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ZnO Nanowires and Their Application for Solar Cells

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1. Introduction

Nanowires (NW) are defined here as metallic or semiconducting particles having a high aspect ratio, with cross-sectional diameters « 1 μm, and lengths as long as tens of microns. Well-aligned one-dimensional nanowire arrays have been widely investigated as photoelectrodes for solar energy conversion because they provide direct electrical pathways ensuring the rapid collection of carriers generated throughout the device (Tang et al., 2008), as well as affording large junction areas and low reflectance owing to light scattering and trapping (Muskens et al., 2008).

Solar energy conversion is a highly attractive process for clean and renewable power for the future. Excitonic solar cells (SCs), including organic and dye-sensitized solar cells (DSSC), appear to have significant potential as a low cost alternative to conventional inorganic photovoltaic (PV) devices. The synthesis and application of nanostructures in solar cells have attracted much attention. Metal oxide nanowire (NW) arrays with large surface area and short diffusion length for minority carriers represent a new class of photoelectrode materials that hold great promise for photoelectrochemical (PEC) hydrogen generation applications. Up to now, various metal oxide nanostructures such as TiO_2, ZnO, Fe_2O_3, ZrO_2, Nb_2O_5, Al_2O_3, and CeO_2 have been successfully employed as photoelectrodes in SCs. Among the above-mentioned metal oxide nanostructures, the study of TiO_2 and ZnO is of particular interest due to the fact that they are the best candidates as photoelectrode used in SCs. However, the advantage offered by the increased surface area of the nanoparticle film is compromised by the effectiveness of charge collection by the electrode. For DSSCs, the traditional nanoparticle film was replaced by a dense array of oriented, crystalline nanostructures to obtain faster electron transport for improving solar cell efficiency. A typical high-efficiency DSSC (Grätzel, 2009) consists of a TiO_2 nanocrystal thin film that has a large surface area covered by a monolayer of dye molecules to harvest sunlight. Comparedwith TiO_2, ZnO shows higher electron mobility with similar bandgap and conduction band energies. ZnO is a direct wide bandgap semiconductor (Eg = 3.4 eV) with large exciton binding energy (~60 meV), suggesting that it is a promising candidate for stable room temperature luminescent and lasing devices. Therefore, ZnO nanowires is an alternative candidate for high efficient SCs.

So far, various ZnO nanostructures have been extensively investigated for SCs. In the early reports on ZnO-based DSSCs, ZnO nanoparticles were often used as the photoanode prepared by a conventional doctor blade technique (Keis et al., 2002; Keis et al., 2002). Lévy-Clément et al. (2005) reported experimental results on a new ETA solar cell fabricated from an electron-accepting layer of free-standing ZnO nanowires. Law et al. (2005) presented first the ordered nanowire DSSC. The nanowire DSSC is an exciting variant of the most successful of the excitonic photovoltaic devices. As an ordered topology that increases the rate of electron transport, a nanowire electrode may provide a means to improve the quantum efficiency of DSSCs in the red region of the spectrum, where their performance is currently limited. Raising the efficiency of the nanowire cell to a competitive level depends on achieving higher dye loadings through an increase in surface area. Law et al. (2006) described the construction and performance of DSSCs based on arrays of ZnO nanowires coated with thin shells of amorphous Al_2O_3 or anatase TiO_2 by atomic layer deposition. Wu et al. (2007) employed mercurochrome and N3 dyes to be the sensitizers in the ZnO-nanowire DSSCs. A lower fill factor is obtained in the N3-sensitized cell which results in comparable efficiencies in both ZnO-nanowire DSSCs although the N3 molecules possess a wider absorptive range for light harvesting. Hsueh et al. (2007) deposited p-Cu_2O onto vertical n-ZnO nanowires prepared on ZnO:Ga/glass templates. With the sputtered Cu_2O, the nanowires became clublike (i.e. nanowire with a head). Leschkies et al. (2007) combine CdSe semiconductor nanocrystals (or quantum dots) and single-crystal ZnO nanowires to demonstrate a new type of quantum dot-sensitized solar cell. An array of ZnO nanowires was grown vertically from a fluorine-doped tin oxide conducting substrate. A significant improvement of the efficiency of the ZnO nanowire DSSC has been achieved by the chemical bath deposition of the dense nanoparticles within the interstices of the vertical ZnO-NW anode (Ku et al., 2007). Greene et al. (2007) evaluated an ordered organic-inorganic solar cell architecture based on ZnO-TiO_2 core-shell nanorod arrays encased in the hole-conducting polymer P3HT. Chen et al. (2009) studied a two-stage growth of a ZnO hierarchical nanostructure consisting of ZnO nanorod at bottom and ZnO nanowire atop in the low pH solutions. The mechanism was explained by hydrothermal reactions and dissolution dynamics. Chen et al. (2009) reported vertically aligned zinc oxide (ZnO) nanorod arrays coated with gold nanoparticles have been used in Schottky barrier solar cells. The nanoparticles enhance the optical absorption in the range of visible light due to the surface plasmon resonance. Recently, Briseno et al. (2010) demonstrated the basic operation of an organic/inorganic hybrid single nanowire solar cell. End-functionalized oligo and polythiophenes were grafted onto ZnO nanowires to produce p-n heterojunction nanowires. Gan et al. (2010) prepared hybrid ZnO/TiO_2 photoanodes for dye-sensitized solar cells by combining ZnO nanowire arrays and TiO_2 nanoparticles with the assistance of the ultrasonic irradiation assisted dipcoating method. Myung et al. (2010) synthesized high-density ZnO-CdS core-shell nanocable arrays by depositing CdS outerlayers on pregrown vertically aligned ZnO (wurtzite) nanowire arrays using the chemical vapor deposition method. Seol et al. (2010) a novel CdSe/CdS/ZnO nanowire array fabricated by a 3-step solution-based method was used as a photoanode of a quantum dot sensitized solar cell, which generated a maximum power conversion efficiency of 4.15%. Wu et al. (2010) reported a 74% enrichment of the efficiency of ZnO nanowire DSSCs is achieved by the addition of a novel light-scattering nanocrystalline film.

In this Chapter, after the brief review of the research progress on ZnO nanowires, some important results obtained on ZnO nanowires are summarized. In the second section, the latest progress in the growth of ZnO nanowires will be described. Their solar cell application will be discussed in detail in the third section. This Chapter ends with a brief summary, which also includes our personal remarks on future research of ZnO nanowires.

2. The growth of ZnO nanowires

A number of methods have been employed to achieve ZnO nanostructured arrays, including chemical and physical vapor deposition, hydrothermal process, metallorganic vapor-phase epitaxial growth, templated growth method and electrochemical deposition technique. Vapor-liquid-solid growth and vapor-solid-solid growth has been conventionally used to synthesize ZnO arrays as reviewed recently by Wang et al. (2009) and Haller et al. (2010).

