

CHAPTER V

STUDY OF QUANTUM DOTS AND MIXED DYES FOR ENHANCE THE CONVERSION EFFICIENCY OF DYE-SENSITIZED SOLAR CELL

5.1 Abstract

The performance of dye-sensitized solar cells (DSSCs) of quantum dots (QDs) prepared by chemical bath deposition (CBD) method with different dipping time and mixed natural dye system were investigated.

In order to enhance the conversion efficiency of DSSC, the quantum dots (QDs) were used to increase the absorption in near infrared (NIR) region and visible region by varying the dipping time of producing QDs. Moreover, the two dyes which one was yellow cotton and another one was indigo, spirulina and red orchid were mixed together to cover the visible absorption range. In this work, three QDs which were ZnS, CdS and Ag₂S were studied. The optical properties which were absorption and emission of QDs which were produced using chemical bath deposition (CBD) method and varying the dipping time were determined using UV-Visible spectrometer and fluorescence spectrometer. The QDs on ZnO film were characterized using X-ray diffractometer and UV-Visible spectrometer. The surface morphology and particle size were measured using Field Emission Scanning Electron Microscope (FE-SEM).

The result of XRD pattern showed that the molecular structure of Ag₂S, CdS and ZnS was acanthite, hexagonal and cubic, respectively. The QDs in ethanol appeared the maximum absorption wavelength at 269, 276 and 290 nm for Ag₂S, CdS and ZnS, respectively. These absorption wavelengths were used to excite the QDs solution to find the emission wavelength using fluorescence spectrometer. For emission spectra, they showed the emission wavelength at 385, 385 and 420 nm for CdS, ZnS and Ag₂S, respectively. Both absorption and emission spectra illustrated that the absorption and emission intensities increased when the dipping time of produced QDs increased. From emission spectra of QDs, the yellow cotton was chosen to be a major dye to mix with

others due to its maximum absorption wavelength was in range of emission wavelength of three QDs. The absorption spectra showed the identity of two dyes when they were mixed together. When fabricated the DSSC with mixed dyes and measured the conversion efficiency of DSSC, it was found that the mixed yellow cotton-spirulina showed highest conversion efficiency equaled to 0.0145 %. Then this mixed dyes system was chosen to fabricate the ZnO/QDs DSSC. The ZnO/QDs DSSCs with mixed yellow cotton-spirulina were fabricated and determined the conversion efficiency. The results indicated that the conversion efficiency of ZnO/QDs DSSCs increased when the dipping time increased. The ZnO/CdS DSSC with mixed yellow cotton-spirulina showed the highest conversion efficiency at dipping time 9 min.

5.2 Introduction

Natural dye-sensitized solar cells (natural DSSCs) have been attracted photovoltaic device because of easy to fabricate, low production cost, abundance supply of raw materials and environmental friendly. The various components of plants including flower petal, leaf, fruit and bark are introduced to use in DSSC. A variety of main chemical component in plant such as anthocyanins, chlorophyll, carotenoids and flavonoids is studied (Narayan, 2011). However, the natural DSSCs still have low conversion efficiency when compare with synthetic DSSC. To solve this problem of natural DSSC, quantum dots (QDs) are used to enhance the conversion efficiency of DSSC not only in synthetic DSSC but also in natural DSSC. In the last few years QDs have widely interested to use in DSSC due to their outstanding optical and electronic properties (Ruhle *et al.*, 2010). QDs are a semiconductor which their bandgap can be tuned by controlling the size of them. Moreover, they have high absorption coefficient ($10^5 - 10^6 \text{ M}^{-1} \text{ cm}^{-1}$) (Choi *et al.*, 2013). The important thing is that they can enhance the conversion efficiency of DSSC by generating more than two electrons from a single photon (electron-hole pair) when they absorb light with higher energy than their bandgap (Sambur *et al.*, 2010). Another approach to improve the conversion efficiency

of DSSC is light scattering. QDs will act as light scatterer to modify the photo paths and extend the traveling distance of incident light (Choi *et al.*, 2013). Therefore, the light absorption possibility of dye will be increased. Meanwhile, mixed dyes which are combined more than two dyes are gotten attention too (Wongcharee *et al.*, 2007). By this way, the absorption of dye is enlarged to get broad absorption and caused the conversion efficiency of natural DSSC increases.

In this work, the optical properties of three QDs which are ZnS, CdS and Ag₂S were studied using UV-Visible spectrometer and fluorescence spectrometer. QDs were produced using chemical bath deposition (CBD) method by varying the deposition time. The given QDs were characterized using X-ray diffractometer and Field Emission Scanning Electron Microscope (FE-SEM). The mixed dyes were combined by two dyes which one had the maximum absorption wavelength closed to the emission wavelength of each QD and another one was other dyes. The optical absorption of mixed dyes was examined using UV-Visible spectrometer. Finally, the DSSC based on QDs with mixed natural dyes was fabricated and measured using Digital Keithley 2400 multimeter.

5.3 Experimental

5.3.1 Materials

Red orchid was purchased from Pak-Khlong market, Bangkok, Thailand. Spirulina powder was purchased from Phu-Fah store in Jatujak market, Thailand. Indigo powder was purchased from Baan Tum-Tao, Sakonnakhon, Thailand. Yellow cotton flower was collected from Nakhon Nayok, Thailand. A commercial ZnO nanoparticle (ZoNoP®, 99.93% ZnO) was purchase from Nano Materials Technology Co., Ltd., in Thailand. Cadmium nitrate was purchased from Fluka. Zinc chloride was purchased from Fluka. Silver nitrate was purchased from Fluka. Sodium sulphate was purchased from Fluka. Acetylacetone ($\geq 99.5\%$) was purchased from Fluka. Triton X-100 (laboratory grade) was purchased from Acros Organics. Polyethylene glycol (PEG, MW 20,000), Lithium iodide beads (99%), 4-tert-butyl pyridine (96%) and hydrogen

hexachloroplatinate (IV) hydrate (~38% Pt basis) were purchased from Aldrich. Iodine was purchase from Suksapan panit, Thailand. Fluorine-doped SnO₂ (FTO) glass (sheet resistance of 8 Ω/cm²) was purchased from Dyesol Company.

5.3.2 Preparation of Natural Dye Sensitizers

Spirulina powder and indigo powder were used as received. Yellow cotton flower and red orchid were cut into small pieces and extracted by using deionized water. The solutions were frozen and dried via freeze-drying process. Then solid dyes were crushed and sieved before used.

5.3.3 Preparation of Mixed Natural Dye Sensitizers

Yellow cotton powder was used to mix with other dyes. The ratio of mixed dyes was 1:1. Finally, mixed dyes powder was dissolved in deionized water to obtain the concentration at 10g/L.

5.3.4 Preparation of ZnO Film

In order to prepare electrodes, the doctor blade method was used to fabricate the ZnO film on conductive glass. The fluorine-doped SnO₂ (FTO) glass plates were washed with water and ethanol, respectively. The FTO-glass plates were fixed area by using transparent tape (size 1.0 cm x 1.0 cm). 1.0 g of ZnO nanoparticles was added into the 5.0 ml of PEG aqueous solution (0.1 g/ml) mixed with 0.1 ml of acetylacetone and 0.4 ml of triton X-100. The mixture was stirred for 1 day then it was extended onto the marked FTO-glass plates and calcined at 550 °C for 1 h to obtain the photoanode film. Then 1 ml of natural dye solutions was dropped on the cooled ZnO film at room temperature for 3 h. The excess dyes were washed out with deionized water.

5.3.5 Preparation of QDs

The chemical bath deposition (CBD) method was used to produce the QDs which are ZnS, CdS and Ag₂S. Firstly, 0.5 M of ZnCl₂, Cd(NO₃)₂, AgNO₃ and

Na₂S in deionized water was prepared. Secondly, ZnO film on FTO glass was dipped into ZnCl₂, Cd(NO₃)₂ and AgNO₃ solution at various time (1-9 minutes) then left them dried. Finally, the same ZnO film on glass was dipped into Na₂S solution as the same time as the previous procedure.

5.3.6 Preparation of Platinum (Pt) Electrode

In order to prepare the Pt electrode, 7 mM of hexachloroplatinic acid in 2-propanol were dropped and spread on FTO-glass which was marked area by using transparent tape (size 0.5 cm x 1.5 cm). Then, it was calcined at 450 °C for 30 min.

5.3.7 Fabrication of DSSC

To fabricate the DSSC, 127 μm-thick transparent parafilm[®] was inserted between photoanode and cathode to prevent the short circuit current by attaching on four edges of photoanode film and the Pt electrode was covered on the top. The redox couple electrolyte solution which contained 0.025 M of iodine (I₂), 0.5 M of lithium iodide (LiI) and 0.2 M of *tert*-butyl pyridine was dissolved in acetonitrile. After that the electrolyte was injected in between two electrodes.

