Chapter

Natural Dyes: From Cotton Fabrics to Solar Cells

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Abstract

This article will discuss natural dyes' role, from colouring the cotton fabrics with some functionality to harvesting sunlight in the dye-sensitized solar cells. Natural dye colourants are identical to the low light- and wash-fastness. Therefore, an approach to improving the colourant's physical properties is necessary. Colouring steps employing silica nanosol and chitosan will be presented. The first part will be these multifunctional natural dye coatings on cotton fabrics. Then, functionality such as hydrophobic surfaces natural dyed cotton fabrics will be discussed. Natural dyes are also potential for electronic application, such as solar cells. So, the second part will present natural dyes as the photosensitizers for solar cells. The dyes are adsorbed on a semiconductor oxide surface, such as TiO_2 as the photoanode. Electrochemical study to explore natural dyes' potential as sensitizer will be discussed, for example, natural dyes for *Batik*. Ideas in improving solar cell efficiency will be discussed by altering the photoanode's morphology. The ideas to couple the natural dyes with an organic–inorganic hybrid of perovskite and carbon dots are then envisaged.

Keywords: natural dyes, cotton fabrics, hydrophobic, multifunctional textiles, dye-sensitized solar cells

1. Introduction

Technology is a means to achieve enhanced goals towards advancing human civilization, as is textile dyeing technology. Dyeing is an integral part of the wet textile processing process, which involves massive amounts of chemicals, both in type and quantity. Recently, the development of the concept of eco-fashion or sustainable textiles has led to the development of dyeing technology using natural dyes that care about aspects of water pollution, the sustainability of raw materials and processed products, biodegradability and other environmentally friendly attributes [1]. Human awareness of a healthy environment has revived interest in products that use natural dyes.

Eco-fashion or Sustainable Fashion as a trend against fast fashion is part of a developing design philosophy to create a system that can support and counteract the impact of human activities on the environment. The focus of eco-fashion is not only on the aspects of the materials used and the environment affected by it but also on the wearer's health and the durability of the clothes. An example is the use of natural pesticide-free materials, the use of materials that can be recycled, clothes that are made to last longer and are not easily damaged, to cover the welfare guarantee for fashion workers. Conventional clothing production is known to involve many resources and produce hazardous waste for the environment. Three criteria attached to environmentally friendly textile creation products include less toxic chemicals, less land or water, and reduction of greenhouse gases. The advantages of nano-sized materials promise exploration opportunities for new technologies with achievements beyond those achieved in computers and biotechnology in recent decades.

The advantage of using natural dyes lies in the smoothness and softness of the colour. This product is highly valued and maintained because it reflects the beauty, prestige, and cultural structures whose existence cannot be replaced by synthetic dyes. However, despite the advantages of natural dyes, several shortcomings of natural dyes have made *Batik* (tradisitional Indonesia fabrics) craftsmen still reluctant to change their *Batik* dyes from synthetic dyes to natural dyes. Among them are the high price, limited availability, long manufacturing process, and low colour resistant to light or washing.

Natural dyes that are currently often used for *Batik* production besides indigo blue are *Tingi* (*Ceriops tagal*) natural dyes. This dye is obtained from the extraction of the bark of the *Tingi* tree, a type of mangrove plant, which has a high tannin content and is used as a dye for *Batik* and tanners. This dye gives the distinctive brown colour of *Batik*. Like most other natural dyes, *Tingi* natural dyes also have a low degree of fastness to washing. So it requires treatment to increase its fastness to washing. Efforts to increase the colour resistance to washing of cotton fabrics coloured by *Tingi* natural dyes will be discussed in the next section. Afterward, works to attach hydrophobic functionality to result in a multifunctional textiles will be described.

Nanotechnology is a technology related to materials or systems at the nanometer scale (1 nm = 10^{-9} m). Unusual changes, which cannot be predicted using classical mechanical models, will be obtained at the nanometer scale, such as changes to electronic properties, mechanical properties, magnetic properties, optical properties and chemical reactivity. The potential for a revival of natural dyes can occur through treaties with nanotechnology.

One of the breakthroughs in photovoltaic technology was the photovoltaic cell's invention based on the photoelectrochemical concept employing nanomaterial by a group of Swiss researchers [2], which became popular as dye-sensitized solar cells (DSSC). The solar cell is composed of a thin layer of semiconductor material, such as titanium dioxide or titania (TiO_2), which has a porous structure, a complex ruthenium (Ru) compound as a sensitizer, and an electrolyte system for the redox pair of iodine compounds. The ruthenium dye complex has a role in absorbing solar radiation, which will generate the dye's electron system so that it flows into the semiconductor material and is connected to a circuit to generate an electric current. The excited electrons from the dye are immediately replaced by the electrons produced from the electrolyte redox pair system, I^-/I_3^-. The natural mechanisms of photosynthesis inspire technology to harvest and use continuous sunlight as a source of energy for all life on earth. Harvesting sunlight ultimately requires the sensitizer to have an absorption character like a black body. So far, ruthenium complex dye as a DSSC photosensitizer has produced a conversion efficiency of ~10% [2]. However, ruthenium is not environmentally friendly. Therefore environmentally friendly sensitizers need to be sought. This environmental demand raises the potential of natural dyes as solar cell sensitizers.

Natural sources of natural dyes for sensitizers are directed to plants that have no potential as a food source and have a large percentage of active colouring agents. Several natural dyes that can be used as solar cell sensitizers have been identified to contain tannins, anthocyanins, betalains, flavonoids, and carotenoids [3]. *Batik*'s natural dyes used for production, mostly are rich of tannins. Potential of this natural dyes will be explored in the fourth section. Finally, some ideas to improve the performance of the natural dyes solar cell will be envisaged in the concluding remarks.

2. Improving the wash-fastness of the natural dyed cotton fabrics

The wood of the *tingi* tree (**Figure 1**) is usually used as firewood. The bark is used as a dye for *Batik* and tanners because of its high tannin content. According to Kasmudjiastuti [4] the tannin content in the bark reaches as high as 26%. The *tingi* bark gives a reddish brown colour with a large enough tannin content. The availability of *tingi* bark as a raw material is very abundant in Indonesia. According to Nazir [5] tannins from *Tingi* dyes fall into the category of condensation tannins, with 26% more tannins than other woody plants such as Avaram, Hemlock, Oak, and Chestnut. Kasmudjiastuti [4] characterised the extract of *tingi* tree wood, resulting in that *tingi* wood contains 70.91% of tannins which are included in procyadinin condensation tannins. However, natural dyes derived from plant extraction have a weakness in their fastness resistance to washing processes and exposure to light. Modification of the dye composition can increase the dye fastness [6].

Dipping the dyed cotton into silica nanosols using the sol–gel method can improve the fastness resistance of a synthetic dye of malachite green b (MG) on cotton fabrics [7, 8]. The hydrogen interaction that occurs between the hydroxyl groups on the cellulose fibers and the hydroxyl groups from the silica sol probably made the silica-MG nanosols to be firmly coated on cotton fabrics. The thin silicon dioxide layer forms a layer that is resistant to heat, light, chemical processes and microbial attack. The oxide thin layer can improve the properties of mechanical strength and resistance to abrasion [7].

The silica nanosol was prepared using the sol gel method with tetraethylortosilicate (TEOS) as a precursor for Si. This process was carried out in an acidic solution of pH 3-4 using HCl as the catalyst and pH regulator [8]. **Figure 2** showed UV–Vis spectra of the *Tingi* extract in water and the mixture of silica nanosol and *Tingi* extract in volume ratio of 1:4 and 1:40. The maximum absorbance of the natural dye is at 473 nm and did not show any shifting after mixing with nanosol silica indicating no structure changes in the dye and the sols. The infrared spectra of the corresponding dried-powder of the mixture dye sols confirmed this, as implied in **Figure 3**. The more the dyes in the mixture sols, the weaker the peaks for Si-O-Si, at around 1080 cm^{-1}.

