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Dye-sensitized solar cells with natural dyes extracted from plant seeds

HATEM S. EL-GHAMRI[1], TAHER M. EL-AGEZ[1], SOFYAN A. TAYA[1*],
MONZIR S. ABDEL-LATIF[2], AMAL Y. BATNIJI[1]

[1]Physics Department, Islamic University of Gaza, Gaza, Palestinian Authority
[2]Chemistry Department, Islamic University of Gaza, Gaza, Palestinian Authority

The application of natural dyes extracted from plant seeds in the fabrication of dye-sensitized solar cells (DSSCs) has been explored. Ten dyes were extracted from different plant seeds and used as sensitizers for DSSCs. The dyes were characterized using UV-Vis spectrophotometry. DSSCs were prepared using TiO_2 and ZnO nanostructured mesoporous films. The highest conversion efficiency of 0.875 % was obtained with an allium cepa (onion) extract-sensitized TiO_2 solar cell. The process of TiO_2-film sintering was studied and it was found that the sintering procedure significantly affects the response of the cell. The short circuit current of the DSSC was found to be considerably enhanced when the TiO_2 semiconducting layer was sintered gradually.

Keywords: *dye sensitized solar cell; TiO_2; ZnO; natural dyes; plant seeds*

1. Introduction

The dye-sensitized solar cell (DSSC) is one of the photochemical electric cells, often called "Grätzel cell" [1]. It is a very promising candidate for next-generation solar cells due to the prospects of low cost and high efficiency [2–9]. A DSSC consists of a porous wide band gap semiconductor thin film layer like (TiO_2, ZnO, SnO_2, Nb_2O_5) coated on a fluorine-doped tin oxide (FTO) photoanode electrode, a dye, a platinum (Pt) thin film counter electrode and an electrolyte normally containing I^-/I_3^- redox couple. The most characteristic feature of the DSSC relative to other types of solar cells is the use of a dye. It is well known that the energy gap size of the applied semiconductors determines the absorption frequency of light in solar cells. An important purpose for using dyes in the DSSC is to expand the absorption spectra to the visible light. The absorption spectra of DSSCs are determined by the combination of the nanocrystalline porous semiconductor and the dye. In this context, investigating these two crucial factors is very important to understand the significant role they play in absorbing sunlight and transforming it into electric energy [2, 3].

Several metal complexes and organic dyes have been synthesized and used as sensitizers including porphyrins [4], platinum complexes [7], and fluorescent dyes [8]. Among these, Ru-based complexes sensitizers have been widely used because they have better efficiency compared to the other ones, and high durability. However, these advantages are offset by their high cost, their complicated synthetic routes, and the tendency to undergo degradation in the presence of water [9].

The increasing interest in natural dyes is attributed to their high availability, harmless, complete biodegradation, low cost, and simple and safe extraction from plants without requiring complex synthetic procedures. Therefore, the investigation of DSSCs using natural dyes is extremely important for practical applications. In fact, natural dyes have been used in DSSCs exhibiting moderate energy conversion efficiency [10–19] For instance, natural chlorophyll dyes have exhibited

*E-mail: staya@iugaza.edu.ps

energy conversion efficiencies over 4 % [20, 21]. However, other natural dyes have not yielded energy conversion efficiencies over 2 % [22].

Although most of the reported works on DSSCs are based on TiO_2 porous thin films, various structures of ZnO are also being used for DSSC fabrication. The advantages of using ZnO over TiO_2 are its direct band gap (3.37 eV), higher exciton binding energy (60 meV) compared to TiO_2 (4 meV), and higher electron mobility (200 $cm^2 \cdot V^{-1} \cdot s^{-1}$) over TiO_2 (30 $cm^2 \cdot V^{-1} \cdot s^{-1}$). Nevertheless, the efficiency of the DSSC based on ZnO nanostructures is still very low [23].

In this study, DSSCs were fabricated using ten different natural dyes extracted from plant seeds. These seeds have no nutritional use, are cheap, and popularly grown in Palestine. The UV-Vis absorption spectra of the extracted dyes were investigated. The photoelectrochemical properties of the fabricated DSSCs using these extracts as sensitizers were studied. Some of the extracted dyes were anchored on another type of metal oxide to make a comparison for the usefulness of both the dyes and the metal oxides in the photovoltaic conversion of the DSSCs. Moreover, the effect of sintering procedure of the porous semiconductor thin film layer on the performance of the DSSC was studied.

