

Bio-Photovoltaic Conversion Device Made from Chitosan Nanofibers and Varieties of Natural Pigments

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Abstract

In this study, the natural pigments anthocyanin, beta carotene, chlorophyll, and curcumin, extracted from red cabbage, carrot, water hyacinth and turmeric, respectively, were used as sensitized dyes in a Bio-photovoltaic Conversion Device (BPV), and the energy conversion efficiencies (η) were compared. The photoelectrodes were designed to use various photoactive layers made of porous TiO_2 or a new TiO_2 :nanofiber interface. The nanofibers were prepared by an electrospinning chitosan solution, a PVA solution (poly(vinylalcohol)), and their mixture at different conditions. Analysis from a scanning electron microscope (SEM) showed that the formation and the density of nanofibers increase with increasing amount of PVA. The highest η was observed in solar cells which used anthocyanin extracted from red cabbage. When considering the photoactive layers made of TiO_2 :nanofibers prepared from the mixture between 1.2 % chitosan in acetic acid and 8 % PVA in aqueous solution at the ratio of 1:1. w/w ([1.2Chitosan]+[8PVA]), it raised the η up to 5.3 times higher than by the TiO_2 alone. Therefore, the utilization of chitosan nanofibers together with the application of natural dyes has the potential to increase η of BPVs.

Keywords: Dye-sensitized solar cells, nanofibers, chitosan, natural pigments

Introduction

The Grätzel photovoltaic cell was first developed by the Swiss scientist Michel Grätzel and his colleagues in the 1990s as a device that used organic pigments to convert the energy of light into direct current [1]. Such cells are now known as dye-sensitized solar cells (DSSCs), which are usually made of an optically active pigment enclosed between two suitable electrodes. A bio-photovoltaic conversion device (BPV) here is defined as a hybrid organic-inorganic DSSC, which represents the state of the art for low cost energy conversion, as well as for minimizing environmental impact. The basis of this interesting type of DSSC involves the coupling between TiO_2 molecules and organic dye molecules to produce photogenerated electrons [1,2]. They are still the object of competitive research and development for energy conversion applications [3,4].

A number of organic molecules can absorb quite a vital part of the solar visible spectrum (400 - 700 nm), which accounts for 60 % of the whole solar energy spectrum. For example, chlorophyll a and b, which act as pure photosensitizers in the photosynthesis of green plants, each have 2 absorption peaks around 425 and 662 nm and 463 and 645 nm, respectively [5]. Anthocyanin are organic molecules belonging to the bioflavonoid group whose energy gap between the last filled state, called the Highest Occupied Molecular Orbital (HOMO), and the first empty state, the Lowest Unoccupied Molecular Orbital (LUMO), corresponds well with the forbidden band of a semiconductor (around 2.2 eV to 2.4 eV) and appears to demonstrate absorption peaks between 520 - 560 nm [6]. Pigments in the carotenoid

group, such as carotene, xanthophyll, and zeaxanthin, can act as antenna pigments in photosystem I and II by absorbing the remaining part of visible light between 400 - 530 nm, and that assists plants to maximize light harvesting efficiency in natural environments [5]. All of this promotes the idea of organic molecule based photovoltaic cells being ideal for absorbing visible light.

Like conventional solid-state solar cells, DSSCs separate the function of light absorption from charge carrier transport. However, in DSSCs, the last is generated when the photons are absorbed by organic dyes, injecting electrons into the conduction band of TiO₂ n-type semiconductors [1,7,8]. The electrons flow to the conductive glass electrode through the TiO₂ network and continue to the counter electrode through an external circuit. The dyes regain the electrons which were transferred from the counter electrode by redox reaction, the process that must be facilitated by either solid or liquid electrolytes. One of the potential causes affecting low conversion efficiency in BPVs is the interfacial charge recombination between the porous semiconductor (TiO₂) coating on the electrode and dye molecules. It has been reported that this drawback could be suppressed by inserting an insulator layer between the semiconductor and the dye [9,10]. On the other hand, many groups have instead improved contact between the dye and semiconductor by increasing the number of carboxylic groups in the dye structures. This is because the more carboxylic groups, the better anchoring ability between the dye and the semiconductor, and thus the better electron injection [11,12]. However, not all natural pigments contain carboxylic groups in their structures, and this could prohibit such a low cost and environmental-friendly dye like chlorophyll to enter into BPV manufacture.

