# Photoconductivity of An Inorganic /Organic Composites Containing Dye-Sensitized (Zinc Oxide)

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## Abstract

In this paper we study the effect of adding Zinc Oxide powder (ZnO) at different ratios (10%,20%,30%,40%,50%) as particles and organic dyes rhodamine B(RhB), rohdamine 6G(Rh6G) and eosin(EO) are added at different doping ratios to polystyrene (PS), to form photosensitized(PS/ZnO/dye) composites, for samples were prepared as films by spin method. Photoconductive properties are investigated.

For I-V characteristic measurements, the photocurrent ($I_{ph}$) and dark current ($I_d$) are generally increased in non linear behavior with increasing light intensity and applied voltage for all composites. The photocurrent goes decrease through its maximum value at high white light intensities or high voltage for 2.4*10-5mol/l RhB/A composites where A=0.06g PS+0.18g ZnO, while the dark current remains nearly constant.

**Key Words** : Photoconductivity of polymers, ZnO, Dyes, Polystyrene

# Introduction

Photoconductivity is defined as an increase of the electrical conductivity by radiator polymers became photoconductive when the charge carriers to transmit electricity are generated by appropriate radiation as light, and also are insulating or poorly conductive in darkness they may be p-type(hole transportation), or n-type(electron transportation)junction or both types.[1,2]

There are many polymers that are conductive or semi conductive in darkness and only slightly more conductive when exposed to light. Since these polymers belong to the glass of conductive polymers. Polystyrene is a linear polymer, much like the crystalline plastics or partially crystalline, its optical properties-color, clarity and the like – excellent, and its high refractive index (1.59-1.6). It is semi-transparent material, therefore its transmission on approximately 90% comparable to glass [3,4]

Photo conducting polymers have been the subject of considerable research due to their applications as solar-energy conversion devices, photovoltaic and photoreceptors in photocopying technology.[1,2]Sensitization of photoconductivity, or ”doping” refers to the addition of small amounts of impurities to the host substance and its technique is often used to increase the dark conductivity and photoconductivity of the host material in molecular crystals and inorganic semiconductors[5].

Sensitized impurities may be classified into dyes and pigments:

1- Dyes are complex organic molecules containing at least one chromospheres. They are usually completely soluble but pigments are insoluble[6].Dyes can be classified as n-type or p-type conductors depending on the influence oxygen and hydrogen exert on the photoconductivity[7],in some dyes (rhodomines) the conductivity decreases when oxygen is absorbed(n-type) conductance[7].
2- Pigments may be classified to organic pigments such as(yellow FGL,benzidene yellow). In organic pigments are usually metallic oxides, which have been calcined at high temperature. Titanium dioxide and zinc oxide and zinc sulfide survey as white pigments and improve the weatherability of plastic and sensitized photoconductivity of polymers [3,5,6].

In this work we will study ZnO as photoconductivity pigment dispersed in polystyrene to obtain photoconductivity film. ZnO is an example of semiconductor sensor that can be used as a monocrystal, thin film or polycrystalline pellt [8].The percolation theory is a very useful tool to probe the pigment distribution within a polymer matrix. The percolation phenomenon also can be observed in semiconductor-polymer composites with similar behavior to metal-polymer composite[7,8]

During the last years, several studying were curried out for using polymers such as PVK, PS and PC as binder materials. Such binders were doped with different photosensitizing materials from which ZnO, RB, R6G, EO in order to get photoconductivity polymer composites.

Also at the present time the majority of studies of polymer photo conductivity are performed on poly(p-phenylen-vinylene)(ppv). Preparing methods of the samples used in that studies are either physical or chemical doping. The studies which are related to our present work will be introduced separately for each material as follow.

Grammatica and mort [9] studies the photosensitization processes in molecular solids.The photosensitization is shown to be controlled by the dye-transport molecule separation. Additional experiments involving the xerographic discharge of dye/transport molecule doped polymers overcoated with an a-Se sensitizing layer the dual sensitizing and trapping role that dye molecules can play.