The dyeing process on the fabric was done by using the dip coating method, which is the direct immersion of the cloth in a solution mixture of silica sol and the

Figure 1.
The Tingi *tree (left) and its corresponding bark for the natural dye's resource (right).*

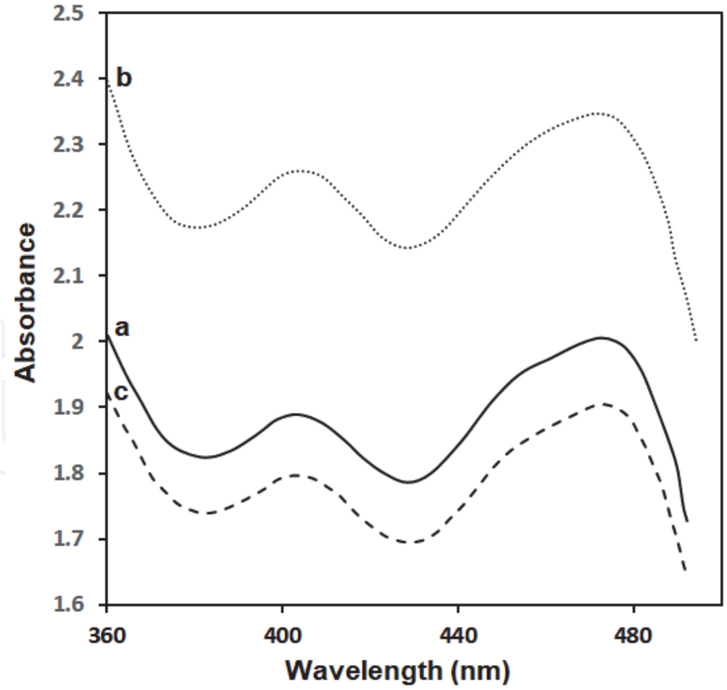

Figure 2.
Electronic spectra of: a. Tingi *extract, and silica sol-*Tingi *extract of: b. 1:4, c. 1:40 by volume.*

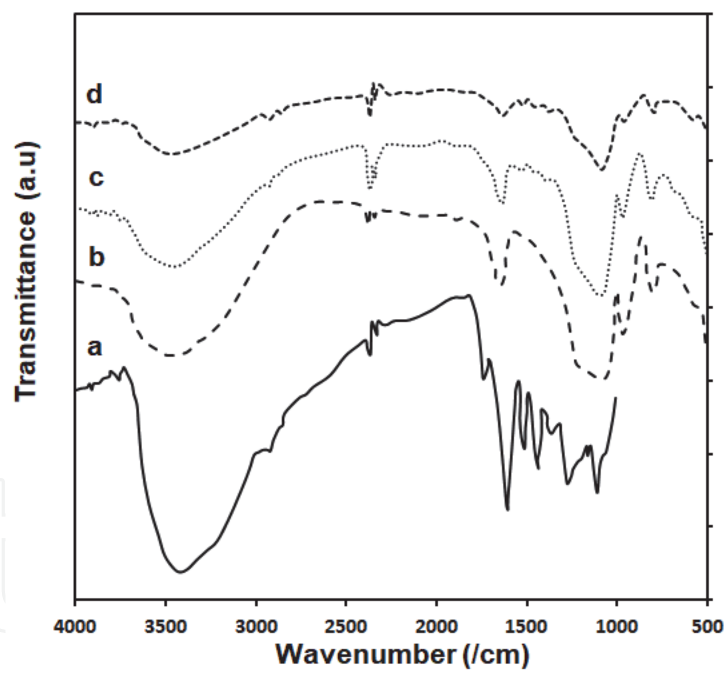

Figure 3.
Infrared spectra of: a. Tingi *extract powder, dried-powder of: b. silica sol, and silica sol-extract* Tingi *of: c. 1:4, d. 1:40.*

dye extract. The variation of the volume ratio of the silica-dye sol was 1:40; 1:8; 1:5; and 1:4 with a total volume of 50 mL. The photos of the dyeing products are displayed in **Figure 4**. The strong dark brown colours are the dominant colour. The colour strength changed as the sols composition changed, with the strongest observed for fabric coloured by 1:4 mixture sols of Si-*Tingi* extract. At other compositions, the colour are almost the same.

The wash-fastness of the dyed fabrics were tested by immersing the testing samples in 1% SDS (sodium dodecyl sulphate) solution (in water) at room

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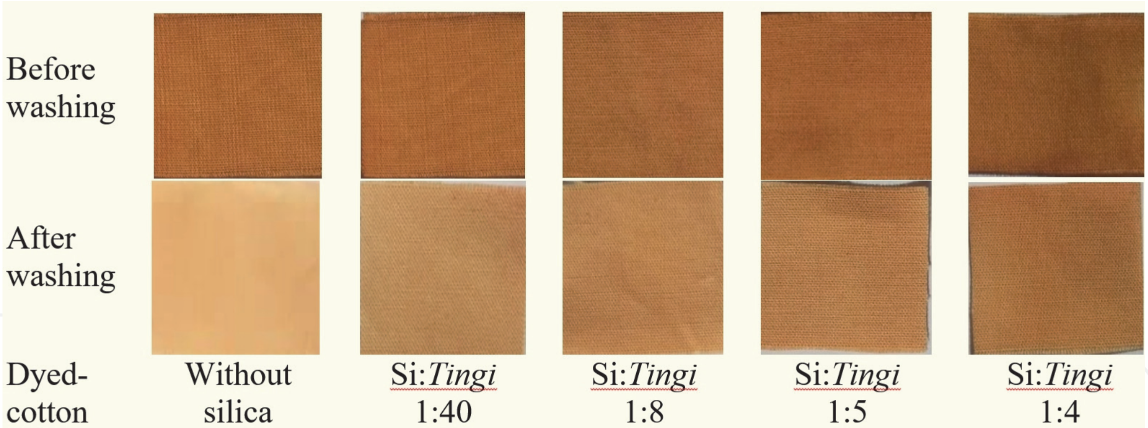


Figure 4.
Dyed cotton fabrics before and after washing under indoor illumination.

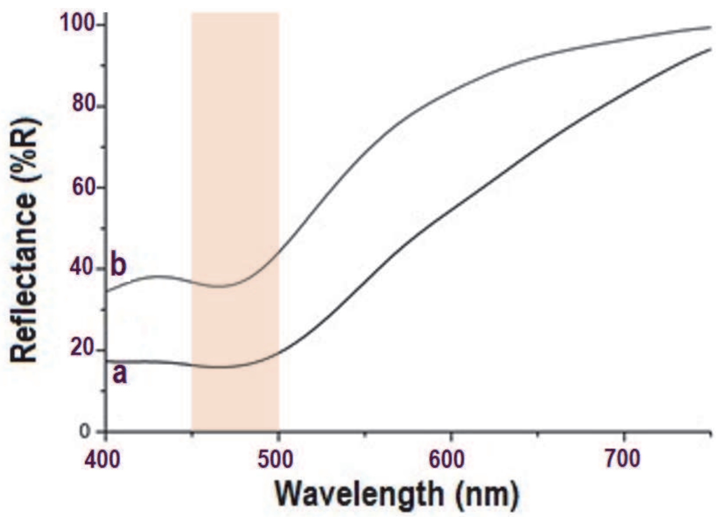


Figure 5.
Reflectance spectra of dyed-cotton without silica coating: a. before washing, b. after washing.

