

## Dye Sensitized Solar Cells Using Natural Pigments from Five Plants and *Quasi-Solid State Electrolyte*

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Células solares sensibilizadas por corantes (DSSCs) foram fabricadas usando corantes naturais extraídos das flores de *Amaranthus caudatus*, *Bougainvillea spectabilis*, *Delonix regia*, *Nerium oleander*, *Spathodea companulata* e uma mistura de extratos. O desempenho da célula fotoeletroquímica (PEC) DSSCs desses corantes mostrou um fator de preenchimento (FF) geralmente maior que 50%, a voltagem de circuito aberto ( $V_{oc}$ ) variou de 0,45 a 0,55 V, e as densidades de fotocorrente de circuito curto ( $J_{sc}$ ) ficaram na faixa de 0,013 a 1,82 mA cm<sup>-2</sup>. A alta voltagem de circuito aberto ( $V_{oc} = 0,55$  V) e a densidade de fotocorrente de circuito curto ( $J_{sc} = 1,82$  mA cm<sup>-2</sup>) foram obtidas a partir de DSSC sensibilizada por extrato etanoico da flor de *Amaranthus caudatus*. A eficiência de conversão de energia ( $\eta$ ) da DSSC com extrato etanoico da flor *Amaranthus caudatus* atingiu 0,61%. O desempenho da PEC DSSC com soluções de corantes misturados também foi investigado. No entanto, extratos misturados não apresentaram sinergia na fotosensibilização quando comparados aos extratos individuais. A célula sensibilizada somente pelo extrato etanoico da flor *Amaranthus caudatus* apresentou o melhor desempenho. Os dispositivos mostraram que a eficiência de conversão fóton-corrente monocromática incidente (IPCE) variou de 4,7% a 52%. Os resultados dos dados de IPCE são consistentes com as curvas J-V.

Dye-sensitized solar cells (DSSCs) were fabricated using natural dyes extracted from flowers of *Amaranthus caudatus*, *Bougainvillea spectabilis*, *Delonix regia*, *Nerium oleander*, *Spathodea companulata* and a mixture of the extracts. The photoelectrochemical cell (PEC) performance of the DSSCs of these dyes showed fill factors (FF) mostly higher than 50%, the open circuit voltages ( $V_{oc}$ ) varied from 0.45 to 0.55 V, and the short circuit photocurrent-densities ( $J_{sc}$ ) ranged from 0.013 to 1.82 mA cm<sup>-2</sup>. High open circuit voltage ( $V_{oc} = 0.55$  V) and short circuit photocurrent-density ( $J_{sc} = 1.82$  mA cm<sup>-2</sup>) were obtained from the DSSC sensitized by the ethanol extract of flower of *Amaranthus caudatus*. The power conversion efficiency ( $\eta$ ) of the DSSC with the ethanol extract of *Amaranthus caudatus* flower reached 0.61%. The PEC performances of DSSCs of mixed dye solutions were also investigated. However, the mixed extract does not show any synergistic photosensitization compared to the individual extracts. Instead, the cell sensitized by the ethanol extract of *Amaranthus caudatus* flower alone showed the best performance. The devices showed incident monochromatic photon-to-current conversion efficiencies (IPCE) varied from 4.7% to 52%. The results from the IPCE data are consistent with the results from the (J-V) curves.

**Keywords:** dye sensitized solar cells, natural pigments, *quasi-solid state electrolyte*

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## Introduction

The world's energy consumption is continuously increasing and this creates a heavy demand for renewable energy sources to be developed. The largest challenge for our global society is to find ways to replace the slowly but inevitably vanishing fossil fuel supplies by renewable resources and, at the same time, avoid negative effects from the current energy system on climate, environment, and health. The worldwide power consumption is expected to double in the next three decades because of the increase in world population and the rising demand of energy in the developing countries.<sup>1</sup> This implies enhanced depletion of easily utilizable fossil fuel reserves in near future, leading to further aggravation of the environmental pollution. The reserves of fossil and even nuclear fuel are also limited: for example, the constantly rising gas prices give indication of exhaustion of crude oil in the future. Solar energy is expected to play a crucial role as a future energy source. More solar energy strikes the earth in one hour ( $4.3 \times 10^{20} \text{ J h}^{-1}$ ) than all the energy consumed on the earth in a year ( $4.1 \times 10^{20} \text{ J year}^{-1}$ ).<sup>1</sup> Solar energy provides clean abundant energy and is therefore an excellent candidate for a future environmentally friendly energy source.

There are various types of solar cells that convert sun light into electrical energy. The commercially available solar cells are currently based on inorganic silicon semiconductors. The demand for silicon will skyrocket within the next decade and its price will rise dramatically. Organic solar cells, therefore, appear to be a highly promising and cost-effective alternative for the photovoltaic energy sector. In this context, dye-sensitized solar cells (DSSC) have attracted considerable attention in recent years.<sup>2</sup>

The DSSC is a device for the conversion of visible light into electricity, based on the sensitization of wide bandgap semiconductors.<sup>3</sup> The performance of the cell mainly depends on a dye used as sensitizer. The absorption spectrum of the dye and the anchorage of the dye to the surface of  $\text{TiO}_2$  are important parameters determining the efficiency of the cell.<sup>4</sup> Generally, transition metal coordination compounds (ruthenium polypyridyl complexes) are used as the effective sensitizers, due to their intense charge-transfer absorption in the whole visible range and highly efficient metal-to-ligand charge transfer.<sup>5</sup> However, ruthenium polypyridyl complexes contain a heavy metal, which is undesirable from point of view of the environmental aspects.<sup>6</sup> Moreover, the process to synthesize the complexes is complicated and costly. Alternatively, natural dyes can be used for the same purpose with an acceptable

efficiency.<sup>4,11</sup> The advantages of natural dyes include their availability, environmental friendliness and low cost.<sup>5</sup>

