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Performance and Impedance Spectroscopy of co-Sensitization of Anthocyanin Dye And Semiconductor Quantum Dots in Sensitizing Solar Cells

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In this work, anthocyanin dye was extracted in ethanol from black rice and used as a sensitizer together with CdS and CdSe quantum dots (QDs) in a QD-dye-co-sensitized TiO_2 solar cell. QDs were prepared via wet solution processed method. Performances of the natural dye-sensitized solar cells with iodide based or cobalt based electrolyte were compared. Solar cells with cobalt-based electrolyte system showed stable performance throughout the measurement period. With the same cobalt based electrolyte, the solar cell co-sensitized with anthocyanin dye and both CdS and CdSe QDs showed the best performance. However, combination of anthocyanin dye and CdS QD as sensitizers showed an overall best performance with iodide-based electrolyte system. The low performance of the cells reported in this study can be attributed to the high recombination rate as observed from electrochemical impedance spectroscopy (EIS) studies.

Keywords: Anthocyanin, quantum dots, cobalt-based electrolyte, electrochemical impedance spectroscopy.

1. INTRODUCTION

Dye-sensitized solar cell (DSSC) and quantum dot-sensitized solar cell (QDSSC) have generated much interest in the past few years due to their ease of fabrication and potential to yield high performance [1,2]. QDSSCs in particular have gained momentum in the solar cell field owing to the excellent optical properties of the sensitizers i.e. semiconductor quantum dots (QDs) as well as the ease of fabrication of the QDs [3,4]. Among the semiconductor materials for QD sensitizers, Ag_2S [5], CdS [6], CdSe [7], $CuInS_2$ [8] and PbS [9] are widely used. Recently, high performing perovskite QD-based solar cell has emerged as a new breakthrough in third generation solar cells [10].

In general, the performance of both DSSC and QDSSC is still lacking behind the commercial thin film photovoltaic. To achieve high performance in sensitized solar cells, various methods have been suggested [1,2]. One of the facile methods is to co-sensitize the titanium dioxide (TiO_2) layer with different dyes and/or semiconductor sensitizers. By using both dye and quantum dots (QDs) as co-sensitizers, there is a potential of achieving better solar cell performance as a result of better light harvesting upon illumination [11]. Although DSSCs based on ruthenium dyes give better performance, the high cost of such dyes has motivated researchers to use natural dyes as alternative sensitizers [12-18]. Some of the commonly used natural dyes are anthocyanin and carotene.

In this work, natural anthocyanin dye extracted from black rice was selected as one of the sensitizers to be used along with QDs. The idea of using natural dye as a co-sensitizer with QDs is aimed at obtaining an alternative and low-cost solar cell. Some considerations that need to be taken in this type of hybrid cell are the choice of electrolyte and counter electrode. As iodide-based electrolyte does not work well with QDs especially CdS and CdSe, a commonly used cobalt-based electrolyte was prepared and tested in the solar cell assembly [19-21].

2. EXPERIMENTAL

2.1 Materials

TiO_2 paste (PST-18NR) was obtained from JGC C&C, Japan. Fluorine doped tin oxide (FTO) conducting glass (8 Ω/sq) and platinum catalyst solution were purchased from Solaronix, Switzerland. Di-isopropoxytitanium bis(acetylacetonate) solution for the preparation of TiO_2 compact layer was purchased from Sigma-Aldrich. A small amount of the solution was then diluted with ethanol to obtain a 0.38 M solution. Cadmium nitrate tetrahydrate, sodium borohydride, selenium dioxide and sulfur were all obtained from Sigma-Aldrich. Sodium sulfide nonahydrate was purchased from Bendosen, Germany.

