Electrical characteristics of chlorophyll-a polyvinyl alcohol photovoltaic cells

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A type of photovoltaic cell was made by sandwiching micro-crystalline chlorophyll-a (chla) layer and polyvinyl alcohol (PVA) film between two semiconductive optical transparent SnO_2 electrodes, such as $SnO_2/chla/PVA/SnO_2$. The cell showed a dark rectifying effect and presented photovaltaic properties on illumination, which was illustrated by the charge distribution in the cell. It was suggested that the $SnO_2/chla$ junction might be responsible for photovaltage and the chla/PVA for the charge separation upon irradiation of visible light. The equivalent electric circuit was discussed and its equivalent component values were calculated.

Keywords   Photovoltaic cell, chlorophyll, polyvinyl alcohol, SnO_2 electrode

Introduction

Because of the photoactivity and high efficiency converting photoenergy to electrical and chemical energy of chla, there has been much interest in photoelectric and photochemical investigation of chla since Tributsch and Calvin studied its photoelectrochemical behavior *in vitro* for the first time in 1971.[1] There are mainly two modes of arrangement to study chla. The first is the incorporation of chla molecules into a small lipid bilayer, which is used as membrane separating two electrolyte solutions.[2,3] Liposomes could also be obtained by this method, and photoredox reactions through the membrane have been studied.[4] But only a relatively low photoconversion efficiency can be yielded due to an inherent high resistivity of the lipid membrane. The other mode is the deposition of ordered chla molecules on solid substrates by means of the Langmuir-Blodgett technique.[5] Although monolayer and multilayer of chla have been obtained by this technique, the observed photoresponse is generally very small.

Consideration about a very efficient quenching of the excited state of chla by free elections in the metal has led scientists to use an optical transparent electrode made of SnO_2, on which an multilayer chla is deposited by electrodeposition.[6] SnO_2 is an electrode material well characterized and has therefore been employed in a number of photoelectrochemical investigations.[7] We demonstrated that the junction of $SnO_2/chla$ was a photo-electric conversion system[6] and a sandwich photoelectric cell of $SnO_2/chla/PVC/SnO_2$ was fabricated in our previous work.[8] The present work is reporting the rectifying characters of chla photovoltaic cells based on SnO_2 electrode, some parameters and electrical properties of the cells.

Experimental

Chla was extracted from fresh spinach leaves and purified according to Iriyama's method,[9] and crystallized with water from its petroleum *tert*-butyl alcohol solution to form its dihydrate aggregates $(chla \cdot 2H_2O)_n$, which had a specific absorption peak at 743 nm in isooctane. Used for both substrate of chla and the counter electrode, SnO_2 optical transparent glass was purchased from

Tianma Company (Shenzhen, China). Only on one side of the glass was present a SnO_2 layer, 100 nm thick, which had a specific resistance of $0.002\ \Omega \cdot cm$ and an optical transmittance of 90% in visible region above 400 nm. PVA was the Rhodia reagent provided by Shanghai Chemicals Company, and its film, 30 μm thick, was prepared with a glass film maker. N-(p-Methoxyben-zylidene)-p-butylanaline (MBBA), hydroquinone (H_2Q), ethylenediamine tetraacetic acid disodium salt ($EDTANa_2$), and all other chemicals were of analytical grade, which were used without further purification. Water was doubly distilled.

Chla dihydrate aggregates were dissolved in isooctane with the help of ultrasonic wave to form 1.0×10^{-4} mol/L chla isooctane solution/dispersion, in which a SnO_2 electrode was used as the anode and a newly-polished Al electrode as the cathode. Under the electric field intensity of 1000 V/cm, the chla was electrodeposited on the SnO_2 electrode from its isooctane solution/dispersion for 10 minutes, forming the SnO_2/chla photoelectrode, on which a PVA film was put and then, after the film was wetted with 40 μL of water, another SnO_2 electrode, forming the chla PVA photovoltaic cell (Fig. 1). The cell was dried in water-saturated atmosphere at room temperature for 24 hours before measurements.
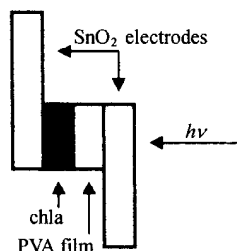

Fig. 1 Scheme of chla PVA photovoltaic cell.

