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Effects of Various Semiconducting Oxides as Photoanode and Counter Electrode for Dye Sensitized Solar Cell Application - A Review

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ABSTRACT

Dye sensitized solar cells (DSSCs) were attractive as a promising photovoltaic technologies alternative. The DSSCs showed a low cost production, high power conversion efficiency and simple fabrication. In DSSCs, the photoanode have significant roles to collects the photo-excitation electrons and dye conducts photo-electrons to the transparent conducting film (TCF). Photoanode have a wide band gap semiconducting metal oxide (e. g. zinc oxide (ZnO) and titanium dioxide (TiO_2)) that were coated onto TCF. Counter electrode (CE) was one of important components in regulating the DSSCs application. The CE was used as mediator to generate the sensitizer after electron injection. The ideal of CE materials must have a low sheet resistance, low cost production, high electrical conductivity, good electro-catalytic activity and excellent stability. The CE materials commonly used for DSSCs application such as platinum (Pt), carbon, carbon nanotubes (CNTs), graphene and conducting polymers. The review has been developed to study the good characteristics of photoanode and CE materials for DSSCs application. Then, it was also used to give information towards the development of photoanode and CE materials for the next research in DSSCs application. In this review, the influence of various semiconducting oxides as photoanode and CE for DSSCs application were discussed.

Keywords : photoanode, counter electrode, dye sensitized solar cells

ABSTRAK

Dye sensitized solar cells (DSSCs) merupakan teknologi alternatif fotovoltaik yang menguntungkan. DSSCs menunjukkan harga yang murah, efisiensi yang tinggi dan proses pembuatan yang sederhana. Dalam aplikasi DSSCs, fotoanoda memiliki peranan yang penting untuk mengumpulkan elektron-elektron yang tereksitasi dan dye berfungsi untuk menyalurkan cahaya elektron-elektron ke *transparent conducting film* (TCF). Fotoanoda mempunyai *band gap* yang lebar pada semikonduktor logam oksida (contoh: *zinc oxide* (ZnO) dan *titanium dioxide* (TiO_2)) yang dilapiskan pada TCF. Counter electrode (CE) adalah salah satu komponen yang penting dalam proses kerja DSSCs. CE digunakan sebagai mediator untuk membangkitkan *sensitizer* setelah masuknya elektron. Bahan CE yang ideal harus mempunyai resistansi yang rendah, biaya produksi yang murah, konduktivitas listrik yang tinggi, aktivitas elektrokatalitik yang bagus dan stabilitas yang tinggi. Bahan-bahan CE yang umum digunakan

untuk aplikasi DSSCs yaitu seperti platina (Pt), karbon, *carbon nanotubes* (CNTs), grafin dan polimer konduktif. Review ini dikembangkan untuk mempelajari sifat-sifat bahan fotoanoda dan CE yang bagus untuk aplikasi DSSCs. Review ini juga digunakan untuk memberikan informasi untuk perkembangan bahan-bahan fotoanoda dan CE pada penelitian selanjutnya dalam aplikasi DSSCs. Dalam review ini, pengaruh bahan-bahan yang digunakan untuk fotoanoda dan CE dalam aplikasi DSSCs didiskusikan.

Kata kunci: fotoanoda, *counter electrode*, *dye sensitized solar cells*

INTRODUCTION

Energy was classified as basic human right in the form of an electricity. Energy is very important to human lives since it could reduce poverty, increase productivity, improves health and standards of living. The energy sources were consisted of three categories, (1) first from the chemical or photo-physical that oxidize some substance, such as solar radiation to generate electricity, (2) second derives from nuclear reactions, (3) and the third derives from thermo-mechanicals (e.g. wind, water, or geological sources) [1].

Among the other sources of energy, fossil fuels (e.g. oil, gas and coal) were used as the main source of energy which will decrease in the next century and shows the finite natural resources. Recently, non-conventional and renewable sources have been explored by many countries [2]. The nuclear, solar, bio and wind were used as source of energy alternative due to low cost production. Commonly, the sunlight was known as a primary source of energy and was usually used to generate electricity.

The development of solar cells has three generations since 1954. The first generation of solar cell was developed by Chapin that used crystalline silicon [3]. The silicon has the high cost production and weak absorption of sunlight. Then, the second generation used cadmium telluride (CdTe), copper indium (gallium) selenide (CIS/CIGS), amorphous and hybrid silicon thin films. However, in this generation has the lower power conversion efficiency than first generation. Finally, the third generation technology was developed by O'regan and Gratzel since 1991. This generation focused on the semiconducting materials due to have wide band gap [4-5], low cost and good performance in DSSCs application [6].

The DSSCs showed the most prominent in the third generation solar cells and better performance than conventional solar cells. The DSSCs were known as a photovoltaic and have low cost production to convert sunlight to electricity. It was also known as a photo-electrochemical cell and have photoelectrode based on a nanostructures metal-oxide film (e. g. ZnO, TiO_2, SnO_2, $SrTiO_3$ and Nb_2O_5) [7-9]. The DSSCs were introduced by O'Regan and Gratzel that were known as inorganic p-n junction solar cells and a promising alternative photovoltaic [8]. Recently, the DSSCs were developed and produced due to have low cost production, high power conversion efficiency, usage of medium purity materials, environmental friendliness, good performance in diverse light conditions, impressive incident photons to electrical current conversion efficiency and long-term stability [11-12].