5.3.8 Characterizations

The absorption and emission spectra of QDs were measured using UV-Visible spectrometer and fluorescence spectrometer at maximum absorbance wavelength (λ_{max}), respectively.

The characterization of QDs on ZnO which produced by chemical bath deposition (CBD) method was examined by X-ray diffractometer (XRD) with 2 theta (2θ) 20-70 degree and Field Emission Scanning Electron Microscope (FE-SEM).

The optical absorption of mixed dyes in deionized water (2.5 g/L) in ratio 1:1 was measured by a UV-Visible spectrophotometer.

The photovoltaic properties of DSSC, short circuit current (J_{sc} , mA/cm²), open circuit voltage (V_{oc} , V), fill factor (FF , %) and efficiency (η , %), which were

calculated from J-V characteristic curve were determined by a digital Keithley 2400 multimeter under an irradiation of white light from 100 mW/cm^2 halogen-tungsten lamp.

5.4 Results and Discussion

5.4.1 Absorption Spectrum of QDs in Ethanol and QDs on ZnO Film.

Figure 5.1 showed the absorption spectra of three QDs which were ZnS, Ag_2S and CdS in ethanol. The maximum absorption wavelength of each QD was 269, 276 and 290 nm for Ag_2S , CdS and ZnS, respectively. The result indicated that all of the QDs absorbed the sunlight in ultraviolet region (UV). Therefore, absorption of QDs in UV region may result in enhancing the performance of DSSC. From this experiment, the maximum absorption wavelength was further used to set condition for fluorescence measurement.

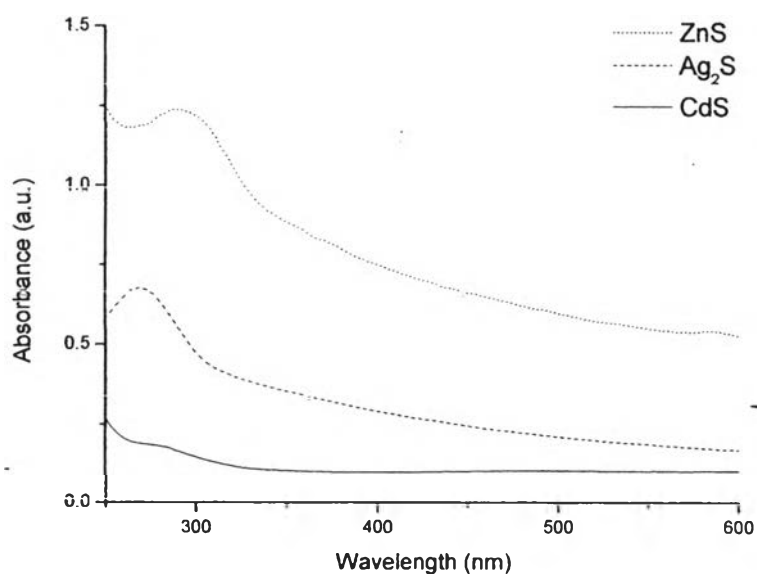


Figure 5.1 UV-Visible absorption spectra of ZnS, Ag_2S and CdS QDs in ethanol.

Figure 5.2 showed the spectra of ZnS QD on ZnO film using CBD method at various dipping times (1-9 min). Due to absorption of all QDs were appeared in UV region. Therefore, the absorption spectra had a lot of noise in range of before 400 nm. The spectra indicated that if the dipping time increased, the absorbance will be increased. This increment dominantly occurred at wavelength which was lower than 400 nm.

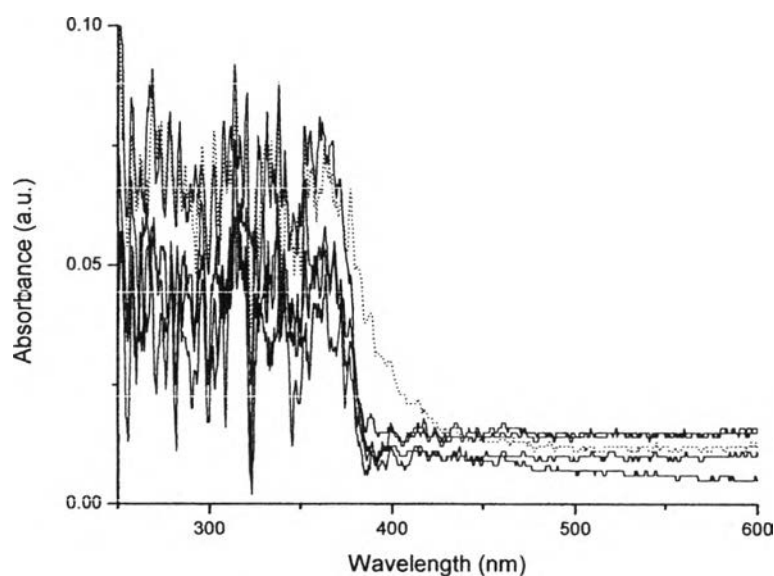


Figure 5.2 UV-Visible absorption spectra of ZnS on ZnO film at various times (—) and 9 min (--).

Figure 5.3 showed the spectra of Ag₂S QD on ZnO film using CBD method at various dipping times (1-9 min). The noise still appeared in the spectra with the same reason above. The absorption spectra showed the relationship between dipping time increment and absorbance. The absorption spectra illustrated that the absorbance will increase when dipping time increased. Moreover, this difference could be seen not only in ultraviolet region but also in visible region.

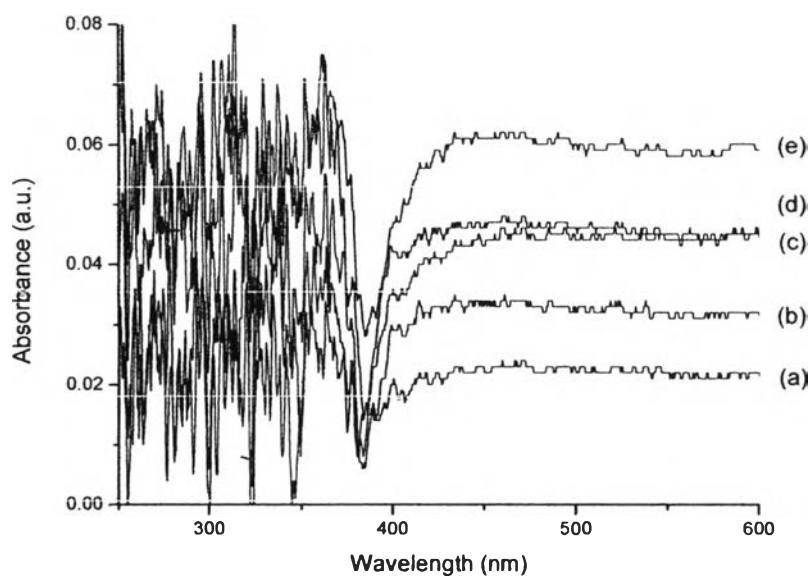


Figure 5.3 UV-Visible absorption spectra of Ag₂S on ZnO at (a) 1 min, (b) 3 min, (c) 5 min, (d) 7 min and (e) 9 min.

Figure 5.4 showed the spectra of CdS QD on ZnO film using CBD method at various dipping times (1-9 min). These absorption spectra showed the divergence when the dipping time was changed. The absorbance trended to increase when the dipping time increased and these phenomena appeared in both ultraviolet and visible region.

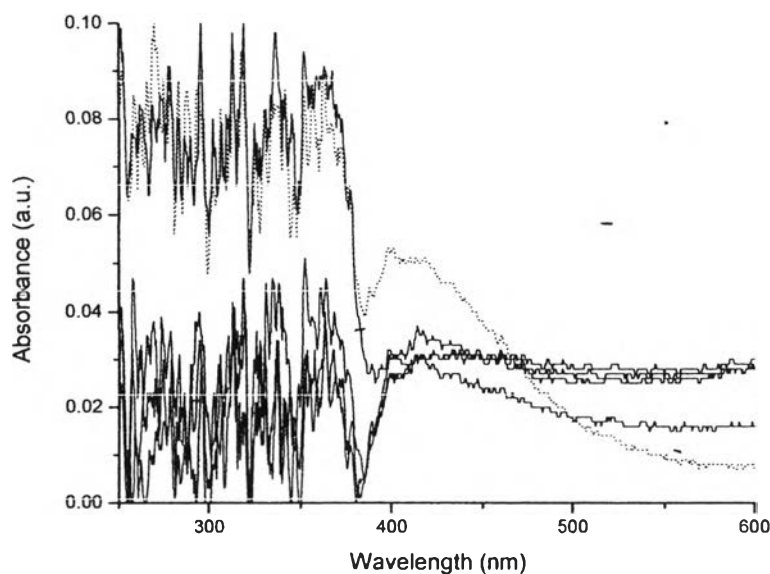


Figure 5.4 UV-Visible absorption spectra of CdS on ZnO film at various times (—) and 9 min (--).