The curves of working voltage vs. working current of the cell were measured under the potential of the chla/SnO_2 electrode controlled by means of a Hokuto Denko potentiostat model HA-501, in totally dark and illumination respectively. The light source was a 150 W halogen lamp , with the intensity of the incident light $1.4 \times 10^{-2}\ W/cm^2$ as measured with a photometer. The cyclic voltammetric curves, time course of photocurrent and photovoltage of the cell were also measured with HA-501 in combination with a 3086 x-y recorder (Tokyo, Japan) and an x-t recorder (Shanghai Dahua Instrument Plant, China), respectively.

Results and discussion

1. Photoelectric parameters

As the cell, SnO_2/chla/PVA/SnO_2, was photovoltaic cell, the open circuit voltage E_{oc} and short circuit current I_{sc} in dark were very low. Under our experimental conditions E_{oc} in dark was only 6 mV and I_{sc} in dark nearly zero. But on illumination the cell gave good photoelectric parameters which could be obtained from the working curve of the cell, which was drawn on the x-y recorder under the voltage scanning speed 1 mV/s.[10] For example, E_{oc} in light was 100 mV and I_{sc} in light 3.1 $\times 10^{-9}$ A/cm.[2] If some electron donors or liquid crystal were added into the cell, its parameters changed greatly as shown in Table 1. But the addition of MBBA and β-carotene into chla layer could only increase I_{sc} a little. Instead of being increased, E_{oc} was decreased by 30 mV with the addition of β-carotene and Asc. The most significant is that whenever H_2Q was added into PVA film, I_{sc} was always enhanced by one to two digital orders.

Table 1 Parameters of photovoltaic cells

Cells	E_{oc} (mV)	I_{sc} (10^{-9} A/cm)	FF^a
SnO_2/chla/PVA/SnO_2	100	3.1	0.23
SnO_2/chla/PVA + H_2Q/SnO_2	137	56	0.23
SnO_2/chla/PVA + $EDTANa_2$/SnO_2	167	28	0.29
SnO_2/chla/PVA + Asc/SnO_2	80	10	0.20
SnO_2/chla + MBBA/PVA/SnO_2	100	5.0	0.24
SnO_2/chla + MBBA/PVA + H_2Q/SnO_2	100	220	0.26
SnO_2/chla + β-car^b/PVA/SnO_2	65	4.0	0.20
SnO_2/chla + β-car/PVA + H_2Q/SnO_2	85	30	0.25

^{a} FF: Fill factor; ^{b} β-car: β-carotene.

As we known, n-SnO$_2$ with 2.4 eV band gap (E_g) is not effective for absorbing the visible light. It is that chla, as a photo-sensitizer, provides one electron when excited, while the enhancement of H$_2$Q or ED-TANa$_2$ as a catalyzer in the PVC film may be attributed to the reduction of the excited chla. As a result, E_{oc} and I_{sc} of the cell increase obviously. In contrast, β-carotene or Asc in the PVA film not only acts as non-effective donor but retards the reduction of the excited chla. The neutral liquid crystal compound, MBBA in the PVA film has little influence on the photoelectric parameters of the cell.

2. Cyclic voltammetry properties

The cyclic voltammetric curves of all the cells in Table 1 were measured between −1.0 V and 0.75 V on

illumination. There was neither anode peak nor cathode one for the SnO$_2$/chla/PVA/SnO$_2$ cell through out the measuring potentials. However, with the addition of H$_2$Q and EDTANa$_2$, the cell gave a cyclic voltammetric curve with both peaks at certain potentials (Fig. 2), which indicated that the potentials should be controlled within the peak potentials when the photovoltaic properties were measured. Otherwise, the measurements would contain the contribution of chemical reactions. ED-TANa$_2$ as a bipolar compound, is both oxidizer and reducer in solution. The peak of oxidation (at about 4.0 V) in Fig. 2 indicates the oxidation of reduced EDTA and the reduction peak at about −0.15V corresponds to the reduction of oxidized EDTA. The redox reversibility of EDTA from the cyclic voltammetric characteristics supports the enhancement of EDTANa$_2$ as a catalyzer in the PVC film to the cell photo-electric parameters.
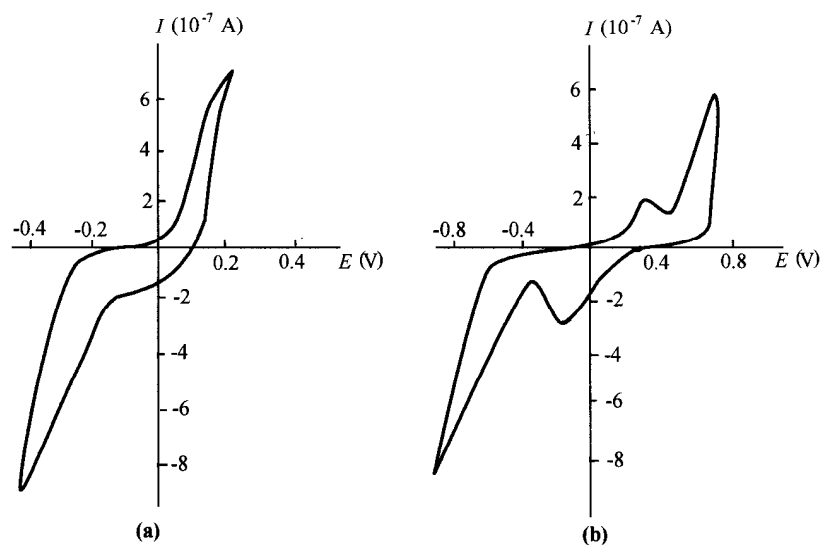