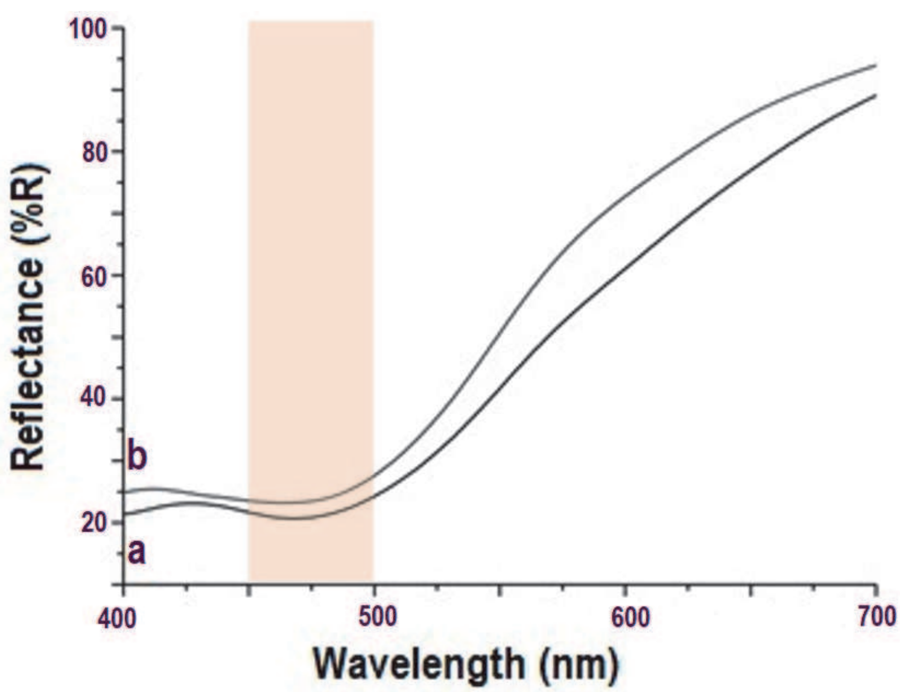


Figure 6.
Reflectance spectra of dyed-cotton with 1:4 silica coating: a. before washing, b. after washing.

temperature for 1 h [7, 8]. Compared to cotton cloth without the addition of silica nanosol, the mixture composition of silica nanosol-dye can increase the wash-fastness resistance of the dye over the washing process. The SiO_2-*Tingi* nanosol ratio of 1: 4 gave the best results, where the colour after the washing process only changed very little when compared to the dyed cotton without nanosol SiO_2. The leaching degree calculated from the reflectance data was 3.18%.

Figures 5 and **6** showed the reflectance spectra to confirm the effect of nanosol silica in the mixture of dye sols. It can be seen that the reflectance difference for fabrics dyed with silica nanosols is relatively smaller than those without silica. Just recently, similar effect can also be obtained by using chitosan coating on the dyed-cotton [9]. It is envisaged that chitosan structure may provide more functional groups for hydrogen bonding with either cellulose of the cotton fabrics or the dye (represented by procyanidin as the active dye for the *Tingi* extract). Therefore, the mixture of chitosan and dye solutions resulted in lower leaching degree to SDS than that of the dye itself. Leaching degree as low as 6.24% has been achieved for dyeing process using a mixture of chitosan and *Tingi* extract [9].

3. Hydrophobic surfaces on natural dyed cotton fabrics

Batik is a work of art with distinctive patterns and motifs on the fabric. The *Batik* cloth used is a cloth that has gone through a pre-treatment preparation process in the textile industry. The pre-treatment process gives a different character to the *Batik* cloth, the *Batik* fabrics commonly used are calico, cotton, and mori. *Batik* fabrics, which are natural textiles, are generally made of cellulose (cotton) and protein (silk) so they are considered more susceptible to microbial attack than synthetic fibers because the porous structure and the constituent polymers are hydrophilic so they are easy to absorb moisture [10]. Fabric surface engineering of *Batik* material needs to be done so that the fabric surface becomes hydrophobic and indirectly provides antimicrobial properties. Topographical engineering of micro-structure and chemical properties on the surface of the fabric was carried out using the sol–gel method.

So far, the surface preparation of hydrophobic fabrics has been done using fluorocarbons which are known to be compounds with low surface energy. Hayn et al. [11] conducted coating of fluorosilane compound (FS) on a nylon-cotton blend fabric resulting in a water contact angle of 148°. However, the use of fluorinated compounds which are commonly used as hydrophobic agents is now starting to be abandoned due to adverse effects such as pollution caused by high toxicity, bioaccumulation in living things and the costs used are also relatively expensive [12]. This has led to research using non-fluorine compounds which are more environmentally friendly. One of them is the compounds of the alkylsilane group which are known to have low surface energy, for example trimethylchlorosilanes (TMCS), octadecyltriclorosilanes (ODTCS), cetyltrimethoxysilanes (CTMS), and hexadecyl-trimethoxysilanes (HDTMS) [13]. Here, we used HDTMS as the hydrophobic agent.

Three types of fabrics commonly used for *Batik* are cotton, *mori* and calico. The three types of clothes are batik fabrics which are differentiated based on the fabrication process. Calico cloth is a cellulose-based cloth that does not go through a pre-treatment process, while cotton and *mori* fabrics go through a pre-treatment process. Therefore, there are differences in fabric properties that will affect the interaction with silica nanosols and HDTMS. **Figure 7** shows the water contact angle obtained from the surface of the three types of *Batik* common fabrics. Cotton and calico clothes resulted in similar basic water contact angle, so similar hydrophobicity. Therefore, for further testing using *Tingi* dyed fabrics, we used cotton.

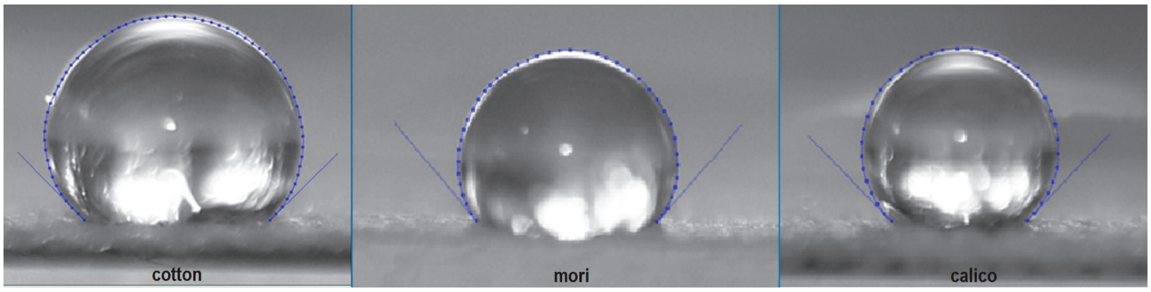


Figure 7.
The water contact angle on different types of Batik*'s fabrics: cotton 135.8°, mori 133.9°, and calico 136.2°.*

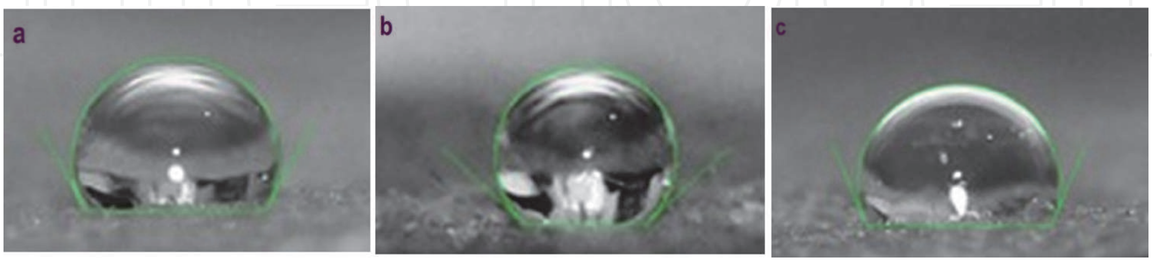


Figure 8.
The water contact angle on cotton fabrics dyed by: a. Tingi *extract (120.1°), b.* Tingi*-silica nanosol mixture (134.7°),* C. tingi *and silica nanosol layer by layer (114.7°).*

Figure 8 displays the water contact angle of *Tingi*-dyed fabrics with and without silica nanosols coated by HDTMS. The mixture nanosol coated cloth showed the best hydrophobicity properties with the greatest water contact angle value of 134.7°, while the fabric coated layer by layer gave the lowest hydrophobicity. This could be due to the weak interaction between HDTMS and the dye molecules. The layer by layer coatings on cotton fabrics were performed in the sequence of silica nanosol, the dye, and the HDTMS.

