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*Research article*

# Influence of the pH value of anthocyanins on the electrical properties of dye-sensitized solar cells

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**Abstract:** In recent years the harvesting of renewable energies became of great importance. This led to a rapid development of dye-sensitized solar cells which can be produced from low-purity materials. The best electrical properties are provided by cells prepared using synthetical, ruthenium based dyes. Unfortunately, most of them are toxic and expensive. The anthocyanins extracted for example from hibiscus flowers yield a more cost-effective and eco-friendly alternative to toxic dyes, however, with a loss of solar cell efficiency. In this article the possibility of improvement of the conversion efficiency by modification of the pH value of the dye is investigated. By decrease of the pH value, an increase of efficiency by a factor of two was achieved.

**Keywords:** dye-sensitized solar cell; pH value; anthocyanin

## 1. Introduction

In recent years, conventional textiles and electronic components have been integrated to produce novel fashion effects, visual displays, or audio and computing systems. Similar systems are also being developed as wearable diagnostic systems for monitoring vital signs in medical and protective textile applications. These sophisticated electronic textile systems will, however, require appropriate energy-generating capabilities to become self-sustaining systems. The 25 years ago discovered dye-sensitized solar cells (DSSC) [1,2], which can be produced from non-toxic, cheap low-purity materials could fill this purpose [3]. Opposite to common silicon-based solar cells, such DSSCs can be prepared from inexpensive, nontoxic, low-purity materials, allowing to integrate them into textiles, while the technical requirements of silicon-based solar cells make it impossible to produce them in usual textile companies. In some regions of Asia and Africa the electricity supply of the off-grid low income population is solved by installation of community and home charging stations [4]. Because of their cost effective production, textile based DSSCs may be also used for this purpose.

As shown in Figure 1, DSSCs consist of two conductive electrodes, of which one has to be transparent. Between the electrodes, a dye is adsorbed on a semiconductor, e.g. $TiO_2$. Between the monomolecular dye layer and the graphite-coated counter electrode, an electrolyte is introduced. The working principle can be described as follows: the absorption of a photon in the dye electronically excites a dye molecule. An electron is injected from this excited state into the semiconductor conduction band and transported through the $TiO_2$ layer to an external load and further to the counter electrode. Next it recombines with acceptors in the electrolyte, which finishes the circuit by reducing the dye cation to its neutral ground state [2,5,6,7].