2. Experiment

2.1. Preparation of natural dye sensitizers

We collected dry seeds of ten different plants. These seeds were thuja, chelidonium majus, ilex paraguariensis, oak, lactuca sativa, rapa, lepidium sativum, corchorus olitorius, allium cepa (onion), and apium graveolens (celery). The seeds were washed with distilled water, dried at 60 °C, and then grinded into fine powders. 10 ml of ethanol (as a solvent) were added to 1 g of the prepared powder. The mixture was filtered after 24 h, then concentrated at 60 °C. After that the extracted dyes were ready to use.

2.2. Preparation of semiconducting films

FTO conductive glass sheets with sheet resistance of 15 Ω/cm^2 and transmission >80 % (Xinyan Technology Ltd., Hong Kong) were first cleaned using an ultrasonic bath for 15 min, rinsed with water and ethanol, and then dried. Plastic adhesive tape was fixed on three sides of the conductive glass sheet to reduce the cell area to 0.25 cm^2. TiO_2 homogeneous paste was prepared by grinding 50 mg of TiO_2 nanopowder with the size of 10 to 25 nm (US Research Nanomaterial, Inc., USA) with 50 mg of polyethylene glycol in a mortar for half an hour until a homogeneous paste was obtained. The paste was spread onto the conductive glass by using a glass rod to form a thin semiconducting film. The films were then dried for 30 min at 60 °C. Finally, the films were sintered at 450 °C for 30 min to ensure that the particles of the TiO_2 thin film were electronically interconnected. After cooling to a temperature of 60 °C, the conductive glass covered with TiO_2 film was immersed in the alcohol solution of a natural dye sensitizer for 24 h to anchor the dye on TiO_2 porous film adequately.

The current work has been divided into three parts. In the first part, the performance of the DSSCs was investigated using TiO_2 as a semiconducting material with all extracts. In the second part, the performance of the DSSCs was investigated with the highest response cells found in part A, using ZnO nanoparticles instead of TiO_2. Part three was devoted to exploring the performance of the cells when the semiconducting layer was sintered continuously to 450 °C and when the sintering process was performed gradually to the same degree in three steps.

2.3. Assembling of DSSC

The TiO_2 porous film electrode (anode) and a conductive glass sheet plated with platinum (cathode, prepared by electrodeposition) were sandwiched to assemble the DSSC. The space between the two electrodes was filled with a liquid electrolyte solution composed of 2 ml acetonitrile (ACN), 8 ml propylene carbonate (p-carbonate), 0.668 g (KI), and 0.0634 g (I_2). Then, the two electrodes were clipped together to form a solar cell.

2.4. Measurements

The dye solutions absorption spectra were measured in a wavelength range of 350 to 800 nm

using a UV-Vis spectrophotometer (Thermoline Genesys 6). The photocurrent-voltage (I-V) curve was measured under simulated sunlight (AM1.5, 100 mW·cm^{-2}) using National Instruments data acquisition card (USB NI 6251) in combination of a Labview program. According to the I-V curves, the fill factor (FF) was calculated as:

$$FF = \frac{I_m V_m}{I_{sc} V_{oc}} \quad (1)$$

where I_m and V_m are the photocurrent and photovoltage for maximum power output (P_m), I_{sc} and V_{oc} are the short-circuit photocurrent and open-circuit photovoltage, respectively.

The overall energy conversion efficiency (η) is defined as:

$$\eta = \frac{FF\, I_{sc} V_{oc}}{P_{in}} \quad (2)$$

where P_{in} is the power of incident light.

3. Results and discussions

Fig. 1 shows the absorption spectra of lepidium sativum (A) and apium graveolens (B) extracts using ethyl alcohol as a solvent. As can be seen from the figure, lepidium sativum extract has an absorption peak in the visible region at 670 nm, whereas apium graveolens extract shows some small peaks between 650 to 800 nm with the most obvious one at 765 nm.