Commonly, the DSSCs consists of five main components: (1) glass substrate of transparent conductive (TCF) (e. g. FTO and ITO); (2) semiconductor metal oxide layer (e. g. ZnO, TiO_2, SnO_2, $SrTiO_3$ and Nb_2O_5) coated on TCF as photoanode [13]; (3) monolayer of organic/inorganic dye molecule on the surface of metal oxide layer in photoanode; (4) liquid phase electrolytes (e. g. iodide/tri-iodide (I^-/I_3^-)) are used to regenerate the oxidized dye and (5) Pt or other materials (e. g. carbon, graphene and CNTs) as CE [14-15].

Objectives of The Present Review

In this review, the influence of photoanode and CE to power conversion efficiency in DSSCs application were discussed. Based on the literatures [15-16], research activities executed toward the modifications of photoanode and CE to increase the power conversion efficiency in DSSCs application. The other articles reported that every constituent (TCF, photoanode, dyes, electrolytes and CE) influenced to the performance of DSSCs. Meanwhile, the role of structural, optical, electrical properties and composition of materials in the photoanode and CE will also affect to the performance of DSSCs [17].

In the present review, we gave an illustration to illustrate the key role of photoanode and CE that will influence to the power conversion efficiency in DSSCs application. This description based on the relevant literatures and investigated about the DSSCs application.

Dye Sensitized Solar Cells

The DSSCs were a photovoltaic device that converts solar radiation into electricity. The schematic diagram of DSSCs and its components were shown in Figure 1. The system DSSCs consists of:

1. Transparent conductive film

The TCF was fabricated by conductive oxide layer on the glass substrate [18]. The conductive glass was used as substrate in photoanode and CE used to enhance the electrical conductivity and light transmittance. Commonly, the fluorine-doped tin oxide (FTO) and indium-doped tin oxide (ITO) were used as substrate in DSSCs application. Meanwhile, the resistivity of FTO substrate (2.5% of F) was $6x10^{-4}\,\Omega cm$ and ITO (6% of Sn) $8x10^{-4}\,\Omega c$ [19-20]. Therefore, the FTO substrate used in DSSCs due to has the higher power conversion efficiency of ~9.4% than ITO ~2.4% [21]. Therefore, the FTO substrate was highly recommended as TCF in this application. Figure 1 showed the structure and components of DSSCs.

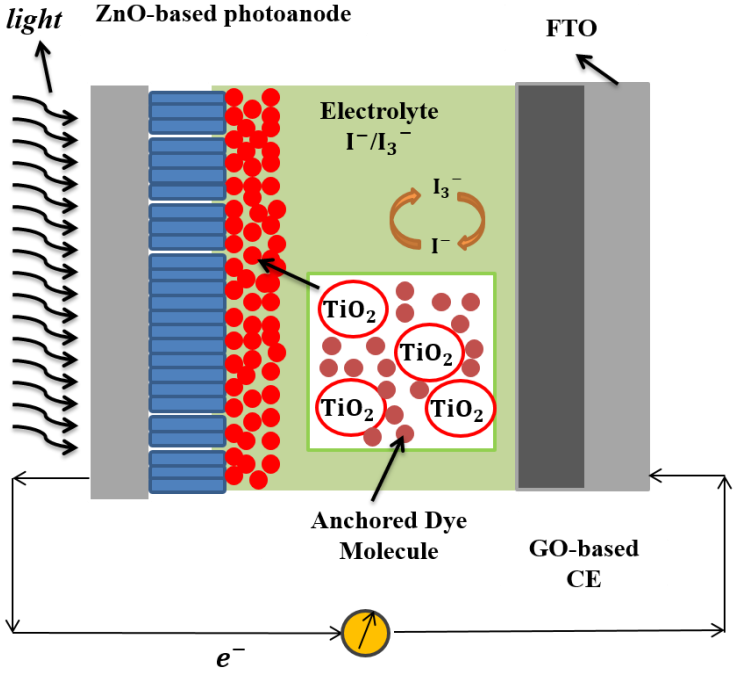

Figure 1. Structure and components of DSSCs.

2. Photoanode

Commonly, the photoanode has a wide band gap and fabricated by semiconducting metal oxides that was coated on TCF. The metal oxides were used to absorb dye molecules, collect the photo-generate electrons from the excited state and conduct photo-electrons from dye to the conducting substrate [11]. Therefore, metal oxides have to have a good electrical and stability properties to against photo-corrosion. Actually, photo-corrosion was caused by oxidation of holes with the redox electrolytes that will influence to the performance in DSSCs application [22]. Meanwhile, the photoanode were used to collect and transport photo-excitation electron from dye to CE. Based on previous research, the ideal photoanode supposedly have high surface area for dye adsorption, high porous for effective mass transport and high electron mobility for efficient electron transport [23]. The metal oxides such as ZnO [15], TiO_2 [23], SnO_2 [24], $SrTiO_3$ [25], Zn_2SnO_4 [26] and Nb_2O_5 [27] have been widely used as photoanode materials for DSSCs application.

