JOURNAL OF MATERIALS SCIENCE **39** (2004) 3587–3591

Preparation and photoconductivity study of azo nanoparticles via liquid phase surfactant-assisted reprecipitation

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4,4′-bis(1′-Azo-2′-hydroxy-3′-naphthoyl-o-chloroanide) oxazole (AZO) nanoparticles in size of 40–60 nm were prepared by the method of liquid phase surfactant-assisted reprecipitation. The AZO nanoparticles were characterized by UV/VIS absorption, X-ray diffraction pattern, and TEM measurements. It revealed that AZO nanoparticles were near spherical in shape and were in amorphous state. The photoconductivity of AZO nanoparticles in single-layered photoreceptors was studied as well. The results showed that the photoconductivity of AZO nanoparticles was improved greatly compared to that of bulk AZO due to nanometer size effect. *© 2004 Kluwer Academic Publishers*

1. Introduction

Azo pigment is a kind of promising candidate for photoactive materials, where it serves as an excellent charge generation material (CGM) in photoconductive devices [1–3]. Organic photoreceptors using azo pigment as a CGM exhibit high photosensitivities. However, one of the problems of azo pigment used in photoreceptors is their intrinsic tendency toward aggregation [4]. This intermolecular association process promotes the nonradiative internal conversion, almost invariably causing a shortening of the triplet lifetime and a drastic reduction of the overall photosensitizing efficiency [5, 6]. This problem is particular serious in polar solvents, where azo pigment tends to self-associate and repels the hydrophobic π systems to form favorable aggregates. One of the strategies to reduce the aggregation of azo pigment in polar solvent media involves the use of dispersants or nanometerization [7–9]. However, it has been found that the former method suffers from low stability, low localizing property, and incompatibility, which limits their use as photosensitizer in photoreceptors. Nanometerization of organic pigments has received significant attention in the past two decades because nanosized organic pigments not only are favorable to reduce the aggregation of organic pigments, but also exhibit unique optic, electric, and magnetic properties compared with those of their bulk counterparts. However, the common techniques, such as vapor-phase and liquid-phase methods, are not suitable for most organic materials [10]. Thus, the development of azo nanoscale materials preserving high photosensitizing property remains a great challenge.

Liquid phase reprecipitation method is often used in the preparation of nanometer pigments such as phthalocyanine [11]. Considering nanometer pigments are very easy to coacervate when the collisions occur, the traditional stabilizers, usually a type of macromolecular substance such as gelatine and poly(vinyl alcohol), are used in preparing pigment nanoparticles. However, such stabilizers are not easy to be removed from the pigment nanoparticles. As a result they may cause trouble when purifying the product and lead to reducing the overall photosensitizing efficiency of photoreceptors based on such pigment nanoparticles [8, 9]. In this paper, we describe a simple method to prepare superstable azo pigment nanoparticles. 4,4′-Bis(1′-Azo-2′-hydroxy-3′-naphthoyl-o-chloroanide) oxazole (AZO) nanometer pigment was prepared by means of a modified liquid phase reprecipitation method, where a mixture of glycerine and poly(4-vinylpyridine bromide) (PVPB) was used instead of the traditional stabilizer. The optical properties and crystal structures of AZO were studied by UV/VIS absorption, X-ray diffraction pattern and TEM measurements. AZO nanometer pigment also functioned as a charge-generation material (CGM) to prepare a single-layered photoreceptor (SLPR) and its photoconductivity was discussed in detail.

2. Experimental

2.1. Materials and equipment

4,4′-Bis(1′-Azo-2′-hydroxy-3′-naphthoyl-o-chloroanide) oxazole (AZO) was prepared and purified according to the literature [12]. N,N′-diethyl-4-aminobenzaldehyde-1-phenyl-1′-(α-naphthyl)-hydrazone (DENPH) was

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commercially available and was recrystallized with butanone before use. Poly(4-vinylpyridine bromide) (PVPB) and bisphenol A type polycarbonate (PC) were commercially purchased and purified before using them. The other reagents were commercially available in analytical grade and used as received.

UV-VIS absorption was recorded by a CARY Bio100 spectrophotometer. Morphology of AZO nanoparticles was observed on a JEM-200CX II electron microscope. X-ray powder diffraction patterns were recorded on a Rigaku D/max 2550 Pe diffraction device, rotating anode X-ray generator working at 40 KV, 300 mA, with Cu K_α monochromatic radiation.

