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Photoelectric Properties

Photoconductivity of Polymeric Copper Phthalocyanine

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Summary Investigations on photoelectric properties of polymeric copper phthalocyanine have been carried out in surface-type photocells. Measurements indicate true photocurrents depending on temperature, intensity, voltage and wavelength.

1. Introduction

Dark- and photoelectric properties of monomeric phthalocyanines have been studied in a series of papers showing, among others, applications in vidicon television pickup tubes (MEIER and ALBRECHT 1969), photoelectrochemical devices (MEIER et al. 1979, MINAMI 1982), xerographic photoreceptors (WEIGL et al. 1972) and photovoltaic cells (MEIER 1963, MEIER an ALBRECHT 1964, GHOSH et al. 1974, FAN and FAULKNER 1978, BENDERSKII et al. 1978, HOR et al. 1983, MARTIN et al. 1983). In addition, recently interest has focussed on the electrical behaviour of polymeric phthalocyanines because of a dramatic enhancement of dark conductivity of monomeric units by the formation of bridged structures (MAKLES et al. 1975) and polymers (MEIER 1974, HANACK et al. 1981, SCHNEIDER et al. 1982). Moreover, relations between structure and conductivity, on the one hand, and catalytic and electrocatalytic activity, on the other hand, point to the possibility of using high-conducting polyphthalocyanines as catalysts, e.g., in fuel-cell cathodes (MEIER et al. 1973, MEIER 1976).

However, in contrast to monomeric phthalocyanines no experimental results are known showing definite photoelectric properties of polymeric phthalocyanines: Photoelectrochemical currents of $Ti/TiO_x/polyPc$ reported by WÖHRLE et al. (1983) may probably be considered as spectral sensitization of TiO_2 photoelectrodes. Furthermore, thermal or bolomeric effects (ELEY et al. 1981) cannot be excluded in experiments showing photocurrents at room temperature in low-resistance polyphthalocyanine discs of films (SCHUMANN and WÖHRLE 1982, MEIER et al. 1982).

Therefore, studies are necessary for a clear decision about real photoconductivity of polymeric phthalocyanines which may be taken as important components, e.g., in organic photovoltaic devices. In this report first results of studies on polymeric copper phthalocyanine are given.

2. Experimental

Polymeric copper phthalocyanine (abbreviated as polyCuPc) has been synthesized by heating pyromellitic dianhydride, copper (II) chloride, urea and catalyst at 180° - 220° according to DRINKARD and BAILAR (1959) and purified by extraction and sublimation at 10^{-2} torr (MEIER et al. 1975). Monomeric copper phthalocyanine (Schuchardt HE 163 α) was used without further purification.

For studies of electrical properties surface-type cells with electrode distances of 0.2 mm have been used. Samples were investigated at pressures of 10^{-5} - 10^{-6} torr in the temperature range of 190 to 350 K. Dark- and photocurrents were measured with a Keithley 480 picoammeter in combination with a fast recorder.

The light source consisted of a 1000 W xenon lamp (Amko), focussed by quartz lenses on the sample. Monochromatic light from 450 to 1100 nm was obtained by using band pass filters with band widths of 50 nm (Schott). Light intensities were varied with neutral density filters and recorded by a Moll thermopile. Action spectra of photoconductivity have been normalized to an incident photon flux of $1.03 \cdot 10^{17}$ photons/cm^2.s corresponding to $6.18 \cdot 10^{15}$ photons/s per sample surface.

3. Results and discussion

In order to recognize the influence of polymerization electrical properties of monomeric and polymeric copper phthalocyanine have been studied and analyzed.

3.1. Dark conductivity

Dark conductivity of Cu-phthalocyanine used in this study increases on transition from the monomer to the polymer analogous to results obtained with many metallophthalocyanines (see, e.g., MEIER et al. 1973). This enhancement ranging at $T = 310$ K from $\sigma_D = 8.8 \cdot 10^{-12}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ to $\sigma_D = 6 \cdot 10^{-8}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ is connected with a corresponding change of activation energy ΔE_D and pre-exponential conductivity σ_0 which have been derived from Arrhenius plots of dark conductivity by Eq. 1:

$$\sigma_D = \sigma_o \exp(-\Delta E_D / 2\,kT) \qquad (1)$$

(k = Boltzmann constant. T = absolute Temperature).

