

# Perylene Nanoparticles Prepared by Reprecipitation Method

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Perylene nanoparticles with different sizes were prepared by reprecipitation method. It is found that the nanoparticles show size-dependent optical property. Electron diffraction patterns indicate that all the nanoparticles of different sizes are in crystalline state. The rapid growth of the nanoparticles during the aging process could be slowed down effectively by the addition of cationic or anionic surfactants.

**Keywords** perylene, nanoparticles, stabilization, surfactant

## Introduction

In the past twenty years, researches on the nanostructured materials have become extremely active due to their interesting quantum confinement effects on optical, optoelectronic, electronic, magnetic and mechanical properties.<sup>1-5</sup> The traditional researches of nanomaterials were mainly focused on the inorganic materials, such as metals, oxides, sulfide, carbon and silicon *et al.* However, organic nanomaterials have drawn more and more attention because of their diversities, controllable functions and tailored structures. Nakanishi's and our research groups have carried out lots of investigations in this field.<sup>6-12</sup> Perylene, the conventional fluorescent dye, is usually used as fluorescent probe in biological, medical and chemical fields. Moreover, as a kind of typical aromatic compound, perylene has a large  $\pi$ -conjugated bond and has a simple structure that is just planar. Therefore, it is suitable for studying the aggregation and growth parameters of organic nanocrystals as a model molecule. And its unique spectra characters exhibit an attractive foreground in tunable optical elements. