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Preparation and characterization of chloroindium phthalocyanine nanoparticles from complexation-mediated solubilization

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Chloroindium phthalocyanine (InClPc) nanoparticles embedded in poly(N-vinylcarbazole) (PVK) are obtained by the method of complexation-mediated solubilization, where InClPc is dissolved in high concentration in the aprotic organic solvent containing Lewis acid for the formation of electron donor-acceptor complexes. The fabricated InClPc nanoparticles are characterized by means of UV/VIS absorption, X-ray diffraction pattern, and TEM. The results show that the InClPc nanoparticles are spherical with a size of 25–50 nm. The broader diffraction peaks and the blue-shifted absorption for InClPc nanoparticles are observed. The photoconductivity of the InClPc nanoparticles in a single layered photoreceptor is investigated as well. © *2003 Kluwer Academic Publishers*

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1. Introduction

Much attention has been paid to the preparation and characterization of nanometer scaled particles or microcrystals recently [1–3]. One important reason for this is that nanoscopic materials may display unique optical, electronic, catalytic, and structural properties, which are not presented in either isolated molecules or macroscopic solids [4–6]. However, most of the research focused on inorganic materials, such as metals, oxides and non-metals, which were formed by a metal bond or a covalent bond. Very few reports were found on the preparation of nanometer particles from organic molecular crystals. So, it is strongly requested to develop new preparation methods for extending studies to organic nanoparticles. In the field of photoconductivity, Koyman *et al.* found that the photoconductivity of the organic azo pigment depended on the size of the crystal in the early 1990s' [7]. Both Enokida [8] and Saito [9] reported the size effect on the absorption properties and charge generation efficiency of metal-free phthalocyanine particles prepared by the traditional milling method. Nanoscaled effects on photoconductivity of conjugated polymers were observed by Zhang in 1996 [10].

Nanoparticles in organic polymers or inorganic glasses are of a particular interest from both a fundamental viewpoint and applications for optoelectronic devices [11]. In our previous work [12, 13], we have fabricated oxotitanium phthalocyanine (TiOPc), an organic photoconductive pigment, into nanoscaled particles embedded in the polymer resin by the methods of mechanical sand grinder and liquid phase direct reprecipitation, and found that the photoconductivity of TiOPc increased with decreasing the size of TiOPc nanoparticles. In this work, we propose a new method of complexation-mediated solubilization for preparing organic nanoparticles of chloroindium phthalocyanine (InClPc) embedded in poly(N-vinylcarbazole) (PVK). The photoconductivities of InClPc nanoparticles in the single layered photoreceptors are investigated as well.

2. Experimental

2.1. Materials

InClPc was synthesized according to the published procedure [14], and was purified via the train sublimation. PVK was purchased from Aldrich and was purified by dissolving it in chloroform and precipitated with ethanol. Trichloroaluminium ($AlCl_3$), nitromethane (NM), nitrobenzene (NB), tetrahydrofuran (THF), N,N′-diethyl-4-aminobenzaldehyde-1-phenyl-1′-(α-naphthyl)-hydrazone (BAH), bisphenol A type polycarbonate (PC), and other reagents were commercially available and of analytical grade.

2.2. Preparation of InClPc nanoparticles

InClPc, $AlCl_3$ and PVK were added into a vial containing NM or NB under an N_2-atmosphere. The solution was heated to about 40–60°C on a hot plate with stirring, during which transparent and black-green InClPc-$AlCl_3$ solution could be formed. The solution was precipitated with ethanol, and the blue powder was dried

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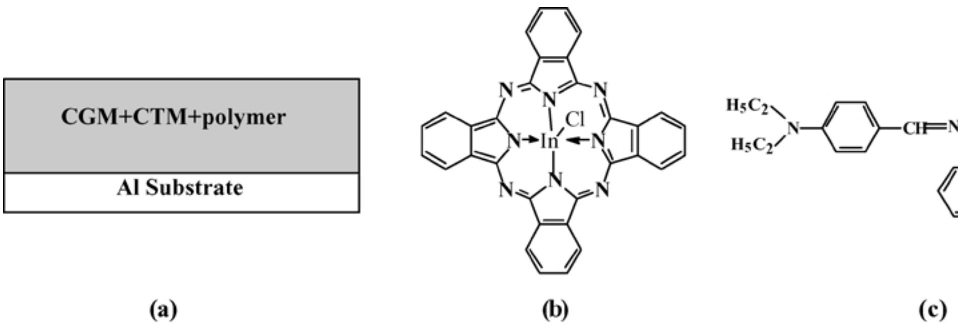

Figure 1 The structure of (a) single layered photoreceptor, and the molecular structures of (b) InClPc and (c) BAH.

at 70°C in the vacuum, leading to the product of InClPc nanoparticles embedded in PVK polymer.

