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# Recent improvements on $TiO_2$ and ZnO nanostructure photoanode for dye sensitized solar cells: A brief review

*Nurnaeimah* Jamalullail[1,2], *Ili Salwani* Mohamad[1,2,3,*], *Mohd Natashah* Norizan[1,2,3], *Norsuria* Mahmed[2,4], and *Bibi Nadia* Taib[1]

[1]School of Microelectronic Engineering, Universiti Malaysia Perlis, Pauh Putra Campus, 02600 Arau, Perlis, Malaysia.
[2]Centre of Excellence Geopolymer and Green Technology (CeGeoGTech), Universiti Malaysia Perlis, Perlis, Malaysia.
[3]Advanced Multi-Disciplinary MEMS-Based Integrated NCER Centre of Excellence (AMBIENCE), Universiti Malaysia Perlis, Perlis, Malaysia.
[4]School of Material Engineering, Universiti Malaysia Perlis, P.O. Box 77, D/A Pejabat Pos Besar, 01000, Kangar, Perlis, Malaysia.

**Abstract.** Dye sensitized solar cell (DSSC) is a promising candidate for a low cost solar harvesting technology as it promised a low manufacturing cost, ease of fabrication and reasonable conversion efficiency. Basic structure of DSSC consists of photoanode, dye, electrolyte and counter electrode. Photoanode plays an important role for a DSSC as it supports the dye molecules and helps in the electron transfer that will determine the energy conversion efficiency. This paper emphasizes the various improvements that had been done on the $TiO_2$ and ZnO photoanode nanostructures synthesized through thermal method. For overall comparisons, ZnO nanoflowers photoanode had achieved the highest energy conversion efficiency of 4.7% due to its ability of internal light scattering that had increased the electron transportation rate. This has made ZnO as a potential candidate to replace $TiO_2$ as a photoanode material in DSSC.

## 1 Introduction

The energy sources that the world primarily depending today is harvested from the non-renewable energy sources which is from fossil fuel [1][2], coal [3][4] and nuclear [5][6]. This energy sources will be run out any time from now. Besides, the process of utilizing the non-renewable energy left us vulnerable to air pollutants because of the emission of carbon dioxide ($CO_2$) [7][8]. The increase of carbon dioxide will lead to the global warming and greenhouse effect [9][10]. Thus, in order to maintain the energy demand and the environmental problem, the world now is urging to find highly effective and carbon-free sources from renewable energy.

Renewable energy is defined as a natural energy that is inexhaustible and abundant such as solar, wind and tidal. Among all those type of renewable energy, solar is the most commonly used as the energy source due to the ability that can be deployed nearly everywhere on earth [11]. Solar energy falls on the surface of the earth everyday on the rate of 120 petawatts which is able to satisfy more than 20 years of energy demand [12][13]. The technology that had been used to convert solar energy into electrical energy is called the photovoltaic effect that is utilized by solar cell.

There are many types of solar cell such as silicon solar cell, thin film solar cell and dye sensitized solar cell (DSSC). Each type of solar cell has its own speciality but the advantages of simplest fabrication process , low cost and the reasonable efficiency has made DSSC as a promising candidate in low power appliances such as outdoor lamp, gadget charger and if it is assembled in a big scale it can be used as smart window power generator [14][15]. The first fabricated DSSC was discovered by O'Regan and Gratzel with the efficiency of 7% [16]. Since then, DSSC has attracted a lot of attention in researches and developments areas.

Basic DSSC structure consists of working electrode that is sandwiched together with semiconductor materials, dye or sensitizer, electrolyte and counter electrode as illustrated in Fig. 1. Photoanode is composed of working electrode that had been coated with semiconductor materials. The semiconductor material plays an important role in electron injection and transportation which will determine the performance of the DSSC [14-16]. As the important component of DSSC, the nanostructure of the semiconductor materials for the photoanode has been widely studied.

