hierarchical nanostructured ZnO for QDSCs

It is well-known that the surface area of photoanodes is a key factor for the loading of QDs. For 1D nanostructured MOS, a fundamental drawback is the insufficient internal surface area owing to a low roughness factor or the considerable free space between adjacent 1D nanostructures[135]. Hierarchical branched nanostructures are derived from 1D nanostructures however with a consideration to enlarge the surface area through using extended “branches”[12], which mainly include branched and dendritic nanowires or nanorods. Our recent work reported a ZnO nanorods branched by nanosheets for QDSCs as shown **Figure 17** [136]. The thin ZnO nanosheets were slowly assembled on the surface of nanorods to form a hierarchically branched photoanode for constructing CdS/CdSe QDSCs. This branched structure had two advantages in improving the PCE of the solar cells: (a) it increased surface area and modified surface profile of the ZnO nanosheets to aid in harvesting more quantum dots (as shown **Figure 17(g)**), which leads to a high short current density J_{sc} ; (b) it facilitated the transportation of the electrons in this compact structure to reduce the charge recombination, which led to the enhancement of V_{oc} and FF. As a result, the QDSC assembled with the hierarchical photoanode exhibited a high PCE of 3.28%, which is twice more than that of NRs photoelectrode (1.37%).

Figure 17. (a) SEM images of the cross section of the ZnO nanorods film, inset shows the cross section of the seed layer and nanorods film; (b) and (c) SEM images of ZnO nanorods, (d) SEM images of ZnO nanorods-nanosheets branched structure, (e) TEM and (f) HRTEM images of the branched ZnO loaded with QDs, (g) Optical absorbance spectra of the ZnO photoelectrodes loaded with QDs, and (h) J-V curves of QDSCs

assembled with different photoelectrodes under simulated AM 1.5, 100 mW/cm² sunlight. Reprinted from reference [131].

Although ZnO hierarchical aggregates show good light scattering for QDSC, its PCE is much lower than that of nanoparticles. In order to utilize the light scattering of the aggregates, a bilayer structure was constructed by ZnO nanoparticles film and ZnO nanosheets aggregates scattering layer as shown in **Figure 18** [137]. The growth orientations of ZnO crystals was controlled to form nanosheets, which attached together and assembled into aggregates due to the high surface energy of the nanosheets. The aggregates were used as a top layer to effectively increase the light diffuse reflection and harvesting to enhance photo-generated current (as shown **Figure 18** (c)). In comparison with ZnO single nanoparticles film, the J_{sc} of QDSC assembled by ZnO bilayer structure is increased from 10.3 mA/cm² to 16.0 mA/cm², which represents an enhancement of 55%. Such structured QDSC exhibited a high PCE of 5.08%.

Figure 18. (a) SEM image of the bilayer structure composed of ZnO NPs film and NSs aggregates layer, (b) SEM image of the ZnO NSs aggregate, and (c) diffuse reflection spectra curves of ZnO films. Reprinted from reference [132].

3.3.3 Surface modification of ZnO for QDSCs

Nanostructured ZnO faces two questions: (1) instability in the electrolyte; (2) a large amount of surface defects. For ZnO based QDSCs, the surface charge recombination is limit factor for improving the performance of the devices. The processes of charge recombination in QDSCs is somewhat different to DSCs, which can be simplified as shown in **Figure 19**. There are seven pathways of recombination in QDSCs [64]: ① recombination of electrons in the QD conduction band and holes in the QD valence band; ② recombination of electrons with the electron acceptors in the electrolyte; ③ trapping of the excited electrons at the surface states of QDs; ④

trapping of the free electrons at the a surface states of QDs; ⑤ back electron injection from ZnO to QDs; ⑥ trapping of the free electrons at the interface states of ZnO particles and ⑦ back electron injection from ZnO to the electrolyte. The electron quenching (①), recombining with the electrolyte (②), trapping (③ and ④) strongly depend on the surface quality of QDs. The pathways ⑤, ⑥ and ⑦ relate directly to the interfaces state of ZnO. Therefore, a lot of interfaces in the nanostructured ZnO provide easy pathways for charge recombination. The state of adjacent surface between QDs and ZnO also propels the free electron trapping. The introduction of surface modification for ZnO is believed to be an effective approach for decreasing the charge recombination and improving the transports of the electrons or holes[59]. For example, the surface modification for ZnO can increase the interfacial resistance and decrease the surface defects, which results in the recombination reduction through the mechanisms ④, ⑤, ⑥ and ⑦. In addition, the surface modification can also change the surface energy of ZnO for loading more QDs[138].

