The Hypersensitization of Photoconduction in Microcrystalline Zinc Oxide

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As is well known, microcrystalline zinc oxide exhibits remarkable photoconduction as long as its surface is covered with chemisorbed oxygen, but it becomes a surprisingly poor photoconductor as the oxygen is removed from the surface.[1] In a previous paper,[2] we have reported that the photoconduction characteristics can be further improved if the chemisorbed oxygen is replaced with appropriate electron-affinitive molecules. In the present paper, an enhancement of the photoconductivity of microcrystalline zinc oxide by the adsorption of some electron-affinitive molecules, such as iodine, phthalic anhydride and *p*-chloranil, will be described. The spectral response of the photocurrent and the temperature dependence of dark- and photo-currents have been studied. Rose Bengal, an organic dye which is widely used for the optical sensitization of zinc oxide photoconduction, was added to the above-mentioned systems, to be adsorved together with the electron-affinitive molecules, and the spectral response of the photoconduction has been measured.

It has been found that the electron-affinitive molecules are chemically adsorbed on zinc oxide not only to change the surface barrier height of zinc oxide, but also to co-operate with the dye molecule on the surface and to increase the photoconductive sensitivity of zinc oxide in its proper (ultraviolet) and also in its dye-sensitized (visible) wavelength regions. We shall call such a co-operative optical sensitization in the visible region " the hyper-sensitization of photoconduction."

Experimental

The microcrystalline zinc oxide used was Merck's reagent, 0.3 μ in particle size. It had a purity of 99.95%, containing calcium (0.015 %), lead (0.01 %) and sulfates (0.01%) as impurities. The adsorption of the electron-affinitive molecule onto the zinc oxide was made in the dark from an alcoholic solution. In order to study the hypersensitization, a small amount of Rose Bengal was further adsorbed by the same method onto thus-prepared zinc oxide, which had already adsorbed the electron-affinitive molecule. During these processes, no attempt was made to remove chemisorbed oxygen from the zinc oxide; therefore, the oxygen is considered to remain on the surface, forming a co-adsorbed layer with the electron-affinitive molecule or with the dye and the electron-affinitive molecule. The prepared samples of zinc oxide were coated in the dark on glass plates to a thickness of 40 to 50 μ. Two aluminum strips used as electrodes were placed 0.5 cm. apart on each of the specimens to accomplish a surface-type arrangement. In order to eliminate any pre-irradiation history of the zinc oxide employed, every specimen was kept in the dark for 50 hr. or more before its electric current was measured with a vibrating-reed electrometer. The contact between the electrode and the specimen was known to be ohmic from the linear relationship observed between the applied voltage (ranging from 5 to 100 V./cm.) and the current. A photographic tungsten lamp was used as the light source for measurement, while white light and a xenon arc were combined with a double monochromator for spectral study.

Results

The Sensitization of the Photoconduction.— When zinc oxide which had chemisorbed oxygen further adsorbed 0.03 mol.% of iodine,

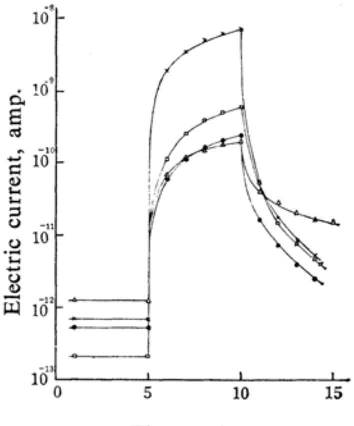

Fig. 1. Rise and decay of photocurrent in zinc oxide-oxygen-electron affinitive molecule systems.

● $ZnO-O_2$
△ $ZnO-O_2$-*p*-chloranil (0.03 mol.%)
□ $ZnO-O_2$-iodine (0.03 mol.%)
× $ZnO-O_2$-phthalic anhydride (0.03 mol.%)

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[1] W. Ruppel, H. J. Gerritsen and A. Rose, *Helv. Phys. Acta*, **30**, 495 (1957).

[2] E. Inoue, I. Maki and T. Yamaguchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 428 (1963).

phthalic anhydride or *p*-chloranil, the photocurrent was found to increase markedly, while the dark current scarcely changed at all or even decreased. Figure 1 shows the photocurrents of zinc oxide-oxygen-electron affinitive molecule systems measured with a white light with an intensity 1.3×10^{-2} W/cm^2.

When the above specimens were dyed with Rose Bengal of 0.0052 mol.%, the photocurrents, upon irradiation with the same light, increased further, as Fig. 2 shows. All the specimens hereto used were prepared by coating the zinc oxide samples with silicone resin (7% by volume) as a binder for convenience. It was assumed that the influence of the resin on the photoconduction in each specimen is similar and that it, therefore, can be disregarded. From these measurements, it has been made clear that the electron-affinitive molecule adsorbed on the zinc oxide surface has a distinct effect on the photoconduction of zinc oxide.