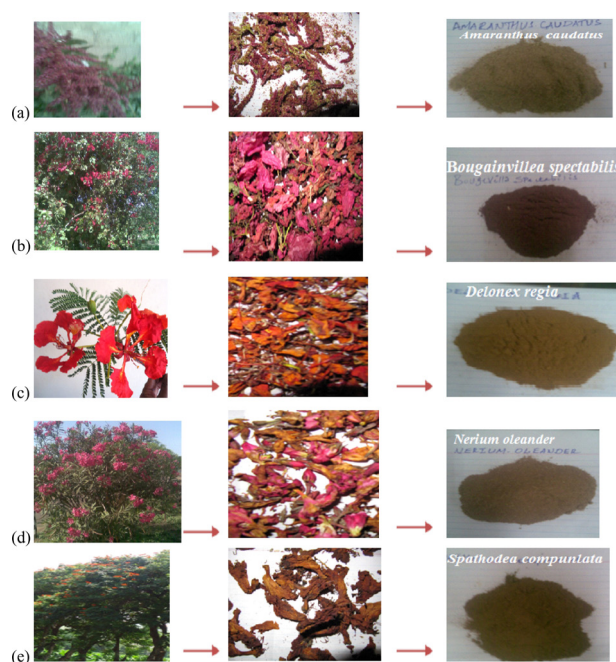
In this study we have extracted natural pigments from five locally available flowers namely *Amaranthus caudatus* (colour of the flower: deep red), *Bougainvillea spectabilis* (colour of the flower: deep red), *Delonix regia* (colour of the flower: red), *Nerium oleander* (colour of the flower: rose) and *Spathodea campanulata* (colour of the flower: red). We studied their photo-responses as sensitizers for dye-sensitized solar cells.

## Experimental

### Preparation of natural dye sensitizers

Enough amounts of the natural flowers namely *Amaranthus caudatus*, *Bougainvillea spectabilis*, *Delonix regia*, *Nerium oleander* and *Spathodea campanulata* were collected. After collection, the plant materials were identified by a taxonomist and dried under shade area for 30 days and crushed to powder for extraction. Figure 1 shows the photographic picture of tree plants, the respective drying flowers and the powder of *Amaranthus caudatus*, *Bougainvillea spectabilis*, *Delonix regia*, *Nerium oleander* and *Spathodea campanulata*.

*Amaranthus caudatus* powder of 3 g and *Bougainvillea spectabilis* powder of 3 g were separately



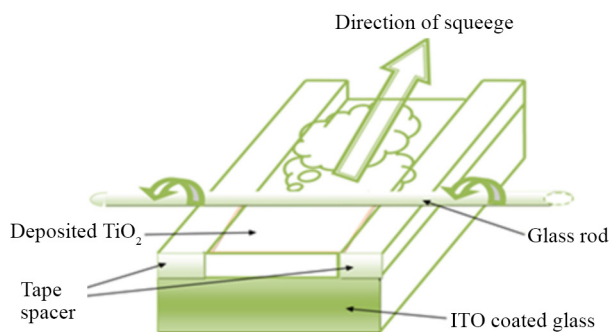
**Figure 1.** Plant materials used in this study (a) *Amaranthus caudatus*, (b) *Bougainvillea spectabilis*, (c) *Delonix regia*, (d) *Nerium oleander* and (e) *Spathodea campanulata*.

extracted in 200 mL of ethanol and 200 mL of 0.1 mol L<sup>-1</sup> HCl, respectively, at room temperature. A mixed dye was prepared by mixing separately ethanol extracted *Amaranthus caudatus* and *Bougainvillea spectabilis* solution to 0.1 mol L<sup>-1</sup> HCl extracted solution at a ratio of 1:1 by volume, respectively. Similarly, 3 g of the powders of the last three plant materials were separately, extracted in 200 mL of 0.1 mol L<sup>-1</sup> HCl at room temperature. The glass containers were covered with aluminium foils to prevent damage from light exposure and were left to shake for one day. Thereafter the solid residues were filtered out to obtain clear dye solutions.

#### Preparation of TiO<sub>2</sub> electrode

Indium tin oxide (ITO) conductive glass sheets (2.5 cm × 1.5 cm) were first cleaned with acetone (Aldrich), 2-propanol (Riedel-de Haen) and ethanol (Fluka) for 30 min in each step using ultrasonic bath.

Preparation of mesoporous titanium dioxide (TiO<sub>2</sub>) paste was done with the method described elsewhere.<sup>12</sup> The preparation of nanocrystalline films employed commercial titanium dioxide nanopowder (P25, Degussa AG, Germany, a mixture of about 30% rutile and 70% anatase). In order to break the aggregates into separate particles, the powder (3 g) was ground in a porcelain mortar with a small amount of water (1 mL) containing acetic acid (0.1 mL) to prevent reaggregation of the particles. After the powder had been dispersed by the high shear forces in the viscous paste, it was diluted by slow addition of water (4 mL) under continued grinding. Finally, a detergent (0.05 mL Triton X-100, Aldrich) was added to facilitate the spreading of the colloid on the substrate. The ITO was covered on two parallel edges with adhesive tape to control the thickness of the TiO<sub>2</sub> film and to provide non-coated areas for electrical contact. The colloid was applied to one of the free edges of the conducting glass and distributed with a glass rod sliding over the tape-covered edges as shown Figure 2. After air



**Figure 2.** TiO<sub>2</sub> film preparation procedure.

drying, the electrode was fired for 30 min at 450 °C in a furnace (Carbolite Model ELF 11/14B).

Coating of the TiO<sub>2</sub> surface with dye was carried out by soaking the film for overnight in the dyes extracted. After completion of the dye adsorption, the electrode was withdrawn from the solution under a stream of dry air. It was stored in dry ethanol or immediately wetted with redox electrolyte solution for testing.

#### Preparation of counter electrode

The poly(3,4-ethylenedioxythiophene) (PEDOT) film on ITO (UNAXIS Corporation, sheet resistance 30 Ωsq<sup>-1</sup>) for the counter electrode was formed by electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) (Aldrich), in a three electrode one-compartment electrochemical cell.

The electrochemical cell consisted of a pre-cleaned ITO-coated glass working electrode, platinum foil counter electrode and *quasi*-Ag/AgCl reference electrode. The solution used for the polymerization contained 0.2 mol L<sup>-1</sup> EDOT and 0.1 mol L<sup>-1</sup> (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub> (Aldrich) in acetonitrile (Sigma-Aldrich). The monomer was used as received. The polymerization was carried out potentiostatically at +1.8 V for 2 s. At this potential, the electrode surface becomes covered with blue-doped PEDOT film. The cell was then rinsed with acetonitrile and dried in air.

