Development in Photoanode Materials for High Efficiency Dye Sensitized Solar Cells

Stephanie Chai Tying Lau *, Jedol Dayou **, Coswald Stephen Sipaut*, Rachel Fran Mansa *‡

* Energy and Materials Research Group (EMRG), Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, MALAYSIA.

** Energy, Vibration and Sound Research Group (e-VIBS), Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, MALAYSIA

(slct88@gmail.com, jed@ums.edu.my, cssums@gmail.com, rfmansa@ums.edu.my)

‡ Corresponding Author; Rachel Fran Mansa, Tel: +60 88320000, Fax:+60 88320286, rfmansa@ums.edu.my

Received: 30.06.2014 Accepted:29.08.2014

Abstract- Dye-sensitized solar cells (DSSC) have been extensively studied due to their promising potential for high efficiency, low production cost and eco-friendly production. The photoanode is one of the main components in DSSCs which determines its performance. The main issues facing in DSSCs are the charge recombinations and low light harvesting capacity. Conventional TiO_2 nanoparticles with large surface area has low light scattering ability and low electron transport rate while one dimensional nanostructures have high electron transport rate and good light scattering ability but has a low surface area. Different approaches such as nanocomposite, light scattering layer and hierarchical structures to improve performance of 1D DSSCs are discussed. Besides that, works done on the optimization of TiO_2 photoanode in cobalt based DSSC is also discussed. Additionally, doping of TiO_2 to improve the properties of TiO_2 and studies on alternative photoanode materials which involved the application of band gap engineering are discussed to further improve the performance of DSSCs.

Keywords- Dye Sensitized Solar Cells; Photoanode; Charge recombination; Light harvesting.

1. Introduction

With the growing demand for sustainable energy sources, dye sensitized solar cells (DSSCs) have been intensively studied as potential alternatives for the next generation solar cells due to their low production cost, relatively high power conversion efficiency (PCE) and eco-friendly production when compared with silicon solar cells [1-4].

DSSC was first reported by Gratzel and coworkers in 1991[1]. Typically, DSSC comprised of a photoanode with sensitizer attached on the surface of the wide band gap semiconductor layer coated on transparent conductive glass (TCO), an iodine based redox-coupled electrolyte and a counter electrode of TCO coated with a platinum layer [1, 5, 6]. To date, a PCE up to 12% has been reported by using the cobalt electrolyte and porphyrin sensitized TiO_2 photoanode [7, 8].

The photoanode which is one of the main components in DSSCs, is usually fabricated using photoanode materials such as TiO_2 due to their large surface area to volume ratios [1, 7, 9]. However, the conversion efficiency of TiO_2 nanoparticles-based DSSCs was limited by the slow transportation of electrons through the randomly arranged nanoparticles as well as the energy losses caused by the recombination [10, 11].

In recent years, many attempts were made to overcome the limitations by improving or varying the structure and morphology as well as the surface properties of the photoanode materials. In this paper, we review the development of photoanode materials in the dye sensitized solar cells to improve the overall power conversion efficiency of the DSSC. The main findings and limitations of each approach are discussed for further development of high efficiency dye sensitized solar cell.

2. Operating Principle of DSSC

DSSCs works based on the photoinjection of electrons from sensitizer (Pathway 1, Figure 1) into the conduction band (E_c) of metal oxide semiconductor (Pathway 2, Figure 1) upon irradiation by sunlight. Subsequently, the excited sensitizer is reduced back to the ground state by electrons donation from the iodide/triiodide redox couples in the electrolyte (Pathway 3, Figure 1). Regeneration of iodide ions, which are oxidized to triiodide in this reaction is achieved by electrons transferred from the counter electrode (Pathway 4, Figure 1). The circuit is completed through the

external load. However, recombination reaction may occur during the process. The injected electrons in the conduction band of semiconductor can recombine with either the excited sensitizer or the oxidized form of the iodide electrolyte as shown in fig.1 (Pathway 5 and 6) [12].

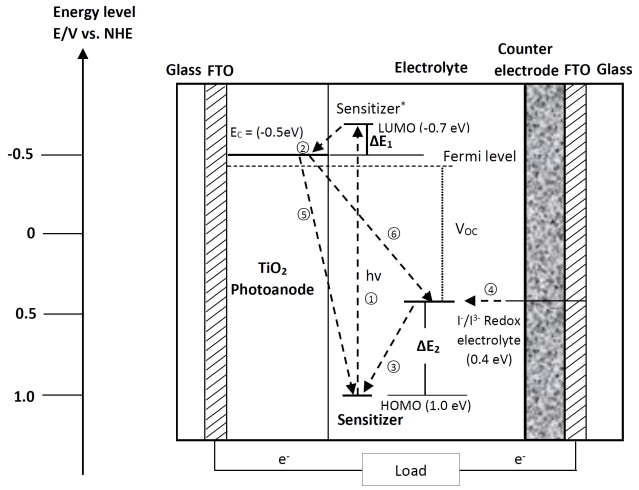

Fig. 1. Schematic energy diagram and operating principle of DSSC. Adapted from [Source: 13].

The performance of a DSSC depends on the energy levels of the component (sensitizer, photoanode and electrolyte) in DSSC. The energy difference between the highest occupied molecular orbital, HOMO and the lowest unoccupied molecular orbital, LUMO of the sensitizer (ΔE_1) will determine the amount of photocurrent obtained in DSSC. The maximum open circuit voltage of DSSC, on the other hand depends on the energy difference between the Fermi level (maximum energy that any electron may possess at absolute zero temperature) [14] and electrolyte redox potential (ΔE_2). For efficient electron injection, the energy level of the LUMO must be sufficiently high (i.e., >0.2 eV) in energy (moving upward in the energy level axis) with respect to the E_c of photoanode. The HOMO level of the sensitizer must be sufficiently low in energy (moving downward in the energy level axis) than the redox potential of the I^-/I_3^- redox electrolyte for efficient regeneration of oxidized dye [13].

The conversion efficiency of the solar cell, η is determined by its current–voltage characteristics, specifically the open-circuit photovoltage (V_{oc}), the photogenerated current density measured under short-circuit conditions (J_{sc}), light irradiance (I_o) and the fill factor of the cell (FF), which depends on the series resistances and on the shunt resistances in the cell [15]. The short-circuit photocurrent (J_{sc}) is essentially related to the amount of sunlight harvested in the visible part of the solar spectrum by the sensitizer. The open-circuit voltage (V_{oc}) is related to the energy difference between the quasi-Fermi level of electrons in the semiconductor and the chemical potential of the redox mediator in the electrolyte. The related equation under standard illumination is shown in equation (1) [15-17].

$$\eta = (J_{sc} \times V_{oc} \times FF)/I_o \quad (1)$$

3. Photoanode Materials in DSSCs

In general, a photoanode material is composed of metal oxide semiconductor which has high surface area for sufficient dye adsorption, highly porous for effective mass transport by diffusion and a suitable band gap that matches with the sensitizer for effective electron injection and fast electron transport. The combined improvements in this factor contribute to a higher charge-collection efficiency [18-22].

