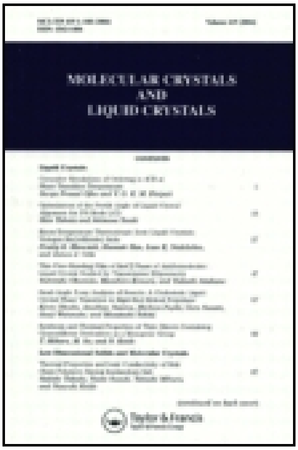

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Liquid Crystal Assisted Photoelectrochemical Solar Cell With Chlorophyll Photoelectrode

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Photoelectrochemical solar cells using chlorophyll photoelectrodes generally give small photovoltages. This paper aims at investigating the possible mechanism for the experimentally observed enhancement of photovoltage when the photoelectrode was chlorophyll-dispersed in a nematic liquid crystal instead of simple chlorophyll. Variation of enhanced photoconductivity, photovoltage and photocurrent at different temperatures after the incorporation of nematic crystal (MBBA) in the chlorophyll electrode are reported. Optical absorption spectra of Chl and Chl + MBBA electrodes have been studied at different temperatures. The overall absorption coefficient increases due to incorporation of MBBA. The increased absorption coefficient decreases with temperature. The enhancement in photovoltage with increasing temperature follows the same pattern as the absorption coefficient.

INTRODUCTION

Chlorophyll is one of the basic constituents of the green plants and its photoexcitable characteristics play an important role in photosynthesis. Ternin[1] showed that chlorophyll film behaves like a p-semiconductor. It is also well known that a magnesium chlorophyll (MgChl) complex, named as P_{700} system, serves as the photochemical pump for the electron for driving the photosystem. Many investigators have tried to use the charge transfer reaction across chlorophyll-metal junction[2-4] or across chlorophyll-electrolyte junction[5-7] for solar energy conversion similar to the corresponding semiconductor devices.[8-10] However, the photovoltages and photocurrents obtained

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in chlorophyll metal or chlorophyll-electrolyte junction are very small. Further investigations revealed that phospholipids surrounding green chlorophyll pigments behave like a liquid crystal and it plays a prominent role in the orientation of these chlorophylls, giving an efficient photochemical reaction field.[11] Recently Aizawa et al[12-14] have demonstrated that incorporation of liquid crystal in a chlorophyll electrode enhances the photovoltage of chlorophyll-electrolyte junction solar cell. However, no valid reason has been given for the role of liquid crystals in the enhancement of the photovoltage.

The present paper deals with the experimental investigation of variation of photovoltage, photocurrent and photoconductivity at different temperatures, before and after incorporation of liquid crystal (MBBA) to chlorophyll electrode. An optical absorption spectra for Chl., and (Chl + MBBA) electrodes have also been studied. These helped us to give a mechanism for enhancement of photoresponse in the liquid crystal incorporated chlorophyll-electrolyte junction solar cell.

EXPERIMENTAL

(a) Materials:

Magnesium chlorophyll (MgChl) was prepared from spinach by crushing fresh spinach in acetone solution and then by putting the extract in a centrifuge machine for three hours. N-(p-Methoxy-benzylidene)p-butylanaline (MBBA) was obtained commercially and had the mesomorphic liquid crystalline range from 20°C to 45°C.

(b) Preparation of photoelectrode:

Solvent evaporation technique was used for preparation of chlorophyll photoelectrode. Chlorophyll was dissolved in acetone and it was uniformly spread on a platinum plate and dried. Chlorophyll-liquid crystal photoelectrode was also prepared in a similar way using petroleum ether as a solvent, Chl. and MBBA was taken in 1:3 ratio. These photoelectrodes are termed as E(chl) and E(Chl-MBBA) in subsequent discussions. E(Chl-MBBA) electrode was rubbed unidirectionally for aligning liquid crystal parallel to the surface.