Chao et al. (2010) reported the ZnO nanowires were grown in a furnace by chemical vapor deposition with gold as catalyst. Figure 1 shows the tilt-view SEM image of ZnO nanowire arrays on the sapphire substrate. This image revealed that the ZnO wires are vertically aligned, the length of nanowire is around 1-2 mm and the diameter is in the range of 70-100 nm. the synthesis and characterization of three-dimensional hetergeneous graphene nanostructures comprising continuous large-area graphene layers and ZnO nanostructures, fabricated via chemical vapor deposition, are reported by Lin et al. (2010). Electron microscopy investigation of the three-dimensional heterostructures shows that the morphology of ZnO nanostructures is highly dependent on the growth temperature. The morphology of the large-area graphene layers was identified via SEM as shown in Figure 2a, indicating regions of monolayers and few-layers. boundary structures of graphene layers enhanced the growth of dense array of ZnO nanostructures, observed as bright regions shown in Figure 2b. The nanowires obtained by chemical and physical vapor deposition have generally a good crystalline quality and an important length (more often they are in nanobelt morphology).

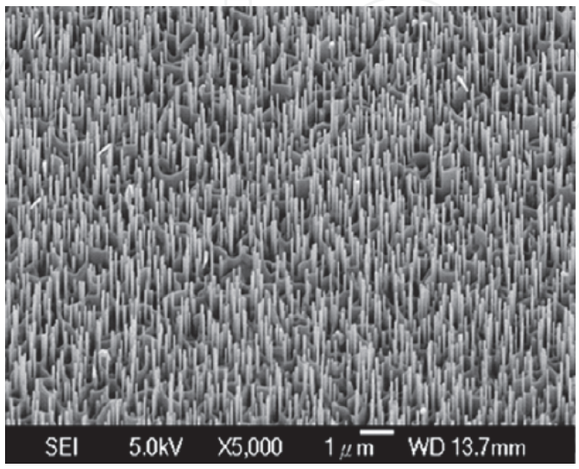


Fig. 1. Tilt-view SEM images of aligned ZnO nanowire arrays. From Ref. (Chao et al., 2010).

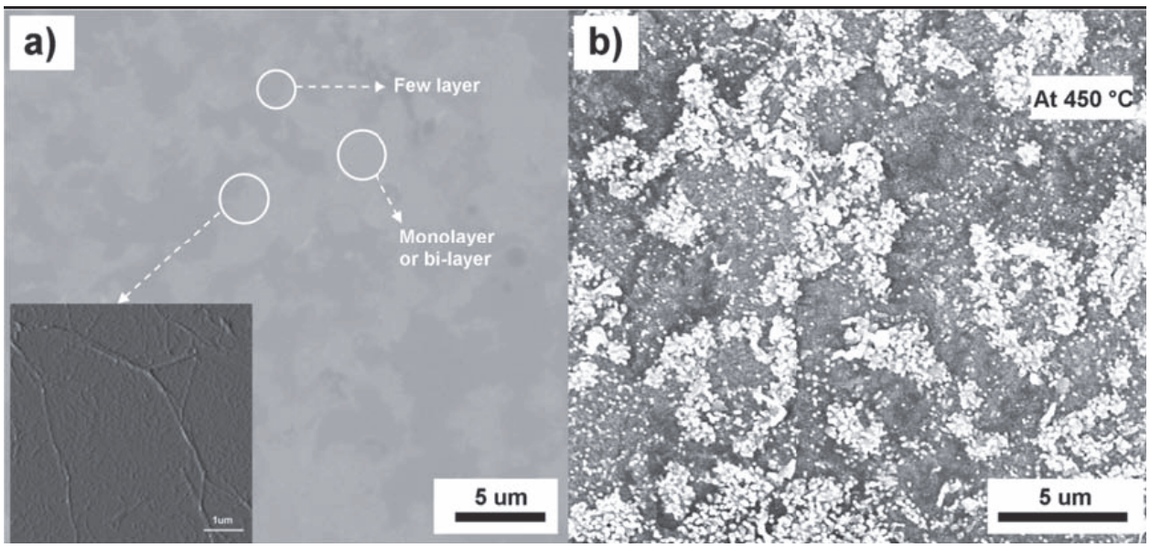


Fig. 2. a) SEM image of a chemical vapor deposition-grown graphene layer on a SiO_2/Si substrate. b) SEM image of ZnO nanostructures grown on the same chemical vapor deposition-graphene film at 450 °C. From Ref. (Lin et al., 2010).

Fang et al. (2006) have successfully synthesized aligned ZnO nanofibers in a dense array from and on a Zn substrate by hydrothermal treatment of Zn foil in an ammonia/alcohol/water mixed solution. Notably, the ZnO nanofibers are ultrathin (3-10 nm) with a length of ≈500 nm. This is the first time that uniform, aligned, and ultrathin ZnO nanofibers have been obtained via a hydrothermal method in the absence of catalysts and at a relatively low temperature. The photoluminescence measurements at room temperature revealed a significantly blue-shifted near-band-edge emission at 373 nm (3.32 eV), which was ascribed to quantum confinement arising from the reduced size of the ultrathin ZnO nanofibers. Then, the hydrothermal synthesis of large-scale, ultralong ZnO nanowire and nanobelt arrays with honeycomb-like micropatterns has been realized by simple surface oxidation of zinc foil in aqueous solutions of NaOH and $(NH_4)_2S_2O_8$ at 150 °C (Lu et al., 2006). This solution approach to fabricate 1D ZnO nanostructures with controlled morphologies and micropatterns can be easily scaled up and potentially extended to the fabrication and assembly of 1D nanostructures of other oxide systems. As shown in Figure 3a, a large scale thin film of long ZnO nanowire (20–50 mm) arrays formed unique micropatterns of honeycomb-like structures typically ranging from 10 to 30 mm in size on the Zn substrate after the Zn foil was immersed in the reaction solution containing 0.48 M NaOH and 0.095 M $(NH_4)_2S_2O_8$ and hydrothermally treated at 150 °C for 2 days. An enlarged image of the honeycomb-like structure is shown in Figure 3b, which indicates that these structures were formed when the collapsing ZnO nanowires from opposite directions met to bundle together between two neighboring areas. The diameter of the ZnO nanowires is measured to range from 60 to 200 nm (Figure 3c) and the electron diffraction (ED) pattern of a single nanowire suggests that each ZnO nanowire is a single crystal oriented along the c-axis (Figure 3d), similar to the growth direction of the ZnO nanorods obtained at room temperature.