Our recent results for chitosan coating mixture have shown improved water contact angle after leaching test using natural detergent (*Sapindus rarak*). Saponin in the *Sapindus rarak* which also classified as the low surface energy compound is presumably responsible for this enhanced hydrophobicity. A ten percent improvement was achieved for the fabrics dyed by a mixture of chitosan-*Tingi* extract dye, resulted in water contact angle of 107.83° [9]. Further studies are still required to explore the potential of *Sapindus rarak* as the co-hydrophobic agent to obtain a hydrophobic *Batik* fabrics.

4. Natural dyes for dye-sensitized solar cells: *Batik* and Algae's extract

A dye-sensitized solar cell (DSSC) is one promising alternative to conventional semiconductor silicon-based solar cells due to its low-cost and moderate efficiency. DSSC is typically constructed of TiO_2 (titania) nanoparticles film sensitized with a monolayer of dye molecules as the photoanode. Upon light illumination, the photoexcited dye molecules inject the electrons. Then, the electrons transport through the photoanode to the counter electrode (e.g., fluorine-doped tin oxide (FTO)). These electrons are collected at the counter electrode through an external load and further shuttled back to the oxidized dye molecules via redox reactions of I^-/I_3^- redox couple in the electrolyte. The dye molecules are critical to the overall device performance since they determine the amount of solar energy absorbed by the device. The efficiencies of the sensitizers are related to some essential criteria. The HOMO potential of the dye should be sufficiently positive compared to the electrolyte redox potential for efficient dye regeneration. The dye's LUMO potential should be negative enough to match the potential of the conduction band edge of the TiO_2. Its orbitals should be located at the acceptor part of the dye to provide efficient electron injection. The common dyes in DSSCs are based on ruthenium metal–ligand complexes (e.g. N3 and N719 dyes). However, the limited availability of ruthenium and the low stability of ruthenium-based dyes could hinder the commercialization of DSSCs. On the other hand, natural dyes are promising sensitizers for DSSC application because of their high extinction coefficient and variable chemical structures for strong and broad absorption of solar energy. In addition to the consideration of environmental aspects, natural dyes can also be extracted easily through water, methanol, or ethanol extraction process directly from the bark, roots, flowers, or leaves, so that they are cost-effective in comparison to the manufactured Ru dyes [14, 15].

Some natural dyes, including dyes extracted from the bark of *Tingi* (*Ceriops tagal, CT*) and *Tegeran* (*Maclura cochinensis, MC*), the dried fruit of *Jalawe* (*Terminalia bellirica(gaertn)roxb, TB*), as well as the leaves of Indigo (*Indigofera tinctoria, IT*), are commonly used in the production of *Batik* (**Figure 9**), a technique of wax-resist dyeing applied to whole cloth originated from Java Island in Indonesia. The bark of *CT* is silvery-grey to orangeish-brown, smooth with occasional pustular lenticels, containing 23-40% tannin. Like *CT*, the smooth, lenticellate, and yellowish-brown bark of *MC* contains a high amount of tannin. The dried fruit of *TB* is yellowish-brown with flavonoids, sterols, and tannins content [16], while the *IT* dye contains 2,2'-Bis(2,3-dihydro-3-oxoindolyliden), known as Indigotin, with a dark blue colour. Since all of those "Batik" natural dyes are able to absorb light, the possibility of using them as photosensitizers for DSSC will then become interesting and important to be further investigated. Considering that the energy level of the photosensitizers will strongly affect the electron transport in DSSC, in this study, the absorption spectra and electrochemical properties of the *Batik* natural dyes were

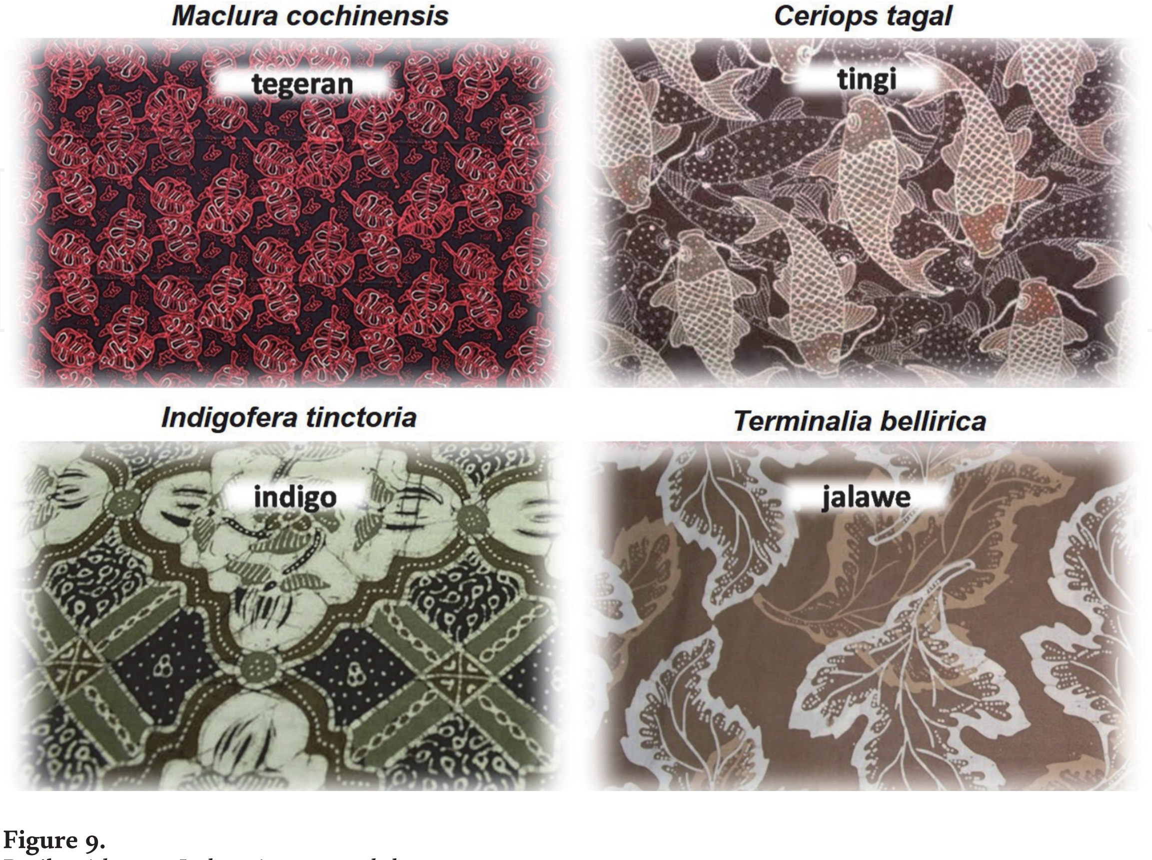


Figure 9.
Batik *with some Indonesian natural dyes.*

presented and discussed. Both data were used to construct the energy of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the corresponding natural dyes to reveal their potential as a light harvester for DSSC.