5.4.2 Emission Spectra of QDs in Ethanol.

Figure 5.5 showed the emission spectra of CdS, Ag₂S and ZnS QDs. The maximum emission wavelength of CdS, Ag₂S and ZnS QDs was 385, 420 and 385 nm, respectively. From the fluorescence spectra, all QDs emitted the fluorescent light due to the relaxation of their molecules at wavelength in visible region. When combined the results of absorption spectra and emission spectra, we can expect that the QDs will enhance the conversion efficiency of natural DSSC by absorbing the ultraviolet light and then emitting the light in visible region. Moreover, if the emission wavelength equals to the absorption wavelength of dye, light absorption probability of dye will be increase. This result in the conversion efficiency of DSSC will be improved. Therefore, the yellow cotton that had maximum absorption wavelength near the emission wavelength of QDs was chosen to be a major dye to mix with other dyes which was indigo, spirulina and red orchid.

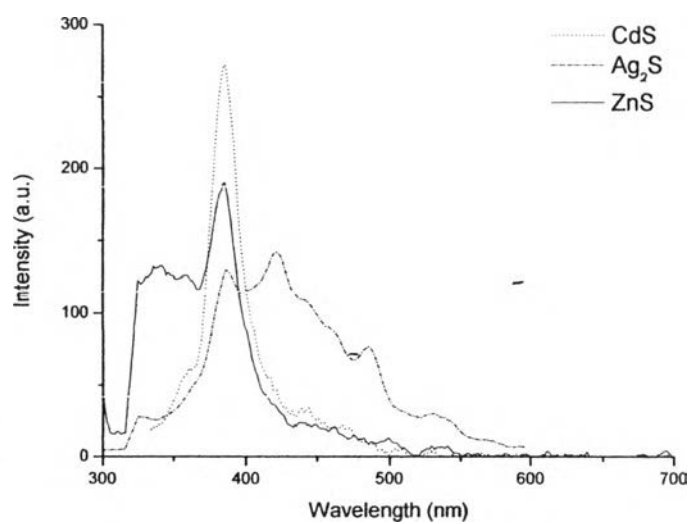


Figure 5.5 Fluorescence emission spectra of CdS, Ag₂S and ZnS QDs in ethanol.

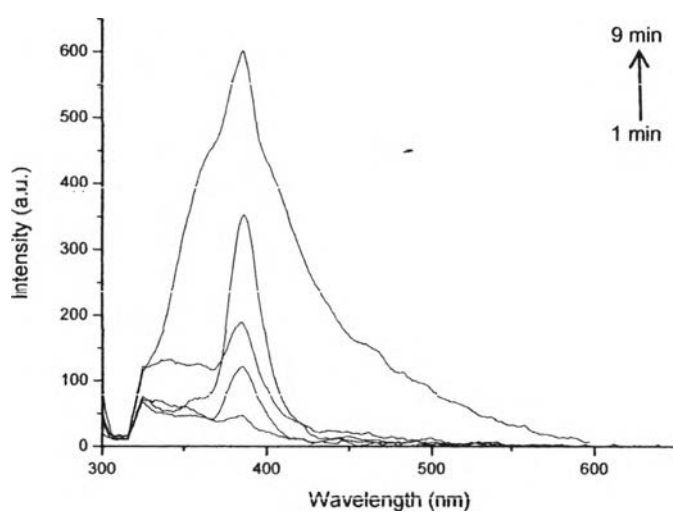


Figure 5.6 Fluorescence emission spectra of ZnS QDs in ethanol at various dipping time (1-9 min).

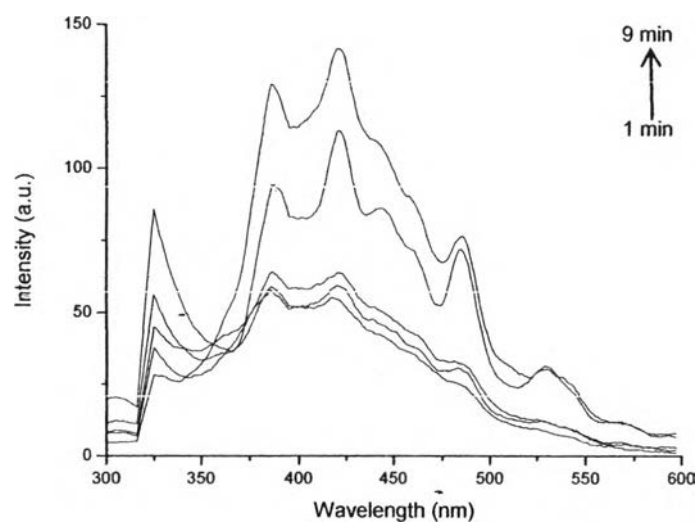


Figure 5.7 Fluorescence emission spectra of CdS QDs in ethanol at various dipping time (1-9 min).

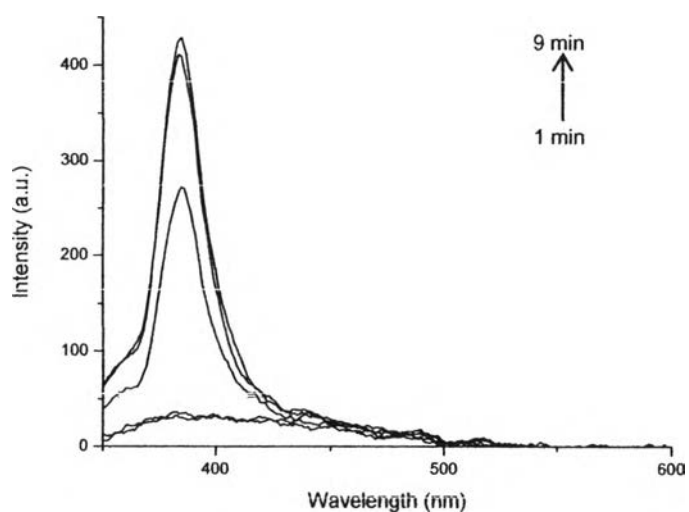


Figure 5.8 Fluorescence emission spectra of Ag₂S QDs in ethanol at various dipping time (1-9 min).

The emission spectra from figure 5.6, 5.7 and 5.8 showed the increment of emission intensity respected to the dipping time. This result indicated that when the dipping time increased the amount of QD was increased causing the intensity increased.

5.4.3 Structure and Morphology of QDs on ZnO Film

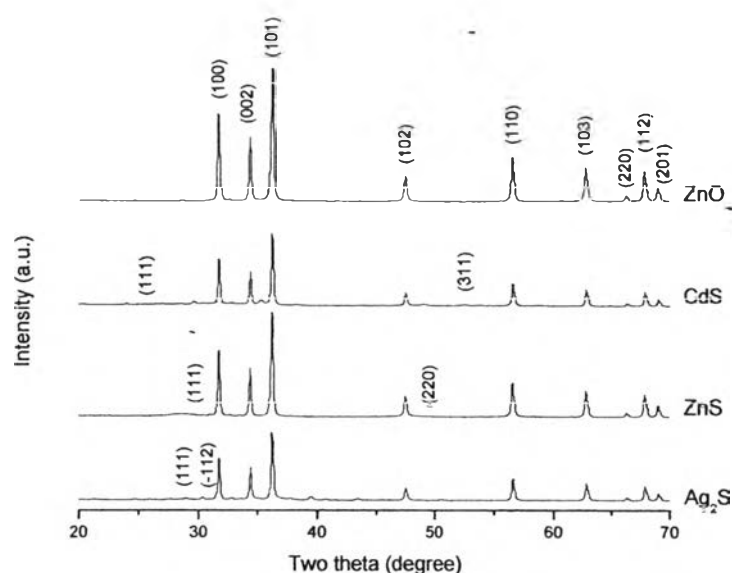


Figure 5.9 The XRD patterns of QDs on ZnO at dipping time 9 minute and ZnO powder.

In the figure 5.9, XRD measurement was used to study the crystal structure of the QDs film which deposited on ZnO using CBD method at dipping time equaled to 9 minute and ZnO film. Figure 5.9 showed the XRD pattern of pure ZnO film, all of the diffraction peaks could be indexed to wurtzite ZnO structure. The diffraction peaks of all QDs presented acanthite, cubic and hexagonal for Ag₂S, ZnS and CdS, respectively. In the Ag₂S/ZnO film, there were two peaks with 2 θ values of 28.1° and 31.1° corresponding to Ag₂S (Subash *et al.*, 2013). The characteristic peaks of (111), (220) and (111), (311) were mentioned to ZnS and CdS, respectively (Rani *et al.*,

2013). Moreover, all of the characteristic peaks of QDs had characteristic peaks which were evident for ZnO. Therefore, the XRD patterns of QDs/ZnO film indicated that all QDs had been successfully deposited on ZnO film.