#### Preparation of electrolyte

The polymer gel electrolyte was prepared by the following process;<sup>13</sup> 0.9 mol L<sup>-1</sup> of 3-ethyl-2-methylimidazolium iodide (EMIM-I) was added into acetonitrile (Aldrich) under stirring to form a homogeneous liquid electrolyte. In order to obtain a better conductivity, 0.5 mol L<sup>-1</sup> of sodium iodide (BDH) was dissolved in the above homogeneous liquid electrolyte, and then 0.12 mol L<sup>-1</sup> iodine and 35% (m/m) of polyvinyl pyrrolidone (PVP) (Aldrich) were added. Then, the resulting mixture was heated at 70-80 °C under vigorous stirring to dissolve the PVP polymer, followed by cooling down to room temperature to form a gel state electrolyte. Finally, the gel electrolyte was deposited in the form of thin film on top of the dye coated TiO<sub>2</sub> electrode. The DSSC was completed by pressing against PEDOT-coated ITO glass counter electrode. The photoelectrochemical cell (PEC) was then mounted in a sample holder inside a metal box with an area of 1 cm<sup>2</sup> opening to allow light from the source. All experiments were carried out at ambient temperature.

## Assembling of the complete DSSCs

The photoelectrode and the counter electrode were overlappingly placed in a holder so that the titanium dioxide covered area of the photoelectrode was the only part of the photoelectrode that was in contact with the counter electrode. The non-titanium dioxide covered area of the photoelectrode and the non-overlapping edge of the counter electrode were attached to the measuring equipment by means of cords and crocodile clips.

## Measurement

The absorption spectra of dye solutions were recorded using GENESYS 2PC UV-Vis spectrophotometer. The photoelectrochemical measurements of the cell were performed using a computer controlled CHI630A electrochemical analyzer. A 150-W Xenon lamp regulated by an Oriel power supply (Model 68830) was used to illuminate the PEC. A grating monochromator (model 77250) placed into the light path was used to select a wavelength between 300 and 800 nm. The measured photocurrent spectra were corrected for the spectral response of the lamp and the monochromator by normalization to the response of a calibrated silicon photodiode (Hamamatsu, model S1336-8BK) whose sensitivity spectrum was known. No correction was made for the reflection from the surface of the sample. The white light intensity was measured in the position of the sample cell with Gigahertz-Optik X1<sub>1</sub> Optometer. The intensity of the incident light was 100 mW cm<sup>-2</sup>.

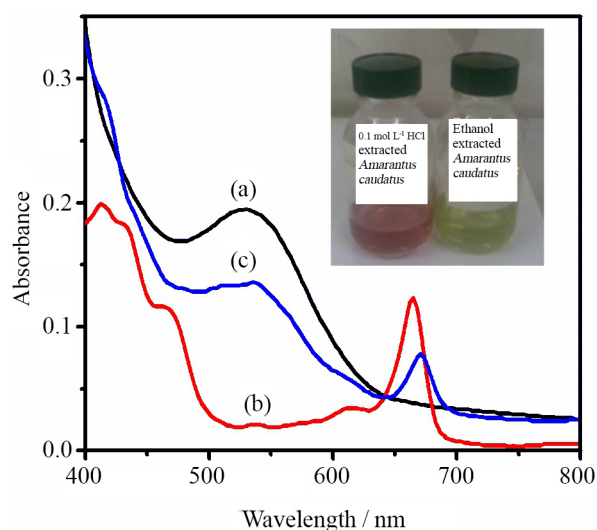
## Results and Discussion

### Absorption spectra of natural dyes

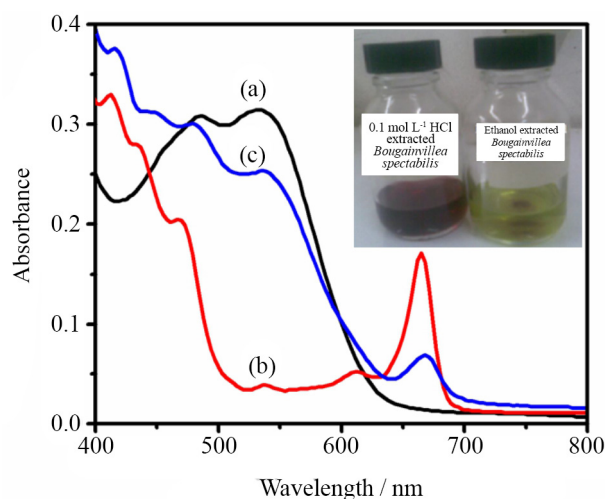
We attempted to use 5 kinds of colorful natural dyes as sensitizers for DSSCs. Figure 3 and Figure 4 show the UV-Vis absorption spectra for the ethanol, 0.1 mol L<sup>-1</sup> HCl, and mixed extracts of 0.1 mol L<sup>-1</sup> HCl and ethanol solutions of *Amaranthus caudatus* and *Bougainvillea spectabilis*, respectively. Figure 3b and Figure 4b show that the ethanol extracts of *Amaranthus caudatus* and *Bougainvillea spectabilis*, whose colors are green, reach a maximum absorption peak of 665 nm and 413 nm. The main component of these two extracts is chlorophyll.

Figure 3a and Figure 4a also demonstrate the 0.1 mol L<sup>-1</sup> HCl extracts of *Amaranthus caudatus* and *Bougainvillea spectabilis*, whose colors are red. *Amaranthus caudatus* extract displayed an intense absorption in the 500-600 nm region, due to the red-purple betacyanines and *Bougainvillea spectabilis*

extract displayed an intense absorption in the 400-600 nm region due to the mixed contributions of the yellow-orange betaxanthins (480 nm) and of the red-purple betacyanines (540 nm).<sup>14</sup> Furthermore, the absorption peaks of mixed dyes of *Amaranthus caudatus* extracts and *Bougainvillea spectabilis* extracts are displayed in Figure 3c and Figure 4c. The absorption peaks of the mixed dyes are in the visible light range about 670 nm, and 536 nm for dyes mixed extract of *Amaranthus caudatus* and about 668 nm, 536 nm, 479 nm, 446 nm, and 416 nm for dyes mixed extract of *Bougainvillea spectabilis*. The light absorption spectrum of the mixed extract contained peaks corresponding to the contributions from the individual extracts.

