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Studies of the absorbance peak on the N719 dye influence by combination between Cadmium Selenide (CdSe)QDs and Zinc Sulfide(ZnS)QDs

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Abstract. The absorption rate of the photoanode can be influenced by the combination between the difference semiconductor quantum dot sensitizer. Six samples were prepared with difference weight percent (wt%) of ZnS from 0% to 50% and constant wt% of CdSe which then will be called as semiconductor QDs were immersed in 0.5mM of N719 dye. The purity of ZnS powder and CdSe powder was determined using x-ray diffraction (XRD).The ultraviolet-visible spectrophotometry (Uv-Vis) use to investigate the absorption spectrum and absorbance peak of this sample. 50 wt% of ZnS is the best composition to increase the absorbance peak of the photoanode. The Cyclic voltammetry (CV) of varying wt% of ZnS, found that the 40 wt% of ZnS is suitable combination for a DSSC's photoanode and produced the higher current.

1 Introduction

Nowadays people are looking for the artificial sources to replace the traditional source. Quantum –dot-sensitized solar cells (QDSSCs) is the most suitable artificial source to replace the traditional sources[1].The benefit using the QDSCs as the artificial source is low cost and the efficiencies boosted up to the traditional Shockley and Queisser limit of 30%[3]. The only difference between the Dye-synthesis solar cell (DSSCs) compare to QDSCs is the replacement of organometallic or organic dye with the narrow band gap semiconductor material QD and the combination between QD and dye is called QDSCs. The most important part in the QDSCs is the photoanode, this part consists of sensitizers which are a semiconductor QD. The semiconductor QDs will be combined with the TiO_2 and coated onto glass sustrate. The semiconductor quantum dot such as InAs, CdSe, CdS, PbSe, and InP have a narrow band gap that is suitable to be used as the sensitized in the QDSCs [3]. The narrow bandgap will couse of easily electron transport when exposes to visible light and even though the light carries a low energy the emitted electron will travel through the TiO2 nanoparticle until it reaches anode, the electron produce current and energy to a device [4]. This electron will arrive at the cathode and move into the electrolyte to be sent back into the QDs in the photoanode [6]. QDs afford extremely optical properties and admirable electrical properties as compared to traditional organic dyes [3]. Furthermore, the various properties of semiconductor QDs make them attractive to take a part in the QDSSCs as a sensitizer. The high absorption coefficients make it suitable for the generation of multiple electrons carrier under high-energy excitation [5].

The high potential of semiconductor QDs sensitizer for light harvesting in the visible –light region, drawn much attention to be explored by the researcher [11]. Semiconductor QDs which is CdSe/ZnS has higher conduction band compared to the TiO_2 layer, this can increase the rate of electron injection of photon excited electrons into the photoanode. The band gap of ZnS is 3.6eV, this will limit the absorption range below a wavelength of 344 nm and the band gap for the CdSe is 1.7 eV [3], therefore the wavelength absorption that can be absorbed is below the 720nm. Because of the low conduction band edge of CdSe compare to ZnS and TiO_2, the efficiency of injection electron could be less.

Light carries the source energy in the form of a photon, this energy will be permeated by a particle in the material [9]. If the particle absorbs the energy of light bigger than their band gap, this particle will emit electron out from their shell [12]. These studies were investigated the variation of absorption spectrum by the photoanode with the difference the weight percent of ZnS/CdSe.

2 Methodology

2.1 Preparation of CdSe/ZnS solution

The two main material are CdSe and ZnS purchased from Sigma Aldrich. Various wt% of the ZnS, were mixed into

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CdSe QDs. 0.045 g ruthenium-based dye (N719) were dissolve in 9mL of ethanol to produce 0.5mM of liquid N719

$$concentration=(number\ of\ mole\ )/(volume\ ) \quad (1)$$

$$molar\ mass=(\ mass)/(number\ of\ mole) \quad (2)$$

Six samples of QDss were prepared with difference weight percent (wt%) of ZnS from 0% to 50% and constant 10% of CdSe. The solution of 0.5mM of N719 was added. The samples were stirred for 24 hours using magnetic stirrer to get a homogenous solution. The mass of QDs ZnS/CdSe powder for each sample were calculated using equation below:

$$Wcdse/zns=(x(wn719))/(1-x)) \quad (3)$$

Where x is the percentage of ZnS/CdSe

Table 1. Percentage of CdSe/ZnS QDs Prepared.

