ISSN 0018-1439, High Energy Chemistry, 2015, Vol. 49, No. 4, pp. 255–258. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © D.A. Afanas'ev, N.A. Davidenko, I.I. Davidenko, N.Kh. Ibraev, E.V. Mokrinskaya, S.L. Studzinskii, V.A. Pavlov, L.S. Tonkopieva, N.G. Chuprina, 2015, published in Khimiya Vysokikh Energii, 2015, Vol. 49, No. 4, pp. 289–292.

PROCESSES AND MATERIALS FOR OPTICAL INFORMATION SYSTEMS

Photovoltaic Properties of Films of Polyvinyl Alcohol–Xanthene Dye Composites

D. A. Afanas'ev[a], N. A. Davidenko[b], I. I. Davidenko[b], N. Kh. Ibraev[a], E. V. Mokrinskaya[b], S. L. Studzinskii[b], V. A. Pavlov[b], L. S. Tonkopieva[b], and N. G. Chuprina[b]

[a] *Institute of Molecular Nanophotonics, Buketov State University of Karaganda,*
ul. Universitetskaya 28, Karaganda, 100028 Kazakhstan

[b] *Taras Shevchenko National University of Kiev, ul. Vladimirskaya 64/13, Kiev, 01601 Ukraine*

e-mail: ndav@univ.kiev.ua

Received September 15, 2014; in final form, November 11, 2014

Abstract—It has been found that films of polymer composites based on polyvinyl alcohol doped with a xanthene dye possess photovoltaic properties, and the photovoltaic response varies little at the dye concentration greater than 10 wt % with respect to the weight of the polymer. The photovoltaic effect is due to photogeneration of charge carriers in the dye aggregates and transport of nonequilibrium charge carriers among them. It is concluded that, in order to reduce the production cost of photoactive media for photovoltaic cells, it is possible to use cheap polymers with a low concentration of organic dyes.

DOI: 10.1134/S0018143915040025

At present, it seems promising to create photovoltaic solar energy converters based on film structures made of organic materials [1–4]. As photogeneration and photoconductive layers, layers of dyes or their aggregates in a polymer binder can be used. The polymer binder may have photoconductive properties, for example, poly-*N*-vinylcarbazole (hole photoconductor), and introduction of acceptor additives (for example, carbon nanotubes) into it increases electron transfer from photoexcited molecules or aggregates of dyes [5]. Aggregates of dyes (for example, polymethines) can be formed in the polymer binder, which provide light absorption and efficient photogeneration of charge carriers in layers of a photovoltaic converter [6, 7]. In this case, of interest is to study the photoelectric and photovoltaic properties of the discussed structures based on a nonphotoconductive polymer binder. Therefore, the aim of this work was to study the photovoltaic and photoelectric properties of film polymer composites (FPCs) based on a nonphotoconductive polymer and an ionic dye, with or without deposited contacts.

EXPERIMENTAL

To prepare FPCs, polyvinyl alcohol (PVA) was used as a polymer matrix. It possesses good film-forming and optical properties and has no intrinsic absorption in the visible light region. To obtain the internal photoelectric effect in the visible region, the xanthene dye Rhodamine C (RC) was used. Its color results from the intense long-wavelength π-π* electronic transition at 550 nm (Fig. 1) [8]. This permits selective excitation of dye RC [9] without affecting the absorption band of PVA.

The samples were prepared in the form of structures with a free surface FPC—glass substrate—ITO—FPC and sandwich structures glass substrate—ITO—FPC—Ag, where ITO is the transparent conducting layer $SnO_2 : In_2O_3$. FPCs were prepared by casting solutions of PVA or PVA doped with RC onto glass substrates with an ITO layer and subsequent centrifugation. Purified and deionized water was used as the solvent. Filtration was performed on an Aquamax device containing carbon, membrane, and ionic filters. The samples were then dried in an oven at 80°C

