EXPERIMENTAL TEST OF THE HYPOTHESIS

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EXPERIMENTAL TEST OF THE HYPOTHESIS OF A $p-n$ MECHANISM OF SPECTRAL SENSITIZATION

In the discussion of two possible mechanisms of spectral sensitization, namely: transfer of excitation energy or transfer of an electron from the dye to the semiconductor, proponents of the latter hypothesis believe that it is confirmed by the existence of an internal photoeffect in a layer of solid dye. The existence of photoconductivity in dye layers has been invoked as evidence for the possibility of electron donation by a dye under the action of a photon of visible light (1–3). At the same time, the identity of the mechanism of sensitization by individual adsorbed molecules and by solid dye layers (4,5) was postulated on the grounds that sensitization is possible not only by monomeric and aggregated forms of the dye, but also at the contact of a semiconductor layer with a dye layer (6,7). After the discovery of a barrier photo-e.m.f. at the contact of dye and semiconductor layers (7–10), the notion was advanced (4,8,9) that, in sensitization, the dye-semiconductor system operates as a photocell with a $p-n$- (or $n-p$-) junction, through which minority carriers pass from the sensitizer to the semiconductor. Hence it follows, in particular, that the efficiency of sensitization will be considerable when the dye and the semiconductor have different types of conductivity, and small when they are of the same type. However, the possibility of applying the results of studies of the photoeffect in solid dye layers to the problem of spectral sensitization requires special consideration.

Meanwhile it is known that sensitization is effected with the greatest efficiency by individual adsorbed dye molecules. It is insignificant at the contact of a semiconductor with a solid dye layer; moreover, in this case sensitization is apparently also effected by individual molecules adsorbed on the surface of the semiconductor (6). But it makes no sense at all to speak of the semiconductor properties of individual molecules and to transfer to them properties inherent in solid layers.

In our opinion, the phenomenon of a barrier photo-e.m.f. at the contact of dye and semiconductor layers has no direct relation to the phenomenon of spectral

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sensitization. In particular, the spectral distribution of this barrier photo-e.m.f. ($^{7-9}$) is similar to the absorption and photoconductivity spectra of a solid dye layer, whereas the sensitization spectrum at the contact of a dye layer with a semiconductor is similar to the absorption spectrum of individual dye molecules (^{6}).

Our numerous experiments have not revealed a direct connection between the sensitizing ability of a dye and the photoelectric properties of their solid layer (^{11,12}). A dye that does not possess photoconductivity in a contact layer, and a dye that is a good photosemiconductor, may be identical in sensitizing quality. In this case the photocurrent in the dye layer is usually 3-5 orders of magnitude smaller than the sensitized photocurrent in the semiconductor. The sensitization spectrum has nothing in common with the photoconductivity spectrum of the dye layer, but coincides with the spectrum

absorption of the adsorbed molecules. No dependence is observed of the sensitization efficiency on the sign of the current carriers in the solid dye layer. The sign of the charge of the photocurrent carriers in the sensitization region is always the same as in the region of intrinsic sensitivity of the semiconductor (n-type in ZnO and AgBr, p-type in TlJ and AgJ). Irrespective of the dye, the sensitized photoeffect in semiconductors can be increased hundreds of times upon adsorption of electron-acceptor molecules (O_2, J_2, Br_2, quinone), despite the fact that such adsorption sharply lowers the photoeffect in dyes with n-type conductivity.

Fig. 1. Spectral distribution of the capacitor photo-e.m.f. of ZnO (n-type) and TlJ (p-type): **1** –in contact with amorphous layers of rhodamine B (n-type); **2** –in contact with the same dye layers after their crystallization (p-type); **3** –in contact with amorphous layers of B3 sulfate (n-type); **4** –in contact with the same layers after their crystallization (p-type).

In order to further test the mechanism of $p-n$ sensitization, in the present work a comparison was made of the efficiency of sensitization of the photoeffect in electron and hole semiconductors (ZnO and TlJ) by dyes having n- or p-type photoconductivity. To exclude any dependence of sensitization on the structure of the dye molecule, the sensitization efficiency of a given semiconductor was compared in contact with a layer of one and the same dye, first with n-, and then with p-conductivity. For this purpose use was made of the previously established fact$^{(13)}$ that in amorphous layers of some dyes the carriers of the dark current and photocurrent are electrons, whereas the same layers, after crystallization, possess hole conductivity. Measurements of the spectra of photoconductivity and of the capacitor photo-e.m.f. were performed on the apparatus described

Fig. 2

Figure 2: Fig. 2

in Ref. (14). Illumination from an incandescent lamp through a double quartz monochromator DMR-2, in contact sensitization of the semiconductor, was carried out through the dye layer(6). The spectral photoeffect curves shown in the figures are given in relative units and referred to equal incident energy.