The construction of schematic energy diagrams in DSSC requires some information regarding the HOMO and LUMO energy levels of the photosensitizer that are determined from its absorption spectra and electrochemical properties. The electronic spectra of the *Batik* natural dye extracts were determined using the UV–Vis spectrophotometry method in the range of 300 to 800 nm, as shown in **Figure 10**. The bark of *MC* and *CT*, as well as the dried fruit of *TB*, were extracted by heating in distilled water, while the *IT* dye was prepared by dissolving a commercial Indigo paste directly in ethanol. The dye extracted from the bark of *MC* shows a single absorption at 490 nm, while several absorptions in the range of 450-500 nm (with the highest peak at 482 nm) were observed from the dye extracted from the bark of *CT*. Both dyes extracted from *IT* and *TB* show a single absorption peak respectively at 665 and 370 nm. The energy band gap of materials was then determined by using the absorption edge of the spectrum. The absorption edge of *MC*, *CT*, *IT*, and *TB* were obtained at observed at 538, 540, 718, and 403 nm, respectively, which attributed to the bandgap energy (E_{gap}) of 2.305, 2.297, 1.729, and 3.078 eV. These E_{gap} values, together with the E_{HOMO} (determined from cyclic voltammetry analysis), were then used to calculate the LUMO energy level.

The electrochemical properties of all *Batik* natural dyes were studied by cyclic voltammetry method using Pt as the working electrode, Pt-wire as the auxiliary electrode, and Ag/AgCI as the reference electrode, with the addition of I^-/I_3^- redox couple as supporting electrolyte. The cyclic voltammograms of all four dyes are shown in **Figure 11**. All cyclic voltammograms results show combined peaks characteristic to

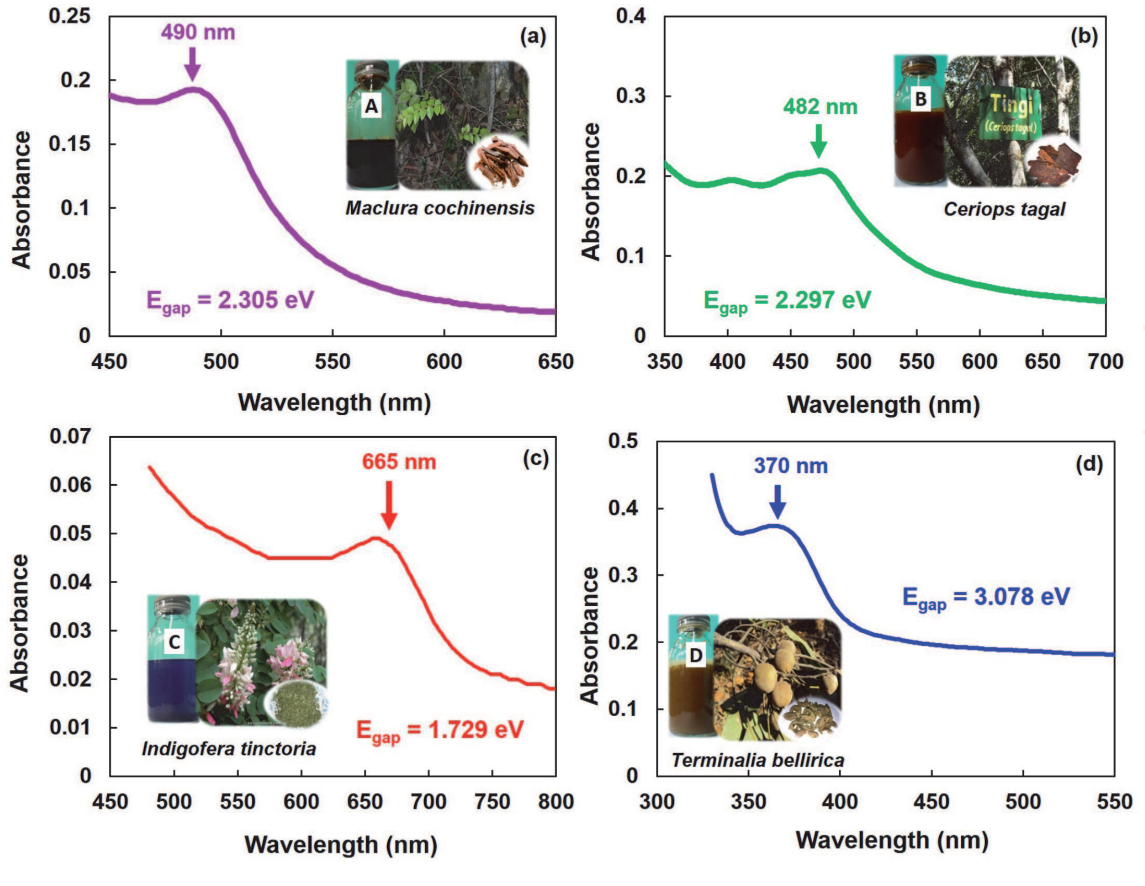


Figure 10.
UV–Vis absorption spectra of four Batik natural dyes: (a) Maclura cochinensis *(MC), (b)* Ceriops tagal *(CT), (c)* Indigofera tinctoria *(IT), (d)* Terminalia bellirica *(TB).*

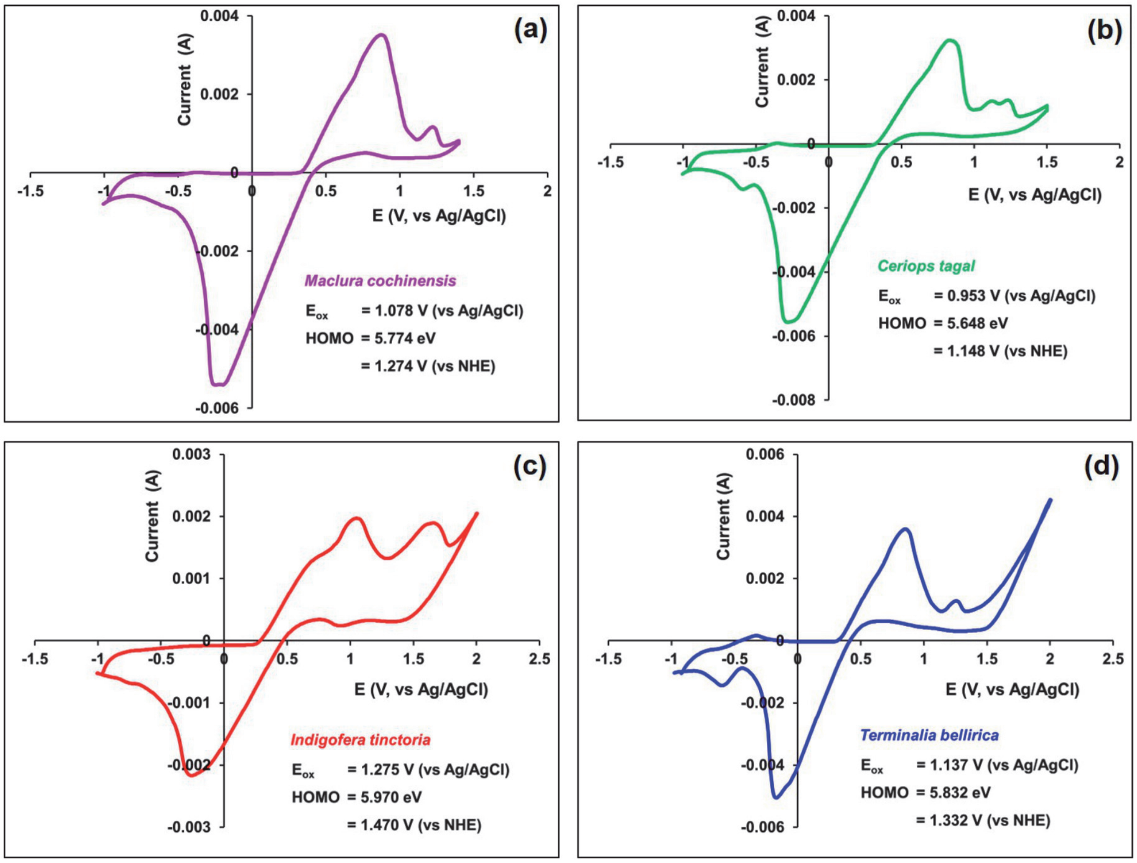


Figure 11.
Cyclic voltammograms of four Batik natural dyes: (a) Maclura cochinensis *(MC), (b)* Ceriops tagal *(CT), (c)* Indigofera tinctoria *(IT), (d)* Terminalia bellirica *(TB).*