Fig. 2 Cyclic voltammetric curves of chla PVA photovoltaic cells.
(a) SnO$_2$/chla/PVA/SnO$_2$. (b) SnO$_2$/chla/PVA + EDTANa$_2$/SnO$_2$.

3. Rectifying characters

All the current vs. voltage curves of the cells were measured in dark. Most of the cells exhibited a rectifying effect. Fig. 3 shows current-voltage characteristics for the SnO$_2$/chla/PVA/SnO$_2$ cell, from which it can be seen that the forward current flows from the SnO$_2$/chla electrode to the counter SnO$_2$ electrode through the cell. From the curve two special voltages, the positive current-turning voltage E_p and the negative current-turning

voltage E_N, which shows the rectifying ability of the cell, could be obtained. One tangent line of the horizontal part of the curve was drawn positively and another tangent of the vertical part in positive area was drawn downward. From the cross point of the two tangents, a vertical line was drawn to the horizontal axis, and thus E_p was pointed. Similarly E_N could also be obtained. The voltage difference, $\Delta E = E_p - E_N$, shows the rectifying ability of the cell. The bigger the difference is, the stronger the ability is. Table 2 shows the rectifying effect

of the tested cells, from which it can be concluded that $SnO_2/chla/PVA/SnO_2$ has a strong rectifying effect that is decreased by H_2Q and $EDTANa_2$, and even dissolved

by β-carotene, but greatly enhanced by MBBA. These appearances of the cells may imply a blocking contact in the cell.

Table 2 Rectifying effect of photovoltaic cells

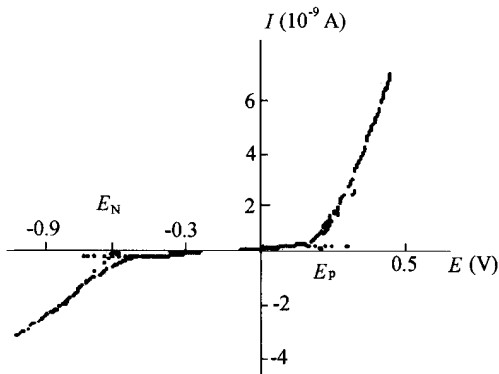| Cells	E_p (mV)	E_N (mV)	ΔE (mV)
$SnO_2/chla/PVA/SnO_2$	250	- 600	850
$SnO_2/chla/PVA + H_2Q/SnO_2$	100	- 400	500
$SnO_2/chla/PVA + EDTANa_2/SnO_2$	100	- 400	500
$SnO_2/chla/PVA + Asc/SnO_2$	500	- 300	800
$SnO_2/chla + MBBA/PVA/SnO_2$	500	- 1000	1500
$SnO_2/chla + MBBA/PVA + H_2Q/SnO_2$	400	- 1000	1400
$SnO_2/chla + β-car/PVA/SnO_2$	—	—	—
$SnO_2/chla + β-car/PVA + H_2Q/SnO_2$	—	—	

Fig. 3 Dark rectifying characters of $SnO_2/chla/PVA/SnO_2$. E_p: positive current-turning potential, E_N: negative current-turning potential, $\cdots$ tangent lines.