Wide band gap metal oxide semiconductor (E_g > 3eV) such as TiO_2, ZnO, SnO_2 and Nb_2O_5 have been commonly used as photoanode materials due to their good stability against photocorrosion (transparent to the major part of the solar spectrum) and good electronic properties [23-26]. Photocorrosion which caused by the oxidation of holes (generated through band gap excitation) with the redox electrolytes may affect the performance of the semiconductor.

The efficiency of the DSSCs fabricated with various photoanode materials is shown in Table 1. At present, TiO_2 nanoparticle which gives the highest recorded efficiencies (12.3 %) has been to be the best photoanode material in DSSCs [7, 27]. Moreover, TiO_2 is a low cost, widely available, non-toxic and biocompatible material. It has been used in health care products as well as domestic applications such as paint pigmentation [28].

On the other hand, ZnO which has a similar conduction band edge and working function as TiO_2, but with the higher carrier mobility than TiO_2 was considered as a promising photoanode of DSSCs. However, the instability of ZnO in the acidic environment and formation of dye aggregates deteriorates its performance [29]. Some other semiconductor materials, such as Zn_2SnO_4 [30], WO_3 [31], $SrTiO_3$ [32], have been applied to the electrodes for DSCs. However, the efficiency of these DSCs still cannot compete with TiO_2-based DSCs.

Table 1. Comparison in performance of DSSCs with different photoanode materials

Photoanode material	Band gap	η (%)	Reference
TiO_2	3.23	12.3	[7]
ZnO	3.3	5.60	[29]
Nb_2O_5	3.49	5.00	[25]
Zn_2SnO_4	3.7	3.70	[30]
$SrTiO_3$	3.2	1.80	[32]
WO_3	2.6-3.0	0.75	[31]
SnO_2	3.6	0.30	[33]

Typically, TiO_2 exists in three crystalline forms which are rutile with energy band, E_g of 3.05 eV, anatase with E_g of 3.23 eV and brookite with E_g of 3.26 eV. The anatase TiO_2 provides a higher surface area for dye loading and a higher electron diffusion coefficient than the rutile nanoparticle photoanode. However, brookite is difficult to produce and is therefore not considered in the DSSC application [34, 35]. Therefore, the anatase TiO_2 nanoparticle is widely used as the main component of the photoanode in DSSCs.

4. The Main Issues Affecting the Performance of TiO_2 based DSSC

Conventional TiO_2 photoanode film usually exhibits high transparency and weak light scattering due to the nanometer particle size, resulting in poor light-harvesting efficiency (LHE). Furthermore, the slow electron transport rate and low electron mobility of TiO_2 nanoparticles also leads to charge recombination in TiO_2 based DSSC. Recently, mass transport issues which causing charge recombination in cobalt electrolyte based DSSC has been raised up. TiO_2 photoanode film prepared in conventional method is no longer suitable for cobalt based DSSC which reported highest PCE recently[7]. In this section, issues on light harvesting efficiency and charge recombination in TiO_2 based DSSC are discussed.

4.1 Light Harvesting Efficiency

As discussed in Section 3, conventional TiO_2 nanoparticles (10-20nm) which has high specific surface area (50 -100 m^2/g) has been used in most DSSC. However, TiO_2 nanoparticles which has large surface area usually have low light-scattering ability. The particle size (20nm) which is smaller than the wavelength of visible light (400 nm) allows transmittance of most of the visible light before being absorbed by the photosensitizer. This may lead to low light harvesting efficiency [36, 37].

To tackle this issue, the concept of the bilayer structure with a scattering layer made of TiO_2 large particle with several hundred nanometers in size as the overlayer has been proposed. This bilayer structure could enhance the LHE by confining the incident light within the photoanode via scattering or diffracting it backward [38-41]. However, the introduction of such large particles would reduce the dye-loading capacity of the photoanode due to the decrease of the specific surface area, and thus leading to the decrease of the photocurrent, to some extent. Thus, new multifunctional TiO_2 photoanode materials, offering both a good capability for light scattering and a high specific surface area for dye loading, should be synthesized for application to the DSSCs [41].

4.2. Charge Recombination

A conventional TiO_2 nanoparticle comes with numorous defects (usually located at the TiO_2/electrolyte interface, in the bulk of the TiO_2 particles, or at grain boundaries) and surface states (the energy states generated below the conduction band of TiO_2 nanoparticles) which limits the electron transportation. Figure 2 shows the electron transportation path in TiO_2 nanoparticles. As the electron diffused within the TiO_2 network via hopping mechanism, this defect in the TiO_2 nanoparticles and surface state will definitely serve as trap centers to retard electron transportation. Once the electron being trapped, it may undergo recombination reaction with the oxidized sensitizer or oxidized iodide in DSSC.

Surface treatment of TiO_2 nanoparticles such as $TiCl_4$ treatment (formed a thin blocking layer on the photoanode surface) and TiO_2 core shell structure (additional energy barrier layer coated on surface of TiO_2 nanoparticle) was often performed to suppress charge recombination and facilitate charge transport [34, 42-45] .

Besides that, one dimensional (1D) nanostructures such as nanowires, nanotube and nanorods which has excellent electron transport and light scattering ability have been studied as photoanode materials in DSSC to reduce charge recombination [46-48]. However, DSSC with this configuration shows lower efficiency (9%) compared to the TiO_2 nanoparticle film (12%) due to its low internal surface area leads to insufficient dye adsorption, and therefore low LHE. Table 2 shows the performance of TiO_2 1D nanostructures compared to the conventional TiO_2 nanoparticle. Until now, it is still remain challenge to improve the electron transport and light scattering abilities without sacrificing its internal surface area.