2.2. Preparation of AZO nanoparticles

Glycerine (5 mL) and poly(4-vinylpyridine bromide) (PVPB) (0.2 g, 1.4 mmol) were added into 400 mL water and were heated at 40°C under stirring to get a transparent colloidal solution. A solution of AZO (0.3 g, 0.4 mmol) in mixed solvents was prepared by magnetically stirring with aluminum chloride ($AlCl_3$) (0.36 g, 2.7 mmol), nitromethane (6 mL) and tetrahydrofuran (THF) (4 mL) in 25 mL flask strictly under nitrogen atmosphere for 24 h, which was then added dropwise to the surfactant solution under vigorously stirring at room temperature. Upon addition, THF, nitromethane and $AlCl_3$ diffused and mixed with water quickly. The insoluble hydrophobic AZO was collapsed and aggregated in water to form nanoparticles, being protected and separated by dispersants of glycerine and PVPB simultaneously and rapidly. The small amount of THF and nitromethane in the mixture was then removed under reduced pressure to give glycerine and PVPB stabilized AZO nanoparticles. After adding several drops of hydrochloric acid, AZO nanoparticles were centrifugated, washed with ethanol to remove most of the excess surfactants, and were then annealed at 65°C in a vaccum overnight.

2.3. Fabrication and photoconductivity measurement of single-layered photoreceptors

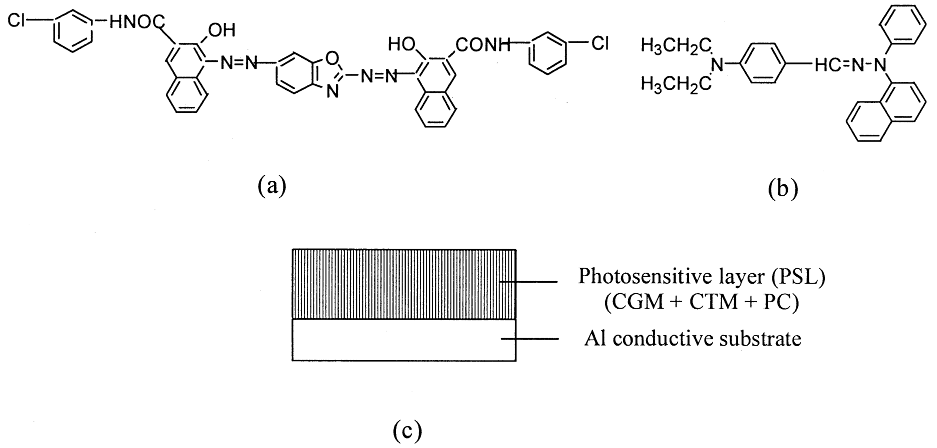
The single-layered photoreceptors (SLPRs) were fabricated as following. AZO pigments were added into a flask containing THF, and the mixture was wet milled for 6 h. Then 1,4-dioxane, PC and DENPH were added into the flask and were mixed uniformly. The resulting slurry was cast onto an A1 substrate by dip coating method, giving a SLPR, where AZO served as the charge generation material CGM), and DENPH acted as the charge transportation material (CTM) (Fig. 1). For a comparison, the bulk AZO was used to prepare the SLPR as well in the same way. After baking for 1 h at 353 K, the formed film was measured as ~20 μm in thickness by ELEKTKO-PHYSIK MINITEST 2000 thin-film-measuring apparatus.

Photoconductive properties were evaluated by the standard xerographic photoinduced discharge technique [13, 14]. Under the same illumination intensity (I), a good photoreceptor is expected to show a high photosensitivity value (S).

3. Results and discussion

3.1. Preparation and characterization of AZO nanoparticles

AZO pigment must be dissolved in a solvent in order to prepare AZO nanoparticles via liquid phase reprecipitation method. However, azo pigments are highly insoluble, making their applications more complicated and limited. Two methods have been adopted to solve this problem. One is to use physical processes such as sulfuric acid solubilization [15], another way is using chemical processes such as direct attachment of flexible or bulky substituents onto pigments molecules [16, 17]. However, the chemical processes are often system specific and thus are less general than the physical ones. Sulfuric acid solubilization is generally used in physical processes, but it is not suitable to general azo pigments because concentrated sulfuric acid could oxidize and decompose azo pigments. It was reported that many heterocyclic pigment classes such as phthalocyanine, perylenebismidazole, azo, and the like can be dissolved through Lewis acid pigment solubilization (LAPS) or complexation-mediated solubilization method by utilizing Lewis acid [18, 19]. In this work, LAPS method is proposed because it not only can solve the problem of insolubility of AZO pigments but also is easy to operate without any pretreatment of AZO pigments.