4. Electrical characters

4.1 Capacitance and resistance of the cells

According to the constructure of the photovoltaic cells, their capacitance, C, was calculated from the formula $C = \varepsilon\varepsilon_0 A/d$ as a flat capacitor, where, in this experiment, dielectric constant of vacuum $\varepsilon_0 = 8.9 \times 10^{-12}$ F/m, relative dielectric constant $\varepsilon \approx 30$, area of electrodes $A = 2 \times 10^{-4}$ m^2, and distance between electrodes $d = 3 \times 10^{-5}$ m. The value obtained was about 1.8×10^{-9} F, which was some three orders of magnitude lower than that obtained experimentally from the current-voltage diagram (Fig. 3) which gave C equal to (2—20) $\times 10^{-6}$ F (Fig. 4). The C^{-2}-E and R-E curves obtained showed that there was not a typical Schottky barrier system in the cell.[11]
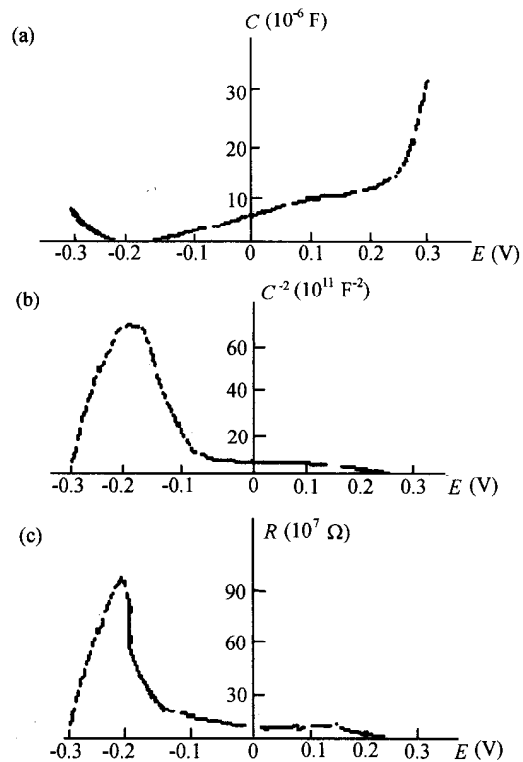

Fig. 4 Electrical properties of the chla PVA photovoltaic cell (in the dark).

(a) capacitance vs. voltage; (b) (capacitance)$^{-2}$ vs. voltage. (c) resistance vs. voltage.

4.2 Photoelectric properties of the cells

The cell has a very high resistance and under short circuit conditions it exhibits no dark current or very low

one. On illumination, however, it induces a much higher current and voltage. This type of solar cells is called photovoltaic cell.

The typical kinetics of the change in current and voltage induced by switching the light on and off is presented in Fig. 5. The short circuit current performed a

high pulse at the moment the light was on, and then fell to a lower and steady value. But the open circuit voltage kept increase to a limit after illumination. As soon as the light was off, both of them decreased and returned to the original.
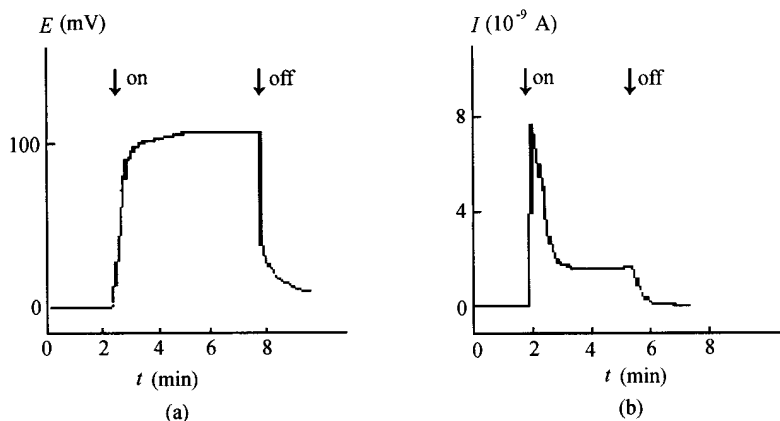

Fig. 5 Photoelectric properties of the chla PVA photovoltaic cell. (a) open circuit potential vs. time. (b) short circuit current vs. time.