Figure 19. Schematic illustrations of charge recombination processes in QDSCs. Reprinted from reference [64].

However, the introduction of shell layer on the ZnO surface will reduce the porosity of the ZnO film, which could result in the decrease of the loading of QDs. Recently, we develop a facile chemical passivation strategy for ZnO mesoporous photoelectrode, which not only enlarged the apertures in the ZnO mesoporous photoelectrode to harvest more QDs, but also introduced a thin TiO₂ nanoparticle layer on the surface of ZnO to decrease the surface charge recombination [139]. The process can be expressed via the following equations [139, 140]:

The reaction (2) and (3) can be shifted to the right by reaction (4), which indicates the dissolution of ZnO can

boost the hydrolyzation of TiF_6^{2-} . **Figure 20** (a) shows the variation of pore size, porosity and surface area of the film during the passivation process. ZnO is dissolved by reacting with H_3O^+ so as to open the apertures and pores, at same time, TiO_2 particles are deposited on the fresh surface and combine with the newly broken chemical bonds to form a passivation layer. **Figure 20** (b) illustrates the recombination pathways of QDSCs. The passivation layer can increase the interfacial resistance and lead to recombination reduction through decreasing the back electron injection from photoanode to electrolyte. According to the results of electrochemical impedance spectroscopy (EIS) and light absorbance as shown in **Figure 20** (c-e), both of QDs loading and electron lifetime have been improved by the surface modification. The PCE of QDSC is also increased from 2.38% to 4.68%, almost doubled the PCE.

Figure 20. (a) Passivation process of the ZnO mesoporous film, (b) surface charge recombination pathways of the QDSC, (c) Nyquist plots curves and (d) bode plot curves of the QDSCs under forward bias (-0.6V) and dark condition, and (e) UV-Vis spectra curves of the ZnO films loaded with QDs. Reprinted from reference [134].

4. Perovskite solar cells (PSCs)

Organic-inorganic hybrid perovskite is a star material for the solar cells. In 2012, there are only several articles of PSCs. But the amounts of the publications of PSCs are more than 600 in the half year of 2015. In fact, the hybrid perovskites ($(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$, $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{SnI}_3$, etc.) had been synthesized several decades ago, which were widely used in organic light-emitting diodes due to high electrical mobility and good optical properties [141]. The band-gap of the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ is 1.5eV, which is very close to the Shockley-Queisser limit optimal band-gap (1.34 eV) for solar cells[142]. So the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ is an

excellent potential light absorber material for the solar cell. There are two structures of PSCs: perovskite-sensitized solar cell and planar heterojunction perovskite solar cell as shown in **Figure 21** [143]. Perovskites were first employed as ‘sensitizers’ on mesoporous TiO_2 and their function in the solar cell was assumed to be analogous to the dye in DSCs (as shown in **Figure 21** (a))[44, 143]. In this case, the working principle is expected to be similar to DSCs. However, the working mechanism is different from DSCs, because of charge transport and charge accumulation properties in the perovskite [45]. So the structure of the solar cell can be evolved into a simple planar heterojunction architecture, where a solid intrinsic perovskite layer is sandwiched between p- and n-type selective contacts (as shown in **Figure 21** (b)) [143].

Figure 21. Illustration of the charge generation processes in a ‘perovskite-sensitized’ solar cell (a) and a planar heterojunction perovskite solar cell (b). m-TiO₂ and c-TiO₂ denote mesoporous and compact TiO₂ layers, respectively, HTM (hole transport material) is the hole transporter material, and FTO (F-doped tin oxide) is the transparent conducting oxide. Reprinted from reference [132].

Figure 22. SEM images of perovskites prepared by (a) static growth process and (b) dynamic growth process, and (c) J-V curves of PSCs and (d) PSCs assembled TiO₂ compact layers prepared by Sol-Gel using different aging time. (a-c) Reprinted from reference [145], (d) reprinted from reference [146].

The perovskites are usually deposited on a substrate by low temperature solution process, including one-step and two-step coating methods. Perovskite forms either by spin-coating a mixed CH₃NH₃I and PbI₂ solution (one-step coating) or by spin coating CH₃NH₃I after coating with PbI₂ (two-step coating). However, the two methods face a problem that is a poor stability of PCE, even under the same fabrication process parameters [144, 145]. One important reason should be attributed to the inhomogeneous perovskite film that fabricated by those methods. Controlling the morphology of perovskite crystallites have been regarded as an essential condition to guarantee reproducibility for high performance PSC [146-149]. Recently, a dynamic growth process was used to fabricate perovskite crystallites. As shown in **Figure 22** (a,b), the coverage rate of perovskites by this method is more than that of perovskites prepared by usual solution process. So the bareness of mesoporous TiO₂ layer is significantly avoided [150]. Due to high quality perovskite capping layer, the PCE of the solar cell is increased from 11% to 13%.