The parameters are $\Delta E = 1.56$ eV (0.88 eV) and $\sigma_0 = 70$ ($1.5 \cdot 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) at $303\ \mathrm{K} \leqslant T \leqslant 353\ \mathrm{K}$ ($243\ \mathrm{K} \leqslant T < 303\ \mathrm{K}$) for monoCuPc and $\Delta E = 0.35$ eV and $\sigma_0 = 4.7 \cdot 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at $193\ \mathrm{K} \leqslant T < 312\ \mathrm{K}$ for polyCuPc. Moreover, dark currents I_D increase with increasing field corresponding to

$$I_D = a \cdot U^s \qquad (2)$$

(U = voltage, a = constant) with parameters s = 1.62 (E = $5 \cdot 10^3 - 10^4$ V/cm) for monoCuPc and s = 1.3 (E = $400 - 2 \cdot 10^3$

V/cm) for polyCuPc showing a transition to space-charge-limited currents.

3.2. Photoconductivity

Analogous to monoCuPc the conductivity of polyCuPc increases rapidly (i.e., within 1 s) on irradiation with visible light. However, there are differences between the photoelectric sensitivity of monomeric and polymeric Cu-phthalocyanines: MonoCuPc used in this study is characterized at T = 180 K by $\sigma_{ph} = 2.5 \cdot 10^{-10}\ \Omega^{-1}\ cm^{-1}$ and poly CuPc by $\sigma_{ph} = 5 \cdot 10^{-8}\ \Omega^{-1}\ cm^{-1}$.

In discussing photoresponse of polyCuPc the following relationships should be taken into account:

1. Photocurrents increase with light intensity I_B yielding curves of

$$I_{ph} = b \circ I_B^{\gamma} \qquad (3)$$

as shown in Fig. 1 (b = constant. γ = intensity parameter).

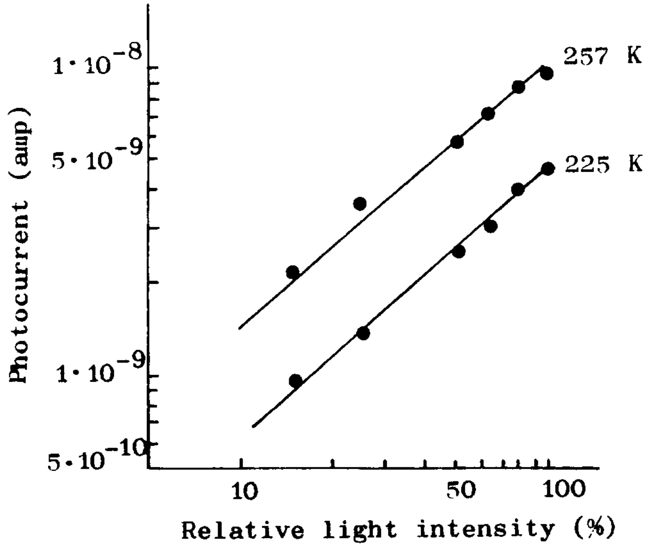

Fig. 1 Dependence of photocurrent on light intensity in polyCuPc. λ = 498 nm. U = 40 volt. I_B (100 %) = $5.9 \cdot 10^{16}$ photons/cm^2 ∘ s.

Parameters γ = 0.85 - 0.87 which have been measured between 192 K and 308 K (λ = 498 nm) point to the control of carrier recombination by exponentially distributed traps (see MEIER 1974, HAMANN 1978).

2. Photocurrents increase with increasing voltage corresponding to

$$I_{ph} = \bar{a} \cdot U^{\bar{s}} \tag{4}$$

as demonstrated in Fig. 2 ($\bar{a}$ = constant. $\bar{s}$ = voltage parameter).

