PHYSICAL CHEMISTRY

{: style="text-align: right;"}

1964

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY {: style= “text-align: right;” }

V. S. MYLNIKOV, Academician A. N. TERENIN

SPECTRAL SENSITIZATION OF THE INTERNAL PHOTOVOLTAIC EFFECT OF COPPER PHENYLACETYLIDE BY DYES

Spectral sensitization of such photosemiconductors as ZnO, AgHal, TlHal, and others to light absorbed by organic dyes adsorbed on their surface is well known (1-3) and has found successful practical application in electrophotography (4-6). The problem of analogous sensitization of the internal photovoltaic effect of organic semiconductors, posed by us long ago, encountered great difficulties associated with the low concentration of photocurrent carriers and their negligible mobility in organic semiconductors of the anthracene type and other polycyclic hydrocarbons. The conducting polymers we used possessed even lower intrinsic photosensitivity. Dyes introduced into films of organic polymers, such as, for example, polyvinyl butyral, polyvinylcarbazole, and others, gave an apparent “sensitized” photosensitivity, evidently associated with dye particles aggregated in the polymer, which was confirmed by photo-emf spectra.*

In connection with our studies on photosemiconducting polymers of the polyacetylene class (7-9), exploratory experiments were carried out on their spectral sensitization by organic dyes, which gave positive results for some polymers. Especially successful results, however, were obtained with the monomeric compound—copper phenylacetylide:

$$\mathrm{Cu-C\equiv C-C_6H_5},$$

the internal photoeffect in which was discovered and studied in detail by us earlier (10). In the present work, the transverse photoconductivity method and the diffusion photo-emf method are used to study the photoeffect. The measurement procedure is described in article (10). Spectral curves were measured with the aid of a high-intensity monochromator with a diffraction grating. The spectra of transverse photoconductivity i_Φ/E and diffusion photo-emf V_Φ/E were recalculated to the same number of incident photons (E is the number of incident photons). Staining of the powder of copper phenylacetylide,** which is yellow in color, was carried out by immersing it in an ethanolic solution of the dye. The optimum concentration of the dye solution for sensitization proved to be 10^{-3} mol/l. Excess dye was washed out in some cases. The absorption spectra of the initial ethanolic solutions were measured on a Unicam SP-700

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

spectrophotometer. In the present article results are given only for chlorophyll a and pinacyanol, as the most typical. Results with other dyes will be published elsewhere.

1. **Chlorophyll a.** The red boundary of the photoeffect of CPA is 2.4 eV (520 nm).

It follows from Fig. 1 that, after staining with chlorophyll a, the photo-emf increases in the region of the intrinsic sensitivity of CPA (curves 1, 2) and a spectrum of sensitized photo-emf appears, with a main maximum at 680 nm and a secondary maximum at 620 nm (curve 2). In the same Fig. 1 the absorption spectrum of a solution of chlorophyll a in ethanol (curve 3) is shown (10^{-3} M). From a comparison of the absorption spectra of the solution and of the photo-emf it follows that the spectrum of the sensitized photo-emf is close to the absorption spectrum of the dilute solution, which above all indicates the molecular dispersion of the dye on the surface of PAA. In addition, a shift of the 680 nm maximum relative to the absorption spectrum of the solution toward longer wavelengths by 10 nm is observed, which is naturally explained by the state of adsorption. The sign of the predominant photocurrent carriers for PAA, previously determined in a capacitor with the aid of a synchronous detector, was positive [10]. PAA colored with chlorophyll showed that in the sensitization region a diffusion photocurrent of the hole type is also observed. Figure 2 gives the spectral distribution of the transverse photoconductivity of PAA before (curve 1) and after (curves 2, 2′) coloring with chlorophyll a. From comparison with Fig. 1 it follows that the photoconductivity spectrum of PAA is shifted relative to the photo-emf spectrum into the long-wavelength region [10]. Therefore the intrinsic photoconductivity spectrum of PAA partially overlaps the absorption spectrum of chlorophyll, which makes observation of sensitization difficult; however, as in the case of the photo-emf method, in the sensitization region the spectral maximum of photoconductivity is located at 680 nm. Let us note that coloring PAA with chlorophyll a practically did not change the dark conductivity of the samples.

---

* Similar apparent spectral sensitization of the photoeffect of a vinyl chloride-vinyl acetate copolymer by crystalline methyl violet and malachite green was reported at the Symposium on Organic Crystals in Ottawa (W. Mehl, H. G. Greig, N. F. Wolf, *Organic Crystal Symposium*, Ottawa. Abstracts, 1962, p. 204). On the same effect in the electrophotographic regime for vinyl chloride copolymers there is a report by Greig in *RCA Review*, **23**, No. 3 (1962), 413.

** Hereafter abbreviated CPA.

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

Fig. 1. Spectral distribution of the photo-emf of copper phenylacetylide: **1** —before coloring with chlorophyll a; **2, 2′** —after coloring with chlorophyll a; **3** —absorption spectrum of a solution (10^{-3} M) of chlorophyll a in ethanol.

Fig. 2. Spectral distribution of the photoconductivity of copper phenylacetylide: **1** —before coloring with chlorophyll a; **2, 2′** —after coloring with chlorophyll a.

