Synergetic enhancement of photoconductivity in chlorodiane blue /oxotitanylphthalocyanine composites*

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Abstract   The nonlinear enhancement of photosensitivity in chlorodiane blue azo (CBA)/ oxotitanylphthalocyanine composites (TiOPc) has been found. Neither evident electronic interaction nor interpenetration between chlorodiane blue and TiOPc molecules is indicated by electronic spectra and X-ray diffraction patterns. Xerographic discharge experiments suggest that the synergetic enhancement of photosensitivity results from contribution of the transition of gap states, which are induced by photoexcitation upon composite photoreceptors. Electron Spin Resonance (ESR) and X-ray Photoelectron Spectroscopy (XPS) data imply that oriented partial charge transfer between TiOPc and CBA molecules occurs when the composites are excited by incident light. This synergetic effect observed in the composite systems with weak electron donor and acceptor provides a novel strategy to design high quality photoconductive materials and devices.

Keywords: chlorodiane blue azo(CBA)/oxotitanylphthalocyanine(TiOPc) composite, photosensitivity, synergetic effect.

Photoinduced charge transfer (PICT) in organic semiconducting composites is an important research subject. PICT has been applied to the designation and fabrication of photo/electronic devices such as organic photocells and photoconducting image sensors[1~4]. The composite materials used in these studies usually contain a typical electron acceptor and a donor. For example, TiO_2 nanocrystals used in Graztel photocells are good electron acceptor as well as electron transport material[1,2]; while in the photovoltaic cell based on the composite of poly [2-methoxy-5-(2'-ethoxyl)-hexyl-*para*-phenylenevin- ylene] (MEH-PPV)/ PCMB (a derivative of C_{60}), PCMB plays the same role as TiO_2 in Graztel cells[3]. In contrary, less research efforts have been made on the PICT mechanism in those composites made from weak electron donors and receptors. Although organic semiconductors with the property of weak donor or acceptor have been commercially applied as photogeneration materials in fax machines, desk-jet printers and photocopy machines, available photoreceptors nowadays are all prepared with single component materials rather than composite materials, and they can only work at high driven field and intense light exposure. Therefore, it is significant to investigate the composite materials of weak electron donor/acceptor and throw light on the insight into related PICT theory.

In our previous studies on the photoconductive properties of phthalocyaninato-compounds[5], we found that ferrophthalocyanine [Fe(Ⅱ)Pc] could be sensitized by copper phthalocyanine [CuPc]. In Fe(Ⅱ)Pc/CuPc composites, a new co-crystal was formed and the co-crystal resulted in an intermolecular partial charge transfer and further led to the enhancement of photoconductivity[6]. The study mentioned above is correspondent to the materials composed of the same kind of dyes or phthalocyanines. In this paper the synergetic enhancement of photosensitivity in composites made from different kinds of dyes (TiOPc and CBA) and the related mechanism will be reported.

1   Experimental

The molecular structures of TiOPc and CBA are shown in Fig. 1. Purified TiOPc and CBA were mixed at a certain ratio and added into a flask previously filled with enough 1, 4-dioxane solvent. Under violent stirring, the mixture was milled with fine glass beards about 6 hours, then a dark blue dispersion was formed, and the particle diameter of the dispersed dyes was no more than 1 μm. After removing the solvent, a series of powder samples was obtained. Their crystallinity was determined on a Rigaku D/max-3B X-ray diffraction instrument, the electron spin resonance data were recorded on an FE-IXG ESR spectrometer, and the electron binding energies of

different elements were determined on an ESCALAB- MK-2 model X-ray photoelectron spectroscopy.
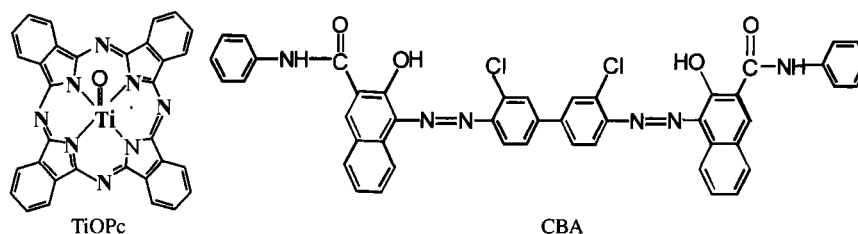

Fig. 1.　Molecular structure of TiOPc and chlorodiane blue azo (CBA).