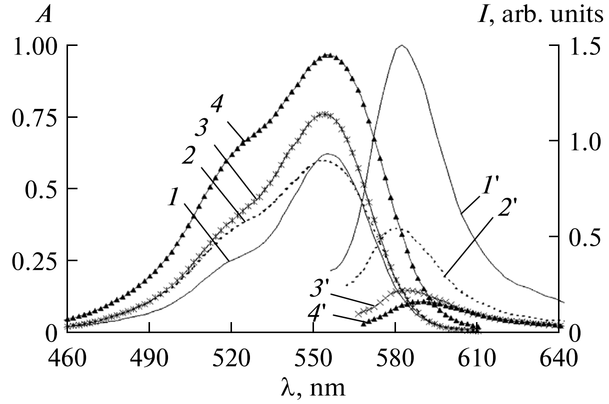

Fig. 1. (*1–4*) Absorption and (*1'–4''*) fluorescence spectra of FPCs based on PVA containing (*1, 1'*) 1, (*2, 2'*) 5, (*3, 3'*) 10, and (*4, 4'*) 20 wt % of dye RC.

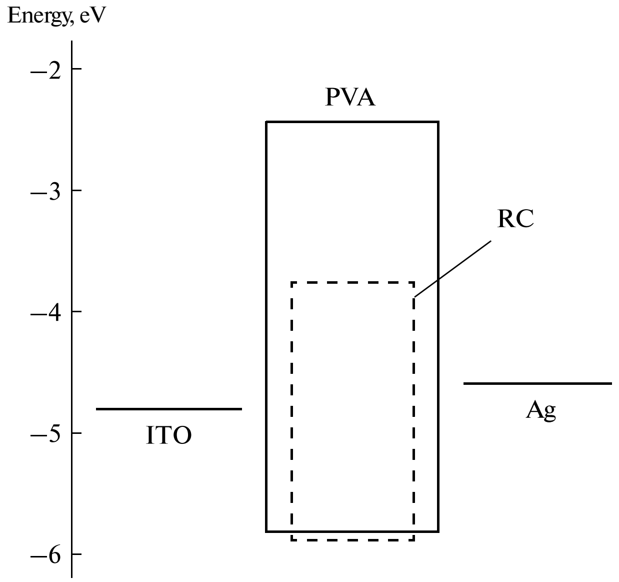

Fig. 2. Energy diagram of the FPC samples.

for 72 hours. The concentration of dye RC was varied from 1 to 20 wt % with respect to the weight of PVA. Thickness of the FPC layers was measured by an MII-4 interference microscope. It was about 1.5 μm. To prepare an Ag electrode, silver paste (ELECTROLUBE) was applied to the surface of FPC, which does not require heat treatment and enables the production of electrical contacts on the surface of FPC like those deposited in the vacuum chamber. This was earlier checked by us by comparing the electrophysical characteristics of samples of sandwich structures with electrical contacts prepared by different methods.

For FPC samples with a free surface, the following parameters were measured: absorbance (*A*) and fluorescence intensity (*I*) spectra; dependence of *I* on time (*t*) after irradiation, that is, kinetics of prompt fluorescence; the value of the electrical potential (V_p) of the free surface of FPC before irradiation with light from the side of the transparent conductive layer ITO, its changes within the irradiation time (*t*) and after turning off light. For the samples of the sandwich structure, tangent of dielectric loss (tan δ) and capacitance (*C*) [10] for sinusoidal alternating voltage with an effective value of 6 V and frequency of 1 kHz were measured, from which the values $\Delta\tan\delta = (\tan\delta_{PH} - \tan\delta)/\tan\delta$ and $\delta C = (C_{PH} - C)/C$ were calculated, where $\tan\delta_{PH}$, C_{PH} and $\tan\delta$, C are the values of tangent of dielectric loss and capacitance after turning on and before turning on light, respectively. Real (Z') and imaginary (Z'') parts of the electrical resistance of FPCs were also measured on a Z500PRO impedance meter in the potentiostatic mode at a given zero constant potential.

The kinetics of prompt fluorescence of FPCs was measured using a pulsed spectrofluorimeter (Becker & Hickl) with picosecond resolution and recording in the time-correlated photon counting mode. Fluorescence excitation of samples was performed using a pulsed semiconductor laser with a generation wavelength of 488 nm and a pulse width at half-maximum of 40 ps.