2.2 Sensitizing TiO_2 electrode

A compact TiO_2 layer was spin-coated on the FTO glass prior to the deposition of TiO_2 paste on the surface using a doctor blade method. In both cases, the as-prepared electrodes were subjected to sintering at 450°C for 30 min. CdS and CdSe QDs were prepared from wet solution process using the common successive ionic layer adsorption and reaction (SILAR) method according to our previous work [22]. In this method, TiO_2 electrode was first dipped into a cationic solution, before rinsing and drying at ambient temperature. The same electrode was then dipped into an anionic solution and ended with rinsing and drying. This two-step dipping is termed as 1 SILAR cycle. The CdS QDs were prepared with 4 SILAR cycles using a dipping time of 5 minutes per dip in 0.5 M cadmium nitrate ethanolic solution (cationic solution) and 0.5 M sodium sulfide methanolic solution (anionic solution) respectively. The CdSe QDs were prepared using 7 cycles having 30 seconds per dip in 0.03 M cadmium nitrate ethanolic solution and pre-prepared selenide ethanolic solution respectively. The QDs prepared are referred to as CdS(*n*) and CdSe(*n*) respectively, where *n* is the number of SILAR cycles used for preparing them. For co-sensitization with CdS and CdSe, CdSe QDs were prepared using 6 cycles instead. After sensitizing TiO_2 electrode with QDs, the electrode was soaked in an ethanolic solution of anthocyanin dye for 48 hours. Anthocyanin dye was extracted from the black rice using alcohol as the medium. Briefly, the extraction was performed by soaking a 50 g batch of black rice in 100 ml of ethanol solution. After 48 hours of soaking, anthocyanin dye from the black rice would percolate through the rice's membrane. As a result, the liquid would turn into dark purple color.

2.3 Electrolyte preparation

Iodide-based liquid electrolyte was prepared from 0.6 M 3-propyl-1-methylimidazolium iodide, 0.1 M lithium iodide, 0.025 M iodine and 0.5 M 4-tert-butylpyridine in acetonitrile. The cobalt-based liquid electrolyte, $[Co(o\text{-}phen)_3](TFSI)_2$ where o-phen = 1,10-phenanthroline, TFSI = bis(trifluoromethanesulfonyl)imide), was prepared based on the procedure described in the literature [21]. Accordingly the electrolyte was prepared from 0.75 M Co^{II} complex, 0.075 M Co^{III} complex and 0.2 M $LiClO_4$ in acetonitrile and ethylene carbonate solution (4:6/v:v). The Co^{II} complex needed was prepared by dissolving $CoCl_2$ in 1,10-phenanthroline followed by reaction with aqueous LiTFSI. The resulting precipitate was subsequently filtered and washed thoroughly. The Co^{III} was obtained by oxidizing Co^{II} with bromine during the solution preparation.

2.4 Device assembly and characterisation

Solar cell assembly was prepared by sandwiching the liquid electrolyte between a sensitized TiO_2 electrode and a Pt counter electrode. The Pt counter electrode was prepared by spin-coating a thin layer of platinum catalyst on the FTO conducting glass followed by sintering at 450°C for 30 min. A parafilm spacer was used to contain the liquid electrolyte. Absorption spectra characteristics of the sensitized TiO_2 electrodes were obtained using Shimadzu PC3101 UV-Vis NIR spectrophotometer. Photocurrent-voltage (*I-V*) behaviours of the solar cells were acquired using Keithley 2400 electrometer under illumination from a xenon lamp at the intensity of 1000 W m^{-2}. Electrochemical impedance spectroscopy (EIS) study on the cells was performed using an Autolab potentiostat/galvanostat in the frequency range 10^6 Hz to 0.1 Hz under the illumination of 1000 W m^{-2}. For this study the cells were biased at 0.5 V and EIS measurements were made with a 15 mV RMS voltage perturbation.

3. RESULTS AND DISCUSSION

Four types of solar cells were fabricated for this study: (a) Anthocyanin DSSC, (b) CdS and anthocyanin dye co-sensitized solar cell, (c) CdSe and anthocyanin dye co-sensitized solar cell, and (d)