Sample	CdSe/Zns QDs composition (wt%)	Mass of N719dye powder	Mass of CdSe/ ZnS QDs powder (g)
A	10	0.045	0.005
B	20	0.045	0.011
C	30	0.045	0.019
D	40	0.045	0.030
E	50	0.045	0.045

2.2 preparation of photoanode

Three steps of cleaning ITO glass using ultrasonic bath where the first step is using the distilled water then acetone and followed by ethanol. Then, the ITO glass was dried at 60^0C for 21 hours. TiO_2 nanoparticle was paste onto ITO glass using the doctor blade technique. The thickness and the area of the TIO_2 on the surface of ITO glass will be control by two parallel adhesive tapes 1cm apart and the area of the TiO_2 film is 1.8 x 1.0 cm before heated in the oven for 24 hours at 450 ^{o}C. The dried TiO_2 film was then immersed in varied wt% of QDs for 24 hours in dark environment. Lastly, ethanol was used to remove and wash dye residue on the surface before dried again in the oven at 60^0C for 24 hours

2.3 Characterization of N719/CdSe-ZnS solution

2.3.1 X-ray diffraction technique (XRD)

XRD was used to study the crystalline structure and phase components of QDs powder. The structure spacing was determined by the high of intensity peak of the spectra. The higher number of count on the same angle prove that the existing components of the CdSe and ZnS.

2.3.2 Uv-vis spectrometry

UV-Vis spectrometry uses to detect the band gap of each sample in the form of a solution. 0.0005 mM CdSe/ ZnS was analyzed at a range of 200 - 900nm and the blank solution is ethanol.

$$E=h(c/\lambda) \quad (4)$$

2.4 Characterization ITO/TiO_2/N719/CdSe-ZnS photoanode

2.4.1 Cyclic voltammetry

The conductivity of co-sensitized of photoanode were be analyzed using the Cyclic voltammetry device. The sample of difference wt% of QDs (ITO/TiO_2/N719-CdSe/ZnS) photoanode were used as a working electrode (W_e), while the counter electrode (C_e) is platinum and Ag/AgCI/3MKCI was act as the reference electrode. The applied voltage on the sample was from -1.0 V to 1.0 V and every sample was run for three cycles to get the average data [11]

3 Results and Discussions

Figure 1 shows the proof of the existing component CdSe and ZnS in the sample powder. From the result in Figure1a the experiment stick pattern of ZnS and CdSe is similar to the reference stick pattern from Institute of Chemical Dependency Studies (ICSD) by xu,y-N ching (1993).The h,k,l peak of CdSe which is(100) is the first clearly produce in the experimental result and another peak such as 002,101,102 also clearly be observed between this two pattern. In Table 2 the first three peak produce at 23.881,25.381,27.101 which is 100,002 and 101 show the strongest proof that this powder is CdSe.