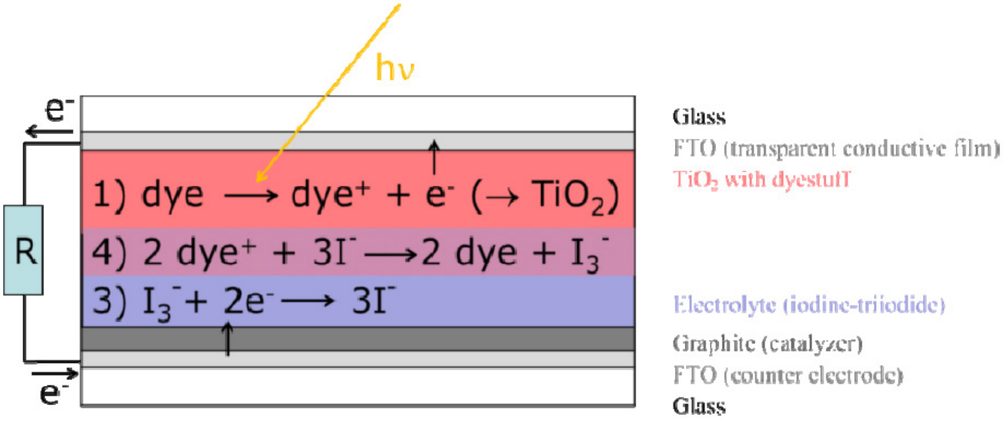

**Figure 1.** Electronic processes in a dye-sensitized solar cell (from Ref. [6], modified).

For an application in textiles, it is necessary that the DSSC is built from nontoxic and cheap materials. Today, in most DSSCs a liquid electrolyte based on Lugol's solution is used. In textile based DSSCs it should be replaced with a biobased, solid or quasi-solid electrolyte. The most promising biopolymers for preparation of electrolytes are carrageenan and cellulose. They are biocompatible and can be cost effectively extracted from seaweeds (carrageenan) or plants (cellulose). Carrageenan was used by Bella et al. as a matrix for a solid electrolyte, which reached a ionic conductivity of 5.53 × $10^{-2}$ s/cm yielding a DSSC with an energy conversion efficiency of 2.06% [8]. Chiappone et al. prepared a composite polymer electrolyte with a good long-term stability using nanoscale microfibrillated cellulose [9]. Willgert et al. achieved a cell conversion efficiency of 1.09% with a gel electrolyte containing polyethylene oxide, cellulose nanocrystals, and $I_3^-/I^-$ [10]. Rudhziah et al. developed biopolymeric electrolytes based on the blend of carboxymethyl-carrageenan/carboxymethyl cellulose. The highest measured ionic conductivity was $2.41 \times 10^{-3}$ s/cm [11]. Buraidah et al. achieved cell efficiencies up to 0.46% using chitosan based gel electrolytes [12].

The highest energy conversion efficiency is achieved by solar cells using ruthenium based dyes, which are very expensive, and most of them are also toxic. Therefore, they are not suitable for integration into smart textiles. Natural dyes could yield a cheap and nontoxic alternative. Unfortunately, natural dyes degrade fast and the cells built with them suffer from a low efficiency. Anthocyanins seem to be a good choice for the use in DSSCs. Several research groups have investigated the possibilities to improve the stability of anthocyanins and found that they are most stable in acidic pH values [12–16]. Many research groups investigated solar cells with natural dyes. Li et al. studied DSSCs with red cabbage extract and achieved an efficiency of 2.9% [17]. Gokilamani et al. achieved efficiencies of 0.73% and 0.67% using extracts of red cabbage and blue pea [18]. Alhamed et al. investigated DSSCs with anthocyanins extracted from raspberries, shami-berries, grapes, hibiscus, and with chlorophyll and found that with an efficiency of 3.04%, a combination of dyes yields better solar cell properties than single dyes [19]. Kumara et al. explored DSSCs sensitized with Nephelium lappaceum and found that the efficiency could be enhanced by adding HCl to the dye extract [20].

In this article DSSCs with anthocyanins extracted from hibiscus flowers are investigated. The influence of the pH value of the dye extract on the electrical properties in order to enhance the efficiency is examined.

## 2. Materials and Methods

### *2.1. Preparation of the dye extract*

15 g hibiscus flowers (*Man Solar*) was pistilled, added to 750 ml distilled water and incubated at room temperature for 30 min. Thereafter the tee extract was filtered. The extract had a pH value of pH = 2.3. The dye extracts with pH values pH = 1.1, 2.0, 2.9, 4.0, 5.1, 7.1, 8.1, and 11.6 were prepared by adding 0.1 M and 0.01 M HCl or 0.5 M and 0.01 M NaOH to the original extract.

### *2.2. Preparation of solar cells*

As working electrodes $TiO_2$ coated glass plates from *Man Solar* were used. Into each dye extract, two $TiO_2$-coated glass plates were immersed for 24 hours. Thereafter, the colored $TiO_2$-coated plates were washed with distilled water in order to remove the unadsorbed dye and dried at room temperature. For the preparation of counter electrodes, fluorine-doped tin-oxide (FTO) coated glass plates from *Man Solar* were cleaned with isopropyl alcohol, washed with distilled water and dried at room temperature. 9 plates were coated with graphite using a pencil, and 9 plates were coated with a graphite spray (CRC Kontakt Chemie Graphit 33) and heated at 200 °C for 30 min. The solar cells were assembled by adding two drops of iodine/potassium iodide based electrolyte from *Man Solar* on each counter electrode. Then, the working and the counter electrodes were put together and fixed with an adhesive tape. In order to enhance the contact surface to the outer circuit, an adhesive conductive band was glued on each electrode. The active area of the cells was 5.9 $cm^2$.

### *2.3. Measurements*

The pH values of the dye extracts were measured by a pH meter pH 3310 by WTW. The electrical properties of the solar cells were determined using two Fluke 45 multimeters and a resistance decade. For illumination of the specimens a daylight lamp at an illuminance of 1000 W/m$^2$ was used.