Stoichiometrical polycarbonate and charge transport material, N, N-diethylamino-α-naphthyl-hydrozone(BAH) were added into the same flask. After adding some more solvent, the mixture was stirred for another 4 hours to form a homogenous blue suspend. A suspend without BAH was prepared in the same procedure. On a polished quartz plate, thin films were cast with the suspend, and the absorption spectra were recorded on a Lambada-20 UV-visible spectroscope. The suspend containing BAH was cast on Al substrates, which were coated previously with a polyimide interlayer (the Al substrates were treated with dilute NaOH solution to remove the Al_2O_3 layer before coating the interlayer). After the solvent evaporated at room temperature, the as-fabricated films were transferred into a vacuum oven, and kept at 60℃ for 24 hours. The photoconductivity of the single-layered photoreceptors was measured on a standard GDP-II photoinduced xerographic discharge apparatus. The incident light intensity was set at 30 lx, the central wavelength of the light source was at 454, 500,570,605,676,703, and 762.5 nm respectively. From this experiment, the half exposure time (defined as the time spanned from the initial of exposure to the time when surface voltage decreased to half of its initial value) and the exposure energy E was recorded, and the photosensitivity of the devices was defined as $S = (Et_{1/2})^{-1}$.

2　Results and discussion

2.1　UV-visible spectra

Fig.2 shows the UV-visible spectra of TiOPc, CBA and their composites respectively. On the feature line of TiOPc, there are two characteristic absorption peaks at 686.5 and 795.6 nm, and they are typical Q-band of phthalocyanines. TiOPc solid usually has two polymorphs: α- and β-type. The Q-band of α-type centers at 830 nm and couples with a pronounced shoulder at around 640 nm, the energy space

is about 180 nm; while in the Q-band of β-type, the central maximum is located at 780 nm, the energy space is smaller than that of α-type. Based on the absorption feature, we assign the polymorph of our TiOPc sample as β-type[7]. There are two absorption peaks (581.7 and 625.5 nm respectively) on the spectrum of CBA. On the spectra of the composites, the position of absorption maximum has shifted. For example, for the composite TiOPc and CBA at 1/1 ratio (by weight) the corresponding absorption bands shifted to 537.03, 624.14, 759.02 and 773.13 nm respectively. But these shifts did not imply the formation of new absorption band, because a precisely similar spectrum can be constructed by linear superposition of the absorption spectra of TiOPc and CBA at 1/1 ratio. The UV-visible spectral study suggests that there is no detectable electronic interaction between TiOPc and CBA at their ground state. This result implies that the photosensitivity can be adjusted by changing the composition of materials, because the carrier's generation efficiency is determined by photoabsorption intensity.
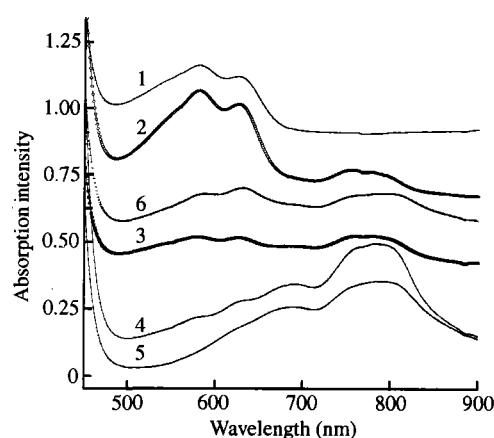

Fig. 2.　Absorption spectra of CBA, TiOPc and their composites. The curves 1 to 5 are the patterns of CBA/TiOPc composite at ratios of 10/0, 8/2, 5/5, 2/8 and 0/10 (by weight) respectively. Curve 6 is simulated by the linear superposition of curve 1 and curve 5 at a ratio of 5/5.

2.2 X-Ray diffraction patterns of the composite powder samples

X-ray diffraction patterns can provide information about the crystalline structure of the components in composite materials. It leads to an elucidation of interaction between the related components before and after they form composites. The X-ray diffraction patterns of TiOPc, CBA and their composites are given in Fig.3, it can be seen from the sharp peaks that the TiOPc powder has high degree of crystallinity, and the peak of 100% intensity is correspondent to the strong diffraction from (001) facets, and the interfacial distance can be calculated to be 3.4 Å. The characteristic diffraction pattern suggests that the polymorph of TiOPc powder sample can be assigned to β-form[7]. This is coincident with the result of UV-visible spectrum. The crystallinity of CBA is relatively low. Diffraction peaks show at 2θ of 6.7°, 7.0°,19.9° and 26.6°, and the related d values are 13.1, 22.5, 4.5 and 3.3 Å respectively. The peaks at 13.1 and 22.5 Å result from the crystal facet arrangement in the axial direction of CBA molecules, which have cis and trans isomers. Isomerization leads to an irregularity and the decrease of the crystallinity. The peaks at 4.5 and 3.3 Å result from the diffraction of conjugated motif stacking in the radial direction, but the assignment of exact stacking modes will be realized by further investigations.