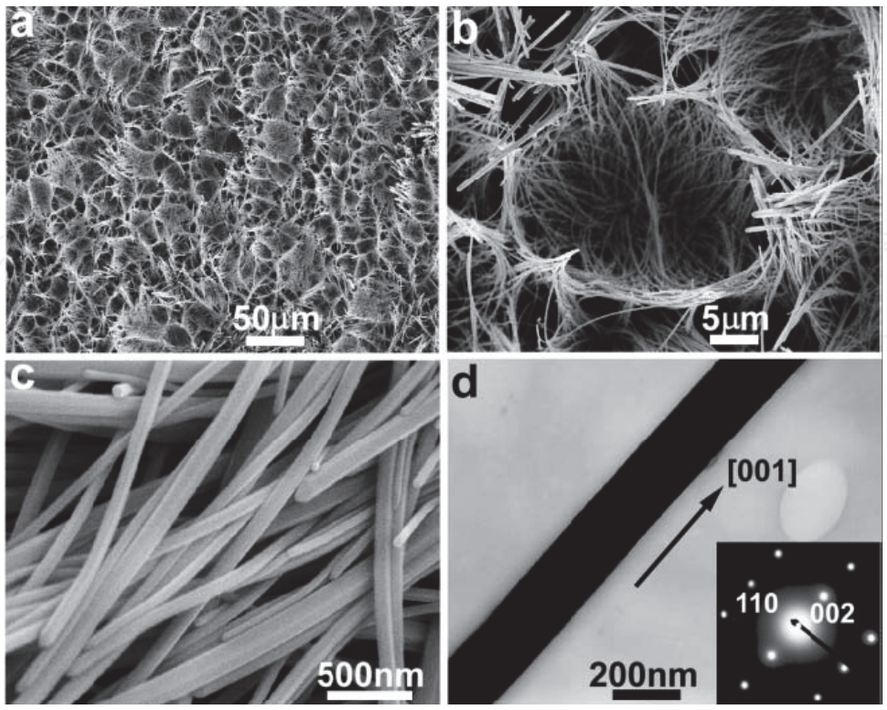


Fig. 3. SEM (a–c) and TEM (d) images of ZnO nanowire arrays hydrothermally grown on Zn foil at 150 °C for 2 days. From Ref. (Lu et al., 2006).

A new method of epitaxial ZnO column deposition that exhibits uniformity and reproducibility over a large surface area were demonstrated by Peterson et al. (2004). This method employs an aqueous solution containing NaOH and $Zn(NO_3)_2$ and substrates coated with sputtered ZnO and does not require the use of complexing agents and can produce micrometer-thick films in less than 1 h. The resulting quasi-epitaxial films of highly ordered columns have the reproducibility and uniformity over large areas to be employed in the development of solar cells and other devices. Liu et al. (2003) reported the fabrication of ordered and homogeneous arrays of ZnO nanowires with a narrow diameter distribution, a high aspect ratio, high wire density, and large-area homogeneity by using anodic aluminum oxide templates and vapor deposition. The nanowire arrays were dense (~10^{10}-10^{11} cm^{-2}) with a high aspect ratio up to ~5×10^6, and homogeneous over a large aera (~20 mm^2). Ultraviolet lasing action of the arrays was observed by photoluminescence at room temperature above an exciting laser (λ = 335 nm) threshold of ~100 kW cm^{-2}.

Because chemical and physical vapor deposition need to work in vacuum and/or at high temperature, these techniques require sophisticated and expensive equipments. The electrochemical deposition technique is becoming an important means for the fabrication of ZnO nanowires due to the low cost, mild conditions, accurate process control and widely used in industry. Electrodeposition of different oxides has been an increasingly active research area in recent years and has been widely used by many research teams because the preparation from aqueous solutions has several advantages over the above techniques. Leprince-Wang et al. (2006) reported on the structure study of ZnO nanowires grown via

electrochemical deposition, a simple and low temperature approach. Figure 4 presents typical TEM images showing the general morphology of the electrodeposited ZnO nanowires. It is found that the nanowires formed from the M90 type membrane are about 130-150 nm in diameter and 2-3 mm in length. Yang et al. (2007) investigated systematically the evolution of electrochemical deposition produced ZnO nanostructures by varying electrochemical conditions, identify important factors for the growth of the ZnO nanorod/nanobelt arrays, deduce possible electrode reactions and pathways, and discuss possible growth mechanisms under the alkaline conditions (Figure 5). Pradhan et al. (2010) have demonstrated a simple electrochemical deposition technique for growing ZnO nanostructures on ITO-glass substrates at 70 ^{o}C in an aqueous $Zn(NO_3)_2 \cdot 6H_2O$ (mixed with KCl) solution. By judiciously manipulating the deposition conditions, the mean ledge thickness of the nanowalls and the diameter of the nanowires can be controlled over the ranges of 50-100 and 50-120 nm, respectively. The KCl supporting electrolyte concentration can be used to control the morphology of ZnO nanostructures growth. Elias et al. (2010) have developed a novel low-cost method to produce large area of single crystal and perfectly-ordered hollow urchin-like ZnO nanowire arrays by a combined colloidal patterning and electrochemical approach at temperature as low as 80 ^{o}C. The process enables a versatile control of dimensions and morphologies of ZnO nanowires as well as control of the core diameter and spatial arrangement (by changing the size of PS spheres) for the first time. The key mechanism for the formation of these architectures is the treatment of PS with $ZnCl_2$ at high concentration which renders them electrically conductive, enabling the deposition of ZnO on their surface. Figure 6 shows the schematic view of the fabrication processes of hollow urchin-like ZnO nanowires. This mechanism opens up new opportunities for processing novel metal oxide or hydroxide materials based on a similar growth mechanisms to that of ZnO.

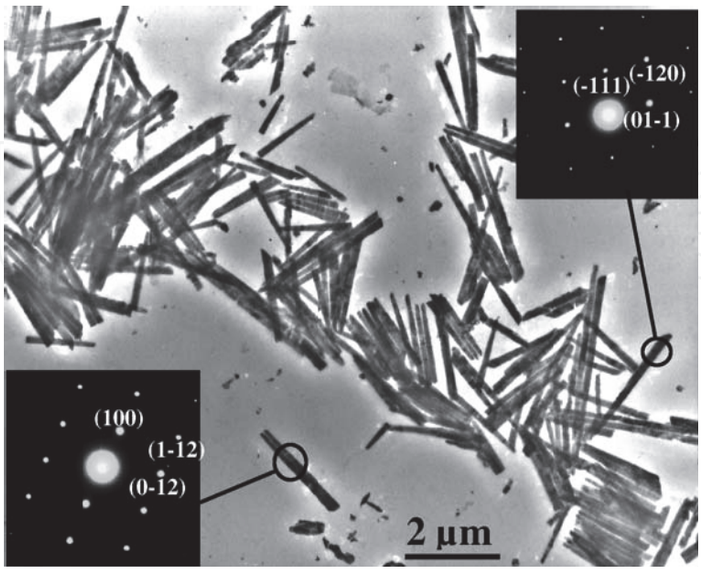


Fig. 4. TEM images showing a general morphology of the electrodeposited ZnO nanowires from M90 type membranes. From Ref. (Leprince-Wang et al., 2006).

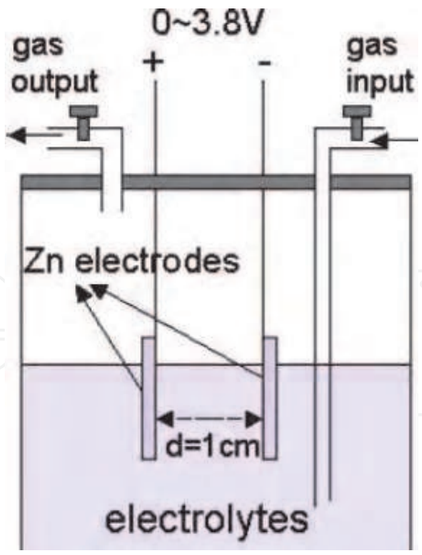


Fig. 5. Schematic diagram of the glass cell setup for the electrochemical synthesis of ZnO nanorod/nanobelt arrays. From Ref. (Yang et al., 2007).