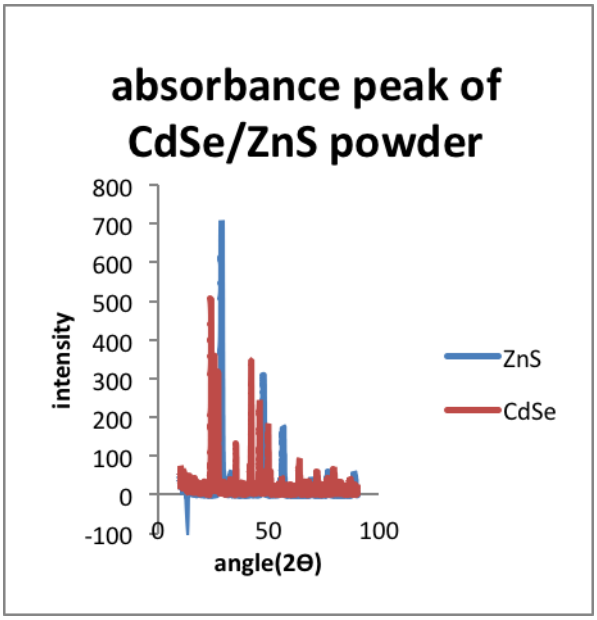


Fig. 1(a). Experimental absorbance peak CdSe/ZnS QDs

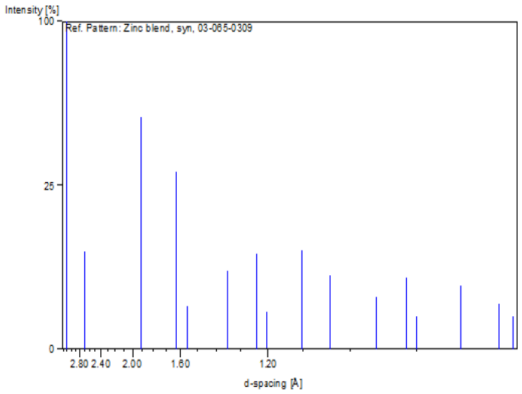


Fig. 1(b): Absorbance Θpeak of CdSe QDs

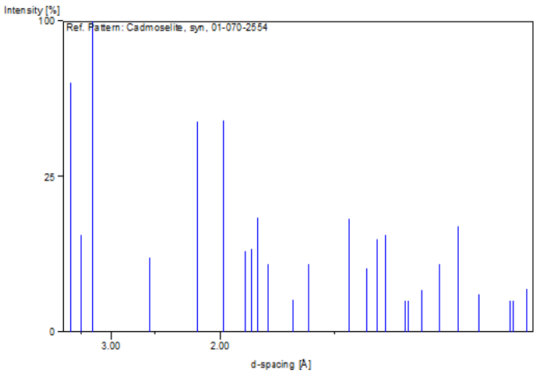


Fig. 1(c): Absorbance Θpeak of ZnS QDs

Table 2. Comparison reference (R) result and experimental (Ep) result of CdSe powder

No	h	k	l	(R) 2Θ	(R) d(A)	(Ep) 2Θ	(Ep) d(A)
1	1	0	0	23.882	3.723	23.881	3.726
2	0	0	2	25.373	3.507	25.381	3.509
3	1	0	1	27.093	3.288	27.101	3.290
4	1	0	2	35.123	2.552	35.129	2.554

Table 3. Comparison reference (R) result and experimental(Ep) result of ZnS powder

No	h	k	l	(R) 2Θ	(R) d(A)	(EP) 2Θ	(EP) d(A)
1	1	1	1	28.609	3.117	28.589	3.122
2	2	0	0	33.153	2.700	33.157	2.702
3	2	2	0	47.591	1.909	47.581	1.911
4	3	1	1	56.473	1.628	56.441	1.630

In table3 the first three peak is at the angle 28.589^0,33.157^0 and 47.581^0 which is the h,k,l peak is 111,200 and 220, this peak is similar to the reference result from NIST by Dubrovin in 1983.

The highest number of count (intensity) by the CdSe samples is 505 at the angle 23.881, this means that the 505 particles reflects the x-ray source to that detector at this angle and from calculation the spacing particle is 3.72651(A), this is the spacing between particles d(A) in the CdSe powder that has been analyzed using XRD method compared to the reference result found that the spacing between the particle is 3.72304 (A) and their percentage difference is about 0.046%.The very small percentage difference between reference d(A) and sample d(A) prove that the powder consists the component of CdSe. For the ZnS powder, the same method is used by comparing the difference between the spacing particle d(A) in the sample with the reference result. The highest peak produce in the ZnS sample is 711 count at 28.569^0 and the spacing between particle is about 3.12264(A), compared to the reference result the highest number count is at 28.609^0 with the spacing between particles is 3.11769(A). The difference particle spacing between the reference value and ZnS sample is 0.0079%, the small difference percentage prove that this powder is ZnS. Table 2 and Table 3 shows the reference (R) and experiment (Ep) peak with comparison of the spacing between first four peaks.

