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ZnO Nanowires for Dye Sensitized Solar Cells

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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.
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$_2$ or inert materials such as Al$_2$O$_3$ 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.
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 TiO$_2$ (anatase) are mostly used as photoelectrode, although alternative wide-band-gap oxides such as ZnO and 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

\[ L_n = \sqrt{D_n \cdot \tau_n}, \]  

(2)

Disordered network of TiO\(_2\) 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$_2$, 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.

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$^{2+}$-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$^{2+}$-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$^{2+}$/dye agglomerates. 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

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

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 photovoltaic electrode 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:

\[
\text{Zn} + \text{O}_2 \rightarrow \text{ZnO}
\]  

(3)

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:

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}
\]  

(4)

where hexamethylenetetramine (HMTA) [40], NH\textsubscript{4}OH [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 nonetheless 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.

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 (Al₂O₃, TiO₂, ZrO₂, 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

Figure 4. Complex structures of ZnO nanowires: (a) nanoforest [47]; (b) hierarchical nanowires (inset shows SEM figure) [48]; (c) tetrapods [49].
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$_2$ shell.

There are several motives why the ZnO-TiO$_2$ core-shell structure is attractive. TiO$_2$ is chemically more stable compared to ZnO in acidic dye solutions [61]. Thus, the presence of TiO$_2$ shell prevents ZnO surface from being dissolved and the formation of Zn$^{2+}$/dye agglomerates. The TiO$_2$ 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$_2$. DFT ab initio study of ZnO-TiO$_2$ core-shell structure [63] shows that TiO$_2$ 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$_4$). 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$^2$, respectively.

In order to increase the surface area of the photoelectrode and without losing the charge-transport 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$_2$ core-shell formed by low-temperature TiCl$_4$ treatment [68].](image-url)
and also effective light scattering. ZnO DSC efficiency can be doubled by decorating ZnO NW photoelectrodes with different nanoparticles of SnO$_2$, TiO$_2$ [69, 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$_2$ 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 ± 0.02 eV) is perfectly aligned with both the LUMO level of P3HT (-3.2 eV) and the conduction band edge of TiO$_2$ (-4.2 eV). This ensures both efficient exciton dissociation at the P3HT/CNP interface and efficient electron extraction. In such a device, ZnO-TiO$_2$ 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].
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.
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$_2$ or other semiconductor layer. Alternatively forming a protective layer from dielectric materials such as Al$_2$O$_3$ 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.

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