Diaz, et al. [10] studies the photo conductivity of ZnO/poly (methylmetlacrylate) particle s RhodamineB was sensitized ZnO-PMMA composites. The result indicates that light and dark conductivity ratio104, and the photoactive response is affected by both the ZnO and the rhodamine B content, and the photocurrent efficiency is comparable to the observed with dye-coated electrodes in electrochemical cell.Nishiguch and Urgu [11] studied the synthesis and photoconductivity of polystyrene containing N- subsitute 5-(p-diethylaminobenzylidene) Rhodamine group inside chains. The content of substitution in polystyrene was 20% mol%. The result shows the wavelength of the peak absorbance of the polymer solution in THF 473nm. Also these composites exhibited very large photoconductivity.

Rafiq[12] studied the double percolation phenomena of blends [(PMMA/PS)/ZnO] composites. Samples were prepared by molded, the effects of filler concentration on the dark current and the photocurrent of above composites were suddenly increased at certain filler content when reached at threshold value. Besides, the experimental results revealed that the polymer has no effect on the intrinsic spectral response of the filler content.

Somani and Radhakrishanan[13] studied the sensitization effect in conducting polyaniline (PANI) by rhodamine 6G. The variation of the dark current($I_d$) and light current($I_{ph}$) with respect to the dye concentration in the linear portion of the current -voltage (I-V) characterization reveals that light current goes through a maximum whereas the dark current remains more or less constant.

# Experimentals

1- Materials:

The polymer material used in this work are commercial, polystyrene(PS) as grain polymer, which supplied by ICI company. The main pigment which was used through this work, Zinc Oxide powder (ZnO), which supplied by Fluka company of purity 97%. The dyes Rhodamine B(RB), Rhodamine 6G(R6G) and Eosin(EO) (Fluka company). Solvents used are methylene chloride(MC) supplied by BDH company of purity 99.99%.

2-Sample preparation:

2-1 Pure polymer film casting

(0.6 gm) of polystyrene were dissolved in (10ml) of methylene chloride to give solutions of 6%(wt/vol). Asmallquantities of the prepared solutions (1-2 ml) was then transferred into a glass slide substrate of 2.5*3.75 cm in dimentions, which predeposited by grade of illuminume electrode, The casted solution on the slide were kept on the almost homogeneous content.

2-2 Polmer film composites

The same above method were repeated to prepare the composite films. The concentrations of the ZnO relative to the pure polymer matrix(inwt/wt ratio) was chosen as(10% to50%). The dyes concentration 10-2(mole/L) is the suitable molar concentration which was chosen for doping polymer/ZnO.

2-3 Measurement

D.C power supply (Philips) were used to study and measure the dark current- voltage($I_d$-V) characteristics of prepared samples, with range (0-40) Volt. Kiethly 616 are used to measure current.

The experimental system for measuring the pohotocurrent is similar to that of dark current only adding light source.

The photocurrent can be calculated from equation $I_{ph}=I_{op}-I_d$

Where $I_{op}$: is the current observed under illumination and $I_d$ is the dark current[14].

3-Optical microscopic:

The morphology of the prepared pure and composites films with various concentrations were examined by an optical microscope, which used to study an investigation the morphology of pure polymeric composites, which indicated the a mount diffusion of ZnO in polymer, The morphology of pure polymeric composites which indicates to excits regular distribution of particles in composite films. As shown in figure(1) with different ZnO concentration

## Results and Discussions

Figure(2,3) shows the variation of dark current ($I_d$) and photo current ($I_{ph}$) as a function of applied voltage for PS/ZnO composites at different ZnO concentrations with light intensity 150mW/cm2 .It is noticed that the both dark and photo current increase with increasing ZnO concentration. These results reveal that the physical mixture system rather than chemical mixture system between ZnO and PS matrix. From these figures we can see, the dark current at low electrical field is low and non linear dependent and then increase linearly with increasing the filled. It was known that the nonlinearly at low voltage region may be attributed to increasing of trapping probability and recombination due to defects and chemical impurities at surface sample. At low electric field the free carrier density is lower and the transit time of these carriers between electrodes is long so that the trapping probability of carriers will be increased by trapping and recombination centers[15,18]. So this leads to fact that the dark current have linear behavior with applied voltage.
The $I_{ph}$-V characteristic was studied by using white light with intensity 150 mW/cm2 , It was observed that the photo current increases at low voltage and then the increase will continue gradually with increased applied voltage up to saturation state of photo current. It is noticed that the trapping and recombination centers are effective at which such centers were relatively unfilled. The saturation of photocurrent caused by the appearance of space charge[7].

