

Poly-N-epoxypropylcarbazole complexes photocapacitive detectors

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In this study a photosensitive organic semiconductor poly-N-epoxypropylcarbazole (PEPC) doped with oligomeric salt of perily (OSP) or tetracyanoquinodimethane (TCNQ) were investigated as a photocapacitive detectors. Thin films of the PEPC complexes were deposited from their solutions in toluene or dioxane on a conductive glass (CG) and a CG/PEPC-OSP/Ag photocapacitive detector was fabricated. A thin film complex of PEPC with TCNQ (20%) in a benzene solution was deposited by drop deposition on conductive glass substrate, and the organic films were then squeezed between CG and Al foil electrodes to fabricate CG/PEPC-TCNQ/Al photocapacitive detector. It was observed that under filament lamp illumination of up to 2000 lx the capacitance of the CG/PEPC-OSP/Ag photocapacitive detectors increased by 8 time with respect to dark conditions when the concentration of OSP in the polymer was equal to 85 wt.%. The photoconductivity of the detectors increased with illumination. It is assumed that the photocapacitive response of the detectors is associated with polarization occurring due to the transfer of photo-generated electrons and holes.

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1. Introduction

At present organic semiconductors and devices have attracted much attention due to their interesting properties and potential applications for use in solar cells, light emitting diodes, field effect transistors and different kinds of detectors [1-3]. Miyasaka and Murakami [4] fabricated and investigated self-charging photocapacitor for direct conversion and storage of solar energy. The photocapacitor was constructed on a multilayered photoelectrode comprising dye-sensitized semiconductor (TiO₂) nanoparticles / hole-trapping layer / activated carbon particles in contact with an organic electrolyte solution, in which photogenerated charges are stored at the electric double layer. A high-voltage photo-rechargeable photocapacitor of three-electrode configuration, comprising a dye-sensitized mesoporous TiO₂ electrode, two-carbon coated electrodes, and two-liquid electrolytes have been reported by Murakami and Kawashima [5]. Similar investigation was made of a piezocapacitive detector with poly-O-phthalanthracenate under uniaxial compression [6].

The current investigation deals with the effect of light irradiation on capacitance of capacitors based on organic semiconductor poly-N-epoxypropylcarbazole (PEPC) that have potential uses in electronics engineering, photoelectric converters and solar cells. The PEPC complexes exhibit high photosensitivity and may be suitable for electrophotography [7]. But their application for use in solar cells may be restricted due to their lower conductivity [8]. Nevertheless, the investigation of current-voltage (*I-V*) characteristics of some PEPC charge-

transfer complexes showed that the *I-V* curves were nonlinear and even exhibits switching-effect from their low conductivity state to high conductivity [7]. Photocapacitive organic semiconductor materials synthesized with PEPC doped by oligomeric salt of perily (OSP) have been reported earlier [9, 10]. It was shown that this material may be used to fabricate photocapacitor sensitive in the visible spectrum. In this paper we continue investigation of these photocapacitive sensors.

2. Experimental

Fig. 1 shows molecular structures of PEPC (here 'n' is about 4 to 6), OSP and TCNQ. The PEPC and OSP were synthesized in the laboratory [7] and commercially produced TCNQ was used to fabricate the photocapacitive detectors. The molecular weights of PEPC and OSP were about 1200 and (600-1220) atomic weight units respectively. A solution of the PEPC and OSP (concentration of OSP in the complex was from 0 to 85 wt.%) was prepared in toluene or dioxane and thin films were deposited by immersion of conductive glass (CG) for 0.5-1.5 hr at slow evaporation of solvent at 60 °C. After that the sample was dried for 24 hrs at room temperature and a thin silver film was deposited on the polymer's surface by vacuum evaporation to fabricate CG/PEPC-OSP/Ag photocapacitive detectors. Terminals of the detector were connected by conductive silver paste. When dioxane was used as a solvent the photocapacitance value was on average higher in comparison to toluene by a factor of 1.5-2.0 times. To fabricate CG/PEPC-TCNQ/Al

photocapacitive detector, the screen printing technology [11] was used: on conductive glass substrate a thin film complex of PEPC with TCNQ (20 wt %) in a benzene

solution was deposited by drop deposition, dried for 10-20 min, and the organic polymer films were then squeezed between CG and Al foil electrodes and dried for 24 hr.