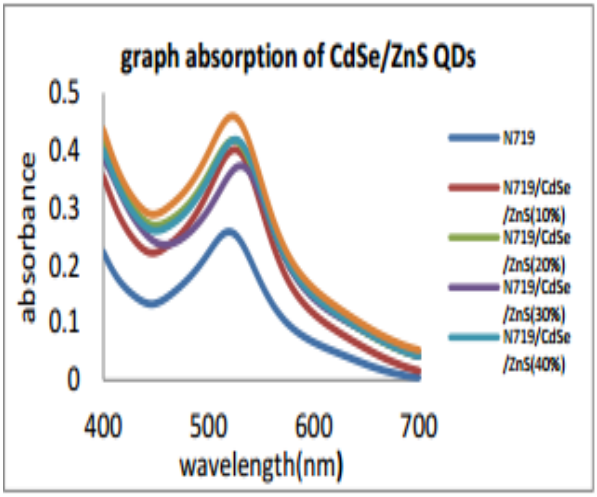


Figure 2. Graph absorption of CdSe/ZnS QDs

Table 4: The value absorbance of CdSe/ZnS QDs with difference weight present (wt%)

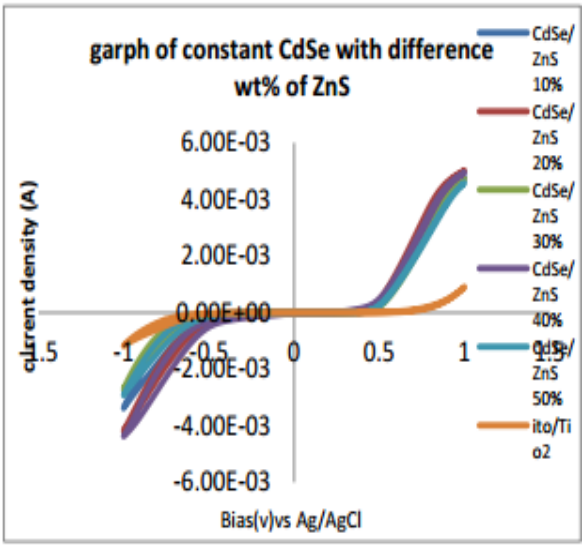
Maximum wavelength (nm)	N719	N719/CdSe/ZnS (10%)	N719/CdSe/ZnS (20%)	N719/CdSe/ZnS (30%)	N719/CdSe/ZnS (40%)	N719/CdSe/ZnS (50%)
525	0.2541	0.4015	0.4173	0.3687	0.4186	0.4584

Figure 2 shows the spectra absorption of six samples with various wt%. The highest peak of spectra is 525 nm of wavelength. This shows that the electron in the sample needs the energy of light with 525 nm to excited one electron out of the particle. Equation 4 was used to calculate the band gap of the CdSe/ZnS resulted 2.36 eV.

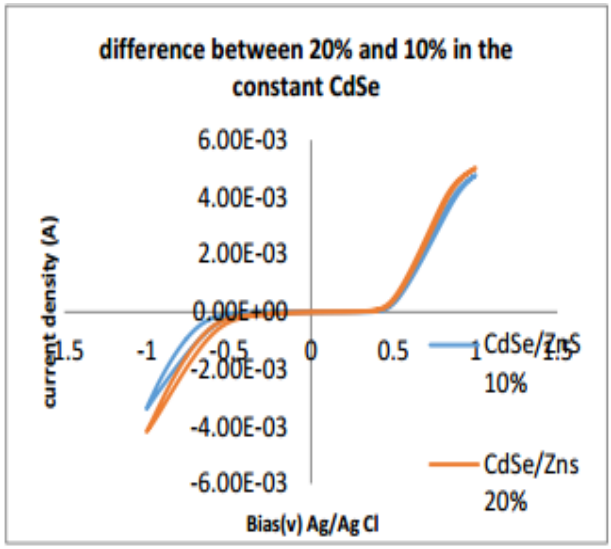
However, control variable, N719 dye showed the absorbance peak at 0.2541 as tabulated in Table 4. As for 10 wt% CdSe/ZnS QDs, the absorbance peak shifted from 0.2541 to 0.4015. This result shows that the combination of N719 and CdSe/ZnS QDs can increase the absorption of light. The 20% ZnS sample have the higher absorbance peak compared to the 10% ZnS sample. The difference between this two peak is 2% may due to formation hole in the 20% ZnS sample is higher compared to the 10 wt%

ZnS. The absorbance peak of 20 wt% ZnS is higher compared to 30 wt% ZnS samples. The absorbance peak of 40 wt% ZnS sample higher than 20 wt% ZnS sample. The absorbance peak of 50 wt% ZnS is higher compared to 40 wt% ZnS sample, this shows that the most suitable material to increase the absorption process is 50wt% of ZnS.