(a) (b) (c)

Figure 1 The molecular structures of AZO (a) and DENPH (b); the structure of single layered photoreceptor based on them (c).

During the preparation of AZO nanoparticles, the mixture of glycerine and PVPB was used instead of traditional stabilizer. It was considered that this glycerine–PVPB mixture had a high viscosity and hydrophilicity, hence reducing the possibility for the emulsion droplets to coalesce. As a result, it was helpful for the formation of AZO nanoparticles. On the other hand, in comparison with other methods that used the traditional stabilizer, the glycerine and PVPB can be easily removed, making the purification of the produced AZO nanoparticles much easier. In the meantime, the multi-hydroxyl structure of glycerine could accelerate the diffusion of organic solution from the nanodrops to the extra water. That is to say, THF, nitromethane and $AlCl_3$ can diffuse and mix with water quickly, while the insoluble hydrophobic AZO precipitated and dispersed stably to form nanoparticles in the mixed water/solvents. Thus the organic solvent can evaporate quickly to form stable AZO nanoparticles.

AZO nanoparticles were prepared following the steps mentioned in the Experimental part. Fig. 2 shows the TEM photographs of AZO nanoparticles. The particle sizes of AZO are in the range of 40–60 nm. The AZO particles are well separated from each other without heavy aggregation as showed in Fig. 2a. Fig. 2b represents a higher magnification AZO nanoparticles, where the membrane is discerned in the projection contrast, and somewhat blurred by a gray halo due to the stabilizer polymer which fix the surface of AZO nanoparticles. It is also found that the morphology of AZO nanoparticles is near spherical. However, in some cases, two AZO nanoparticles were observed in close contact as shown in Fig. 2b. They deformed and the adjacent AZO nanoparticles became parallel and planar, indicating that the spherical shape is not rigid in fact (probably due to above treated processes of solvent or dispersants). From Fig. 2b, we can estimate the polymer membrane thickness to be between 13 and 25 nm. The suspension of AZO nanoparticles in water is stable for at least 4 months at room temperature (no coalescene or breakdown was detected even after high-speed centrifugation).

The UV-VIS spectra were used to compare the optical absorption changes between the nanoscale AZO and bulk AZO. Fig. 3 shows the UV-VIS spectra of AZO nanoparticles and bulk AZO thin films dispersed in PC, respectively. It is found that, when compared with the UV-VIS spectrum of bulk AZO film, the nanoscale

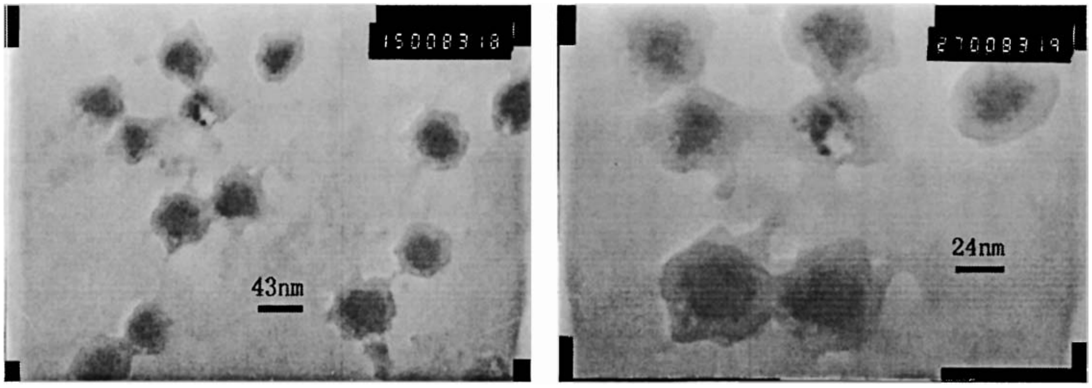


Figure 2 TEM images showing the morphology of AZO nanoparticles: (a) 200,000 times magnification and (b) 270,000 times magnification.