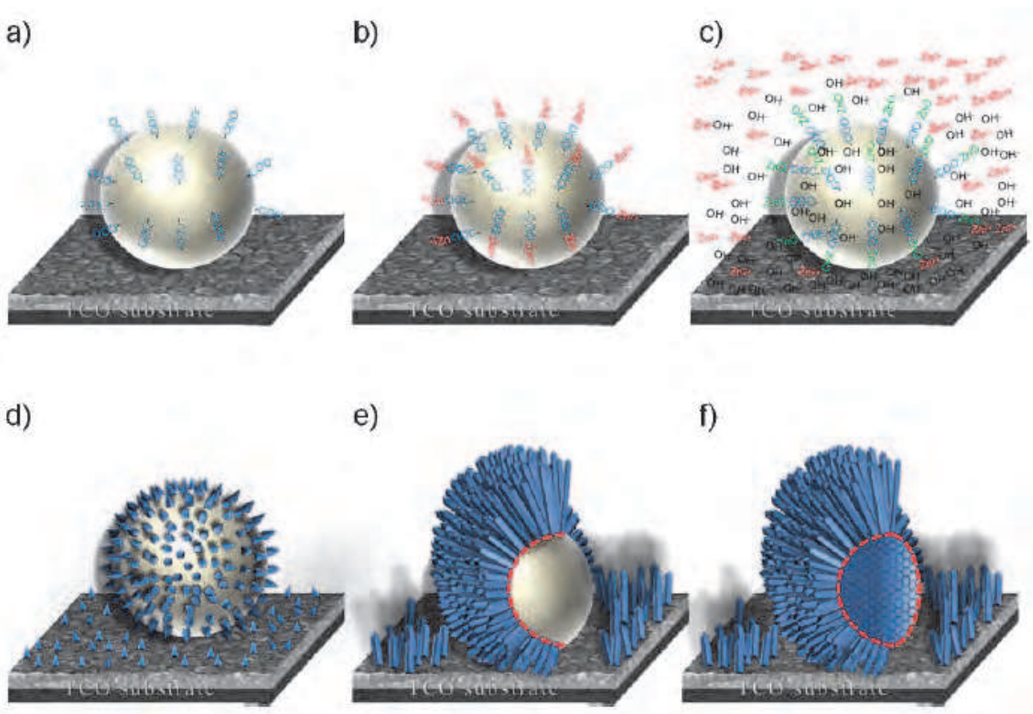


Fig. 6. Schematic view of the fabrication processes of hollow urchin-like ZnO nanowires. From Ref. (Elias et al., 2010).

3. ZnO nanowires for solar cell application

Nanostructured metal oxide materials is an intensive research area today with many potential applications. Dye-sensitized nanoporous materials are especially of interest for

solar cells. ZnO/CdSe/CuSCN extremely thin absorber (*eta*)-solar cells based on ZnO nanowires have been successfully realized using easily accessible electrochemical and solution deposition techniques (Tena-Zaera et al., 2006). The ZnO/CdSe nanowire layer exhibited a high light-trapping effect, with an effective absorbance of ~89% and effective reflectance of ~8% in the 400–800 nm region of the solar spectrum (AM1.5). High density aligned ZnO nanotube arrays were synthesized using a facile chemical etching of electrochemically deposited ZnO nanorods (Luo et al., 2010). Cadmium selenide nanoparticles as sensitizers were assembled onto the ZnO nanotube and nanorods arrays for solar cell application. A conversion efficiency of 0.44% was achieved for CdSe/ZnO nanotube-based solar cell under the white light illumination intensity of 85 mW/cm^2. An 8% enhancement in conversion efficiency was observed between the CdSe/ZnO nanotube-based and nanorod-based solar cell due to the enhancement of the photocurrent density. This approach to design photovoltaic electrode would give a direction in the field of multi-junction solar cell materials.

Due to its low cost and high efficiency, DSSC is a promising candidate to be a new renewable energy device. Several attempts have been made to use ZnO in DSSC. Baxter et al. (2006) used ZnO nanowires as the photo-electrode in DSSCs. A schematic diagram of the nanowire DSSC is shown in Figure 7. Typical solar cell photocurrent, photovoltage, fill factor and overall efficiencies were 1.3 mAcm^{-2}, 0.7 V, 0.35–0.40 and 0.3%, respectively. Electron transport through the nanowires is not constrained by nanowire dimensions.

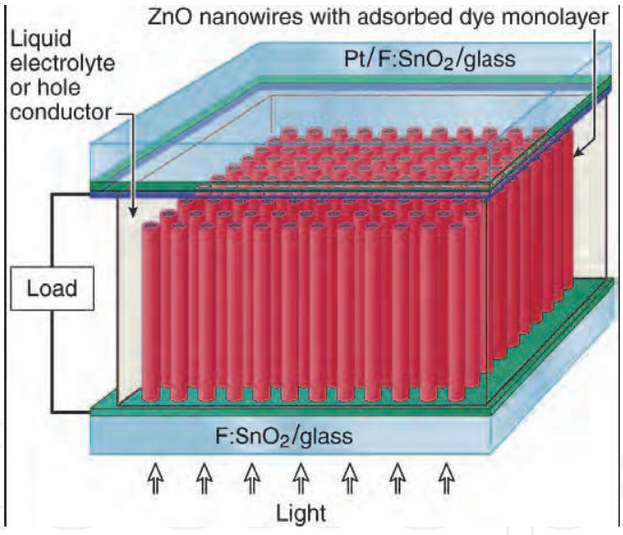


Fig. 7. Schematic diagram of the nanowire-based dye-sensitized solar cell. From Ref. (Baxter et al., 2006).

Pradhan et al. (2007) have fabricated DSSCs by using vertical nanowires of ZnO. Vertical growth of the nanowires was achieved via a simpler chemical route. In addition, they have introduced a new organic dye, namely Rose Bengal in xanthene class, as a photosensitizer. The new class of dye, whose energy matches the ZnO and usual KI-I_2 redox couple for DSSC applications, provides an alternative over conventional ruthenium complex-based DSSCs. Figure 8 shows the schematic band diagram showing the working principle of the DSSC. The maximum IPCE of the system is about 5.3% at 570 nm. The short circuit current of the cells increased linearly with illumination intensity.

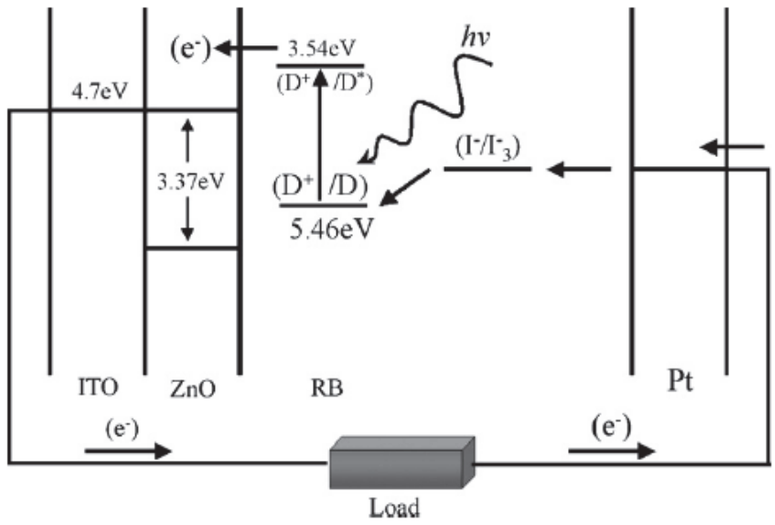


Fig. 8. Schematic band diagram showing the working principle of the DSSC. From Ref. (Pradhan et al., 2007).

