We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists



185,000

200M



Our authors are among the

TOP 1% most cited scientists





WEB OF SCIENCE

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

# Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected. For more information visit www.intechopen.com



## ZnO Nanowires for Dye Sensitized Solar Cells

Simas Rackauskas, Nadia Barbero, Claudia Barolo and Guido Viscardi

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/67616

#### Abstract

This chapter provides a broad review of the latest research activities focused on the synthesis and application of ZnO nanowires (NWs) for dye-sensitized solar cells (DSCs) and composed of three main sections. The first section briefly introduces DSC-working principles and ZnO NW application advantages and stability issues. The next section reviews ZnO NW synthesis methods, demonstrating approaches for controlled synthesis of different ZnO NW morphology and discussing how this effects the overall efficiency of the DSC. In the last section, the methods for ZnO NW interface modification with various materials are discussed, which include ZnO core-shell structures with semiconductive or protective layers, ZnO NW hybrid structures with other materials, such as nanoparticles, quantum dots and carbon nanomaterials and their benefit for charge and light transport in DSCs. The review is concluded with some perspectives and outlook on the future developments in the ZnO nanowire application for DSCs.

**Keywords:** Nanowires, ZnO nanowire, Synthesis, dye-sensitized solar cell, DSC, Photovoltaics, surface modification, hybrid materials

### 1. Introduction

World energy demand is rapidly increasing; therefore, a clean and reliable energy source is fundamental to global economy. The environmental impact of the fossil fuel use urges the need for the search of alternative energy resources. Many different renewable energy technologies were developed recently aiming for efficient solutions of clean energy supply; however, a price competitiveness is a biggest drawback. Solar energy is considered as a key solution for environmental challenge, because of its carbon neutral nature and high abundance. The conversion of solar energy to electricity is fulfilled by solar cells based on the photovoltaic effect.



© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. (cc) BY Dye-sensitized solar cells (DSCs) have gained widespread attention because of the ease of fabrication, low production costs and tuneable optical properties, such as colour and transparency [1]. The most attractive properties of DSCs are their low cost and simple manufacturing processes together with their advantageous attributes such as lightweight, low toxicity and good performance in diverse light conditions [2].

ZnO attracted attention as an alternative photoelectrode material for DSCs due to multiple advantages, that is, excellent optoelectronic properties, low cost, easy synthesis, non-toxicity and others. Moreover, ZnO has the diversity of one-dimensional (1D) structures, which suggest attractive approach for photoelectrode scaffolding.

ZnO nanowire (NW) application as DSC photoelectrode shows multiple advantages, such as higher electron mobility and increased optical way because of refraction; moreover, additional functionalities such as flexible DSCs with the help of ZnO NW photoelectrode can also be obtained. The efficiency of ZnO nanowire DSCs is rapidly increasing in recent years; therefore, the interest in ZnO NW application for DSC is rapidly growing. In order to reach higher efficiency of ZnO NW DSCs, further surface modifications with an additional protective layer of TiO<sub>2</sub> or inert materials such as  $Al_2O_3$  are used. Other possibilities lie in tailoring the morphology of NWs, or employing hybrid structures of ZnO nanowires with other materials.

The application of ZnO NW for DSCs is an interesting topic for nanowire community and also to researchers from diverse scientific fields, since much effort was put in this topic, numerous approaches were tried and a definite improvement was reached. Still, there is a need to direct the effort in understanding more deeply the ZnO NW interaction with other materials, processes of light and charge transfer and master the synthesis methods in order to achieve the optimal structure for application in DSCs.

This chapter will provide a comprehensive review of the state-of-the-art research activities focused on the synthesis and application of ZnO nanowires for dye-sensitized solar cells. The first section briefly overviews fundamentals of the DSC and introduces ZnO NW synthesis, divided into vapour and solution phase methods, demonstrating approaches to obtain different ZnO NW morphology. Next, the methods for ZnO NW surface modification are discussed, which include ZnO core-shell structures with semiconductive layers or protective layers and their benefit for charge and light transport in DSCs. In the last part, we will review ZnO NW hybrid structures with other materials, such as nanoparticles, quantum dots or carbon nanomaterials. The chapter will then conclude with the perspectives and the outlook on the future developments in the ZnO nanowire application for DSCs.

### 2. Fundamentals of dye-sensitized solar cells

The concept of a dye-sensitized solar cell was introduced in 1991, by O'Regan and Grätzel [3]. A schematic diagram showing the operation of a typical DSC is shown in **Figure 1**.

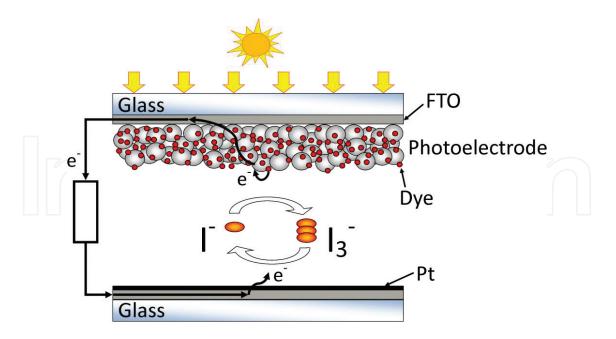


Figure 1. Schematic overview of the typical dye-sensitized solar cell (DSC).

Typical DSCs are composed of a transparent conducting oxide (such as fluorine-doped tin oxide, FTO) on glass, a nanoparticle photoelectrode covered in a monolayer of sensitizing dye, a hole-conducting electrolyte and a platinum-coated, FTO-coated glass back-contact.

Nanoparticles of  $\text{TiO}_2$  (anatase) are mostly used as photoelectrode, although alternative wide-band-gap oxides such as ZnO and  $\text{SnO}_2$  have also been investigated. A monolayer of the sensitizer is attached to the surface of the nanoparticle photoelectrode. Under illumination, sensitizer photo-excitation results in the injection of an electron into the conduction band of the oxide. The dye is regenerated by electron donation from the electrolyte, mostly from a redox system (iodide/triiodide couple) in an organic solvent. The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The iodide is regenerated, in turn, by the reduction of triiodide at the counter-electrode, and the circuit is completed via electron migration through the external load. The voltage, which is obtained under illumination, corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte. Overall, there are no permanent chemical transformations involved in the generation of electric power from light.

The photoelectrode serves as a support for sensitizer loading and at the same time transport media of photo-excited electrons from sensitizer to the external circuit. Hence, to ensure high dye loading, a large surface area is necessary. Moreover, a fast charge-transport rate is required to ensure high electron collection efficiency. These two properties are the defining characteristics of an ideal photoelectrode [4].

Insight into the factors limiting DSC performance is gained by comparing theoretical cell efficiencies with those of current state-of-the-art cells. The power conversion efficiency (PCE) of a solar cell is given as

$$PCE = \frac{J_{sc} V_{oc} FF}{P_{in}},$$
(1)

where  $J_{sc}$  is the absolute value of the current density at short circuit,  $V_{oc}$  is the photovoltage at open circuit, *FF* is the fill factor and *P*in is the incident light power density. In principle, the maximum  $J_{sc}$  of a DSC is determined by how well the absorption window of its dye overlaps the solar spectrum. Much of the shortfall is due to the poor absorption of low-energy photons by available dyes. Thickening of the photoelectrode to increase its optical density in order to improve the absorption of red and near-infrared light is unsuccessful because the film thickness comes to exceed the electron diffusion length through the nanoparticle network.