oxidation and reduction potential of the reference electrolyte and the natural dyes. The HOMO energy level of the dyes was then calculated from the onset anodic potential of the cyclic voltammograms. The onset anodic potential (E_{ox}) is a cross-section of the baseline and the oxidation peak of the dye [17]. $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox couple was used as an external standard to calculate the E_{HOMO} of the natural dyes. The onset anodic potential of *MC*, *CT*, *IT*, and *TB* were observed respectively at 1.078, 0.953, 1.275, and 1.137 V, which are attributable to the E_{HOMO} of 1.274, 1.148, 1.470, and 1.332 V (vs NHE), respectively. The E_{LUMO} was then calculated based on the bandgap energy and the E_{HOMO} of the dyes. They are −1.031, −1.149, −0.259, and − 1.746 V (vs NHE), respectively for *MC*, *CT*, *IT*, and *TB*. The half-wave redox potential ($E_{p/2}$) of I^-/I_3^- redox couple that was used as supporting electrolyte was observed at around 0.478 V vs. Ag/AgCl or 0.701 V vs. NHE. The values of E_{gap}, E_{HOMO}, and E_{LUMO} of all *Batik* natural dyes were summarized in **Table 1**.

Figure 12 shows a schematic energy level diagram of DSSC using *Batik* natural dyes as photosensitizer and I^-/I_3^- a couple as redox electrolyte. All the HOMO levels of the dyes are sufficiently more positive than the half-wave redox potential

Dyes	Absorption Edge (nm)	E_{gap} (V)	HOMO (V vs. NHE)	LUMO (V vs. NHE)
MC	538	2.305	1.274	−1.031
CT	540	2.297	1.148	−1.149
IT	718	1.729	1.470	−0.259
TB	403	3.078	1.332	−1.746

Table 1.
The values of E_{gap}, E_{HOMO}, and E_{LUMO} of the four Batik *natural dyes.*

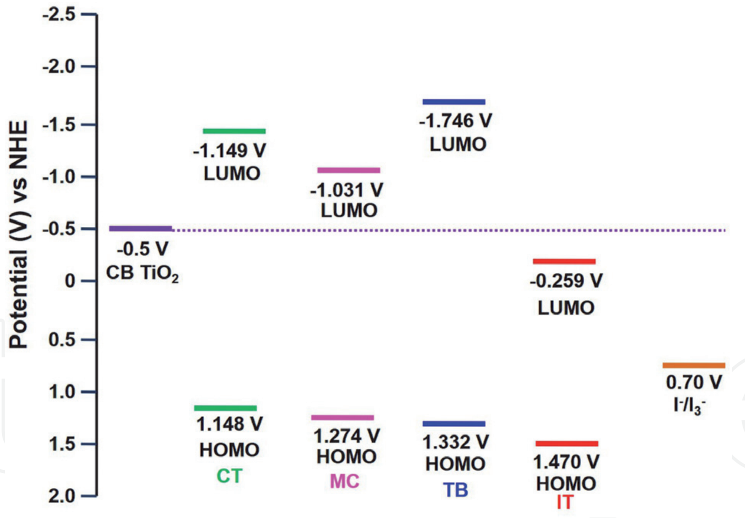
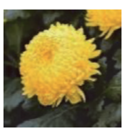
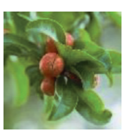
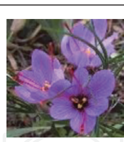
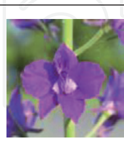
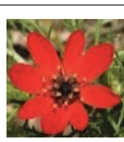
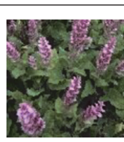


Figure 12.
Schematic energy level diagram of DSSC using Batik *natural dyes as photosensitizer and* I^-/I_3^- *couple as redox electrolyte.*

of I^-/I_3^- couple, suggesting an efficient regeneration of the oxidized dye by the I^-/I_3^- redox couple as the hole transport material. Meanwhile, the LUMO level of the dyes is sufficiently more negative than the conduction band edge of the TiO_2 (E_{CB}), except for IT, which ensure the necessary driving force for electron injection from the excited state of the dye into the conduction band of TiO_2 semiconductor [18, 19]. Therefore, in this DSSC system, we can expect that the *Batik* natural dyes would be regenerated by I^-/I_3^- redox couple and allow the electron injection to the semiconductor and complete the electron flow through an external circuit. **Table 2** lists the solar cell parameters of some *Batik* dyes. The order of efficiency of the solar cell corresponds to the ease of electron injection from the dyes into the conduction band of TiO_2. Thermodynamically, the LUMO of MC to the conduction band of TiO_2 is closer than the LUMO of CT and TB (**Figure 12**). Thus, facilitating the electron injection from the dyes to the semiconductor oxide. However, the cell efficiency is still low. It is probably due to the poor cell construction as indicated by the low values for all solar parameters (**Table 2**).

Kay and Gratzel [27] has studied photosensitization of TiO_2 solar cells with chlorophyll derivatives and related natural porphyrins. Mechanism for sensitization has been revealed [28]. Here, spectral sensitization of TiO_2 films with natural chlorophylls extracted from algae is reported. The crude chlorophylls extracts are obtained by methanol extraction of the dried algae. The algae were harvested from Krakal beach, Yogyakarta on September 2007. They were washed with water and air-dried before use. **Figure 13** shows the absorption spectra of some chlorophylls extracted from algae and the corresponding sensitized titania film.

Based on the UV–Vis absorption spectra of the algal methanol extract in **Figure 13**, it appears that the spectra show the two main absorption characters in the visible light region, around 416-422 nm and 660-666 nm. These results are consistent with the results of Kay and Gratzel [27] who have extracted chlorophyll a and b from spinach using methanol as a solvent. The visible light absorption ability of each algal methanol extract can be assessed by determining the solution's light absorption coefficient. In this study, the light absorption coefficient was determined by measuring the uptake of algae methanol extract at different concentrations. Then the absorption coefficient can be determined by applying the Lambert–Beer law (A = a.b.c., where A is the absorbance, a is the absorption coefficient, b is the thickness of the sample and c is the concentration of the solution). The concentration of algae extract that is not a pure isolated chlorophyll extract is expressed in