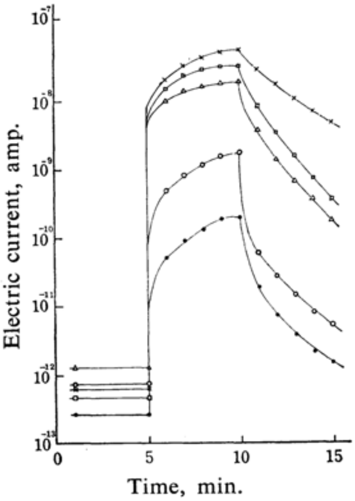

Fig. 2. Rise and decay of photocurrent in zinc oxide-oxygen-electron affinitive molecule-dye systems.

● $ZnO-O_2$
○ $ZnO-O_2$-Rose Bengal (0.0052 mol.%) (1)
△ (1)+0.01 mol. % *p*-chloranil
□ (1)+0.01 mol. % iodine
× (1)+0.01 mol. % phthalic anhydride

Figure 3 illustrates the spectral response of photoconduction in the zinc oxide-oxygen-electron-affinitive molecule systems. The sensitization of the photoconductivity occurs only in the ultraviolet region, not in the visible region, except in the case of *p*-chloranil. In the case of phthalic anhydride, which was found to be the most effective, a double peak was found in the action spectrum. The cause of the double peak has not yet been determined. The system with *p*-chloranil showed a slight response in the visible region which was too small to be shown in Fig. 3. The wavelength where the small response appears coincides with that of light absorption by *p*-chloranil. The results in Fig. 3 indicate a process whereby the electron-affinitive molecule is chemisorbed on the zinc oxide surface and there draws an electron from the crystal, making a depletion layer which decreases the dark conductivity of zinc oxide. When the system is irradiated with the light which zinc oxide absorbs, the chemisorbed molecule may get physisorbed or desorbed into the atmosphere. This process will lead to an increase in the photocurrent, as is the case in the zinc oxide-oxygen system mentioned at the beginning of this paper.[1] Therefore, the sensitization of the photoconduction under investigation should be considered to be caused by the chemisorption of the electron-affinitive molecule and, therefore, not by the optical sensitization effect. Here, the optical sensitization refers to a type of sensitization caused by light absorption by the sensitizer itself, as has been found in dye-sensitized silver halide in the photographic process.

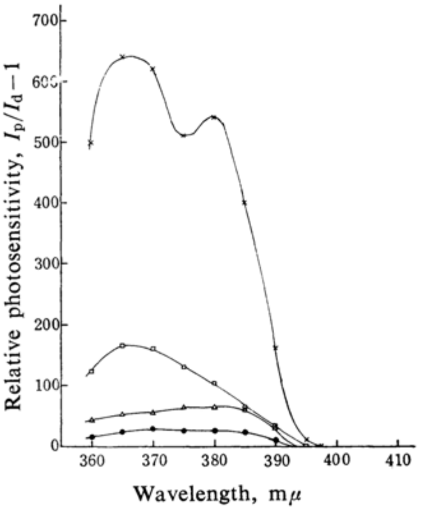

Fig. 3. Spectral response of photoconduction in zinc oxide-oxygen-electron affinitive molecule systems.

● $ZnO-O_2$
△ $ZnO-O_2$-*p*-chloranil (0.03 mol. %)
□ $ZnO-O_2$-iodine (0.03 mol. %)
× $ZnO-O_2$-phthalic anhydride (0.03 mol. %)

The spectral response of photoconduction in the zinc oxide-oxygen-electron affinitive molecule-Rose Bengal systems is shown in Fig. 4. A remarkable optical sensitization is found in the visible region, where the light is strongly absorbed by Rose Bengal (420~600 mμ); *p*-chloranil, is an exceptional case, for it shows

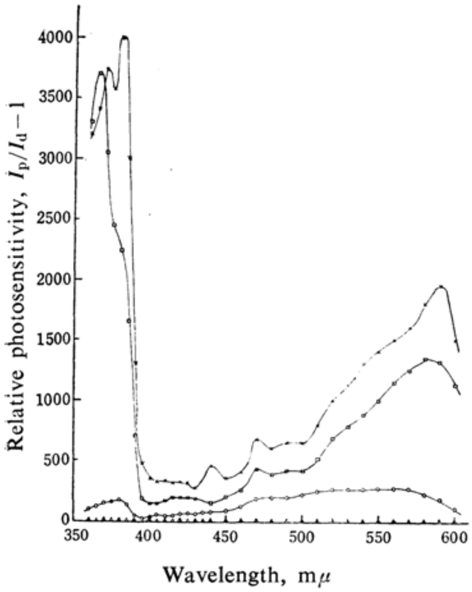

Fig. 4. Spectral response of photoconduction in zinc oxide-oxygen-electron affinitive molecule-dye systems.