The dynamic scale of the processes involved in light to electricity conversion (**Figure 2**) shows that the initial events of electron injection and dye regeneration leading to photoinduced charge separation occur on a femto- to nanosecond or microsecond time scale [6], while the electron transport across the photoelectrode takes place within milliseconds or even seconds [7]. However, for the efficient functioning of the DSC, the diffusion length of the electron should be greater than the thickness of the photoelectrode. Electron diffusion length  $L_n$  can be expressed through electron lifetime  $\tau_n$  and electron diffusion coefficient  $D_n$  as

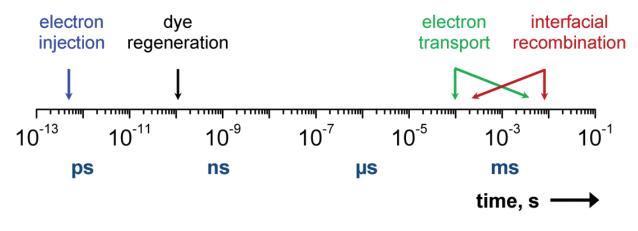
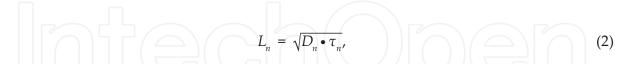


Figure 2. Dynamics competition of the processes involved in the conversion of light to electric power by typical DSCs [5].



Disordered network of TiO<sub>2</sub> nanoparticles with numerous grain boundaries weakens electron mobility and results in slow transport and recombination of photo-excited electrons [8]. This greatly hinders the overall PCE of such devices. The mentioned problems associated with the standard architecture of the photoelectrode oblige a search for more effective nanostructured photoelectrode materials and morphologies [9–11].

### 3. ZnO nanowire synthesis and application in DSCs

The relatively low transport resistance of transparent high-mobility materials, such as ZnO compared to that of anatase  $TiO_2$  nanoparticles, is one of the major advantages for the application in charge injection and collection for DSCs [12–15]. ZnO, which has an energy

bandgap similar to that of the ordinarily used TiO<sub>2</sub> but possesses higher electron mobility, is an alternative photoelectrode material for DSCs [16]. Another advantage of ZnO is the diversity of 1D structures. Structurally, ZnO has several fast-growth directions; therefore, various morphologies can be easily obtained.

ZnO nanowires were widely considered as an alternative photoelectrode material (**Figure 3**), since they address many of the mentioned problems; however, up to date the highest power conversion efficiency of ZnO-based DSC reported [18] is still lower than  $TiO_2$ -based DSC. The main reason may be that best DSC dyes are designed for  $TiO_2$  photoelectrode, and since ZnO is less stable especially in acid, therefore there is still no efficient dye available for ZnO anode [19, 20]. It was found that electron injection from traditional Ru-based dye to ZnO is much slower than to  $TiO_2$  [21]. However, much research is conducted in order to find modifications for ZnO photoelectrodes and further increase the overall PCE of the DSCs.

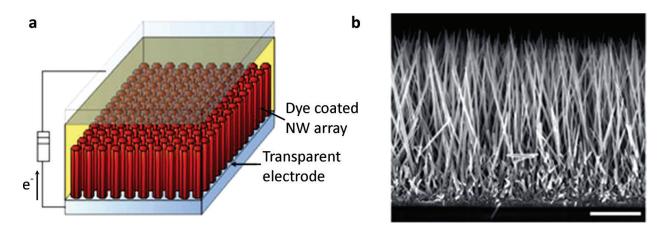


Figure 3. ZnO nanowire-based DSC: (a) a schematic of the cell; (b) SEM image of a nanowire array. Scale bar, 5 µm [17].

### 3.1. ZnO nanowire DSC stability

ZnO has a low chemical stability in acidic environment. After the DSC assemble, ZnO photoelectrode degrades through the carboxylic groups of the acidic dye attached to it, and thus leads to the formation of Zn<sup>2+</sup>-dye agglomerates.

On the other hand, the time of dye loading is crucial for the performance of an all-ZnO-based DSC, because longer dye-loading time leads to the formation of more Zn<sup>2+</sup>-dye agglomerates and shorter immersion time is insufficient for dye adsorption. For this reason, other than traditional Ru-based dyes could be used, such as porphyrin and indoline dyes [22]. Indoline dyes have been found to be a comparatively good match with ZnO because of its lower acidity and the lack of complexing agent. The CR147 dye-sensitized ZnO film is almost free from Zn<sup>2+</sup>/dye agglomerations. A ZnO DSC with CR147 dye has high PCE of 6.89%, 40% higher than the cell with traditional N719 dye [23]. A metal-free organic dye D149 allows to use lower-sensitizing times, moreover a PCE of 5.14% was reported [24]. A mix of several specially engineered dyes could also be advantageous. Compared to only D149-sensitized cell, the YD2-o-C8-TBA and D149 co-sensitized ZnO DSSC with a wavelength ranging from 475–700 nm exhibited improved photon-to-current conversion efficiencies with cell PCE of 5.6% [25]. Vegetable tannin

and their Fe complexes could be used for their low cost and can be obtained from renewable sources, but the efficiencies are up to 0.99% [26].

Other stability problems are associated with a liquid electrolyte used, which tends to leak in time. Device instability and the need for good device packaging have become major problems for commercial application of DSCs. This problem is common to most DSCs; liquid electrolyte could be substituted with quasi-solid-state electrolytes [27]. Metal oxide nanoparticle gelators are applied [28], ZnO nanoparticles gel [29] shows PCE of 4.17%, and the optimized DSC shows a stability of 95% on the PCE value for 150 days. The hole transport is presumably done by Grotthuss-type ion exchange mechanism.

#### 3.2. ZnO nanowire synthesis

As it was earlier stated, competition between the transport and the recombination of photoexcited carriers is one of the main obstacles for developing higher conversion efficiency photoelectrode. To date, numerous morphologies of low-dimensional ZnO nanostructures such as nanowires, nanobelts, nanotubes and nanoflakes have been synthesized and are expected to improve the electron diffusion length in the photoelectrode.

This paragraph reviews the most important approaches of the ZnO NW synthesis with the aim of application in DSCs. In order to obtain an optimal structure for the photoelectrode of DSC, the growth of ZnO NWs should be carefully controlled. ZnO nanowires can be synthesized in a variety of methods; two main synthesis groups can be distinguished: vapour phase and solution phase synthesis.

*Vapour phase ZnO NW synthesis* involves temperatures typically 400–1100°C, needed to vapourize and transport the precursors. A typical reaction involves ZnO NW growth by vapour-liquid-solid mechanism (VLS) [30, 31] using catalyst particles such as Au, Pt or Ag, or by vapour solid mechanism (VS) [32] without the use of catalysts. Zn vapour is obtained by heating the mixture of ZnO and C [33] or directly from Zn powder [34]. A direct growth on Zn metallic substrate is also interesting for its simplicity [35–37]. ZnO NW growth by vapour phase synthesis typically involves a direct Zn oxidation:

 $Zn + O_2 \rightarrow ZnO$ 

*Solution phase ZnO NW synthesis* is especially interesting for its low-temperature approach and high-output possibilities. Since the typical synthesis conditions apply temperatures lower than 200°C, the variety of materials can be used as substrates. In the solution phase synthesis, the ZnO NW growth process is carried out in aqueous or organic solvents from zinc salts. Normally, aqueous solutions are used and the methods are often referred to as hydrothermal growth [38]. However, other solutions such as ethanol [39] are also used. A typical ZnO NW solution phase growth involves the following reaction:

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_{2} \rightarrow ZnO + H_{2}O$$
(4)

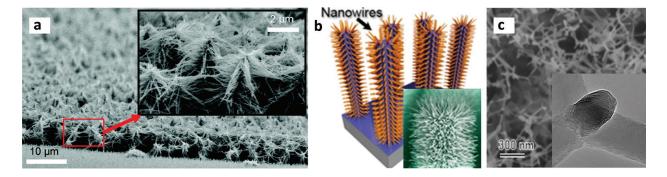
(3)

where hexamethylenetetramine (HMTA) [40],  $NH_4OH$  [41] or NaOH [42] may be used as the hydroxide source. High aspect ratio can be achieved by controlling the preferential growth

with catalytic Au nanoparticles [43] or polymers such as polyethylenimine (PEI) [44], or polyethylene glycol (PEG) [45]. ZnO NW aspect ratio can be further improved by sequential growth [46].