From the structure of PSCs, the compact MOS layer (such as c-TiO₂ as shown in **Figure 21**) that plays an important role in charge transfer, which reduces the energy barrier between FTO and perovskites to increase the charge collection. As n-type semiconductor, the compact layer can transport the electrons and prevent the transfer of the holes. So it reduces the charge recombination at the interface of FTO and perovskite. Recently, some methods, such as ALD, magnetron sputtering, thermal spraying and sol-gel, have been used in the fabrication of the compact MOS layer [45, 61, 62, 143]. Among these methods, the sol-gel method is one of the most widely used methods due to flexible adjustability and low cost without complex equipment. For sol-gel process, the aging time and temperature are two key factors for the compact layer. In our recent work, the PCS with greater than 15% of PCE was obtained by controlling the sol-gel aging of TiO₂ compact layer as shown in **Figure 22** (d) [151]. It

was found that the sol-gel aging time is 4h under room temperature, PCS shows the best performance: the highest and average values of PCEs are 15.6% and 14.01%, respectively.

Most recently, scanning Kelvin probe force microscopy (SKPM) and photoconductive atomic force microscopy (pcAFM), were used in the investigation of the variation of the surface potential, photo-generated voltage, and photocurrent networks of the PSCs with different film topography [152]. Three perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ films with different morphologies and crystallite sizes as well as the corresponding complete PSC devices based on those three films were prepared as shown in **Figure 23** [152]. It has been found that the defect regions on the capping layer showed little photovoltaic response while exhibited good conductivity, which can establish form small current paths for the photo-charge recombination. Accordingly, even though the P52 film with largest grain size shows most significant photovoltaic response in the KPFM measurement, the V_{oc} of P52-based PSCs was suppressed due to the existence of defect regions. Meanwhile, the insufficient exciton generation in the grain boundary region was also observed by the pcAFM measurement. Hence, P15 film with the smallest grain size can eliminate the defect region, while it can also reduce the I_{sc} due to the increase of the grain boundary region.

Figure 23. Three of perovskite-based films with different roughness and coverage rate have been studied in this experiment. The low (a, d, g) and large (b, e, h) magnified SEM images of the film surfaces and their corresponding three-dimensionally SPM images(c, f, i). The roughness were 52, 25, and 15 nm for (a-c), (d-f), and (g-h) films, respectively. For clarification, they are noted as P52, P25, and P15. (j) *I-V* curves measured for the perovskite solar cells employing these P52, P25, and P15 films from 0 V to 1 V bias voltage with 200 ms speed rate under AM 1.5 G one sun (100 mW/cm^2). (i) Photovoltaic parameters obtained from *I-V* curves. Reprinted from reference [147].

5. Inverted organic photovoltaic (OPVs)

Figure 24. Schematic illustration of device structures of (a) inverted and (b) conventional OPVs with bulk heterojunction active layer. Reprinted from reference [13].

Figure 24(a) shows a schematic of an inverted OPV with a stacked structure of a transparent electrode (e.g., ITO, FTO and AZO), an interfacial layer named as cathode buffer layer (CBL), a BHJ active layer, an anode buffer layer (ABL) usually made of PEDOT:PSS, and a metal electrode with high-work-function such as Ag and Au [13]. The structure of conventional PSCs is also schematically presented in **Figure 24(b)** for comparison. In the inverted device architecture, the contact between the ITO and PEDOT:PSS is avoided, and meanwhile Al for top electrode adopted in conventional PSCs is replaced with an air stable high-work-function metal, such as Au or Ag [153, 154]. As a result, the inverted PSCs exhibit greatly improved ambient stability as compared to the PSCs with a conventional structure, overcoming one big hurdle for possible widespread application of PSCs [155-160]. The MOS used in the inverted OPVs deposited on ITO glass substrate serves as a CBL and is a critically important

component. Its composition, morphology, structure, and crystallinity can largely affect the solar cell performance.