To determine the photovoltaic characteristics of FPC samples with a free surface, the technique of measurement of the surface potential using a dynamic probe (the Kelvin method [11, 12]) was used. The choice of this technique was based on the fact that in this case there is no influence of the contact potential difference that appears in samples of a sandwich structure with the electrodes made of different materials on photoprocesses in FPCs. An Ag plate 4 mm in diameter was used as a probe. The vibration frequency of the probe was 4 kHz. Kinetics of changes in V_p in FPC samples with a free surface and in samples with the sandwich structure was recorded using a Tektronix TDS1001B storage oscilloscope. For irradiation of the samples, a light emitting diode was used with maximum emission at a wavelength of 532 nm, which is close to the wavelength of maximum absorption of the dye. The light intensity of about 40 W m^{-2} incident on the sample to the active area of the probe from the side of the glass substrate was provided by radiation of a light emitting diode with a light intensity of 30 Candela. The real and imaginary parts of the resistance were measured by the impedance method [13]. All measurements were carried out at room temperature (20°C), at which the use of photovoltaic cells based on FPC is assumed.

RESULTS AND DISCUSSION

Figure 1 shows the absorption and fluorescence spectra of FPCs with different concentrations of dye RC. The changes in the shape of the curves and the position of their maximums with increasing the concentration indicate the formation of aggregates of RC molecules in FPCs [8]. This is confirmed by a decrease in the lifetime of prompt fluorescence of RC in the FPCs studied: with increasing the RC concentration from 1 to 5, 10, and 20 wt %, the lifetime of the prompt fluorescence decreases from 2.42 to 1.85, 1.15, and 0.95 ns, respectively. This is due to a decrease in the difference of the energies of the allowed states between which the radiative transition occurs in relaxation of the excited states of light absorption centers.

Figure 2 shows locations of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the polymer PVA, dye RC, as well as of the working electrodes. The values of the energy levels of the components of the samples are given in the works [14–16]. Since LUMO of the polymer PVA is located significantly higher than LUMO of dye RC, then, upon optical excitation of the dye, we can exclude the process of electron transfer from LUMO of the dye to LUMO of the polymer.

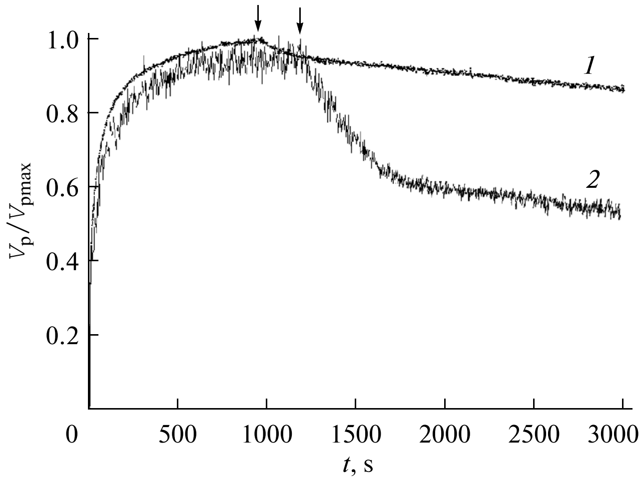

Fig. 3. Normalized plots of the dependence $V_p(t)$ for the FPC samples based on PVA containing (*1*) 1 and (*2*) 10 wt % of dye RC. The moment of turning off light is marked with an arrow.

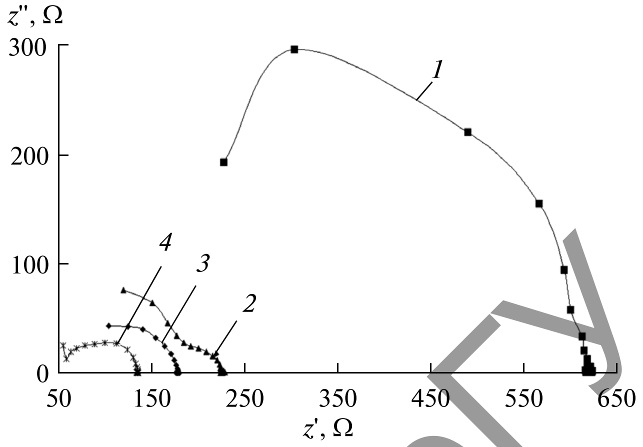

Fig. 4. Plots of electrical impedance spectra for the FPC samples (*1*) based on PVA and (*2–4*) containing dye RC: (*2*) 5, (*3*) 10, and (*4*) 20 wt % of dye RC.

