Recent developments on the photoanodes employed in dye-sensitized solar cell

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Abstract

The emergence of dye sensitized solar cell (DSSC) as an alternative device for silicon based solar cell has gained a lot of attention from researchers due to its cost-effective, easy fabrication and environmentally friendliness. Photoanodes are semiconductor and as one of the four components of DSSC plays a major role for dye loading and electron conduction. A good photo anode should provide an efficient surface area in dye loading, nanostructure for high light harvesting opportunity, fast electron transport ability and good band gap architecture. Several nanostructures materials have been studied and employed as photoanode in DSSC. They include TiO₂, ZnO, Nb₂O₅, SnO₂, among others. The problem associated with photoanodes used in fabricating DSSC is high recombination rate of electrons that emanate from the number of grains. The dispersed nature of progress reports on developments of photoanodes calls for summary. Hence this review gives a general summary of the progress made in various materials used as photoanode in DSSC and the methods adopted in synthesizing them. In this present review, our attention is not only on synthesis and characterization of the materials alone but also on the effect of different factors influencing photovoltaic characteristics of photoanode for DSSC application.

Keywords: Nanostructure, photoanode, conversion efficiency, DSSC, photovoltaic
1. Introduction

The continuous depletion of fossil fuel reserves coupled with the associated environmental hazards emanated from combustion calls for more concerted effort for the development of clean, sustainable and renewable energy. Solar energy, with the sun producing over 120,000 TW of energy each year, seems to be the most apparent response [1]. There is no other source of energy as enormous as solar energy radiation. However, it can be considered limitless on the degree of humankind and harnessed at low cost. Profuse energy from the sun is received on earth which is projected to be $3 \times 10^{24} \text{ J/yr}$, which is about $10^4$ times more than what the earth uses currently. In other words, it covers only 0.1% of the earth surface with the conversion efficiency of around 10% which would be enough to suit our current needs [2]. Photon energy from the sun can be converted to direct electricity using solid state devices (photovoltaic device) i.e. solar panels, which have undergone three generations with an evolution from the first generation which are silicon based solar cell to the second generation that are based on thin films [3-5] and now to the third generation which are dye-sensitized solar cell (DSSC), Perovskite Solar cell, Quantum-dot Sensitized solar cell (QDSC) and Nanocrystal based solar cell [6-9]. The third generation solar cell shows a relatively low conversion efficiency when they are compared with the silicon based solar cell and thin film based solar cell that have an approximate conversion efficiency of 20-30% [10, 11].

Ever since the O’regan and Gratzel discovery in 1991, dye sensitized solar cell (DSSC) have captured public view and acquired more research consideration over the following 18 years as shown in Figure 1 [12]. Dye-sensitized solar cell (DSSC) have some advantages over the first two generations which is their simple manufacturing processes and low-cost of production coupled with their other advantages e.g. flexibility, low toxic and good performance in varied light condition [14]. Figure 2 schematically showed components of DSSC, a typical DSSC consists of photoanode made from semiconductor (e.g. TiO$_2$, ZnO, SnO$_2$ among others) film deposited on a conductive substrate, a sensitizer (i.e. dye; e.g. Ruthenium dye, organic dyes) by monolayer adsorption or quantum dots (e.g. CdS, CdSe or PbS), an electrolyte (e.g. $\Gamma/\Gamma^-$ and $\text{Co}^{2+/3+}$ redox couples) that is deposited between the counter electrode and sensitizer, and the last component of a DSSC is a counter electrode deposited on another conductive substrate [15].
Figure 1. Evolution of the number of publications for Dye-sensitized solar cell [13]

Supply of light by visible light irradiation on the photoanode triggers photo-excitation of the absorbed dye molecules to produce excited electrons that are consequently injected into the wide conduction band of the semiconductor and quickly transferred to the peripheral circuit through the conductive substrate; an electric current is produced in these processes. The initial nature of the dye is consequently returned by electron contribution from the redox electrolyte. Charges are returned by the counter electrode from the external circuit back to the cycling circuit in the cell [15].