The measurements of I-V characteristic curves of ten DSSCs dyed with different seed extracts have been carried out under the illumination with white light of intensity of 100 mW/cm^2 from a high pressure mercury arc lamp. The I-V characteristic curves for DSSCs sensitized with rapa, lepidium sativum, allium cepa (onion), and apium graveolens are shown in Fig. 2. The DSSC output power has been calculated as P = I·V using the I-V data corresponding to each cell. Fig. 3 represents the output power plotted as a function of voltage. The photocurrent (I_m) and photovoltage (V_m) corresponding to the maximum power point (P_m) were then obtained for each cell from the P-V curve. The values of the fill factor and the cell conversion efficiency were then calculated using equations 1 and 2. All these results were summarized in Table 1. It is clear from the table that the DSSCs sensitized with rapa, allium cepa (onion) and lactuca sativa have the highest short circuit current densities with values of 2.9, 2.6, and 2.5 mA/cm^2, respectively. The dye extracted from chelidonium majus has the lowest value of 0.345 mA/cm^2. On the other hand, the cell sensitized with the extract of lepidium sativum has the maximum open circuit voltage of 0.65 V, whereas the minimum value for V_{oc} is 0.49 V for the cells dyed with thuja and chelidonium majus. The fill factor of the fabricated cells changes in the range of 0.21 to 0.53. The highest fill factor was obtained for the DSSC sensitized with the extract of allium cepa (onion). Moreover, the dye with the maximum fill factor had the highest output power and conversion efficiency value of 0.875 %. These results are similar to those of the DSSCs sensitized by other natural dyes in previous works [11–19]. Moreover, Table 1 shows the photoelectrochemical parameters of a DSSC sensitized with Ru complex cis-dicyano-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II), Ruthenizer 505, (Solaronix, Switzerland), which is widely used in DSSCs. The V_{oc} and the fill factors of the DSSCs sensitized with the extracts of rapa, lepidium sativum, allium cepa (onion) and apium graveolens are very close to that of the DSSC sensitized by Ru complex. The main difference between the results of the cells fabricated with natural dyes in the current work, compared to that sensitized by Ru complex, is the low efficiency, which is due to the low short circuit current.

TiO_2 is recognized as the most common electrode material for DSSCs because the TiO_2-based cells generally have relatively high-energy conversion efficiencies. However, many kinds of metal oxide semiconductors have also been applied in the fabrication of DSSCs. Among them, ZnO is widely investigated in terms of transport of the injected electrons.

In the second part of this work we investigated the performance of some of our dyes with ZnO semiconducting films instead of TiO_2. ZnO electrodes were prepared from ZnO powder with an approximate nanoparticle size of 50 nm (MTI Corporation, USA). DSSCs with ZnO thin film

Table 1. The photoelectrochemical parameters of the DSSCs sensitized by dyes extracted from plant seeds.

Dye	J_{sc} (mA/cm^2)	V_{oc} (V)	J_m (mA/cm^2)	V_m (V)	FF %	η %
Thuja	0.81	0.49	0.48	0.313	38	0.15
Chelidoniumma	0.345	0.49	0.22	0.281	37	0.062
Llexpuraguariensis	0.7	0.57	0.357	0.364	33	0.13
Quercus (Oak)	1.77	0.53	1.1	0.345	40	0.38
Lactuca sativa	2.5	0.59	1.55	0.42	21	0.31
Rapa	2.9	0.63	1.9	0.45	47	0.86
Lepidium sativum	1.72	0.65	1.2	0.48	51	0.575
Corchorus olitorius	0.55	0.54	0.4	0.3	40	0.12
Allium cepa(Onion)	2.6	0.635	1.95	0.45	53	0.875
Apium graveolens	1.8	0.635	1.14	0.43	43	0.49
Ruthenium	12	0.621	9.78	0.373	49	3.65

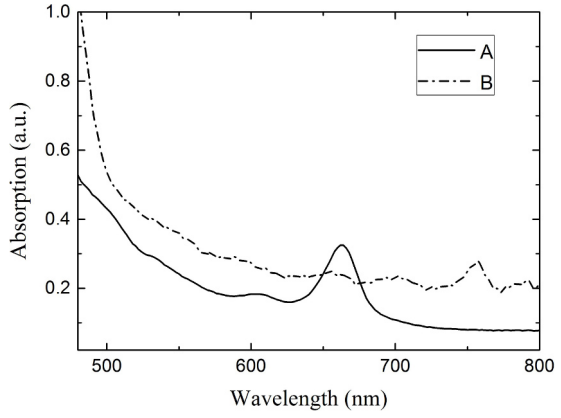

Fig. 1. Absorption spectra of the extracts of lepidium sativum (A) and apium graveolens (B) using ethyl alcohol as solvent.