Table 2. Performance of TiO_2 1D nanostructures based on highest efficiency

1D nanostructures	Efficiency, %	References
TiO_2 nanowire	9.33	[49]
TiO_2 nanorod	9.00	[50]
TiO_2-nanotube arrays	9.1	[51]
TiO_2 nanoparticle	12.3	[7]

Apart from that, DSSC based on cobalt electrolyte which had achieved higher PCE compared to the iodide based DSSC also suffered from recombination issues. The photovoltaic performance of DSSC based on electrolytes consisting cobalt complexes is constrained by mass transport limitations of the mediator. In this case, the thickness and the porosity of the photoanode was found to be very crucial. Conventional TiO_2 nanoparticles with pore size of 20 nm allows effective mass transport and electrolyte penetration in iodide based DSSC but not in the case of cobalt based DSSC. This increases the risk of charge recombination. Thus, TiO_2 film porosity should be optimized to enhance the performance of cobalt based DSSC.

5. Development of TiO_2 Morphology in High Efficiency DSSC

As has been discussed before, the main issues facing in conventional TiO_2 nanoparticles based DSSC are high charge recombination and low LHE. Introduction of light scattering layer of large TiO_2 particles increase the LHE but also reduce the surface area for dye loading. 1D TiO_2 nanostructures has excellent electron transport to reduce charge recombination and light scattering abilities for excellent LHE. However, its performance was limited by the low surface area causing poor dye loading. Thus, a photoanode materials with high surface area, fast electron transport and good light scattering ability is needed for high efficiency DSSC.

Recent development in TiO_2 photoanode materials focused on solving surface area limitations in 1D nanostructures by introducing nanocomposite and hierarchical structures in DSSC. Besides that, alternative scattering layer which include various nanoctructures has been studied to substitute the conventional large particle

TiO_2 scattering layer. Therefore, in this section, development in TiO_2 photoanode materials which is divided into nanocomposite, hierarcical structure and light scattering layer will be discussed. Besides that, works done in optimizing TiO_2 photoanode for application in cobalt based DSSC.

5.1. Nanocomposite

As discussed in Section 4.1, 1D TiO_2 nanostructures suffer from low internal surface area which caused the poor dye loading and thereby lower performance compare to the TiO_2 nanoparticle films. Mixing one-dimensional materials with the nanoparticles has been a successful approach in improving the surface area for dye loading and thus, device performance [52, 53]. Besides that, highly electrically conductive carbon materials, such as carbon nanotubes (CNTs) [58], and graphene [54] was incorporated into TiO_2 to improve the charge collection efficiency [55]. Table 3 shows the performance of TiO_2 nanocomposite with different materials.

Table 3. Performance of TiO_2 nanocomposite (NC) in DSSC

Nanomaterial/nanoparticle (NP)	Efficiency (%) of NC/NP	References
TiO_2 nanotube/2% NP	8.43/5.01	[56]
TiO_2 nanorod/NP	7.12/5.82	[57]
TiO_2 nanowire/NP	3.8/2.45	[58]
0.025%wt MWCNT/TiO_2 NP	10.29/6.31	[18]
1%wt graphene/ TiO_2 NP	6.86/5.98	[54]

From Table 3, the blending and mixing of 1D nanostructures with nanoparticles showed an improved efficiency compared to the bare TiO_2 nanoparticles. TiO_2-MWCNT (Multiwall Carbon Nanotube) nanocomposite shows the highest efficiency of 10.29% and highest increment due to the unique electrical properties of CNT. CNT not only have a large electrons-storage capacity, but also show electronic conductivity similar to that of metals. Besides that, incorporation of graphene into the TiO_2 matrix also enhance electron transport while reduce charge recombination. However, recombination reaction may happen in this monolayer structure which affects the performance. Furthermore, single layer film cannot harvest light well due to its shorter electron path.

5.2 Light Scattering Layer

In order to improve light scattering and dye loading simultaneously, bilayer structure with one dimensional material overlayer has been proposed to replace the conventional TiO_2 large particles scattering layer which has low dye loading ability together with TiO_2 nanoparticles as the under-layer [59, 60]. Table 4 shows the effect of light scattering overlayer on the performance of double layer DSSCs.

Table 4. Effect of light scattering overlayer on the performance of double layer DSSCs

Light Scattering layer (SC)	Underlayer	Jsc ($mAcm^{-2}$) with SC (without SC)	η (%) with SC (without SC)	Reference
Hollow spherical TiO2	TiO_2 Nanoparticle	15.8(12.5)	9.43(7.79)	[36]
400 nm-sized TiO2	TiO_2 Nanoparticle	14.6(12.5)	8.96(7.79)	[36]
TiO_2 beads	TiO_2 Nanoparticle	15.47(13.25)	8.84(7.38)	[61]
400-nm TiO_2	TiO_2 Nanoparticle	14.56(13.25)	7.87(7.38)	[61]

From Table 4, the highest conversion efficiency of 9.43% was being achieved after hollow spherical TiO_2 was introduced as the scattering layer. When comparing the photovoltaic performance of hollow spherical TiO_2 overlayer and 400 nm-diameter TiO_2 overlayer, hollow spherical TiO_2 overlayer shows a higher J_{SC}. The TiO_2 hollow spherical particles are believed to be able to adsorb dye efficiently and has good light scattering ability compared to the commonly used which only provide light scattering ability.

Besides that, DSSC prepared with the beads as a scattering layer have also shown similar result. This shows that bilayer structured photoanodes with nanocrystalline aggregates as light-scattering particles is a promising approach to enhance the efficiency of DSSCs. However, the increase in thickness with the use of multilayer structure films may lead to the higher recombination rate.

5.3 Hierarchical Structrures

Hierarchical structures such as spherical, quasi-1D or 1D micro/nanoscale aggregates that could function as light scattering centers without sacrificing the internal surface and exhibit better electron transport properties has attracted much interest [62]. Hierarchically structured materials usually consists of assemblies of small building blocks, such as nanoparticles, nanorods, nanowires, nanoplates, etc which is small in size so that high surface area can be retained in the new photoanode film, leading to a high load of the dye molecules [12]. Table 5 shows the performance of different nanostructured TiO_2 electrodes in DSSCs.

Table 5. Performance of different nanostructured TiO_2 electrodes in DSSCs

Hierarchical Structure	Assemble by	Efficiency (Hierarchical)	Efficiency (NP)	Reference
TiO_2 sphere	nanorods and nanoparticles	10.34	8.10	[63]
Yolk –shell TiO_2 beads	TiO_2 nanoparticle	9.05	7.56	[64]
nanoporous TiO_2 spheres	TiO_2 nanoparticles	8.44	7.30	[65]

From the table, we have demonstrated that the photoanode derived from spherical nanoparticle aggregates could generate efficiencies comparable to or even higher than those made with TiO_2 nanoparticles due to their ability to generate effective light scattering without sacrificing internal surface area, the facilitation of electrolyte diffusion through the relatively open structure and the improvement of electron transport resulting from compact interconnection of nanoparticles.