Figure 2. Schematic Diagram of the Working Principle of DSSC
Production of nanostructured semiconductor photoanodes with effective architectures for high dye loading and fast electron transport have gained a lot of interest by researchers; the utilization of adaptable sensitizers with noticeable light harvesting ability, the use of strong redox electrolytes with favorable compositions for proficient transport of the hole, the optimization of the counter electrode as well as the development of other equivalent alternatives at lower costs [16-19]. Hence, this review highlights latest developments with insights into the photoanodes of DSSC. A general overview of this aspect in DSSC will be given. Detailed information and comprehensive discussion of different issues for DSSC can be found in some special articles [20-24].

2. Recent Developments on Photoanode
A good DSSC photoanode should offer large surface for dye absorption and also transfer the photo-generated electrons from sensitizer to peripheral circuit efficiently. It should have a band gap that matches well with the band structure of the sensitizer for effective injection of photoelectron. Typically, this involves the conduction band of semiconductor 0.2-0.3 eV lower than that of the sensitizer. Owing to these conditions, nanostructured semiconductor materials such as TiO₂, ZnO, graphene, NbO₂ and SnO₂ [25-30] are often employed as photoanode in DSSC.

An efficient surface area for dye loading can be obtained from a nanoscale structure of the semiconductor. Good interconnected semiconductor nanostructure semiconductors give room for effective charge transfer within the hole-transfer and anode to the redox mediator because of the penetration of the electrolyte back of the semiconductor film [26].

3. Materials Used as Photoanode
Nanoparticles, nanorod, nanofiber, nanotube, hierarchical nanostructure, and nanosphere are the different nanostructure of semiconductors that have been studied to improve the photovoltaic performance of the DSSC [31]. Also, different methods have been adopted to prepare effective nanostructured photoanodes (e.g. TiO₂, ZnO, Nb₂O₅ and SnO₂) including nanoparticle, nanorod, nanofiber, nanotube, hierarchical nanostructure, and nanosphere such as hydrothermal/solvothermal processes, sol-gel, electrospining, spray pyrolysis, electrochemical anodization [32-38] and atomic deposition [39].
3.1 Titanium (IV) Oxide (TiO$_2$)
Anatase, brooktie and rutile are the three forms of TiO$_2$ with energy band gap 3.23eV, 3.26eV and 3.05eV respectively. Higher electron dispersion coefficient and large surface area for dye-loading are provided by the anatase form of TiO$_2$ than the rutile form. However, the brooktie form is not considered for DSSC due to difficulty in its production, making the anatase form the most considered DSSC photoanode [40, 41]. Since the inception of researches on DSSC photoanode, TiO$_2$ nanoparticles gained more attention due to the large surface area provided and dye molecules absorption used for charge production. However, enormous number of grain boundaries and grain size between nanoparticles often cause a high charge recombination rate and inefficient energy conversion behavior. So far, 11.18% conversion efficiency has been obtained using TiO$_2$ nanoparticles as photoanode [42]. Figure 3 shows the crystal structure of the three forms of TiO$_2$.

![Image of crystal structures](image)

(a) Anatase  
(b) brooktie  
(c) Rutile

**Figure 3.** Crystal structure of the three forms of TiO$_2$ [43]

Recently, TiO$_2$ nanoflower (NF) was used in fabrication DSSC by doctor blade method. TiO$_2$ nanoflower was deposited over the edge of fluorine-doped Tin oxide (FTO) glass substrate with a sensitizer of N719 dye at standard temperature. A thin layer of platinum was used as the counter electrode and I$_2$ as the electrolyte. The fabricated DSSC have an energy conversion
efficiency of approximately 3.64% [44]. Titanium corrosion was used to prepare TiO$_2$ nanowire (NW) for DSSC fabrication in 2017. Ti foil reaction in alkaline potassium hydroxide at different corrosion time of (6, 12, 24 and 48 h) respectively was used to prepare the TiO$_2$ nanowire. Back illumination was used to illuminate the fabricated DSSC; metallic substrate used account for the back illumination. The conversion efficiencies obtained at different corrosion time of 6, 12, 24, 48 h were 0.27, 0.42, 0.80, 1.03% respectively. The photovoltaic parameters connected to the efficiency at 1.03% respectively are short circuit current $J_{sc} = 2.08 \text{ mA/cm}^2$, open circuit voltage $V_{oc} = 0.69 \text{ V}$ and fill factor $FF = 71.5 \%$ [45].