○ ZnO-O_2-Rose Bengal (1)
× (1)+Phthalic anhydride
□ (1)+Iodine
△ (1)+*p*-Chloranil

very little effect. The efficiency of sensitization, however, varies from one electron-affinitive molecuce to another. It should be noticed here that the photoconductivity in the ultraviolet region is also much increased by the presence of Rose Bengal. Since Rose Bengal does not absorb light of this wavelength region, the increase can not be caused by optical sensitization. It is most likely that the sensitizing effect by the electron-affinitive molecule is intensified by the co-adsorption of Rose Bengal.

With the zinc oxide co-adsorbed *p*-chloranil and Rose Bengal, this effect has not been observed (see Fig. 4), though quite a large effect of sensitization was observed upon irradiation with the intense white light (see Fig. 2). The discrepancy between the two results can probably be explained by the difference between the incident light—white light and monochromatic light. A superposing effect of the photocurrent, which seems to be responsible for this discrepancy, will be described in the next paragraph.

The photocurrents in the zinc oxide-oxygen-Rose Bengal system and in the zinc oxide-oxygen-*p*-chloranil-Rose Bengal system were measured with ultraviolet (365 mμ), visible (577 mμ) and combined (365 mμ+577 mμ) lights. Here the intensities of the ultraviolet light and the visible light were held constant at 3.24×10^{-6} W/cm². As may be seen in Fig. 5, the photocurrents under co-irradiation were considerably larger than the sum of the photocurrents under separate irradiation. Evidently, there is a co-operative process for the sensitization of the photoconduction in the system,

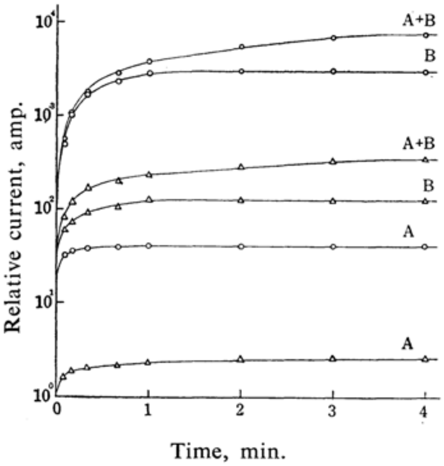

Fig. 5. Rise of photocurrent in dyed zinc oxide irradiated with light of 365 mμ (A), 577 mμ (B) or 365 mμ+577 mμ (A+B).

○ ZnO-O_2-Rose Bengal
△ ZnO-O_2-*p*-chloranil-Rose Bengal

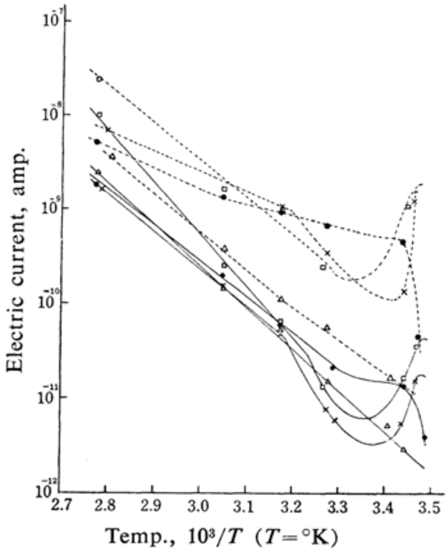

Fig. 6. Temperature dependence of dark- (solid line) and photo-current (broken line). (Light intensity 1.0×10^{-6} W/cm², applied voltage 40 V./cm.)

	Activation energy, eV.	
	dark-	photo-
● ZnO-O_2 (1)	0.89	0.66
△ (1)+*p*-Chloranil	0.76	0.47
□ (1)+Iodine	0.90	0.76
× (1)+Phthalic anhydride	0.79	0.30

which takes place when the system is irradiated simultaneously with ultraviolet and visible lights. We shall call such an effect "the superposing effect of the photocurrent."

The Temperature Dependence of the Electric Current. — The change in photoconductivity upon the adsorption of an electron-affinitive molecule can be caused by the change in the electron density of the zinc oxide crystal and also by the change in surface barrier height. The latter can be roughly estimated from a measurement of the thermal activation energy of the dark-current, which is determined from the temperature dependence of the dark-current.

Figure 6 illustrates the temperature dependence of dark- and photo-currents from 20°C to 90°C in each system without Rose Bengal. The thermal activation energy of the zinc oxide-oxygen system in the dark ($\sim$0.9 eV.) is maintained in the zinc oxide-oxygen-iodine system too, but those of other systems are smaller. The photoconduction requires less activation energy than the dark conduction in each of the systems investigated. It is certain that the adsorption of the electron-affinitive molecule causes a change in the activation energy of conduction which corresponds to a change in the barrier height or surface level.