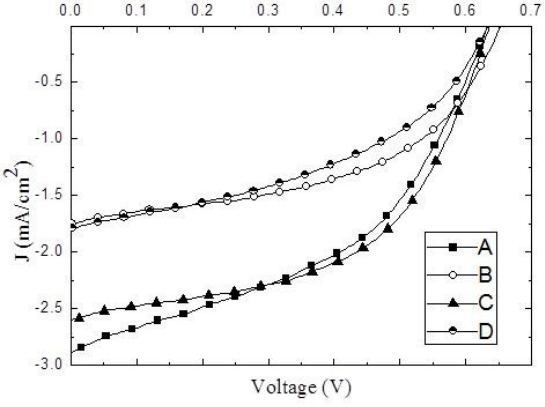

Fig. 2. I-V curves for the DSSC sensitized by rapa (A), lepidium sativum (B), allium cepa (C), and apium graveolens (D) at light intensity 100 mW/cm^2.

semiconducting layer were prepared using the same procedure as described above. Three extracts were chosen (rapa, lepidium sativum and allium cepa) as sensitizing dyes. Fig. 4 illustrates the I-V characteristic curves of these DSSCs under illumination with light intensity of 100 mW/cm^2. The photoelectrochemical parameters of these cells are summarized in Table 2. It is clear that the cell parameters are much less than those listed in Table 1 for the same extracts. As Table 2 shows, J_{sc} changes in the range of 0.5 to 1.53 mA/cm^2, V_{oc} varies from 0.33 to 0.38 V, the lowest value of the fill factor is 0.21, but the highest one is 0.33, and the conversion efficiency changes from 0.035 to 0.19 %. If you look closer at the results of the three chosen extracts, the DSSC sensitized with rapa exhibits a conversion efficiency of 0.86 % when using TiO_2 as a semiconducting layer and 0.035 % when using ZnO. Similarly, when using lepidium sativum as a sensitizing dye, the conversion efficiency of 0.575 % obtained with TiO_2 has declined to 0.07 % with ZnO. Finally, the conversion efficiency of the DSSC sensitized with allium cepa decreased from 0.875 % to 0.19 %. In agreement with many previous works [3], DSSCs fabricated with TiO_2 as a semiconducting layer exhibit much

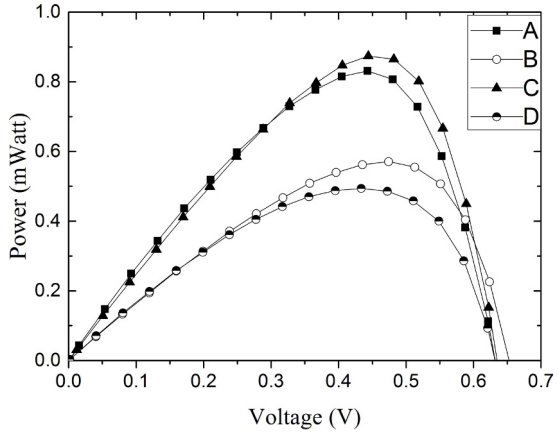

Fig. 3. P-V curves of the DSSC sensitized by rapa (A), lepidium sativum (B), allium cepa (C), and apium graveolens (D).

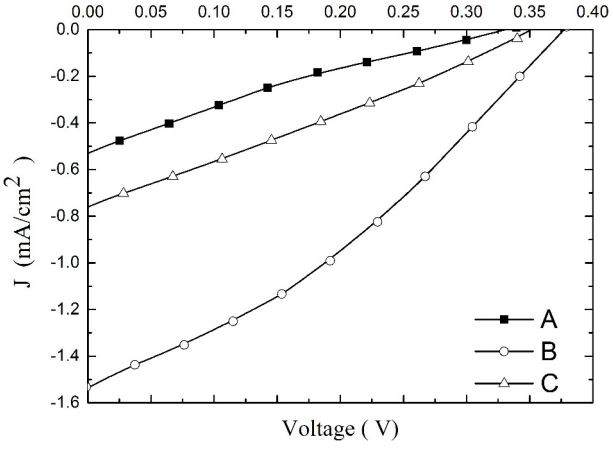

Fig. 4. I-V curves of the DSSCs sensitized by using ZnO nanoparticles as semiconductor and sensitized by rapa (A), lepidium sativum (B), and allium cepa (C) sensitizing dyes.

better performance in photoelectric conversion of light compared to those employing ZnO as a semiconductor. One of the reasons of the poor response of ZnO cells is the lower open-circuit voltage of ZnO-based cells compared to that of TiO_2-based cells. The difference in V_{oc} is possibly due to a recombination, namely, capturing the electrons photogenerated in the conduction band of the metal oxide semiconductor layers by oxidized species in an electrolyte.

