

Synergetic enhancement of photoconductivity in oxotitanium phthalocyanine nanocrystalline/ fluoronone-based azo/ BAH composite photoreceptors^{*}

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Abstract A simple method of liquid phase direct precipitation (LPDP) is employed to prepare oxotitanium phthalocyanine (TiOPc) nanoparticles. By encapsulation within casein coating, the TiOPc nanoparticles exhibit uniform and well-controlled particle sizes. The results of photoinduced discharge experiment demonstrates that the photoconductivity of the photoreceptors fabricated with TiOPc nanoparticles and fluoronone-based azo pigments as composite carrier generation materials was substantially enhanced. The photosensitivity has been improved three times as the TiOPc particle size decreased from 100 nm to 40 nm.

Keywords: nanocrystalline photosensitivity, composite.

Oxotitanium phthalocyanine (TiOPc) is widely used as photogeneration material in xerographic photoreceptors due to its better thermal and chemical stability, and a high photogeneration efficiency^[1,2]. The photoreceptors based on the blends of TiOPc and polymer binders have excellent sensibility in near infrared spectral region, so that they are commercially employed to the desk-jet printers and fax machines. Recently, Wang et al.^[3-6] reported that the photoreceptors fabricated with TiOPc and azo composite pigments showed both wide spectral sensitization and synergetic enhancement in photosensitivity. The tri-component composite photogeneration material of TiOPc/ chlorodiane blue/ *para*-N, N'-diethylphenyl- α -naphthyl-hydrazone (BAH) system exhibited the enhanced photosensitivity in full visible spectral range^[7]. The enhancement has been ascribed to a step-wise photoinduced charge transfer mechanism. Based on this model, we employed a fluoronone-based azo instead of the chlorodiane blue to prepare a tri-component composite photogeneration material of TiOPc/ fluoronone based azo /BAH system, which showed a higher photosensitivity than that of TiOPc/ chlorodiane blue/BAH system. In consideration that nanoparticles have drastically enlarged surfaces, which is helpful to the charge transfer process between photogeneration and transport materials, we prepare TiOPc nanoparticles using the liquid phase di-

rect reprecipitation (LPDP) method. The photosensitivity of TiOPc nanoparticles under the monochromic light of 762.5 nm is higher than that of the microparticles under the same conditions^[8]. In this paper, the synergetic enhancement of photoconductivity in composite photoreceptors fabricated from TiOPc nanoparticles /fluoronone-based azo/BAH systems will be reported. The experimental results revealed that the nanofication of the TiOPc component led to a substantial enhancement in the photoconductivity and a size-dependent effect of photosensitivity.

1 Experimental

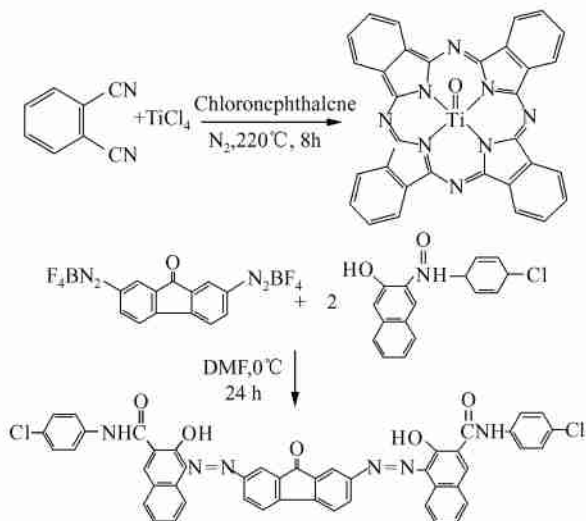
1.1 Materials

TiOPc was prepared by the standard synthetic method, and the synthetic route towards fluoronone-based azo is shown in Scheme 1. Casein was purchased from Alrich. The charge transport material *para*-N, N'-diethylphenyl- α -naphthyl-hydrazone (BAH) was commercially available and used directly. Polycarbonate (PC) was purchased from Aldrich and purified by dissolving in chloroform and precipitating with ethanol twice, and used as the binder. Polyamide was purchased from Acros and used in the interface layer between aluminum substrate and the charge generation layer (CGL). The aluminum was treated by dilute basic solution and cleaned with pure

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water for removal of surface oxide layer. Other chemicals or solvents were of AR grade.