### 1.1 Working principle

Dye sensitized solar cell working principle is applied from photosynthesis process and diffusion is a major mechanism for electron to travel through the components [16-18]. The working principle of dye sensitized solar cell involved several steps as shown in Fig. 1. During the day, the sun will release energy called photon. Photon will strike a dye molecule and bring it to the excited

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[*] Corresponding author: ilisalwani@unimap.edu.my

state. The excited dye molecule is then injects an electron into the semiconductor material, leaving a hole in the molecule. The electron will diffuse through the semiconductor material, reaching both working and counter electrode. On the counter electrode, electron will regenerate the oxidized dye through the iodide ($I_3^-$) and form triiodide ($3I^-$). Meanwhile, the triiodide ($3I^-$) will recover its missing electron ($e^-$) from cathode and regenerating the iodides. The process will continue with the presence of sunlight.

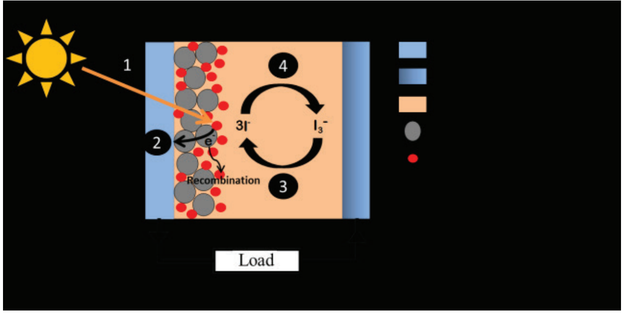

**Fig. 1.** The structure of DSSC.

## 2 Improvements in Photoanode Semiconductor Materials

In order to perform as a good photoanode semiconductor materials, the selected materials must have wide energy and direct bandgap [21][22], high electron mobility [23][24] and ideal surface morphology [25][26]. In DSSC, diffusion is a major route for electron to travel through [16-18]. Upon dye excitation caused by the photon, the electron from the excited dye is injected into the semiconductor material. The reduction of the oxidized sensitizer dye by the electrolyte is in competition with the unfavorable recombination of the injected electron with the oxidized dye [27] as illustrated in Figure 1. Thus, it is obvious that the electron transportation is a very important for the energy conversion process. Henceforth, the selection of the photoanode need to be taken seriously so that the electron can be transferred efficiently.

### 2.1. Titanium Dioxide ($TiO_2$)

$TiO_2$ is the most commonly used semiconductor material for photoanode [28][29]. $TiO_2$ is a semiconductor material with wide energy bandgap that is existed in three crystalline phase; rutile [26][31], anatase [31][32] and brookite [31][33]. This type of material is not only differs in the crystalline phase but also in the energy bandgap as rutile have the energy bandgap of 3.02 eV, 3.2 eV for anatase and 2.96 eV for brookite [30][31]. Anatase is the most commonly used in DSSC [34][35]. However, $TiO_2$ has been suffering from high recombination losses and low electron mobility properties [31][36]. In DSSC, the recombination takes place between the injected electron in the semiconductor and the oxidized dye that will lead to inefficiency [27].

Thus, in order to enhance the electron mobility in the $TiO_2$, several studies in surface area, porosity, grain size, particle diameter, orientation, and crystal phase of the nanostructures had been studied. Recent studies have involved the fabrication of $TiO_2$ anatase as nanoparticles [37][38], nanowires [34-36], nanotubes [37-40] and nanorods [41-43]. Taleb et. al demonstrated that the aggregation of $TiO_2$ nanoparticles (Fig. 2 (a)) strongly influences the performance of DSSC by achieving 4.3% of energy conversion efficiency [46]. According to the research, the high energy conversion efficiency is achieved due to the large surface area for dye attached, enhanced light scattering and improved connectivity for charge transport and thus lowering the recombination process.