(c) Fabrication of photoelectrochemical solar cell (PESC):

Figure 1 shows PESC that we have fabricated using chlorophyll or chlorophyll + liquid crystal photoelectrode. E(Chl) or E(Chl + MBBA)

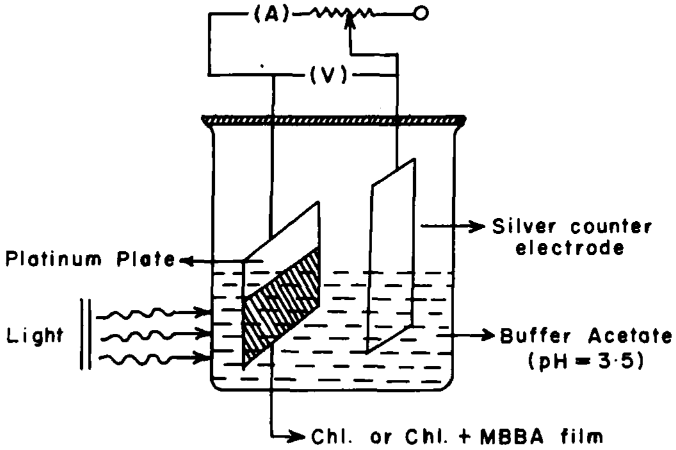

FIGURE 1: Photoelectrochemical solar cell with Chl. or Chl. + MBBA photoelectrode.

was one electrode and silver plate was used as a counter electrode. M/30 buffer acetate with pH = 3.5 was used as an electrolyte. A 300 W tungsten lamp was used for illumination with illuminating intensity 100 mW/cm^2 at the cell, The photo-energy conversion system can be represented as:

E(Chl + MBBA) or E(Chl)	Buffer acetate (pH = 3.5)	Silver plate

Photovoltage and photocurrent of the PESC was measured by a digital multimeter. Temperature of PESC was kept constant within the range of ±0.5°C. For maintaining the PESC at different temperatures it was put on an automatic temperature controlled hot plate. A magnetic stirrer was used for attaining uniformity in temperature.

(d) Recording of absorption spectra:

Absorption spectra of chlorophyll, chlorophyll + liquid crystal (MBBA) and liquid crystal (MBBA) were recorded by an optical spectrometer.

(e) photoconductivity measurement:

For photoconductivity measurement, chlorophyll or chlorophyll + liquid crystal film (thickness ~10μ) was sandwiched between a platinum electrode and a transparent conducting glass plate. This cell

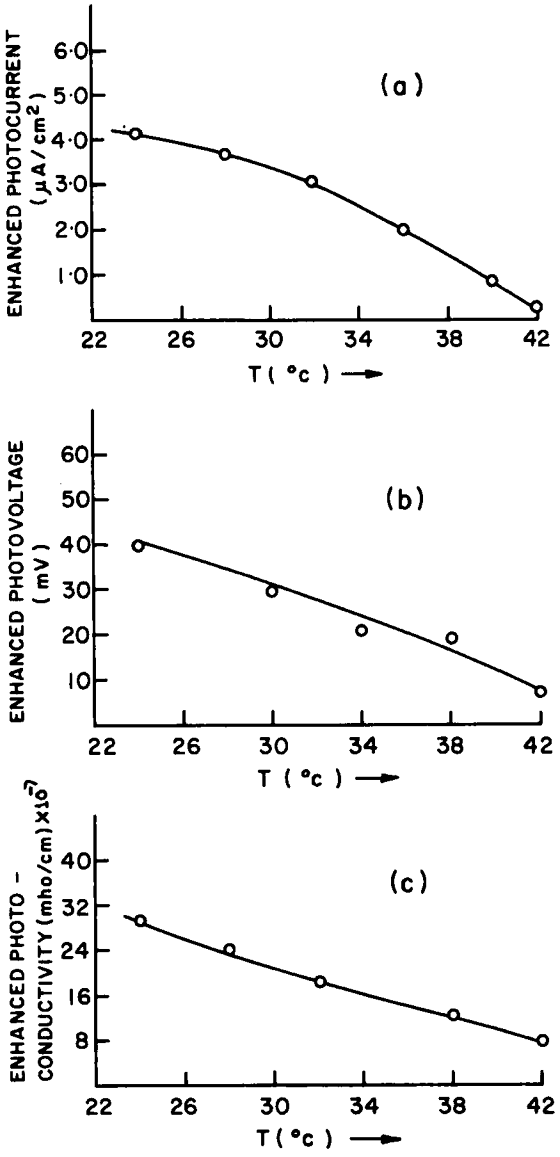

FIGURE 2: Variation of enhanced photovoltage, photocurrent and photoconductivity of E(Chl. + MBBA). Solar cell with temperature.

was illuminated from the transparent glass side with an illumination intensity of 40 mW/cm^2 at the cell. Temperature variation of the photoconductivity was also recorded. Photoconductivity, σ_{ph} was measured at 400 Hz and at 25 mV a.c. signal level using Hewlett-Packard LCR Bridge.