Comparing the vapour and liquid phase synthesis, it is important to note that the vapour phase growth of ZnO NWs uses higher temperatures; therefore for low-melting substrates an efficient post synthesis, transferring and attachment methods should be developed, but none-theless high crystallinity can be obtained without further annealing. On the contrary, most of the solution growth methods use low temperatures, therefore NWs can be directly grown on a variety of low-melting materials and surfaces; however, the synthesis of high aspect ratio structures with high crystallinity is demanding.

Applying the mentioned methods, ZnO NWs could be synthesized in complex forms (**Figure 4**) such as nanoforest [47], tetrapods [49, 50], hierarchical nanowires [48], coral-shaped nanostructures [51], nanocactus [24], flower-like [52] and many others [53–55] by simply controlling the crystal grow direction.



**Figure 4.** Complex structures of ZnO nanowires: (a) nanoforest [47]; (b) hierarchical nanowires (inset shows SEM figure) [48]; (c) tetrapods [49].

### 4. ZnO NW interface modifications

The advantage of fast electron transfer is often counterbalanced by faster electron recombination dynamics with the oxidized electrolyte via intrabandgap surface states which ultimately limits the PCE [15]. In order to slow down the recombination and to increase the photovoltage and photocurrent, the ZnO NW interfaces can be covered by a thin layer of various capping materials ( $Al_2O_3$ ,  $TiO_2$ ,  $ZrO_2$ , etc.). Alternatively, hole transfer can be modified by forming ZnO NW hybrid structures with conductive polymers, or various nanostructures such as quantum dots (QDs), nanocrystals (NCs) and carbon nanomaterials.

#### 4.1. ZnO NW core-shell structure in DSC

The purpose of NW coating with an insulating or semiconducting oxide layer is to diminish the recombination by forming a potential barrier on NW surface, to physically separate electrons from ions and to increase the dye adsorption on the surface. Moreover, band edge can be shifted by using higher bandgap layer to increase the open-circuit voltage. In addition to acting as an effective protection layer for the chemically unstable ZnO against the acidic dye solution, the complete coverage of the NWs with a dense layer can passivate surface traps [12]. ZnO NW core-shell structures with different metal oxides can be obtained with atomic layer deposition (ALD) technique [56, 57]. The coverage of ZnO NWs with an insulating materials results in a low-efficiency DSCs [58–60]; by contrast, ZnO NW core-shell structures with semiconductors have several advantages, especially interesting is TiO<sub>2</sub> shell.

There are several motives why the ZnO-TiO<sub>2</sub> core-shell structure is attractive. TiO<sub>2</sub> is chemically more stable compared to ZnO in acidic dye solutions [61]. Thus, the presence of TiO<sub>2</sub> shell prevents ZnO surface from being dissolved and the formation of  $Zn^{2+}/dye$  agglomerates. The TiO<sub>2</sub> shell can also increase the injected electrons and more dye absorption, which lead to a higher light-harvesting efficiency. Moreover, the shell reduces recombination by forming a tunnelling barrier to confine the photoinjected electrons within the core, and by passivating the recombination centres on the core surface [62]. The charge transfer is significantly improved since ZnO has much higher electron mobility compared to TiO<sub>2</sub>. DFT ab initio study of ZnO-TiO<sub>2</sub> core-shell structure [63] shows that TiO<sub>2</sub> coating induces changes in surface states and shifts the conduction and valence band edges to higher energies; therefore, an increase in open-circuit voltage and a decrease in short-circuit current are expected.

 $TiO_2$  shell on ZnO NWs can be formed by dip coating in Ti precursors, such as tetrabutyl titanate (TBOT) [64, 65], titanium isopropoxide (TTIP) and titanium tetrachloride (TiCl<sub>4</sub>). ZnO NW coated with a thin shell layer of  $TiO_2$  (**Figure 5**) showed an increased PCE up to 6% [66]. A comparative study [67] showed that at the same conditions TBOT-treated ZnO DSC showed the best performance with the highest PCE and short-circuit current density of 4.92% and 12.49 mA/cm<sup>2</sup>, respectively.

In order to increase the surface area of the photoelectrode and without losing the chargetransport properties, hierarchical structures could be used. A hierarchical structure of ZnO NWs could also increase the efficiency of DSCs by providing a high area for dye absorption

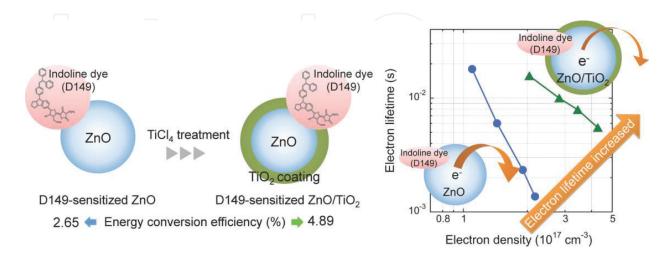


Figure 5. ZnO-TiO<sub>2</sub> core-shell formed by low-temperature TiCl<sub>4</sub> treatment [68].

and also effective light scattering. ZnO DSC efficiency can be doubled by decorating ZnO NW photoelectrodes with different nanoparticles of  $SnO_2$  [69], TiO\_2 [70, 71] or in situ-synthesized ZnO nanoparticles [72]. Even though the large surface area of nanoparticles empowers a high dye-loading capacity, yet the disordered network with numerous grain boundaries weakens electron mobility and results in slow transport and recombination of photo-excited electrons [8]. The application of ZnO NW with semiconductive nanoparticles has advantages of both high surface area and fast charge transport. A complex structure of hierarchical NWs improves the PCE up to five times compared to the initial NW, the reported efficiencies for nanotrees 2.63% [73], coral-shaped nanostructure gives 4.58% [51], nanocactus 5.14% [24] are encouraging.

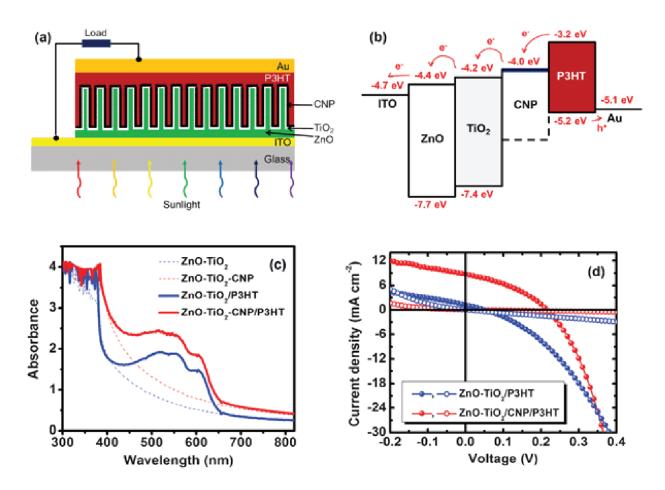
ZnO tetrapods used with  $SnO_2$  nanoparticles provided large roughness factors, good charge collection and tunable light-scattering properties. High PCE of 6.31% was attributed to  $NH_3$  treatment, which was believed to create ZnO shell on  $SnO_2$  nanoparticles [74]. A hierarchical core-shell ZnO NW with TiO<sub>2</sub> nanosheets resulted in an outstanding performance with a solid-state electrolyte, showing the conversion efficiencies of up to 7.46% [75].