2.3. Characterization of InClPc nanoparticles

The dried powder above was dispersed in THF, and then was deposited as a thin film on quartz plates for UV/VIS absorptions recorded on a Lambda-20 spectrophotometer. A piece of copper net was dipped into the mentioned InClPc-$AlCl_3$ solution, submerged in ethanol in order to remove $AlCl_3$, dried in air, and then used to record the image of InClPc nanoparticles on a Hitachi 600-4 transmission electron microscopy (TEM). The dried powder of InClPc nanoparticles embedded in PVK was used directly to record the X-ray diffraction patterns on a Rigaku D/max-3B X-ray diffraction device.

2.4. Photoreceptor fabrication and photoconductivity measurement

InClPc nanoparticles embedded in PVK was added into 1,4-dioxane solution dissolving BAH and PC. The single layered photoreceptor (PR) was prepared by dip-coating the mentioned mixed suspension onto an Al substrate with a thickness of about 20 μm, where InClPc nanoparticles served as the charge-generation material (CGM) and BAH as charge-transportation material (CTM) (Fig. 1). For a comparison, the single layered PR was prepared as well in the same way by changing InClPc nanoparticles embedded in PVK to the bulk InClPc, and the concentration of InClPc was the same for the PR formed with the nanoparticles and bulk materials.

Photoconductivity measurements were carried out by the photoinduced xerographic discharge technique on a GDT-II model photoconductive measuring device. A halogen lamp (5 W, 24 V) was used as light source. The monochromatic wavelengths of 678, 703 and 762 nm were obtained by optical filters. In the measurement, the surface of the single layered PR was negatively charged in the dark, and the light intensity of the exposure (**I**) was controlled at 5 μW. Upon the exposure, the surface potential decreased, and the photoinduced discharge curve of the device was recorded, from which the time from the original potential to half under exposure ($t_{1/2}$) and the half decaying exposure energy ($E_{1/2}$, the product of $t_{1/2}$ multiplied by **I**) were obtained [15]. The photosensitivity was characterized by the reciprocal of $E_{1/2}$. The bigger the $E_{1/2}^{-1}$, the higher the photosensitivity.

3. Results and discussion

3.1. Preparation of InClPc nanoparticles

Due to their molecular structures and strong intermolecular interactions, metal phthalocyanines, such as ZnPc, CuPc, TiOPc and InClPc, have a great solubility in concentrated sulfuric acid but a poor one in common organic solvents, which inhibits the preparation of their nanoparticles by liquid-phase method. In the present paper, properties of InClPc solutions in the aprotic organic solvents, e.g., $AlCl_3$/NM and $AlCl_3$/NB, are investigated.

As shown in Table I, InClPc has a poor solubility in NM, NB, DMF, DMSO and acetone with blue color. After adding $AlCl_3$, the solubility in NM and NB solvents increases greatly by changing the color from blue to green, but no changes are observed in DMF, DMSO, and acetone solvents in terms of solubility and color. It can be seen from the absorption intensity in Fig. 2 that the solubility of InClPc

TABLE I Properties of organic solvents and InClPc solutions

Solvent	Boiling point[a] (°C)	Dielectric constant [a] (ε)	Donor number[b]	Acceptor number[b]	Solubility (without $AlCl_3$)	Solubility (with $AlCl_3$)	Solution color before & after adding $AlCl_3$
NM	101	35.9	2.7	20.5	Poor	Good	blue → green
NB	211	34.82	4.4	14.8	Poor	Good	blue → green
DMF	153	36.7	26.6	16.0	Poor	Poor	blue → blue
DMSO	189	46.68	29.8	19.3	Poor	Poor	blue → blue
Acetone	56	21.6	17.0	12.5	Poor	Poor	blue → blue

[a] J. A. Riddick, W. B. Bunger, Techniques of Organic Chemistry. Organic Solvents, 3rd ed, Wiley-Interscience: New York, 1970, Vol. 2.

[b] V. Gutmann, The Donor-Acceptor Approach to Molecular Interactions, Plenum Press: New York, 1978.

