

Photoconductive Composite Films Based on Cobalt (II) and Nickel (II) Organic Salts Doped with Polymethine Dyes

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Photoconducting film compositions based on cobalt (II) and nickel (II) octanoates doped by cationic and/or anionic polymethine dyes are obtained. Their electric and photoconductive properties are investigated. Anomalous for semiconductor materials peculiarities of the photocurrent were observed in these compositions. Effect of memory of preliminary illumination with light was observed in the obtained films. The scheme of non-equilibrium charge carriers photogeneration process in these compositions are suggested.

Keywords: Photoconductive composites, Dyes, Photocurrent kinetics, Photogeneration, Charge carriers.

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1. INTRODUCTION

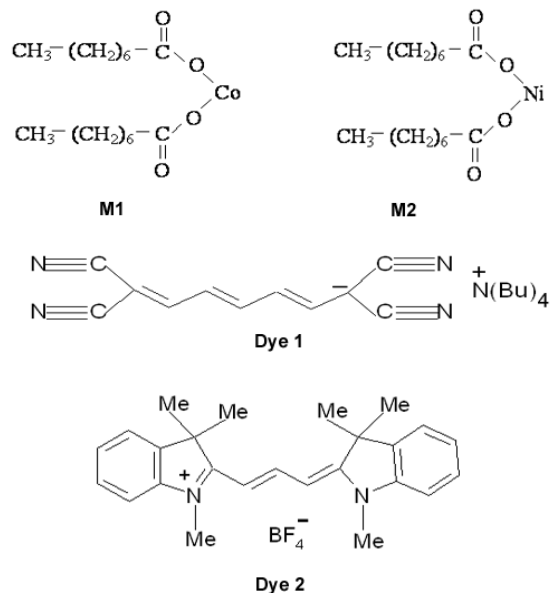
The films of organic metal-containing composites (FC) doped with organic dyes are commonly used in photonics media [1-3]. In FC monomeric dye molecules play role of centers of light absorption and photogeneration of non-equilibrium charge carriers. Considerable progress is reached in control of photophysical and electrophysical properties of FC by adjustment of chemical structure of the dye and composite-matrix. The polymethine dyes [11] are the most interesting amongst organic dyes for photonics applications. The work is aimed in obtaining of new cobalt- and nickel-contained film composites doped with low concentration of organic dyes and investigation of their photoconductive properties.

2. THE SAMPLES AND EXPERIMENTAL TECHNIQUE

Cobalt (II) and nickel (II) octanoates (M1 and M2) as well as anionic (Dye1) and cationic (Dye2) polymethine dyes were used as FC components.

The samples were prepared as the structures with free surface [glass substrate – electroconducting SnO₂ : In₂O₃ (ITO) layer – FC] and sandwich-structures [glass substrate – electroconducting ITO layer – FC – Ag]. Concentration (N) of Dye was 1 mas.%, FC thickness was ~2 μm.

The technique of measurement of optical density (D) within the range λ = 400 – 800 nm, density (j_{PH}) of photocurrent is described in [2, 12]. Green light-emitting diode with maximum of irradiation at λ₁ = 540 nm was used for investigation of photoconducting properties of FC. Parameters δD_E = (D_E - D₀)/D₀ and δI_{LE} = (I_{LE} - I_{L0})/I_{L0}, where D₀ and I_{L0} are the values D and I_L before application of the field (E), D_E and I_{LE} are the values D and I_L after application of the field, were calculated using experimental results. Light intensity (I) at λ₁ and



λ₂ was changed by neutral light filters within the range 1 – 50 W/m². The value of electric voltage (U) which was applied to electric contacts in the samples of sandwich-structure was changed within the range 1 – 200 V. For measurements of fluorescence spectra and for excitation of fluorescence in FPC spectral fluorometer Solar CM2203 was used. All measurements were done at room temperature which corresponds to conditions of FPC practical applications.