Nanofibers are ultrafine fibers, as thin as several nanometers, prepared from various kinds of organic (e.g. DNA, collagen and chitosan) and inorganic (e.g. polyvinyl alcohol and polyvinylpyrrolidone) polymers. Nanofibers became highly valuable because of their amazing characteristics, such as very large surface area-to-volume ratios and high porosity with very small pore sizes. Therefore, nanofibers can be promising materials for many biomedical applications, such as artificial organs, tissue engineering, medical prostheses, wound dressing, pharmaceutical composition, drug delivery, and so on. One of the techniques which are widely used for nanofiber preparation is called "electrospinning". This technique mainly involves the application of electrostatic repelling force to overcome the surface tension force of polymer solution which drips from a tip of a needle into an electric field. The outcome is an extremely fine continuous filament, with simultaneous rapid evaporation [13]. By electrospinning chitosan solution, chitosan nanofibers are successfully deposited on indium tin oxide (ITO) substrates. Then, enzyme polyoxometalate (α -[P₂W₁₈O₆₂])⁶⁻ are immobilized onto the modified electrode to create a biosensor for nitrite (NO₂⁻) detection [14]. Here, the authors propose a deposition of nanofibers onto the porous TiO₂ to produce a new semiconductor interface (TiO₂:nanofiber). The nanofibers not only act as insulator layers between the semiconductors and the dyes, but probably improve adhering capacity between non-carboxylic natural dyes and the photoactive layers as well.

In addition, the performance of several BPVs prepared from varieties of natural photoactive pigments (extract of red cabbage, carrot, water hyacinth and turmeric) making contact with the new TiO₂:nanofiber interface are reported. Scanning electron microscopy (SEM) analysis is used to study the surface morphology of the TiO₂ and TiO₂:nanofiber films.

Materials and methods

Preparation of natural dye sensitizers

The alcohol extracts of red cabbage and turmeric result in anthocyanin and curcumin, whereas the acetone extracts of water hyacinth and carrot result in chlorophyll and beta carotene, respectively. Extraction of pigments is obtained according to the following steps: the clean flesh of red cabbage, carrot, water hyacinth, and turmeric is dried at 40 °C in a vacuum drying oven and then crushed into a fractionlet. The raw materials are put in either 95 wt.% ethanol or acetone solution and kept in ambient temperatures, without exposure to direct sunlight, to extract natural dyes in the solution adequately. Solid residues are filtrated out and the natural dye solutions are concentrated to one quarter with a rotary evaporator at 40 °C. After that, the natural dye sensitizer solutions either in alcohol or acetone are

prepared. The absorption spectra of the extract solution are conducted with spectrophotometer (Jasco V-530) scanning from 400 - 800 nm.

Preparation of BPVs

The TiO₂ paste is prepared by mixing 5 g of TiO₂ powder with 12 cm³ of polyethylene glycol solution (6 % by weight in water); then, TiO₂ paste is coated on the conducting glass (FTO, F-doped SnO₂, sheet resistance is 8 Ω/cm²) by the screen painting technique, covering the film area of 0.5 × 2 cm² with a thickness of about 50 μm, and is followed by sintering at 450 °C for 1 h with a heating rate of 5 °C/min. The semiconductor layer in the photoelectrodes is fabricated by spin coating with the nanofiber of chitosan and PVA in 4 conditions, called *1.2Chitosan*, [*1.2Chitosan*]+[*8PVA*], [*1.2Chitosan*+*8PVA*] and *8PVA*, where *1.2Chitosan* is TiO₂ + nanofiber of chitosan 1.2 % w/w in acetic acid, [*1.2Chitosan*]+[*8PVA*] is TiO₂ + nanofiber of a mixture between the same chitosan 1.2 % w/v and PVA 8 % w/v in aqueous solution at a ratio of 1:1, [*1.2Chitosan*+*8PVA*] is TiO₂ + nanofiber prepared by dissolving both chitosan and PVA in acetic acid to achieve a final concentration of chitosan 1.2 % and PVA 8 % w/v, and *8PVA* is TiO₂ + nanofiber of PVA 8 % w/v in aqueous solution. For a control sample [*TiO₂*], TiO₂ is screened on the conductive glass without nanofiber fabrication. In each condition, samples are soaked in either dye solutions extracted from red cabbage, carrot, water hyacinth and turmeric for 3 h.