4.3 Junctions and charge distribution of the cells

As it is shown in Fig. 1, the cell contains 4 layers and 3 junctions: SnO_2/chla, chla/PVA and PVA/SnO_2. SnO_2 is a typical n-type semiconductor and chla can be regarded as a p-type semiconductor.[12] PVA film is an insulator when it is dry and can conduct when wet. The PVA molecules can form hydrogen bonds with water, which make it conductive although the resistance is very high.[13] Fig. 6 shows the possible charge distribution of the cells. At SnO_2/chla p-n junction, the charge density is much more higher than at the other two, chla/PVA and PVA/SnO_2, which are ohmic or near ohmic contacts. These structural characteristics are responsible for the low potential difference, only several millivolts in general, and zero current in dark, as well as the dark rectification behavior. When the cell is illustrated by light, chla molecules are radiated from base/ground state to single or triplet state, which intense the p-n junction and induce the positive photovoltage for chla-coated SnO_2 electrode with respect to the counter SnO_2 electrode. If the external circuit is on, the radiated chla gives out electrons throughout PVA film and the time profile of photocurrent shows a sharp spike pattern (Fig. 5).
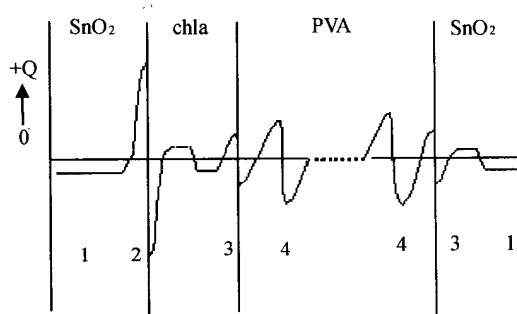

Fig. 6 Scheme of charge density (Q) distribution in the chla PVA photovoltaic cell.
1: space charge, 2: p-n junction charge, 3: surface charge, 4: Helmholtz double layer.

5. Equivalent circuit of the cell

As discussed above, the equivalent electric circuit of the photovaltaic solar cell is shown in Fig. 7.[14,15] The cell's power output character is described by its filling factors, $FF = P_m/P_t$, where P_m is the maximum power of the cell and $P_t = I_{sc} \cdot E_{oc}$, the theoretical power. All other notations are given in Fig. 7. If the parasitic resistances R_s and R_F did not exist, the theoretical value of FF would be: $FF_o = [E_{oc} - \ln(E_{oc} + 0.72)]/(E_{oc} + 1)$, where the one-digitized open-circuit voltage of the cell $E_{oc} = 1.61$ V in our experiment. Hence, from the

equation, we can get $FF_o = 0.29$, to which the experi-
mental FF is very near (Table 1). According to the fol-

lowing two equations:

$$FF = FF_o(1 - r_s); \qquad FF = FF_o[(1 - FF_o(E_{oc} + 0.7)/E_{oc}r_F]$$

we can calculate the one-digitized resistance of the cell
$r_s = 0.207$ and the one-digitized shunt resistance $r_F = 2.01$. On the other hand, the characteristic resistance
of the cell $R_H = E_{oc}/I_{sc} = 2.18 \times 10^7 \ \Omega$, we can obtain
the values of the equivalent components in Fig. 7: $R_s = R_H \cdot r_s = 4.51 \times 10^6 \ \Omega$, $R_F = R_H \cdot r_F = 4.38 \times 10^7$
Ω. Compared with R_H, R_s is not very small, but also
R_F is not very big, so the R_s and R_F would have some
effect on the filling factors of the cell. In conclusion,
the chla PVA photovoltaic cells exhibit an obvious dark
rectifying behavior and a strong photovoltaic effect, for
which the asymmetric distribution of charges at $SnO_2/$
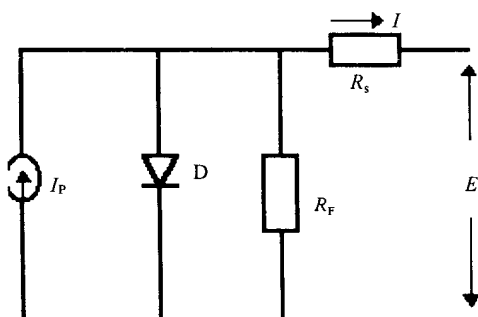chla junction is responsible.

Fig. 7 Equivalent electric circuit of the chla PVA photovoltaic
cell. E: applied potential difference, I_p: current of
source, D: p-n junction, R_s: series resistance, R_F:
shunt resistance.

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