The power conversion efficiency of metal oxides as photoanode is showed in Table 1. Theoretically, wide band gap was needed in photoanode due to an electron with energy ($h\upsilon$) will be excited to the conduction band when has high exceeds the band gap of a semiconductor. Consequently, electron was excited leave hole (positive charge) at the valence band. These charges can be changed to electrical current by chemical reaction [28]. Among the semiconducting metal oxides, the TiO_2 was mostly used as photoanode material. Actually, the TiO_2 has three crystalline forms such as rutile, anatase and brookite phase. The rutile phase has band gap of 3.05 eV with tetragonal structure. Then, the anatase phase has band gap of 3.23 eV that has been also tetragonal structure and orthorhombic structure for brookite with band gap of 3.26 eV [29]. However, the rutile and anatase phase of TiO_2 nanoparticles have been studied for DSSCs application.

The rutile phase was widely used in photoanode due to has better light scattering, more stable than anatase phase and higher refractive index of 2.71 than the anatase phase 2.53 [30]. Meanwhile, the rutile phase has higher wavelength in incident photon-to-current conversion efficiency (IPCE) of 400-750 nm than anatase phase 500-550 nm [31]. However, the rutile crystals were usually formed in high temperature process, whereas the anatase phase stable at low temperature [32]. Commonly, the brookite phase was not used as photoanode in the DSSCs application due to difficult in production [33].

Table 1. Comparison performance of photoanode materials (metal oxides) in DSSCs application

Photoanode Material	Band gap (eV)	Method	η (%)	References
TiO_2	3.2	Hydrothermal	7.13	[34]
ZnO	3.3	Blending	4.59	[35]
Nb_2O_5	3.4	Doctor Blade	0.64	[27]
Zn_2SnO_4	3.6	Hydrothermal	3.36	[26]
$SrTiO_3$	3.2	Hydrothermal	5.07	[36]
WO_3	2.6 - 3.0	Sol-gel	4.63	[37]
SnO_2	3.8	Electrospinning	3.41	[38]

Besides of TiO_2, the ZnO was a promising alternative metal oxide due to wide band gap, relatively high electron mobility (~100 $cm^2v^{-1}s^{-1}$) than TiO_2 and large excitation binding energy (60 meV) [15]. However, the TiO_2 has the highest power conversion efficiency than ZnO in DSSCs performance. The TiO_2 and ZnO nanostructures can be produced with a large surface area that showed a primary factor in maximizing dye absorption of photoanode for DSSCs application [7, 39].

The ZnO has three crystalline forms: hexagonal wurtzite, cubic zinc blende and cubic rock salt. Among these crystalline forms, the hexagonal wurtzite was the most stable at ambient condition that showed the majority form of crystal [40]. Meanwhile, the ZnO nanostructures have category of 1-D, 2-D and 3-D. However, the 1-D nanostructures were usually used in DSSCs application due to the electrons can easily migrate, compared with nanoparticles. Meanwhile, the 1 -D nanostructures have a high light scattering to enhance the cells performance and high surface area to absorb dye molecules [14]. The nanostructures were used as photoanode due to have trigger fast electron transport and capable to absorb dye effectively [39].

The microstructures, particle size, porosity and pore size distribution in the metal oxides showed a key role in photoanode that was used to enhance the photovoltaic performance. Moreover, the doping on the metal oxides materials will affect to the structural, optical and electrical properties of photoanode. The technique preparation will also influence to the results of performance in DSSCs application [15].

2.1 Effect of doping in photoanode materials

In semiconducting metal oxides, doping cation/anion will change band gap and improve the electrical properties. Meanwhile, the ion doping was used to reduce recombination resistance in photoanode [41]. Injection and transportation of photo-excitation electrons will influence to the power conversion efficiency of DSSCs [14]. Hence, the cations were used as dopant in metal oxides due to large dipole moment that will affect to the electron transfer [42]. The ZnO and TiO_2 were usually used as photoanode in DSSCs application which can absorbs UV light due to have wide band gap of 3.2 - 3.3 eV. In TiO_2, cations and anions were used as dopant that can improve the power conversion efficiency in this application. Based on literature, the different of cationic dopants and power conversion efficiency in TiO_2 material were shown in Table 2. Then, Table 3 showed the performance of DSSCs with the different anionic dopants in TiO_2 as photoanode in DSSCs application.

Table 2. Comparison performance of DSSCs with different cationic dopants in TiO_2 material as photoanode

Cationic Dopant	η (%)	References
Scandium (Sc)	9.6	[43]
Magnesium (Mg)	8.04	[44]
Niobium (Nb)	7.3	[45]
Chrome (Cr)	3.89	[46]
Cuprum (Cu)	0.44	[47]
(Tantalum (Ta))	8.18	[48]
(Vanadium (V))	7.8	

Among the cationic dopants in TiO_2, the Sc showed the highest power conversion efficiency than the others due to size Sc^{3+} rather similar with the Ti^{4+}. Therefore, the Sc cationic dopant can decrease defects in TiO_2 as photoanode [43]. Meanwhile, Ta and Mg dopant can also improve the power conversion efficiency in DSSCs application.