5.4.4 Absorption of Mixed Dyes and Mixed Dyes on ZnO.

Figure 5.10 showed the absorption spectra of pure and mixed dyes between yellow cotton and indigo in deionized water at 2.5 g/L. It was found that the absorption peaks of mixed yellow cotton-indigo combined both absorption peak of yellow cotton about 420 nm and absorption peak of indigo about 630 nm. However, the absorption peak which represented yellow cotton in yellow cotton-indigo was not dominant when compared with absorption peak at 630 nm which represented indigo.

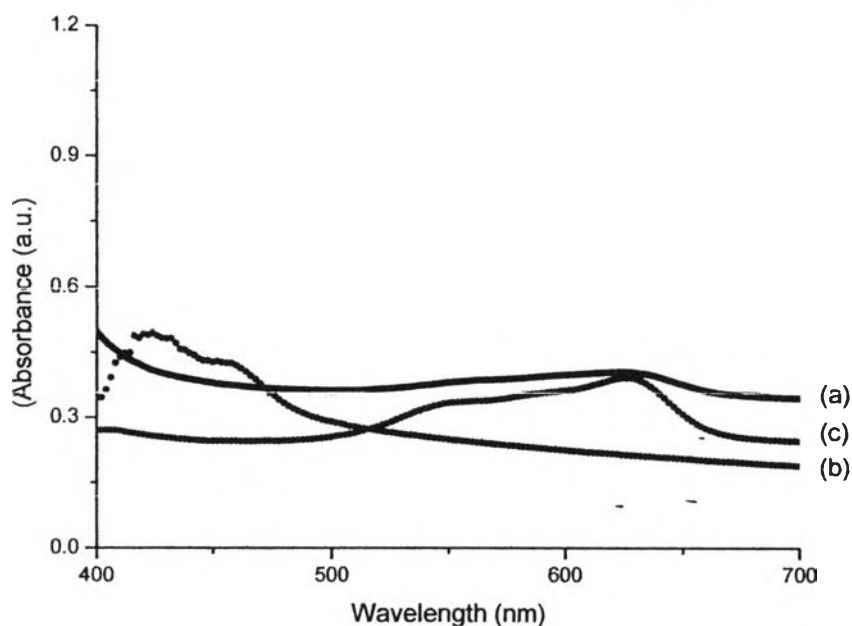


Figure 5.10 UV-Visible absorption spectra of dyes solution of: mixed yellow cotton-indigo (a), yellow cotton (b) and indigo (c) extracts in deionized water.

Figure 5.11 showed the absorption spectra of pure and mixed dyes between yellow cotton and red orchid in deionized water at 2.5 g/L. Although the

absorption peaks of mixed yellow cotton-red orchid showed the absorption peaks which represented both yellow cotton and red orchid around 410 and 520 nm, respectively but the absorption peak of red orchid was more legible than absorption of yellow cotton.

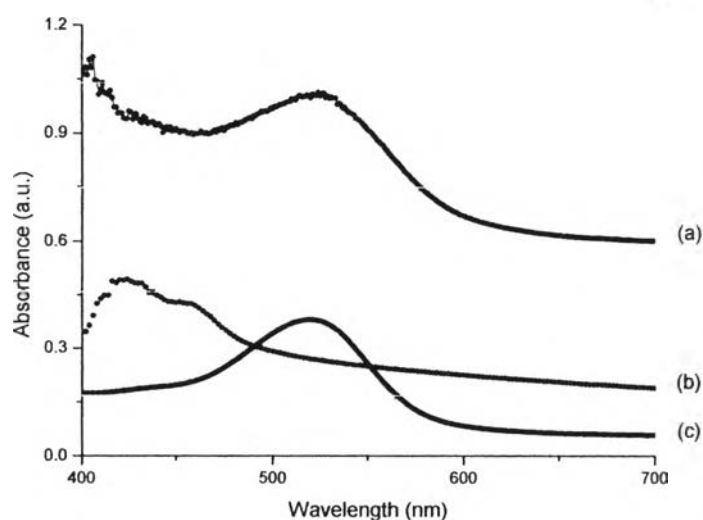


Figure 5.11 UV-Visible absorption spectra of dyes solution of: (a) mixed yellow cotton-red orchid, (b) yellow cotton and (c) red orchid extracts in deionized water.

Figure 5.12 showed the absorption spectra of pure and mixed dyes between yellow cotton and spirulina in deionized water at 2.5 g/L. These spectra indicated that the absorption peaks combination of yellow cotton and spirulina appeared. The mixed yellow cotton-spirulina spectrum showed absorption peaks about 450 nm which represented yellow cotton and 620 nm which represented spirulina. Moreover, the mixed yellow cotton-spirulina is the best of mixed combination because their spectra showed distinctive absorption peaks both yellow cotton and spirulina.

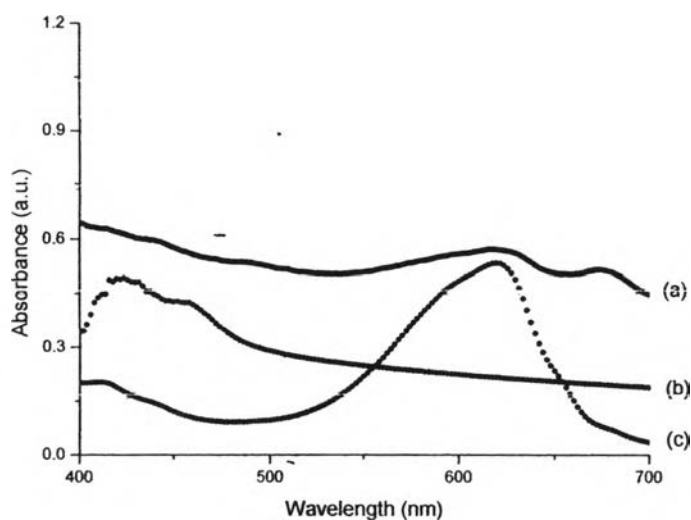


Figure 5.12 UV-Visible absorption spectra of dyes solution of: (a) mixed yellow cotton-spirulina, (b) yellow cotton and (c) spirulina extracts in deionized water.

Figure 5.13 showed the absorption spectra of pure and mixed dyes between indigo and spirulina in deionized water at 2.5 g/L. Although we chose yellow cotton to mix with others due to the absorption of yellow cotton was matched with the emission of QDs but in order to confirm this hypothesis, we set the experiment that used the dyes showing the higher conversion efficiency as indigo and spirulina mixed together. The absorption spectra indicated that spectrum of mixed dyes did not show the maximum absorption peaks which represented the indigo and spirulina. Therefore, the indigo and spirulina interact together causing the maximum absorption peaks were shifted. This may result in lower conversion efficiency of DSSC because the dye molecule has not the functional group or active site to bind with ZnO. Therefore, the electron which is excited from dye will be transferred to ZnO harder than other mixed dye systems.

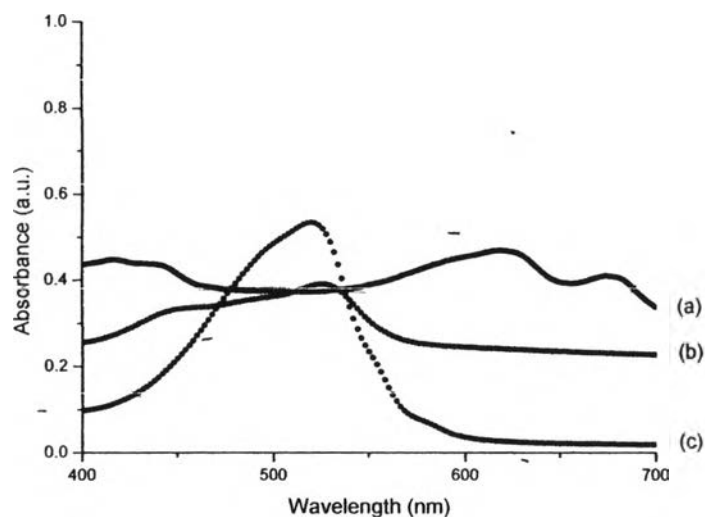


Figure 5.13 UV-Visible absorption spectra of dyes solution of: (a) mixed indigo-spirulina, (b) indigo and (c) spirulina extracts in deionized water.

5.4.5 Absorption of Mixed Dyes on ZnO/QDs.

Figure 5.14 showed the absorption spectra of mixed dyes on ZnO. The absorption spectrum of mixed yellow cotton-spirulina appeared absorption peaks both yellow cotton about 430 nm and spirulina about 610 nm. For mixed yellow cotton-indigo, it was found that the absorption spectrum showed absorption peaks about 420 and 600 nm which were yellow cotton and indigo, respectively. Furthermore, the spectrum of mixed yellow cotton-red orchid showed the absorption peak about 420 nm. The results indicate that the mixed dyes were successfully added to ZnO film and also showed the identical absorption peaks of mixed dyes system as in mixed dyes solution. Moreover, the maximum absorption wavelength of each mixed dyes system was a little shift due to the interaction between mixed dyes and ZnO film.