Electrospinning experiments are conducted with the apparatus parameters as described by the following: the polymeric solution is placed into a 5 mL syringe attached with a hypodermic needle tip which points downward. A copper wire connected to the positive electrode is connected with the metal needle tip when a copper collector plate with the photoelectrodes placed on it is connected to the ground. To prevent excessive polymeric solution drooping on the photoelectrodes due to gravitational force, the collector plate is tilted 45° and placed 1 cm away from a vertical baseline. A high voltage power supply is employed to generate the electric field. The applied voltage and the tip-to-collector distance are fixed at 19 kV and 10 cm, respectively. The resulting chitosan nanofibers are dried at room temperature prior to further investigation.

The counter electrode is a thermally platinized conducting glass (5 mM H₂PtCl₆ in acetone solution, sintered at 450 °C on a conducting glass substrate for 1 h). The photoelectrode and counter electrode is incorporated into a thin layer sandwich-type solar cell, with a thick PARA film sheet as a spacer. The electrolyte solution, a mixture of 0.03 M I₂ + 0.3 M LiI in an acetone nitrile, is encapsulated between the photoelectrode and counter electrodes. The photoelectrochemical characteristics of BPVs are tested under simulated sunlight at 1.5 AM produced by a solar simulator (Solar Light Co., Model XPS 400) with a radiant power of 100 mW/cm² (emitted from 400 W Xenon short arc lamp). The current density versus voltage characteristics is measured with a DC voltage and current source which is interfaced and controlled by a computer. The short current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and the overall photoconversion efficiency (η) are determined from the J-V curves.

Results and discussion

Absorption spectra of natural dye sensitizers

Figure 1 shows the UV-VIS absorption spectra of extract from red cabbage, water hyacinth, carrot, and turmeric. It can be seen that the absorbance peak of red cabbage (522 nm), water hyacinth (410, 664 nm), carrot (501 nm) and turmeric (421 nm) corresponded well with the natural pigments anthocyanin, chlorophyll, beta- carotene, and curcumin, respectively [15].