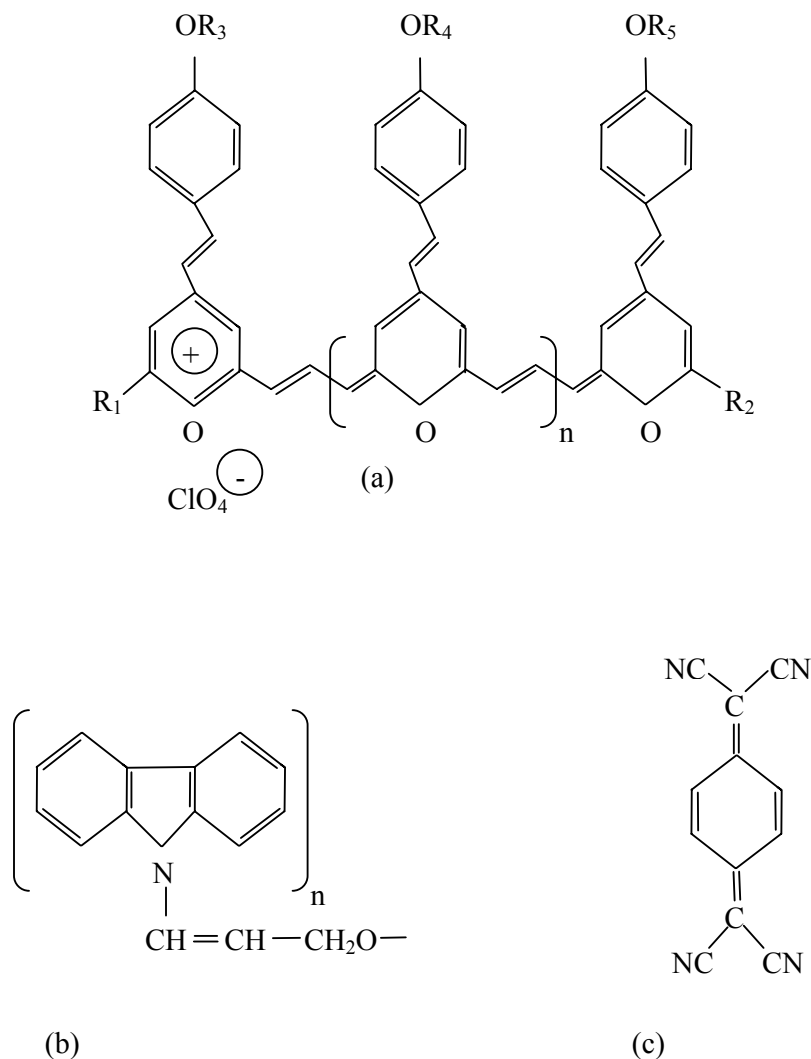


Fig. 1. Molecular structures of (a) oligomeric salt of perily OSP, (b) Poly-N-poxypropylcarbazole PEPC and (c) tetracyanoquinodimethane TCNQ.

Fig. 2 shows schematic diagrams of the capacitive detectors. The size of the CG substrates for the CG/PEPC-OSP/Ag and CG/PEPC-TCNQ/Al was $1 \times 1 \text{ cm}^2$ and $1 \times 2 \text{ cm}^2$ respectively. The thickness of the organic polymer

films were 4.0 to 4.2 μm . Measurement of the capacitance was done by conventional instruments at the frequency of 1 kHz, at room temperature. The capacitive detectors were illuminated by filament lamp.