Figure(4) shows the variation of dark current and photo current as a function of applied voltage at range of light intensities (61.33 mW/cm2 to 180 mW/cm2 ), for high concentration of ZnO (50% PS +50% ZnO). This composite selected to study the effect of light intensity on $I_{ph}$-V characteristic because it has a linear behavior for photocurrent. The result shows increase the photocurrent with increase of light intensity in which the light is lowering of the potential barrier between PS/ZnO interface [7,13], causing increase in photocurrent up to the saturation $I_{ph}$ with respect to applied voltage occurred due to the maximum carrier concentration to be injected by the electrode coincides with the carrier density of the solid[7,15].

Figure(5) shows the variation of current as a function of intensity of light for various typical composites which have. The polymer matrix such as A=(0.06 gm PS+ 0.18 gm ZnO), 4*10-5 mol/l Rh6G/A, 1.22*10-5 EO/A and 2.44*10-5mol/l RhB/A. generally the results show non linear dependence of light intensity for all composites. At low intensity the results refer to low dependent of photocurrent because the strong effects of free traps on few photogenerated carriers, but at medium intensity the photocurrent increases rapidly because the major traps were filled by electrons, while at high intensity the photocurrent approach the saturation state[15].

Figure (6) shows the variation of photo and dark current as a function of applied voltage at various intensities of light for 2.4*10-5 mol/l RhB/A composites (where A=0.06 gm PS+ 0.18 gm ZnO).The results show that the photocurrent increases with increasing applied voltage. This result is explained with the efficient charge separation that resulted from the transfer of the photoexcited electrons from dye to ZnO[16]. Also the photocurrent after that goes through maximum whereas the dark current remains more or less constant. Also the photocurrent increases with increasing light intensity for up to 106.6 mW/cm2 and then decreases with increasing the light intensity. The decreasing of photocurrent for RB concentration due to increase light intensity or applied voltage attributed to limitation by space charge effect [12,17]. One notices that certain RhB doping not only introduces the desired shallow donor states but also alarge concentration of defect[18].These defects help to form space charge by which increasing light intensity or applied voltage leads to increase space charge by trapping process.

# Conclusions

1- The Zinc Oxide (ZnO) is the fundamental additive which results in dark and photoconductivity in polymer/ZnO/dye composites better than polymer/ZnO. The dependence of dark and photo conductivity on the ZnO/dye content suggests that the charge transfer process can be described by percolation theory.

2- Photocurrent obtained due to increase applied voltage or light intensity is less stability than dark current, and the stability of the current at ZnO composites is better than ZnO/dye composites with polymer.