La et al. in his previous research have developed a method to synthesize anatase $TiO_2$ nanowires with the energy conversion efficiency of 4.12% by employing salinization treatment to the $TiO_2$ nanowire [41]. Through the salinization treatment, it can prevent the detachment of dyes from the surface of $TiO_2$ nanowires which allowing more sunlight energy to be absorbed and converted. In other hand, $TiO_2$ nanorods structure also had been synthesized with the aim to provide direct pathways for electron transportation and thus increase the energy conversion rate with the energy conversion efficiency of 1.86% [47]. However, the energy conversion efficiency recorded is still lower due to numbers of the grain boundary for the electrons to pass through. Meanwhile, $TiO_2$ nanotubes also had been studied, according to Liu et al. in his research, the energy conversion efficiency recorded for $TiO_2$ nanotubes photoanode is 4.59% [48]. $TiO_2$ nanotubes provides hollow structure that gives large surface area for the dye attachement and allow the electron to move in one direction. Ameen et. al in had developed highly dense and well-defined $TiO_2$ nanoflowers photoanode grown by the hydrothermal process [49]. The fabricated DSSC with $TiO_2$ nanoflowers photoanode reveal that the surface morphology is in the form of uniform clover-like petals and had accomplished a reasonably good energy conversion efficiency of 3.64%. The efficiency improvement on $TiO_2$ nanostructure photoanode is illustrated in Table 1.

### 2.2 Zinc Oxide (ZnO)

ZnO is a semiconductor with hexagonal crystalline wurzite structure with direct wide energy bandgap (3.37 eV) [50][51]. ZnO is also a favorable semiconductor material for photoanode due to large free excitation binding energy (60 meV) and high electron mobility (155 $cm^2\ V^{-1}.S^{-1}$) [52][53]. Up to now, ZnO has been considered as a promising candidate to replace $TiO_2$. Interestingly, ZnO crystal structure enables various morphological changes including nanoparticles [54][55], nanowires [40][51], nanorods [56][57], nanotubes [40][58], nanoflowers [59][60] and etc. The variety of nanostructures can boost the electron mobility and enhance the energy conversion efficiency of DSSC.

To achieve high energy conversion efficiency performance, the photoanode needs to possess a large surface area for the dye attached and good electron transport capability [61][62]. Pandey et al. in his research have achieved energy conversion efficiency of 3.35% through ZnO nanoparticles photoanode [63]. ZnO nanoparticle film provides a large enough surface area; however, electron transport is difficult because of the need for electrons to hop across neighboring nanoparticles and thus slow down the electron mobility that leads to inefficiency [64]. In other hand, Jung et al. have fabricated DSSC with ZnO nanowires photoanode that improved light scattering and facilitating electron with energy conversion efficiency of 0.26% [65]. However, small surface area for dye attach and too many path for the light scattering direction causing it to slow down the electron mobility and leads to inefficiency. Rouhi et al. research have synthesized ZnO nanorods photoanode in his research and achieved energy conversion efficiency of 0.93% [66]. Based on the theory, nanorods will provide direct pathways for the electron to pass through the semiconductor materials. However, since the nanorods mainly lie down on the glass, electrons still need to face many grain boundaries that slow down their speed to the electrode. Meanwhile, Han et. al had develop ZnO nanotubes photoanode with the energy conversion efficiency of 1.18% [67]. This research compares the performance of DSSC with ZnO nanorods and nanotubes where the nanotubes was modified from the nanorods structure. The research shows significant improvement with nanotubes that achieved higher energy conversion efficiency compared to nanorods. Next, Wahyuono et. al in his research has reported energy conversion efficiency of 4.7% [68] through the fabrication of DSSC with ZnO nanoflowers photoanode which recorded as the highest efficiency compared to others that had been stated before. In the research, ZnO nanoflowers have shown a suitable structure with improved inner light scaterring compared to $TiO_2$ nanoflowers structure

The energy conversion efficiency of fabricated DSSC with ZnO photoanode is comparable with $TiO_2$ photoanode which has made ZnO as a potential candidate to replace $TiO_2$ as a photoanode material in DSSC. The summary of the electrical performance on improvements in ZnO nanostructures compared to $TiO_2$ nanostructures is summarized in Table 1 and illustrated in Figure 2.