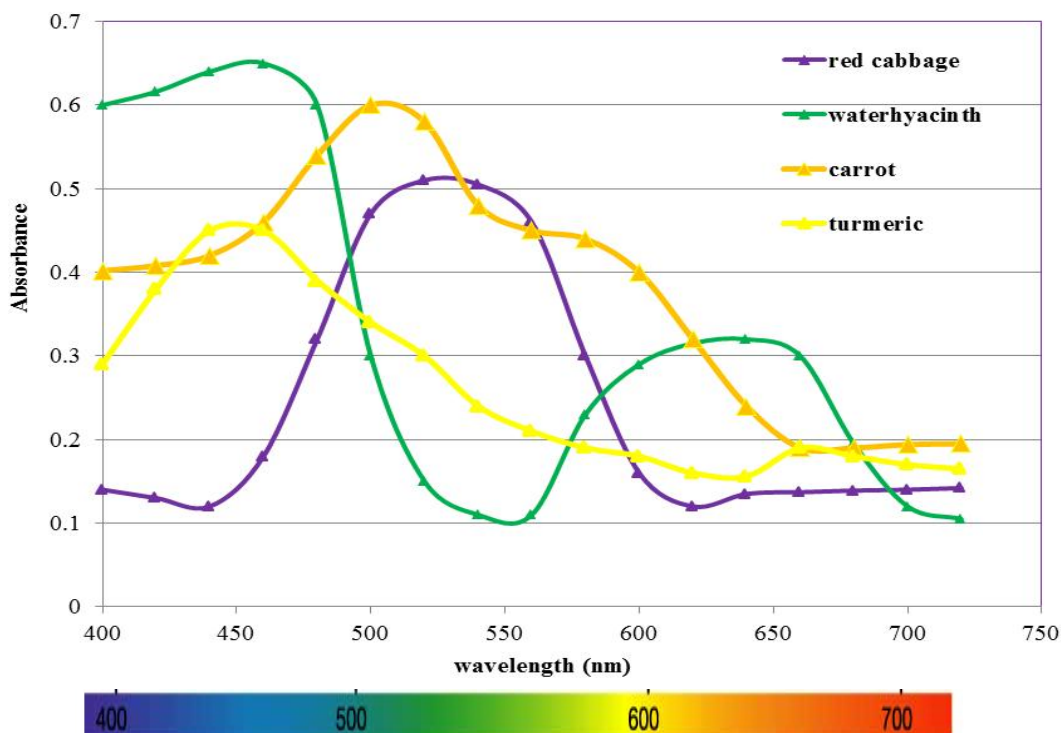


Figure 1 The absorption spectra of the extracts of red cabbage and turmeric in 95 % alcohol solution and water hyacinth and carrot in acetone solution. The color bar displays the corresponding color in the solar visible spectrum.

Anthocyanin is the main component of some natural dyes, and usually expresses strong color in several parts of plants, ranging from fruits, flowers and leaves. Because anthocyanin shows color in the range of visible light from red to blue, it promises to become a highly efficient sensitizer for wide bandgap semiconductors [16]. Chlorophyll and beta carotene are 2 common photosynthetic pigments widely found in terrestrial plants. They function to capture photon energy used to drive electron transport in photosynthesis light reaction. It has been reported that both pigments were used together as sensitized dyes in the DSSCs to imitate the photosynthetic electron transport observed in plants with satisfying results [17].

Curcumin is an antioxidant and widely used in traditional medicine. Due to its strong yellow-orange color, it was used as food additive to provide edible color to numerous cuisines [18]. Recently, curcumin was used as a sensitized dye in DSSCs and successfully produced a current density of 0.53 mA/cm² with a conversion efficiency of 0.41 % [19]. When curcumin was modified by adding two carboxylic groups into its structure, it became a new photoactive dye with a strong surface attachment [20].

Morphology of photoelectrodes and natural sensitized dyes

Figures 2a - e show SEM topographies of TiO₂ film and the new TiO₂:nanofiber interfaces. The surface morphology of the nanofiber deposition (Figures 2b - e) is quite distinguishable from that of bare TiO₂ semiconductors (Figure 2a). It is clear that chitosan solution alone failed to form nanofibers (Figure 2b), while the chitosan/PVA blend successfully produced the nanofibers onto TiO₂ film (Figures 2c, d). Chitosan is a derivative of chitin, the second-most abundant natural polysaccharide next to cellulose, which is embedded in the protein matrix of a squid pen or a crustacean shell [21]. It is widely accepted that electrospinning of pure chitosan is difficult because of its high surface tension [13]. To

overcome this problem, chitosan is recommended to dissolve in a high concentration of acetic acid to reduce surface tension force. The protocol reported in the literature was followed, but failed to produce chitosan nanofibers (**Figure 2b**). This was probably due to the in-house built electrospinning apparatus not being able to produce electrostatic repelling forces high enough to initiate the formation of chitosan nanofibers (19 kV, compared to 40 kV in the literature). The blend between chitosan and long chain polymers, such as PVA, PEG (poly ethylene glycol) and trifluoroacetic acid (TFA), was reported to form fine nanofibers [14,22,23] and here chitosan nanofibers were successfully produced by adding PVA to chitosan solution. By doubling the amount of PVA in the polymeric mixture ($[1.2\text{Chitosan}+8\text{PVA}]$ compared to $[1.2\text{Chitosan}]+[8\text{PVA}]$), the density of chitosan composite nanofibers increased dramatically (**Figures 2d, c**).