In FPC samples with a free surface, the photovoltaic effect is observed upon excitation at the absorption region of the dye. When changing the dye concentration from 1 to 10 wt %, the maximum value of V_p (V_{pmax}), which was determined in the course of irradiation of the samples with light, varies from +(350 ± 30) to +(500 ± 50) mV. At dye concentrations ranging from 10 to 20 wt %, the value of V_{pmax} is practically unchanged. Figure 3 shows the normalized plots of the dependence $V_p(t)$ in samples with different concentrations of the dye in FPC. In the dependences $V_p(t)$, after turning on light, two components are observed: first V_p rather quickly increases with the time constant of the process being about 10 ± 2 s, but then the rate of this process is slowed down (Fig. 3). After turning off light, first the value of V_p decreases rapidly, and then slowly relaxes, and this is more noticeable in samples with greater dye concentrations in FPCs. Relaxation of V_p after turning off light occurs for tens of minutes and is not described by a simple exponential function. It can be assumed that the fast component of the kinetics $V_p(t)$ is associated with the movement of nonequilibrium charge carriers. The slow component of the kinetics $V_p(t)$ and its non-exponential character may be associated with slow recombination of charge carriers.

The photovoltaic effect in the samples studied can be explained by photogeneration of charge carriers in dye aggregates and transport of nonequilibrium charge carriers among these aggregates even in nonphotoconductive polymer (in our case, in PVA). This is confirmed by the results of the studies presented in Figs. 4, 5. Figure 4 shows the spectra of the electrical impedance of FPCs with different concentrations of dye RC. It follows from these measurements that with increasing concentration of dye molecules, the resistance of FPCs decreases, and hence, their conductivity increases. Figure 5 shows plots of time dependences of Δtanδ (*1*) and Δ*C* (*2*) for the samples with the sandwich structure ITO–FPC–Ag and the RC concentration of 10 wt %. The moment of turning off light is indicated by an arrow. The kinetics of the increase in tanδ and *C* after turning on light correlates with the kinetics of development of the photovoltaic response (Fig. 3) in these samples. The latter corresponds to the fact that, upon irradiation with light, nonequilibrium carriers of electric charge appear in the bulk of FPCs. In the FPC samples with a free surface, containing dye RC, an internal electric field, whose force lines are perpendicular to the film surface, should not be realized. The appearance of free electric charges on the free surface of FPCs upon their irradiation with light is probably due to diffusion of photogenerated holes

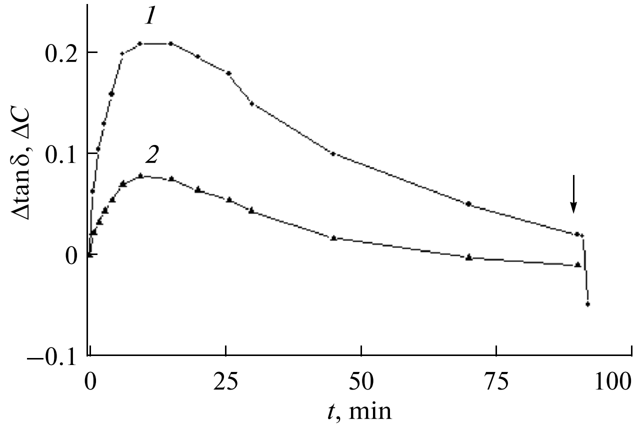

Fig. 5. Plots of time dependences of (*1*) Δtanδ and (*2*) Δ*C* for the FPC samples based on PVA containing 10 wt % of dye RC. The moment of turning off light is marked with an arrow.

from the irradiated ITO contact to the free surface. The diffusion of carriers is caused by the emergence of a concentration gradient of mobile charge carriers, which is greater nearby the irradiated ITO electrode. Such a diffusion mechanism of appearance of the photovoltaic effect (the Dember effect) is characteristic of photosemiconductor materials, in which, upon irradiation, opposite charge carriers (electrons and holes) with different mobility are formed [17, 18].