Discussion

The sensitization of the photoconduction in the ultraviolet region in microcrystalline zinc oxide is considered to be due to the chemisorption and not to the optical effect. This is evident from Fig. 3, where the enhancement of the photoconductivity is not found in the visible region in spite of the fact that the adsorbed molecules more or less absorb light of this region. The chemisorption of the electron-affinitive molecule would increase the dark resistivity of the system by decreasing the electron density in the zinc oxide crystal as well as by changing the surface barrier height, while the chemisorbed molecule may get desorbed or physisorbed when the system is irradiated with the light which is absorbed by zinc oxide, leading to the marked decrease in resistivity. This change in resistivity upon irradiation may depend upon the electron affinity of the chemisorbed molecule and also on the concentration of chemisorbed molecules on the surface. When the electron-affinitive molecule is adsorbed on zinc oxide, the surface level may become more shallow than when only oxygen is present, and at the same time the surface level density may increase.

When both the electron-affinitive molecule and Rose Bengal are adsorbed on zinc oxide, the hypersensitization of the photoconduction takes place (cf. the visible region of Fig. 4). Here, supposedly the electron-affinitive molecule co-operates with Rose Bengal in the optical sensitization process. In other words, the optical sensitization of the photoconduction is intensified by the chemisorbed molecule. Such a process may be understood by adopting Weigl's postulate⁽⁴⁾ on the dye-sensitization mechanism. When the system is irradiated with visible light, the Rose Bengal molecule absorbs the light and injects an electron into the conduction band of zinc oxide. The positively-charged dye ion thus formed captures an electron from a chemisorbed negative molecular ion, e. g., iodine ion or phthalic anhydride ion, returns to the original neutral molecule, and absorbs light again. By repeating this, the chemisorbed molecular ion density on the surface gradually decreases and the surface barrier of zinc oxide is finally eliminated. Therefore, the photosensitivity depends upon the nature and on the surface density of both the dye and the electron-affinitive molecule. However, another possible process, in which an exciton produced by light in dye aggregates elevates an electron from the chemisorbed negative ion directly up to the conduction band of zinc oxide, can not be excluded. One of the present authors (E. I.) and Maki have reported that the photodesorption of oxygen from dye-sensitized zinc oxide occurs upon irradiation with light absorbed by the dye.⁽⁵⁾ This fact supports the processes hypothesized above.

The co-operative effect of the electron-affinitive molecule and dye in the ultraviolet region (Fig. 4) may differ from the above-discussed effect in the visible region. In this case, the fact that Rose Bengal does not absorb ultraviolet light of 350$\sim$400 mμ eliminates the possibility of the optical sensitization. This co-operative effect is probably to be attributed to the change in the surface level of zinc oxide upon the chemisorption of the electron-affinitive molecule.

The superposing effect of the photocurrent in the zinc oxide-oxygen-dye system upon irradiation with the mixed light of the ultraviolet and visible regions (Fig. 5) can be explained as follows. When the dye-sensitized zinc oxide is irradiated with ultraviolet⁽⁶⁾ or visible⁽⁵⁾ light separately, the photodesorption of the oxygen occurs and photocurrent increases,

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3) S. R. Morrison, *Advances in Catalysis*, **7**, 259 (1955).

4) J.W. Weigl, Preprint in "Internationales Kolloquiume über Wissenshaftliche Photographie," Zürich, September, 1961.

5) E. Inoue and I. Maki, The 16th Annual Meeting of Chemical Society of Japan, Tokyo, April. 1963.

6) D. J. W. Bevan and J. S. Anderson, *General Discussion Faraday Soc.*, **8**, 238 (1950).

in different processes. The rate of photocurrent increase should depend on the rate of photodesorption. Under ultraviolet light irradiation, the chemisorbed atomic oxygen ion combines with a hole photo-produced in the valence band of zinc oxide and becomes an neutral atom. Then two oxygen atoms recombine on the surface to form a molecule which gets desorbed into the ambient. On the other hand, under visible light irradiation, oxygen atoms produced by the process mentioned in the discussion of the hypersensitization recombine to form molecules which leave the surface. In both processes, the rate-determining step would be the recombination of the oxygen atoms, a step which is proportional to the square of the oxygen atom concentration on the surface. The rate of the photo-desorption oxygen by co-irradiation with ultraviolet and visible lights will thus become larger than the sum of the rates by separate irradiation. This is considered to be the best possible explanation for the superposing effect of the photo-conduction.

The above findings on the sensitization of the photoconduction in microcrystalline zinc oxide can well be employed in order to raise the photosensitivity of the electrophotographic layer in which zinc oxide powder is dispersed in dielectric resin.

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