CdS, CdSe and anthocyanin dye co-sensitized solar cell. Sensitization of the TiO_2 electrode was confirmed visually and via UV-Vis spectroscopy measurements. Figure 1 shows the visual appearance of the sensitized electrodes. With only anthocyanin dye as the sensitizer, the TiO_2 layer appears as dark purple. With the addition of CdS the colour changed to yellow and with CdSe QD the colour became brown. With both type of QDs added, the colour changed to dark brown. The colour changes indicate that good QD sensitizer uptake before the sensitization with anthocyanin dye. The extracted anthocyanin dye solution was not characterised in this study. The UV-Vis absorption spectra were measured on the sensitized electrodes in order to give a fair and better comparison. The absorption spectra of the four sensitized electrodes are shown in Figure 2. The absorbance spectrum of the anthocyanin dye-sensitized electrode shows an absorption edge at 675 nm. For the CdS and anthocyanin dye co-sensitized electrode, the absorption edge is seen at almost the same wavelength. However, the absorption rate is higher for the latter electrode in the lower wavelength region (400 – 500 nm). When the CdS QD is replaced with CdSe QD as the co-sensitizer the absorption edge shifts to a higher wavelength of 700 nm. This shift is attributed to the better optical absorption properties of the CdSe QD. The absorption rate for the CdSe sensitized electrode has also increased throughout the entire visible spectrum region (400 – 700 nm). However, when both types of QDs are used to co-sensitize with anthocyanin dye, the absorption edge remains at 675 nm and the absorption rate is lower than that of the electrode co-sensitized with CdSe QD and anthocyanin dye. The low absorption rate is plausible as the amount of CdSe QD sensitizers in this electrode is almost half of that in CdSe and anthocyanin dye co-sensitized electrode.

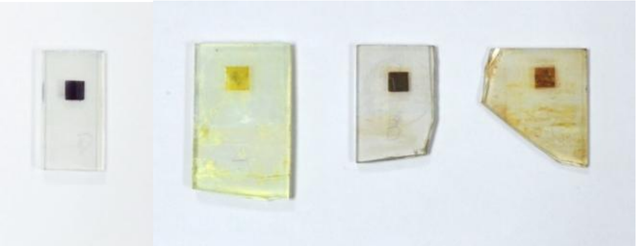

Figure 1. Samples of photoanode electrodes. From left to right: Anthocyanin dye; CdS(4) + Anthocyanin dye; CdSe(7) + Anthocyanin dye; CdS(4)/CdSe(6) + Anthocyanin dye.

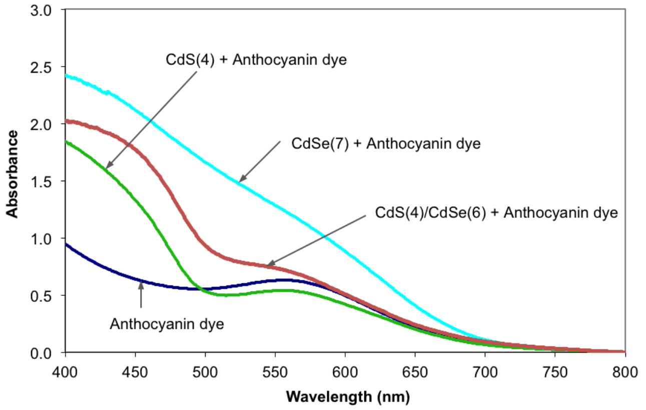

Figure 2. UV-Vis spectra of anthocyanin dye with/without CdS, CdSe QD-sensitized TiO_2 electrodes.

Figure 3 shows the photocurrent density–voltage (*J-V*) characteristics for the four types of the solar cells with QD and anthocyanin dye-sensitized TiO_2 and iodide/cobalt based electrolytes. Their respective performance parameters are tabulated in Table 1. With only anthocyanin as the sole sensitizer, the solar cells show low performances having efficiencies of 0.04% and 0.11% with iodide-based and cobalt-based electrolyte respectively. The short-circuit current density obtained in both electrolyte systems is low with values less than 0.50 mA cm^{-2}. The low performance of the DSSC with the natural dye as sensitizer as the sole sensitizer is not uncommon as most such DSSCs reported in the literature have low performance with efficiency values typically less than 1% [13].