Comparative studies show that although TiO_2 adsorb less dye molecules, they could effectively retard charge recombination and achieve longer electron lifetime than ZnO; as a result, the DSSCs composed of TiO_2 exhibit higher performance than those of ZnO.

The sintering process plays a significant role in improving the efficiency of charge collection by promoting both more rapid electron transport and slower charge recombination. This affects the electrically connected network of TiO_2 particles [24]. This condition improves TiO_2 performance as an electron transport material. Besides electron transporting, the porosity of TiO_2 nanoparticles offers large surface area for dye adsorption. Particularly, this affects the number of dye molecules that can be adsorbed [25–28]. At a certain level of porosity, TiO_2 particles can adsorb the maximum amount of dye which affects the performance of the DSSC.

In the last part of this work, the effect of sintering process on the characteristics of TiO_2-based DSSC is presented. It is well known that semiconducting film porosity is related to sintering duration and temperature, which affects the photocurrent density and the amount of adsorbed dye.

FTO substrates covered with a TiO_2 film were sintered in a furnace by raising the temperature gradually from 60 °C to 180 °C, the sample was stabilized at 180 °C for 10 min., then from 180 °C to 320 °C, the sample was stabilized at 320 °C for 10 min., and finally the temperature was raised to 450 °C for another 10 min. We have called this process gradual sintering. Other samples were sintered continuously from 60 °C to 450 °C for 30 min. This sintering process has been called continuous sintering. The same procedure of cooling and immersing in the dye was followed for gradual and continuous sintered samples. Four dyes were used in this investigation. Two of them, i.e. rapa and allium cepa, were natural, whereas the others included two different Ru-complexes: cis-dicyano-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II) Ruthenizer 505 (Ru1) and cis-bis(isothiocyanato) bis(2,2 bipyridine-404-dicarboxylate) Ruthenium(II)957 – N_3 (Ru2). Each dye was used with a gradually and a continuously sintered samples.

Table 2. Photoelectrochemical parameters of the DSSCs sensitized by various natural dyes with ZnO semiconducting layer.

Dye	J_{sc} (mA/cm^2)	V_{oc} (V)	J_m (mA/cm^2)	V_m (V)	FF %	η %
Rapa	0.50	0.33	0.25	0.14	21	0.035
Lepidium sativum	0.75	0.35	0.39	0.18	27	0.07
Allium cepa	1.53	0.38	1.00	0.19	33	0.19

Fig. 5 shows the I-V characteristic curves for four DSSCs dyed with Ru1 and Ru2 complexes. It is clear that the gradually sintered cells for both dyes show a considerable enhancement in the short circuit current as well as the efficiency compared to the continuously sintered ones. The J_{sc} increases from 11.38 to 20.23 mA/cm^2 for DSSCs sensitized with Ru1 and from 7.48 to 17.08 mA/cm^2 for those sensitized with Ru2. Moreover, the efficiency of these cells has enhanced from 3.5 % to 5.3 % for Ru1 dye and from 2.7 % to 5.5 % for Ru2 due to the gradual sintering. In a similar manner, Fig. 6 shows the results obtained for the rapa and allium cepa as sensitizing dyes for DSSCs sintered gradually and continuously. In analogy to the results obtained in case of Ru-complexes, the curves show an enhancement from 2.88 to 3.43 mA/cm^2, for the cells sensitized with rapa dye, and from 2.39 to 2.69 mA/cm^2 for the cells sensitized with allium cepa. The photoelectrochemical parameters of these cells are summarized in Table 3.