2. Pinacyanol. Pinacyanol, a representative of the polymethine dyes, is a good sensitizer of photographic emulsions, and also of the internal photoeffect in ZnO and in the halides of Tl and Ag. Figure 3 gives, on two scales, the spectral distribution of the photoconductivity of PAA colored with pinacyanol from an ethanol solution (10^{-3} M). The spectral distribution of the photo-emf for a sample colored with pinacyanol is given in Fig. 4. The absorption spectrum of pinacyanol in ethanol

shown in Fig. 3 (curve 2). As in the case of chlorophyll *a*, in both methods a shift of the maximum of the spectral sensitivity toward the long-wavelength region, by about 10 nm relative to the absorption spectrum of the solution, is observed. The increase in the intensity of the maximum at 570 nm relative to the maximum at 620 nm in the spectra, as compared with the solution, indicates an increase in aggregation of the dye upon adsorption, as is also known for inorganic adsorbents. In addition, this shows that the aggregated form of the dye also produces the sensitization effect. Unlike chlorophyll *a*, dyeing with pinacyanol led to a severalfold decrease in the intrinsic photoconductivity and photo-e.m.f., especially marked for the former. The magnitude of the dark conductivity of FAM did not change upon dyeing with pinacyanol, as in the case of chlorophyll *a*. Measurements showed that, when FAM is dyed with pinacyanol, the predominant carriers of the photocurrent in the sensitization region are holes. A similar sensitization effect was also observed when FAM was dyed with methylene blue, erythrosine, phthalocyanines, and others.

Fig. 3. 1, 1′—spectral distribution of the photoconductivity of copper phenylacetylide dyed with pinacyanol; 2—absorption spectrum of a pinacyanol solution in ethanol (10^{-3} M)

Fig. 4. 1, 1′—spectral distribution of the photo-e.m.f. of copper phenylacetylide dyed with pinacyanol

Quite recently a paper was published [11], carried out by the Philips firm, in which spectral sensitization of the photoconductivity of a thin single crystal of anthracene in contact with liquid electrodes was effected using dyes (rhodamine B, proflavin, methylene blue) dissolved in one of the polar compartments. It is possible that this phenomenon is to some extent similar to the sensitized photovoltaic effect observed by Rigollo in 1893 when illuminating a copper oxide electrode immersed in an electrolyte and dyed with organic dyes [12, 13].

The results we have obtained give grounds to suppose that the mechanism of spectral sensitization of the photoeffect in an organic semiconductor is similar to the mechanism of photosensitization of inorganic semiconductors. First of all, dyes of the most diverse classes exert a sensitizing action: cationic (methylene blue, pinacyanol), anionic (erythrosine), neutral (chlorophyll *a*, phthalocyanines, etc.), belonging both to the types of photographic sensitizers and to desensitizers. As for inorganic semiconductors, sensitization of PAM causes, in the case of pinacyanol, an aggregated dye (maximum 570 nm) that possesses its own photoconductivity, the carriers of which have the sign (−) ⁽²⁾, opposite to the sign (+) of the photocurrent carriers in the spectral region of semiconductor sensitization. This and a number of other facts compel us to give preference to the sensitization mechanism in which it is precisely the quantum of energy absorbed by the dye, and not an electron, that is transferred to the semiconductor, causing traps to be filled with electrons in the case of hole photoconductivity*. From the preceding paper ⁽¹⁰⁾ it follows that such traps exist in PAM. What is essentially new is the fact established here of a sharp change in the intrinsic photosensitivity of PAM upon dyeing. If the adsorbed dye captures the majority carriers (holes) under illumination in the intrinsic sensitivity region of PAM, then the photo-e.m.f. in this region should decrease, as is indeed observed for pinacyanol. An increase in the intrinsic photo-e.m.f. of PAM, on the other hand, should occur if the dye captures the minority current carriers, i.e., electrons. In this case the transverse photoconductivity, in contrast to the photo-e.m.f., should always decrease, as was observed for the majority of the dyes studied. The anomalous increase in the intrinsic photoconductivity of PAM upon dyeing with chlorophyll may be explained by the fact that the dye has absorption bands in this region and can exert a photosensitizing action here.

Received
30 XII 1963

CITED LITERATURE

1. E. K. Putseiko, A. N. Terenin, *ZhFKh*, **23**, 676 (1949).
2. A. Terenin, E. Putzeiko, I. Akimov, *J. chim. phys.*, **54**, 716 (1957).
3. A. Terenin, I. Akimov, *Zs. phys. Chem.*, **217**, 307 (1961).
4. I. I. Zhilevich, E. L. Nemirovskii, *Elektrografiya*, Moscow, 1961.

5. N. N. Markevich, *Optiko-mekhanicheskaya prom.*, **4**, 21 (1963).
6. E. G. Giaimo, *RCA Rev.*, **23**, 96 (1962).
7. V. S. Mylnikov, A. M. Sladkov et al., *DAN*, **144**, 840 (1962).
8. V. S. Mylnikov, *DAN*, **148**, 620 (1963).
9. V. S. Mylnikov, E. K. Putseiko, A. N. Terenin, *DAN*, **149**, 897 (1963).
10. V. S. Mylnikov, A. N. Terenin, *DAN*, **153**, No. 3 (1963).
11. I. W. Steketee, J. de Jonge, *Proc. (B) Phys. Sci. Nederland.*, **66**, 76 (1963).
12. M. H. Rigollot, *C. R.*, **116**, 878 (1863).
13. M. H. Rigollot, *J. Phys.*, **6**, 520 (1897).

---

* When methylene blue is used as the sensitizer, under certain conditions a photo-e.m.f. of the electronic type is observed in the sensitization region. Whether this gives grounds to assert that in the present case transfer of an electron, rather than of energy, takes place requires further investigation.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.