## 3. Results and Discussion

Figure 2 shows the comparison of the current density-voltage characteristics and the power density of solar cells which were coated by graphite layers using a pencil to the same properties of cells with sprayed graphite layer for pH values of the dye pH = 1.1 and pH = 2.0. For both pH values, both cells yield similar open circuit voltages. However, the cells with a pencil-coated graphite layer yield higher current densities and therefore higher power densities than the cells with a sprayed graphite layer for the same pH value of the dye. The short-circuit current density and the maximal power of cells with a graphite layer made by a pencil are higher by 17.3% and 28.8% for pH = 1.1 and by 7.7% and 13.3% for pH = 2.0, respectively. The cells with a pencil-coated graphite layer are apparently more efficient; therefore, in the rest of the paper only the results for those cells are shown.

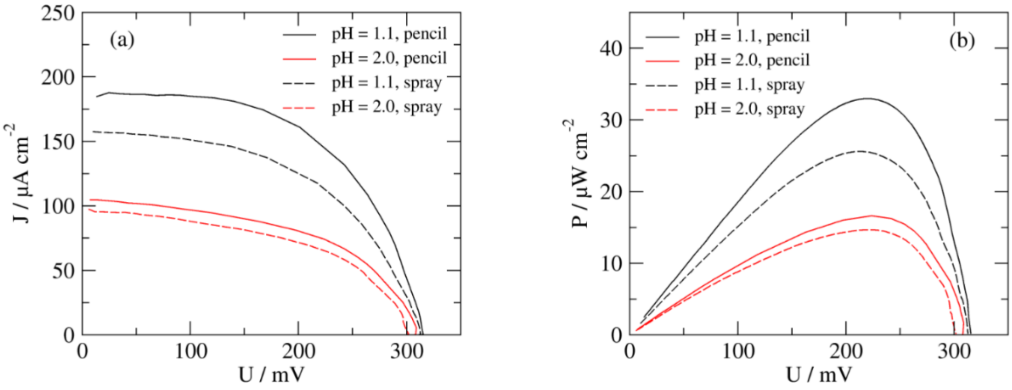

**Figure 2.** (a) Current density-voltage characteristics and (b) power density vs. voltage of cells with manually coated graphite layers, where the pH values of the dye are pH = 1.1 (black, solid line) and pH = 2.0 (red, solid line), and of cells with graphite layers made by a spray, whit the pH values of the dye pH = 1.1 (black, broken line) and pH = 2.0 (red, broken line) measured just after preparation.

Figure 3a depicts the current density-voltage characteristics of solar cells for several pH values of the dye. For pH values between pH = 1.1 and pH = 4 the open circuit voltages are nearly identical. For higher pH values a decrease of the open circuit voltage with increasing pH can be observed. The current density depends much stronger on the pH value of the dye than the open-circuit voltage. The pH value of the original dye extract is pH = 2.3.

With increasing pH value, the current density is decreasing. This effect may have two reasons. First, the absorption spectrum of anthocyanins extracted from the hibiscus flowers shows two maxima, one at the wavelength l = 300 nm and one at = 521 nm (see Figure 4). For the DSSCs the second maximum at = 521 nm is more relevant than the maximum at = 300 nm. The height of the second maximum decreases with increasing pH value, and at pH = 5 the maximum nearly vanishes (see Figure 4). This effect leads to a decreased number of available electrons, which can be excited by light, and therefore to a decrease of the current density. Opposite, the decrease of the pH value below pH = 2.3 leads to an increase of the current density, which is a consequence of the increased height of the maximum at = 521 nm in the absorption spectrum of the dye.