Scheme 1. Synthetic route to TiOPc and fluorinone-based azo.

1.2 Fabrication of nano-TiOPc

Casein is an amphiphilic botanical polypeptide and was used directly to prepare a 2% solution with pH 11. Because the solubility of TiOPc is extremely low in most of organic solvents but it can be dissolved in concentric sulfuric acid, we added TiOPc/concentric H₂SO₄ solution (~0.01 g/mL) from a dropping funnel into casein solution with vigorous stirring at different temperature. The mixture turned to blue rapidly and finally became a dark blue viscose solution. TiOPc-coated casein particles were precipitated by adjusting the pH value. The deposit was filtrated and washed with pure water to pH 7, then dried in a vacuum oven for 48 h at 60 °C. The obtained dry powder could be readily or after removing the casein layer blended with host polymers to fabricate casting or spin-coating films for photoconductivity measurements.

1.3 Fabrication of the photoreceptors

Stoichiometric amounts of TiOPc and fluorinone-based azo solvent were added into a nitrogen flushed flask with violent stirring at ambient temperature for 6 h, then stoichiometric amounts of BAH and PC were introduced into the system and stirring was continued for 4 h, finally a dark blue suspension was obtained. During the stirring, a charge blocking layer with a thickness of ~1 μm was cast from a 5% polyamide ethanol solution onto the clean surface of as-treated aluminum substrates. After the interface layer was dried, the blue suspension was cast onto it

to form the dual-functioned layer for charge generation and transport. The whole device was transferred into a vacuum oven at about 50 ~70 °C for 2 h, and a single layered photoreceptor was fabricated.

1.4 Measurement of photoconductivity

The photoconductivity of the obtained single-layered photoreceptors was measured using a standard photoinduced discharge technique, which constitutes the basis of xerographic process in the photocopying system. The surface of a photoreceptor was firstly negatively corona charged to a surface potential V_0 , after a dark discharge for 3 seconds and the surface potential dropped to V_i , the photoreceptor was exposed to a light of intensity I . The photoinduced electron-hole pairs were immediately generated upon the photon absorption. The photogenerated pairs dissociated to give rise to free carriers with the aid of external field and the free holes migrated towards the negatively charged surface following the applied field through the conductive channels provided by the transport materials^[9]. Thus the surface charges were neutralized and only a rather low potential V_r remained. From the discharge experiment we can obtain the parameter of half-discharge exposure energy, i.e. $E_{V/2} = t_{V/2} I$, where $t_{V/2}$ is the time from initial potential V_i to its half value under exposure to light. Photosensitivity S is defined as the reciprocal of $E_{V/2}$, $S = 1/E_{V/2}$. The light source used in our experiments was a halogen lamp (5W, 24V), and the monochromatic wavelengths were 500, 570, 605, 678.7, 703 and 762.5 nm by penetrating through optical filters respectively. Based on these parameters, and under an identical illumination intensity I , a promising photoreceptor will give high S values.

2 Results and discussion

2.1 TEM of nanoparticles

TEM photographs of TiOPc particles coated with casein layer at different temperature are shown in Fig. 1. It can be seen that a light gray layer wrapping the dark TiOPc particles for the film of casein has a lower electron density. These photographs indicate that the grain size of nanoparticles decreases with the rising of the temperature. The grain size of nanoparticles is about 100 nm at 25 °C, while it is about 60 nm at 40 °C and is about 40 nm at 60 °C. The classical physical methods such as milling with glass beads in organic solvent can also obtain nano-

sized TiOPc particles, but the size distribution ranged from several ten up to several hundred nanometers even to several micrometers. Such a large discreteness in particle size often results in an instable photoconductive performance and the fatigue of the photoreceptors. As a result, the surface modification method provides a reliable approach for obtaining uniform-sized organic nanoparticles.