5.1 Nanostructured TiO₂ CBLs for OPVs

5.1.1 TiO₂ mesoporous film

Figure 25. Top-view SEM images of (a) dense TiO₂, (b) mesoporous TiO₂ and (c) macroporous TiO₂ films, respectively; (d) The cross section SEM of an OPV using a porous TiO₂ films. Reprinted from reference [153].

Besides facilitating the PCBM to form a continuous layer, CBL may play a role in enhancing the solar cell performance. We [161] found that, in the case of a TiO₂ mesoporous oxide film with the pore size of ~10-20 nm as cathode buffer layer, the PCE of the OPV could reach a value as high as 3.4%, while they were 1.7% and 1.9% when using a macroporous film with the size of 2-50 nm and a dense film, respectively. **Figure 25** shows SEM images of dense, mesoporous and macroporous TiO₂ CBLs [161]. When the conduction band bottom of the oxide such as TiO₂ is lower than the LUMO level of PCBM and meanwhile the film thickness is not much larger than the electron diffusion length, the electron can transport within the oxide film efficiently, and the transport is much more efficient than within a polymer such as PCBM. When the CBL has a suitable structure, for example in this work it is a mesoporous film, the polymers can penetrate into the mesoporous film, leading to the formation a much large interface between the polymers and the oxide. This makes the electrons in the PCBM have a significantly increased probability to transport into the oxide before they get trapped during transport within the PCBM. Since the electron transport in an oxide is much more efficient than in a polymer, the use of nanostructure

which stretches into the polymers to extract electrons can largely enhance the electron collection efficiency, resulting in the high efficiency. However, in the case of macroporous film, which was prepared by spin-coating a precursor solution which contains a sol of TiO_2 and PVP additive stirred for a longer time (60 min) compared to the time (30 min) for the preparation of a mesoporous film, the nanocrystallites agglomerate to larger aggregates than in the mesoporous film, and the electron transport in the oxide becomes less efficient resulting from the size of aggregates larger than the diffusion length of electrons within the corresponding oxide. Consequently, the macroporous film achieved a PCE of 1.7%, much lower than the 3.4% efficiency achieved by using a mesoporous film. This work illustrates that there is a trade-off between the nanostructure forming a large interface with the polymers to improve electron collection and it hindering electron transport in case of its size much larger than the electron diffusion length.

5.1.2 TiO_2 nanorod array

Figure 26. The top-view and cross section SEM images of TiO_2 nanorods with length of 140 nm (a, b), and nanorod with length of 500 nm (c, d). (e) SEM image of TiO_2 dense film. The scale bars are all 100 nm. (f) Schematic of the OPV based on TiO_2 nanorods array CBL. Reprinted from reference [154].

Nanostructured TiO₂ for the enhancement of electron collection in OPVs have also demonstrated in another work with regard to the use of TiO₂ nanorod array grown on a FTO glass substrate through a hydrothermal method as shown **Figure 26** [162]. By controlling the time for hydrothermal growth, the length of nanorods (i.e., the height of the nanorod array) could be adjusted. When the nanorod arrays were used as the CBL in OPVs, it was observed that the solar cell efficiency could be much affected by the length of nanorods. For the nanorods ~150 nm in length, the solar cell reached a high PCE of ~3.21%, which was apparently higher than the efficiency of ~2.70% when using the nanorods with a length of ~500 nm, and was also higher than the efficiency of 2.79% when using a very thin TiO₂ dense film. The high efficiency obtained for the solar cell using the nanorods with a relatively small length was explained that, similar to the mechanism in the case of mesoporous film mentioned above, the nanorods stretching into the polymers resulted in a large oxide/polymer interface and could thus improve the electron transport and collection. However, when the nanorods were as long as 500 nm (which is much larger than the electron diffusion length in TiO₂), although the TiO₂ nanorods were single crystalline, the electron transport through the entire nanorods became somewhat difficult, leading to electron traps to a large extent and thus giving rise to a smaller photocurrent density than in the case of short nanorods (9.05 mA/cm² for 500 nm and 10.06 mA/cm² for 150 nm). This eventually yielded a low PCE. It had also been observed that the solar cell with the long nanorods presented a fill factor (FF), 51.3%, lower than the fill factor of 53.6% for short nanorods and 53.8% for dense film. This can be explained that, in the case of too long nanorods, the polymers is hard to penetrate into the entire nanorod array so that the bottom area of the nanorod array is not fully covered by the polymers, resulting in an increase in the series resistance of the solar cell.