As shown in the table, DSSC with TiO_2 sphere assemble by the nanorods and nanoparticle achieved highest increment compared to the other spherical TiO_2 assemble by TiO_2 nanoparticles. This may due to its superior light scattering ability which contributed to the increase in the light harvesting efficiency. However, its poor contact with the FTO glass which leaves large uncovered space on FTO glass may lead to a higher interface resistance. Therefore, to obtain a higher efficiency, combination of hierarchical structure layer and nanoparticles which has good contact with FTO glass within one film electrode is a promising approach.

5.4 Optimization of TiO_2 Photoanode Materials for Cobalt Based DSSC

Recently, efficiencies of up to 12.3% have been obtained in DSSC employing cobalt based electrolyte [7]. However, optimization of conventional TiO_2 is pivotal to achieve high performance in cobalt based DSSC. Previous investigations have suggested that the performance of cobalt redox mediators in DSCs is limited by rapid recombination from electrons in the TiO_2 conduction band to the cobalt(III) species and mass transport problems in the mesoporous TiO_2 electrode [66, 67].

To retard the fast recombination between TiO_2 conduction band electrons and the oxidized species of the cobalt(III/II) electrolyte, blocking layer has been incorporated on the TiO_2 surface[66, 68]. Cobalt complexes are bulky and therefore need sufficiently large pores to avoid mass transport limitations in TiO_2 based DSSC [7]. A mixed TiO_2 macroporous–mesoporous morphology has been introduced to assist the diffusion of cobalt electrolyte [69]. Yella and coworkers (2013) manage to solve the mass transport issues in cobalt based DSSC by increasing TiO_2 pore size (from 23 nm to 32 nm) and reducing thickness of TiO_2 film [7].

6. Band Gap Engineering to Improve Performance of Photoanode Materials

As discussed from Section 4.2, oxygen vacancy defects was found in the conventional TiO2 photoanode material. These defects trap the electrons, causing the recombination reaction to occur. To improve the performance of TiO_2 photoanode, it is necessary to tailor the band gap of TiO_2 so that the properties of TiO_2 can be improved. Another possible solution is to discover new photoanode materials to substitute TiO_2 nanoparticles. The band gap of semiconductors such as nanosilica (> 4 eV) can be tuned to be used in DSSC applications.

6.1 Doping to Tailor the Band Gap of Photoanode Materials

Recently, doping TiO_2 with metal or nonmetal ions has been considered as a promising way to improve the properties of TiO_2 photoanode. Doping could change the surface properties such as the band edge or surface states of TiO_2 [70]. The positive shift of conduction band (moving downward in y axis) results in an increased injection driving force of electrons which improve the electron injection efficiency from the LUMO of the dye to the TiO_2 conduction band. Fast electron transport can improve charge-collection efficiency and thus increase photocurrent density [71].

Metal doping such as Nb, Sn, Zn and W doped TiO_2 has been found to exhibit a positive shift in a conduction band edge which increase the electron injection efficiency and suppressed the carrier recombination [72, 73]. Doping of nonmetals such as nitrogen, carbon, sulfur, and fluorine also shifts the conduction band edge of TiO_2 and decreases the concentration of oxygen vacancy by replacing the oxygen atoms which reduce the trapping of electrons at the defect sites [74]. Figure 2 shows the positive shift of E_c with W doping. Performance of doped and undoped TiO_2 in DSSC was shown in Table 6.

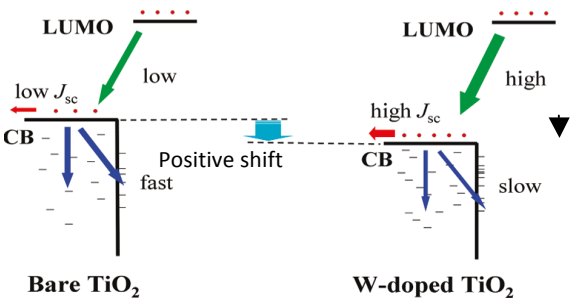

Fig. 2. Positive shift in E_c of TiO_2 with W doping increases the driving force for electron injection (increases in J_{sc}) and suppress recombination [Source:75].

Table 6. Performance of doped and undoped TiO_2 in DSSC

Photoanode materials	J_{SC} ($mAcm^{-2}$) (Doped/Undoped)	V_{oc} (V) (Doped/Undoped)	η (%) (Doped/Undoped)	Reference
W-doped TiO2	8.94/7.05	0.61/0.62	4.20/3.37	[75]
Sn-doped TiO_2	16.01/15.15	0.72/0.70	8.31/7.45	[76]
Nb-doped TiO_2	17.67/11.87	0.70/0.79	7.8/6.6	[77]
N-doped TiO2	11.56/9.35	0.68/0.68	6.25/5.08	[78]
F-doped TiO2	19.39/16.86	0.66/0.66	8.07/7.25	[79]

From Table 6 we can see that doping of TiO_2 improved the conversion efficiency of DSSC. Photocurrent, Jsc which depends on the driving force for electron injection, namely the difference between the conduction band and the LUMO is increased with the doping of TiO_2. However, the V_{oc} which is dependent on the difference between the E_c of TiO_2 and the redox potential of the redox couples electrolyte, is remain or slightly change with the doping of TiO_2 due to the positive shift in E_c. Although extensive studies have been made on doping TiO_2, none of which could both enhance the J_{SC} and V_{OC}.

6.2. Band Gap Modification in Developing New Oxide Semiconductor

It is well known that photoanode materials in DSSCs usually consists of wide band gap (> 3 eV) semiconductor oxide which is stable against photocorrosion. Besides that, the conduction band of semiconductor oxide must be lower than the LUMO level of sensitizer for efficient electron injection from sensitizer. Conventional TiO_2 nanoparticles with the band gap of 3.2 eV has fullfilled the requirement of photoanode materials. However, silica which has wide band gap of 8.9 eV will definitely have a higher conduction band edge than the excited state energy level of sensitizer. This may affect the working mechanism of a DSSC as the electron cannot be injected from sensitizer. Thus, narrowing band gap is needed in order to use it as a photoanode materials [80].