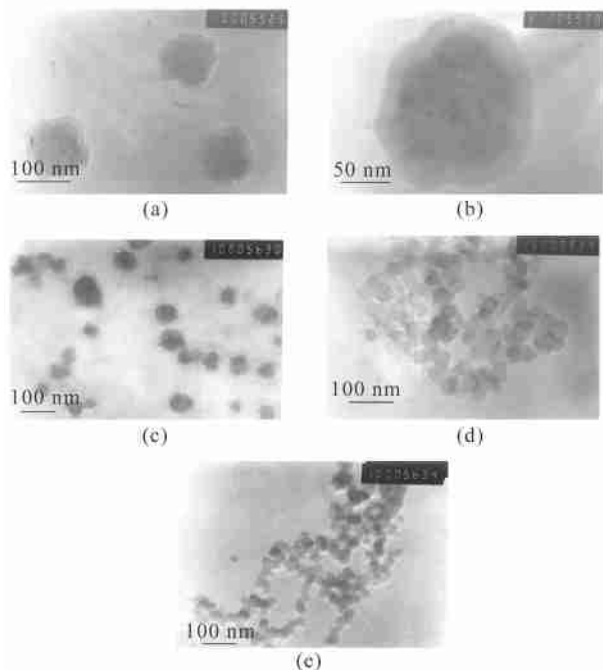


Fig. 1. TEM images of the TiOPc nanoparticles prepared at different temperature of (a) 25 °C, (b) 25 °C, (c) 40 °C, (d) 60 °C and (e) 80 °C, respectively. The TEM image (b) clearly demonstrates the encapsulating of TiOPc into the casein layer.

It is well known that blends of polymer and organic/inorganic particles tend to phase separate on account of low mixing entropy. Furthermore, for the typical planar π -conjugated molecules, the existence of strong π - π interaction between TiOPc molecules will result in self-assembly to form large aggregates. These two factors will cause degrading of the properties of photoreceptors. While the casein encapsulated TiOPc nanoparticle we prepared could be dissolved in KOH/H₂O solution and kept clear blue for at least a whole year. And they can disperse in polycarbonate matrix, forming the stable and uniform film without any detectable morphology changes during the fabrication. Thus this approach is a new strategy to making stable composites of bi- or multi-components that are incompatible to each other.

2.2 X-ray diffraction of nanoparticles

The X-ray diffraction patterns of pristine TiOPc

and decoated TiOPc nanoparticles are depicted in Fig. 2. It can be seen from the sharp peaks that the pristine TiOPc powder has a 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^[10]. The X-ray diffraction pattern of the decoated TiOPc nanoparticle shows a typical feature of low crystallinity and the diffraction peaks can be partly indexed to the alpha polymorph of TiOPc.

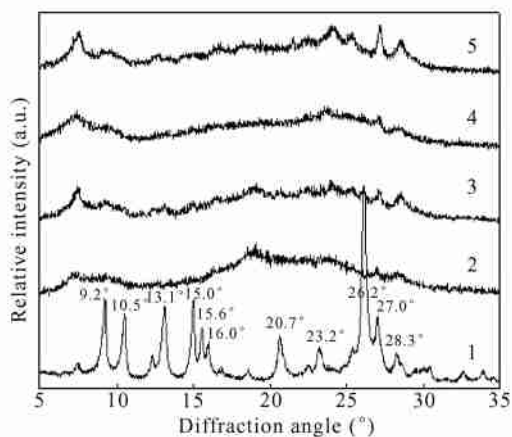


Fig. 2. X-ray diffraction patterns of different TiOPc powders. Curve 1, bulk sample; 2, 100 nm; 3, 60 nm; 4, 40 nm; 5, 30 nm.

2.3 Photoconductive properties

Summarized in Table 1 are the photoconduction parameters obtained from the photoinduced discharge experiment. According to the principle of photoinduced discharge experiment, small $t_{1/2}$ value implies a high photogeneration efficiency and the high S value corresponds to a good photoconductivity. A quantitative comparison of the $t_{1/2}$ values for different sizes of TiOPc nano-particles reveals that shorter $t_{1/2}$ and higher photosensitivity are associated with a smaller nanoparticle size. For example, upon illumination at $\lambda = 762.5$ nm, the photosensitivity S approached $0.615 \text{ cm}^2/\mu\text{J}$ when the average size of TiOPc nanoparticles is 40 nm. Such an S value is three times bigger than that observed from 100 nm TiOPc nanoparticles.