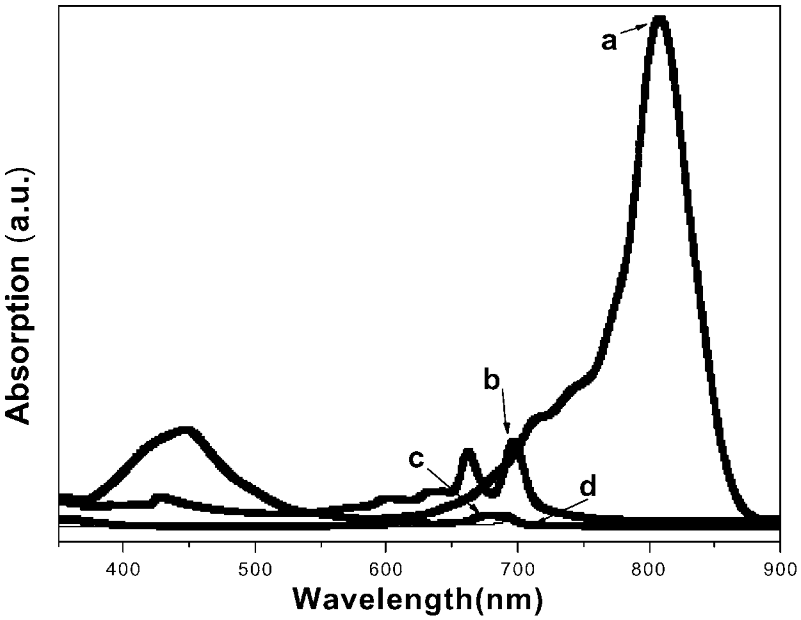

Figure 2 UV/VIS spectra of InClPc in (a) concentrated H_2SO_4, (b) $AlCl_3$/NB, (c) DMF, and (d) NB.

in solvents are in the decreasing order: concentrated $H_2SO_4 > AlCl_3/NB >$ DMF > NB. The concentration of InClPc in $AlCl_3$/NB is 8 and 16 times higher than that in DMF and NB, respectively. These observations indicate that there must exist a strong interaction between $AlCl_3$ and InClPc molecules which favors the solubility of InClPc.

There exist two competitive reactions during dissolving InClPc in the organic solvent/Lewis acid system. One is the reaction between InClPc and the Lewis acid. Since InClPc is a good electron donor due to the 4 nitrogen atoms with unshared electron pairs, it can react with the Lewis acid such as $AlCl_3$, an electron acceptor, to form electron donor-acceptor complexe which facilities the dissolving of InClPc in the organic solvent/$AlCl_3$. Another is the reaction between the organic molecules and the Lewis acid, which definitely will decrease the solubility of InClPc. To a typical Lewis acid as $AlCl_3$, the reaction depends on the donor number and the dielectric constant of the organic solvent. The high dielectric constant and the low donor number mean a high molecular polarity and a strong electron withdrawing ability, which can avoid the possible competing reaction between the solvent and $AlCl_3$. Therefore, to increase the solubility of InClPc in the aprotic organic solvent/$AlCl_3$, the solvent with high dielectric constant and low donor number is preferred. It is found from Table I that the good organic solvents, which would dissolve InClPc in the presence of $AlCl_3$, are exact those combining a low donor number and a high dielectric constant, such as NM and NB in our case.

It has been demonstrated by Jenekhe [16] that the reversible formation of electron donor-acceptor complexes of heteroaromatic rigid-chain polymer with Lewis acid allows dissolution to form viscous solutions, which can be processed by conventional methods. Since metal phthalocyanines with both the π-electron conjugated structures and the heteroaromatic molecular structures are similar to the mentioned heteroaromatic rigid-chain polymer, the solubilization of metal phthalocyanines in the aprotic organic solvents/Lewis acid are considered to have the same mechanism. Therefore, the main idea of our proposed method of solubilization of metal phthalocyanines is to form the electron donor-acceptor complexes between the metal phthalocyanines and the Lewis acid. In this work, polymer PVK is used to avoid InClPc nanoparticles aggregation. This method proposed here is also suitable for preparing many other nanosized phthalocyanine materials, such as ZnPc, CuPc, TiOPc and H_2Pc.

3.2. Characterization of InClPc nanoparticles

The fabricated InClPc nanoparticles were characterized by means of UV/VIS absorption, X-ray diffraction pattern, and TEM.