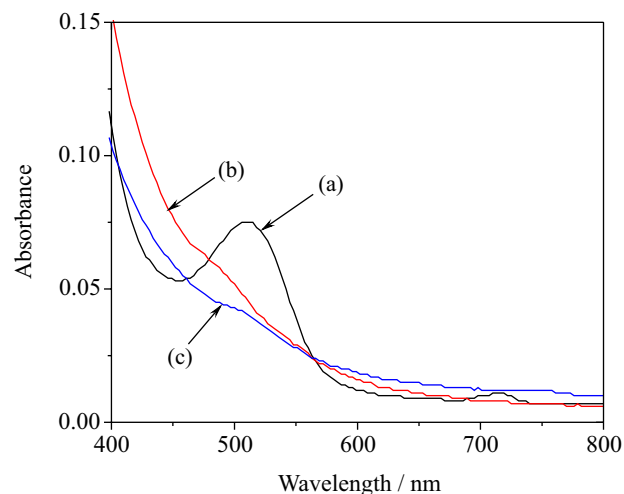


**Figure 3.** UV-Vis absorption spectra of dye solutions of: (a) 0.1 mol L<sup>-1</sup> HCl extracted *Amaranthus caudatus* extract, (b) ethanol *Amaranthus caudatus* extract and (c) mixture of dyes extracted in 0.1 mol L<sup>-1</sup> HCl and ethanol. Inset: extract of *Amaranthus caudatus* in 0.1 mol L<sup>-1</sup> HCl and ethanol.



**Figure 4.** UV-Vis absorption spectra of dye solutions of: (a) 0.1 mol L<sup>-1</sup> HCl *Bougainvillea spectabilis* extract, (b) ethanol *Bougainvillea spectabilis* extract and (c) mixture of dyes extracted in 0.1 mol L<sup>-1</sup> HCl and ethanol. Inset: extracts *Bougainvillea spectabilis* in 0.1 mol L<sup>-1</sup> HCl and ethanol.

Figure 5 shows the UV-Vis absorption spectra of *Delonix regia*, *Nerium oleander* and *Spathodea companulata* in 0.1 mol L<sup>-1</sup> HCl solution. From Figure 5a, it can be seen that there is an absorption peak at about 516 nm for the extract of *Delonix regia*. This absorption ascribes to their identical components, namely, anthocyanins, a group of natural phenolic compounds.<sup>15</sup> Anthocyanin is the core component of some natural dyes and is often found in the fruits, flowers, and leaves of plants. Because anthocyanin shows color in the range of visible light from red to blue,



**Figure 5.** UV-Vis absorption spectra of dye solutions of: (a) *Delonix regia*, (b) *Nerium oleander* and (c) *Spathodea companulata* extracted with 0.1 mol L<sup>-1</sup> HCl.

it is predicted to become a highly efficient sensitizer for wide band gap semiconductors.<sup>16</sup> The *Nerium oleander* and *Spathodea companulata* in 0.1 mol L<sup>-1</sup> HCl solution do not show obvious maximum absorption peaks in the visible light region as observed in Figure 5b and Figure 5c. This is because the anthocyanin extracted was dominantly found in the colorless quinonoidal form and do not absorb in the visible region. However, upon acidifying, it turned out to be colored since the equilibrium shifts to the highly conjugated flavylium cation form. Anthocyanin usually exists as equilibrium system between quinonoidal and flavylium cation form.

#### Photoelectrochemical properties of DSSCs sensitized with natural dyes

Photovoltaic tests of DSSCs using these natural dyes as sensitizers were performed by measuring the current density-voltage (J-V) curves under irradiation with white light (100 mW cm<sup>-2</sup>). The performance of natural dyes as sensitizers in DSSCs was evaluated by short circuit current density ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor (FF), and power conversion efficiency ( $\eta$ ). The photoelectrochemical parameters of the DSSCs sensitized with natural dyes are listed in Table 1. It presents the performance of the natural pigments based DSSCs in this work in terms of  $J_{sc}$ ,  $V_{oc}$ , FF and  $\eta$  compared to those of the results found in the literature.

**Table 1.** Photoelectrochemical parameters of the DSSCs sensitized by ethanol extracted natural dyes, 0.1 mol L<sup>-1</sup> HCl extracted natural dyes and mixture of dyes extracted in 0.1 mol L<sup>-1</sup> HCl and ethanol (dye mixed solution)

Natural dye	$J_{sc}$ / (mA cm <sup>-2</sup> )	$V_{oc}$ / V	FF / %	$\eta$ / %	Reference
<i>Amaranthus caudatus</i> <sup>a</sup>	1.82	0.55	61	0.610	This work
<i>Amaranthus caudatus</i> <sup>b</sup>	0.102	0.53	61	0.033	
<i>Amaranthus caudatus</i> <sup>c</sup>	0.44	0.45	58	0.114	
<i>Bougainvillea spectabilis</i> <sup>a</sup>	1.11	0.5	58.6	0.325	
<i>Bougainvillea spectabilis</i> <sup>b</sup>	0.081	0.45	48.3	0.018	
<i>Bougainvillea spectabilis</i> <sup>c</sup>	0.648	0.47	54	0.164	
<i>Delonix regia</i> <sup>b</sup>	0.114	0.47	57.9	0.031	
<i>Nerium oleander</i> <sup>b</sup>	0.046	0.5	57.5	0.013	
<i>Spathodea companulata</i> <sup>b</sup>	0.013	0.46	44	0.003	
<i>Begonia</i> <sup>a</sup>	0.63	0.537	72.2	0.240	17
<i>Bauhinia tree</i> <sup>a</sup>	0.96	0.572	66	0.360	
<i>China loropetal</i> <sup>a</sup>	0.84	0.518	62.6	0.270	
<i>Tangerine</i> <sup>a</sup>	0.74	0.592	63.1	0.280	
<i>Rhododendron</i> <sup>a</sup>	1.61	0.585	60.9	0.570	
<i>Lithospermum</i> <sup>a</sup>	0.14	0.337	58.5	0.030	
<i>Mangosteen pericarp</i> <sup>a</sup>	2.69	0.686	63.3	1.170	
<i>Fructus lycii</i> <sup>a</sup>	0.53	0.689	46.6	0.170	

<sup>a</sup>Ethanol extracted natural dye; <sup>b</sup>0.1 mol L<sup>-1</sup> HCl extracted natural dye and <sup>c</sup>mixture of natural dyes extracted from ethanol and 0.1 mol L<sup>-1</sup> HCl.