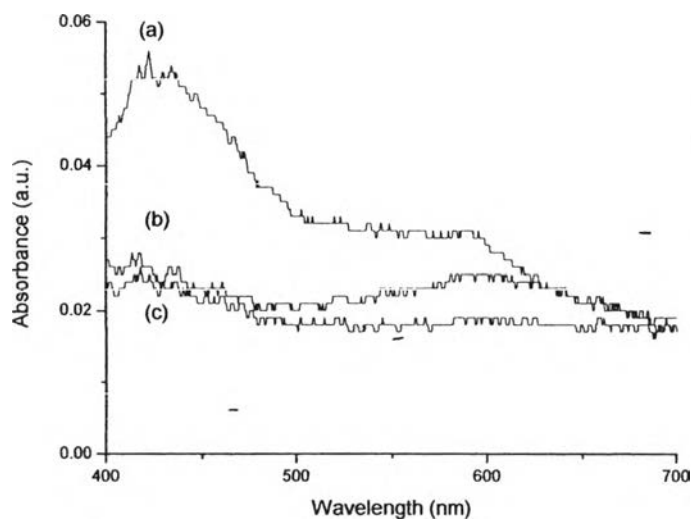


Figure 5.14 UV-Visible absorption spectra of mixed dyes on ZnO of: (a) mixed yellow cotton-indigo, (b) mixed yellow cotton-spirulina and (c) yellow cotton-red orchid.

5.4.6 Surface Morphology of ZnO/QDs.

Figure 5.15, 5.16 and 5.17 display the cross-section view of ZnO/QDs with various dipping time based platinum coated by ion sputtering. It can be seen that the small and smooth particle was shown in (a) which was ZnO. When the dipping time increased, the particle size tended to increase too. Furthermore, ZnO/QDs showed rough surface when compared with pure ZnO. At high dipping time such as 7 and 9 min showed that the some particle aggregated together. Overall the average particle size of ZnO/QDs was showed in the table 5.1

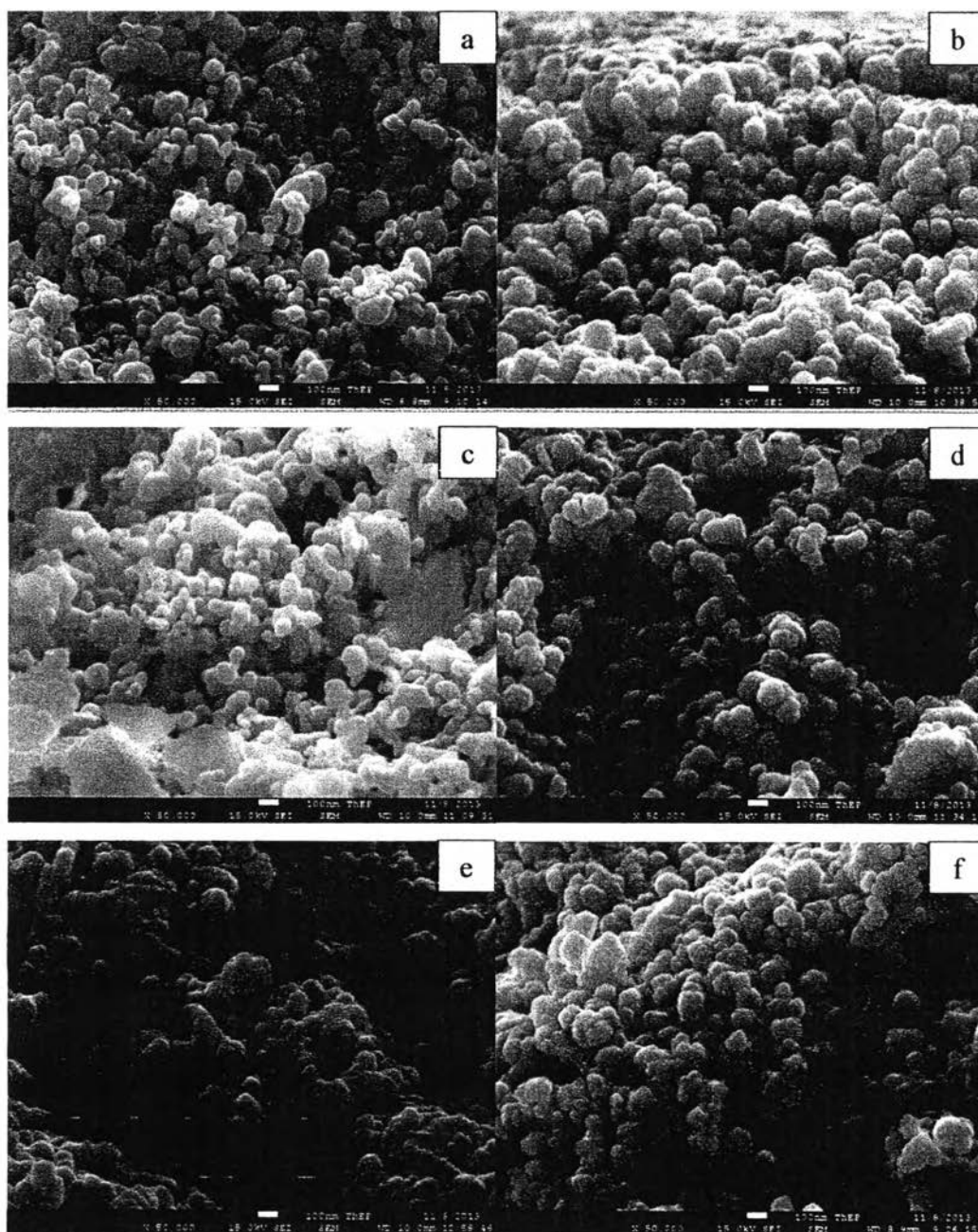


Figure 5.15 FE-SEM cross-section images of the ZnO/CdS QD at (a) 0 min, (b) 1 min, (c) 3 min, (d) 5 min, (e) 7 min and (f) 9 min.

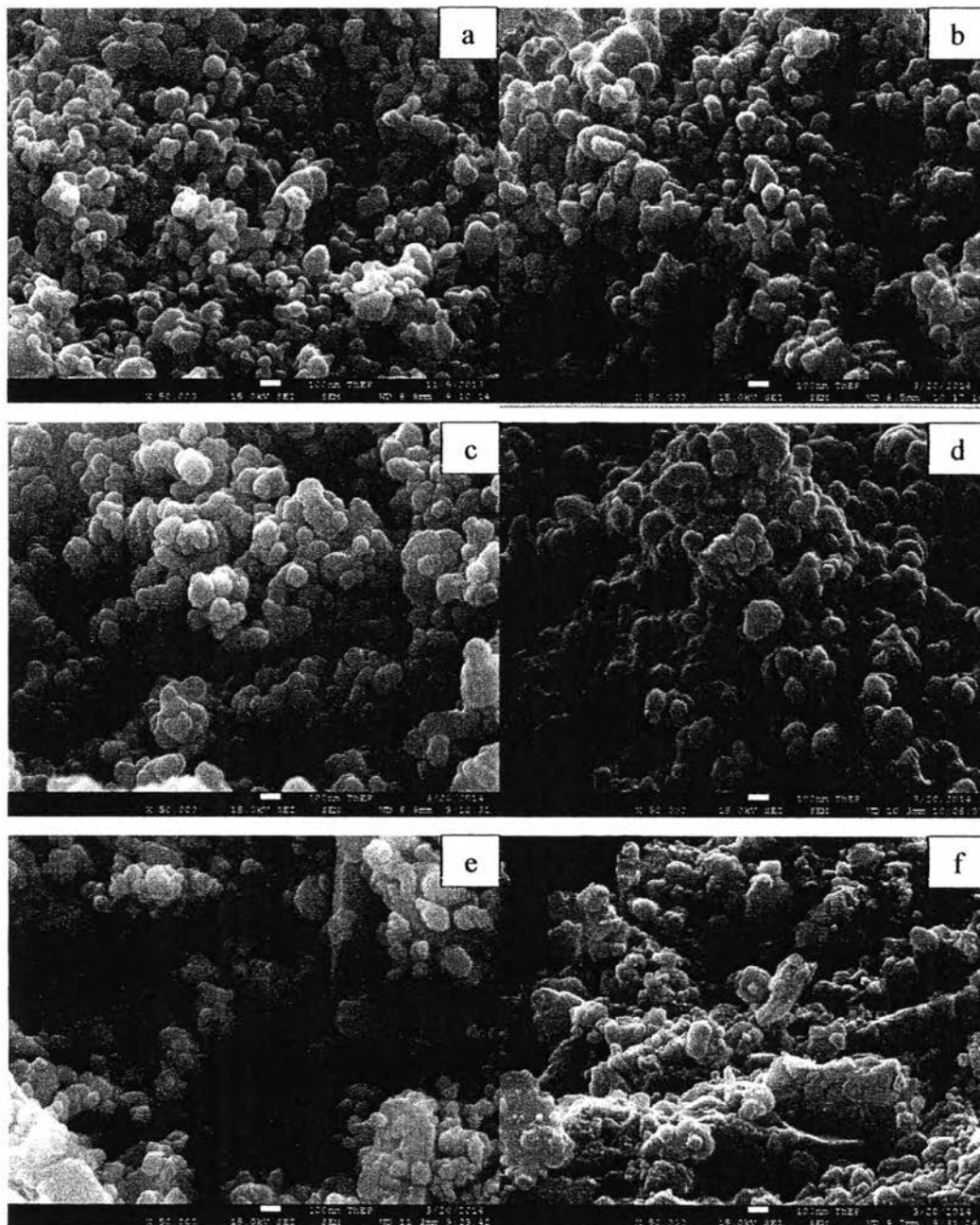


Figure 5.16 FE-SEM cross-section images of the ZnO/ZnS QD at (a) 0 min, (b) 1 min, (c) 3 min, (d) 5 min, (e) 7 min and (f) 9 min.