The variation of the photoconductivity with the changing of TiOPc nanoparticle size can be directly observed in Fig. 3. With the decreasing size of TiOPc nanoparticles, the related photoconductivity increases accordingly, except for TiOPc nanoparticles with the average size of 30 nm obtained at 80 °C. At such a high temperature the TiOPc reacted with sul-

uric acid and the photosensitivity of sulfonated TiOPc was lower than that of TiOPc. The results suggest that the photoconduction property of the composite photoreceptors can be substantially improved by using nanoscale photogeneration materials. The enhanced photoconductivity can be ascribed to the mechanism of the improved interface charge transfer efficiency. It is well-accepted that smaller nanoparticles have larger specific surfaces; as a result, the smaller TiOPc nanoparticles have larger contact areas with the charge transport materials. The carriers generated in the smaller TiOPc nanoparticles are easier to be injected into the conduction band of the transport materials. On the other hand, the primary photoexcitation in organic solid is usually excitonic, and the excitons disassociated more easily in the smaller particles because of their smaller Frenkel radii.

Table 1. Photoconductivity parameters for various TiOPc nanoparticles at different wavelengths (at intensity of $50 \mu\text{W}/\text{cm}^2$)

Particle size (nm)	Wavelength (nm)	$t_{1/2}$ (s)	S ($\text{cm}^2/\mu\text{J}$)
100	500	0.71	0.113
	570	0.66	0.121
	605	0.71	0.113
	678.5	0.41	0.195
	703	0.24	0.333
	762.5	0.39	0.205
60	500	0.63	0.127
	570	0.60	0.133
	605	0.45	0.178
	678.5	0.25	0.320
	703	0.18	0.444
	762.5	0.23	0.348
40	500	0.42	0.190
	570	0.32	0.250
	605	0.31	0.258
	678.5	0.12	0.667
	703	0.15	0.533
	762.5	0.13	0.615
30	500	0.49	0.163
	570	0.40	0.200
	605	0.40	0.200
	678.5	0.15	0.533
	703	0.19	0.421
	762.5	0.14	0.571

3 Conclusions

In summary, our study shows that TiOPc nanoparticles can be readily obtained by treating TiOPc sulfuric acid solution with an amphiphilic polymer—casein. Casein-coated nanoparticles are stable both in KOH solution and in the suitable polymer matrix. The single-layer photoreceptors based on deoated

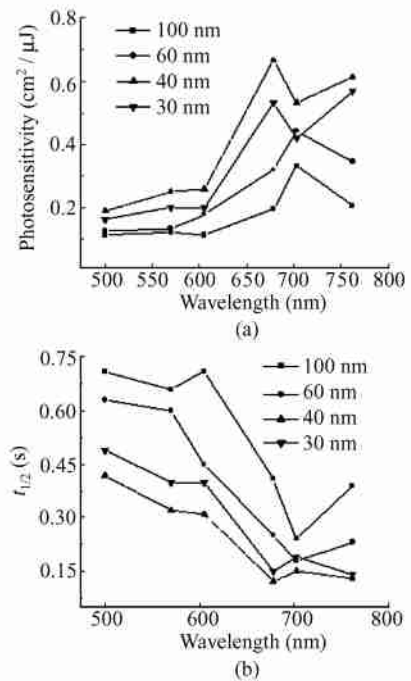


Fig. 3. Variation of S (a) and $t_{1/2}$ (b) values with the TiOPc nanoparticle sizes at different illumination wavelengths.

TiOPc nanoparticles and fluorone-based azo composites show enhanced photoconductivity. In the regime of our experiments, the photoconductivity of the composite photoreceptors is improved as the size of TiOPc nanoparticles decreased from 100 nm to about 40 nm. These composite organic photogeneration nano materials provide the opportunities for potential applications in development of high performance photoreceptors.

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