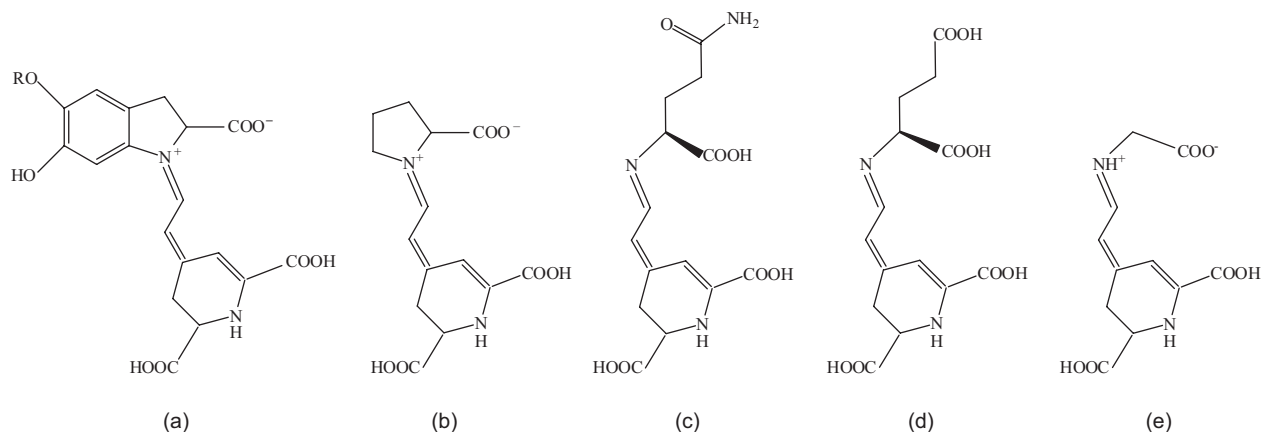
The typical current density-voltage (J-V) curves of the DSSCs using the sensitizers extracted from *Amaranthus caudatus*, *Bougainvillea spectabilis*, *Delonix regia*, *Nerium oleander*, and *Spathodea campanulata* are shown in Figure 6, Figure 7 and Figure 8, respectively. As shown in Table 1, Figure 6, Figure 7 and Figure 8, the fill factors of these DSSCs are mostly higher than 50%. The  $V_{oc}$  varies from 0.45 to 0.55 V, and the  $J_{sc}$  ranges from 0.013 to 1.82 mA cm<sup>-2</sup>. Specifically, a high  $V_{oc} = 0.55$  V and  $J_{sc} = 1.82$  mA cm<sup>-2</sup> were obtained from the DSSC sensitized by the dye of *Amaranthus caudatus* extracted with ethanol; the efficiency of the DSSC reached 0.61%. These data are significantly higher than those of the DSSCs sensitized by other natural dyes in this work and showed a comparable performance to the DSSCs prepared from other natural dyes done by other groups (Table 1).<sup>17</sup> This is due to a broader range of the light absorption of the extract adsorbed on TiO<sub>2</sub>, and the higher interaction between TiO<sub>2</sub> and chlorophyll in the *Amaranthus caudatus* extract leads to a better charge transfer. Moreover, chlorophyll in the *Amaranthus caudatus* extract may have the shortest distance between the dye skeleton and the point connected to TiO<sub>2</sub> surface compared to that of other extracts in this work.<sup>18</sup> This could facilitate an electron transfer from chlorophyll in the *Amaranthus caudatus* extract to the TiO<sub>2</sub> surface and could be accounted for a better performance of *Amaranthus caudatus* extract sensitization.<sup>18</sup> Even though ethanol extract of *Bougainvillea spectabilis* is also chlorophyll, the photoelectrochemical performance of the DSSC from the ethanol extract is lower compared with the respective ethanol extract of *Amaranthus caudatus*. This is because the concentration of chlorophyll in *Bougainvillea spectabilis* is higher than its concentration in the ethanol extract of *Amaranthus caudatus* as it is evident from the absorption measurement. The high concentration of chlorophyll leads to dye aggregation on the TiO<sub>2</sub> film, which intern leads to concentration quenching resulting in lower photoelectrochemical performance in DSSC of ethanol extract of *Bougainvillea spectabilis*. Chlorophyll plays an important role in plant photosynthesis; the DSSCs using chlorophyll derivatives as sensitizers obtained a relatively high conversion efficiency.<sup>19,20</sup> This is because there are available bonds between the dye and TiO<sub>2</sub> molecules through which electrons can transport from the excited dye molecules to the TiO<sub>2</sub> film.<sup>21</sup> This result indicates that the interaction between the sensitizer and the TiO<sub>2</sub> film is significant in enhancing the power conversion efficiency of DSSCs.

The photovoltaic properties of the DSSCs sensitized by the dyes extracted from *Amaranthus caudatus* and *Bougainvillea spectabilis* with various solvents were studied

by measuring current density-voltage (J-V) curves, and the corresponding photoelectrochemical parameters are listed in Table 1. As observed, the efficiencies of the DSSCs using ethanol extracts and 0.1 mol L<sup>-1</sup> HCl extracts as sensitizer are 0.61% and 0.033% for *Amaranthus caudatus* and 0.325% and 0.018% for *Bougainvillea spectabilis*, respectively. The photoelectrochemical performances of DSSCs using the mixed dye solutions were also investigated. The efficiencies of mixed dye solutions are 0.114% for *Amaranthus caudatus* and 0.164% for *Bougainvillea spectabilis*, respectively. The efficiency of DSSC using mixed dye solution as sensitizer is much lower than the sum of the efficiencies of the DSSCs sensitized with ethanol extracts and 0.1 mol L<sup>-1</sup> HCl extracts. This result indicates that the mixed extract adsorbed on TiO<sub>2</sub> does not show synergistic photosensitization compared with individual extracts, which is in accordance with the results reported by Wongcharee *et al.*<sup>22</sup> However, this is rather different from the result reported by Kumara *et al.*,<sup>23</sup> in which a DSSC fabricated using chlorophyll and shisonin dyes showed synergistic effect of both dyes. We hypothesize two possible reasons for this phenomenon in which the mixed extract of *Amaranthus caudatus* and *Bougainvillea spectabilis* did not show synergistic photosensitization. First, although the DSSC sensitized with the mixed extracts of *Amaranthus caudatus* and *Bougainvillea spectabilis* utilize the light of several spectral regions, the coadsorption suppresses electron injection possibly due to the increase in concentration quenching. Second, the strong steric hindrance of basic molecular structures for the main components of the extracts of *Amaranthus caudatus* and *Bougainvillea spectabilis* with various solvents prevents the dye molecules from effectively arraying on the TiO<sub>2</sub> film. Hence, this leads to a deficiency of electron transfer from dye molecules to conduction band of TiO<sub>2</sub>.