Fig. 3 shows the UV/VIS spectra of thin films from PVK, InClPc nanoparticles embedded in PVK, and the bulk InClPc dispersed in PVK. It is found that, PVK

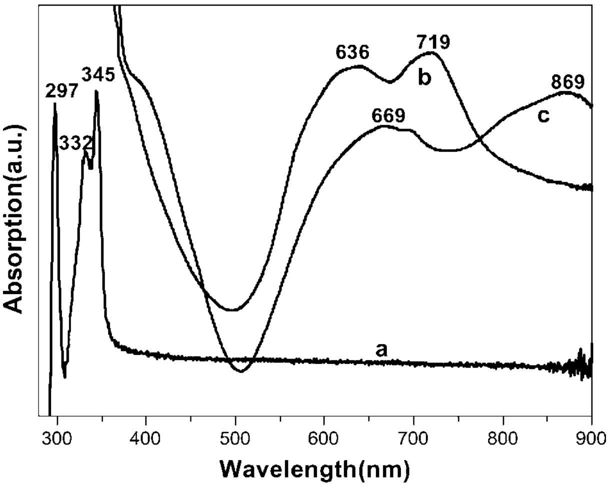

Figure 3 UV/VIS spectra of the thin films from (a) PVK, (b) InClPc nanoparticles embedded in PVK, and (c) the bulk InClPc dispersed in PVK.

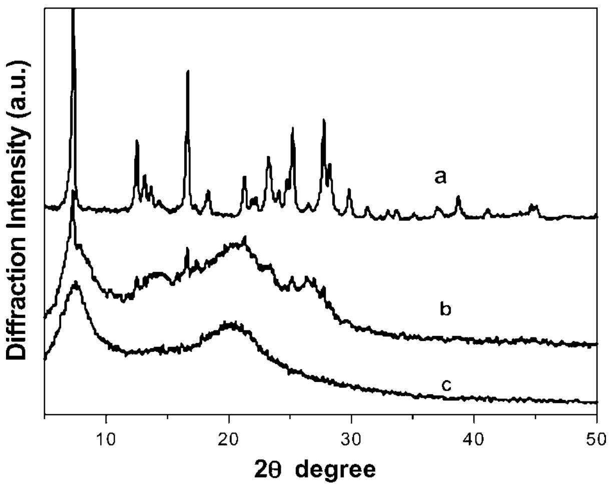

Figure 4 X-ray diffraction patterns of (a) bulk InClPc powder, (b) InClPc nanoparticles embedded in PVK, and (c) PVK powder.

has three absorption peaks centered at 297, 332, and 345 nm, but no absorption peak is found in the range of 500–900 nm, therefore, the absorption in the region should be assigned to InClPc. As shown in Fig. 3b, the spectrum of the InClPc nanoparticles embedded in PVK comprised two broad peaks of 636 and 719 nm in the near-IR region, which has been reported in our previous work [17]. These two peaks of the InClPc nanoparticles are blue-shifted when compared to those of the bulk InClPc dispersed in PVK at 669 and 869 nm, and about 33 and 150 nm shift can be observed, respectively. The blue shift of absorption in inorganic nanometer materials has been widely reported. It is accepted generally that the effect of quantum size of nanometer material makes peaks shift to shorter wavelength [18]. Phthalocyanine and other functional dyes can form molecular aggregates in solution state or molecular crystals in solid state with close intermolecular spacing and strong coupling interaction [19]. The coupling interaction can in turn result in the splitting of the HOMO and LUMO energy levels of molecules in the aggregates or solid. The energy gap between HOMO and LUMO increased with decreasing particle size. So, the nanometer particles need absorb at shorter wavelengths (higher energies) to realize electron hopping.

As shown in X-ray diffraction patterns (Fig. 4), the PVK powder just has two broad peaks because it is not a crystal but a polymer with amorphous state. X-ray powder diffraction patterns of bulk InClPc powder and InClPc nanoparticles embedded in PVK were measured, and both of them show diffraction peaks at Bragg angle (2θ) of 7.3, 12.5, 16.6, 21.3, 23.2, 25.2, and 27.2°. This clearly indicates that both of them are in the same crystalline form. However, diffraction peaks of InClPc nanoparticles embedded in PVK are broader than those of bulk InClPc powder, which might be resulted from the nanometer size effect.