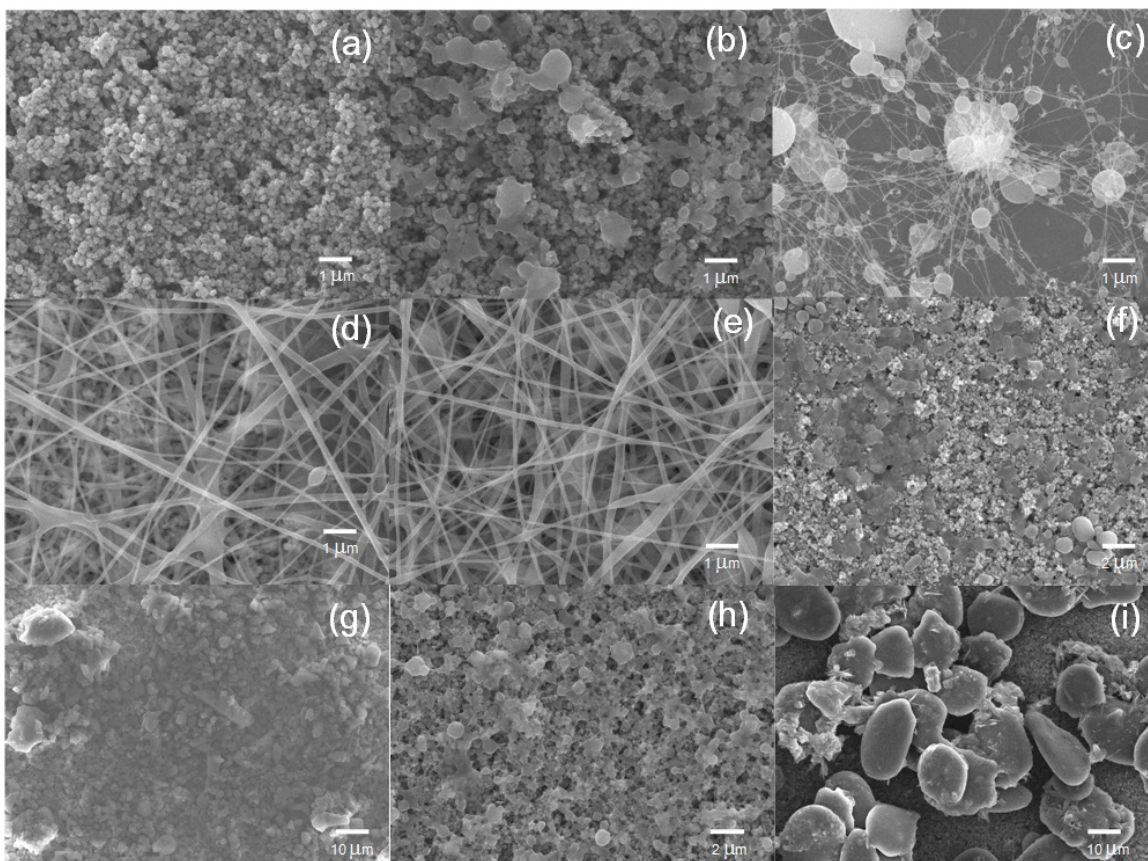


Figure 2 SEM micrographs of photoelectrodes (a) TiO_2 , (b) 1.2Chitosan , (c) $[1.2\text{Chitosan}]+[8\text{PVA}]$, (d) $[1.2\text{Chitosan}+8\text{PVA}]$ and (e) 8PVA , as well as the morphology of natural dyes on the photoelectrodes (f) anthocyanin, (g) beta-carotene, (h) chlorophyll and (i) curcumin.

Figures 2f - i are SEM micrographs showing the morphology of all natural dyes in this experiment, and reveal that particles of all of the dyes were in the magnitude of micrometers.

Photoelectric properties of DSSCs prepared from different photoactive layers

Photovoltaic tests of BPVs using different kinds of photoactive layers in the photoelectrodes were carried out by measuring the J-V characteristic curves (**Figure 3**). Additionally, tests were carried out

with different kind of natural dyes extracted from those plants mentioned above. The J-V curves indicated that all BPVs prepared in this project were obviously able to generate photocurrent, although they were in the magnitude of mA (Figure 3). The miniscule amount of photocurrent observed here is typical for any BPVs which were prepared from natural dyes elsewhere. For example, beta carotene, chlorophyll, and anthocyanin, have been reported to produce a photocurrent of 0.35, 0.43 and 0.65 mA, respectively, when coated on porous TiO₂ [17,24,25].