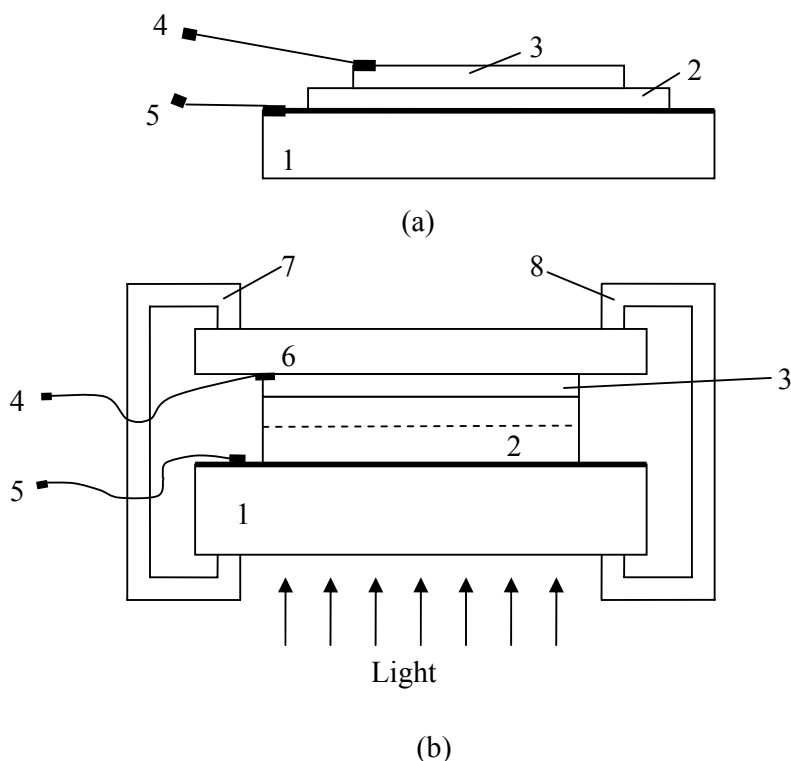


Fig. 2. Schematic diagrams of the photocapacitive detectors (a) CG/PEPC-OSP/Ag and (b) CG/PEPC-TCNQ/Al; 1- conductive glass, 2- PEPC complex with OSP or TCNQ, 3- Ag or Al, 4 and 5- terminals, 6- glass, 7 and 8- fixer.

3. Results and discussion

Fig. 3 shows relative capacitance – composition relationship for the CG/PEPC-OSP/Ag photocapacitive detector under filament lamp illumination of 2000 lx. Here C is photocapacitance (capacitance under illumination), C_d is capacitance in under dark condition, X is concentration of the OSP in a PEPC-OSP complex. As seen from Figure 3 that photocapacitance increases with increase of X . For X above 85 %, the properties of the detector became unstable due to the heterogeneous structure of the polymer film. The relative dielectric constant ϵ_d under dark conditions was equal to 8.0 at $T = 20\text{ }^{\circ}\text{C}$ and frequency of 1 kHz with $C_d = 1690\text{ pF}$. The later was calculated from the following expression for a plane capacitor [12]:

$$C_d = \frac{\epsilon_d \epsilon_0 A}{d}, \quad (1)$$

where A is area of the capacitor (in this case $A = 1\text{ cm}^2$), ϵ_0 is permittivity of free space and d is distance between plates of the capacitor. For the pure PEPC capacitive detector ($X = 0$), C/C_d was equal to 1.002 under illumination of 2000 lx.

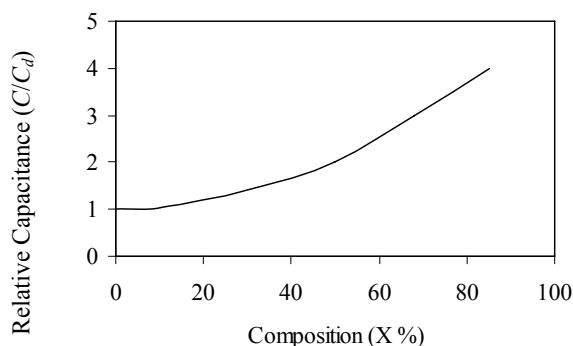


Fig. 3. Relative capacitance V_s composition relationship for the CG/PEPC-OSP/Ag photocapacitive detector under filament lamp illumination of 2000 lx. C is photocapacitance under illumination, C_d is capacitance under dark condition, X is concentration of the OSP in a PEPC-OSP complex.

Fig. 4 shows relative conductivity – composition relationship for the CG/PEPC-OSP/Ag photocapacitive detector under filament lamp illumination of 2000 lx. Here σ is photoconductivity (conductivity under illumination); σ_d is conductivity under dark condition. It is seen that σ/σ_d increases with increase of X .

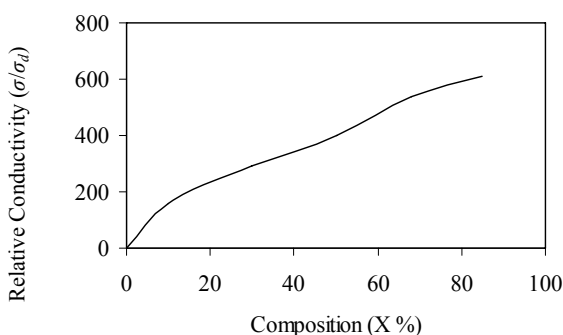


Fig. 4. Relative conductivity Vs composition relationship for the CG/PEPC-OSP/Ag photocapacitive detector under filament lamp illumination of 2000 lx. Here σ is photoconductivity under illumination, σ_d is conductivity under dark condition, X is concentration of the OSP in a PEPC-OSP complex.

Figs. 5 and 6 show relative capacitance - illumination and relative conductivity - illumination relationships respectively for the CG/PEPC-OSP/Ag photocapacitive detector when $X=85\%$. It is seen that there is a correlation, both capacitance and conductivity increase with increase of illumination.