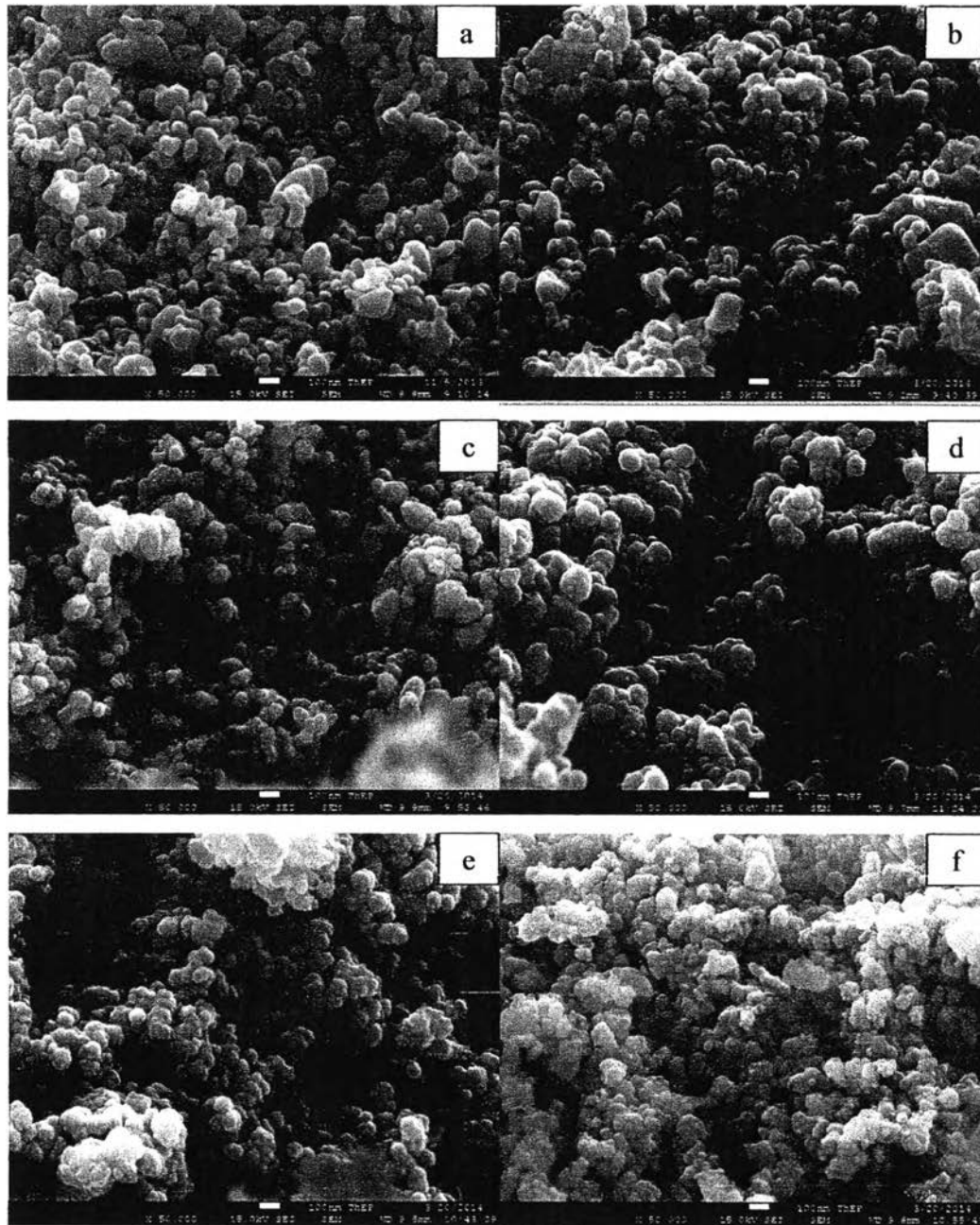


Figure 5.17 FE-SEM cross-section images of the ZnO/Ag₂S QD at (a) 0 min, (b) 1 min, (c) 3 min, (d) 5 min, (e) 7 min and (f) 9 min.

Table 5.1 The particle size of ZnO/QDs at various dipping times

QDs	Dipping time	Average particle size
	0 min	92.35
CdS	1 min	125.25
	3 min	104.41
	5 min	144.0
	7 min	150.39
	9 min	132.45
ZnS	1 min	126.13
	3 min	137.80
	5 min	137.30
	7 min	127.03
	9 min	154.78
Ag ₂ S	1 min	114.17
	3 min	136.31
	5 min	140.95
	7 min	114.02
	9 min	118.03

5.4.7 Performance of QDs on ZnO DSSCs

In order to study the function of QDs, the DSSC without dye was fabricated to compare with DSSC with dye. The DSSC of all QDs on ZnO showed that the conversion efficiency was very low when compared with normal DSSC (with dye) which was showed in table 5.2 This indicated that the QDs is not a sensitizer but they are semiconductor that provides more light to dye by releasing the fluorescence from relaxation process of their molecules.

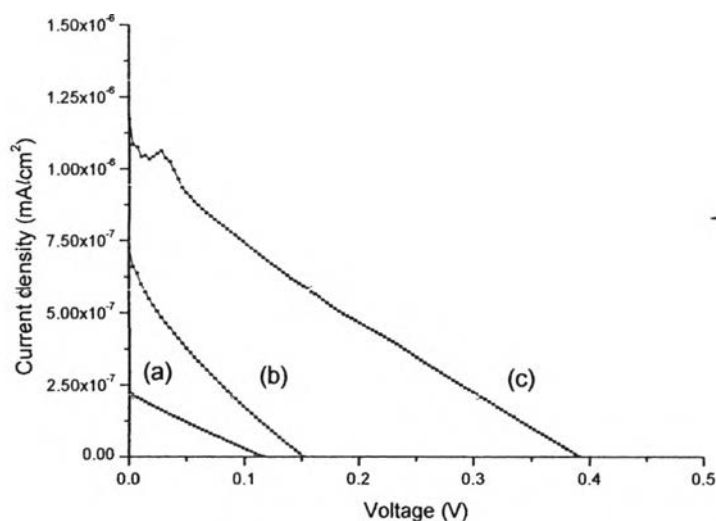


Figure 5.18 The J-V characteristics of DSSC with QDs: (a) CdS, (b) Ag₂S and (c) ZnS.

Table 5.2 The efficiency parameters of QDs on ZnO for DSSC

QDs	J_{sc} (nA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
CdS	236.1	115.9	24.0	6.534E-6
Ag ₂ S	708.4	148.9	18.9	1.996E-5
ZnS	1080.0	369.8	20.4	8.147E-5

5.4.8 Performance of Mixed Dyes on ZnO DSSCs

Figure 5.19 showed J-V characteristic of DSSC that sensitized with mixed natural dyes based on yellow cotton. Table 5.3 showed the data acquired from measuring the photoelectric conversion efficiency of DSSC. The highest efficiency of DSSC prepared by yellow cotton-spirulina with 0.526 mA/cm² (J_{sc}) of short-circuit current, 0.302 V of open circuit voltage (V_{oc}) and 9.1 % of fill factor. Then the efficiency of DSSC which was prepared by yellow cotton-indigo with 0.225 mA/cm² of short-circuit current (J_{sc}), 0.167 V of open circuit voltage (V_{oc}) and 10.1 % of fill factor. Finally, the lowest efficiency of DSSC which was prepared by yellow cotton-red orchid

with 0.017 mA/cm^2 of short-circuit current (J_{sc}), 0.410 V of open circuit voltage (V_{oc}) and 19.1% of fill factor. The efficiency of yellow cotton was improved when used indigo and spirulina to mix together. In mixed yellow cotton-red orchid system, the efficiency of DSSC was lower than DSSC with pure yellow cotton due to the efficiency of DSSC with pure red orchid was lower than pure yellow cotton. From this experimental data, the mixed yellow cotton-spirulina was chosen to use in next point.