Fig. 5 shows the TEM micrography from the InClPc nanoparticles embedded in PVK. The TEM micrography is bright field and the image reveals the spherical microcrystals with a size of 25–50 nm. It can be seen clearly that InClPc nanoparticles in dark color are coated and packed by a thin layer of PVK polymer in lighter color. It is the embedding effect of PVK polymer that prevents the InClPc microcrystals from aggregating into a large size, in other words, PVK has prevented agglomeration of the InClPc nanoparticles.

3.3. Photosensitivity of InClPc nanoparticles embedded in PVK

The photosensitivity of InClPc nanoparticles was investigated in single layered photoreceptors that consisted of InClPc nanoparticles embedded in PVK as CGM and BAH as CTM. Fig. 6 shows the photosensitivities of InClPc nanoparticles embedded in PVK and bulk InClPc in the single layered photoreceptors. We can find that the photosensitivities of the InClPc nanoparticles embedded in PVK are higher than that of the bulk InClPc in the near-IR region. For example, when $\lambda = 762$ nm, a 30% increase in photosensitivity (from 1.31 to 1.70 cm^2/μJ) is observed. Because PVK has no absorption in the near-IR region, the changes of photosensitivities in the near-IR region will be brought from InClPc. According to the reports of Umeda [20, 21], Wang [22] and Chen [12, 13] that photocarriers are generated at the CGM/CTM interface, we believe that the huge surface area of the InClPc nanoparticles plays an important role in the improvement of photosensitivity.

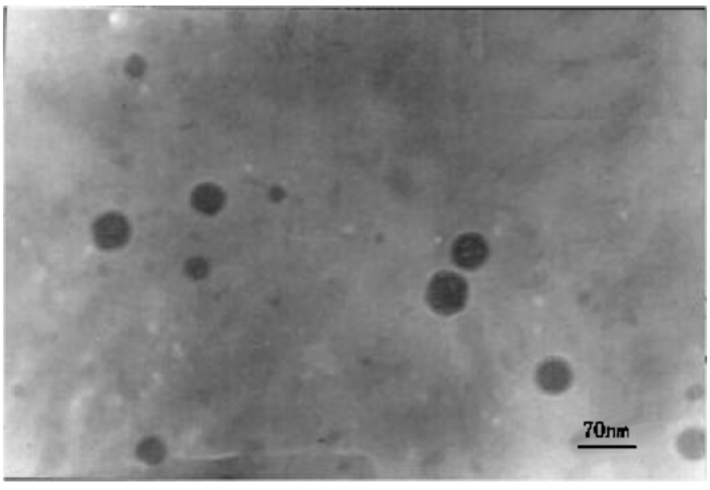

Figure 5 TEM micrography from the InClPc nanoparticles embedded in PVK matrix.

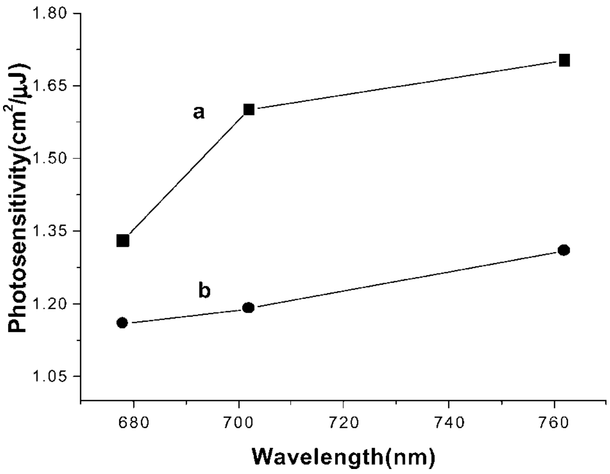

Figure 6 Photosensitivity vs. wavelength for the single layered photoreceptors made from (a) InClPc nanoparticles embedded in PVK and (b) bulk InClPc.

The larger surface area of the CGM/CTM interface in the single layered PR made from the InClPc nanoparticles can result in much more photocarrier generation sites, and consequently the higher photosensitivity. Following this argument, it can be concluded that photoconductivity of InClPc might increase with decreasing the size of InClPc particles.

4. Conclusions

Spherical InClPc nanoparticles embedded in PVK with a size of 25–50 nm are successfully obtained via a new method of complexation-mediated solubilization. The InClPc nanoparticles exhibit a blue shift of absorption compared to the bulk InClPc, and remain the same crystalline form as the bulk InClPc with broader diffraction peaks. The enhanced photoconductivity of the InClPc nanoparticles in the single layered photoreceptor is resulted from the enlarged surface area of the CGM/CTM interface.

Acknowledgments

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