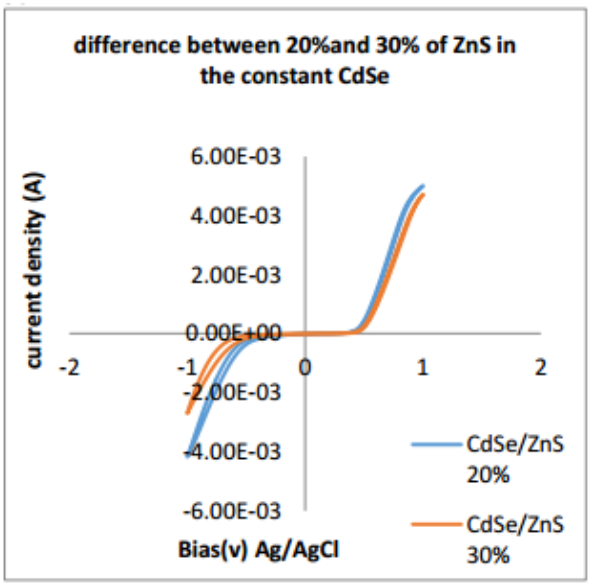
3a



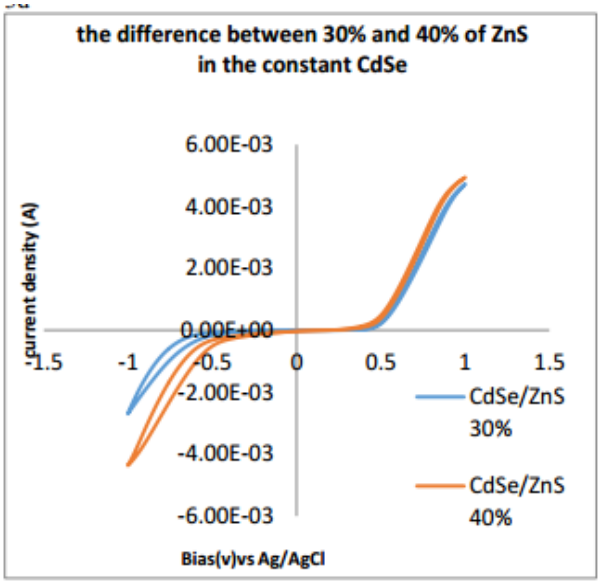
3b



3c



3d



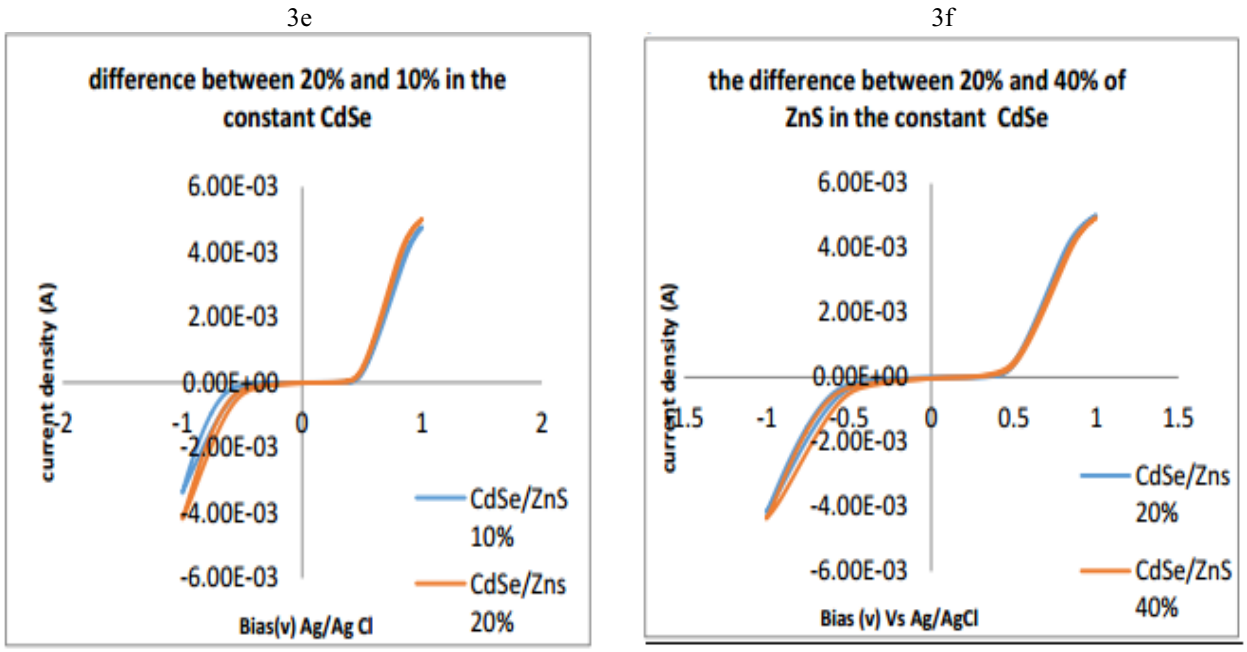


Fig. 3. Cyclic voltammetry of difference wt% of QDs

The I-V behavior of different sample with difference wt% of ZnS QD showed in Figure 3. Figure 3a shows the comparison of current produced between sample photoanode with difference wt% QD and sample without QDs. ITO/TiO_2 shows -0.00118 A while the combination of ITO/TiO_2/CdSe-ZnS(10%) is -0.00338 A, gives the difference of 0.00220 A. The current produced by the movement of an electron in the circuit, the more electrons flow the more current was produced [4]. However, the current from TiO_2 photoanode in Figure 3a is low may be due to the structure of the material which have a medium recombination process [6]. This recombination process reduces the acceleration of the electron to move from one particle to another in the structure of the TiO_2 thin film. Hence, the QDs photoanode consists of CdSe/ ZnS QDs provide a lot of hole at the valence shell of the particle, this valence shell is known as the hole act as the platform for the electron to jump from one particle to other until it reaches the conducting side of ITO glass [4]. The combination of ITO/TiO_2 with CdSe/ZnS QDs could increase the total number of the hole. As the result, the electron could flow easily.

Figure 3b shows the tabulated data of 10 wt% and 20wt% of ZnS. The current produce in CdSe/ZnS (20 wt%) is higher compared to the CdSe/ZnS(10 wt%). The 20 wt% ZnS produces -0.00418 A of current while the 10 wt% of ZnS is -0.00337952 A the difference between this two sample is -0.000801 A.