Table 1 presents the electrical data recorded based on previous works that had been done for both $TiO_2$ and ZnO nanostructure. According to the data, the highest efficiency recorded is from ZnO nanoflowers photoanode with the energy conversion efficiency of 4.7%. ZnO nanoflowers can work as a good photoanode due to its ability of internal light scattering that had increased the electron transportation rate. This has made ZnO as a potential candidate to replace $TiO_2$ as a photoanode material in DSSC.

**Table 1.** Summary of performance on improvements in nanostructures of photoanode.

| Photoanode | Nanostructures | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF | Efficiency (%) | Ref |
|---|---|---|---|---|---|---|
| **$TiO_2$** | Nanoparticles | 15.00 | 0.62 | 0.55 | 4.30 | [46] |
| | Nanowires | 8.31 | 0.76 | 0.65 | 4.12 | [41] |
| | Nanorods | 4.15 | 0.76 | 0.59 | 1.86 | [47] |
| | Nanotubes | 8.65 | 0.76 | 67.7 | 4.59 | [48] |
| | Nanoflowers | 9.60 | 0.67 | 0.57 | 3.60 | [49] |
| **ZnO** | Nanoparticles | 8.82 | 0.62 | 0.58 | 3.35 | [63] |
| | Nanowires | 1.13 | 0.73 | 0.26 | 0.26 | [65] |
| | Nanorods | 4.90 | 0.43 | 0.44 | 0.93 | [66] |
| | Nanotubes | 3.24 | 0.68 | 0.58 | 1.18 | [67] |
| | Nanoflowers | 19.60 | 0.57 | 0.42 | 4.70 | [68] |

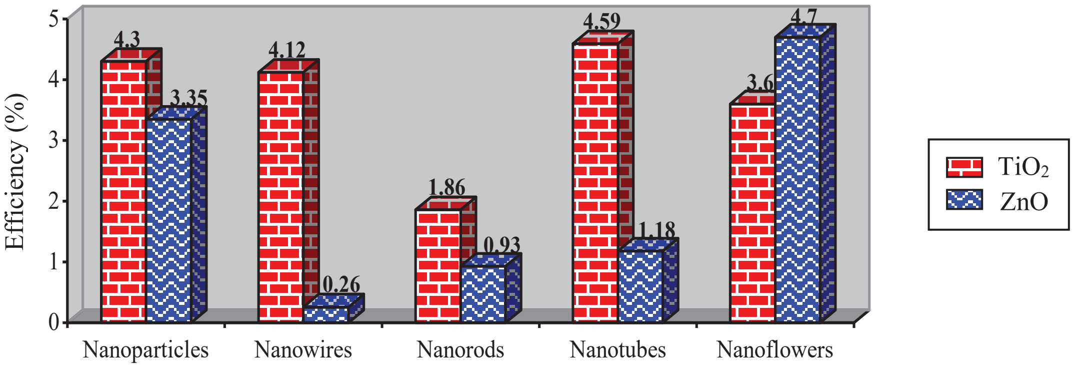

**Fig. 2.** Efficiency improvements in nanostructures of photoanode.

## 3 Conclusions

Many studies have been devoted to enhance the performance of the DSSC especially in the nanostructure of photoanode materials since photoanode is an important component that provides the electron transportation for the energy conversion process. This paper emphasizes the various improvements that had been done on the $TiO_2$ and ZnO photoanode nanostructures (nanoparticles, nanowires, nanorods, nanotubes and nanoflowers) synthesized through thermal method where all of the above works have shown some significant improvement in the performance of the DSSC. In conclusion, ZnO nanoflowers photoanode had achieved the highest energy conversion efficiency of 4.7% due to its ability of internal light scattering that had increased the electron transportation rate. This is also supported by the chemical properties of ZnO itself where it has the high electron mobility (155 $cm^2$ $V^{-1}.S^{-1}$) and large free excitation binding energy (60 meV). Hence, the development and innovation of the photoanode material should be continued to enhance the performance of DSSC.

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