It has been reported that the band gap of a semiconductor material is a function of the particle size [81, 82]. According to Brus and coworkers [82], the density of defects or surface states of semiconductor oxide increases with the decrease in particle size below a certain threshold. These defects create deep and shallow traps near the band edge of its electronic state causing reduction in band gap, that is, red-shift in absorption spectrum [81, 82]. However, when the size of semiconductor particle decreases from its bulk to that of Bohr radius, the band gap of semiconductor material increases. This may due to the arising of size quantization effect [82]. Padavettan and coworkers (2009) studied on the effect of particle size on the band gap of synthesized nanosilica and found that the decrease in particle size from 400 nm to 7 nm, the band gap decreased from 6.03 to 5.89 eV [83]. Besides that, Yelil Arasi and coworkers (2013) also reported reduction in band gap (3 - 4 eV) with the nanosilica of 78 to 85 nm [84]. This shows a large reduction of band gap from the reported band gap of bulk silica (11 eV) [85]. Lin and coworkers (2006) also reported the similar result where the band gap of TiO_2 decreased from 3.239 to 3.173 eV when the particle size decreased from 29 to 17 nm [86].

From the above reported result, we can conclude that the band gap decreased (red shift) to a certain minimum value (critical size) with the decrease in particle size from its bulk particle. Further decrease in particle size from the critical size caused the band gap to increase (blue shift). Thus, band gap of semiconductor such as silica can be narrowed with the decrease in particle size from bulk to its critical size.

7. Conclusions and Summary

DSSCs have been extensively studied due to their promising potential for high efficiency, low production cost and eco-friendly production. However, recombination and light harvesting issues occurs in conventional TiO_2 nanoparticles limits its improvement in efficiency. Surface treatment such as $TiCl_4$ treatment and core shell structure is advantageous in retarding recombination. Hierarchical structures which consists of assemblies of nanoparticles or 1D nanoparticles is the most promising photoanode due to its excellent properties without compromising surface area of the particles. Mass transport limitation in cobalt based DSSC can be overcome by optimizing the pore size and thickness of TiO_2 photoanode. Meanwhile, band gap tailoring of TiO_2 and studies on alternative photoanode materials for future development of DSSCs can be done through band gap engineering to overcome the limits in TiO_2 nanoparticles. Thus, it is believed that with the above accomplishment, DSSCs will become one of the most promising solar devices in next generation.

Acknowledgments

This research is supported by the Malaysian Ministry of Education under the research grant number ERGS0022-TK-1-2012 and ERGS0019-TK-1/2012, and is greatly acknowledged.

References

[1] B. O'Regan, and M. Graetzel, "Low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films", Nature, vol. 353, pp. 737, 1991.

[2] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, and L. Han, "Dye-sensitized solar cells with conversion efficiency of 11.1%", Japanese Journal of

Applied Physics, Part 2: Letters, vol. 45, pp. L638-L640, 2006.

[3] L. Yang, B.-g. Zhai, Q.-l. Ma, and Y.M. Huang, "Effect of ZnO decoration on the photovoltaic performance of TiO2 based dye sensitized solar cells", Journal of Alloys and Compounds, vol. 605, pp. 109-112, 2014.

[4] R.F. Mansa, G. Govindasamy, Y.Y. Farm, H.A. Bakar, J. Dayou, and C.S. Sipaut, Hibiscus flower extract as the natural dye sensitizer for dye-sensitized solar cell, in, Journal of Physical Science, 2013, Accepted.

[5] M. Grätzel, "Photoelectrochemical cells", Nature, vol. 414, pp. 338-344, 2001.

[6] R.F. Mansa, A.R.A. Yugis, K.S. Liow, S.C.T. Lau, M.C. Ung, J. Dayou, and C.S. Sipaut, A Brief Review on Photoanode, Electrolyte, and Photocathode Materials for Dye-Sensitized Solar Cell Based on Natural Dye Photosensitizers, in: P. Ravindra, A. Bono, C.M. Chu (Eds.) Developments in Sustainable Chemical and Bioprocess Technology, Springer, pp. 313-319, 2013.

[7] A. Yella, H.W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.G. Diau, C.Y. Yeh, S.M. Zakeeruddin, and M. Grätzel, "Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency", Science, vol. 334, pp. 629-634, 2011.

[8] W.Q. Wu, J.Y. Liao, H.Y. Chen, X.Y. Yu, C.Y. Su, and D.B. Kuang, "Dye-sensitized solar cells based on a double layered TiO2 photoanode consisting of hierarchical nanowire arrays and nanoparticles with greatly improved photovoltaic performance", Journal of Materials Chemistry, vol. 22, pp. 18057-18062, 2012.

[9] S. Ito, P. Chen, P. Comte, M.K. Nazeeruddin, P. Liska, P. Péchy, and M. Grätzel, "Fabrication of screen-printing pastes from TiO2 powders for dye-sensitised solar cells", Progress in Photovoltaics: Research and Applications, vol. 15, pp. 603-612, 2007.

[10] Q. Huang, G. Zhou, L. Fang, L. Hu, and Z.S. Wang, "TiO2 nanorod arrays grown from a mixed acid medium for efficient dye-sensitized solar cells", Energy and Environmental Science, vol. 4, pp. 2145-2151, 2011.

[11] M. Wang, Y. Wang, and J. Li, "ZnO nanowire arrays coating on TiO2 nanoparticles as a composite photoanode for a high efficiency DSSC", Chemical Communications, vol. 47, pp. 11246-11248, 2011.

[12] H.Y. Chen, D.B. Kuang, and C.Y. Su, "Hierarchically micro/nanostructured photoanode materials for dye-sensitized solar cells", Journal of Materials Chemistry, vol. 22, pp. 15475-15489, 2012.

[13] K. Hara, and H. Arakawa, Dye-sensitized Solar Cells, in: S.H. Antonio Luque (Ed.) Handbook of Photovoltaic Science and Engineering, England:John Wiley & Sons Ltd, 2003.

[14] B. Grob, and M.E. Schultz, Basic electronics, vol. Gregg Division, 1977.

[15] L.R. Andrade, and A.H.A. Mendes, Dye-sensitized Solar Cells: An Overview in Energy Production and Storage: Inorganic Chemical Strategies for A Warming World, pp. 53-72, 2010.

[16] L. Andrade, J. Sousa, H. Aguilar Ribeiro, and A. Mendes, "Phenomenological modeling of dye-sensitized solar cells under transient conditions", Solar Energy, vol. 85, pp. 781-793, 2011.

[17] J. Maçaira, L. Andrade, and A. Mendes, "Review on nanostructured photoelectrodes for next generation dye-sensitized solar cells", Renewable and Sustainable Energy Reviews, vol. 27, pp. 334-349, 2013.