Obviously, the efficiency of the cell sensitized by the ethanol extract was significantly higher than the one sensitized by the 0.1 mol L<sup>-1</sup> HCl extract for *Bougainvillea spectabilis* and *Amaranthus caudatus*. This is due to the difference in the kinds of dyes extracted. The ethanol extracts in both cases is chlorophyll whereas the respective 0.1 mol L<sup>-1</sup> HCl extracts are betalains. The other extracts mainly contain anthocyanins in both the 0.1 mol L<sup>-1</sup> HCl and ethanol extracts. Anthocyanins are much soluble in ethanol than 0.1 mol L<sup>-1</sup> HCl, which makes better performance of the ethanol extract. This is because of higher solubility of anthocyanin in ethanol,<sup>24</sup> which reduces the aggregation of dye molecules. A good dispersion of dye molecules on the oxide surface could in fact improve the efficiency of the system.

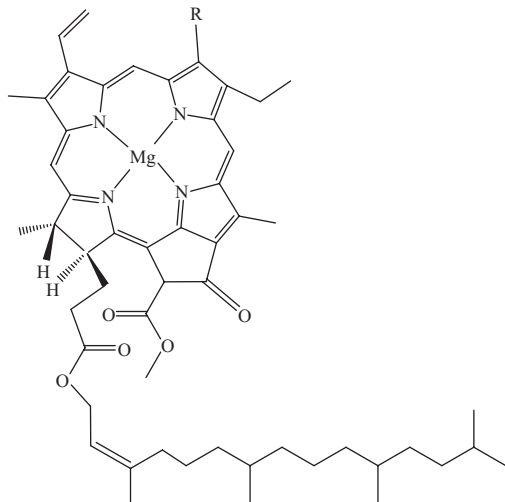
The prevailing pigment coloration of *Bougainvillea spectabilis* and *Amaranthus caudatus* varies from orange to



**Scheme 1.** Chemical structure of betacyanins, (a) R =  $\beta$ -D-glucose (betanin), R = H (betanidin) and betaxanthins [(b) indicaxanthin; (c) vulgaxanthin I; (d) vulgaxanthin II; (e) portulaxanthin].

red, due to the combination of two main dyes: betacyanin (red-purple) and betaxanthin (yellow-orange), whose schematic structures are reported in Scheme 1.<sup>25</sup> Both dyes contain carboxylic functional groups that facilitate  $\text{TiO}_2$  surface binding.

The major component of the ethanol extract of *Amaranthus caudatus* and *Bougainvillea spectabilis* is chlorophyll. Scheme 2a and 2b show these families of compounds.

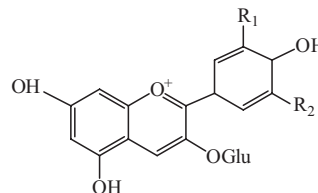


**Scheme 2.** General structures of the chlorophyll dyes: (a) R =  $\text{CH}_3$ , chlorophyll-a (b) R = CHO, chlorophyll-b.

As noticed, the efficiencies of the DSSCs using  $0.1 \text{ mol L}^{-1}$  HCl extracts as sensitizers are 0.03% for *Delonix regia*, 0.013% for *Nerium oleander* and 0.003% for *Spathodea companulata*. In the case of *Delonix regia*, the dye component is anthocyanin. The DSSCs sensitized by natural dyes mainly composed of anthocyanin (extract of *Delonix regia*) in this work, did not offer high conversion efficiency. This is because anthocyanins have no carboxyl functional groups to chemically bind with  $\text{TiO}_2$  and

facilitate electron injection from the LUMO of the dye to the conduction band of  $\text{TiO}_2$ . Instead of this, weak physical adsorption by intermolecular forces between the hydroxyl of the anthocyanin and  $\text{TiO}_2$  exists leading to a possibility of desorption of the dye from  $\text{TiO}_2$ .

The main component of the dye extracted from flower of *Delonix regia*, *Nerium oleander*, and *Spathodea companulata* is anthocyanins. The structure of these classes of compounds is as depicted in Scheme 3.



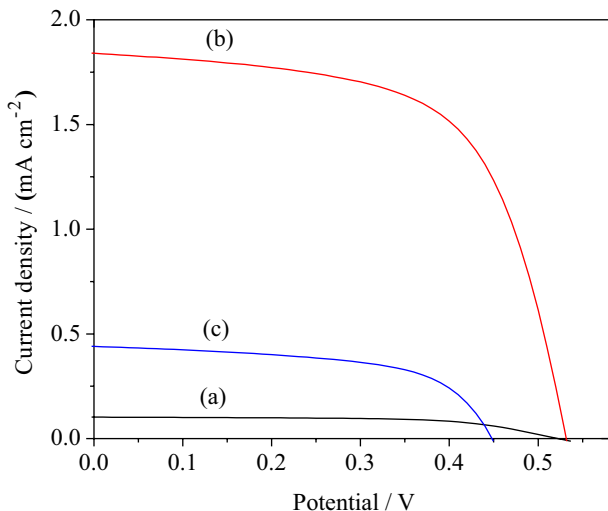
**Scheme 3.** Chemical structures of anthocyanines.  $\text{R}_1 = \text{OH}$ ,  $\text{R}_2 = \text{H}$  (cyanidin-3-glucoside),  $\text{R}_1 = \text{R}_2 = \text{OH}$  (delphinidin-3-glucoside),  $\text{R}_1 = \text{R}_2 = \text{OCH}_3$  (malvidin-3-glucoside).