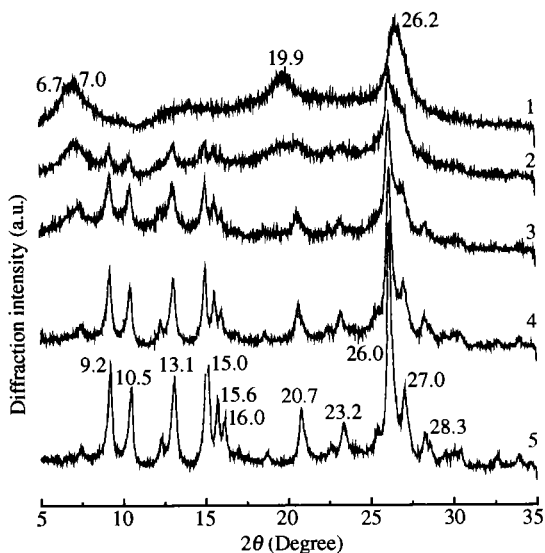In the composite of TiOPc/CBA = 1/1, every characteristic peak of TiOPc and CBA is clearly

shown up in its diffraction pattern, and the 2θ value and the feature of every peak are the replica of that in TiOPc and CBA sample. This result indicates that there is no interpenetration or complexion between TiOPc and CBA molecules, and the composite is simply a mixture of two components. β-form is a thermal-dynamically stable state for TiOPc solid, it can be transformed to other polymorphs by treating with suitable solvent, or by heating to its phase transition temperature. In our experiment, β-form TiOPc is stable in the presence of 1,4-dioxane solvent and CBA molecules. Fig.4 shows the molecular stacking of β-form TiOPc in (001) direction. The d value of 3.4 Å in this direction facilitates a π-π interaction between adjacent TiOPc molecules. The geometric shapes of TiOPc and CBA molecules are greatly different, this intrinsic discrepancy leads to the fact that they cannot form co-crystals as those in composites of Fe(Ⅱ)Pc/CuPc[5,8].
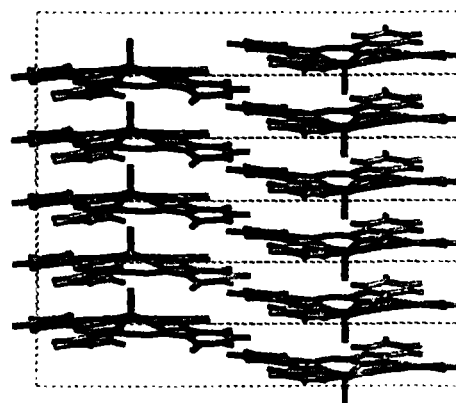

Fig. 4. Molecular stacking along c axial direction in β-polymorph of TiOPc.

2.3 Photoconductive properties of TiOPc/CBA composites

The photoconductive properties of TiOPc, CBA and TiOPc/CBA composites measured with standard photoinduced discharge (PIDC) method, and the experimental data are summarized in Table 1. As a reference, the data obtained from composite of TiOPc/CBA = 8/2 are also listed in the table. These data reveal that the photosensitivity values of pure TiOPc and CBA are 0.4702 and 0.1927 (lxs)$^{-1}$ under an exposure to a light of 762.5 nm and 30 lx, while at the same conditions, the composite materials (TiOPc/CBA = 5/5 and 8/2) reach 3.3333 (lxs)$^{-1}$, which is about 7 and 20 times of that in pure TiOPc and CBA respectively, so the enhancement in photosensitivity is effective. Furthermore, the data suggest

Fig. 3. X-ray diffraction patterns of CBA, TiOPc and their composites. The curves 1~5 are the patterns of CBA/TiOPc composite at ratios of 10/0,8/2,5/5,2/8 and 0/10 (by weight) respectively.

that the photosensitivity of the composite materials is not a linear superposition of those of TiOPc and CBA, but shows a synergetic enhancement. This fact implies that the photoreceptors fabricated by suitable composites can attain desirable photosensitivity at lower driven field, which provides the possibility to develop photoconductive devices working at low electric field.