The prepared ZnO photoelectrode can be further treated to improve the conductance and porosity parameters. Hot-press treatment of the ZnO photoelectrode was demonstrated to improve PCE of the DSC by 45% [76]. Another powerful technique, the room-temperature chemical bath deposition, was used to increase the surface area of the ZnO photoelectrode, a PCE of 5.24% was obtained [77].

### 4.2. ZnO NW hybrid solar-cell structures

Hybrid polymer solar cells composed of metal oxide nanostructures and polymers have attracted great interest mostly due to the good physical and chemical stability. In such solar cells, p-type donor polymers are combined with n-type acceptor ZnO nanostructures [78] among other oxides. Nanowires are one of the most attractive forms for such solar cells because they provide a direct path for charge transport, high carrier motilities and a high electron affinity necessary for charge injection from the complementary organic donor material [79]. Mostly used conducting polymer poly(3-hexylthiophene) (P3HT) composite with ZnO nanowire shows hybrid solar-cell PCE in the range of 0.2-0.5% [80-82] and can be further increased to 2% by adding dye [83]. Such low-power conversion efficiencies are associated with poor polymer infiltration and therefore low-active interfacial area between polymer and ZnO NWs. An interfacial layer of carbon nanoparticles (CNPs) can be employed to enhance the charge-transfer properties in hybrid ZnO NW solar cells. The energy-level diagram of the solar cells is shown in Figure 6b. The LUMO level of the CNPs (- $4.00 \pm 0.02$  eV) is perfectly aligned with both the LUMO level of P3HT (-3.2 eV) and the conduction band edge of TiO<sub>2</sub> (-4.2 eV). This ensures both efficient exciton dissociation at the P3HT/CNP interface and efficient electron extraction. In such a device, ZnO-TiO<sub>2</sub> core-shell works as electron collector and transporter, P3HT acts as electron donor, and the CNP layer acts as electron acceptor [84].

The other possibility is to use quantum dots (QDs) for hole transfer. The use of PbS quantum dots (QDs) is promising because of the tunable, size-dependent bandgap from 0.7 to 1.3 eV [85].



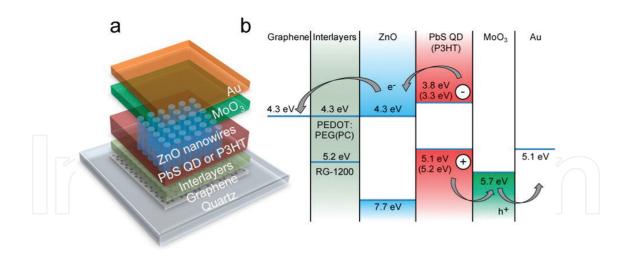
**Figure 6.** Hybrid solar cell with ZnO-TiO<sub>2</sub> core-shell, carbon nanoparticles (CNP) and conductive polymer P3HT. (a) Device structure; (b) energy-level diagram; (c) absorption spectra of the active films on ITO glass substrates; (d) J-V characteristics (empty: dark; filled: illuminated) of the solar cells with and without CNP [84].

Pairing ZnO with PbS QDs for photovoltaic applications shows high stability in ambient atmosphere. An advantage of using ZnO NWs instead of ZnO planar or nanoparticle layer is demonstrated [86]. Vertically oriented ZnO NW arrays are fully infiltrated with QDs, increasing considerably the light absorption and carrier collection. Ordered interface architecture of ZnO NW arrays can decouple absorption from collection, extending the effective depletion width throughout a thick QD film.

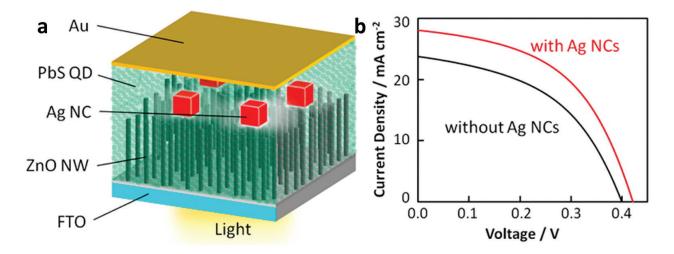
The ZnO NW performance was tested in both earlier mentioned hole conductor configurations: conducting polymer P3HT and PbS QDs [82]. As it is shown in **Figure 7b**, band alignment is similar; however, the PCE of 4.2% and 0.5% for QDs and P3HT, respectively, was obtained. It is worth noting that graphene was used as the conductive electrode instead of the traditional ITO, which demonstrates the flexibility of application for various substrates.

ZnO NW solar-cell absorption in the near-infrared region can be enhanced by using plasmonic nanocrystals (NCs). Ag NC enhances ZnO NW solar-cell (**Figure 8**) PCE from 4.5 to 6.0% [87].

A plasmonic NC traps a photon on the basis of localized surface plasmon resonance, and generates a strong oscillating electric field (i.e. optical near field) that is localized in the vicinity of the NC. The optical near field excites a dye molecule or semiconductor more efficiently than incident far-field light, and therefore photocurrents are enhanced.



**Figure 7.** Hybrid ZnO NW solar cells. (a) Schematic diagram of ZnO NWs (400 nm) infiltrated and covered with PbS QDs (300 nm) or P3HT (700 nm); (b) flat-band energy-level diagram of the solar cell [82].



**Figure 8.** PbS QD/ZnO NW solar cell with embedded Ag NCs. (a) Schematic; (b) J-V characteristics without and with Ag NCs [87].

### 5. Conclusions

Several conclusions could be made with the proposal for the future trends:

- 1. First of all, since one of the main parameters for high efficiency of DSC is surface area, more attention should be paid in order to obtain ZnO NW with a structure of high surface, at the same time a virtue of high crystallinity should not be lost. Several possible methods are worth of interest: the obvious trend would be to synthesize nanowires with lower diameter, but the other ways, such as adding NP to the photoelectrode and using NW as charge delivery highway, are also interesting.
- 2. Non-catalytic growth methods are uncomplicated and much cheaper compared to catalytic ones. Hydrothermal methods have multiple advantages in application since they are low cost and versatile; however, it is problematic to obtain a high aspect ratio structures

with good crystallinity. Nevertheless, these methods are unbeatable for high-yield deposition. A variety of substrates can be used for hydrothermal ZnO NW growth because of the low temperatures used. By contrast, vapour phase growth of ZnO NWs uses higher temperatures, therefore for a low-melting substrates an efficient post-synthesis transferring and attachment methods should be developed; however, high crystallinity can be obtained without further annealing.

- 3. ZnO NW surface is decomposed in acidic environment of best-to-date dyes, therefore special dyes for ZnO should be developed or alternatively surface modification of ZnO is needed. Best-to-date results are obtained by covering the NW surface with TiO<sub>2</sub> or other semiconductor layer. Alternatively forming a protective layer from dielectric materials such as Al<sub>2</sub>O<sub>3</sub> lowers the conductance of photoelectrode, except for an extremely thin layer.
- 4. Hybrid structures of ZnO NWs are primarily interesting for their high physical and chemical stability, but can also boost other properties such as charge transfer or light absorption; however, more work should be done to understand the underlying mechanisms of ZnO NW interaction with hybrid materials.

### Acknowledgements

The work has received funding from the European Union's Seventh Framework programme for research and innovation under the Marie Sklodowska-Curie grant agreement No 609402 – 2020 researchers: Train to Move (T2M).