[18] T. Sawatsuk, A. Chindaduang, C. Sae-kung, S. Pratontep, and G. Tumcharern, "Dye-sensitized solar cells based on TiO2-MWCNTs composite electrodes: Performance improvement and their mechanisms", Diamond and Related Materials, vol. 18, pp. 524-527, 2009.

[19] S.R. Jang, R. Vittal, and K.J. Kim, "Incorporation of functionalized single-wall carbon nanotubes in dye-sensitized TiO2 solar cells", Langmuir, vol. 20, pp. 9807-9810, 2004.

[20] T.Y. Lee, P.S. Alegaonkar, and J.B. Yoo, "Fabrication of dye sensitized solar cell using TiO2 coated carbon nanotubes", Thin Solid Films, vol. 515, pp. 5131-5135, 2007.

[21] S.L. Kim, S.R. Jang, R. Vittal, J. Lee, and K.J. Kim, "Rutile TiO2-modified multi-wall carbon nanotubes in TiO2 film electrodes for dye-sensitized solar cells", Journal of Applied Electrochemistry, vol. 36, pp. 1433-1439, 2006.

[22] H. Usui, H. Matsui, N. Tanabe, and S. Yanagida, "Improved dye-sensitized solar cells using ionic nanocomposite gel electrolytes", Journal of Photochemistry and Photobiology A: Chemistry, vol. 164, pp. 97-101, 2004.

[23] M. Saito, and S. Fujihara, "Large photocurrent generation in dye-sensitized ZnO solar cells", Energy & Environmental Science, vol. 1, pp. 280-283, 2008.

[24] B. Onwona-Agyeman, S. Kaneko, A. Kumara, M. Okuya, K. Murakami, A. Konno, and K. Tennakone, "Sensitization of nanocrystalline SnO2 films with indoline dyes", Japanese Journal of Applied Physics, Part 2: Letters, vol. 44, pp. L731-L733, 2005.

[25] P. Guo, and M.A. Aegerter, "RU(II) sensitized Nb2O5 solar cell made by the sol-gel process", Thin Solid Films, vol. 351, pp. 290-294, 1999.

[26] M. Grätzel, "The advent of mesoscopic injection solar cells", Progress in Photovoltaics: Research and Applications, vol. 14, pp. 429-442, 2006.

[27] R. Jose, V. Thavasi, and S. Ramakrishna, "Metal Oxides for Dye-Sensitized Solar Cells", Journal of the American Ceramic Society, vol. 92, pp. 289-301, 2009.

[28] M. Grätzel, "Dye-sensitized solar cells", Journal of Photochemistry and Photobiology C: Photochemistry Reviews, vol. 4, pp. 145-153, 2003.

[29] H. Minoura, and T. Yoshida, "Electrodeposition of ZnO/dye hybrid thin films for dye-sensitized solar cells", Electrochemistry Tokyo, vol. 76, pp. 109, 2008.

[30] B. Tan, E. Toman, Y. Li, and Y. Wu, "Zinc stannate (Zn2SnO4) dye-sensitized solar cells", Journal of the American Chemical Society, vol. 129, pp. 4162-4163, 2007.

[31] H. Zheng, Y. Tachibana, and K. Kalantar-Zadeh, "Dye-sensitized solar cells based on WO3", Langmuir, vol. 26, pp. 19148-19152, 2010.

[32] S. Burnside, J.-E. Moser, K. Brooks, M. Grätzel, and D. Cahen, "Nanocrystalline mesoporous strontium titanate as photoelectrode material for photosensitized solar devices: increasing photovoltage through flatband potential engineering", The Journal of Physical Chemistry B, vol. 103, pp. 9328-9332, 1999.

[33] N. Nang Dinh, M.C. Bernard, A. Hugot-Le Goff, T. Stergiopoulos, and P. Falaras, "Photoelectrochemical solar cells based on SnO2 nanocrystalline films", Comptes Rendus Chimie, vol. 9, pp. 676-683, 2006.

[34] N.G. Park, G. Schlichthörl, J. Van De Lagemaat, H.M. Cheong, A. Mascarenhas, and A.J. Frank, "Dye-sensitized TiO2 solar cells: Structural and photoelectrochemical characterization of nanocrystalline electrodes formed from the hydrolysis of TiCl4", Journal of Physical Chemistry B, vol. 103, pp. 3308-3314, 1999.

[35] N.G. Park, J. Van De Lagemaat, and A.J. Frank, "Comparison of dye-sensitized rutile- and anatase-based TiO2 solar cells", Journal of Physical Chemistry B, vol. 104, pp. 8989-8994, 2000.

[36] H.J. Koo, Y.J. Kim, Y.H. Lee, W.I. Lee, K. Kim, and N.G. Park, "Nano-embossed hollow spherical TiO2 as bifunctional material for high-efficiency dye-sensitized solar cells", Advanced Materials, vol. 20, pp. 195-199, 2008.

[37] J.H. Park, S.Y. Jung, R. Kim, N.G. Park, J. Kim, and S.S. Lee, "Nanostructured photoelectrode consisting of TiO2 hollow spheres for non-volatile electrolyte-based dye-sensitized solar cells", Journal of Power Sources, vol. 194, pp. 574-579, 2009.

[38] Z.S. Wang, H. Kawauchi, T. Kashima, and H. Arakawa, "Significant influence of TiO2 photoelectrode morphology on the energy conversion efficiency of N719 dye-sensitized solar cell", Coordination Chemistry Reviews, vol. 248, pp. 1381-1389, 2004.

[39] A. Usami, "Theoretical simulations of optical confinement in dye-sensitized nanocrystalline solar cells", Solar Energy Materials and Solar Cells, vol. 64, pp. 73-83, 2000.

[40] J. Ferber, and J. Luther, "Computer simulations of light scattering and absorption in dye-sensitized solar cells", Solar Energy Materials and Solar Cells, vol. 54, pp. 265-275, 1998.

[41] K. Guo, M. Li, X. Fang, L. Bai, M. Luoshan, F. Zhang, and X. Zhao, "Improved properties of dye-sensitized solar cells by multifunctional scattering layer of yolk-shell-like TiO< sub> 2</sub> microspheres", Journal of Power Sources, vol. 264, pp. 35-41, 2014.

[42] D.B. Menzies, R. Cervini, Y.B. Cheng, G.P. Simon, and L. Spiccia, "Nanostructured ZrO2-coated TiO2 electrodes for dye-sensitised solar cells", Journal of Sol-Gel Science and Technology, vol. 32, pp. 363-366, 2004.