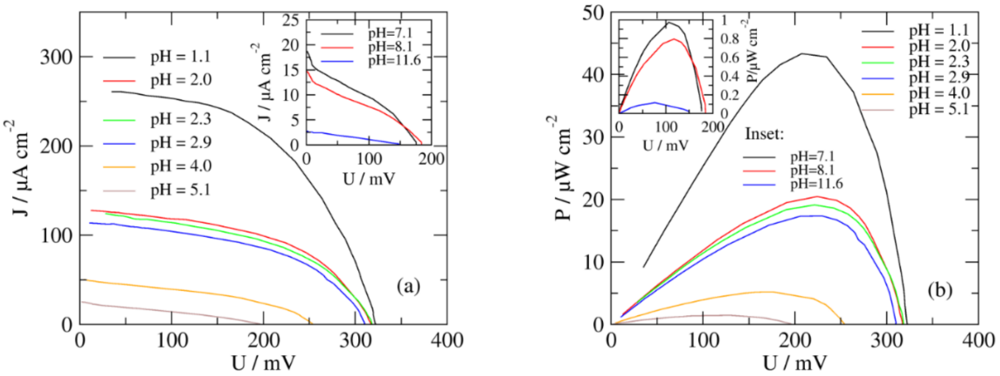

**Figure 3.** (a) Current density-voltage characteristics and (b) power density vs. voltage of cells, measured one day after preparation, where the pH values of the dye are pH = 1.1 (black line), 2.0 (red line), 2.3 (green line), 2.9 (blue line), 4.0 (orange line), and 5.1 (brown line). In the inset of subfigure (a) the current-voltage characteristics and in the inset of subfigure (b) the power density vs. voltage, measured one day after preparation of cells, with dye-pH values of pH = 7.1 (black line), 8.1 (red line), and 11.6 (blue line) are shown.

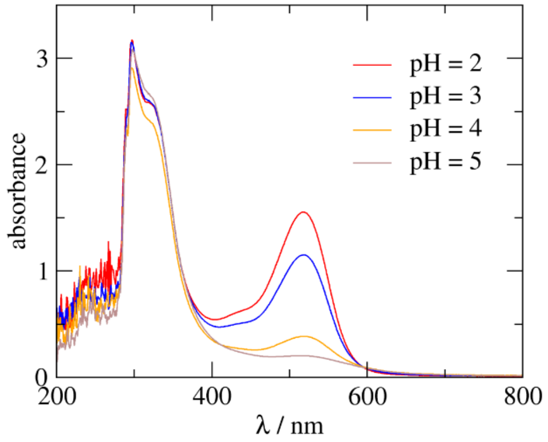

**Figure 4.** Absorption spectra of the dye extracts with pH = 2 (red line), 3 (blue line), 4 (orange line), and 5 (brown line).

Anthocyanins can exist in more chemical forms which have different colors. Which of these forms is most stable, depends on the pH value. At pH = 1 the anthocyanins are mainly present as flavylium cations, which are red. At higher pH values other forms become more stable [12]. The decrease of the absorbance at = 521 nm by increasing pH value can be explained by the change of the chemical form of anthocyanins contained in the dye extract, which leads to the decrease of the concentration of flavylium cations which are responsible for the absorption of light in the region about = 521 nm.

The second reason for decreasing of the current density by increasing the pH value of the dye extract may be that the dye with higher pH value adsorbs poorly to the $TiO_2$ surface. In order to test this hypothesis, we performed a desorption measurement (washing test) as described in the Reference [21]. $TiO_2$-coated glass plates were immersed into dye extracts of different pH values which were prepared as described in Section 2.1. After three hours, the colored $TiO_2$-coated glass plates were removed from the dye extracts, rinsed with distilled water and dried. Thereafter, each plate was immersed into 10 ml of 0.2 Mol/l NaOH. Three hours later all glass plates were completely decolored. Then, they were removed from the NaOH and the absorption spectrum of the resulting solutions of desorbed dye in NaOH was measured by a UV-Vis spectrophotometer between 200 nm and 800 nm. The spectra showed only one maximum at 300 nm, while the maximum at 521 nm has vanished. Taking into account, that according to Figure 4 the maximum at 521 nm vanishes for pH > 5 and that the pH value of the NaOH containing the resorbed dye was about pH = 13.25 for each sample, this behavior was expected. According to Lambert-Beer law, the absorbance is proportional to the concentration, i.e. in our case to the concentration of the desorbed dye in the NaOH, and hence to the amount of the desorbed dye. If we assume, that the resorption was complete, the amount of the desorbed dye is equal to the amount of dye which was adsorbed on the $TiO_2$-coated glass plates. In order to see the influence of the pH value of the dye extracts on the dye uptake, the ratio of the dye amount adsorbed by a $TiO_2$-coated glass plate immersed into a dye extract with a given pH and the dye amount adsorbed by a $TiO_2$-coated glass plate immersed into a dye extract of pH = 2.3 was calculated by division of the absorbances at 300 nm of corresponding dye solutions in NaOH. The results are shown in Figure 5. The highest dye uptake is found for the pH = 2.9. It is