Wang et al. (2008) reported success in synthesizing ZnO/ZnSe core/shell nanowires on a large-area, transparent, conducting substrate, using a relatively simple and low-cost approach. They have characterized their structural and optical properties by applying a comprehensive set of techniques. Absorption and photoconductivity studies show an extension of photoresponse into the region well below the ZnO bandgap.

Recently, Qiu et al. (2010) used synthesized ZnO nanowires to assemble DSSC, and to see if the further increase of nanowire length can improve the device performance. Figure 9a shows the photocurrent–voltage (*J*–*V*) characteristics of ZnO nanowire DSSCs dye-sensitized solar cells with various lengths. The Nyquist plots of both the measured data points and fitted curves are shown in Figure 9b. The performance of DSSCs increased with increasing length of the ZnO nanowire arrays, indicating that the ultralong ZnO nanowire arrays have great potential in improving the performance of DSSCs.

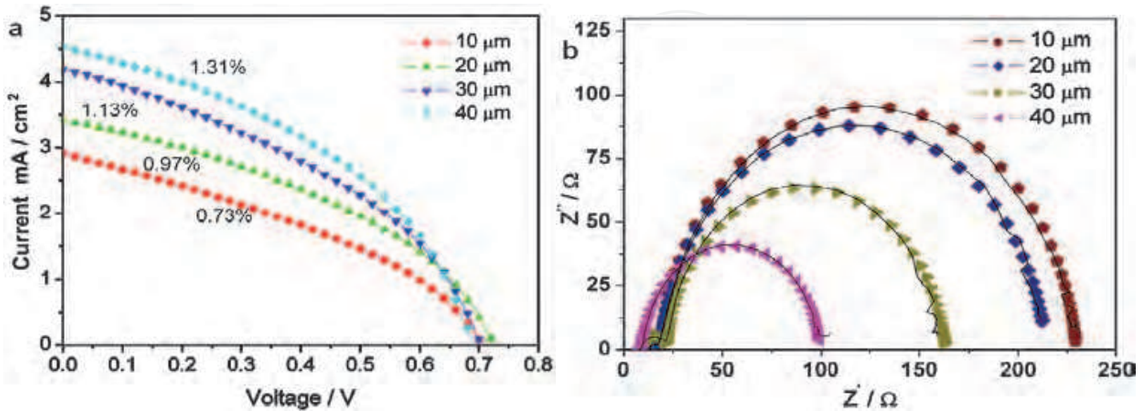


Fig. 9. a) *J* –*V* curves of the ZnO nanowire DSSCs fabricated from different lengths; and b) Nyquist plots of the impedance data of the ZnO nanowire DSSCs constructed from different lengths. From Ref. (Qiu et al., 2010).

Umar et al. (2009) reported a very rapid and large-scale synthesis and DSSCs application of well-crystallized hexagonal-shaped ZnO nanorods. The as-grown nanorods based DSSCs exhibited an overall light to electricity conversion efficiency (ECE) of 1.86% with a fill factor of 74.4%, shortcircuit current of 3.41 mA/cm² and open-circuit voltage of 0.73 V. Qurashi et al. (2010) demonstrated DSSCs performance of dumb bell-shaped hexagonal nanorods and well-aligned ZnO nanorod arrays. ZnO nanostructures were used as the wide band gap semiconducting photoelectrode in DSSCs. Well-aligned ZnO nanorod arrays were greatly enhances dye adsorption, leading to improved light harvesting and overall efficiencies. Solar cells made from aligned ZnO nanorod arrays showed photocurrents of 2.08 mA/cm², internal quantum efficiencies of 34.5%, and overall efficiencies of 0.32%. However, DSSC made from the randomly formed dumbbell-shaped hexagonal ZnO nanorods showed efficiency about 0.26%, with internal quantum efficiency of 31.5% respectively. A 74% enrichment of the efficiency of ZnO nanowire (NW) dye-sensitized solar cells (DSSCs) is achieved by the addition of a novel light-scattering nanocrystalline film (nanofilm) (Wu et al., 2010). *J*sc, *V*oc, and FF of the nanofilm/ZnO NW DSSCs are all enhanced compared to those of the ZnO NW DSSCs. The significant enhancement of the efficiency of the ZnO NW DSSC by the lightscattering layer of nanofilm is mainly attributed to the successful reflection of unabsorbed photons back into the NW anode.

Xu et al. (2010) have demonstrated that the DSSC based on hierarchical ZnO nanowire-nanosheet architectures with better dye loading and light harvesting showed a power conversion efficiency of 4.8%, which is nearly twice as high as that of the DSSCs constructed using the primary ZnO nanosheet arrays. The the schematic diagram of the DSSC based on the hierarchical ZnO nanoarchitectures is illustrated in Figure 10. The improvement in the photovoltaic performance can benefit from the enlargement of the internal surface area within the photoanode without sacrificing a direct conduction pathway for the rapid collection of photogenerated electrons. Further, the concept of the hierarchical nanowire-nanosheet architectures is anticipated to be applicable to other semiconductor

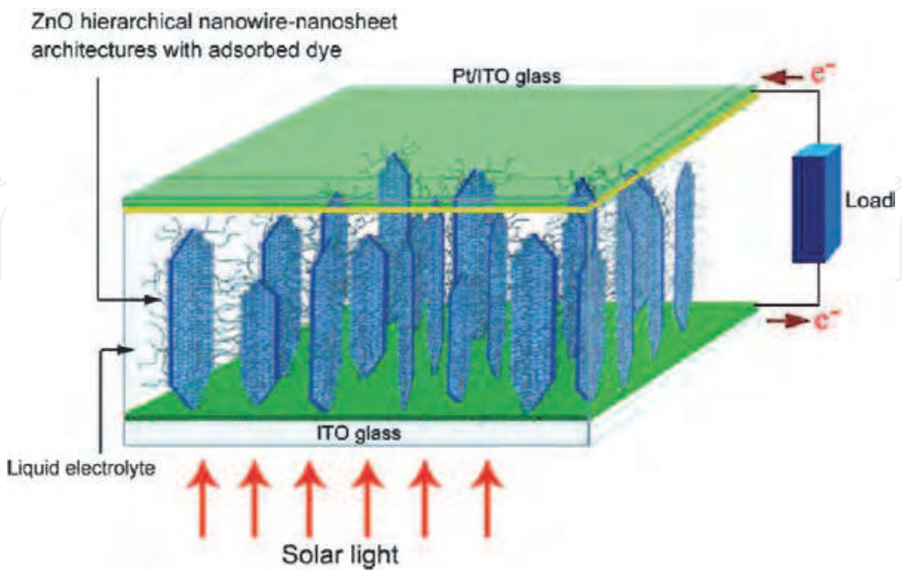


Fig. 10. Schematic diagram of the DSSCs based on the hierarchical ZnO nanowire-nanosheet architectures. From Ref. (Xu et al., 2010).