When co-sensitized with CdS QDs, the performance of the anthocyanin dye sensitized solar cell is improved due to increased current density and open-circuit potential. As can be seen from Table 1, the highest efficiency of 0.64 % was obtained for the cell sensitized with CdS and anthocyanin and operated in iodide-based electrolyte. The observed photocurrent density value of 2.10 mA cm^{-2} for this cell is good when compared to the reported values of the order of 1.50 mA cm^{-2} for most of the similar cells [12,13]. When cobalt-based electrolytes are used, the efficiency of the anthocyanin dye-CdS co-sensitized DSSC improved to just a mere 0.18%. This seems to suggest that iodide-based electrolyte works well with CdS QDs. However, the performance of the cell with iodide based electrolyte was found to decrease rapidly with prolonged period implying that the solar cell with iodide-based electrolyte system has a stability problem. It has been opined that iodine/iodide redox mediator will slowly dissolve CdS QDs [23,24].

Co-sensitization of anthocyanin dye with CdSe QDs does not yield the same improvement as observed in the case of co-sensitization with CdS QDs (see Table 1). The performance of the cell with cobalt-based electrolyte system is low with an efficiency of 0.09% and current density of 0.40 mA cm^{-2}. The performance of the same cell with iodide-based electrolyte system is found to be better with an efficiency of 0.15% and current density of 0.57 mA cm^{-2} when compared to the values obtained in the cell with anthocyanin dye as the sole sensitizer. The better results with iodide-based electrolyte system indicate that the recombination rate of the electron transfer from TiO_2 matrix to the iodide-based electrolyte is slower than that to the cobalt-based electrolyte [23].

It has been observed that on co-sensitization of the TiO_2 layer with anthocyanin and both CdS and CdSe QDs, the solar cell has the best performance. With iodide-based electrolyte, an efficiency of 0.62% with a current density of 2.03 mA cm^{-2} and open circuit voltage of 0.68V is observed. These values are slightly lower than the values in the cell without CdSe QDs as co-sensitizers since the presence of CdSe QDs might not have significant impact towards the cell performance. With cobalt-based electrolyte, the solar cell with the all three sensitizers has the highest current density of 1.09 mA cm^{-2} with a better efficiency of 0.23%. In comparing with performance observed with the iodide-based electrolyte system, we opine that the improvement in the cell with cobalt electrolyte is largely due to the presence of CdS QD as well as the natural sensitizer. It is also to be noted that solar cells with cobalt-based electrolyte were observed to be stable throughout the characterisation activities.