In 2016, Xia and co-workers fabricated hierarchical anatase form of TiO$_2$ using one step hydrothermal process. The fabricated film was studied under four different reaction times (3, 6, 9 and 12 h) to achieve different morphology and thickness photoanode. It was discovered that as the reaction time increases, the surface area also increases which gives way to high dye absorption. The fabricated DSSC achieve its highest efficiency at 9 h when the thickness was about 2 µm and the conversion efficiency obtained was 4.11% associated with $J_{sc} = 8.53 \text{ mA/cm}^2$, $V_{oc} = 7.4 \text{ V}$ and $FF = 66.37 \%$. The highest efficiency obtained from TiO$_2$ at 9 h among the four tested samples may be due to its higher Voc and Jsc, which might be credited to large surface area for dye loading [46].

TiO$_2$ nanotube (NT) boast immense prospect to prevail over the deficiencies of TiO$_2$ nanoparticles, seeing as their exceptional structure promotes electron transfer and charge parting by forging straight path and as well accelerate charge transport between interfaces [47-49]. The conversion efficiency of DSSC can be improved by TiO$_2$ nanotube due to their orderly and vertically-oriented characteristic as well as their intrinsic advantage. In other to harness the benefits of TiO$_2$ nanotube arrays maximally, its structure is to be taken into consideration. TiO$_2$ nanotube produced from Ti foil of 96% purity via anodization with which three morphologies of nanotube are generated which are grassy tube, open tube with nucleation layer on top and highly ordered nanotube. However, the conversion efficiencies of DSSC are obtained from 4.32%, 4.8% and 5.2% respectively [50]. Slightly higher result can be obtained from TiO$_2$ NT/NP composite [50, 51]. Figure 4 shows SEM image of highly ordered nanotube array formed on Ti foil for DSSC usage [52]. Electrons in TiO$_2$ nanotubes have much longer lifetime than those in nanoparticles [53].
Figure 4. SEM image of highly ordered TiO$_2$ nanotubes [52]

3.2 Composites of TiO$_2$ Photoanode

The compositions of TiO$_2$ semiconductor with other semiconductor have a great impact on DSSC fabrication. Recently, coaxial electrospinning method was employed to prepare Zn doped/TiO$_2$ hollow fibers. The light absorption was affected by the thickness of the Zn doped/TiO$_2$, most especially the short circuit current. The conversion efficiency obtained from this composition was 3.12% associated with $J_{sc} = 15.81$ mA/cm$^2$, $V_{oc} = 0.566V$ and $FF = 34.91\%$ [54]. DSSC fabricated with TiO$_2$ nanorod/nanoparticle (NR/NP) via hydrothermal process gives a conversion efficiency of 7.7%, $V_{oc} = 0.732V$, $J_{sc} = 17.06$ mA/cm$^2$ and $FF = 61.7\%$ [55].

TiO$_2$ nanorod(NR)/nanoflower(NF) based DSSC with some ratio of (HCl:H$_2$O) have improvement in DSSC application. Hierarchical TiO$_2$ nanorod(NR)/nanoflower (NF) photoanode produced by hydrothermal method composed of (H$_2$O:HCl = 5:5) shows an largely energy conversion efficiency of 0.85% associated with a $J_{sc} = 2.11$ mA/cm$^2$, $V_{oc} = 0.63V$ and $FF = 64\%$, which is much than that of microsphere 0.71% and nanowires of 0.61% efficiency [56]. DSSC with TiO$_2$ Nanowire (NW)/Nanoparticle (NP) composite with I$_3$/I$^-_3$ as electrolyte had an efficiency of 5.5% [57].