Table 1.   Photosensitivity in CBA/TiOPc composites [$(lxs)^{-1}$]

AZO/ TiOPc	Wavelength (nm)						
	454	500	570	605	678	703	762
10/0	0.2489	0.4762	0.1927	0.3333	2.5641	0.5291	0.1927
8/2	0.2506	0.3184	0.1406	0.3030	3.3333	2.5641	3.3333
5/5	0.4505	0.3968	0.1792	0.1650	0.7937	1.1111	3.3333
0/10	0.1065	0.1138	0.1149	0.0894	0.2778	0.3764	0.4762

The UV-visible spectra and X-ray diffraction patterns have confirmed that at ground state there is no evident interaction between TiOPc and CBA, thus the synergetic enhancement in photosensitivity must come from photoinduced excited states. In Fig. 5 we demonstrate the change in photosensitivity with the wavelength of action light and the absorption spectrum of the CBA. The most sensitive wavelength for the photoconductivity of CBA is longer than the wavelength of the absorption maximum. Such an asymbatic phenomenon between absorption and photoconductive action spectra has been observed in many researehes on other organic photoconductive properties[9]. A well accepted explanation is as follows: there exist large amount of defects in organic semiconducting materials, which result in the formation of gap states, and these gap states are located between conducting band and valance band, and they can be thermally excited or excited by the radiations whose energy is lower than the energy gap. Such gap states can substantially contribute to the photoconductivity. The X-ray diffraction patterns show that CBA has rather low crystallinity, while TiOPc exists in the powder sample of polymorph state; the crystallinity of TiOPc/CBA composites decreases and the corresponding structural defects increase. On the other hand, the geometric shapes of azo and phthalocyanine molecules are extremely different, and the structural difference leads to the nonlinear amplifying of the defects, thereby leads to the nonlinear increasing of gap states which contribute to the synergetic enhancement in photosensitivity, although the nonlinear amplifying of the defects cannot be revealed evidently on X-ray diffraction patterns.
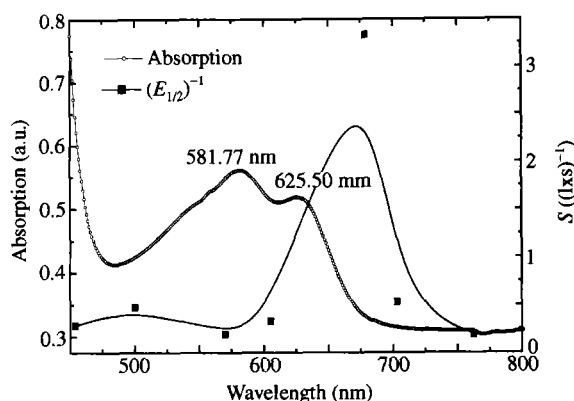

Fig. 5.   Absorption intensity and change in photosensitivity of CBA with the wavelength of incident light.

2.4   ESR and XPS spectra of TiOPc/CBA composites

In an ideal state, no ESR signal should be detected because there is no single or uncoupled electron in TiOPc and CBA molecules, but as organic semiconductors, both TiOPc and CBA can be excited by light or thermal to form single electron state, so detectable electron spin resonance can be measured under ambient temperature and light exposure. For TiOPc, CBA and their composites, the data of spin concentration recorded before and after the radiation of UV light are listed in Table 2, all the data have been calibrated with a diamond thin film. The obtained results indicate that the radical concentrations for both TiOPc and CBA are boosted up by UV light; but in the composites, the radical concentration becomes lower after exposing the sample to UV light. This is also true for the composite of TiOPc/CBA = 8/2.

Table 2.   Radical concentration of the CBA/TiOPc composites

TiOPc/ AZO	UV light	N_x ($\times 10^{17}$/g)	P ($\times 10^{-4}$)	N_x' ($\times 10^{17}$/g)	P' ($\times 10^{-4}$)
10/0	No	1.338	1.279	1.338	1.279
	Yes	1.615	1.545	1.615	1.545
8/2	No	1.129	1.144	1.082	1.096
	Yes	1.227	1.243	1.308	1.325
5/5	No	0.951	1.058	0.698	0.777
	Yes	0.900	1.001	0.847	0.942
0/10	No	0.059	0.079	0.059	0.079
	Yes	0.078	0.103	0.078	0.103

N_x is the radical concentration and P is the probability with which a molecule of composites becomes free radical. N_x' and P' are obtained by calculation.