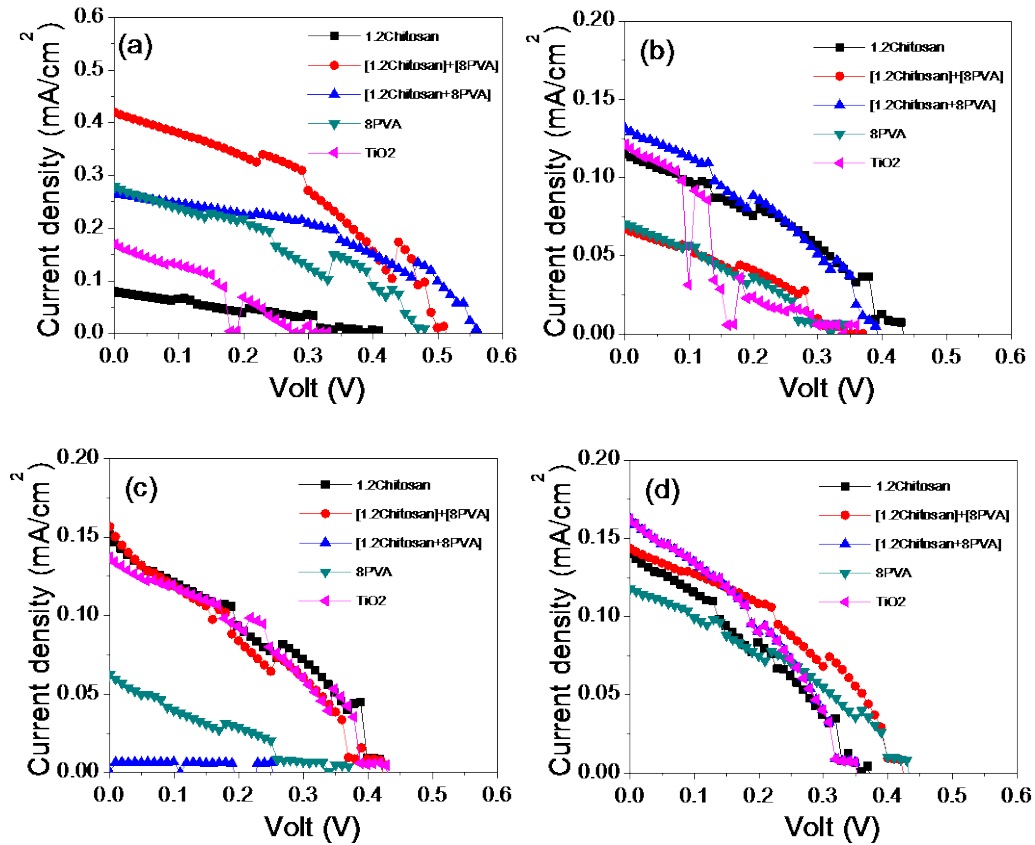






Figure 3 Current density versus voltage curve of BPVs prepared with various dyes, (a) anthocyanin, (b) beta carotene, (c) chlorophyll and (d) curcumin.

The photoelectric parameters of BPVs prepared from different photoelectrodes, as well as different natural dyes were measured and calculated; the results are summarized in Table 1. From Table 1, all calculated photoelectrical parameters can be seen in detail. For example, the fill factor (FF) of most BPVs range from 0.3 - 0.4; this is considered to be very low compared to the literature [2,9,10]. Conversion efficiency (η) should be paid attention to, and this was compared according to the types of photoactive layers. The results show that the new TiO₂ nanofibers interface significantly increased η more than by the TiO₂ film alone in the case of anthocyanin dye (Table 1, ↑). In contrast, the new interface caused a reduction in η when compared to the TiO₂ alone in the case of chlorophyll dye (↓). For the sake of convenient comparison, the η values are presented in the form of bar chart (Figure 4).

Table 1 Photoelectrical parameters of BPVs prepared by different photoactive layers and sensitized by different natural dyes.