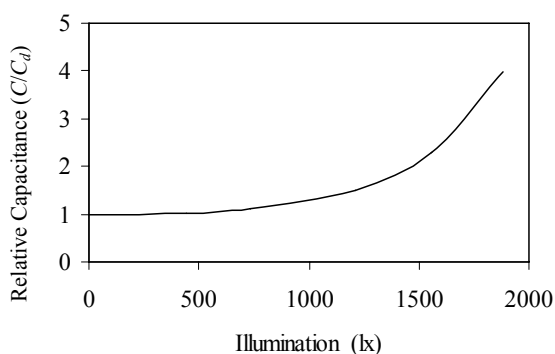


Fig. 5. Relative capacitance Vs illumination relationship for the CG/PEPC-OSP/Ag photocapacitive detector for $X=85\%$.

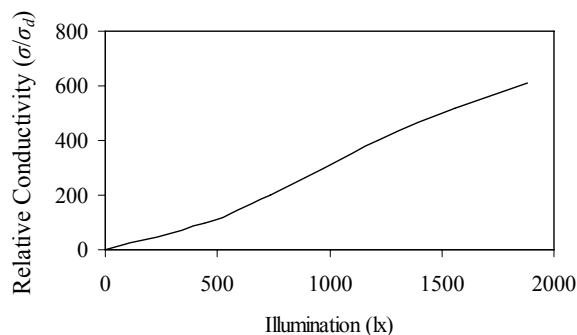


Fig. 6. Relative conductivity Vs illumination relationship for the CG/PEPC-OSP/Ag photocapacitive detector for $X=85\%$.

It was observed that when dioxane is used as solvent the relative photocapacitance increases up to 8.0 times in CG/PEPC-OSP/Ag detectors at a doping concentration of $X=85\%$. This may be due to formation of more compact donor-acceptor structure in the complex or due to incorporation of solvent molecules into the complex that activate the photoexcitation and charge generation processes.

For CG/PEPC-TCNQ/Al capacitive detector with $X=20\%$, it was found that C/C_d was equal to 1.05 under filament lamp illumination of 2000 lx. Also, the relative capacitance-illumination and relative conductivity-illumination relationships in this case were actually similar to the relationships shown in Figures 5 and 6. Undoubtedly, the photocapacitive effect was stronger in CG/PEPC-OSP/Ag detectors.

It is known that the capacitance value depends on polarizability α of the material [12, 13] and basically there are several sources such as dipolar α_{dip} , ionic α_i and electronic α_e . The later is most universal and arises due to relative displacement of the orbital electrons. As the PEPC-OSP or PEPC-TCNQ are charge-transfer complexes we can assume that ionic polarization also takes place in these organic semiconductors. However we may neglect dipolar polarizability α_{dip} here in comparison to ionic and electronic. The ionic and electronic polarizability probably affect dark capacitance at low frequency (1kHz) measurements of capacitance. Investigation of the polarizability due to the transfer of charge carriers α_{td} such as electrons and holes have been reported [14-16] that is present at normal, as well under dark conditions. We may write for the total polarizability under dark conditions α_d

$$\alpha_d = \alpha_i + \alpha_e + \alpha_{td} \quad (2)$$

For the illuminated samples the total polarizability α may be written as:

$$\alpha = \alpha_i + \alpha_e + \alpha_t \quad (3)$$

where α_t is polarizability under illumination due to the transfer of electrons/holes charge carriers. Here we take into consideration that concentration of charge carriers and α are illumination dependent.

The relationship between relative dielectric constant and molecular concentration N , (or concentration of the electrons/holes under dark conditions N_d) and polarizability α_d of the molecule is determined by Clausius-Mosotti relation [13]:

$$\frac{(\epsilon_d - 1)}{(\epsilon_d + 2)} = \frac{N_d \alpha_d}{3 \epsilon_0} \quad (4)$$

From this equation relative dielectric constant may be found as:

$$\varepsilon_d = \frac{\left(1 + \frac{2N_d\alpha_d}{3\varepsilon_0}\right)}{\left(1 - \frac{N_d\alpha_d}{3\varepsilon_0}\right)}. \quad (5)$$

And similar equation can be obtained for dielectric constant under illumination ε

$$\varepsilon = \frac{\left(1 + \frac{2N\alpha}{3\varepsilon_0}\right)}{\left(1 - \frac{N\alpha}{3\varepsilon_0}\right)}, \quad (6)$$

and thus

$$\frac{C}{C_d} = \frac{\varepsilon}{\varepsilon_d} = \frac{\left(1 + \frac{2N\alpha}{3\varepsilon_0}\right)}{\left(1 - \frac{N\alpha}{3\varepsilon_0}\right)\varepsilon_d}. \quad (7)$$