5.2 Nanostructured ZnO CBLs for OPVs

5.2.1 ZnO dense layer

ZnO has drawn much attention in serve as the buffer layer because it has good transparency across the whole visible spectral range, relatively high electron mobility, and environmental stability [13, 163]. Recently, we compared the efficiencies of OPVs constructed with ZnO dense CBL having different thickness and roughness achieved by changing the concentration of the ZnO sol used for the fabrication of cathode buffer layer [163]. It was revealed that, when the thickness of ZnO film varied from 20 nm to 65 nm, the PCE basically remained the same, around 3.1%. In other words, the solar cell efficiency is not sensitive to the thickness of the CBL. This makes sense considering that the film thicknesses in 20-65 nm are comparable to the electron diffusion length in ZnO and, therefore, the electron transport within the CBL is not affected perceptibly by varying the film thickness.

However, it was found that the solar cell efficiency could be significantly affected by the roughness of the cathode buffer layer; a smaller roughness gave rise to higher power conversion efficiency, which increased from 1.82% to 3.30% when the roughness (as shown in **Figure 27** measured with AFM) decreased from 4.25 nm to 2.86 nm. It was explained that the ZnO cathode buffer layer with small roughness could lead to a good contact with the polymer, which benefited the electron transport at the polymer/ZnO interface and meanwhile gave rise to the solar cell with low series resistance; in the case of large roughness, there likely formed some voids at the polymer/ZnO interface, which hindered the electron transport and increased the series resistance of the solar cell. Such a speculated mechanism was in line with the experimental observation that higher photocurrent density and larger fill factor were obtained in the case of smaller roughness.

Figure 27. 3D AFM images of the ZnO buffer layers of devices A, B, C, D, E, and F, which were deposited by spin-coating 0.02, 0.05, 0.1, 0.3, 0.6, and 1 M sol one time. Reprinted from reference [155].

5.2.2 *SrTiO₃:ZnO composite layer*

Compared with ZnO, SrTiO₃ has a higher dielectric constant ($\sim 10^4$), similar band gap structure, but lower electron mobility. It was hypothesized that the material with larger dielectric constant and spontaneous polarization, such as SrTiO₃, may create an internal electric field while PSCs operation. Such a high dielectric constant material would favor the effective charge transfer in OPVs. SrTiO₃:ZnO CBL was used in OPVs as shown in **Figure 28** (a, b) [164]. The fabrication of SrTiO₃:ZnO CBL was achieved by mixing a sol of SrTiO₃ and a sol of ZnO in certain molar ratios and then spin coating on a ITO glass substrate followed by a heat treatment at 350 °C to enable the formation of SrTiO₃:ZnO composite. The ratios of SrTiO₃ to ZnO changed from 5:95, 10:90, 15:85, 20:80, to 25:75. It was revealed that the solar cell efficiency increased from 3.58% for pure ZnO to 4.10% for the ratio of SrTiO₃:ZnO being 10:90; a further increase of the SrTiO₃:ZnO ratio however led to a decrease in

the efficiency, which dropped to 2.38% when the ratio was 25:75 as shown in **Figure 30** (c). The increase in the solar cell efficiency was found to result from an increase in the FF of the solar cell while the open-circuit voltage and short-circuit photocurrent density didn't show an apparent change. The increase in the FF likely suggests that the contact between the polymers and the CBL is improved in view of the addition of suitable amount of SrTiO_3 to ZnO , which changes the surface status of ZnO (possibly due to local spontaneous polarization of the SrTiO_3) and results in the interface between the polymers and cathode buffer layer with a relatively low energy barrier; a low energy barrier is beneficial to the electron transport over the polymer/CBL interface especially when the kinetic energy of electrons is small, corresponding to the high voltage range (adjacent to open-circuit voltage) during the I-V measurement. The allowing of the electrons with small kinetic energy to transport through the polymer/CBL interface straightforwardly leads to an increase in the FF.

Figure 28. (a, b) OPVs and the corresponding energy level diagram of the components of the devices, (c) I-V curve at 1 sun and dark condition with various $\text{SrTiO}_3:\text{ZnO}$ films as the cathodic buffer layer and (d) IPCE results of various $\text{SrTiO}_3:\text{ZnO}$ films as CBLs. Reprinted from reference [156].