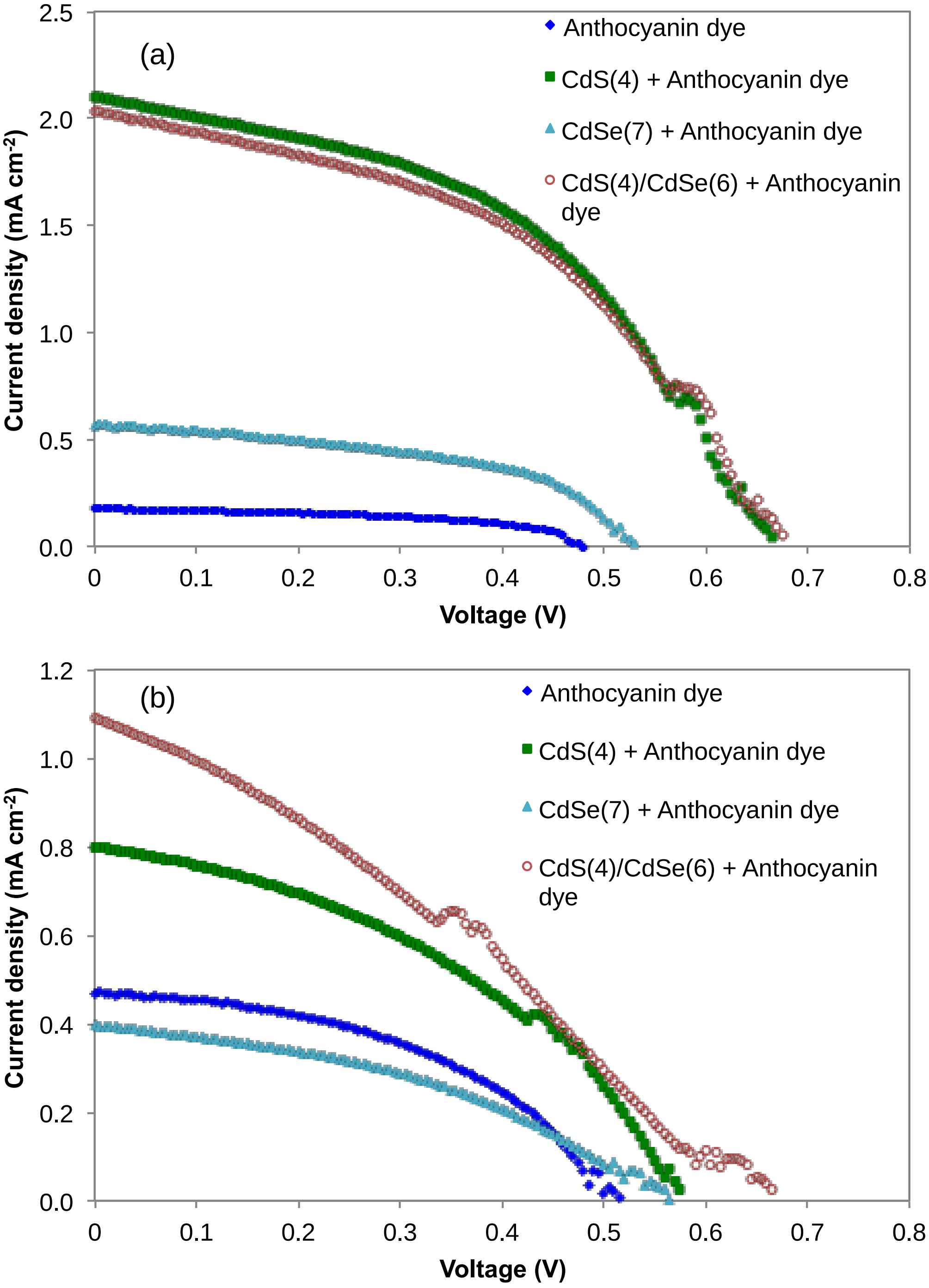

Figure 3. *J*-*V* curves of all four types of solar cells (a) with iodide-based electrolyte, (b) with cobalt-based electrolyte. All measurements were made under 1000 W m^{-2} illumination.

The solar cell performance can be further explained with EIS results plotted in the form of Nyquist plots as shown in Figure 4 (a) and (b). Nyquist plots provide the necessary information to understand the kinetics within the electrode/electrolyte interface. The values of the recombination resistance (R_r), constant phase element (CPE) and electron lifetime (τ) obtained from the Nyquist plots for the cells with different sensitizers are shown in Table 2. Electron lifetime (τ) was calculated using the equation (1) where R_r is the recombination resistance and C_μ is the true chemical capacitance [25].

$$\tau = R_r C_\mu \qquad (1)$$

The true chemical capacitance for a CPE can be expressed as

$$C_\mu = Q^{1/n} R_r^{(1-n)/n} \qquad (2)$$

where Q represents the capacity of the interface and n is the power value ($0 < n < 1$). When n = 1, equation (2) represents a perfect capacitor. On substituting for C_μ from equation (2), the equation (1) can then be expressed as

$$\tau = (Q \times R_r)^{1/n} \qquad (1a)$$

Table 1. Performance parameters of all solar cells under 1000 W m^{-2} illumination with iodide based or cobalt based electrolytes

Electrolyte	Sensitizers	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)
Iodide-based	Anthocyanin dye	0.18	0.48	0.51	0.04
	CdS(4) + Anthocyanin dye	2.10	0.67	0.46	0.64
	CdSe(7) + Anthocyanin dye	0.57	0.53	0.49	0.15
	CdS(4)/CdSe(6) + Anthocyanin dye	2.03	0.68	0.45	0.62
Cobalt-based	Anthocyanin dye	0.47	0.52	0.45	0.11
	CdS(4) + Anthocyanin dye	0.80	0.58	0.40	0.18
	CdSe(7) + Anthocyanin dye	0.40	0.57	0.39	0.09
	CdS(4)/CdSe(6) + Anthocyanin dye	1.09	0.67	0.32	0.23