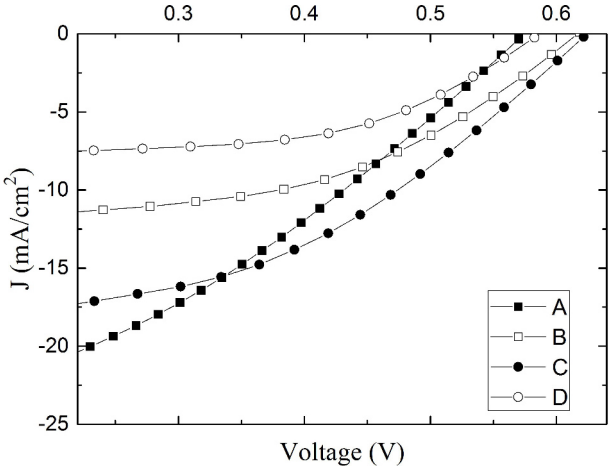

Fig. 5. I-V curves of DSSCs sensitized by Ru1 (A and B) when TiO_2 film was sintered gradually (A) and continuously (B). The curves C and D represent DSSCs sensitized by Ru2 when TiO_2 film was sintered gradually (C) and continuously (D).

This improvement in the short circuit current of the gradually sintered cells can be attributed to making the thin film layer more homogeneous with less cracks in the step sintering process. Rapid and continuous sintering led to cracking of the films that could be easily peeled from the FTO substrate.

4. Conclusion

Dye sensitized solar cells were fabricated using two semiconducting materials: TiO_2 and ZnO. Natural extracts from plant seeds were used to sensitize these cells. The extracted dyes were characterized by UV-Vis absorption spectroscopy. The I-V characteristic curves were measured and the photoelectrochemical properties were determined. The highest conversion efficiency of 0.875 % was obtained for the DSSC fabricated using TiO_2 semiconducting layer and sensitized by allium cepa extract. The open circuit voltage of the DSSCs sensitized with the extracts of rapa, lepidium sativum, allium cepa, and apium graveolens are very close to that of the cells sensitized by ruthenium complex. It has been confirmed that when using TiO_2 as a semiconducting layer, the cells exhibit much better performance in photoelectric conversion of light than the cells using ZnO. Moreover, it was found that the sintering procedure affected the response of the cell. The short circuit current density of the DSSC was found to significantly enhance when the TiO_2 semiconducting layer was sintered gradually.

Table 3. Photoelectrochemical parameters of the DSSCs when TiO_2 film was sintered gradually and continuously.

Dye	Sintering process	J_{sc} (mA/cm^2)	V_{oc} (V)	J_m (mA/cm^2)	V_m r (V)	η %
Rapa	gradual	3.43	0.633	2.26	0.442	0.99
	continuous	2.88	0.629	1.89	0.442	0.82
Allium cepa	gradual	2.69	0.610	1.75	0.427	0.75
	continuous	2.39	0.605	1.56	0.439	0.70
Ru1	gradual	20.23	0.571	16.14	0.321	5.3
	continuous	11.38	0.615	9.8	0.372	3.5
Ru2	gradual	17.08	0.625	13.8	0.417	5.5
	continuous	7.48	0.583	6.25	0.417	2.7

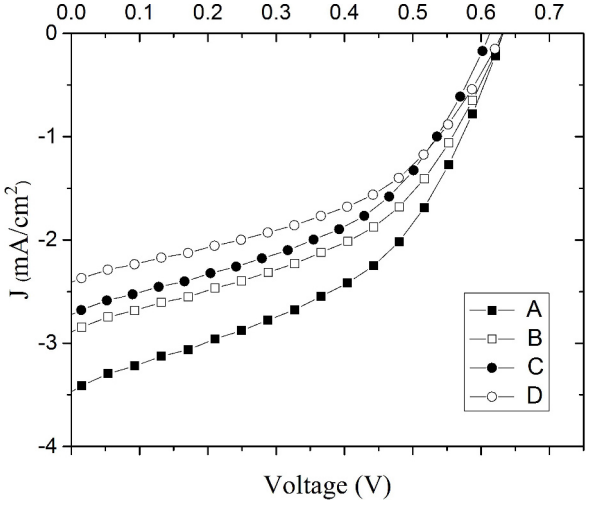

Fig. 6. I-V curves for DSSCs sensitized by rapa (A and B) when TiO_2 film was sintered gradually (A) and continuously (B). The curves C and D represent DSSCs sensitized by allium cepa when TiO_2 film was sintered gradually (C) and continuously (D).

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