Incident monochromatic photon to current conversion efficiency

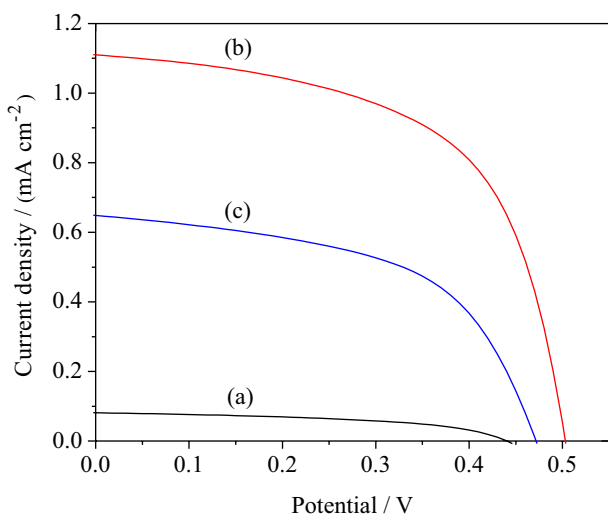
Incident photon to current-conversion efficiency (IPCE) is defined as

$$IPCE = \frac{1240 (eV \text{ nm}) \cdot I_{SC} (mA \text{ cm}^{-2})}{\lambda (nm) \cdot P_{in} (mW \text{ cm}^{-2})} \quad (1)$$

Figure 9 shows the action spectra for the DSSC sensitized with natural pigments extracted from *Amaranthus caudatus*. In the wavelength range of 300-800 nm, the IPCE plot exhibits a maximum of 52% at 430 nm with ethanol extract for *Amaranthus caudatus* pigment-sensitized solar cell. Whereas the IPCE peaks of  $0.1 \text{ mol L}^{-1}$  HCl extract and mixed dye extract for *Amaranthus caudatus* pigment-sensitized solar cells shows maximum at 350 nm with 6.8%



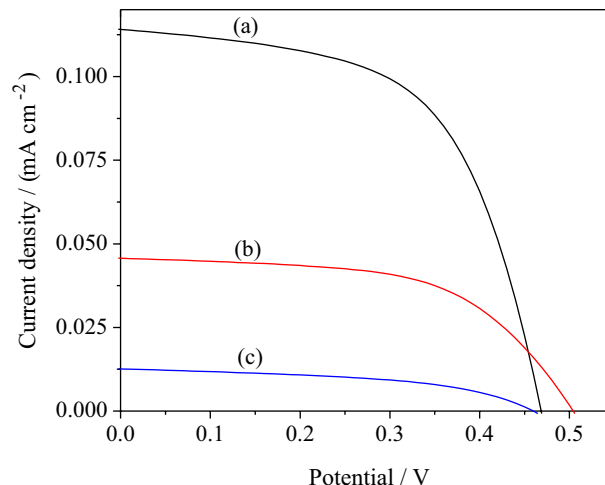
**Figure 6.** J-V curves for DSSCs sensitized by the extract of *Amaranthus caudatus* extracted from: (a) 0.1 mol L<sup>-1</sup> HCl, (b) ethanol and (c) mixture of dyes extracted in 0.1 mol L<sup>-1</sup> HCl and ethanol.



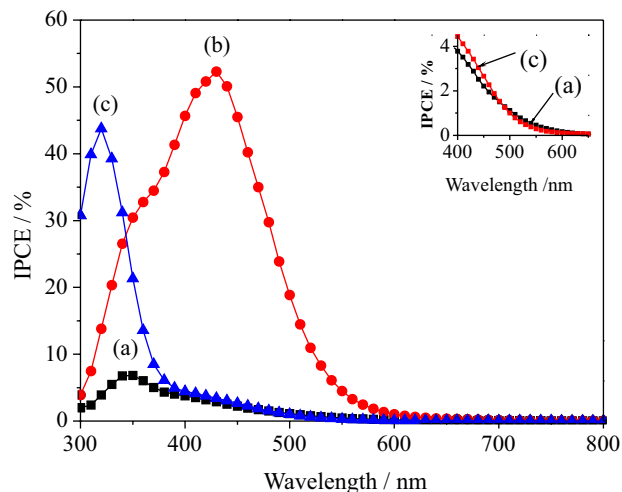
**Figure 7.** J-V curves for DSSCs sensitized by the extract of *Bougainvillea spectabilis* extracted from: (a) 0.1 mol L<sup>-1</sup> HCl, (b) ethanol and (c) mixture of dyes extracted in 0.1 mol L<sup>-1</sup> HCl and ethanol.

and at 320 nm with 43.5%, respectively. These peaks are due to direct light harvesting by bare TiO<sub>2</sub> semiconductor.<sup>26</sup> However, the action spectra in the wavelengths 400-600 nm originates from the dye molecules adsorbed on the TiO<sub>2</sub> surface.

Figure 10 shows the action spectra for the DSSC sensitized with natural pigments extracted from *Bougainvillea spectabilis*. In the wavelength range of 300-800 nm, the IPCE plot shows a maximum of 27.7% at 410 nm with ethanol extract pigment-sensitized solar cell. The IPCE peaks of 0.1 mol L<sup>-1</sup> HCl extract and a mixed dye extract for *Bougainvillea spectabilis* pigment-sensitized solar cells occur at 345 nm with 5.8% and at 330 nm with 16.7%, respectively. These peaks are due to direct light



**Figure 8.** J-V curves for DSSCs sensitized by: (a) the extract of *Delonix regia*, (b) the extract of *Nerium oleander* and (c) the extract of *Spathodea companulata* extracted from 0.1 mol L<sup>-1</sup> HCl.

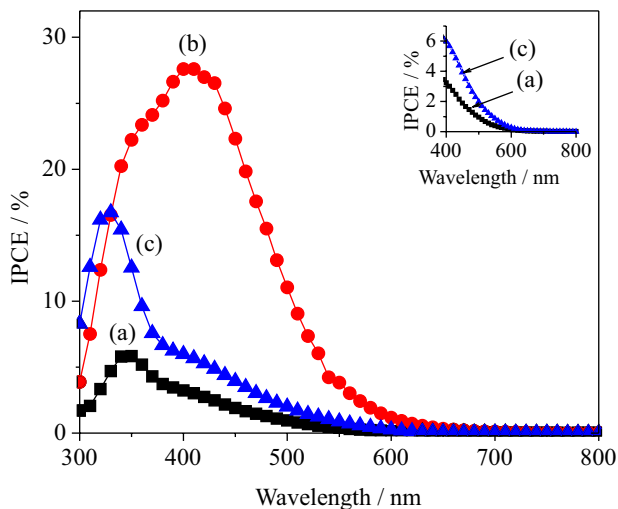


**Figure 9.** IPCE curves for DSSCs sensitized by the extract of *Amaranthus caudatus* extracted from: (a) 0.1 mol L<sup>-1</sup> HCl, (b) ethanol and (c) mixture of dyes extracted in 0.1 mol L<sup>-1</sup> HCl and ethanol. Inset represents the IPCE of curves (a) and (c) in the wavelength range from 400-600 nm.

harvesting by bare TiO<sub>2</sub> semiconductor.<sup>26</sup> However, the action spectra at wavelengths 400-600 nm originates from the dye molecules adsorbed on the TiO<sub>2</sub> surface.