The results of some experiments are presented in Fig. 1. First the spectral curve of the sensitization efficiency was measured when a thin (0.05 μm) amorphous layer of rhodamine B (n-type) was pressed against a ZnO layer (n-type). After crystallization of this dye layer, which converted it into a p-semiconductor(13), the sensitization spectrum was again measured under the same conditions in its contact with ZnO. In an analogous manner, the sensitization curve of the photoeffect in the hole semiconductor was determined.

TlJ upon contact with a layer (initially amorphous, then crystallized) of the same dye. Thus, the semiconductor–dye pair was studied in all possible combinations: $n-n$, $n-p$, $p-n$, $p-p$. According to the mechanism of $p-n$ sensitization, the sensitization efficiency should be maximal only in two cases of pairs: $n-p$ and $p-n$, and insignificant for the combinations $n-n$ and $p-p$. However, as shown in the left half of Fig. 1, no noticeable difference in the sensitization efficiency of amorphous and crystalline layers of rhodamine B is observed.

Fig. 2. Spectral distribution of photo-emf and photoconductivity of ZnO powders (n-type) and TlJ (p-type), colored by grinding with powders of brilliant green sulfate (p-type) (1) and brilliant green oxalate (n-type) (2) (weight proportion $10000:1$); 3—photo-emf of a powder of brilliant green sulfate alone; 4—photo-emf of a powder of brilliant green oxalate

In the right-hand part of the figure are given the results of analogous experiments with another dye—brilliant green (BG) sulfate, whose amorphous layers also possess electron conductivity, while the crystallized layers possess hole conductivity. Here too, the sensitization efficiency did not correspond to that predicted by the hypothesis under discussion. In the case of both semiconductors, sensitization by amorphous layers of this dye somewhat exceeded sensitization by crystallized layers.

For a further check, use was made of the fact that microcrystalline powder of brilliant green sulfate (BGS) possesses hole photoconductivity, while the carriers of photocurrent in the oxalate of this dye (BGO) are electrons.

A uniformly colored semiconductor was prepared by grinding, in a mortar, weighed portions of dye powder (BGS or BGO) and semiconductor (ZnO or TlJ) in the proportion $1:10000$. Then, to prepare photoresistances, the powder, in the form of a paste formed upon addition to it of petroleum ether (the dye does

Fig. 3. Spectral distribution of the photo-emf and photoconductivity of ZnO and TlJ powders colored with sulfate (1) and oxalate (2) of BG from ethanolic solutions, concentration 10^{-5} mol/l

Figure 3: Fig. 3. Spectral distribution of the photo-emf and photoconductivity of ZnO and TlJ powders colored with sulfate (1) and oxalate (2) of BG from ethanolic solutions, concentration 10^{-5} mol/l

not dissolve in it), was applied to a quartz substrate with platinum electrodes, on which, upon drying, a sufficiently strong layer of the colored semiconductor was formed. Here also all combinations of conductivity types of the sensitizer and semiconductor were produced. The spectra of the capacitor photo-emf and photoconductivity of these layers are given in Fig. 2. The same figure gives the spectral curves of capacitor photo-emf in powders of the dyes-sensitizers themselves (curves 3 and 4). Their photoelectric sensitivity was approximately three orders of magnitude lower than the photoeffect sensitized by these dyes in ZnO and TlJ at coatings not reaching monomolecular thickness.

The results shown in Fig. 2 also do not confirm the view of the sensitization mechanism as a *p*—*n* junction. The efficiency of sensitization of the photoeffect both in *n*-ZnO and in *n*-TlJ by brilliant green sulfate is somewhat greater than by the oxalate. The latter is also observed in molecular sensitization by these dyes, as is seen from Fig. 3.

It is necessary to note that the spectral curves of the sensitized photoeffect under any procedures—namely, adsorption of the dye from solution, rubbing dry powders of the dye and semiconductor, or contact of layers of dye and semiconductor—are similar to the absorption spectra of the dyes adsorbed on these semiconductors and differ from the absorption and photoeffect spectra of solid dye layers (Fig. 3, compare 3 and 4 with 1 and 2).

Fig. 3. Spectral distribution of the photo-emf and photoconductivity of ZnO and TlJ powders colored with sulfate *(1)* and oxalate *(2)* of BG from ethanolic solutions, concentration 10^{-5} mol/l.

The results obtained again confirm our data that the sensitizing ability of dyes is not determined by their own photoelectric properties. Moreover, the explanation (^{4,9}) of sensitization in the dye—semiconductor system by electron transfer, occurring like the photoeffect with a *p*—*n* junction, is completely ruled out. On the contrary, the results described are in full agreement with the mechanism of energy (and not electron) transfer from the dye to the semiconductor and the liberation, under its action, of an electron from the trapping level of the semiconductor into the conduction band (^{11,12}).

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