CONCLUSIONS

The results obtained permit us to believe that, upon increasing the concentration of a xanthene dye in films based on nonphotoconductive polymer, aggregates of dye molecules are formed, with the photovoltaic signal increasing in the region of dye absorption. The photovoltaic effect is related to photogeneration of charge carriers and transport of nonequilibrium carriers in the bulk of the films among the aggregates. The value of the photovoltaic signal changes little with increasing dye concentration above 10 wt % with respect to the weight of the polymer. This means that, when creating photoactive layers in photovoltaic converters, to reduce their production costs by reducing the amount of expensive dyes, it is not necessary to use the technology of spraying dye or a high concentration of the dye in polymer films.

REFERENCES

1. Alferov, Zh.I., *Usp. Khim.*, 2013, vol. 82, no. 7, p. 587.
2. Heeger, A.J., *Adv. Mater.*, 2014, vol. 26, p. 10.
3. *Physics of Organic Semiconductors*, Brutting, W., Ed., Weinheim: Wiley–VCH, 2012.
4. Meng, H.-F., *Polymer Electronics*, Singapore: Pan Stanford, 2013.
5. Tameev, A.R, Pereshivko, L.Ya., and Vannikov, A.V., *Polym. Sci., Ser. A*, 2009, vol. 51, no. 2, p. 182.
6. Fan, B., De Castro, F.A., Heier, J., Hany, R., and Nuesch, F., *Org. Electron.*, 2010, vol. 11, no. 4, p. 583.
7. Tameev, A.R., Vannikov, A.V., and Schoo, H.F.M., *Thin Solid Films*, 2004, vol. 451/452, p. 109.
8. Terenin, A.N., *Fotonika molekul krasitelei i rodstvennykh organicheskikh soedinenii* (Photonics of Dyes and Related Organic Compounds), Leningrad: Nauka, 1967.
9. Davidenko, N.A., Ishchenko, A.A., and Kuvshinskii, N.G., *Fotonika molekulyarnykh poluprovodnikovykh kompozitov na osnove organicheskikh krasitelei* (Photonics of Semiconducting Molecular Composites Based on Organic Dyes), Kiev: Naukova Dumka, 2005.
10. Lushcheikin, G.A., *Metody issledovaniya elektricheskikh svoistv polimerov* (Methods of Investigation of Electric Properties of Polymers), Moscow: Khimiya, 1988.
11. Nonnenmacher, M., *Appl. Phys. Lett.*, 1991, vol. 58, p. 2921.
12. Blythe, T. and Bloor, D., *Electrical Properties of Polymers*, Cambridge: Cambridge University Press, 2005.
13. Lvovich, V.F., *Impedance Spectroscopy: Applications to Electrochemical and Dielectric Phenomena*, Hoboken: *Wiley–Blackwell*, 2012.
14. El-Mansy, M.K., Sheha, E.M., Patel, K.R., and Sharma, G.D., *Optics*, 2013, vol. 124., issue 13, p. 1624.
15. Takirawa, T., Watanabe, T., and Honda, K., *J. Phys. Chem.*, 1978, vol. 82, no. 12, p. 1391.
16. Mashford, B.S., Nguyen, T.L., and Wilson, G.J., *J. Mater. Chem.*, 2010, vol. 20, p. 167.
17. Ryvkin, S.M., *Fotoelektricheskie yavleniya v poluprovodnikakh* (Phoot5oelectic Phenomena in Semiconductors), Moscow: Fizmatlit, 1962.
18. Gurevich, Yu.G. and Meriuts, A.V., *Phys. Lett. A*, 2013, vol. 377, no. 38, p. 2673.

Translated by A. Tatikolov