Excited by incident light, part of the valance electrons experience a transition to excited states and

form single electrons, then the spin concentration increases logically. It is an abnormal observation that the spin concentration in the composites decreased after exposure to UV light, and a reasonable explanation is photoinduced charge transfer — the decrease of ESR signals in composites could be ascribed to the coupling or annihilation of single electrons generated in TiOPc and CBA molecules by light excitation. Two ESR signals have been recorded at $g = 1.997$ and $g = 2.222$ respectively. Considering that the free electrons give signal at $g = 2.0012$, the data in Table 2 show only the change of the signal of $g = 1.997$, which is corresponding to the single electrons being weakly bounded. It is obvious that the signal of TiOPc is much stronger than that of CBA. When keeping the samples in a dark chamber, the magnitude of ESR signal decreases with the decreasing TiOPc amount in TiOPc/CBA composites. When the samples are exposed to the visible light centered at 570 nm, the CBA molecules, which are sensitive to this band, will absorb the photons and become excited, and then the electrons will transfer from the excited molecules to the molecular orbit in TiOPc resulting in the annihilation of the single electrons in TiOPc molecules. However, in a single component charge generation layer, or in the composites kept in dark, the annihilation process cannot occur, consequently, in TiOPc/CBA composites the ESR signal will decrease when the samples are exposed to light source. It is well known that the photogenerated excitons can only be dissociated to form weak bounded electron-hole pairs at high applied field, the ESR signals cannot be ascribed to the electrons generated by $\pi\text{-}\pi^*$ transition but to those dissociated from gap states. This deduction is in agreement with the results of photoinduced discharge experiment.

In order to further investigate the synergetic enhancement of photoconductivity in TiOPc/CBA composites, we conducted XPS measurement on powder samples of TiOPc, CBA and their composites. The XPS measurement revealed profound information about electronic structure of organic dyes and pigments in solid states[5,10]. We have summarized the binding energies of C_{1s}, N_{1s}, $Ti_{2p3/2}$ in Table 3, the binding energy of C_{1s}(284.6eV) was used as the reference for calibration. Theoretical calculation suggests that 8 C atoms and 8 N atoms of phthalocyanine contribute 18 electrons to form an aromatic phthalocyaninato- macrocycle, and when it acts as ligand coordinating with metal ions, the 8 N atoms are in the same

chemical environment; only a sharp single peak at 400.02 eV is found on the XPS spectrum of TiOPc. There are two kinds of N atoms in a CBA molecule, one is in the imide group and the other is in azo group; they appeared at 399.5 and 400.48 eV respectively.

Table 3.   Electron binding energy(eV) of CBA/TiOPc composites

AZO/TiOPc	C_{1s}	N_{1s}(CBA)	N_{1s}(CBA)	N_{1s}(TiOPc)	$Ti_{2p3/2}$
10/0	284.6	399.50	400.48		
8/2	284.6	399.64	400.70	398.51	456.99
5/5	284.6	399.94	400.84	398.79	457.85
0/10	284.6			400.02	459.16

The change of binding energy reflects the change of the distribution of electron density over the atomic nucleus; when the electron density in the valance shell decreases, the binding energy of electrons in the inner shell increases because they are less shielded by valance electrons and vice versa. From Table 3 it can be found that in composite of TiOPc/CBA = 5/5, the N_{1s} binding energy of azo group shifts from 400.48 eV to 400.84 eV, while the N_{1s} binding energy of TiOPc shifts from 400.02 eV to 398.79 eV; the $Ti_{2p3/2}$ binding energy shifts from 459.16 eV to 457.85 eV. These results indicate the dropping of electron density in azo group or CBA molecules and the rising of electron density in TiOPc molecules. Based on the above data, we argue that a photoinduced charge transfer from CBA to TiOPc molecules takes place in the composite. The XPS measurement results confirm the conclusion derived from ESR experiment and the photoinduced discharge experiment.

3   Conclusions

A synergetic enhancement of photoconductivity has been found in composite photoreceptors with weak electron donors (CBA) and weak electron acceptors (TiOPc). The absorption spectra of the composites show that there is no detectable electronic interaction between TiOPc and CBA molecules in the ground state. X-ray diffraction patterns demonstrate that composing TiOPc and CBA in the same charge generation layer do not result in the complex and co-crystals, but lead to a decrease of crystallinity and an increase of defects. The gap states incurred from defects can make the photoconductive action spectrum of CBA greatly asymmetrical from the absorption spectrum, and steady state photoconduction begins before the absorption edge. The ESR and XPS measurements confirm the process of photoinduced electron transfer from CBA to TiOPc. The nonlinear increase

of defects and gap states that result from composing different dyes can be ascribed to the synergetic enhancement of photoconductivity in TiOPc/CBA composites. This synergetic enhancement effect found in the system with weak electron donors and acceptors is promising in the field of developing photocopier, fax-machine, laser jet printer and photoconductive image sensors.

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