Table 3. Comparison performance of DSSCs with different anionic dopants in TiO_2 as photoanode

Anionic Dopant	η (%)	References
Fluoride (F)	8.31	[49]
	5.24	[48]
Nitrogen (N)	4.7	[50]
Sulfur (S)	6.91	[51]
Boron (B)	4.61	[52]
Carbon (C)	3.9	[53]

Based on the Table 3, F dopant showed the highest power conversion efficiency than the others anionic dopants. The F dopant can enhance the power conversion efficiency, reduce the charge recombination and contact resistance in photoanode [49]. Therefore, the F dopant can improve the TiO_2 properties and can be developed in this application. Meanwhile, N and S anionic dopant in TiO_2 can also increase the power conversion efficiency in DSSCs. Besides in TiO_2, the ZnO can be also doped with the cationic dopants that was used to

enhance the absorption of visible light. Table 4 showed the performance of DSSCs with different cationic dopants into ZnO as photoanode in DSSCs performance.

Table 4. Comparison performance of DSSCs with different cationic dopants in ZnO as photoanode

Cationic Dopant	η (%)	References
Gallium (Ga)	3.19	[54]
Magnesium (Mg)	4.19	[55]
Aluminum (Al)	1.02	[56]
Potassium (K)	0.012	[57]

Among the cationic dopants in ZnO, the Mg has the highest power conversion efficiency than the others. The Ga, Mg and Al dopants in ZnO will affect to the photovoltaic properties and improve the power conversion efficiency in DSSCs performance [55]. Overall, doping cations/anions were promising affect in photoanode performance in DSSCs application.

2.2 Effect of ZnO and TiO_2 layer in the photoanode properties

In photoanode, semiconducting metal oxides layer influenced the structural, optical and electrical properties. The researchers used TiO_2 as photoanode due to improve the power conversion efficiency in DSSCs application [23]. Besides TiO_2, the ZnO was also used as photoanode in DSSCs application.

Among these metal oxides materials, TiO_2 and ZnO have high power conversion efficiency in DSSCs performance. Hence, the TiO_2 and ZnO were used as photoanode materials in DSSCs application. Moreover, Table 5 showed the various morphology of TiO_2 and its performances as photoanode. The TiO_2 has good chemical stability under visible irradiation, cheap, non-toxic, and ready available due to its stability and better of power conversion efficiency [32]. Meanwhile, the power conversion efficiency of TiO_2 as photoanode was strongly depended on light harvesting [58].

Based on Table 5, the 1-D of TiO_2 nanorods were usually used as photoanode. The TiO_2 nanorods were used in this alippcation due to can decrease the interconnections between crystalline titania particles that were compared to a porous titania film [59]. The TiO_2 nanorods have diameters around of 99 nm and length 310 nm [39]. The nanorods structures have rapid transport of charge carriers and power conversion efficiency ~9.21% [60]. Meanwhile, the TiO_2 nanotubes structures can also attribute to the synergistic effect due to have large surface area, fast charge transport and superior light scattering [61].

Table 5. Various morphologies and performances of TiO_2 as photoanode in DSSCs application

Morphology	Method	η (%)	References
Nanoflowers	Hydrothermal	6.63	[62]
Nanorods	Hydrothermal	1.86	[63]
Nanotubes	Electrochemical Anodization	7.24	[61]
Nanowires	Hydrothermal	4.32	[64]
Nanosheets	Hydrothermal	7.51	[65]
Nanoflakes	Hydrothermal	4.5	[66]

Among the methods in Table 5, the TiO_2 nanostructures were usually grown by hydrothermal method. This method was used to grow TiO_2 nanoflowers, nanorods, nanowires, nanosheets, nanoflakes and to get highly crystalline [39]. The hydrothermal method was a powerful to synthesis of inorganic nanocrystal and high crystallinity without post synthetic annealing. Meanwhile, this method results the highest power conversion efficiency than the other methods. The hydrothermal method has a low temperature and simple to produce photoanode in DSSCs application. This method has also fast diffusion process reactions compared to the other methods. Besides the hydrothermal method, electrochemical anodization method was also used to grow TiO_2 nanotubes due to high power conversion efficiency in DSSCs application.

Besides TiO_2, the ZnO was also used as photoanode due to wide band gap energy [5] and higher electron mobility than TiO_2 [67]. The ZnO presented superior electron mobility that enabled faster transport of photo injection electrons [69]. However, the power conversion efficiency of ZnO still lower compared to the TiO_2 [16]. Therefore, the researchers were suggested to improve the ZnO metal oxides properties that was used to increase the power conversion efficiency in DSSCs performance. The overall power conversion efficiency of ZnO can be improved by increasing the dye capacity and decreasing the recombination effect in the cell. The ZnO nanostructures were fabricated to improve power conversion efficiency and light harvesting of the cell. Various morphologies and performances of ZnO as photoanode in DSSCs application were shown in Table 6. The structures such as nanorods, nanotubes and nanowires were usually used in photovoltaic cells due to photoactive materials as well as electrodes.