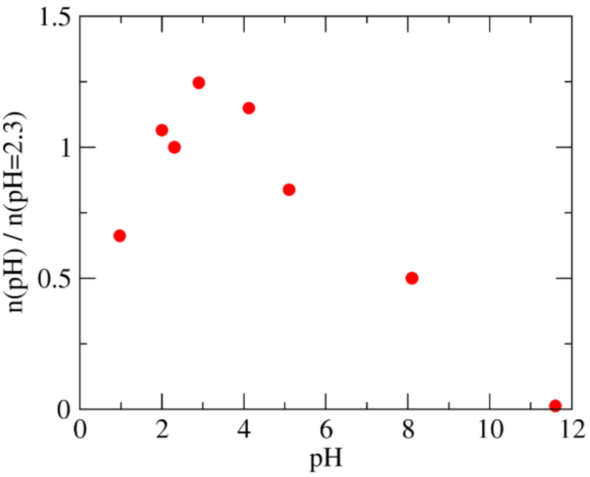

**Figure 5.** Ratio of the amount of the dye n(pH) adsorbed by a glass plate which was immersed into a dye extract with a given pH value and the amount of the dye n(pH = 2.3) adsorbed by a glass plate immersed into the dye extract with pH = 2.3 (original, unadjusted value) in dependence on the pH value of dye extracts.

two times higher than the dye uptake at pH = 1.1. Oppositely, the current density for DSSCs made with the dye extract of pH = 1.1 is two times higher than the current density of DSSCs made with a dye extract of pH = 2.9 (see Figure 3a). For pH > 2.9, with increasing pH the dye uptake is decreasing, as we have expected. However, the decrease of the dye uptake is much slower than the decrease of the current density. Hence, the rapid decrease of the current density for pH > 2.9 can be mainly ascribed to the decreased light absorption through the change in the molecular structure of the dye, and not to the poor dye adsorption.

This effect can be used to enhance the efficiency of the solar-cell. Then, the increase of current density leads to an increase of the maximal power density yielded by the solar cell (see Figure 3b), which is proportional to its efficiency. For example, the short-circuit current density and the maximal power density increase by a factor 2.1 and 2.3, i.e. by 110% and 126%, respectively, by decreasing the pH value from pH = 2.3 to pH = 1.1. In Figure 6 the time dependence of the open-circuit voltage and the short-circuit current density of cells with different pH values of the dye extract is shown. As mentioned above, both the voltage and the current density decrease with increasing pH value. After a slight increase in the first three days after preparation of the solar cells, the open-circuit voltage remained nearly constant during the next seven days, while opposite to our expectation, the short-circuit current density showed a slight increase in a period of ten days of the measurement. This could be caused by the slow distribution of electrolyte through the $TiO_2$ layer, by which the pores become better filled with electrolyte enhancing therewith the transport of electrons through the cell. We think that after several days, as the electrolyte fills equally all pores, the short-circuit current will saturate and remain constant over some period of time. The open-circuit voltage of cells with a sprayed graphite layer showed a slight decrease after a small increase in the first days. The short-circuit current density decreased rapidly after five days. This indicates that the spray is less suitable for the preparation of solar cells.

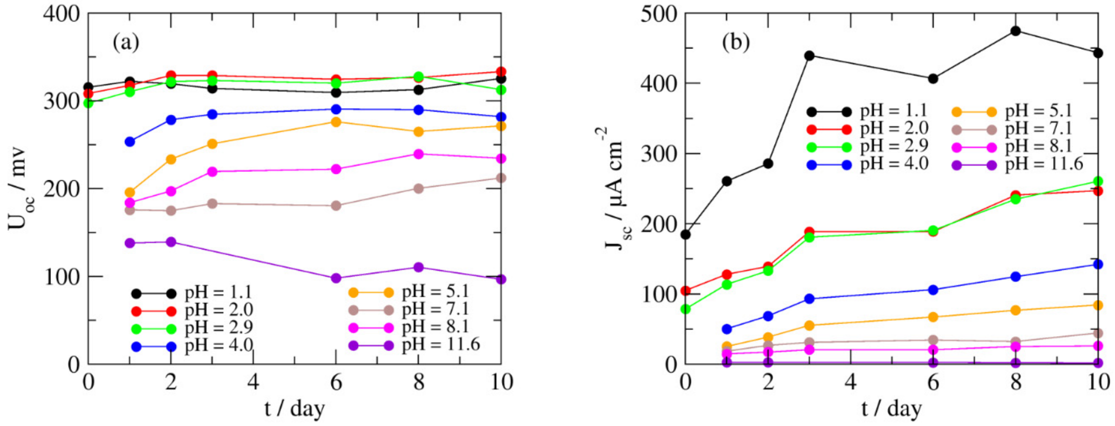

**Figure 6.** Time dependence of (a) open-circuit voltage and (b) short-circuit current density of DSSCs with dye pH values of pH = 1.1 (black dots), 2.0 (red dots), 2.9 (green dots), 4.0 (blue dots), 5.1 (orange dots), 7.1 (brown dots), 8.1 (pink dots), and 11.6 (violet dots). The lines in both subfigures serve only as guides for the eyes.