RESULTS AND DISCUSSION

The enhanced photovoltage (V'_{ph}), photocurrent (J'_{ph}) and photoconductivity (σ'_{ph}) after the incorporation of MBBA are shown in Figures 2a, 2b and 2c respectively for different temperatures. It may be seen from these figures that the extent of enhancement is different for different temperatures. V'_{ph}, J'_{ph} and σ'_{ph} plotted in Figure 2 are obtained from the following equations:

$$V'_{ph} = V_{ph}[E(\mathrm{Chl.} + \mathrm{MBBA})] - V_{ph}[E(\mathrm{Chl.})]$$

$$J'_{ph} = J_{ph}[E(\mathrm{Chl.} + \mathrm{MBBA})] - J_{ph}[E(\mathrm{Chl.})]$$

$$\sigma'_{ph} = \sigma_{ph}[E(\mathrm{Chl.} + \mathrm{MBBA})] - \sigma_{ph}[E(\mathrm{Chl.})]$$

Figure 3 shows J−V characteristics for E(Chl.)/Buffer Acetate/Ag and E(Chl + MBBA)/Buffer Acetate/Ag solar cells. It is evident from this figure that the area covered in the case of E(Chl + MBBA) is many times higher than that of E(Chl.).

Figure 4 shows the schematic diagram of chlorophyll or liquid crystal + chlorophyll-electrolyte (Buffer acetate) junction. When this junction is illuminated, photons ($h\nu \approx 1.6$ eV) excite chlorophyll to the lowest vibrational level of its first singlet excited state. Photons with higher energy excite the chlorophyll to high vibrational and electronic singlet states, but the extra energy is very rapidly lost to the environment as the random translation energy of heat, until the lowest vibrational level of the first singlet excited state is reached. Life time of singlet excited state is $\approx 10^{-9}$ sec. From singlet excited state, the Chl* decays to the triplet excited state (Chl′). Life time of the triplet excited state is $\approx 10^{-3}$ sec which is much higher than the life time of the singlet excited state. Thus, most of the photochemical reaction occurs through the triplet state. Suppose there is an oxidised species (e.g. H^+) whose energy level is just lower than the energy level of the triplet excited state (Chl′). Then, the Chl′ may donate

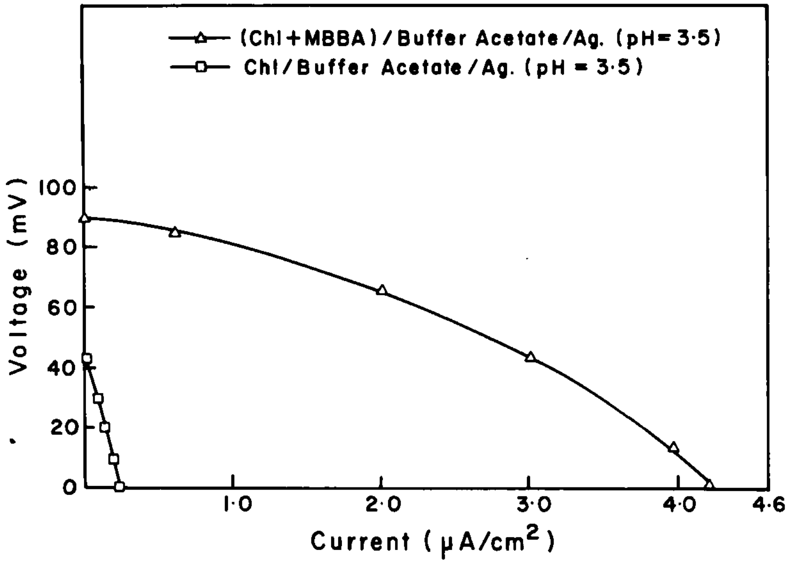

FIGURE 3: J-V characteristics for E(Chl.)/buffer acetate/Ag and E(Chl. + MBBA)/ buffer acetate/Ag solar cell.