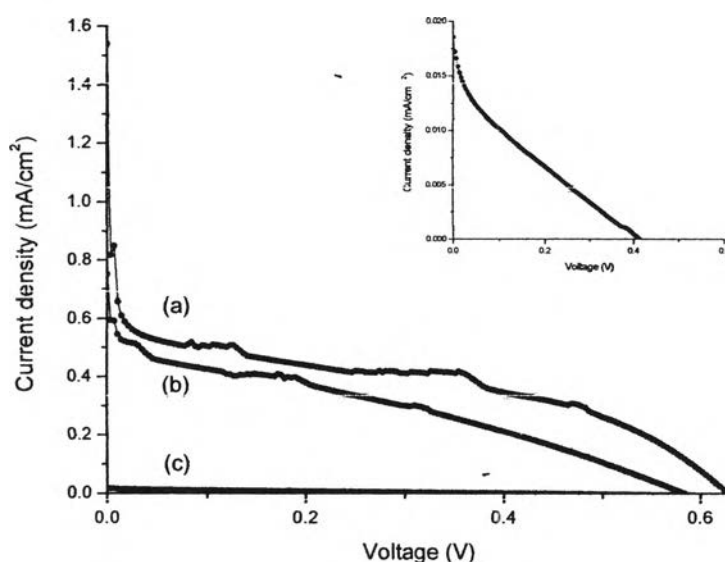


Figure 5.19 The J-V characteristics of DSSC with mixed natural dyes: (a) mixed yellow cotton-spirulina, (b) mixed yellow cotton-indigo and (c) mixed yellow cotton-red orchid. Inset shows the enlarge J-V curve of mixed yellow cotton-red orchid.

Table 5.3 The efficiency parameters of mixed dyes on ZnO for DSSC

Natural mixed dyes	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
Yellow cotton-indigo	0.255	0.167	10.1	0.0043
Yellow cotton-red orchid	0.017	0.410	19.1	0.0013
Yellow cotton-Spirulina	0.526	0.302	9.1	0.0145

5.4.9 Performance of Pure Dyes on ZnO/QDs Semiconductor DSSC

To study effect of QDs to the conversion efficiency of DSSC, the DSSC with natural dye and natural dye/CdS QD were fabricated. The result showed that when added the CdS QD in the DSSC the conversion efficiency was improved. From the table 5.4, only J_{sc} value which was increased. The QDs caused the amount of electron increased due to they can absorb the light in NIR region and emit the light in visible region that natural dyes can absorb. Therefore, intensity of light will be increase causing the amount of electron increase and result in higher conversion efficiency.

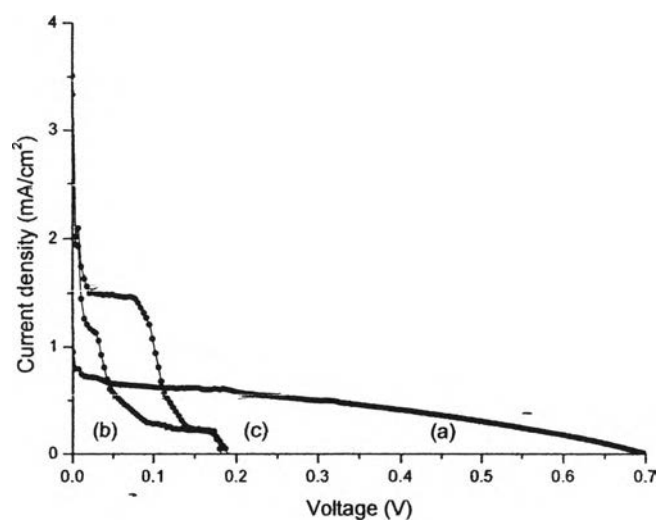


Figure 5.20 The J-V characteristics of DSSC with yellow cotton dye and CdS QD: (a) yellow cotton, (b) yellow cotton/CdS 5 min and (c) yellow cotton/CdS 9 min.

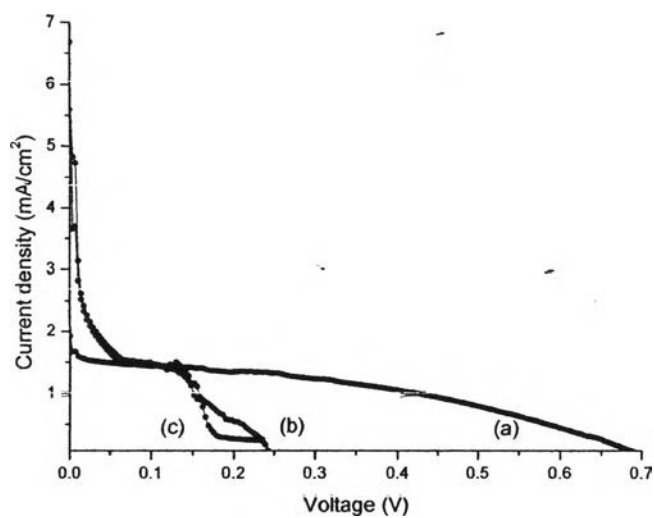


Figure 5.21 The J-V characteristics of DSSC with indigo dye and CdS QD: (a) indigo, (b) indigo/CdS 5 min and (c) indigo/CdS 9 min.

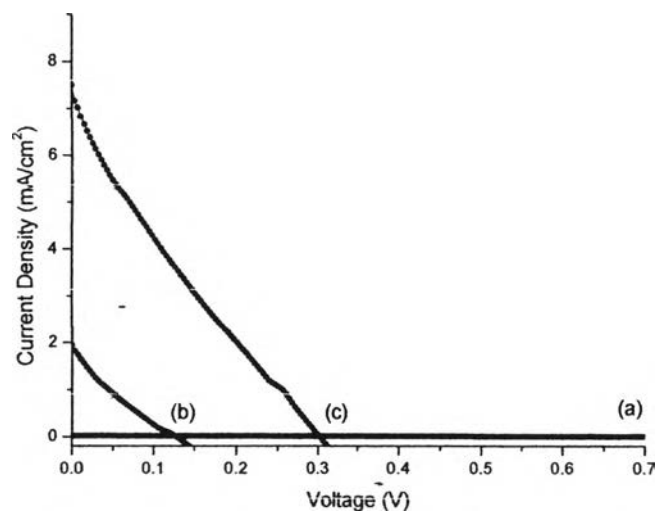


Figure 5.22 The J-V characteristics of DSSC with red orchid dye and CdS QD: (a) red orchid, (b) red orchid/CdS 5 min and (c) red orchid/CdS 9 min.

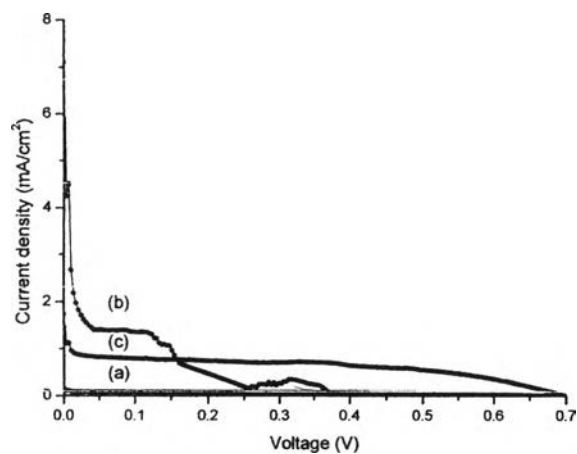


Figure 5.23 The J-V characteristics of DSSC with spirulina dye and CdS QD: (a) spirulina, (b) spirulina /CdS 5 min and (c) spirulina /CdS 9 min.

Table 5.4 The efficiency parameters of natural dyes and natural dye/CdS QD on ZnO for DSSC

Natural dye	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
Red orchid	0.013	0.368	14.8	0.0005
Red orchid /CdS 5m	0.019	0.126	19.1	0.0005
Red orchid /CdS 9m	0.007	0.303	20.9	0.0005
Spirulina	0.039	0.507	15.6	0.0171
Spirulina /CdS 5m	0.509	0.313	10.7	0.0170
Spirulina /CdS 9m	0.495	0.325	12.3	0.0198
Yellow cotton	0.203	0.168	11.4	0.0041
Yellow cotton/CdS 5m	0.255	0.167	10.1	0.0043
Yellow cotton /CdS 9m	0.264	0.172	25.5	0.0116
Indigo	0.426	0.234	20.1	0.0200
Indigo /CdS 5m	0.461	0.224	18.9	0.0196
Indigo /CdS 9m	0.638	0.223	14.4	0.0206

5.4.10 Performance of Mixed Dyes on ZnO/QDs Semiconductor DSSC

Figure 5.24 showed the J-V curves of DSSCs with mixed yellow cotton-spirulina based on ZnO/ZnS semiconductors and the results of these DSSC are listed in Table 5.5 It was found that the conversion efficiency of DSSC which had various dipping time was increase and the maximum conversion efficiency was 0.0239 % at 9 min dipping time. The result indicated that QDs improved the all parameters of DSSC performance. Therefore, QDs not only increase the absorption in NIR region but also help the electron flow well causing J_{sc} and V_{oc} increase, respectively.