Among the other methods to grow ZnO nanostructures as shown in the table 6, the solvothermal has the highest power conversion efficiency than the others. This method was used to grow ZnO nanorods and nanoflakes structures. Moreover, the solvothermal method has low temperature, simplicity, high purity and good homogenecity [69]. Meanwhile, the sol-gel immersion method was also used to prepare of metal oxide structures and film coatings. Usually, this method also to grow aligned ZnO nanorods thin film on a glass substrate. Sol-gel immersion has high quality of aligned ZnO nanorods. This method was started with preparing the solution by a sonicated sol-gel and immersion method to grow ZnO nanorods [70]. Moreover, this method has low cost production, simplicity, capability to control the growth of ZnO nanorods and low temperature deposition process.

Table 6. Various morphologies and performances of ZnO as photoanode in DSSCs application

Morphology	Method	η (%)	References
Nanowires	Hydrothermal	5.7	[71]
Nanorods	Solvothermal	5.2	[72]
	Sol-gel Immersion	0.59	[73]
	Hydrothermal	0.22	[74]
Nanosheets	CBD (Chemical Bath Deposition)	5.16	[75]
Nanoflakes	Solvothermal	3.64	[76]
Nanoflowers	Hydrothermal	3.0	[77]

The hydrothermal method was also used to grow ZnO nanorods, nanowires and nanoflowers. The hydrothermal method has low temperature and simplicity. However, this method required a long time in order to get a good crystallinity and low efficiency than solvothermal method when used to grow ZnO nanorods. Then, the chemical etching method was used to grow ZnO nanotubes that has a low temperature, good electrical properties but low power conversion efficiency in DSSCs application. Meanwhile, the ZnO nanosheets were grown by CBD method. The CBD method has advantages such as simple to fabricate, low cost, low evaporation temperature and high power conversion efficiency in DSSCs.

Based on types of morphologies, the ZnO nanorods showed the higher power conversion efficiency than ZnO nanoparticles that grown by solvothermal method [79]. The ZnO nanorods used as photoanode due to good performance in DSSCs application that provide a better electron transport [59]. The ZnO nanorods usually grown on seeded catalyst that used to reduce the thermodynamic barrier [78]. The materials were usually used as seeded catalyst such as aluminium (Al) [79], magnesium (Mg) [7], magnesium oxide (MgO) [80], silicon dioxide (SiO_2) and aurum (Au) [81].

Hence, the presence of seeded catalyst has benefit to reduce the lattice mismatched effect during the growth of ZnO nanostructures on Si or FTO substrate by sol-gel immersion method. Seeded catalyst was influenced by speed up the rate of chemical reaction during the synthesis process. Meanwhile, the seeded catalyst used as the growth of ZnO nanorods [82]. Among the seeded catalyst materials, Mg showed a good seeded catalyst for growth of ZnO nanorods. The Mg used as seeded catalyst due to has almost similar ionic radii of Mg^{2+} (0.72 Å) and Zn^{2+} (0.74 Å) that was believed to give less lattice distortion when Zn^{2+} was replaced with Mg^{2+} [83].

The ZnO nanowires have type like ‘nanoforest’ that have high density, long branched ‘treelike’ hierarchical by hydrothermal method. The branch network of crystalline ZnO nanowires can increase the electron diffusion and enhance rate of electrons transportation [16]. The ZnO nanowires has power conversion efficiency of ~5.7% that were grown by hydrothermal method [71]. The superior performance of DSSCs was affected by a better light scattering, adequate dye loading and good electron transport [14].

Beside of TiO_2 and ZnO, bilayer Zn-doped TiO_2 was also used as photoanode in DSSCs application. The Zn on TiO_2 layer in photoanode used to change the existing crystalline phases as well as degree of crystallinity, morphology, distribution and particle size. Meanwhile, the Zn can enhance photo-catalytic activity of TiO_2 [84]. The synthesis of

bilayer Zn-doped TiO_2 with Zn over TiO_2 layer was fabricated by hydrothermal method [85]. The bilayer Zn-doped TiO_2 has the lower density and good for efficient electron in photoanode. The Zn on TiO_2 layer can improve the performance of DSSCs that showed the higher power conversion efficiency (~8%) than mono-layer TiO_2 [86]. Bilayer structures consisted of an over and under layer that were used light scattering for boosting the optical absorption of photoanode [16]. Consequently, the more light can be absorbed and the electron-hole pair injections were occurred.

3. Photo-sensitizer

In DSSCs, dye was used as photo-sensitizer on the surface of photoanode. Dye molecules adsorbed light photons in visible region and near infrared region of solar spectra. Meanwhile, the dye created photo-excitation electrons due to the presence of sun light. Afterwards, the photo-excitation electrons were injected into the conduction band of the semiconducting metal oxides that dye can rapidly regenerate over electron donation from the liquid electrolyte [14]. The dye has properties such as photo-stable, stable chemically, thermally and does not forms aggregates [87]. Moreover, the dye must has efficient electron injection into the conduction band of the semiconductor and strong adsorption onto the semiconductor surface [32]. Actually, the dye has three categories: inorganic, organic and natural dyes.