Photoelectrode			DSSC characteristics				
Dye sensitizer	λ_{max} (nm)	Photoactive layers	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	Efficiency (%)	Eff comparison* (fold)
Anthocyanin 	522	<i>1.2Chitosan</i>	0.078	0.408	0.33	0.0107	↓ 0.64
		<i>[1.2Chitosan]+[8PVA]</i>	0.420	0.459	0.46	0.0897	↑ 5.37
		<i>[1.2Chitosan+8PVA]</i>	0.266	0.560	0.45	0.0665	↑ 3.98
		<i>8PVA</i>	0.279	0.479	0.38	0.0509	↑ 3.05
		<i>TiO₂</i>	0.169	0.329	0.30	0.0167	1.00
Beta carotene 	501	<i>1.2Chitosan</i>	0.115	0.429	0.36	0.0179	↑ 1.63
		<i>[1.2Chitosan]+[8PVA]</i>	0.067	0.370	0.33	0.0082	↓ 0.75
		<i>[1.2Chitosan+8PVA]</i>	0.131	0.390	0.36	0.0182	↑ 1.65
		<i>8PVA</i>	0.071	0.340	0.30	0.0073	↓ 0.66
		<i>TiO₂</i>	0.121	0.359	0.25	0.0110	1.00
Chlorophyll 	410, 664	<i>1.2Chitosan</i>	0.147	0.419	0.36	0.0220	↓ 0.99
		<i>[1.2Chitosan]+[8PVA]</i>	0.157	0.420	0.29	0.0192	↓ 0.86
		<i>[1.2Chitosan+8PVA]</i>	0.007	0.180	0.01	0.0009	↓ 0.04
		<i>8PVA</i>	0.063	0.370	0.25	0.0057	↓ 0.26
		<i>TiO₂</i>	0.134	0.428	0.39	0.0223	1.00
Curcumin 	421	<i>1.2Chitosan</i>	0.140	0.369	0.32	0.0167	↓ 0.85
		<i>[1.2Chitosan]+[8PVA]</i>	0.143	0.420	0.39	0.0233	↑ 1.19
		<i>[1.2Chitosan+8PVA]</i>	0.162	0.349	0.35	0.0196	→ 1.00
		<i>8PVA</i>	0.118	0.429	0.35	0.0176	↓ 0.90
		<i>TiO₂</i>	0.162	0.349	0.35	0.0196	1.00

*Each value was calculated by dividing the photoconversion efficiency of each photoactive layer by the efficiency of the control (TiO₂). The arrow indicates the direction of difference in photoconversion efficiency between each photoactive layer and the control in each dye. ↑ = higher than the control, ↓ = lower than the control and → = equal to the control.