ZnO tetrapods was used together with TiO$_2$ (ZnO/TiO$_2$), the ZnO/TiO$_2$ composite was prepared via screen printing method. The structure of ZnO tetrapod/TiO$_2$ composite obtained via screen
printing is homogeneously porous and can excite the surface area and improve absorption of dye. It was reported that DSSC based on TiO₂/ZnO/TiO₂, ZnO tetrapod/TiO₂ and ZnO nanorod/TiO₂ photoanode had efficiency of 1.87%, 0.34% and 0.24%, respectively. Figure 5 shows SEM images of different techniques used in obtaining ZnO tetrapod/TiO₂ composites [58]. The photovoltaic parameters of synthesized TiO₂ nanostructures are presented in Table 1.

**Figure 5.** SEM image of (a) ZnO tetrapods/TiO₂ photoanode fabricated via screen printing (b) ZnO tetrapods/TiO₂ photoanode fabricated through colloidal spray coating and (c) ZnO tetrapods/TiO₂ photoanode fabricated via electrophoretic deposition [58].

**Table 1.** Photovoltaic parameters TiO₂ nanostructures with their synthesis methods

| TiO₂ Photoanode       | Method            | Jsc (mA/cm²) | Voc (V) | FF (%) | η (%) | Ref.  |
|-----------------------|-------------------|--------------|---------|--------|-------|-------|
| TiO₂ nanoflower       | Doctor Blade      | 7.80         | 0.69    | 67     | 3.64  | [44]  |
| TiO₂ nanowire         | Titanium corrosion| 2.08         | 0.69    | 71     | 1.0   | [45]  |
| TiO₂ nanoparticle     | Hydrothermal      | 8.53         | 0.74    | 66.37  | 4.11  | [46]  |
| TiO₂ nanotube         | Anodization       | 13.48        | 0.67    | 48     | 4.32  | [50]  |
| TiO₂ nanotube         | Anodization       | 13.45        | 0.70    | 55     | 5.2   | [50]  |
| TiO₂ nanotube         | Anodization       | 12.68        | 0.70    | 54     | 4.8   | [50]  |
| Zn doped/TiO₂         | Electrospinning   | 15.81        | 0.56    | 34.9   | 13.12 | [54]  |
| TiO₂ NR/NP            | Hydrothermal      | 17.06        | 0.73    | 61.7   | 7.7   | [55]  |
| TiO₂ NR/NF            | Hydrothermal      | 0.85         | 2.11    | 63     | 0.64  | [56]  |
3.3 ZnO as Photoanode

The wide-band gap characteristic of ZnO with the energy-band structure and its physical characteristics make ZnO suitable for DSSC application. It also has a higher electronic mobility that makes it encouraging for transportation of electrons which is one of the major characteristics for a proficient photoanode [59]. The high electron mobility of ZnO can be linked to the characterization and syntheses of different nanostructures of ZnO such as nanotubes, nanobelts, nanorods, nanoparticles, nanoflowers, nanosheets and nanotetrapods [60]. However, ZnO is unstable with acidic dye and higher charge recombination which account for lower conversion efficiency of ZnO based solar cell than that of TiO₂ [61]. Recently, ZnO nanorods (NR) was synthesized using chemical bath deposition (CBD) alongside electrodeposition; the synthesized ZnO has a large surface area that leads to its large short circuit current. The conversion efficiency of 0.8%, $J_{sc} = 3.47 \text{ mA/cm}^2$ and $FF = 51.7\%$ are obtained with high electron transfer and more injected electrons [62]. Hydrothermal process was used recently to grow nanoflowered shape ZnO on an FTO substrate which was employed to DSSC fabrication. The large grain size of the ZnO nanoflower accounts for its great Voc and FF and high recombination rate. The fabricated DSSC has $J_{sc} = 4.2 \text{ mA/cm}^2$, $V_{oc} = 0.62V$, $FF = 54\%$ and conversion efficiency of 1.4% [63].