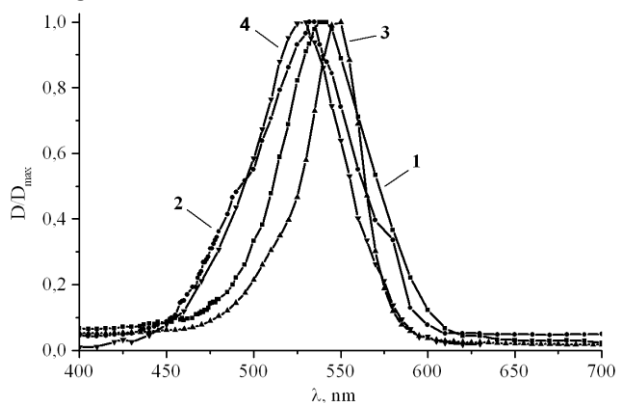
Quantum-chemical calculations of molecules N-methylcarbazole (as a model monomer of PEPC) and anion An5 were done by non-empirical method DFT/B3LYP in 6-31G(d,p) basis using program package PC Gamess/Firefly [13].

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3. EXPERIMENTAL RESULTS AND DISCUSSION

In the samples of sandwich-structure based on M1- and M2-films without dyes-additives photocurrent was not observed. In the samples with 1 mas. % dye photocurrent was observed both for Dye1 and for Dye2. In the samples with $N = 10$ mas. % An5 for $U = 100$ V, $I = 50$ W/m² the value j_{PH} is 10^{-3} A/m² under illumination with light with λ_1 and $2 \cdot 10^{-4}$ A/m² under illumination with light with λ_2 .



In the similar structures with PVB photocurrent was not observed. Dependencies j_{PH} on U can be described by analytical function $j_{PH} \sim U^{m_{PH}}$, which is usually used for analysis of currents in semiconductor materials. Power exponent $m_{PH} \approx 2.1$ for λ_1 and 1.4 for λ_2 . The value j_{PH} weakly depend on polarity U . The dependencies of j_{PH} on I with λ_1 and λ_2 are close to linear. The last fact means that effect of photoconductivity which is not caused by two-quantum processes was discovered.

Discovered in the work photoeffect is unusual. It can not be explained by formation of electron-hole pairs (EHP) caused by electron transfer from carbazole fragment PEPC to excited molecule An5 due to difference HOMO energy (HOMO energy of the polymer which was calculated for N-methylcarbazole is -5.3280 eV and it is -2.2205 eV for An5 anion).

Additional investigations were carried out for determination of reasons of appearance of inner photoeffect upon growth of An5 concentration. Influence of external electric field on spectra of absorption and photoluminescence was observed in all investigated samples based on PEPC (Fig.1).

When electric field is switched on the values D_0 and I_{L0} reach the values D_E and I_{LE} during time interval ~ 1 s, which is close to time of electric charge of geometric capacity of the sample. After electric field switching off all changes of spectra stop. Peculiarities of spectra changes depend on dye concentration. In FPC with $N < 5$ mas. % when electric field is switched off within short wavelength range absorption intensity increases ($\delta D_E > 0$), intensity of photoluminescence decreases ($\delta I_{LE} < 0$). Within the long wavelength range the effects are opposite ($\delta D_E < 0$, $\delta I_{LE} > 0$) (Fig.1, c). Earlier

[2, 14] the similar changes were observed in photoconducting and non-photoconducting FPC with low concentration of symmetric polymethine dyes. These changes were explained by intramolecular redistribution of electronic density under influence of external electric field. But we have ascertained that upon N growth the dependency $\delta D_E(\lambda)$ does not change whereas the dependency $\delta I_{LE}(\lambda)$ essentially transforms. The last fact reveals itself in quenching of luminescence upon application of electric field ($\delta I_{LE} < 0$) in FPC with $N > 5$ mas. %. This quenching increases upon N growth (Fig.1, d). That corresponds to the model considerations described in [1, 2]. Luminescence quenching of organic dyes in photoconducting FPC under electric field influence is explained by formation and dissociation of EHP, namely by decrease of probability of radiative recombination of EHP.