Dye Sources		Active Ingredients	J_{SC} (mA.cm^{-2})	V_{OC} (V)	FF	η (%)	Ref.
	Rhododendron	carotenoid	1.61	0.585	0.609	0.57	[20]
	Yellow rose	carotenoid	0.74	0.609	0.571	0.26	[20]
	Tangerine peel	flavonoid	0.74	0.592	0.631	0.28	[20]
	Mangosteen pericarp	anthocyanin	2.69	0.686	0.633	1.17	[20]
	Achiote seed	bixin	1.10	0.57	0.59	0.37	[21]
	Chrysanthemum	xanthophyll	0.09	0.31	0.26	0.01	[22]
	Pomegranate leaf	chlorophyll	2.05	0.56	0.52	0.597	[23]
	Mulberry	anthocyanin	1.89	0.555	0.49	0.548	[23]
	Saffron petal	anthocyanin	2.77	0.36	0.52	0.52	[24]
	*Consolida orientalis*	delphinidin	0.56	0.60	0.53	0.18	[25]
	*Adonis flammea*	astaxanthin	0.40	0.59	0.66	0.16	[25]
	*Salvia sclarea*	eupatilin	0.10	0.37	0.54	0.02	[25]
	Green algae	chlorophyll	0.13	0.41	0.21	0.01	[26]

Dye Sources		Active Ingredients	J_{SC} (mA.cm^{-2})	V_{OC} (V)	FF	η (%)	Ref.
	*Maclura cochinensis* (MC)*	phenolic	0.0064	0.10	0.38	0.0100	this work
	*Ceriops tagal* (CT)*	phenolic	0.0032	0.07	0.21	0.0020	this work
	*Terminalia bellerica* (TB)*	phenolic	0.0064	0.10	0.31	0.0080	this work
	*Sargassum mcclurei* Setchell (SM)‡	chlorophyll	3×10^{-5}	0.06	0.25	0.0009	this work
	*Hypnea esperi* Bory (HE)‡	chlorophyll	0.013	0.055	0.31	0.0044	this work

$^{*}P_{input}$ = 25.6 mW/cm^2, vapor deposited Au counter electrode.
$^{‡}P_{input}$ = 50.0 mW/cm^2, vapor deposited Au counter electrode.

Table 2.
Photoelectrochemical parameters of DSSC with Batik *and other natural dyes.*

the weight concentration of the extract against the volume of solvent (mg/L), so that a is also expressed in mg^{-1} mL cm^{-1}. It appears that the methanol extract of the algae *Sargassum mcclurei* Setchell (SM) has the greatest ability to absorb visible light (a = 0.027), while the algae *Hypnea esperi* Bory (HE) has the ability to absorb less light (a = 0.006). The value of a is characteristic and expresses the intrinsic property of a chemical species to absorb light at a particular wavelength. Based on the electronic spectra of the algae's methanol extract in **Figure 13**, it can be confirmed that chlorophyll a is the main component of the algae's extracts. The concentration of chlorophyll a (Ca) can be calculated using the equation $Ca = 12.7 \bullet A_{663} - 2.69 \bullet A_{646}$ [29]. It turns out that the value of a is in line with the chlorophyll concentration (Ca) contained in the algae methanol extract. The Ca algae SM and HE were 2.59 and 0.96 mg/L, respectively. While, the Ca of extract HA and AF were 0.35 and 0.98 mg/L, respectively. Algae SM has green leaves, but the others are brown to red. Based on the character of visible light absorption and the Ca, the algae SM has the best character as a DSSC sensitizer. Two dye extracts of SM and HE were set for I-V measurement. The extract of Hypnea espery Bory is chosen for I-V testing due to its rich spectra absorption from UV to visible region compared to the other two algaes. **Table 2** presents the solar cell parameters as the results from SM and HE solar cells. It is confirmed that SM resulted in better solar cell parameters compared to HE as predicted.

The absorption spectra of four methanol extract dyes of algae as adsorbed on TiO_2 surface, depicted in **Figure 13**, are all relatively broadened forward to both red and blue sides of visible region compared to their respective spectra in methanol solution. These indicate pronounced aggregation occurred as the dyes adsorbed on

TiO_2 surface. However, the absorption pattern of SM is quite different. The electronic absorption of methanol extract of SM exhibits similar pattern to its respective spectra on TiO_2 surfaces. Two main peaks of chlorophyll *a* are still observed. The Soret band experienced hypsochromic shift (blue-shifted), while the Qy band was red-shifted. This indicates that chlorophyll *a* of SM adsorbed on the TiO_2 surface with limited aggregation [30, 31]. Absorption spectrum in the visible region resembles the absorption spectra of chlorophyll *a* in a mixture of methanol or ethanol-water upon completion of transition of monomer into aggregates [32]. A weak shoulder around 445 nm, close to the Soret band is also observed. This may ascribe to the presence of chlorophyllin *b* [33]. Chlorophyllin is chlorophyll derivative in which the cyclopentanone ring is opened as well as the carbonyl of the phytyl ester bond [33]. Compared to the parent chlorophyll, the Qy band of chloropyllin is much weaker than the Soret band. The presence of chlorophyllin affects mainly the intensity of the Qy bands of the crude extracts of algae. In general, the Qy bands of chlorophyll contained in methanol extracts of algae are slightly lower related to the synthetic chlorophyll a presented in the previous reference [33]. The presence of chlorophyllin as observed in **Figure 13** is predicted to facilitate aggregation due to intermolecular bonding induced by the –COOH groups. Efficient photosensitization