Low temperature hydrothermal process was used to synthesize ZnO flower shaped nanostructure. The axial arrangement of nanoneedles which are accumulated formed the flower shape of the ZnO. The purity of the flowers was high and has good optical characteristics. The light harvesting efficiency result to the reasonable high dye absorption by the photoanode. The fabricated DSSC were reported to have an efficiency of ~1.1% coupled with $J_{sc} = 3.532 \text{ mA/cm}^2$, $V_{oc} = 0.611V$ and $FF = 51\%$ [64].

A nanoporous ZnO photo-anode formed from pre-dyed ZnO (Pd-ZnO), the pre-dyed ZnO is made by mixing dyeing procedure with ZnO nanoparticles. The pd-ZnO paste used in fabrication of DSSC which gives $J_{sc} = 1.97 \text{ mA/cm}^2$, $V_{oc} = 0.57V$, $FF = 80\%$ and energy conversion efficiency of 0.90%. Using hot-press system on the fabricated DSSC of Pd-ZnO a $J_{sc} = 2.97 \text{ mA/cm}^2$, $V_{oc} = 0.59V$, $FF = 75\%$ and efficiency of 1.31% were obtained. However, the
pre-dyeing process has insufficient connection with zinc oxide nanoparticles which may serve as the drawback for pd-ZnO [65].

Kumara et al. [66], fabricated DSSC with a dense ZnO layer and also mesoporous ZnO layer with spray pyrolysis methods. Higher efficiency of 5.02 % was obtained for dense layer fabricated DSSC and 4.2% for mesoporous layer fabricated DSSC under the same circumstances. High surface area for dye absorption was recorded for the DSSC with dense ZnO layer than that with mesoporous ZnO layer. Other parameters connected to the dense ZnO layer are $J_{sc} = 13.68 \ mA/cm^2$, $V_{oc} = 0.537V$ and $FF = 66.3\%$ while those connected to the mesoporous layer have $J_{sc} = 12.06 \ mA/cm^2$, $V_{oc} = 0.565V$ and $FF = 62.4\%$ [66].

Nanosheets ZnO was used to produce Zinc Oxide (ZnO) nanoarchitecture film by a simple two-step synthesis procedure for DSSC photoanode. The ZnO nanoarchitecture was then compared with DSSC with an upright-standing ZnO nanosheet photoanode. ZnO nanoarchitecture was fabricated using dense ZnO nanowire that is grown of primary ZnO nanosheet. Electrodeposition and Aqueous Chemical Growth (ACG) respectively are the two methods used to obtain the ZnO nanoarchitecture. The ZnO nanoarchitecture (nanosheet/nanowire) was dyed on Indium Tin Oxide (ITO) in an ethanol, ruthenium (N719) used as dye, Platinum as the counter electrode and Iodide as the electrolyte [67]. The structure of ZnO nanoarchitecture was analyzed using X-ray diffraction (XRD) which shows that the peak of all diffraction can be indexed to hexagonal ZnO, and the structure contains no impurities. The ZnO (nanosheet/nanowire) based DSSC was compared with conventional ZnO nanosheet array with the same thickness of 5 µm. The conversion efficiency obtained from ZnO nanoarchitecture was 4.8% associated with $J_{sc} = 10.9 \ mA/cm^2$, $V_{oc} = 0.68V$ and $FF = 65\%$ as well as the conventional ZnO nanosheet with the efficiency of 2.3% associated with $J_{sc} = 7.2 \ mA/cm^2$, $V_{oc} = 0.61V$ and $FF = 52\%$. The efficiency of ZnO nanoarchitecture is as twice as that of ZnO nanosheet. The higher conversion efficiency is said to be obtained due to large internal surface area of the film (Figure 6) without losing the straight conduction pathway for swift collection of electrons [67].

ZnO nanoflower (NF) prepared hydrothermally for DSSC application with a chosen size of 8µm compared with ZnO nanoparticles (NP) has a higher dye-loading and also higher light scattering, due to its large surface area. ZnO nanoflower has a high short-circuit current (Jsc) and higher open-circuit voltage (Voc) because of straight conduction path it possesses. ZnO nanoflower has an efficiency of 5.96% as compared to ZnO nanoparticles that has 4.39% efficiency. However,
both structures have nearly the same value of Voc and FF. ZnO nanoflower array has $J_{sc} = 13.5 \text{ mA/cm}^2$, $V_{oc} = 0.682V$ and $FF = 64.6\%$ while the ZnO nanoparticles have $J_{sc} = 10.1 \text{ mA/cm}^2$, $V_{oc} = 0.680V$ and $FF = 64\%$. Figure 7 showing the current-voltage (I-V) characteristics of the comparison of ZnO nanoflower and ZnO nanoparticles [68].