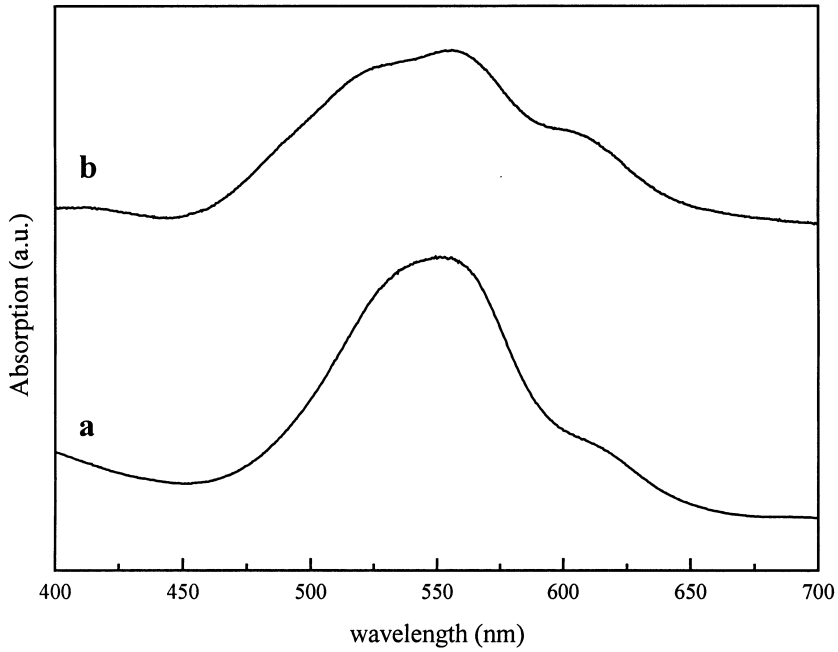


Figure 3 UV-vis absorption spectra of (a) bulk AZO and (b) AZO nanoparticles.

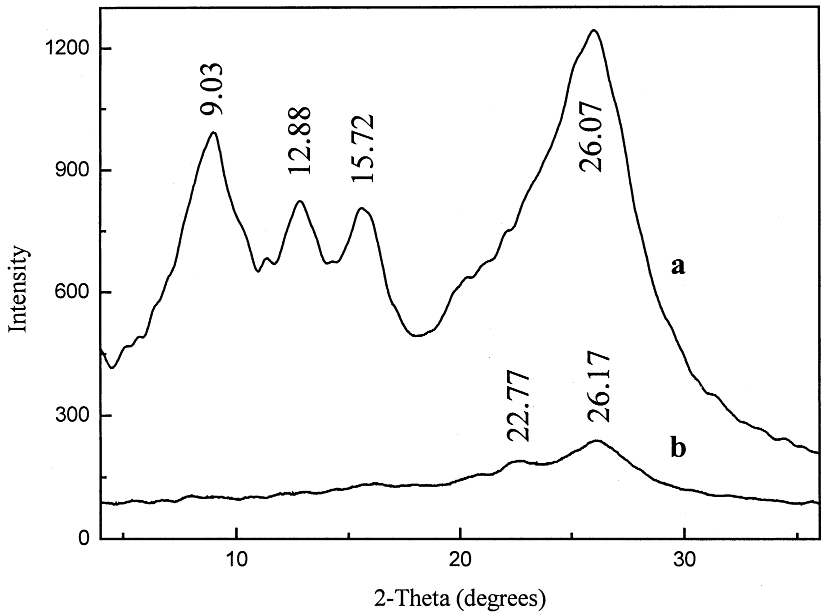


Figure 4 XRD patterns of (a) bulk AZO and (b) AZO nanoparticles.

AZO exhibited a broader absorption band. The peaks of the nanoscale AZO are blue-shifted about 20 nm (from 470 to 450 nm) and red-shifted about 15 nm (from 635 to 650 nm), in other words, the absorption range of nanoscale AZO particles becomes broader. Furthermore, the peak absorption shape of nanoscale AZO particles becomes flater and smoother, which might be due to the decreased size of AZO particles to nanoscale.

AZO nanoparticles were also studied by X-ray diffraction (XRD). The results obtained from AZO nanoparticles and bulk AZO are shown in Fig. 4. Compared to bulk AZO, which exhibits clear peaks mainly at $2\theta = 9.03$, 12.88, 15.72 and 26.07°, the nanoscale AZO powder only have two weak and broad peaks at $2\theta = 22.77$ and 26.17°, indicating an almost amorphous state, which may be the results of nanosize effect of AZO nanoparticles coated by polymer of PVPB. Because the amount of AZO molecules was very limited in each nanoparticle and the nanoparticles were embedded with the polymer membrane, AZO molecules could not stack up into a long-ordered state as the bulk AZO do, but only into short-ordered or no-ordered state, resulting in broad and vanished peaks in the X-ray diffraction pattern.