growth of intensity of short wavelength band of creates conditions for higher reaction ability as compare to the state S_0 . Possibility of such mechanism is confirmed by quantum-chemical calculations. Upon formation of neutral radical (An5 \cdot) HOMO energy decreases until -6.0138 eV. This value is lower than HOMO of N-methylcarbazole (-5.3280 eV). Thus, the radical An5 \cdot can play role of effective acceptor of electron from carbazole fragment of PEPC. It can create positive charge carrier – hole.

Effect of FPC photoconductivity on the light wavelength λ_2 also is unusual. The matter is, that λ_2 is outside the absorption band of An5 monomer. Therefore, irradiation of He-Ne laser can not involve inner photoeffect in FPC. Unusual is also kinetics of the photocurrent $j_{PH}(t)$ (Fig.2, c and Fig.2, d) with slow growth of photocurrent and quite quick its relaxation when illumination is ceased. The kinetics of photocurrent is the same for different values U and I .

Addition of conductivity current j_{PH1} and j_{PH2} for stationary dark conductivity current is similar to kinetics of j_{PH} change.

4. CONCLUSIONS

Investigations of electroconducting and photoconducting properties of the Co(II)- and Ni(II)-octanoates composite films doped with different types of polymethine dyes (anionic and cationic) are carried out. Influence of external electric field on spectra of absorption and photoluminescence, electric and photoconductivity of PEPC films doped with anion dye is studied. Widening of absorption and photoluminescence bands, quenching of photoluminescence intensity, arising of photoconductivity effect within visible range of spectrum were observed upon growth of dye concentration. These effects can be explained by formation of associates of dye molecules. The reason of photoconductivity can be attributed to photogeneration and transport of charge carriers in the associates.