Figure 11 shows the action spectra for the DSSC sensitized with natural pigments extracted from *Delonix regia*, *Nerium oleander* and *Spathodea companulata*. In the wavelength range of 300-800 nm, the IPCE plot exhibits a maximum of 5.1% at 340 nm for *Delonix regia* pigment-sensitized solar cell and of 4.7% at 330 nm for *Nerium oleander* pigment sensitized solar cell, which is the action spectral response of the bare TiO<sub>2</sub> semiconductor,<sup>26</sup> but beyond 400 nm there is still action spectral response which is contributed by sensitization of extracts.





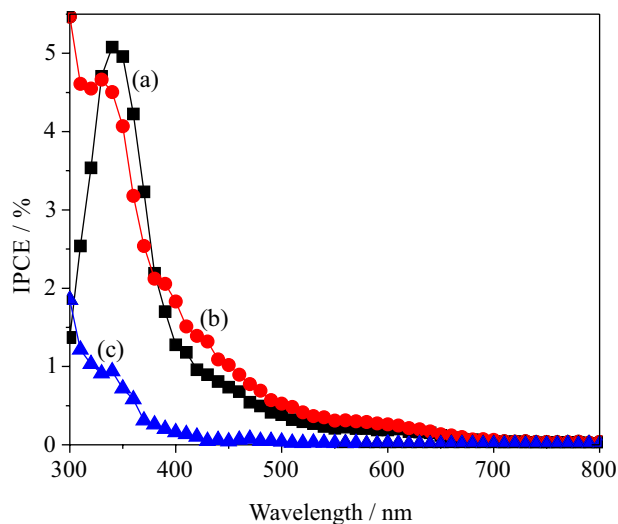
**Figure 10.** IPCE curves for DSSCs sensitized by the extract of *Bougainvillea spectabilis* extracted from: (a) 0.1 mol L<sup>-1</sup> HCl, (b) ethanol and (c) mixture of dyes extracted in 0.1 mol L<sup>-1</sup> HCl and ethanol. Inset represents the IPCE of curves (a) and (c) in the wavelength range from 400-600 nm.

For *Amaranthus caudatus*, *Bougainvillea spectabilis*, and *Delonix regia* pigment sensitized solar cells, the spectral response shows a blue-shift due to the electronic coupling between dye and TiO<sub>2</sub>. The results from the IPCE data are consistent with the results from the J-V curves. The IPCE of the DSSC depends on the incident light harvesting and light scattering.<sup>27</sup> The former is due to the surface area of TiO<sub>2</sub> and the amount of adsorbed dye, whereas the later is related to the morphology of TiO<sub>2</sub>.

Table 2 presents the wavelength at maximum absorbance in the visible region of the dye solutions extracted from 0.1 mol L<sup>-1</sup> HCl and ethanol and maximum IPCE% of the dye sensitized solar cells of the respective plant materials studied in this work.

**Table 2.** Wavelength at maximum absorbance of the dye solutions in the visible region and maximum IPCE of the dye sensitized solar cells of the respective dyes

Natural dye	Solvent	Absorption spectra $\lambda_{\max}$ / nm	Photocurrent action spectra	
			$\lambda_{\max}$ / nm	IPCE / %
<i>Delonix regia</i>	Ethanol	–	–	–
	0.1 mol L <sup>-1</sup> HCl	510	590	33.8
<i>Spathodea companulata</i>	Ethanol	–	–	–
	0.1 mol L <sup>-1</sup> HCl	–	340	56
<i>Nerium oleander</i>	Ethanol	–	–	–
	0.1 mol L <sup>-1</sup> HCl	–	330	4.7
<i>Amaranthus caudatus</i>	Ethanol	433, 466, 618, 664	430	52
	0.1 mol L <sup>-1</sup> HCl	530	350	6.8
<i>Bougainvillea spectabilis</i>	Ethanol	433, 469, 608, 664	410	27.7
	0.1 mol L <sup>-1</sup> HCl	485, 532	345	5.8



**Figure 11.** IPCE curves for DSSCs sensitized by: (a) the extract of *Delonix regia*, (b) the extract of *Nerium oleander*, and (c) the extract of *Spathodea companulata* extracted from 0.1 mol L<sup>-1</sup> HCl.

## Conclusions

Dyes obtained from flowers of five different plants were used as sensitizers in DSSCs. The dyes extracted from these materials contained anthocyanins, betalains and chlorophyll. The photoelectrochemical performance of the DSSCs based on these dyes showed a V<sub>OC</sub> ranging from 0.45-0.55 V, and J<sub>SC</sub> was in the range of 0.013-1.82 mA cm<sup>-2</sup>. The DSSC sensitized by *Amaranthus caudatus* pigment extracted with ethanol offered the highest conversion efficiency of 0.61% among the extracts. This is due to the better charge transfer between the *Amaranthus caudatus* dye molecule and the TiO<sub>2</sub> surface, which is related to a dye structure. The photoelectrochemical performance for the extracts of *Amaranthus caudatus* and

*Bougainvillea spectabilis* with different solvents indicated that the extracting solvent has an effect on the efficiency of DSSCs. DSSC fabricated using ethanol extract shows a higher efficiency than that of 0.1 mol L<sup>-1</sup> HCl extract, reported as 0.61% and 0.033%, respectively for *Amaranthus caudatus*, where as it was 0.325% and 0.018%, respectively for *Bougainvillea spectabilis*. Therefore, the ethanol extract of *Amaranthus caudatus* should be an alternative chlorophyll source for DSSC preparation in geographical regions that *Amaranthus caudatus* is widely available. Overall, natural dyes as sensitizers of DSSCs are promising because of their environmental friendliness, low-cost of production and simple and energy-efficient manufacturing.

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