Figure 6. SEM images of the hierarchical ZnO nanowire/nanosheet obtained by aqueous chemical growth after 0, 1, and 4 h, respectively [67]

ZnO nanoparticles doped with Niobium used as photoanode in DSSC has been investigated by Anuntahirunrat and colleagues recently as a means of improving the efficiency of solar cell. Five (5) samples of the dopant were taken in weight percent (wt%) for comparison and to ascertain the most effective one, starting from 1wt% - 5wt% using spin-coating technique. The highest efficiency was recorded at 3wt% with an efficiency of 9.02% associated with $J_{sc} = 16.3 \text{ mA/cm}^2$, $V_{oc} = 0.63V$ and $FF = 38.26\%$. However, doping of the Niobium with ZnO does not affect the structure of ZnO, and also as the content of Niobium increases light absorption of ZnO [69]. The samples were characterized using scanning electron microscopy (Figure 8).

Figure 7. I-V characteristic of ZnO nanoflower and ZnO Nanoparticle photoanode based DSSC [68].
In 2009, Lai et al. [70] fabricated DSSC without transparent conducting oxide (TCO) using ZnO film as a replacement for the TCO and ZnO nanorods as the photoanode. Two methods were used to grow ZnO nanorods (NR)/ZnO film which were chemical vapour deposition (CVD) and chemical bath deposition (CBD) respectively. In the first method, one-step chemical vapor deposition (CVD) technique was used to grow ZnO nanorods on ZnO film, while two-step chemical bath deposition (CBD) technique that involved (1) growing of ZnO film on a glass substrate and (2) Deposition of ZnO nanorod array on ZnO substrate. The ZnO film/ZnO nanorods without TCO were compared with ZnO nanorod with TCO which was grown using CBD technique. However, there is uniformity in the thickness of one-step CVD growth technique used than the two-step CBD growth technique. The conversion efficiency obtained from one-step CVD is 0.73% having $J_{sc} = 1.97\ mA/cm^2$, $V_{oc} = 0.80V$ and $FF = 39.4\%$, while the two steps CBD grown sample has an efficiency of 0.66% with $J_{sc} = 3.96\ mA/cm^2$. 

Figure 8. SEM images different samples of fabricated Nb-doped ZnO nanoparticles [69]

(a) 1wt % Nb-ZnO (b) 2wt % Nb-ZnO (c) 3wt % Nb-ZnO
(d) 4wt % Nb-ZnO (e) 5wt % Nb-ZnO
The efficiency is obtained from the two technique above is low when compared with conventional ZnO based DSSC grown on FTO substrate with an efficiency of 1.37% having $J_{sc} = 5.51 \text{ mA/cm}^2$, $V_{oc} = 0.65\text{V}$ and $FF = 38.2\%$. It could be noted that the conventional DSSC system has a lower $V_{oc}$ when compared with DSSC without transparent conducting oxide [70]. Recently, ZnO nanoparticles (ZnO NP) were synthesized by Musleh and coworkers [71] using two methods which are sol-gel and hydrothermal technique. Three samples of dye were also adopted in fabrication of DSSC which are Eosin Y (EY), Eosin B (EB) and Rhodamine B (RB). These three dyes were used to replace the conventional dye. X-ray Diffraction (XRD) was used to measure the crystal structure and it size. The precise composition of the structure was done using High Resolution Transmission Electron Microscopy (HRTEM) and Spectrofluorimeter was used to check for the photoluminescence properties. It can be deduced from their work that the highest efficiency was obtained from DSSC based on sol-gel technique synthesized with EY dye and the lowest efficiency DSSC was obtained from hydrothermal technique synthesized with EB dye. The factors that may lead to higher efficiency in Sol-gel synthesized with EY dye may be due to the ability of injected electrons, amount of the absorbed dye and the surface structure. The highest efficiency obtained is 1.08% with photovoltaic parameters of $J_{sc} = 4.25 \text{ mA/cm}^2$, $V_{oc} = 0.51\text{V}$ and $FF = 50.08\%$, while the lowest efficiency obtained may be due to low dye absorption and weak bonding that exist between dye molecules and ZnO nanoparticles with the efficiency of 0.29% with photovoltaic parameters of $J_{sc} = 1.60 \text{ mA/cm}^2$, $V_{oc} = 0.37\text{V}$ and $FF = 49.76\%$ [71]. The photovoltaic parameters of ZnO nanostructures are presented in Table 2.