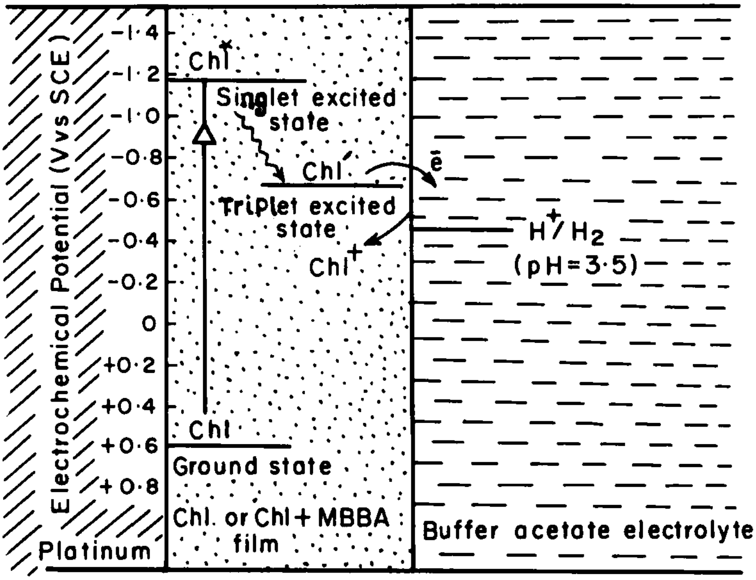

FIGURE 4: Schematic diagram of photoinduced charge transfer reaction at Chl. or (Chl. + MBBA) – electrolyte interface.

an electron to H^+ and become Chl^+. This phenomena gives rise to the photovoltage and photocurrent at the chlorophyll or liquid crystal + chlorophyll – electrolyte junction. Electrode reactions can be written as:

$$\mathrm{Chl} \xrightarrow{h\nu} \mathrm{Chl}^*$$

$$\mathrm{Chl}^* \rightarrow \mathrm{Chl}'$$

$$\mathrm{Chl}' \rightarrow \mathrm{Chl}^+ + e^-$$

$$e^- + H^+ \rightarrow \frac{1}{2} H_2$$

Chl^+ is neutralised by an electron from the counter electrode through the external circuit.

It is obvious that the photovoltage and photocurrent of chlorophyll – electrolyte junction would depend upon the population of the triplet excited state. The photo-response may enhance if the population of Chl′ is increased by some method.

Figure 5 shows the absorption spectrum for Chl.,(Chl + MBBA) and MBBA at room temperature (25°C). It may be observed that the spectrum for Chl has an absorption peak at 652 nm ($h\upsilon \approx 1.7$ eV). A greater absorption of photoenergy in Chl + MBBA film gives an additional photoexcitation of singlet/triplet state and subsequently yields higher photo-response.

Figure 6 shows the absorption spectra of Chl. + MBBA at three temperatures (25°C, 30°C, 35°C). This clearly shows that absorption of photoenergy decreases with the increase in temperatures. Temperature variation studies of photovoltage, photocurrent and photoconductivity also show decrease with the increase in temperature (Figure 2). Thus we have two facts: (a) Incorporation of MBBA increases absorption coefficient and (b) this increased absorption decreases with temperature. A parameter which is known to decrease in a similar manner is order parameter. If we presume that some liquid crystalline order continues to exist even with 30% chlorophyll in MBBA, then a correlation between order parameter and enhanced photoresponse can be made. However, in the absence of any study on liquid crystalline property of the mixture Chl. + MBBA, this correlation is at best a conjecture and enhanced photovoltage can only be attributed to enhanced absorption coefficient.