photoelectrodes in organic-inorganic nanocomposite solar cells and hierarchical heterojunction nanostructures for future potential applications. Hierarchical ZnO nanostructures with high surface to volume ratio are built in direct contact with conductive FTO substrate (Fu et al., 2010). The formation of the hierarchical ZnO structure follows an organic amine assisted growth mechanism. The bifunctional diamine, EDA, causes slight etching of the primary ZnO crystal, thus initiating the site-specific heterogeneous nucleation of hierarchical structure. The morphology and the branch density of hierarchical structure can be tuned easily by changing the molar ratio of [EDA]/[Zn^{2+}], and the growth temperature can be efficiently lowered by addition of HMT. Current density-voltage characterizations on DSSCs suggest that the conversion efficiencies were improved by increasing the surface area with hierarchical ZnO nanowires.

Recently, ZnO nanorod-based DSSCs have been investigated. The strategy to increase the surface area was investigated because ZnO nanorods have a surface area that is one-fifth of TiO_2 particles. DSSCs were fabricated using vertically aligned ZnO nanorod arrays on FTO glasses. The DSSCs with an annealed ZnO seed layer exhibited greater cell performance than those that were not annealed. It is noted that annealing of the seed layer improved adhesion between the FTO and the seed layer, and ZnO nanorods were grown into effective electrodes. The DSSCs with annealed ZnO nanorods produced greater cell efficiency than those that did not receive annealing. Figure 11 illustrates the ZnO nanorod-based DSSC fabrication process. Zinc oxide nanorods annealed in N_2/H_2 or O_2 exhibited greater dye loading due to a higher OH concentration and a hydrophilic surface property. In addition, annealing of ZnO nanorods slightly increased the grain size of the ZnO crystal and greatly reduced the defectd ensity in the ZnO crystal. Therefore, the improved cell efficiency of the DSSC in which ZnO nanorods were annealed resulted from the increases in J_{SC} and the fill factor.

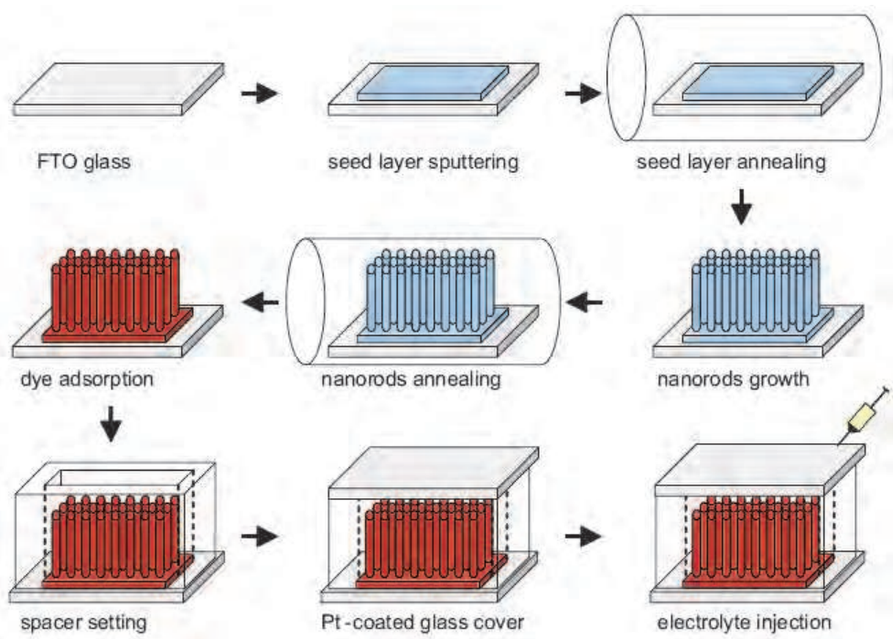


Fig. 11. Schematic diagrams of the fabrication process of ZnO nanorod-based DSSCs. From Ref. (Chung et al., 2010).

Organic solar cells are the another attracting enormous attentions to date, as low cost, light weight, solution process ability. Conjugated low band gap polymer is blended with fullerene to achieve the bulk heterojunction devices. Low band gap polymer materials and their application in organic photovoltaics have been reviewed by Bundgaard et al. (2007). Krebs et al. (2009) presented a complete polymer solar cell module prepared in the ambient atmosphere using all-solution processing with no vacuum steps and full roll-to-roll (R2R) processing. The completed modules (Figure 12) were flexible and quite robust. They have detailed the transfer of the P3CT/ZnO technology to methods giving full R2R compatibility in the ambient atmosphere with no vacuum coating steps being involved during the processing of the five layers of the modules.



Fig. 12. Photograph of one of the final modules in front of the R2R coater. From Ref. (Krebs et al., 2009).

Organic solar cell devices were fabricated using P3HT and PCBM, which play the role of an electron donor and acceptor, respectively (Park et al., 2009). Organic solar cells based on Al-doped ZnO as an alternative to ITO. Organic solar cells with intrinsic ZnO inserted between the P3HT/PCBM layer and AZO were also fabricated (Figure 13). The intrinsic ZnO layer prevented the shunt path in the device. The performance of the cells with a layer of intrinsic ZnO was superior to that without the intrinsic ZnO layer.

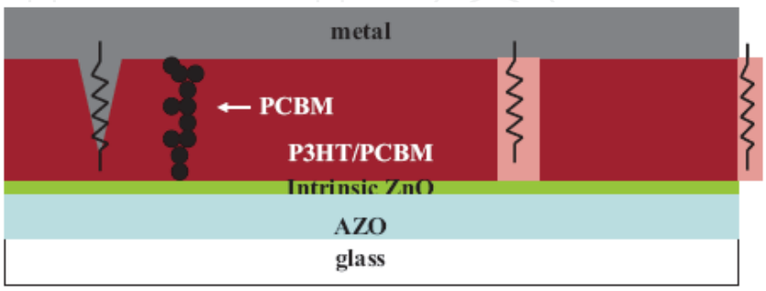


Fig. 13. Schematic diagram of the shunt path in organic solar cells with the intrinsic ZnO buffer layer. From Ref. (Park et al., 2009).