### 3.4 Other materials employed as photoanode

The efficient band gap of Tin Oxide (SnO$_2$) makes it valuable for DSSC application. Spherical SnO$_2$ nanoparticles were synthesized using solvothermal method. Two samples of the SnO$_2$ were prepared at pH 8 and 10; the size of particles in the synthesized SnO$_2$ increased with the pH value. The two samples have 4.76 and 4.53 band gap respectively. The conversion efficiency of DSSC of SnO$_2$ samples with pH 8 = 0.0044% and pH 10= 0.0042%. Solid electrolyte used for the fabrication may have accounted for the poor efficiency of the solar cell. The efficiency of the
DSSC dropped to 0.0013% and 0.0014% respectively after 40 days. The methylene blue dye of poor chemical stability might also account for the reduction in the efficiency of the solar cell [72]. Recently, an architecture of SnO2 was prepared by combining nanocrystallite aggregate (SnO2 NA) of SnO2 synthesized by hydrolysis method at standard room temperature with SnO2 nanosheet (NS) synthesized via hydrothermal method. A freeze drying treatment was adopted for the SnO2 synthesized with hydrolysis method.

**Table 2.** Photovoltaic parameters ZnO nanostructures with their synthesis methods

| ZnO Photoanode     | Method              | Jsc (mA/cm²) | Voc (V) | FF (%) | η (%) | Ref.  |
|--------------------|---------------------|--------------|---------|--------|-------|-------|
| ZnO nanorod        | CBD                 | 3.47         | 0.64    | 51.7   | 0.8   | [62]  |
| ZnO NF             | Hydrothermal        | 4.2          | 0.62    | 54     | 1.4   | [63]  |
| ZnO NF             | Hydrothermal        | 3.53         | 0.61    | 51     | 1.1   | [64]  |
| Pd-ZnO             | Dyeing              | 1.97         | 0.57    | 80     | 0.90  | [65]  |
| ZnO dense layer    | Spray pyrolysis     | 13.68        | 0.54    | 66.3   | 5.02  | [66]  |
| ZnO mesoporous     | Spray pyrolysis     | 12.06        | 0.57    | 62.4   | 4.2   | [66]  |
| Zno NF             | Hydrothermally      | 13.5         | 0.68    | 64.6   | 5.96  | [68]  |
| ZnO NS             | Electrodeposition   | 7.2          | 0.61    | 52     | 2.3   | [67]  |
| ZnO NS-NW          | Electrodeposition/ACG | 10.9      | 0.68    | 65     | 4.8   | [67]  |
| ZnO/Nb             | Spin-coating        | 16.3         | 0.63    | 38.26  | 9.02  | [69]  |
| Zno NR             | CBD                 | 1.97         | 0.80    | 39.4   | 0.73  | [70]  |
| Zno NR             | CVD                 | 3.96         | 0.72    | 20.0   | 0.66  | [70]  |
| ZnO NP             | Sol-gel             | 4.25         | 0.51    | 50.08  | 1.08  | [71]  |