### Author details

Simas Rackauskas\*, Nadia Barbero, Claudia Barolo and Guido Viscardi

\*Address all correspondence to: simas.rackauskas@gmail.com

Department of Chemistry, NIS Interdepartmental Centre and INSTM Reference Centre, University of Turin, Turin, Italy

### References

- [1] Mathew S, Yella A, Gao P, Humphry-Baker R, Curchod BFE, Ashari-Astani N, et al. Dyesensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. Nat. Chem. [Internet]. 2014 [cited 2016 Sep 16];6:242-7. Available from: http://www.nature.com/doifinder/10.1038/nchem.1861
- [2] Grätzel M. The advent of mesoscopic injection solar cells. Prog. Photovoltaics Res. Appl. [Internet]. John Wiley & Sons, Ltd.; 2006 [cited 2016 Sep 16];14:429-42. Available from: http://doi.wiley.com/10.1002/pip.712

- [3] O'regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films. Nature. Nature Publishing Group; 1991;353:737-40.
- [4] Maçaira J, Andrade L, Mendes A. Review on nanostructured photoelectrodes for next generation dye-sensitized solar cells. Renew. Sustain. Energy Rev. 2013;27:334-49.
- [5] Grätzel M. Solar energy conversion by dye-sensitized photovoltaic cells. Inorg. Chem. American Chemical Society. 2005:6841-51.
- [6] Bach U, Tachibana Y, Moser J-E, Haque SA, Durrant JR, Grätzel M, et al. Charge separation in solid-state dye-sensitized heterojunction solar cells. J. Am. Chem. Soc. American Chemical Society. 1999;121:7445-6.
- [7] Grätzel M. Solar energy conversion by dye-sensitized photovoltaic cells. Inorg. Chem. American Chemical Society. 2005;44:6841-51.
- [8] Ye M, Wen X, Wang M, Iocozzia J, Zhang N, Lin C, et al. Recent advances in dye-sensitized solar cells: From photoanodes, sensitizers and electrolytes to counter electrodes. Mater. Today. 2015;18:155-62.
- [9] Colodrero S, Forneli A, López-López C, Pellejà L, Míguez H, Palomares E. Efficient transparent thin dye solar cells based on highly porous 1D photonic crystals. Adv. Funct. Mater. [Internet]. WILEY-VCH Verlag; 2012 [cited 2016 Sep 16];22:1303-10. Available from: http://doi.wiley.com/10.1002/adfm.201102159
- [10] Wang J, Lin Z. Dye-sensitized TiO<sub>2</sub> nanotube solar cells: Rational structural and surface engineering on TiO<sub>2</sub> nanotubes. Chem. An Asian J. [Internet]. WILEY-VCH Verlag; 2012 [cited 2016 Sep 16];7:2754-62. Available from: http://doi.wiley.com/10.1002/asia.201200349
- [11] Feng X, Zhu K, Frank AJ, Grimes C a, Mallouk TE. Rapid charge transport in dye-sensitized solar cells made from vertically aligned single-crystal rutile TiO<sub>2</sub> nanowires. Angew. Chem. Int. Ed. [Internet]. WILEY-VCH Verlag; 2012 [cited 2016 Sep 16];124:2781 [4. Available from: http://doi.wiley.com/10.1002/ange.201108076
- [12] Tétreault N, Arsenault É, Heiniger LP, Soheilnia N, Brillet J, Moehl T, et al. Highefficiency dye-sensitized solar cell with three-dimensional photoanode. Nano Lett. [Internet]. American Chemical Society; 2011 [cited 2016 Sep 16];11:4579-84. Available from: http://pubs.acs.org/doi/abs/10.1021/nl201792r
- [13] He C, Zheng Z, Tang H, Zhao L, Lu F. Electrochemical impedance spectroscopy characterization of electron transport and recombination in ZnO nanorod dye-sensitized solar cells. J. Phys. Chem. C [Internet]. American Chemical Society; 2009 [cited 2016 Sep 16];113:10322-5. Available from: http://pubs.acs.org/doi/abs/10.1021/jp902523c
- [14] Martinson ABF, Goes MS, Fabregat-Santiago F, Bisquert J, Pellin MJ, Hupp JT. Electron transport in dye-sensitized solar cells based on ZnO nanotubes: Evidence for highly efficient charge collection and exceptionally rapid dynamics. J. Phys. Chem. A [Internet]. American Chemical Society; 2009 [cited 2016 Sep 16];113:4015-21. Available from: http:// pubs.acs.org/doi/abs/10.1021/jp810406q

- [15] Martinson ABF, McGarrah JE, Parpia MOK, Hupp JT. Dynamics of charge transport and recombination in ZnO nanorod array dye-sensitized solar cells. Phys. Chem. Chem. Phys. [Internet]. The Royal Society of Chemistry; 2006 [cited 2016 Sep 16];8:4655-9. Available from: http://www.ncbi.nlm.nih.gov/pubmed/17047762
- [16] Zhang Q, Dandeneau CS, Zhou X, Cao G. ZnO nanostructures for dye-sensitized solar cells. Adv. Mater. [Internet]. WILEY-VCH Verlag; 2009 [cited 2016 Sep 16];21: 4087-108. Available from: http://onlinelibrary.wiley.com/doi/10.1002/adma.200803827/ abstract%0Ahttp://onlinelibrary.wiley.com/doi/10.1002/adma.200803827/abstract;jses sionid=28F0008F38AEB7367E640662E9AD0B66.f01t04%0Ahttp://onlinelibrary.wiley. com/store/10.1002/adma.200803827/asset/
- [17] Law M, Greene LE, Johnson JC, Saykally R, Yang P. Nanowire dye-sensitized solar cells. Nat. Mater. [Internet]. Nature Publishing Group; 2005 [cited 2016 Jul 19];4:455-9. Available from: http://www.nature.com/doifinder/10.1038/nmat1387
- [18] Memarian N, Concina I, Braga A, Rozati SM, Vomiero A, Sberveglieri G. Hierarchically assembled ZnO nanocrystallites for high-efficiency dye-sensitized solar cells. Angew. Chem. Int. Ed. [Internet]. WILEY-VCH Verlag; 2011 [cited 2016 Sep 16];50:12321-5. Available from: http://doi.wiley.com/10.1002/anie.201104605
- [19] Anta JA, Guille E. ZnO-based dye-sensitized solar cells. J. Phys. Chem. C [Internet]. American Chemical Society; 2012 [cited 2016 Sep 16];116:11413-25. Available from: http://dx.doi.org/10.1021/jp3010025
- [20] Jiang WT, Wu C Te, Sung YH, Wu JJ. Room-temperature fast construction of outperformed ZnO nanoarchitectures on nanowire-array templates for dye-sensitized solar cells. ACS Appl. Mater. Interfaces [Internet]. American Chemical Society; 2013 [cited 2016 Sep 16];5:911-7. Available from: http://pubs.acs.org/doi/abs/10.1021/am302570r
- [21] Borgwardt M, Wilke M, Kampen T, Mähl S, Xiao M, Spiccia L, et al. Charge transfer dynamics at dye-sensitized ZnO and TiO<sub>2</sub> interfaces studied by ultrafast XUV photoelectron spectroscopy. Sci. Rep. [Internet]. Nature Publishing Group; 2016 [cited 2016 Dec 20];6:24422. Available from: http://www.nature.com/articles/srep24422
- [22] Syu Y-K, Tingare Y, Yeh C-Y, Yang J-S, Wu J-J. Panchromatic engineering for efficient zinc oxide flexible dye-sensitized solar cells using porphyrin and indoline dyes. RSC Adv. [Internet]. The Royal Society of Chemistry; 2016 [cited 2016 Sep 30];6:59273-9. Available from: http://xlink.rsc.org/?DOI=C6RA09262D
- [23] Lee CP, Chen PW, Li CT, Huang YJ, Li SR, Chang LY, et al. ZnO double layer film with a novel organic sensitizer as an efficient photoelectrode for dye-sensitized solar cells. J. Power Sources. 2016;325:209-19.
- [24] Jiang WT, Wu C Te, Sung YH, Wu JJ. Room-temperature fast construction of outperformed ZnO nanoarchitectures on nanowire-array templates for dye-sensitized solar cells. ACS Appl. Mater. Interfaces [Internet]. American Chemical Society; 2013 [cited 2016 Sep 12];5:911-7. Available from: http://pubs.acs.org/doi/abs/10.1021/am302570r