The dye ruthenium based inorganic (e.g. N3, N719, Z907 and black dye) was used as photo-sensitizer that has a high power conversion efficiency around of 10-11% [88]. However, this inorganic dye has a high cost. Meanwhile, the organic dyes were also used as photo-sensitizer in DSSCs application. The green porphyrin was used as organic dye sensitizer in the aryl group and as an electron donor that malonic acid groups acted as an acceptor [89]. Based on the other researchers, dyes have an electron donor-acceptor that were used to make ease in charge transfer and power conversion efficiency up to ~12.5% [90]. Actually, the organic dyes were cheaper, more environmental friendliness than inorganic dyes and good performance as sensitizers in DSSCs application, but narrow absorption spectra [87].

Besides synthetic inorganic and organic dyes, natural dyes were also used as a photo-sensitizer in DSSCs application. The natural dyes (e.g. carotenoid, betalain, chlorophyll and anthocyanin) were extracted from flowers, fruits and leaves that were used as photo-sensitizer [91]. The natural dyes were easily extracted, readily available, no need further purification, low cost production and environmental friendly [2]. Usually, natural dyes have a high efficiency up to ~0.56% with high stability [92]. Compare to the other dyes, inorganic dyes were selected as photo-sensitizer due to its high power conversion efficiency than organic and natural dyes in DSSCs application.

4. Electrolyte

The electrolyte in DSSCs acted as a medium to transfer electrons from the CE to the oxidized dye and also regenerated the oxidized dye. Based on their physical state, the electrolytes can be classified mainly into three categories namely liquid, quasi-solid and solid electrolyte.

4.1 Liquid electrolyte

The types of liquid electrolyte were redox couple, organic solvent and additives. However, the iodide/tri-iodide (I^-/I_3^-) redox couple system was mostly studied and developed in DSSCs application [17]. The redox couple was made by mixing parts of chemical species in different oxidation states that can oxidize the agent in an electrochemical reaction. The good properties of redox electrolytes must have ionic mobility, solubility of a redox couple, driving force for the dye regeneration, fast electron transfer kinetics [17], high conductivity, relative high stability, not cause desorption of the dye from the photoanode, low cost and easy preparation [87]. Meanwhile, the significant characteristics of electrolyte were stability and efficiency in DSSCs performance [92]. Commonly, the iodide/tri-iodide (I^-/I_3^-) redox couple was used as electrolyte due to have a better performance in DSSCs application. The iodide/tri-iodide (I^-/I_3^-) electrolyte has advantages in kinetic properties, such as fast oxidation of I^- at the photoanode/electrolyte for efficient dye regeneration and slow reduction of I_3^- at the electrolyte/CE interface for high carrier collection [92].

The I^-/I_3^- electrolyte has drawbacks such as the absorption of visible light at 430 nm and corrosion of the metal CE (e.g. Pt, and Au) [93]. Then, the power conversion efficiency of I^-/I_3^- electrolyte around ~11% in DSSCs application [94]. The concentration of I^-/I_3^- redox couple has a key role in DSSCs performance. The low iodine concentration will difficult to maintain sufficient electrolyte conductivity and rapid redox reaction. Meanwhile, the high iodine concentration, electron recombination at the semiconducting metal oxide interface will decrease the performance of DSSCs and redox couple will increase the rate of light absorption [95]. The major drawback of I^-/I_3^- redox couple was the higher driving force for reduction of the dye [87].

Then, the organic solvent (e.g. acetonitrile, 3-methoxy propionitrile, ethylene carbonate) not used in DSSCs application due to have a low viscosity, high dielectric constant and optimum donor number (14-20) of solvents [96]. Moreover, the additives were used as electrolyte and to adsorb on titanium surface (semiconducting metal oxide). It served as a barrier to the recombination reaction between the injected electrons in the metal oxide semiconductor [97].

4.2 Quasi–solid electrolyte

Besides on liquid electrolytes, quasi-solid electrolytes and solid-state electrolytes were also used in DSSCs application. The quasi-solid electrolyte such as ionic liquid (e.g. bis (imidazolium), 1-propargyl-3-methylimidazolium) iodides and polymer gel (e. g. polyvinyl acetate and poly (ethylene oxide)) contained redox couple. The couple redox was used as quasi-solid electrolyte to overcome the problems and volatile of liquid electrolyte [98]. The power conversion efficiency of DSSCs used quasi-solid electrolyte around 8-9% [98]. However, the quasi-solid electrolyte has thermodynamic instability under high temperature, still suffer from solvent leakage and also require sealing when were used in high environment temperature [97].

4.3 Solid state electrolyte

Solid state electrolyte has various hole transporting materials that was investigated as a hole acceptors to replace liquid electrolytes [97]. Moreover, solid state electrolyte has a better mechanical stability and simply fabrication process. The power conversion efficiency of solid-state electrolyte ~5% in DSSCs application. However, the solid state electrolyte has a high recombination reaction, low conductivity and ineffective contact with the CE [99].