[43] E. Palomares, J.N. Clifford, S.A. Haque, T. Lutz, and J.R. Durrant, "Slow charge recombination in dye-sensitised solar cells (DSSC) using Al2O3 coated nanoporous TiO2 films", Chemical Communications, pp. 1464-1465, 2002.

[44] E. Palomares, J.N. Clifford, S.A. Haque, T. Lutz, and J.R. Durrant, "Control of charge recombination dynamics in dye sensitized solar cells by the use of conformally deposited metal oxide blocking layers", Journal of the American Chemical Society, vol. 125, pp. 475-482, 2003.

[45] S. Ito, P. Liska, P. Comte, R. Charvet, P. Pechy, U. Bach, L. Schmidt-Mende, S.M. Zakeeruddin, A. Kay, M.K. Nazeeruddin, and M. Grätzel, "Control of dark current in photoelectrochemical (TiO2/I--I3-) and dye-sensitized solar cells", Chemical Communications, pp. 4351-4353, 2005.

[46] Y. Wang, H. Yang, and H. Xu, "DNA-like dye-sensitized solar cells based on TiO2 nanowire-covered nanotube bilayer film electrodes", Materials Letters, vol. 64, pp. 164-166, 2010.

[47] J.Y. Liao, B.X. Lei, H.Y. Chen, D.B. Kuang, and C.Y. Su, "Oriented hierarchical single crystalline anatase TiO2 nanowire arrays on Ti-foil substrate for efficient flexible dye-sensitized solar cells", Energy and Environmental Science, vol. 5, pp. 5750-5757, 2012.

[48] K. Zhu, N.R. Neale, A. Miedaner, and A.J. Frank, "Enhanced charge-collection efficiencies and light scattering in dye-sensitized solar cells using oriented TiO2 nanotubes arrays", Nano Letters, vol. 7, pp. 69-74, 2007.

[49] M. Adachi, Y. Murata, J. Takao, J. Jiu, M. Sakamoto, and F. Wang, "Highly efficient dye-sensitized solar cells with a titania thin-film electrode composed of a network structure of single-crystal-like TiO2 nanowires made by the "oriented attachment" mechanism", Journal of the American Chemical Society, vol. 126, pp. 14943-14949, 2004.

[50] B.H. Lee, M.Y. Song, S.Y. Jang, S.M. Jo, S.Y. Kwak, and D.Y. Kim, "Charge transport characteristics of high efficiency dye-sensitized solar cells based on electrospun TiO2 nanorod photoelectrodes", Journal of Physical Chemistry C, vol. 113, pp. 21453-21457, 2009.

[51] C.J. Lin, W.Y. Yu, and S.H. Chien, "Transparent electrodes of ordered opened-end TiO2-nanotube arrays for highly efficient dye-sensitized solar cells", Journal of Materials Chemistry, vol. 20, pp. 1073-1077, 2010.

[52] B. Tan, and Y. Wu, "Dye-sensitized solar cells based on anatase TiO2 nanoparticle/nanowire composites", Journal of Physical Chemistry B, vol. 110, pp. 15932-15938, 2006.

[53] Y. Alivov, and Z.Y. Fan, "Efficiency of dye sensitized solar cells based on TiO2 nanotubes filled with nanoparticles", Applied Physics Letters, vol. 95, 2009.

[54] T.-H. Tsai, S.-C. Chiou, and S.-M. Chen, "Enhancement of dye-sensitized solar cells by using graphene-TiO2 composites as photoelectrochemical working electrode", Int. J. Electrochem. Sci, vol. 6, pp. 3333-3343, 2011.

[55] M. Zhu, X. Li, W. Liu, and Y. Cui, "An investigation on the photoelectrochemical properties of dye-sensitized solar cells based on graphene–TiO2 composite photoanodes", Journal of Power Sources, vol. 262, pp. 349-355, 2014.

[56] S. Ngamsinlapasathian, S. Sakulkhaemaruethai, S. Pavasupree, A. Kitiyanan, T. Sreethawong, Y. Suzuki, and S. Yoshikawa, "Highly efficient dye-sensitized solar cell using nanocrystalline titania containing nanotube structure", Journal of Photochemistry and Photobiology A: Chemistry, vol. 164, pp. 145-151, 2004.

[57] S. Pavasupree, S. Ngamsinlapasathian, M. Nakajima, Y. Suzuki, and S. Yoshikawa, "Synthesis, characterization, photocatalytic activity and dye-sensitized solar cell performance of nanorods/nanoparticles TiO2 with mesoporous structure", Journal of Photochemistry and Photobiology A: Chemistry, vol. 184, pp. 163-169, 2006.

[58] P. Sun, X. Zhang, C. Wang, Y. Wei, L. Wang, and Y. Liu, "Rutile TiO2 nanowire array infiltrated with anatase nanoparticles as photoanode for dye-sensitized solar cells: Enhanced cell performance via the rutile-anatase heterojunction", Journal of Materials Chemistry A, vol. 1, pp. 3309-3314, 2013.

[59] A.M. Bakhshayesh, M.R. Mohammadi, and D.J. Fray, "Controlling electron transport rate and recombination process of TiO2 dye-sensitized solar cells by design of double-layer films with different arrangement modes", Electrochimica Acta, vol. 78, pp. 384-391, 2012.

[60] Y. Qiu, W. Chen, and S. Yang, "Double-layered photoanodes from variable-size anatase TiO2 nanospindles: A candidate for high-efficiency dye-sensitized solar cells", Angewandte Chemie - International Edition, vol. 49, pp. 3675-3679, 2010.

[61] F. Huang, D. Chen, X.L. Zhang, R.A. Caruso, and Y.B. Cheng, "Dual-function scattering layer of submicrometer-sized mesoporous TiO2 beads for high-efficiency dyesensitized solar cells", Advanced Functional Materials, vol. 20, pp. 1301-1305, 2010.

[62] F. Xu, X. Zhang, Y. Wu, D. Wu, Z. Gao, and K. Jiang, "Facile synthesis of TiO2 hierarchical microspheres assembled by ultrathin nanosheets for dye-sensitized solar cells", Journal of Alloys and Compounds, vol. 574, pp. 227-232, 2013.

[63] J.Y. Liao, B.X. Lei, D.B. Kuang, and C.Y. Su, "Tri-functional hierarchical TiO2 spheres consisting of anatase nanorods and nanoparticles for high efficiency dye-sensitized solar cells", Energy and Environmental Science, vol. 4, pp. 4079-4085, 2011.