- [25] Syu Y-K, Tingare Y, Yeh C-Y, Yang J-S, Wu J-J. Panchromatic engineering for efficient zinc oxide flexible dye-sensitized solar cells using porphyrin and indoline dyes. RSC Adv. [Internet]. Royal Society of Chemistry; 2016 [cited 2016 Sep 12];6:59273-9. Available from: http://xlink.rsc.org/?DOI=C6RA09262D
- [26] Çakar S, Güy N, Özacar M, Findik F. Investigation of vegetable tannins and their iron complex dyes for dye sensitized solar cell applications. Electrochim. Acta. Elsevier Ltd. 2016;209:407-22.
- [27] Tao L, Huo Z, Ding Y, Li Y, Dai S, Wang L, et al. High-efficiency and stable quasi-solid-state dye-sensitized solar cell based on low molecular mass organogelator electrolyte.
   J. Mater. Chem. A [Internet]. The Royal Society of Chemistry; 2015 [cited 2016 Dec 20];3:2344-52. Available from: http://xlink.rsc.org/?DOI=C4TA06188H
- [28] Dkhissi Y, Huang F, Cheng Y, Caruso RA. Quasi-solid-state dye-sensitized solar cells on plastic substrates. J. Phys. Chem. C [Internet]. American Chemical Society; 2014 [cited 2016 Dec 20];118:16366-74. Available from: http://pubs.acs.org/doi/abs/10.1021/ jp408844q
- [29] Chang WC, Sie SY, Yu WC, Lin LY, Yu YJ. Preparation of nano-composite gel electrolytes with metal oxide additives for dye-sensitized solar cells. Electrochim. Acta. 2016;212:333-42.
- [30] Yang P, Yan H, Mao S, Russo R, Johnson J, Saykally R, et al. Controlled growth of ZnO nanowires and their optical properties. Adv. Funct. Mater. 2002;12:323-31.
- [31] Huang MH. Room-temperature ultraviolet nanowire nanolasers. Science (80-.). [Internet]. 2001 [cited 2016 Dec 19];292:1897-9. Available from: http://www.sciencemag.org/cgi/ doi/10.1126/science.1060367
- [32] Pan ZW, Dai ZR, Wang ZL. Nanobelts of semiconducting oxides. Science (80-. ). 2001; 291:1947-9.
- [33] Zhang Z, Wang SJ, Yu T, Wu T. Controlling the growth mechanism of ZnO nanowires by selecting catalysts. J. Phys. Chem. C [Internet]. American Chemical Society; 2007 [cited 2014 May 28];111:17500-5. Available from: http://dx.doi.org/10.1021/jp075296a
- [34] Sekar A, Kim SH, Umar A, Hahn YB. Catalyst-free synthesis of ZnO nanowires on Si by oxidation of Zn powders. J. Cryst. Growth. 2005;277:471-8.
- [35] Rackauskas S, Nasibulin AG, Jiang H, Tian Y, Kleshch VI, Sainio J, et al. A novel method for metal oxide nanowire synthesis. Nanotechnology [Internet]. 2010;20:165603. Available from: http://stacks.iop.org/0957-4484/20/165603
- [36] Kleshch VI, Rackauskas S, Nasibulin AG, Kauppinen EI, Obraztsova ED, Obraztsov AN. Field emission properties of metal oxide nanowires. J. Nanoelectron. Optoelectron. [Internet]. 2012 [cited 2016 Nov 28];7:35-40. Available from: http://openurl.ingenta.com/ content/xref?genre=article&issn=1555-130X&volume=7&issue=1&spage=35

- [37] Rackauskas S, Nasibulin AG, Jiang H, Tian Y, Statkute G, Shandakov SD, et al. Mechanistic investigation of ZnO nanowire growth. Appl. Phys. Lett. [Internet]. 2009 [cited 2013 Oct 3];95:183114. Available from: http://link.aip.org/link/APPLAB/v95/i18/p183114/ s1&Agg=doi
- [38] Nam D, Park J, Park S, Min Y, Noh Y, Lee D. High-density hydrothermal growth of zincoxide nanowires using printed resistive heater. Mater. Lett. 2015.
- [39] Wu C, Shen L, Yu H, Huang Q, Zhang YC. Synthesis of Sn-doped ZnO nanorods and their photocatalytic properties. Mater. Res. Bull. 2011;46:1107-12.
- [40] Parize R, Garnier J, Chaix-Pluchery O, Verrier C, Appert E, Consonni V. Effects of hexamethylenetetramine on the nucleation and radial growth of ZnO nanowires by chemical bath deposition. J. Phys. Chem. C [Internet]. 2016 [cited 2016 Dec 19];120:5242-50. Available from: http://pubs.acs.org/doi/abs/10.1021/acs.jpcc.6b00479
- [41] Cho J, Salleh N, Blanco C, Yang S, Lee C-J, Kim Y-W, et al. Novel synthetic methodology for controlling the orientation of zinc oxide nanowires grown on silicon oxide substrates. Nanoscale [Internet]. 2014 [cited 2016 Dec 19];6:3861-7. Available from: http://www.ncbi. nlm.nih.gov/pubmed/24584438
- [42] Xu S, Wang ZL. One-dimensional ZnO nanostructures: Solution growth and functional properties. Nano Res. 2011;4:1013-98.
- [43] Gu C, Shanshan L, Huang J, Shi C, Liu J. Preferential growth of long ZnO nanowires and its application in gas sensor. Sens. Actuators, B Chem. 2013;177:453-9.
- [44] Hu X, Shen X, Li H, Masuda Y, Ohji T, Kato K. Polyethylenimine-assisted synthesis of transparent ZnO nanowhiskers at ambient temperatures. Thin Solid Films. 2014;558:134-9.
- [45] Panigrahy B, Aslam M, Misra DS, Bahadur D. Polymer-mediated shape-selective synthesis of ZnO nanostructures using a single-step aqueous approach. CrystEngComm [Internet]. Royal Society of Chemistry; 2009 [cited 2016 Dec 19];11:1920. Available from: http://xlink.rsc.org/?DOI=b904833m
- [46] Caicedo N, Thomann J-S, Leturcq R, Lenoble D. Aspect ratio improvement of ZnO nanowires grown in liquid phase by using step-by-step sequential growth. CrystEngComm [Internet]. The Royal Society of Chemistry; 2016 [cited 2016 Dec 19];18:5502-11. Available from: http://xlink.rsc.org/?DOI=C6CE00904B
- [47] Ko SH, Lee D, Kang HW, Nam KH, Yeo JY, Hong SJ, et al. Nanoforest of hydrothermally grown hierarchical ZnO nanowires for a high efficiency dye-sensitized solar cell. Nano Lett. [Internet]. American Chemical Society; 2011 [cited 2016 May 17];11:666-71. Available from: http://dx.doi.org/10.1021/nl1037962
- [48] Bielinski AR, Kazyak E, Schlepütz CM, Jung HJ, Wood KN, Dasgupta NP. Hierarchical ZnO nanowire growth with tunable orientations on versatile substrates using atomic

layer deposition seeding. Chem. Mater. [Internet]. 2015 [cited 2016 Dec 18];27:4799-807. Available from: http://pubs.acs.org/doi/abs/10.1021/acs.chemmater.5b01624