Table 5. The maximum current produced in each sample

Sample	Applied voltage (v)	Current produce (A)	The difference current (A) between Tio2 and QDs(wt%)
ITO/TIO2	-1.00098	-0.00118	
ITO/TIO2/ N719/CdSe-ZnS(10%)	-1.00098	-0.00338	-0.00220
ITO/TIO2/ N719/CdSe-ZnS(20%)	-1.00098	-0.00418	-0.00300
ITO/TIO2/ N719/CdSe-ZnS(30%)	-1.00098	-0.0027	-0.00152
ITO/TIO2/ N719/CdSe-ZnS(40%)	-1.00098	-0.00437	-0.00319
ITO/TIO2/ N719/CdSe-ZnS(50%)	-1.00098	-0.00292	-0.00174

The process of reduction in the system involved the donation of electrons from the electrolyte (Ag/AgCl 1M KCI) to the photoanode (CdSe/ZnS, QDs). The unstable particle which has the hole on their valence particle produce the easy way for an electron to pass through the barrier [6]. Table 5, shows the maximum current value produced by each sample. The highest value of current produced is CdSe/ZnS(40 wt%) which is -0.00437 A. The lowest current produce for the QDs photoanode is CdSe/ZnS(10%). The current increase -0.0008 A from 10 wt% to 20 wt% and -0.00167 from 30 – 40 wt% but the

current reduce-0.00148 A from 20 wt% to 30 wt% and -0.00145 A from 40 wt% to 50 wt% of CdSe/ZnS.

4 Conclusions

CdSe/ZnS QDs immersed in N719 could increase the movement of electrons in the photoanode materials. 50 wt% of ZnS is the best composition to increase the absorbance peak of the photoanode. The Cyclic voltammetry (CV) of varying wt% of ZnS, found that the 40 wt% of ZnS at 0.00437 A is suitable combination to make a photoanode and could produce the highest current.

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