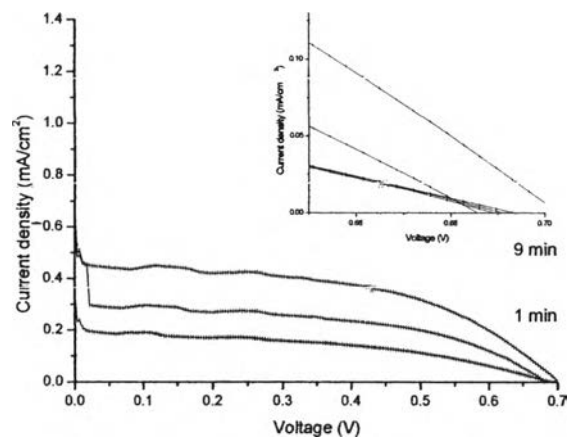


Figure 5.24 The J-V characteristics of DSSCs with mixed yellow cotton-spirulina on ZnO/ZnS QD. Inset shows the enlarge J-V curves.

Table 5.5 The efficiency parameters of mixed dyes (yellow cotton- spirulina) on ZnO/QDs for DSSC

QDs	Dipping time	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
ZnS	1 min	0.571	0.233	11.2	0.0148
	3 min	0.581	0.237	10.9	0.0149
	5 min	0.571	0.234	11.4	0.0151
	7 min	0.585	0.249	13.5	0.0198
	9 min	0.769	0.242	12.8	0.0239
CdS	1 min	0.872	0.266	8.4	0.0195
	3 min	0.888	0.268	8.4	0.0201
	5 min	0.895	0.270	8.5	0.0206
	7 min	1.220	0.244	11.4	0.0339
	9 min	1.200	0.245	11.7	0.0345
Ag ₂ S	1 min	0.557	0.242	13.4	0.0180
	3 min	0.577	0.247	13.3	0.0190
	5 min	0.690	0.317	10.5	0.0229
	7 min	0.727	0.334	11.0	0.0266
	9 min	0.830	0.346	11.2	0.0321

Figure 5.25 showed the J-V curves of DSSCs with mixed yellow cotton-spirulina based on ZnO/CdS semiconductors and the results of these DSSC are listed in Table 5.5 This results indicate that when the dipping time of produced QD increased, the conversion efficiency of DSSC raised. The highest conversion efficiency of DSSC based on ZnO/CdS QD equaled to 0.0345 % with dipping time 9 min.

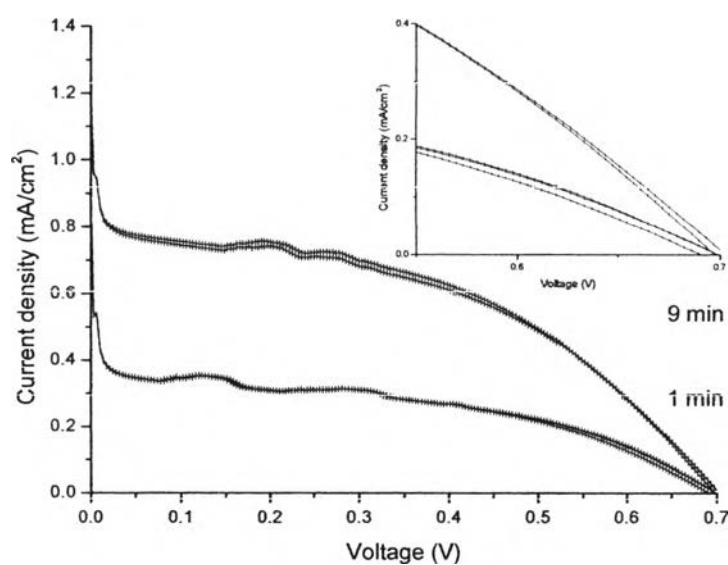


Figure 5.25 The J-V characteristics of DSSC with mixed yellow cotton-spirulina on ZnO/CdS QD. Inset shows the enlarge J-V curves.

Figure 5.26 showed the J-V curves of DSSCs with mixed yellow cotton-spirulina based on ZnO/Ag₂S semiconductors and the results of these DSSC are listed in Table 5.5 The results show that if dipping time increase, the conversion efficiency will be increased. The DSSC with dipping time 9 min showed the highest conversion efficiency which equaled to 0.0321 %.

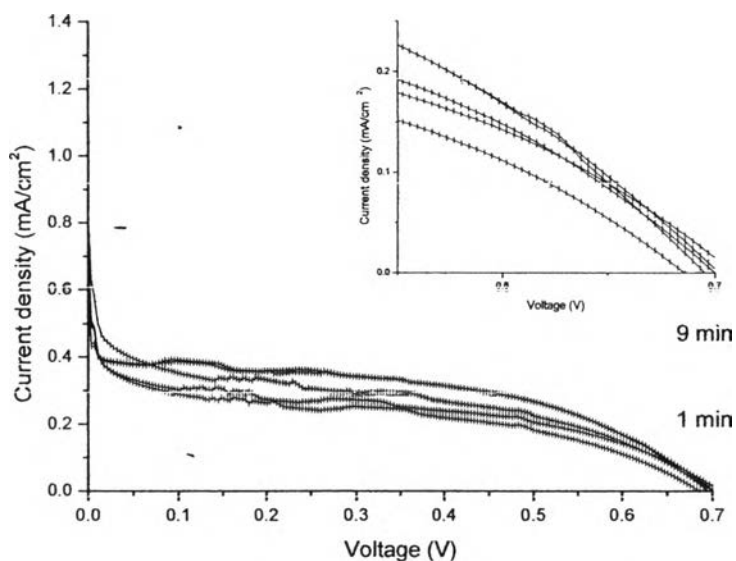


Figure 5.26 The J-V characteristics of DSSC with mixed yellow cotton-spirulina on ZnO/Ag₂S QD. Inset shows the enlarge J-V curves.

5.5 Conclusions

In summary, the emission spectra show the emission wavelength at 385, 385 and 420 nm for CdS, ZnS and Ag₂S, respectively. Therefore, the yellow cotton is chosen to use to be a main dye to mix with other dyes because its absorption wavelength is near the emission wavelength of QDs. Moreover, when the dipping time increases the intensities of both absorption and emission increase. The mixed natural dyes have been combined based on yellow cotton. The UV spectra of three mixed dyes system: mixed yellow cotton-spirulina, mixed yellow cotton-indigo and mixed yellow cotton-red orchid illustrate the identical characteristic of both of two dyes in mixed system. The solar testing is used to measure the conversion efficiency of DSSC with mixed dyes. It is found that mixed yellow cotton-spirulina shows the highest conversion efficiency equaling to 0.0145 %. Therefore, the mixed yellow cotton-spirulina is chosen to use to

be sensitizer for ZnO/QDs DSSC. Then effect of type of QDs to the conversion efficiency is studied. The results indicate that the highest conversion efficiency is found in mixed yellow cotton-spirulina with ZnO/CdS which conversion efficiency equals to 0.0345 %.

5.6 Acknowledgements

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5.7 References

- Choi, H., Nahm, C., Kim, J., Kim, C., Kang, S., Hwang, T., Park, B. (2013) Review paper: Toward highly efficient quantum-dot- and dye-sensitized solar cells. Current Applied Physics, 13, S2-S13.
- Narayan, M. R. (2011) Review: Dye sensitized solar cells based on natural photosensitizers. Renewable and Sustainable Energy Reviews
- Rani, G., Sahare, P. D. (2013) Study of the structural and morphological changes during the phase transition of ZnS to ZnO. Applied Physics A
- Ruhle, S., Shalom, M., Zaban, A. (2010) Quantum-dot-sensitized solar cells. Chemphyschem, 11(11), 2290-2304.
- Sambur, J. B., Novet, T., Parkinson, B. A. (2010) Multiple exciton collection in a sensitized photovoltaic system. Science, 330(6000), 63-66.
- Subash, B., Krishnakumar, B., Swaminathan, M., Shanthi, M. (2013) Ag₂S-ZnO--an efficient photocatalyst for the mineralization of Acid Black 1 with UV light. Spectrochimica Acta. Part A: Molecular and Biomolecular Spectroscopy, 105, 314-319.

Wongcharee, K., Meeyoo, V.,Chavadej, S. (2007) Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers. Solar Energy Materials and Solar Cells, 91(7), 566-571.