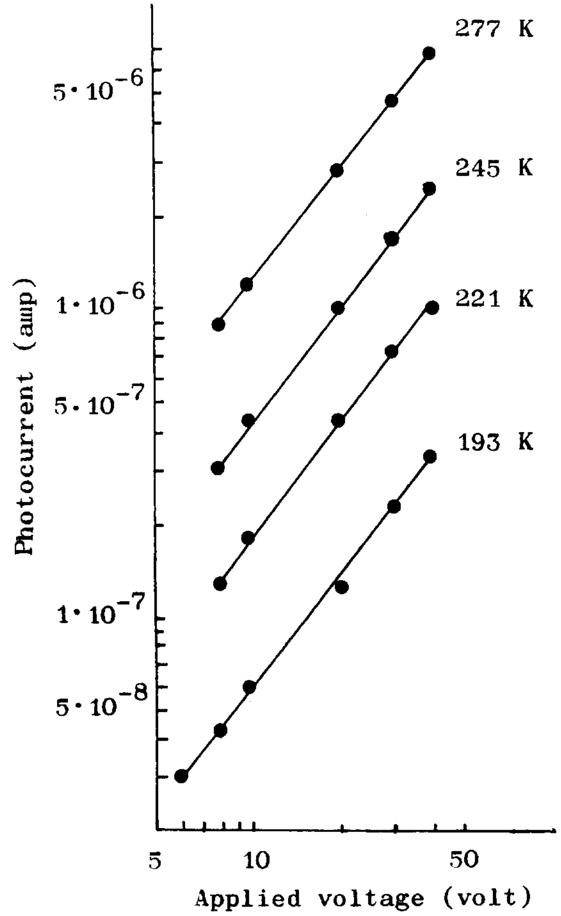

Fig. 2 Dependence of photocurrent on applied voltage in polyCuPc. I_B (unfiltered) ≃ 20 mW/sample.

Parameters $\bar{s}$ between E = 250 V/cm and E = $2 \cdot 10^3$ V/cm measured in the temperature region of 193 K to 277 K yield values of 1.31. These values coincide with parameters s of dark currents and indicate space charge effects.

3. The temperature dependence of photoconductivity can be expressed by

$$\sigma_{ph} = \sigma_{o,ph} \cdot \exp(-\Delta E_{ph}/kT) \qquad (5)$$

as indicated in Fig. 3 by an Arrhenius plot.

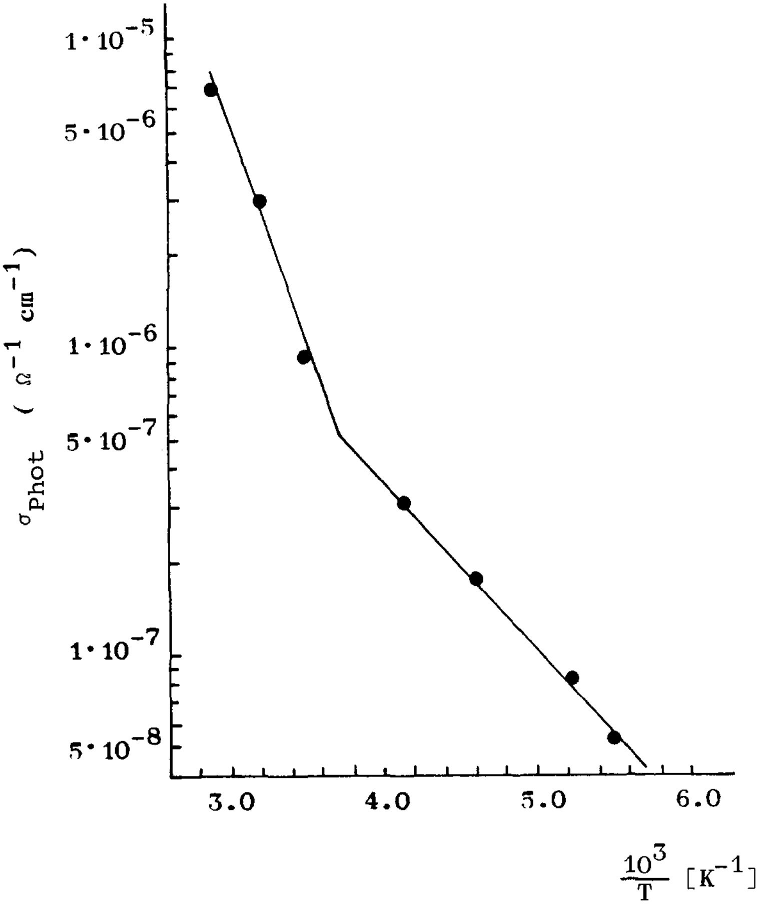

Fig. 3 Temperature dependence of photoconductivity of polyCuPc. I_B (unfiltered) ≈ 20 mW/sample.