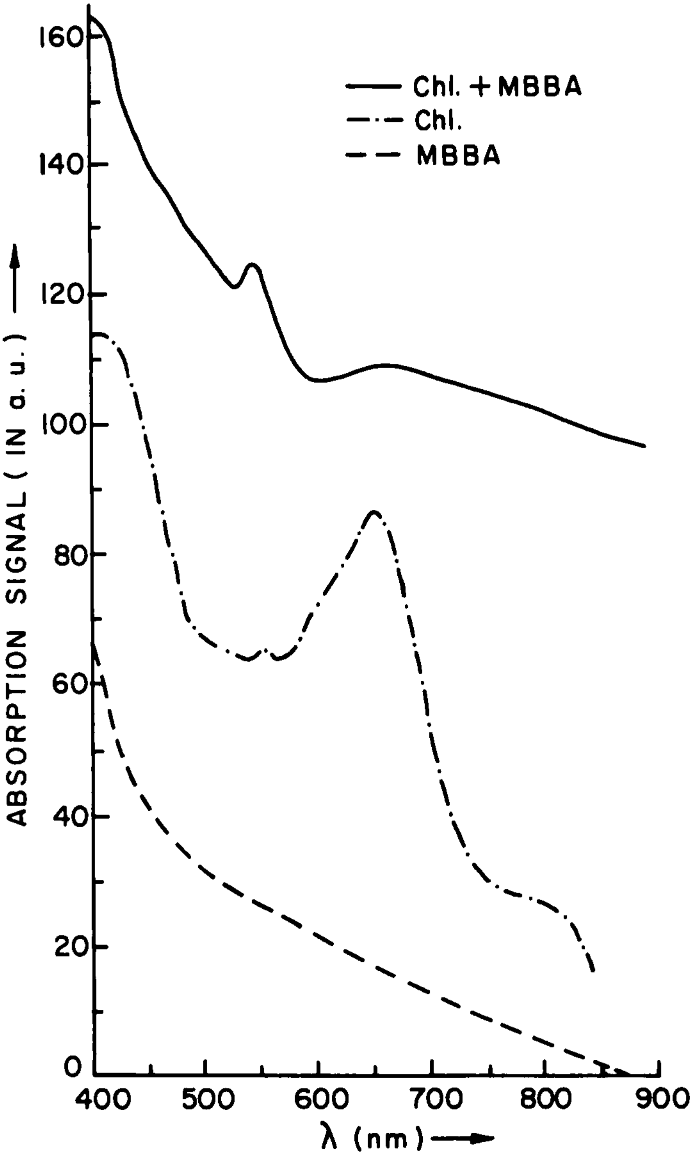

FIGURE 5: Absorption spectra of Chl., (Chl. + MBBA) and MBBA at room temperature (25°C).

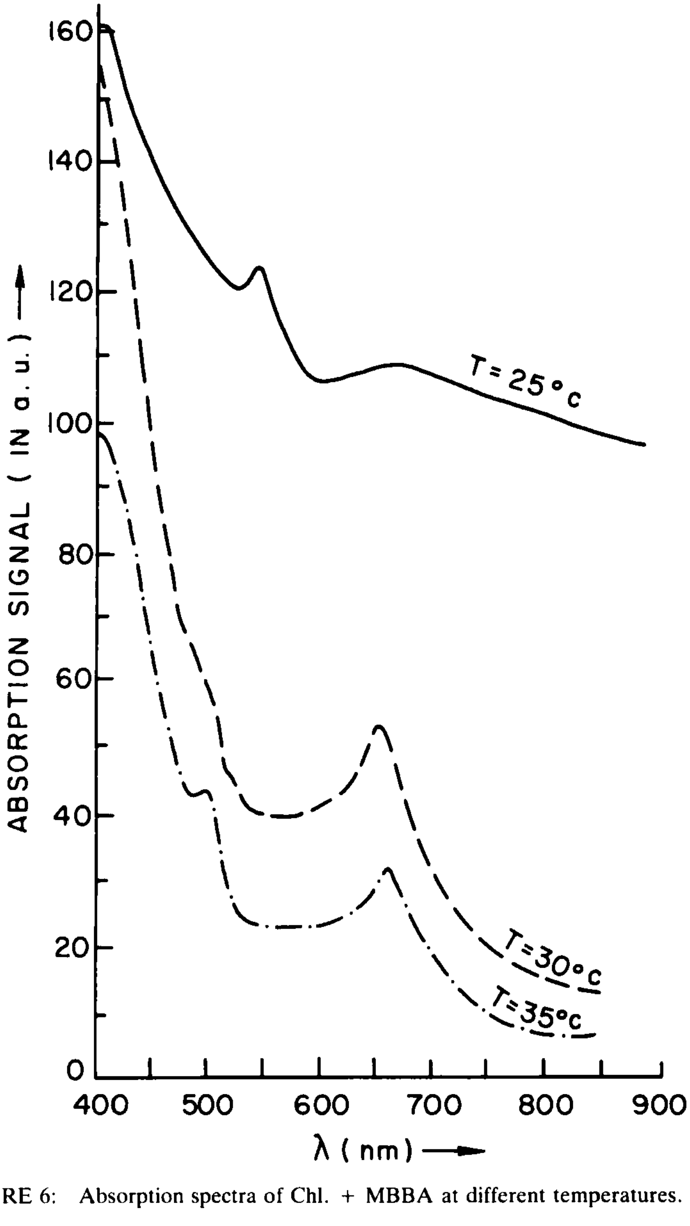

FIGURE 6: Absorption spectra of Chl. + MBBA at different temperatures.

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