5. Counter Electrode

The CE was one of the important components in DSSCs application. The main tasks of CE were (a) to regulate the DSSCs by catalysing the reduction of the iodide-tri-iodide redox species and as a mediator to generate the dye sensitizer after electron injection, or (b) to collect the hole from the transport materials in a solid state of DSSCs [100]. The ideal CE materials must have a low sheet resistance, low cost, good chemical stability, high electrical conductivity to charge transport and good electro-catalytic activity to reduce the redox couple [93, 101].

The metal Pt was popular catalyst as CE material in DSSCs application. The Pt has a high electro-catalytic activity to the reduction of redox couples in liquid electrolytes, highly transparent, high power conversion efficiency [102] and high electrical conductivity. The Pt catalyst was used as CE due to can help in regeneration of I^- from I_3^- and collect of electron from the external load to the electrolyte [100]. However, Pt was expensive metal, diminishing supply and corrosion in liquid electrolyte. Recently, much effort has been made to reduce or replace Pt-base electrodes as CE in DSSCs application [16]. Consequently, other materials such as carbon, CNTs, graphene and conducting polymers have been also used as CE materials [103–104]. Carbonaceous were used to replace Pt as CE in DSSCS due to inexpensive and readily available.

5.1 Carbon

Carbon was mainly produced by incomplete combustion in industry. It was a promising material for CE due to has a high electrical conductivity, low cost, high surface area and high electro-catalytic activity towards the I^-/I_3^- redox species [105]. Meanwhile, carbon has also high crystallinity favourable. The thickness of carbon layer on the substrate was important due to affect the catalysis and resistance of material. Carbon has a power conversion efficiency up to ~6.97% by thermal deposition method in DSSCs application [106].

5.2 Carbon nanotubes

The CNTs were actually a carbon and successfully attract the attention of researcher community in 1991. The CNTs have three structures due to their number of roll walls such as single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs) and double-walled carbon nanotube (DWCNTs). The CNTs have chemical stability, high electrical conductivity, mechanical properties and thermal conductivity [15]. The structure of SWCNTs and MWCNTs were usually used as CE in DSSCs application. The MWCNTs

have efficiency of ~4.2% by using electrochemical deposition method, good electro-catalytic activity and higher surface area than Pt [107]

5.3 Graphene

Graphene has been extensively explored to replace noble metal (Pt) as CE. Graphene has become the main research h object for the last few decades due to its outstanding properties. It has high thermal and electrical conductivity [108-109]. Meanwhile, graphene has high surface area around of $2630\ m^2g^{-1}$ that the higher than CNTs and decrease the charge transfer resistance [110]. Graphene has also high chemical and mechanical robustness [111]. Meanwhile, graphene has a low-cost production, simple preparation, high optical transparency, good electro-catalytic activity, environmental friendliness. Graphene has been intensively used as CE and yielded high-performance in DSSCs application [137].

In addition to photovoltaic, graphene has been also recognized in other application such as electronics and energy storage devices [113]. Actually, graphene has similar characteristics with CNTs. Graphene can be applied to DSSCs, fuel cells, supercapasitor and chemical sensor devices. Meanwhile, graphene as a new material for CE and has a high power conversion efficiency of ~8.03% was successfully fabricated by using spin coating method [112]. Whereas, the power conversion efficiency used Pt as CE of ~5.09% in DSSCs application [104]. These results showed that the graphene higher power conversion efficiency than Pt for CE in DSSCs application.

Graphene has nanosheets and nanoplatelets structure as CE in DSSCs application. However, graphene nanosheets were usually used as CE. The graphene nanosheets were prepared from graphite by oxidation-reduction. The graphene oxide (GO) can be synthesized by electrochemical exfoliation method [7]. Commonly, this method was assisted by surfactant. The commercial sodium dodecyl sulphate (SDS), sodium dodecylbenzene sulphonate (SDBS), poly (sodium 4-styrenesulfonate) (PSS) and custom-made surfactant used was sodium 1, 4-bis (neopentyloxy)-3-(neopentyloxycarbonyl)-1, 4-dioxobutane-2-silphonate (TC14) can be used as surfactant in this method. However, the commercial SDS and custom-made TC14 surfactants were used to assist during the electrochemical exfoliation method [15]. This method consumes a less chemicals and suitable to produce graphene flakes due to simple preparation, low cost production and low temperature [7]. Hence, the electrochemical exfoliation method was the most efficient method to produce GO.

Meanwhile, hummers method was also used to produce GO [114]. Hummers method gained intensive attention due to has a high efficiency, safety reaction and short reaction time [115]. However, this method was included non-cost effective due to high consumption of strong acids, high defects level on the sample and difficult to control the thickness of graphene sheets. Besides electrochemical exfoliation and hummers method, GO can be also produced by chemical vapour deposition (CVD) [116]. This CVD method can produce a low defect graphene on substrate that used argon as the carrier gas in the chamber. However, this method used a high temperature to oxidize graphite that caused less efficient and high energy consumption. Nowadays, this method was rarely used to produce graphene.

In addition, hydrazine hydrate was used as reducing agent to produce reduced graphene oxide (rGO) from GO by using reduction process. The reduction process was used to reduce

the oxygen content in GO solution. The rGO showed a better electro-catalytic activity than the GO [117]. The rGO was attractive and unique due to has a capability to produce single-layer graphene and low cost production. Commonly, the transfer process of GO and rGO to fabricate thin film was prepared by using spray deposition method.