[64] J.Y. Liao, H.P. Lin, H.Y. Chen, D.B. Kuang, and C.Y. Su, "High-performance dye-sensitized solar cells based on hierarchical yolk-shell anatase TiO2 beads", Journal of Materials Chemistry, vol. 22, pp. 1627-1633, 2012.

[65] Y.J. Kim, M.H. Lee, H.J. Kim, G. Lim, Y.S. Choi, N.G. Park, K. Kim, and W.I. Lee, "Formation of highly efficient dye-sensitized solar cells by hierarchical pore generation with nanoporous TiO2 spheres", Advanced Materials, vol. 21, pp. 3668-3673, 2009.

[66] B.M. Klahr, and T.W. Hamann, "Performance Enhancement and Limitations of Cobalt Bipyridyl Redox Shuttles in Dye-Sensitized Solar Cells", The Journal of Physical Chemistry C, vol. 113, pp. 14040-14045, 2009.

[67] K.S. Liow, C.S. Sipaut, R.F. Mansa, and J. Dayou, "Dye Sensitized Solar Cell Based on Polyethylene Glycol/4,4'Diphenylmethane Diisocyanate Copolymer Quasi Solid State Electrolyte", Applied Mechanics and Materials, vol. 625, pp. 140-143, 2014.

[68] S.M. Feldt, E.A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo, and A. Hagfeldt, "Design of organic dyes and cobalt polypyridine redox mediators for high-efficiency dye-sensitized solar cells", Journal of the American Chemical Society, vol. 132, pp. 16714-16724, 2010.

[69] T.T. Trang Pham, T.M. Koh, K. Nonomura, Y.M. Lam, N. Mathews, and S. Mhaisalkar, "Reducing Mass-Transport Limitations in Cobalt-Electrolyte-Based Dye-Sensitized Solar Cells by Photoanode Modification", ChemPhysChem, vol. 15, pp. 1216-1221, 2014.

[70] Y. Duan, N. Fu, Q. Zhang, Y. Fang, X. Zhou, and Y. Lin, "Influence of Sn source on the performance of dye-sensitized solar cells based on Sn-doped TiO2 photoanodes: A strategy for choosing an appropriate doping source", Electrochimica Acta, vol. 107, pp. 473-480, 2013.

[71] J.K. Lee, and M. Yang, "Progress in light harvesting and charge injection of dye-sensitized solar cells", Materials Science and Engineering B: Solid-State Materials for Advanced Technology, vol. 176, pp. 1142-1160, 2011.

[72] X. Lü, X. Mou, J. Wu, D. Zhang, L. Zhang, F. Huang, F. Xu, and S. Huang, "Improved-Performance Dye-Sensitized solar cells using Nb-Doped TiO2 electrodes: Efficient electron Injection and transfer", Advanced Functional Materials, vol. 20, pp. 509-515, 2010.

[73] M. Yang, D. Kim, H. Jha, K. Lee, J. Paul, and P. Schmuki, "Nb doping of TiO2 nanotubes for an enhanced efficiency of dye-sensitized solar cells", Chemical Communications, vol. 47, pp. 2032-2034, 2011.

[74] H. Tian, L. Hu, C. Zhang, W. Liu, Y. Huang, L. Mo, L. Guo, J. Sheng, and S. Dai, "Retarded charge recombination in dye-sensitized nitrogen-doped TiO2 solar cells", Journal of Physical Chemistry C, vol. 114, pp. 1627-1632, 2010.

[75] X. Zhang, F. Liu, Q.-L. Huang, G. Zhou, and Z.-S. Wang, "Dye-sensitized W-doped TiO2 solar cells with a tunable conduction band and suppressed charge recombination", The Journal of Physical Chemistry C, vol. 115, pp. 12665-12671, 2011.

[76] Y. Duan, N. Fu, Q. Liu, Y. Fang, X. Zhou, J. Zhang, and Y. Lin, "Sn-doped TiO2 photoanode for dye-sensitized solar cells", The Journal of Physical Chemistry C, vol. 116, pp. 8888-8893, 2012.

[77] X. Lü, X. Mou, J. Wu, D. Zhang, L. Zhang, F. Huang, F. Xu, and S. Huang, "Improved-Performance Dye-Sensitized Solar Cells Using Nb-Doped TiO2 Electrodes: Efficient Electron Injection and Transfer", Advanced Functional Materials, vol. 20, pp. 509-515, 2010.

[78] Y. Xie, N. Huang, Y. Liu, W. Sun, H.F. Mehnane, S. You, L. Wang, W. Liu, S. Guo, and X.-Z. Zhao, "Photoelectrodes modification by N doping for dye-sensitized solar cells", Electrochimica Acta, vol. 93, pp. 202-206, 2013.

[79] S. Yang, S. Guo, D. Xu, H. Xue, H. Kou, J. Wang, and G. Zhu, "Improved efficiency of dye-sensitized solar cells applied with F-doped TiO2 electrodes", Journal of Fluorine Chemistry, vol. 150, pp. 78-84, 2013.

[80] S.C.T. Lau, C.S. Sipaut, J. Dayou, and R.F. Mansa, "Sol gel synthesized nanosilica as photoanode material for dye sensitized solar cells (DSSCs) system", Applied Mechanics and Materials, vol. 625, pp. 110-113, 2014.

[81] J.-P. Rino, and N. Studart, "Structural correlations in titanium dioxide", Physical Review B, vol. 59, pp. 6643-6649, 1999.

[82] L.E. Brus, "Electron–electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state", The Journal of chemical physics, vol. 80, pp. 4403-4409, 1984.

[83] V.A.L. Padavettan, Synthesis And Characterization Of Silica Nanoparticles And Their Application As Fillers In Silica-Bismaleimide Nanocomposite, PhD Thesis, Universiti Sains Malaysia, 2009.

[84] A. Yelil Arasi, M. Hemma, P. Tamilselvi, and R. Anbarasan, "Synthesis and characterization of SiO_2 nanoparticles by sol-gel process", Indian Journal of Science, vol. 1, pp. 6-10, 2012.

[85] A.N. Trukhin, L.N. Skuja, A.G. Boganov, and V.S. Rudenko, "The correlation of the 7.6 eV optical absorption band in pure fused silicon dioxide with twofold-coordinated silicon", Journal of Non-Crystalline Solids, vol. 149, pp. 96-101, 1992.

[86] H. Lin, C. Huang, W. Li, C. Ni, S.I. Shah, and Y.-H. Tseng, "Size dependency of nanocrystalline TiO2 on its optical property and photocatalytic reactivity exemplified by 2-chlorophenol", Applied Catalysis B: Environmental, vol. 68, pp. 1-11, 2006.