5.2.3 $\text{Ta}_2\text{O}_5:\text{ZnO}$ composite layer

Similar to SrTiO_3 , Ta_2O_5 is also known for its high dielectric constant and index of refraction, which is helpful for the effective charge transfer in OPVs. $\text{Ta}_2\text{O}_5:\text{ZnO}$ is another composite studied for CBL of OPVs [165]. The results are very similar to what are obtained for $\text{SrTiO}_3:\text{ZnO}$ as shown in **Table 3**. It was observed that the

PCE of OPV increased gradually when the percentage of Ta₂O₅ in the composite increased from 0 to 18% (in molar), and when the percentage is higher than 18%, the efficiency dropped quickly. For pure ZnO (i.e., 0% Ta₂O₅), the PCE was 3.70%. The maximum efficiency corresponding to 18% Ta₂O₅ was 4.12%. When the Ta₂O₅ was 30%, the efficiency was as low as 1.26%. When the CBL only consisted of Ta₂O₅, the solar cell efficiency was nearly close to zero. Same as the case of SrTiO₃:ZnO, when the content of Ta₂O₅ increased from 0 to 18%, the increase in PCE mainly resulted from an increase in FF, from 0.61 for pure ZnO to 0.67 for 18% Ta₂O₅, while the solar cell's open-circuit voltage and short-circuit current density didn't show an apparent change. When the content of Ta₂O₅ exceeded 18%, it was found that the electron mobility of the SrTiO₃:ZnO films decreased greatly with increasing the amount of Ta₂O₅ in the composite, and as a result the series resistance of the solar cell increased significantly, which were 7.28 Ωcm² for 18% Ta₂O₅, 10.07 Ωcm² for 24% Ta₂O₅, and 243.9 Ωcm² for 30% Ta₂O₅. The mechanism of Ta₂O₅:ZnO composite CBL enhancing the solar cell efficiency is same as what was depicted above for SrTiO₃:ZnO. The addition of Ta₂O₅ to ZnO gives the cathode buffer layer with a surface status different from that of ZnO film. When the amount of Ta₂O₅ is suitable, it seems that the use of Ta₂O₅:ZnO composite can improve the contact between the polymers and the cathode buffer layer, so as to enable the formation of an interface with low energy barrier, which benefits the solar cell with increasing its fill factor. However, when the composite contains too much Ta₂O₅, for example, over 18% as revealed by this work, a dramatic decrease in the electron mobility will largely increase the series resistance of the solar cell and result in a low efficiency. So the study of the use of composites for CBL of OPVs delivers new understanding to the criteria for choosing material for the CBL.

Table 3. Properties of OPVs with various Ta₂O₅:ZnO CBLs [165].

Ta ₂ O ₅ / %	V _{oc} / V	J _{sc} /mA cm ⁻²	FF	PCE / %	R _{sh} /kΩ cm ²	R _s /kΩ cm ²
0	0.636	9.49	0.613	3.70	0.67	8.72
6	0.637	9.75	0.649	4.03	1	7.58
12	0.634	9.73	0.661	4.08	5	7.20
18	0.637	9.64	0.670	4.12	3.3	7.28
24	0.631	9.75	0.616	3.79	1.67	10.07
30	0.563	8.61	0.260	1.26	0.2	243.9
100	0.564	0.04	0.374	0.0009	11	125000

As it was mentioned in the beginning of section 5, one of the biggest attraction of inverted OPVs is its

excellent ambient stability in comparison with the conventional OPVs. The PCE of the unencapsulated inverted organic photovoltaics was periodically measured for 42 days to monitor their long-term stability in air (**Figure 29**). All devices retained around 100% of the magnitude of their original power conversion efficiency after being exposed to ambient conditions for 42 days. This explicitly demonstrates the superior air stability of inverted organic photovoltaics.

Figure 29. The long term stability of inverted OPVs with ZnO or Ta₂O₅:ZnO films as CBL; the devices were stored in ambient conditions. Reprinted from reference [160].

6. Concluding remarks

As the essential component, MOSs, such as TiO₂, ZnO and SnO₂ have been widely used in the ESCs including DSCs, QDSCs, PSCs and OPVs. With the development of nanotechnology, a big breakthrough in ESCs will be made due to the novel nano-architectures of MOSs. For example, hierarchical nanostructured MOSs not only offer large specific surface area for loading a large amount of active materials (dyes, quantum dots or perovskites), but also have strong light scattering to capture a sufficient fraction of photons. This review summarized the recent works on the structure design, fabrication, and surface modification of MOSs to enhance PCE of ESCs. In addition to the design and fabrication of the nanostructured MOSs, it was also found that the poor chemical stability and lots of surface defects of nanostructured MOSs caused much high surface charge recombination of the solar cells, which resulted in the decrease of PCE. So the rational design and engineering surface and interface chemistry would favor charge transfer and at the same time prevent or minimize the charge recombination of the solar cells.

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