A higher value of τ is favourable as electron recombination is delayed at the photoanode/electrolyte interface. The equivalent circuit of the cells is indicated in the inset of Figure 4. It consists of a series resistance (R_S) which represents the resistance at the conducting oxide glass, and two time-constant elements [26]. The two time-constant elements correspond to the charge transfer activity at the counter electrode and electrolyte interface (CPE1 and R_{CE}), and, the electron transfer in sensitized TiO_2 layer as well as the recombination process (CPE2 and R_r), respectively.

The low performances of the solar cells as exhibited in cell with anthocyanin dye as the sole sensitizer and CdSe QD with anthocyanin dye as co-sensitizers are due to the lower chemical capacitance values at the electrode/electrolyte interface which result in low electron lifetimes (see Table 2). Although CdSe QD co-sensitized with anthocyanin dye has a high recombination resistance, the low chemical capacitance is not able to yield a longer electron lifetime. Both of these cells have low electron lifetimes when compared to other solar cells with either iodide- or cobalt-based electrolyte system. In the case of co-sensitization with CdS QD and anthocyanin dye, the better performance is due to the higher chemical capacitance value obtained. This could yield a longer electron lifetime.

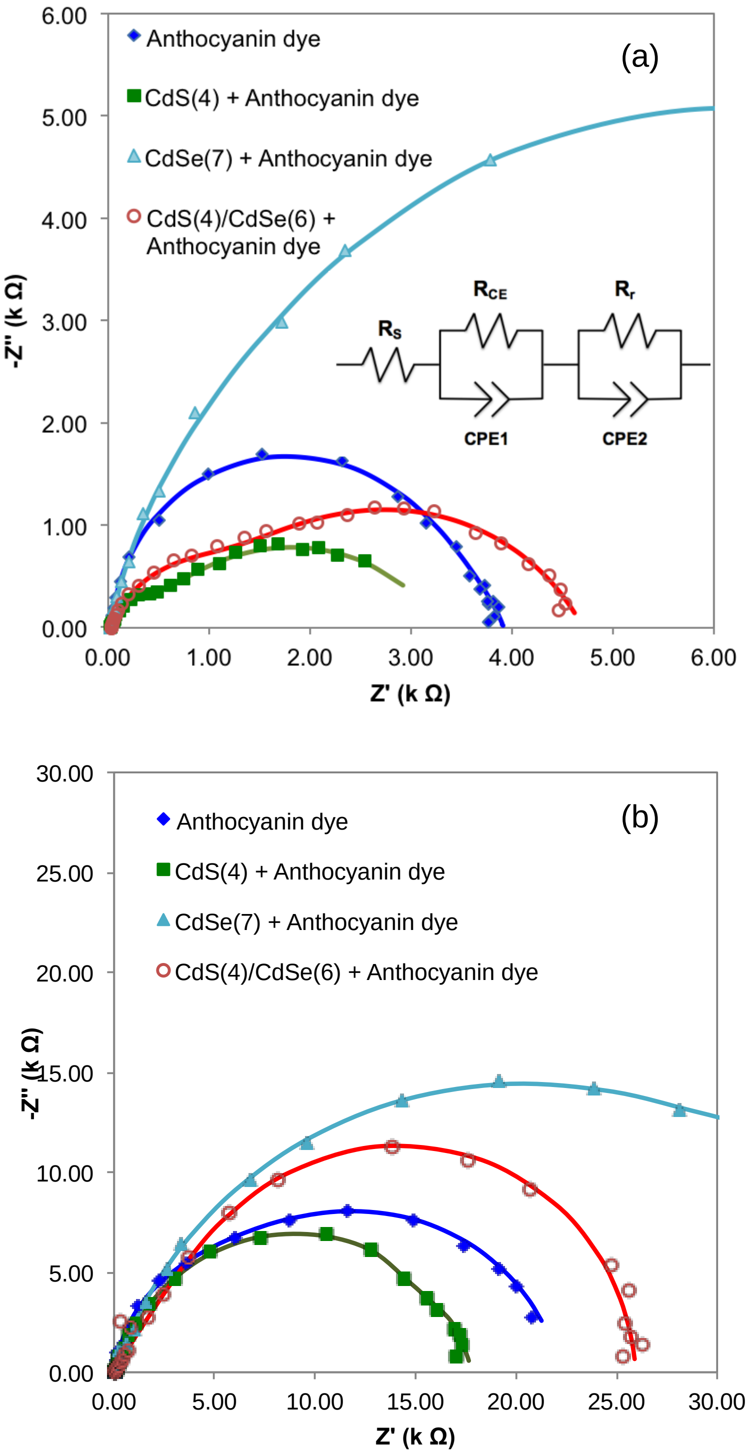

Figure 4. Nyquist plots of all four types of solar cells (a) with iodide-based electrolyte, (b) with cobalt-based electrolyte. All cells were measured under 1000 W m^{-2} illumination with 0.5 V bias. The equivalent circuits of the cells are shown in the inset with the representation of series resistance (subscript s), impedance at photoanode TiO_2/electrolyte (subscript r) and counter electrode/electrolyte interface (subscript CE). The symbol *R* denotes the resistance while CPE is the constant phase element.

With iodide-based electrolyte system, this cell has an electron lifetime of 213 ms. Meanwhile with cobalt-based electrolyte system, a longer electron lifetime of 94 ms is observed although it is not the longest since the cell is not the best performer. When anthocyanin dye is used along with both CdS and CdSe QDs, the lifetime of electrons increased to 140 ms for cobalt-based electrolyte system.