An inverted polymer solar cell geometry comprising a total of five layers was optimized using laboratory scale cells and the operational stability was studied under model atmospheres (Krebs et al., 2009). The device geometry was substrate-ITO-ZnO-(active layer)-

PEDOT:PSS-silver with P3HT-PCBM as the active layer. The inverted model device was then used to develop a new process giving access to fully R2R processed polymer solar cells entirely by solution processing starting from a PET substrate with a layer of ITO. All processing was performed in air without vacuum coating steps and modules comprising eight serially connected cells gave power conversion efficiencies as high as 2.1% for the full module with 120 cm^2 active area (AM1.5G, 393 W m^{-2}) and up to 2.3% for modules with 4.8 cm^2 active area (AM1.5G, 1000 W m^{-2}). An inverted-type organic bulk-heterojunction solar cell inserting ZnO as an electron collection electrode, fluorine-doped tin oxide (FTO)/ZnO/(PCBM:P3HT)/(PEDOT:PSS)/Au, was fabricated in air and characterized by an alternating current impedance spectroscopy (Kuwabara et al., 2009). The photo *I-V* measurement gave a PCE of 2.49%, and the impedance spectroscopy measurements in the dark and under light irradiation gave Nyquist plots consisting of two components. According to this result, it was proven that the depletion layer functioning to take out the photocurrent to the external circuit was formed in both of the ZnO and PCBM:P3HT layers at the ZnO/PCBM:P3HT interface. The inverted polymer solar cell based on a sol-gel derived ZnO thin film as an electron selective layer is investigated by Liu et al. (2010). Figure 14 shows the schematic diagram of inverted polymer solar cell based on ZnO thin film. the average grain size of the P3HT/PCBM layer and oxidation of the Ag electrode have a direct relationship with the evolution of device performance. The improvement of Jsc and FF is attributed to the grain growth of the P3HT/PCBM layer and the enhancement of Voc is due to the increase in work function of the Ag electrode. The highest PCE of 3.8% is thus achieved for the device placed in air for six days without the use of PEDOT:PSS and encapsulation.

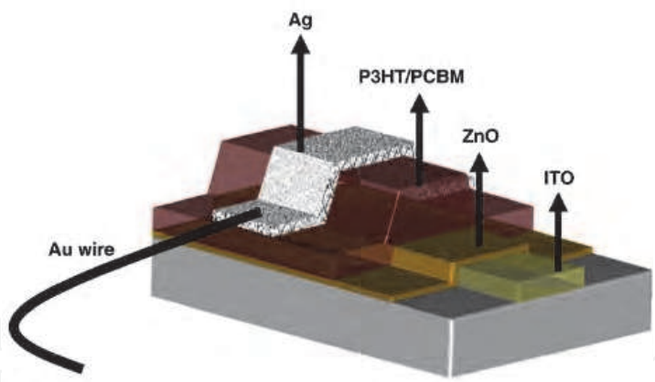


Fig. 14. Schematic diagram of inverted polymer solar cell based on ZnO thin film. From Ref. (Liu et al., 2010).

Hybrid solar cell is an alternative type of the promising device, which combined the organic semiconductor as donor material together with inorganic semiconductor as acceptor material. Huynh et al. (2002) demonstrated that semiconductor nanorods can be used to fabricate readily processed and efficient hybrid solar cells together with polymers. Hybrid P3HT/nanostructured oxide devices were fabricated using solution-based methods with efficiencies greater than 0.5% (Olson et al., 2006). The P3HT/ZnO device was limited in photocurrent due to the large spacing between the ZnO fibers. This was overcome by blending PCBM into the P3HT film. As shown in Figure 15, the polymer can be effectively intercalated into the ZnO fiber film thus making a hybrid nanostructured oxide/conjugated polymer composite device.

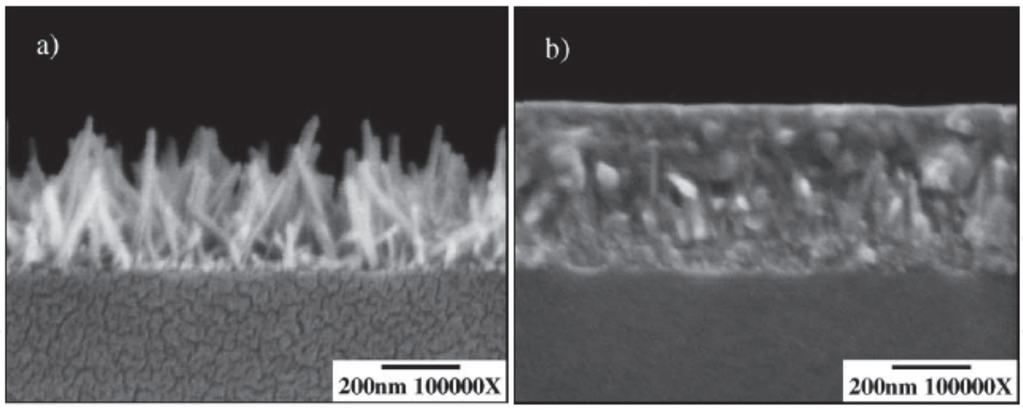


Fig. 15. (a) SEM image of a glass/ZnO nucleation layer/ZnO nanocarpet structure. (b) SEM image of P3HT intercalated into the nanocarpet structure. From Ref. (Olson et al., 2006).

Different layered ZnO/MEH:PPV composite solar cells have been fabricated by Plank et al. (2008) to assess the role of the ZnO backing layer on the open circuit voltage of nanowire composite solar cells. The thickness dependence of the blocking sputtered blocking layer is investigated. A 130 nm ZnO layer gives in a cell configuration with MEH-PPV an open circuit voltage of 0.41 V, which decreases with thicker ZnO layers to 0.28 V at 650 nm. The sputter ZnO/MEH:PPV devices have been shown to have reproducible I-V characteristics over many pixels indicating the high quality of the sputtered ZnO films. It has been clearly observed that the quality and thickness of the ZnO backing layer influence the device performance of simple geometry flat junction semiconductor and polymer composite solar cells. Uniform, pinhole-free oxide films are essential for the fabrication of working solar cells and to ensure reproducibility of results. 3D-ordered mesoporous ZnO films were fabricated by electrodeposition in DMSO solution (Wang et al., 2008). The porous electrode hybrid solar cells were made by infiltrating P3HT or P3HT:ZnO composite into the ordered porous ZnO films. The photocurrent of the ITO/ZnO(IO)/P3HT/Al device was limited because of the large diffusion distance for exciton to reach ZnO frameworks. This was obviously improved by using the P3HT:ZnO composite. A significant higher photocurrent was observed owing to the enhanced exciton dissociation and electron transfer efficiency. Solar decay analyses showed lifetime of ITO/ZnO(IO)/P3HT:ZnO/Al device could be improved by the application of a UV filter. a soluble perylene-derivative dye, N, N'-didodecyl-3,4,9,10-perylene tetracarboxylic diimide (PDI) was used in this work to enhance the photoelectric efficiency of the hybrid P3HT/ZnO bulk-heterojunction solar cells (Wang et al., 2008). PDI can absorb the sunlight in a broad wavelength range. By blending with PDI, the light absorption and exciton separation of the P3HT/ZnO solar cells can be significantly improved.