Actually the N in equation (6) may be considered as concentration of electrons/holes under illumination. The product $N\alpha$ depends on intensity of light J , i.e. with increase of illumination concentration of electrons/holes and, probably, mobility of charge carriers will change as well. If we assume that

$$N\alpha = N_d\alpha_d(1 + kJ), \quad (8)$$

where k , we may call, a photocapacitive factor. Then equation (7) may be rewritten as the following empirical expression that can be used for simulation of the relative capacitance-illumination intensity relationships of photocapacitive detector:

$$\frac{C}{C_d} = \frac{\left(1 + \frac{2N_d\alpha_d(1 + kJ)}{3\varepsilon_0}\right)}{\left(1 - \frac{N_d\alpha_d(1 + kJ)}{3\varepsilon_0}\right)\varepsilon_d}. \quad (9)$$

From equation (9) the product $N_d\alpha_d = 18.6 \times 10^{-12}$ F/m may be calculated in the case of dark conditions ($J=0$, $\varepsilon_d = 8$ and $C_d = 1690$ pF).

Fig. 7 shows comparison of simulated and experimental results of relative capacitance-illumination relationship. Both graphs show reasonable agreement as seen from figure 7. In this case $k = 1.6 \times 10^{-4}$ (1 / lx).

Fig. 8 shows equivalent circuit of the photocapacitive detector. The equivalent circuit reflects the point that photocapacitance and photoconductivity phenomena have a common physical reason and are due to photogeneration of electrons/holes under illumination that was observed in

both CG/PEPC-OSP/Ag and CG/PEPC-TCNQ/Al detectors.

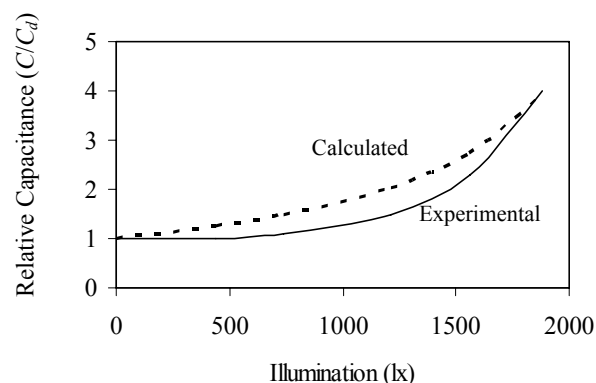


Fig. 7. Calculated relative capacitance V_s illumination relationship of the CG/PEPC-OSP/Ag photocapacitive detector for the $X=85\%$, compared with the results obtained from experiment.

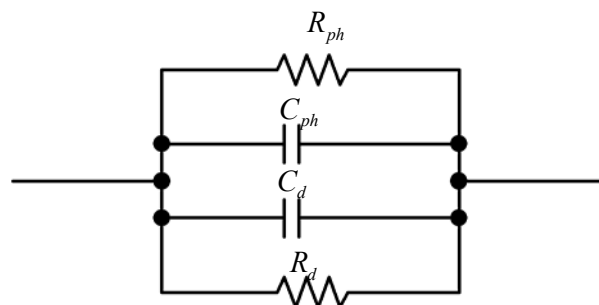


Fig. 8. Equivalent circuit of the CG/PEPC-OSP/Ag photocapacitive detector: C_{ph} and R_{ph} are capacitance and resistance due to photo-effect only; C_d and R_d are dark capacitance and resistance.

4. Conclusions

Complexes of poly-N-epoxypropylcarbazole with oligomeric salt of perily and tetracyanoquinodimethane were prepared. CG/PEPC-OSP/Ag and CG/PEPC-TCNQ/Al photocapacitive detectors were fabricated and their properties were investigated. It was found that under filament lamp illumination up to 2000 lx the capacitance of the CG/PEPC-OSP/Ag detector increased up to 8 time with respect to dark condition when doping concentration in polymer was optimal (85 wt %). Under the same illumination conditions the capacitance of the CG/PEPC-TCNQ/Al detector increased by 5 % at a doping concentration of the polymer with $X=20\%$. An increase in photoconductivity was also observed with increase of illumination. It is assumed that the photocapacitive response of the detectors is associated with polarization due to transfer of photo-generated electrons and holes that

significantly depend on the nature of low molecular impurities (OSP or TCNQ) and also on their doping concentration in the polymer. The calculated results reasonably matched with the experimental values.

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