- [49] Rackauskas S, Klimova O, Jiang H, Nikitenko A, Chernenko KA, Shandakov SD, et al. A novel method for continuous synthesis of ZnO tetrapods. J. Phys. Chem. C [Internet]. American Chemical Society; 2015; Available from: http://dx.doi.org/10.1021/acs.jpcc. 5b03702
- [50] Rackauskas S, Mustonen K, Järvinen T, Mattila M, Klimova O, Jiang H, et al. Synthesis of ZnO tetrapods for flexible and transparent UV sensors. Nanotechnology [Internet]. 2012;23:95502. Available from: http://www.ncbi.nlm.nih.gov/pubmed/22327417
- [51] Lamberti A, Gazia R, Sacco A, Bianco S, Quaglio M, Chiodoni A, et al. Coral-shaped ZnO nanostructures for dye-sensitized solar cell photoanodes. Prog. Photovoltaics Res. Appl. [Internet]. 2014 [cited 2016 Jul 18];22:189-97. Available from: http://doi.wiley. com/10.1002/pip.2251
- [52] Pugliese D, Bella F, Cauda V, Lamberti A, Sacco A, Tresso E, et al. A chemometric approach for the sensitization procedure of ZnO flowerlike microstructures for dye-sensitized solar cells. ACS Appl. Mater. Interfaces [Internet]. American Chemical Society; 2013 [cited 2016 Dec 19];5:11288-95. Available from: http://pubs.acs.org/doi/abs/10.1021/ am403527m
- [53] Kuo S-Y, Yang J-F, Lai F-I. Improved dye-sensitized solar cell with a ZnO nanotree photoanode by hydrothermal method. Nanoscale Res. Lett. [Internet]. 2014 [cited 2016 Dec 19];9:206. Available from: http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=4 022993&tool=pmcentrez&rendertype=abstract
- [54] Zhang S, Chen H-S, Matras-Postolek K, Yang P. ZnO nanoflowers with single crystal structure towards enhanced gas sensing and photocatalysis. Phys. Chem. Chem. Phys. [Internet]. The Royal Society of Chemistry; 2015 [cited 2016 Dec 19];17:30300-6. Available from: http://xlink.rsc.org/?DOI=C5CP04860E
- [55] Gao R, Tian J, Liang Z, Zhang Q, Wang L, Cao G. Nanorod-nanosheet hierarchically structured ZnO crystals on zinc foil as flexible photoanodes for dye-sensitized solar cells. Nanoscale [Internet]. Royal Society of Chemistry; 2013 [cited 2016 Dec 19];5:1894-901. Available from: http://dx.doi.org/10.1039/C2NR33599A%5Cnhttp://pubs.rsc.org/en/ content/articlepdf/2013/nr/c2nr33599a
- [56] Law M, Greene LE, Radenovic A, Kuykendall T, Liphardt J, Yang P. ZnO-Al<sub>2</sub>O<sub>3</sub> and ZnO-TiO<sub>2</sub> core-shell nanowire dye-sensitized solar cells. J. Phys. Chem. B. American Chemical Society ; 2006;110:22652-63.
- [57] Zhang Y, Lu H-L, Wang T, Ren Q-H, Chen H-Y, Zhang H, et al. Photoluminescence enhancement of ZnO nanowire arrays by atomic layer deposition of ZrO<sub>2</sub> layers and thermal annealing. Phys. Chem. Chem. Phys. [Internet]. The Royal Society of Chemistry; 2016 [cited 2016 Dec 19];18:16377-85. Available from: http://xlink.rsc.org/?DOI=C6CP01900E

- [58] Bu IYY. Effects of post annealing temperature on formation of alumina core shell on zinc oxide nanowire: optoelectronic properties and dye sensitized solar cell applications. J. Mater. Sci. Mater. Electron. [Internet]. Springer US; 2014 [cited 2016 Dec 19];25:4458-65. Available from: http://link.springer.com/10.1007/s10854-014-2188-4
- [59] Li TC, Góes MS, Fabregat-Santiago F, Bisquert J, Bueno PR, Prasittichai C, et al. Surface passivation of nanoporous TiO<sub>2</sub> via atomic layer deposition of ZrO<sub>2</sub> for solid-state dye-sensitized solar cell applications. J. Phys. Chem. C [Internet]. American Chemical Society; 2009 [cited 2016 Jul 19];113:18385-90. Available from: http://pubs.acs.org/doi/ abs/10.1021/jp906573w
- [60] Loh L, Dunn S. Recent progress in ZnO-based nanostructured ceramics in solar cell applications. J. Nanosci. Nanotechnol. American Scientific Publishers; 2012;12:8215-30.
- [61] Greene LE, Yuhas BD, Law M, Zitoun D, Yang P. Solution-grown zinc oxide nanowires [Internet]. Inorg. Chem. 2006 [cited 2016 Jul 20]. p. 7535-43. Available from: http://pubs. acs.org/doi/abs/10.1021/ic0601900
- [62] Law M, Greene LE, Radenovic A, Kuykendall T, Liphardt J, Yang P. ZnO-Al<sub>2</sub>O<sub>3</sub> and ZnO-TiO<sub>2</sub> core-shell nanowire dye-sensitized solar cells. J. Phys. Chem. B [Internet]. American Chemical Society; 2006 [cited 2016 Jul 19];110:22652-63. Available from: http:// pubs.acs.org/doi/abs/10.1021/jp0648644
- [63] Pazoki M, Nafari N, Taghavinia N, O'Regan B, Gratzel M, Hagfeldt A, et al. Ab initio study of electronic effects in the ZnO/TiO<sub>2</sub> core/shell interface: application in dye sensitized solar cells. RSC Adv. [Internet]. The Royal Society of Chemistry; 2014 [cited 2016 Jul 19];4:301-7. Available from: http://xlink.rsc.org/?DOI=C3RA45973J
- [64] Feng Y, Ji X, Duan J, Zhu J, Jiang J, Ding H, et al. Synthesis of ZnO@TiO<sub>2</sub> core–shell long nanowire arrays and their application on dye-sensitized solar cells. J. Solid State Chem. [Internet]. 2012 [cited 2016 Jul 19];190:303-8. Available from: http://dx.doi.org/10.1016/j. jssc.2012.02.026
- [65] Ji X, Liu W, Leng Y, Wang A, Ji X, Liu W, et al. Facile synthesis of ZnO@TiO<sub>2</sub> coreshell nanorod thin films for dye-sensitized solar cells. J. Nanomater. [Internet]. Hindawi Publishing Corporation; 2015 [cited 2016 Jul 19];2015:1-5. Available from: http://www. hindawi.com/journals/jnm/2015/647089/
- [66] Gan X, Li X, Gao X, Zhuge F, Yu W. ZnO nanowire/TiO<sub>2</sub> nanoparticle photoanodes prepared by the ultrasonic irradiation assisted dip-coating method. Thin Solid Films. 2010;518:4809-12.
- [67] Wang D, Wang W, Ma X, Zhang C, Zhao J, Zhang X. Comparative study on the influence of TiO<sub>2</sub> precursors on ZnO-based dye-sensitized solar cells. Ind. Eng. Chem. Res. [Internet]. American Chemical Society; 2015 [cited 2016 Dec 20];54:12639-45. Available from: http://pubs.acs.org/doi/abs/10.1021/acs.iecr.5b03627
- [68] Sakai N, Miyasaka T, Murakami TN. Efficiency enhancement of ZnO-based dye-sensitized solar cells by low-temperature TiCl<sub>4</sub> treatment and dye optimization. J. Phys.