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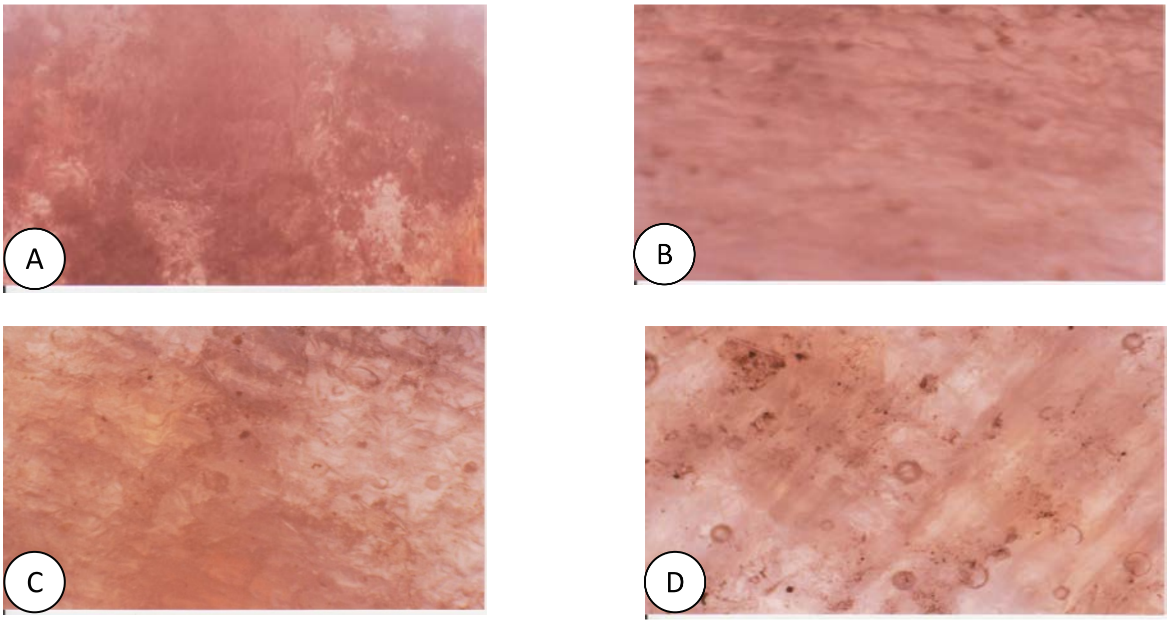
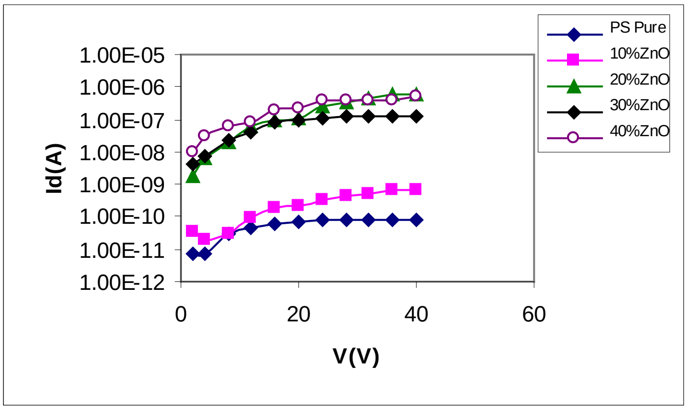



**Fig(1): Photomicrograph (*100) of PS/ZnO composites :**
**(A)10% ZnO , (B) 20% ZnO , (C) 30% ZnO , (D) 40% ZnO**




**Fig(2): Variation of dark current ($I_d$)versus applied voltage (V) for several concentration of ZnO content in PS**

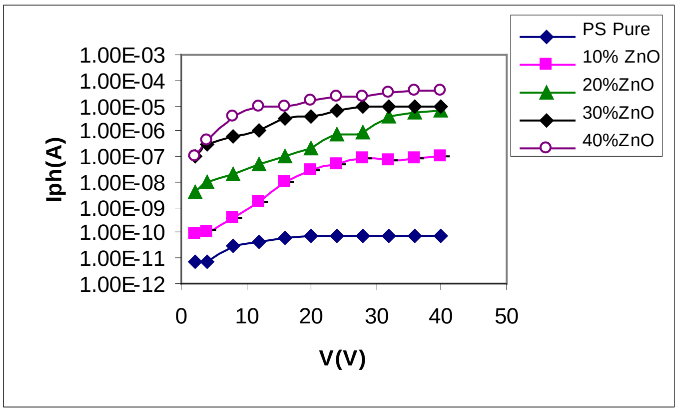



**Fig.(3): Variation of photocurrent($I_{ph}$) versus applied voltage(V) fo r several concentration of ZnO content in PS at white light intensity 150 mW/cm2**