3.2. Photoconductive properties of single-layered photoreceptors based on AZO nanoparticles

The xerographic properties of AZO nanoparticles and bulk AZO were investigated in single-layered photoreceptors (SLPRs) that consisted of AZO pigment as CGM, DENPH as CTM and PC as binder polymer under the exposure of various wavelengths. Shown in Fig. 5, the data indicate that almost in the entire spectrum the photosensitivities of SLPRs containing AZO

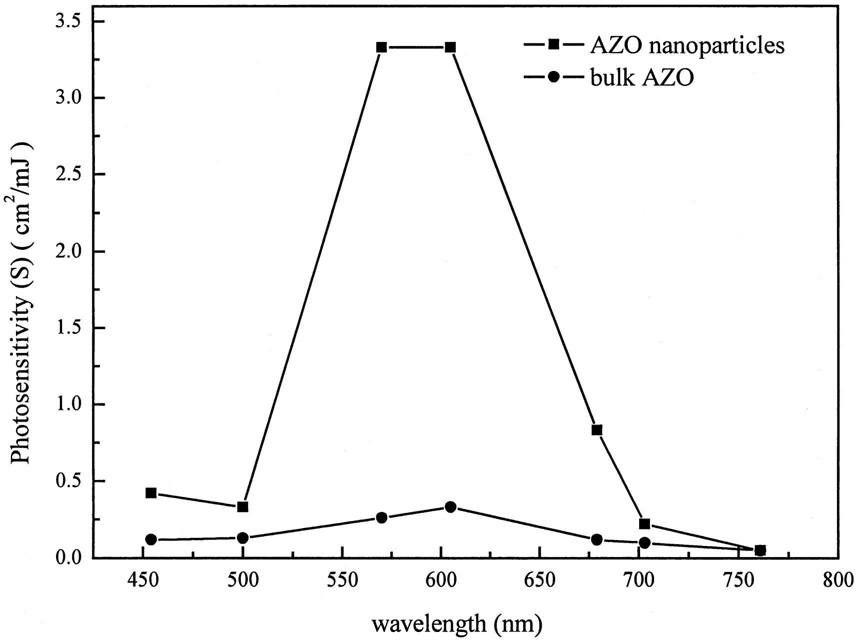


Figure 5 The effect of the illumination wavelength on the photosensitivity of the SLPRs based on the bulk AZO and AZO nanoparticles.

nanoparticles as CGM are evidently higher than that containing bulk AZO as CGM. For example, under the exposure of 600 nm wavelength, S value for AZO nanoparticles is about 10 times higher than that for bulk AZO (from 0.33 to 3.33 $\mathrm{cm}^2/\mu\mathrm{J}$). These results suggest that nanoscale material is promising in fabrication of high photosensitive photoreceptors.

Photogeneration mechanism now available holds that the formation and migration of charge carriers is an interface process: the photocarriers are generated at the CGM/CTM interface resulted from the CTM penetration into the CGL [20]. The larger the surface area of the CGM/CTM interface is, the more the photocarrier generation sites, and consequently the higher the photosensitivity. In our case, with decreasing particle size of AZO pigment to nanoscale, the ratio of surface molecules becomes much larger, the specific surface area and the surface energy also increase, leading to much more photocarrier generation sites as well as higher carrier injection efficiency from CGM to CTM. So it is understandable that the photosensitivity is remarkably enhanced with decreasing AZO particle size to nanoscale in SLPRs.

4. Conclusions

AZO nanoparticles in size of 40–60 nm were successfully obtained by using a simple method of modified liquid phase surfactant-assisted reprecipitation. The photoconductivity of AZO nanoparticles in single-layered photoreceptors showed enhanced photoconductivity than the bulk AZO did due to the great increase of the photocarrier generation sites resulted from the enlarged surface area of CGM/CTM interface.

Acknowledgments

This work was financed by the National Natural Science Foundation of China (No: 90201009) and by the Natural Science Foundation of Zhejiang Province, China (No: ZC0101).

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Received 8 August 2003
and accepted 5 January 2004