The SnO2 architecture was characterized using Transmission Electron Microscopy (TEM), UV-vis spectrometer and X-ray diffraction (XRD). The combined architecture provides an efficiency of 5.59% associated with Jsc of high value and low Voc and FF value was reported. The efficiency obtained from the SnO2 NA/SnO2 NS was attributed to large surface area and light scattering ability of the SnO2 NA [73]. Teh et al. [74] synthesized a nanoporous SnO2 in
ammonia aqueous solution and compared with conventional SnO₂ nanoparticles. It was revealed that the nanoporous SnO₂ has low charge transfer and high charge recombination account for the high DSSC performance of the nanoporous SnO₂ based photoanode. The conversion efficiency recorded for nanoporous SnO₂ is 1.66% as against 1.02% for SnO₂ nanoparticles based DSSC [74]. A microsphere SnO₂ structure was hydrothermally synthesized and employed as photoanode in DSSC. Improved light harvesting factor and efficient light scattering ability of the structure propel the good performance of the DSSC. An energy conversion efficiency of 4.55% was obtained from the SnO₂ microsphere based DSSC [75].

In 1999, Burnside and co synthesized a nanocrystal form of strontium titanate (SrTiO₃) using hydrothermal technique [76]. The synthesized SrTiO₃ was used as photoanode is fabrication of DSSC. However, SrTiO₃ has low photocurrent value which could result low dye loading of the material. The SrTiO₃ based DSSC have a power conversion efficiency of 1.8% as compared to anatase TiO₂ based DSSC with 6.0% power conversion efficiency [76]. Reduced graphene oxide (r-GO) and titanium dioxide was adopted as photoanode in DSSC recently. The reduced graphene oxide was synthesized by chemical reduction process and mixed with powder of TiO₂. An efficiency of 2.02% was achieved for reduced graphene oxide based solar cell [77]. Nanowire of three forms (monoclinic, pseudo-hexagonal and orthorhombic) of Nb₂O₅ was synthesized via electrospinning of Nb₂O₅ polymeric solution and employed as photoanode in DSSC; the fabricated DSSC with pseudo-hexagonal nanowire form of Nb₂O₅ has greater conversion efficiency. However, monoclinic has a low recombination of charge, efficient electron lifespan and high dye loading ability than orthorhombic and pseudo-hexagonal form. The conversion efficiencies of monoclinic, pseudo-hexagonal and orthorhombic are 1.92%, 3.05% and 2.53% respectively [78]. The photovoltaic parameters of other materials that have been adopted as photoanode in DSSC are shown in Table 3.
Table 3. Photovoltaic parameters of other materials that have been adopted as photoanode in DSSC

| Photoanode | Method        | Jsc (mA/cm²) | Voc (V) | FF (%) | η (%) | Ref. |
|------------|---------------|--------------|---------|--------|-------|------|
| SnO₂MH     | Solvothermal  | 10.4         | 7.65    | 57.3   | 4.55  | [75] |
| Nb₂O₅      | Electrospining| 6.68         | 0.77    | 59.06  | 3.05  | [78] |
| SrTiO₃     | Hydrothermal  | 3.00         | 7.89    | 70.0   | 1.8   | [76] |
| R-GO       | Chemical reduction | 10.8   | 6.24    | 30.0   | 2.02  | [77] |

4. Conclusion

Previous work done and series of attempts to improve the conversion efficiency of DSSC using different nanostructure of semiconductors as photoanodes and with different synthesis method have been summarized in this review. Few of the discussed work can be compiled and applied by researchers to obtain a better efficiency. Combination of two or more nanostructure ranging from nanorods, nanofibers, nanoparticles, nanosphere, nanoflower and nanosheet of photoanodes have proven to enhance the performance efficiency of DSSC. DSSC still has lower conversion efficiency when compared to conventional silicon based solar cell despite the notable improvements. Photoanodes with high electron transfer efficiency with lower recombination electron rate and large surface area are highly anticipated from researchers. Also, composition of TiO₂ nanoparticles as well as 3D nanostructure of Silicon with efficient electron transport and large surface capability could be synthesized via hydrothermal technique and applied as photoanode in DSSC. The counter electrode, electrolytes and sensitizers can also be optimized and the whole structure can enhance the conversion efficiency of DSSC.

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