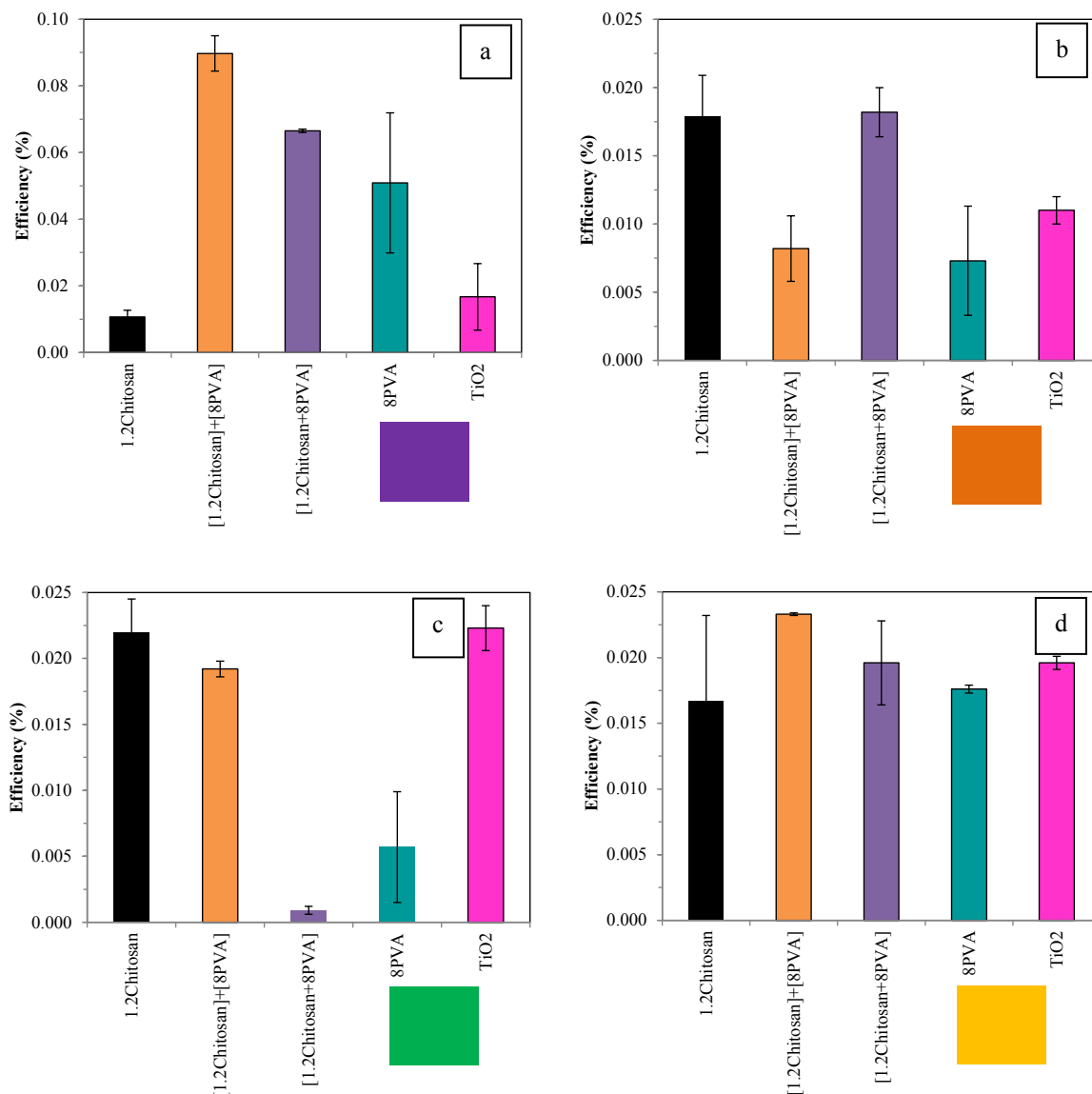


Figure 4 Energy conversion efficiency (η) of BPVs prepared from various dyes (a) anthocyanin, (b) beta carotene, (c) chlorophyll and (d) curcumin.

Overall, BPVs which used anthocyanin as sensitized dyes showed the highest η compared to other natural dyes (**Figure 4**). The reason for the high η may be due to the high stability of anthocyanin extract *in vitro*. According to Jenshi roobha *et al.* anthocyanin extract has 4 different structures which are in equilibrium, flavylium cation, quinoidal base, carbinol pseudobase and chalcone. They observed that purified anthocyanin in aqueous solution can maintain its optical properties at temperature as high as 30 °C for pH 6.0 - 7.0 in light [26], a similar environmental condition experienced by sensitized dyes during the photoelectrical testing. The researchers suggested that this condition was possibly in favor of flavylium cation construction, the structure which is highly tolerant to decomposition caused by

hydrolysis [26]. When considering the new TiO₂:nanofiber in each graph (**Figure 4**), η tended to be highest in the case of [1.2Chitosan]+[8PVA] followed by [1.2Chitosan+8PVA], 1.2Chitosan and 8PVA, respectively. The results indicate that chitosan helped increase η regardless of photoactive layer morphology, whereas PVA tended to reduce η . PVA caused the reduction in η and may result from its high solubility in water. It is likely that PVA nanofibers lost their nanostructure when in contact with a water-soluble electrolyte during the photoelectrical testing, leading to low η . This explanation is supported by the fact that PVA is a hydrophilic polymer for which its aqueous gel has been widely used in many industries because of its easy preparation as well as its versatile benefits [27,28]. In the case of curcumin dye, no effect of the photoactive layers on η was observed (**Figure 4d**). Because curcumin has such high attachment ability, it is possible that curcumin can bind to any kind of photoactive layer and penetrate to any depth of it. It has been previously demonstrated that curcumin is strongly bound to human protein through hydrogen bonding, which was a result of charge delocalization in its structure [29]. It is presumed that a similar phenomenon occurred here between curcumin and the new interface in the photoactive layers.

Conclusions

BPVs prepared from the new TiO₂:nanofiber interface successfully generated electricity, with the highest photocurrent density of 0.42 mA/cm² if used with anthocyanin dyes. The highest η were observed in the new interface made from [1.2Chitosan]+[8PVA] nanofibers at a value of 0.089 %, i.e. 5.37 times higher than those using the porous TiO₂ film alone. Therefore, the utilization of chitosan nanofibers together with natural anthocyanin dye has the potential to increase η of BPVs.

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