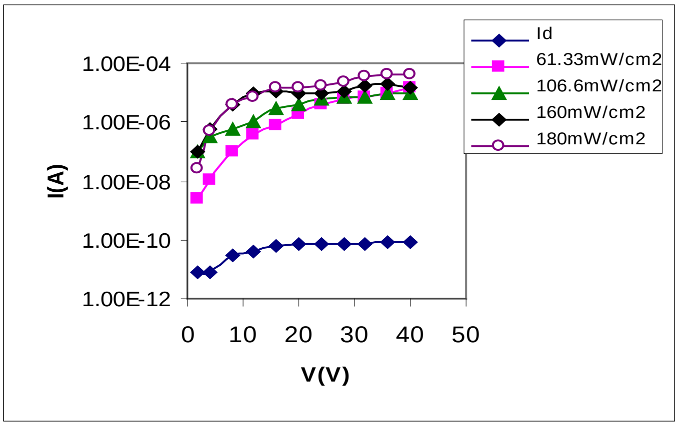
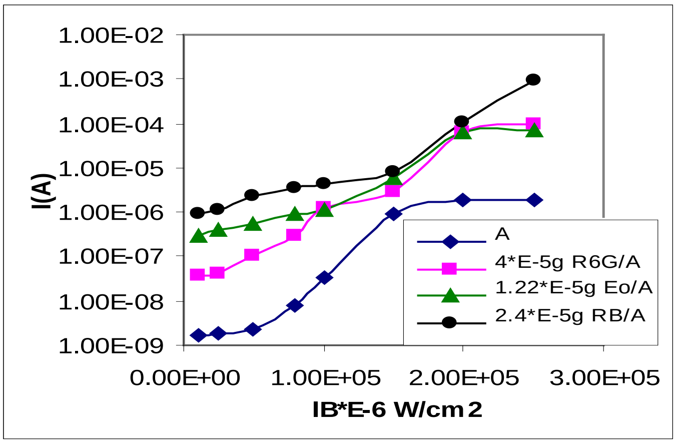



**Fig.(4): Variation of dark current (Id) and photocurrent(Iph) for (50% PS+ 50% ZnO) at different wihte light intensities**




**Fig(5) Current versus white light intensity ($I_B$) of a composite doped with different dyes at 40V. (A=0.06 gm PS+0.18 gm ZnO)**

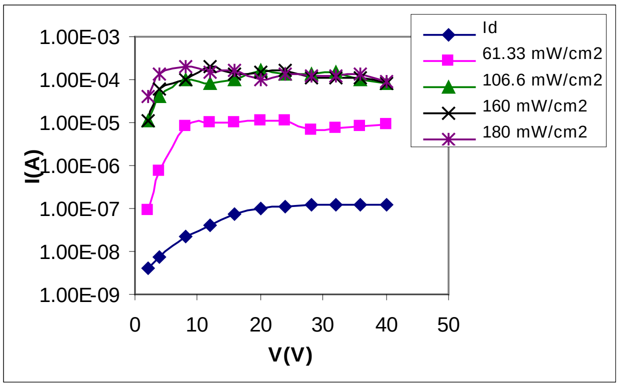



**Fig.(6): Variation of dark current ($I_d$) and photocurrent($I_{ph}$) for (2.44*10-5 gm RhB/A) at different white light intensites, A=0.06 gm PS+ 0.18 gm ZnO**

# التوصيلية الضوئية لمتراكبات عضوية- غير عضوية لأوكسيد الزنك المطعم بالصبغات

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## الخلاصة

في هذا البحث تمت دراسة تاثير اضافة مسحوق اوكسيد الزنك (ZnO) بنسب وزنية (10%,20%,30%,40%,50%)واضافة بعض الاصباغ العضوية مثل رودامين RhB) B) ورودامي6G (Rh6G) والايوسين (EO) الى البولي ستايرين (PS) للحصول على متراكب(PS/ZnO/dyes ). و تأثير هذه الاضافات في التوصيلية الضوئية لهذا المتراكب. اعدت العينات بشكل افلام وبطريقة (Spin method) .حسب تيار الضوء وتيار الظلام من مواصفات منحني تيار- جهد واظهرت النتائج زيادة غير خطية لتيار الضوء والظلام بزيادة الجهد و بزيادة شدة الضوء الابيض لكل المتراكبات وكذلك اظهرت النتائج ان التيار الضوئي يتناقص عن قيمته العظمى للمتراكب 2.4*10- 5mol/l RhB/A (A=0.06g PS+ 0.18g ZnO)بينما يبقى تيار الظلام اكثر ثباتا.

**الكلمات المفتاحية** : التوصيلية الضوئية للبوليمرات،اوكسيد الزنك،دايز،بولي ستايرين