Chem. C [Internet]. American Chemical Society; 2013 [cited 2016 Dec 6];117:10949-56. Available from: http://pubs.acs.org/doi/abs/10.1021/jp401106u

- [69] Chen W, Qiu Y, Yang S. A new ZnO nanotetrapods/SnO<sub>2</sub> nanoparticles composite photoanode for high efficiency flexible dye-sensitized solar cells. Phys. Chem. Chem. Phys. [Internet]. The Royal Society of Chemistry; 2010 [cited 2016 Dec 18];12:9494-501. Available from: http://xlink.rsc.org/?DOI=c000584c
- [70] Liu J, Wei A, Zhao Y, Lin K, Luo F. Dye-sensitized solar cells based on ZnO nanoflowers and TiO<sub>2</sub> nanoparticles composite photoanodes. J. Mater. Sci. Mater. Electron. [Internet]. Springer US; 2014 [cited 2016 Dec 19];25:1122-6. Available from: http://link.springer. com/10.1007/s10854-013-1698-9
- [71] Yang J, Lin Y, Meng Y, Lin Y. Oriented ZnO nanotubes arrays decorated with TiO<sub>2</sub> nanoparticles for dye-sensitized solar cell applications. Appl. Phys. A Mater. Sci. Process. 2014;114:1195-9.
- [72] Gao R, Cui Y, Liu X, Wang L, Cao G. A ZnO nanorod/nanoparticle hierarchical structure synthesized through a facile in situ method for dye-sensitized solar cells. J. Mater. Chem. A [Internet]. The Royal Society of Chemistry; 2014 [cited 2016 Dec 18];2:4765. Available from: http://www.scopus.com/inward/record.url?eid=2-s2.0-84897711028&partnerID=t ZOtx3y1
- [73] Ko SH, Lee D, Kang HW, Nam KH, Yeo JY, Hong SJ, et al. Nanoforest of hydrothermally grown hierarchical ZnO nanowires for a high efficiency dye-sensitized solar cell. Nano Lett. [Internet]. American Chemical Society; 2011 [cited 2016 Dec 19];11:666-71. Available from: http://pubs.acs.org/doi/abs/10.1021/nl1037962
- [74] Chen W, Qiu Y, Zhong Y, Wong KS, Yang S. High-efficiency dye-sensitized solar cells based on the composite photoanodes of SnO<sub>2</sub> nanoparticles/ZnO nanotetrapods. J. Phys. Chem. A. American Chemical Society; 2010;114:3127-38.
- [75] Miles DO, Lee CS, Cameron PJ, Mattia D, Kim JH. Hierarchical growth of TiO<sub>2</sub> nanosheets on anodic ZnO nanowires for high efficiency dye-sensitized solar cells. J. Power Sources. 2016;325:365-74.
- [76] Haque Choudhury MS, Kishi N, Soga T. Hot-compress: A new postdeposition treatment for ZnO-based flexible dye-sensitized solar cells. Mater. Res. Bull. [Internet]. 2016 [cited 2016 Dec 18];80:135-8. Available from: https://www.scopus.com/inward/record. uri?eid=2-s2.0-84964068595&partnerID=40&md5=50ce3ec4267cd7360fa5c41dc52d7463
- [77] Chang G-J, Lin S-Y, Wu J-J. Room-temperature chemical integration of ZnO nanoarchitectures on plastic substrates for flexible dye-sensitized solar cells. Nanoscale [Internet]. The Royal Society of Chemistry; 2014 [cited 2016 Dec 19];6:1329-34. Available from: http://www.ncbi.nlm.nih.gov/pubmed/24362771
- [78] Oosterhout SD, Wienk MM, van Bavel SS, Thiedmann R, Koster LJA, Gilot J, et al. The effect of three-dimensional morphology on the efficiency of hybrid polymer solar cells.

Nat. Mater. [Internet]. Nature Publishing Group; 2009 [cited 2016 Dec 20];8:818-24. Available from: http://dx.doi.org/10.1038/nmat2533

- [79] Briseno AL, Holcombe TW, Boukai AI, Garnett EC, Shelton SW, Fréchet JJM, et al. Oligoand polythiophene/ZnO hybrid nanowire solar cells. Nano Lett. [Internet]. American Chemical Society; 2010 [cited 2016 Dec 20];10:334-40. Available from: http://pubs.acs.org/ doi/abs/10.1021/nl9036752
- [80] Ravirajan P, Peiró AM, Nazeeruddin MK, Graetzel M, Bradley DDC, Durrant JR, et al. Hybrid polymer/zinc oxide photovoltaic devices with vertically oriented ZnO nanorods and an amphiphilic molecular interface layer. J. Phys. Chem. B. American Chemical Society ; 2006;110:7635-9.
- [81] Olson DC, Lee YJ, White MS, Kopidakis N, Shaheen SE, Ginley DS, et al. Effect of polymer processing on the performance of poly(3-hexylthiophene)/ZnO nanorod photovoltaic devices. J. Phys. Chem. B [Internet]. American Chemical Society ; 2007 [cited 2016 Dec 20];111:16640-5. Available from: http://pubs.acs.org/cgi-bin/doilookup/?10.1021/ jp0757816
- [82] Park H, Chang S, Jean J, Cheng JJ, Araujo PT, Wang M, et al. Graphene cathode-based ZnO nanowire hybrid solar cells. Nano Lett. [Internet]. American Chemical Society; 2013 [cited 2016 Dec 20];13:233-9. Available from: http://pubs.acs.org/doi/abs/10.1021/ nl303920b
- [83] Thitima R, Patcharee C, Takashi S, Susumu Y. Efficient electron transfers in ZnO nanorod arrays with N719 dye for hybrid solar cells. Solid. State. Electron. 2009;53:176-80.
- [84] Li Y, Li S, Jin L, Murowchick JB, Peng Z. Carbon nanoparticles as an interfacial layer between TiO<sub>2</sub>-coated ZnO nanorod arrays and conjugated polymers for high-photocurrent hybrid solar cells. RSC Adv. [Internet]. Royal Society of Chemistry; 2013 [cited 2016 Dec 20];3:16308. Available from: http://xlink.rsc.org/?DOI=c3ra42614a
- [85] Moreels I, Lambert K, Smeets D, De Muynck D, Nollet T, Martins JC, et al. Size-dependent optical properties of colloidal PbS quantum dots. ACS Nano [Internet]. American Chemical Society; 2009 [cited 2016 Dec 21];3:3023-30. Available from: http://pubs.acs.org/ doi/abs/10.1021/nn900863a
- [86] Jean J, Chang S, Brown PR, Cheng JJ, Rekemeyer PH, Bawendi MG, et al. ZnO nanowire arrays for enhanced photocurrent in PbS quantum dot solar cells. Adv. Mater. [Internet]. WILEY-VCH Verlag; 2013 [cited 2016 Dec 20];25:2790-6. Available from: http://doi.wiley. com/10.1002/adma.201204192
- [87] Kawawaki T, Wang H, Kubo T, Saito K, Nakazaki J, Segawa H, et al. Efficiency enhancement of PbS quantum Dot/ZnO nanowire bulk-heterojunction solar cells by plasmonic silver nanocubes. ACS Nano [Internet]. American Chemical Society; 2015 [cited 2016 Dec 20];9:4165-72. Available from: http://pubs.acs.org/doi/abs/10.1021/acsnano.5b00321