Larger lifetime indicates lower rate of recombination electrons which results in larger short circuit current and ultimately produces the observed best efficiency. The same cell configuration with iodide-based electrolyte system also has a longer electron lifetime of 171 ms. This slightly lower lifetime compared to that in the cell with CdS QD and anthocyanin dye as co-sensitizers is partly attributed to the slightly higher recombination resistance although its true chemical capacitance is the highest.

Table 2. EIS results of solar cells measured under 1000 W m^{-2} illumination: series resistance, charge-transfer resistance and impedance values of the constant phase element (CPE2).

Electrolyte	Sensitizers	R_S (Ω)	R_r (kΩ)	Q (μS.s^n)	n (0<n<1)	τ (ms)
Iodide-based	Anthocyanin dye	27.27	3.09	1.82	0.99	5.40
	CdS(4) + Anthocyanin dye	23.30	2.96	0.01	0.62	213.16
	CdSe(7) + Anthocyanin dye	22.88	8.97	3.96	1.00	35.53
	CdS(4)/CdSe(6) + Anthocyanin dye	25.80	3.67	0.64	0.82	171.61
Cobalt-based	Anthocyanin dye	28.71	4.00	9.66	1.00	38.69
	CdS(4) + Anthocyanin dye	33.53	17.67	6.04	0.95	94.16
	CdSe(7) + Anthocyanin dye	34.53	37.19	1.26	0.80	21.76
	CdS(4)/CdSe(6) + Anthocyanin dye	35.60	20.99	6.67	1.00	140.09

4. CONCLUSIONS

Anthocyanin dye was successfully extracted from black rice. The extraction was then used as the natural sensitizer in DSSCs with iodide- and cobalt-based electrolytes. The low performance of these DSSCs was found to improve on co-sensitization with CdS and CdSe QDs. For the cobalt-based electrolyte system, the solar cell co-sensitized with anthocyanin dye and both CdS and CdSe QDs produced the best performance with an efficiency of 0.23%. However, the best overall performance with an efficiency of 0.64 % was obtained with iodide-based electrolyte system when anthocyanin dye and CdS QDs were used as co-sensitizers. In general, the solar cell performances were low compared to ruthenium-based DSSC due to relatively high recombination rate in the cell as indicated from the EIS studies. Further optimization is necessary in order to improve these hybrid sensitizers based DSSCs.

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