Thitima et al. (2009) demonstrated the charge injection efficiency of hybrid solar cell consisting of P3HT and PCBM/ZnO with and without N719 dye molecule. After the modification of ZnO nanorod arrays with N719, short-circuit current density (*Jsc*) of 8.89 mA/cm^2 was obtained, and it was 1.5 times higher than that of without the N719. The power conversion efficiency was enhanced from 1.16% to 2.0% through the additional surface modification of the ZnO nanorod array with N719 dye. Lin et al. (2009) have

demonstrated an improvement of photovoltaic performance based on the nanostructured ZnO/P3HT hybrid through interface molecular modification on ZnO nanorod surface (Figure 16). By probing the carrier dynamics at ZnO/P3HT interfaces, they have found that the interfacial molecules can play the role of assisting charge separation and suppression of back recombination at interfaces, which accounts for the observed enhanced short circuit current (*Jsc*) and open circuit voltage (*Voc*) in photovoltaic performance. Ji et al. (2010) demonstrated a hybrid solar cell which was made by blending nanocrystalline ZnO and conjugated polymer regioregular P3HT as the active layer of the solar cell. It can be seen that the efficiency of this new type of solar cells obviously varied as the size and morphology of ZnO nanostructures. The short-circuit photocurrent, fill factor, and power conversion efficiency were enhanced while the smaller nc-ZnO was utilized in such a device.

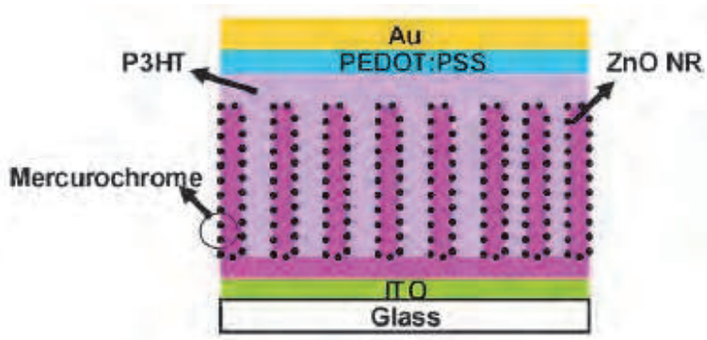


Fig. 16. The schematic structure of the nanostructured ZnO/P3HT hybrid photovoltaic device. From Ref. (Lin et al., 2009).

Wu et al. (2010) investigated hybrid photovoltaic devices based on P3HT and an ordered electrospun ZnO nanofibrous network (Figure 17). The performance of the P3HT/ZnO hybrid solar cell is dependent on fabrication conditions, especially the thickness of the nanofibrous film. It has been found that the lifetime of carriers is lower in the device consisting of thicker ZnO nanofibrous films due to the higher density of surface traps in the ZnO nanofibers. The device with optimum fabrication conditions exhibits a power conversion efficiency of 0.51%.

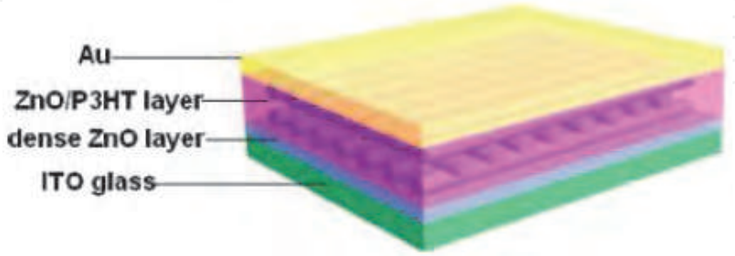


Fig. 17. Stucture of the hybrid solar cell based on electrospun ZnO nanofibers and P3HT. From Ref. (Wu et al., 2010).

A hybrid solar cell is designed and proposed as a feasible and reasonable alternative, according to acquired efficiency with the employment of ZnO nanorods and ZnO thin films at the same time (Hames et al., 2010). Both of these ZnO structures were grown

electrochemically and P3HT:PCBM was used as an active polymer blend, which was found to be compatible to prepared ITO substrate base. This ITO base was introduced with mentioned ZnO structure in such a way that, the most efficient configuration was optimized to be ITO/ZnO film/ZnO nanorod/P3HT:PCBM/Ag. Efficiency of this optimized device is found to be 2.44%. All ZnO works were carried out electrochemically, that is indeed for the first time and at relatively lower temperatures. Das et al. (2010) fabricated hybrid polymer-metal oxide bulk heterojunction solar cell by blending of ZnO and regioregular P3HT through solution process and flow coating on the flexible substrate. The decrease in the photoluminescence emission intensity more than 79% for ZnO:P3HT composites film indicates high charge generation efficiency. The cell shows the *Voc* and *Isc* of 0.33 V and 6.5 mA/cm^2, respectively. Cheng et al. (2010) fabricated the P3HT/ZnO NWs hybrid prototype device. The I-V and time-depend photocurrent wasmeasured for both the pristine ZnO NWs array and the hybrid structure. An ultraviolet (UV) light of λ = 350nm was used to investigate the photo-electric properties of the pristine ZnO NWs array and the hybrid structure in measurement. The P3HT coating process resulted in a higher and faster photoelectric response for the hybrid structure, which is benefit from the charge transfer process and the eliminating of adsorbed oxygen. The present work provides profound understandings on the electron transport of ZnO NWs array in a working hybrid polymer solar cell.

Nadarajah et al. (2008) reported first results on a new solar cell structure which incorporates n-type ZnO nanowires, an undoped CdSe layer, obtained from quantum dot precursors, and a p-type polymer layer as the main components (Figure 18). In the fabrication process the quantum dot layer is converted to a conformal ~30 nm thick polycrystalline film. MEH-PPV as well as P3HT have been explored for this contact, best results were obtained with P3HT. The fabrication of the cell occurs in lab air at temperatures below 100 °C. Several intermittent annealing steps raise the energy conversion efficiency to approximately 1%.

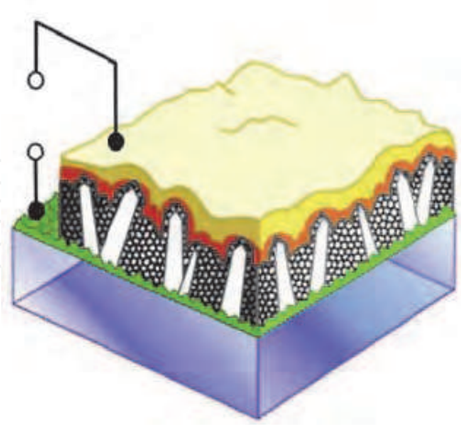


Fig. 18. Schematic diagram of the solar cell structure. From Ref. (Nadarajah et al., 2008).

4. Summary

In summary, we have reviewed the research progress on ZnO nanowires and some important results obtained on ZnO nanowires. And we have reviewed the latest progress in

the growth of ZnO nanowires and their solar cell application. A number of methods have been employed to achieve ZnO nanostructured arrays. Several attempts have been made to use ZnO in solar cells. In our opinion, more work is still needed to make further progress on this topic. First, the quality and stability of the ZnO nanowires need to be further improved. This will require even better control the background conductivity, development of new growth methods and search for new acceptor dopants. Second, The techniques used in fabricating these solar cells have still to be optimized. Once these milestones are achieved, the ZnO nanowire arrays have great potential in improving the performance of SCs.

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This potentially unique work offers various approaches on the implementation of nanowires. As it is widely known, nanotechnology presents the control of matter at the nanoscale and nanodimensions within few nanometers, whereas this exclusive phenomenon enables us to determine novel applications. This book presents an overview of recent and current nanowire application and implementation research worldwide. We examine methods of nanowire synthesis, types of materials used, and applications associated with nanowire research. Wide surveys of global activities in nanowire research are presented, as well.

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