Spray deposition method was used due to low cost, fast and simple to fabricate highly conductive films for electronic device applications [7]. Prior spray process, solution was sonicated (commercial SDS and custom-made TC14 surfactants) for 5 mins. Then, GO and rGO were sprayed onto preheated substrates (e. g. FTO, Si) at 120˚C by using an airbrush with pressure of ~40 psi [118]. The distance of nozzle and substrates around ~10 cm, and spray time will affect to the thickness of film.

Meanwhile, graphene thin film can be fabricated as CE by using dip coating method. The substrate was dipped into solution and withdrawn at a constant speed. Alcohols were usually used as solvents due to have low surface tension and relatively fast evaporation. The balance of thickness depended on the density, viscosity and the surface tension of the fluid. The dip coating method was potentially used due to low cost and less equipment required. Besides of spray and dip coating method, sputtering method was also used to fabricate graphene thin film as CE. Plasma was generated between substrate and target of the material that was used to deposit thin film. In this method, substrate was placed as the anode and target as the cathode that was emitted atoms to the surface substrate under vacuum condition [119].

5.4 Polymer materials

Conducting polymers were spectacular materials as CE in DSSCs application. Conducting polymer was used to replace Pt [100]. The conducting polymer like PEDOT was preferred as CE due to have electrochemical activity, transparency and high stability [120]. PEDOT as CE has power conversion efficiency of ~4.99% by polymerization method that has high electrical conductivity to improve performance in DSSCs application [120].

6. Operational Principle of Dye Sensitized Solar Cells

Photovoltaic devices have two important steps to convert sunlight into electrical energy: (1) radiation absorption with electron excitation, (2) charge carrier's separation. The dye molecules under exposure of sunlight became photo-excitation and injection electrons into the conduction band of the semiconducting metal oxide. The configuration of dye will be regenerated by electron donation from the electrolyte. Electrolyte regenerates the dye by recombination of photo-excitation electrons that flow into the photoanode. Then, the electrolyte was regenerated at the CE when the circuit was completed by an external load.

CONCLUSIONS

The power conversion efficiency has important role in DSSCs application. The present review was given explanation about the good materials that can be used as photoanode and CE in DSSCs. The good properties of photoanode materials supposedly have a high surface area for sufficient dye adsorption, highly porous for effective mass transport by diffusion, high electron mobility for efficient electron transport and to be transparent to visible light for minimizing the loss of incident photon. The TiO_2 was used as photoanode materials due

to has the highest power conversion efficiency than the other semiconductor materials. However, the TiO_2 has low electron mobility. Besides of TiO_2, the ZnO was also used as photoanode due to have a higher electron mobility than TiO_2. However, ZnO has a low power conversion efficiency in DSSCs application.

The ZnO and TiO_2 have the similar band gap (>3eV). Hence, bilayer Zn on TiO_2 layer was used as photoanode in DSSCs application. The Zn on TiO_2 layer was used to change the existing crystalline phases as well as degree of crystallinity, morphology, distribution and particle size. Meanwhile, Zn can enhance the photo-catalytic activity of TiO_2. The synthesis of Zn-doped TiO_2 used hydrothermal method. The Zn-doped TiO_2 has the lower density that good for efficient electron in DSSCs performance. The Zn on TiO_2 layer can improve the power conversion efficiency. This bilayer has a power conversion efficiency of ~8% which the higher than mono-layer of TiO_2. Bilayer structures consisted of an over and under layer that were used by light scattering for boosting the optical absorption of photoanode. Consequently, the more light absorbed and electron-hole pair injections were occurred.

Meanwhile, an excellent photoanode material supposedly has a low sheet resistance, low cost, good chemical stability, high electrical conductivity to charge transport, high reflecting properties, good electro-catalytic activity to reduce the redox couple and excellent stability. The metal Pt was popular catalyst as CE materials due to high electro-catalytic activity to the reduction of redox couples in liquid electrolytes, highly transparent and high power conversion efficiency. However, Pt was highly cost, diminishing supply and corrosion in liquid electrolyte. Consequently, other materials such as carbon, CNTs, graphene and conducting polymers have been also used as CE materials. Carbonaceous were used to replace Pt as CE in DSSCS due to inexpensive and readily available.

Meanwhile, graphene has been extensively explored to replace noble metal such as Pt as CE due to low cost, simple preparation, good electro-catalytic activity, high transparency, high electrical conductivity, high thermal stability, environmental friendliness, chemical and mechanical robustness and high surface area. Graphene has been intensively used as CE that has yielded high-performance of DSSCs. Graphene as CE has power conversion efficiency of ~5.09% and same goes with Pt, while used as CE has efficiency of ~5.09% in DSSCs application. Therefore, graphene well-known has a high power conversion efficiency and Pt as well. Then, the GO can be synthesized by using electrochemical exfoliation method. Afterward, the hydrazine hydrate was used as reducing agent to produce rGO from GO by reduction process. The reduction process was used to reduce the oxygen content in GO solution. The rGO showed the better electro-catalytic activity than the original GO.

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