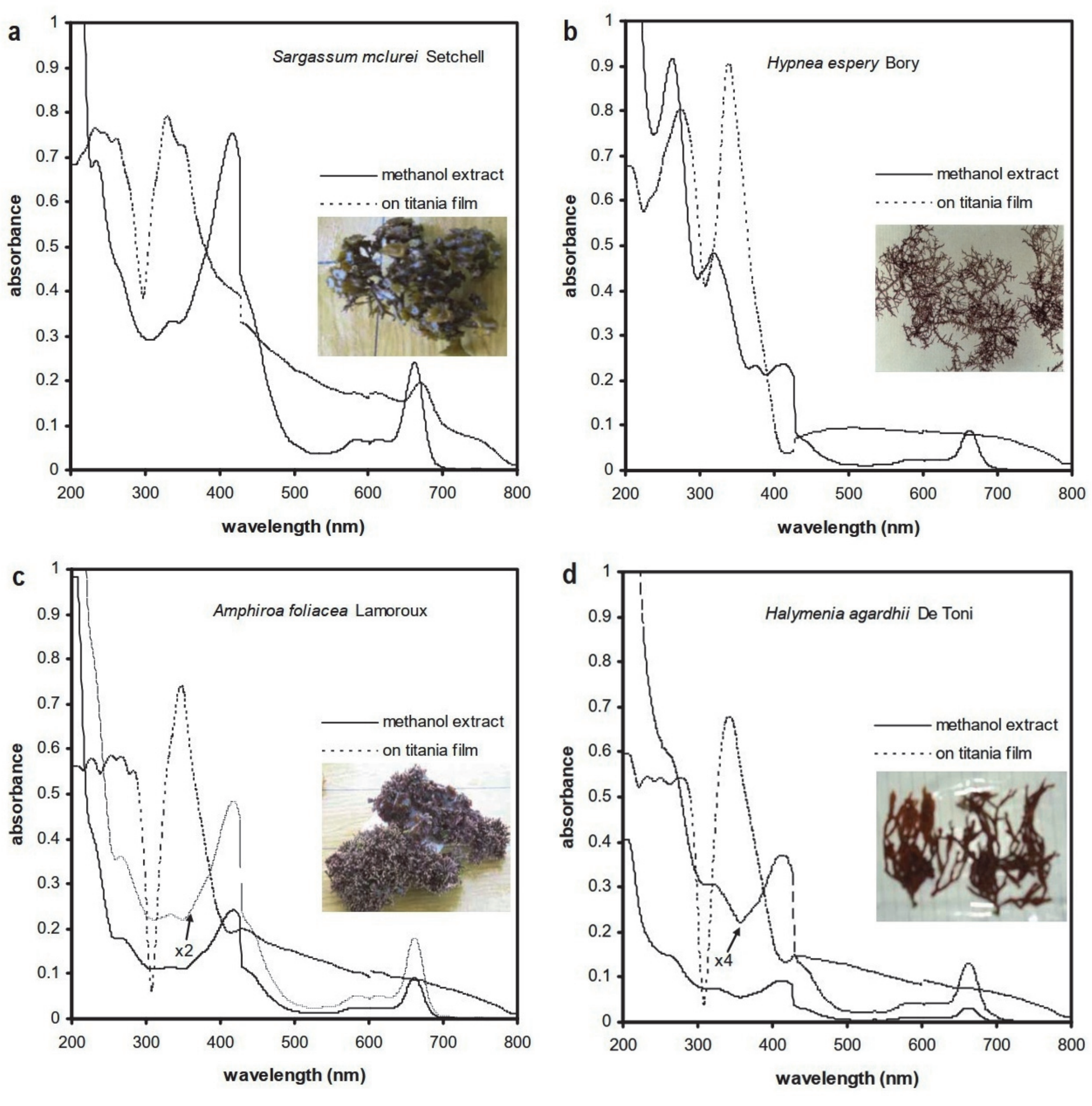


Figure 13.
The electronic absorption of methanol extract of algae adsorbed on titania film and their corresponding solution spectra of: a. Sargassum mclurei *Setchell (SM) b.* Hypnea espery *Bory (HE), c.* Amphiroa foliacea *Lamoroux (AF), and d.* Halymenia agardhii *De Toni (HA).*

may result from efficient electron injection through the bonding formed between TiO_2 and the pigment. Large difference in the photocurrent density of the SM and HE cells rather than in photovoltage suggesting that the solar cell performance of the cells are influenced by the efficiency of the electron injection from the sensitisers into TiO_2 [34].

Natural dyes can be used as a sensitizer, which will require making and purifying dyes more efficiently and rapidly in order to lower production costs, reduce the risk of solar cell toxicity, and use an environmentally sustainable manufacturing method. Some also can be extracted from fruit waste [20, 21], thus it is green technology. Improved efficiency are still intensively researched by employing a cocktail of dyes [20–26, 35], adsorbed dyes on clay [36], optimizing solvent extraction [37]. Amongst, combination of dyes has shown two to three times increased efficiency, while the use of clay has decreased the cell efficiency. It has been shown that TiO_2 is still superior compared to ZnO semiconductor as the photoanode materials [38]. Therefore, discussion will focus on the improvement of natural dyes PEC solar cells due to the use of nanostructured titania. TiO_2 has band gap energy (E_g) in the range of 3.0-3.2 eV. The crystalline phase of TiO_2 found in nature includes anatase, rutile, brookite, and TiO_2-B. Among all the crystalline TiO_2 phases, anatase is the most photoactive crystalline phase. The energy of the upper TiO_2 band gap is 3.2 eV, higher than rutile (3.0 eV). The width of the TiO_2 band gap gives the nature of photostability due to the electron recombination.

The next strategy is to take advantage of the sophistication of nanotechnology, namely utilizing the features of 1D nanostructures such as nanofibers, nanotubes, nanorods; which allows a toll path for electrons from the sensitizer to the back contact of the titania photoanode [39, 40]. The TiO_2 nanorod photoanode gave a value of Voc 0.802 V, Isc 7.01 mA and efficiency of 2.9% [41], whereas TiO_2 nanowire produced Voc 0.752 V, Isc 3.73 mA and efficiency of 1.81% [42]. The TiO_2 nanotube photoanode gave characteristic values of Voc 0.846 V, Isc ~9.63 mA and efficiency of 4.03% [43]. Bijarbooneh et al. [44] used mesoporous TiO_2 nanofibers and obtained Voc 0.76 V, Isc 15.23 mA and were able to increase energy efficiency from 7.28% to 8.14%. The cell performance of nanotubes titania was three-times higher than that constructed from nanoparticle titania (P25) using mangosteen pericarp ethanol extract as the sensitizer [45]. These studies encourage the use of 1D nanostructured TiO_2 to improve performance of the natural dyes solar cells.

Another possibility to improve the natural dyes solar cells is the invention of perovskite material for hybrid DSSCs. Methylammonium lead (II) iodide ($MAPbI_3$) is a perovskite material where the A cation is the organic $CH_3NH_3^+$ cation, B is the Pb^{2+} metal cation, and X is the halide anion such as I^-. Since having a band gap energy of 1.55 eV, which is equivalent to the absorption at a wavelength of 800 nm, this material is potential as visible light absorber. The solar cells efficiency with perovskite structure has achieved up to 25.2% [46]. This high conversion efficiency provides the opportunity to be combined with natural dye sensitised solar cells. Dey et al. [47] has shown that a perovskite and carotene dye layers resulted in a conversion efficiency of up to 5.01%, which was almost ten times than that of solar cells using carotene alone [20]. This new perovskite material feature is expected to be another way to the revival of natural dyes as solar cell sensitisers. However, the presence toxic elements of lead in the perovskite could be a challenge for sustainability.

Recent computational study has shown potential of nanohybrid of graphene quantum dots (GQD), a one type of carbon dots, with porphyrin as the solar cell [48]. It was found that the electron transfer from porphyrin to GQD is faster for larger size of GQD. Nanocomposite carbon dots-polymer [49] has also resulted promising results for quasi solid state solar cells. The carbon dot in the electrolyte composition resulted in improved efficiency up to 6.05% by absorbing unused higher energy of visible light. These findings pave a way to more efficient green natural dyes solar cells.

Our fast-moving time demands creating and innovating science and technology in natural dye's application. Intrinsic properties of the natural dyes of having rich antioxidant are rendering the potential for multifunctional antibacterial textiles. The soft and shady colour of natural dye dyed fabrics with low impact on the environment also drive the fashion industry into the more sophisticated functions of sustainable fashion. It is not only for textile colouring but also for bringing prestige and dignity. The more sophisticated natural dyes function as photosensitisers for photodynamic therapy (PDT) requires intensive purification [50, 51]. Advanced nanotechnology may direct the applications to the photochromic and sensor materials [52, 53].

5. Concluding remarks

Some works on the use of natural dyes for textiles have been presented. The use of natural dyes supports the shifting paradigm in the world fashion to the sustainable fashion. Although, past researches have endorsed essential growth in the application of the natural dyes for fabrics, but still there are a number of technical challenges of natural dye application that must be overcome. The composite formation with green resources such as chitosan, silica may result in enhance dyeing performance to cotton fabrics. Functional such as hydrophobic surface may also be introduced by using natural ingredients such as *Sapindus rarak*.

This work also presents the investigation of the absorption and electrochemical properties of four *Batik* natural dyes to be considered as environmentally friendly photosensitisers for dye-sensitised solar cells. All *Batik* natural dyes extract exhibit absorption peaks in the visible wavelength ensuring their sunlight harvesting ability and HOMO-LUMO energy levels ideal for DSSC. It is noteworthy to blend all the *Batik* dyes to obtain superposition of absorption spectra covering a visible light region from 350 to 800 nm, thus resulting in more efficient panchromatic dyes as required for DSSC. Most of the HOMO-LUMO of the *Batik* dyes have satisfied the thermodynamic requirement as a sensitizer to allow electron transport in DSSC.

Natural dye solar cell technology is still promising as an alternative green and renewable energy. Improved efficiency could be sought through the application of 1D nanostructured titania, the hybrid formation with perovskite organic–inorganic hybrid, and graphene quantum dots or carbon dots. Both, the organometallic perovskite halide and the carbon dots can be used as the co-sensitizer for the realisation of the more efficient natural dyes solar cells.

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