From this graph two regions of photoconductivity can be derived which are characterized by the following parameters:

Temperature below 273 K: $\Delta E_{ph} = 0.11$ eV, $\sigma_{o,ph} = 6.3 \cdot 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$

Temperature above 273 K: $\Delta E_{ph} = 0.28$ eV, $\sigma_{o,ph} = 8.7 \cdot 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

Values of activation energy are lower than values for ΔE_D below 273 K. Therefore, thermal effects can be excluded in the photoresponse of polyCuPc.

4. The photoconductivity spectrum of monoCuPc is characterized by a remarkable change on transition to the polymer as shown in Fig. 4.

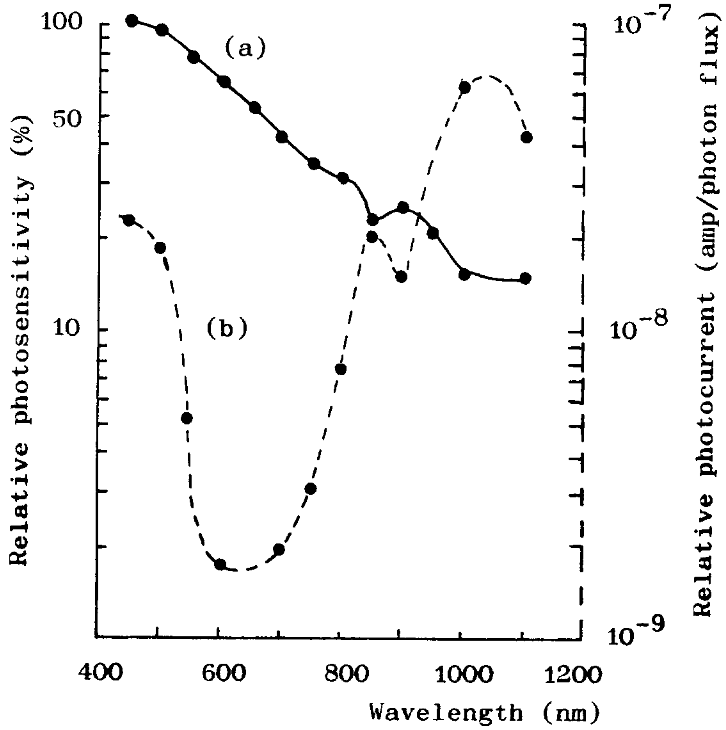

Fig. 4 Photoconductive spectra of phthalocyanines

(a) PolyCuPc (plotted as $I_{ph}^{1/\gamma}/N_q$ with n = 0.88)

(b) MonoCuPc (plotted for constant photon flux $N_q = 1.03 \cdot 10^{17}$).

The main points of this change are

- the removal of photoconductivity peaks at about 850 nm and 1050 nm which are characteristic of monoCuPc (see HARRISON 1969, MINAMI 1982)
- the formation of a broad photoconductivity band covering the visible region in polyCuPc.

5. PolyCuPc is about two orders of magnitude more photosensitive as monoCuPc. An estimation of the photoconductive gains G, defined as the number of charge carriers passing through the sample per absorbed photon, gives $G_{polyCuPc} \simeq 7 \cdot 10^{-5}$ and $G_{monoCuPc} \simeq 5 \cdot 10^{-7}$ (λ = 4983 Å; E = 2000 V/cm).

4. Conclusion and Acknowledgement

In conclusion it can be stated that in surface-type devices polyCuPc reveal true photocurrents at low temperatures where dark conductivity is strongly reduced. Further experiments are now necessary on the mechanism of the photocarrier generation and on the photoelectric properties of polyphthalocyanines with different metals.

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