Figure 7 depicts the pH and the time dependence of the energy-conversion efficiency of DSSCs. As we can see in Figure 7a, in the region around the original pH value of 2.3, the efficiency changes only slightly. However, by decreasing the pH value below pH = 2, the efficiency increases rapidly, corresponding to the rapid increase of the current density by decreasing pH, illustrated in Figure 3 and Figure 6. In this way, the efficiency can be increased almost by a factor of two. In the region between pH = 4 and pH = 5 the efficiency decreases fast and is very low for higher pH values because of the small current densities. During the ten days of measurement, a slight increase of the efficiency was observed. The reason is the increase of the current density during this period.

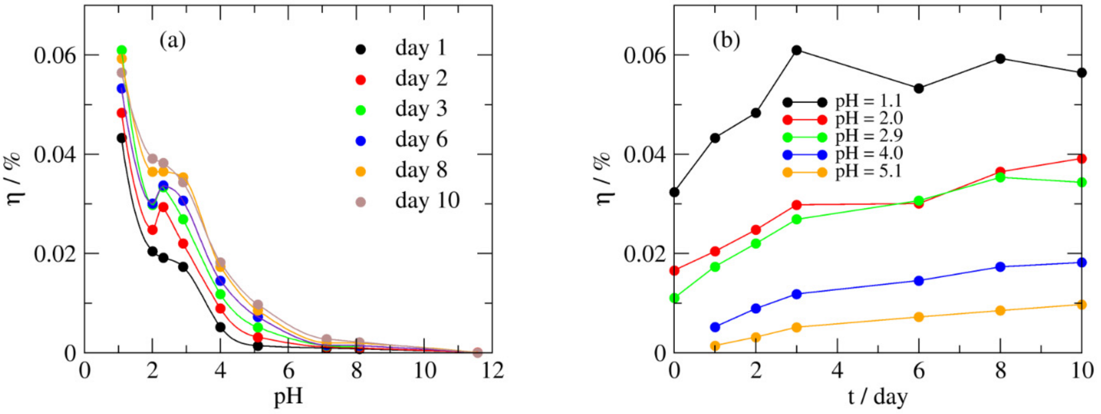

**Figure 7.** (a) Dependence of the energy-conversion efficiencies on the pH value of the dye of DSSCs, measured one day (black dots), two days (red dots), three days (green dots), six days (blue dots), eight days (orange dots), and ten days (brown dots) after the preparation. (b) Time dependence of the energy-conversion efficiencies of DSSCs with graphite layer prepared by a pencil, where the pH values of the dye were pH = 1.1 (black dots), 2.0 (red dots), 2.9 (green dots), 4.0 (blue dots), and 5.1 (orange dots). The lines in both subfigures serve only as guides for the eyes.

## 4. Conclusion

In this paper DSSCs using the anthocyanins extracted from hibiscus flowers as natural dye were investigated. The possibility of an enhancement of the electrical properties of DSSCs by a modification of the pH value of the dye extract was examined. It was found that the open-circuit voltage and the short-circuit current-density depend strongly on the pH value of the dye extract. By decreasing the pH value to pH = 1.1 the efficiency of the solar cell could be doubled with respect to the efficiency at the original pH = 2.3.

The influence of the way of preparation of the graphite layer on the electrical properties of the DSSCs was also examined. It was found that the cells with a pencil-coated graphite layer and the cells with a spray-made graphite layer yield similar open-circuit voltages. However, the cells with the spray-made graphite layer yield lower current densities and lower efficiency than the other cells. In order to use it in the textile industry, the spray coated graphite layer should be improved, or an alternative method for preparation of the graphite layer should be found.

## Conflict of Interest

All authors declare no conflicts of interest in this paper.

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