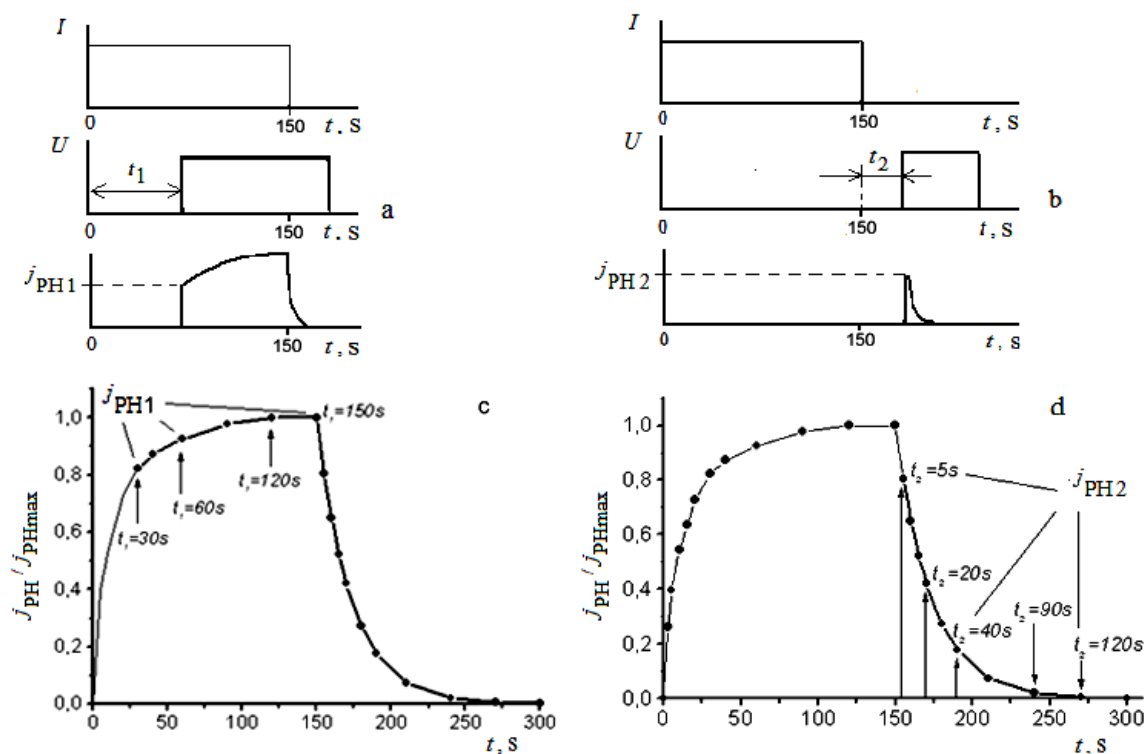


Fig. 2 – Diagrams explaining the technique of measurements of j_{PH1} depending on time of delay t_1 of electric field application after start of illumination of the samples with light (a), Diagrams explaining method of change of j_{PH2} depending on time interval t_2 of delay of application of electric field after illumination is ceased (b), kinetics of photocurrents j_{PH} and j_{PH1} for different t_1 values (c) and kinetics of photocurrents j_{PH} and j_{PH2} for different t_2 values (d)

REFERENCES

1. N. Davidenko, A. Ishchenko, N. Kuvshynsky, *Photonics of Molecular Semiconducting Composites Based on Organic Dyes* (Kyiv: Naukova Dumka: 2005).
2. N.A. Davidenko, N.A. Derevyanko, A.A. Ishchenko, S.L. Studzinsky, V.A. Pavlov, A.D. Chetyrkin, N.G. Chuprina, *Opt. Spectrosc.* **106** No2, 229 (2009).
3. N.A. Davidenko, S.V. Dehtyarenko, Yu.P. Getmanchuk, A.A. Ishchenko, A.V. Kozinetz, L.I. Kostenko, E.V. Mokrinskaya, S.L. Studzinskii, V.A. Skryshevskii, N.A. Skulskii, O.V. Tretyak, N.G. Chuprina, *Semiconductors* **43** No11, 1473 (2009).
4. A.A. Ishchenko, G.P. Grabchuk, *Theor. Exp. Chem.* **45** No3, 143 (2009).
5. N.A. Davidenko, S.V. Dehtyarenko, A.V. Kozinetz, A.S. Lobach, E.V. Mokrinskaya, V.A. Skryshevsky, N.G. Spitsyna, S.L. Studzinsky, O.V. Tretyak, L.S. Tonkopyyeva, *Tech. Phys.* **56** No2, 259 (2011).
6. *Physics of Organic Semiconductors* (Ed. V. Brutting) (Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA: 2005).
7. N.A. Davidenko, V.A. Skryshevsky, A.A. Ishchenko, A.Yu. Karlash, E.V. Mokrinskaya, *Semiconductors* **43** No5, 640 (2009).
8. R. Naaman, D.N. Beratan, D.H. Waldeck, *Electronic and Magnetic Properties of Chiral Molecules and Supramolecular Architectures* (London - New York: Springer: 2011).
9. *Photophysics of Molecular Materials* (Ed. G. Lanzani) (Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA: 2006).
10. V. Agronovich, *Thin Films and Nanostructures Electronic Excitations in Organic Based Nanostructures, Volume 31* (New York: Elsevier Academic Press: 2003).
11. A. Ishchenko, *Structure and Spectral-Luminescent Properties of Polymethine Dyes* (Kyiv: Naukova Dumka: 1994).
12. N.A. Davidenko, M.A. Zabolotny, A.A. Ishchenko, *Spectrochim. Acta A*, **61**, 213 (2005).
13. <http://classic.chem.msu.su/gran/firefly/index.html>.
14. N.A. Davidenko, N.A. Derevyanko, A.A. Ishchenko, S.L. Studzinsky, *Theor. Exp. Chem.* **44** No6, 351 (2008).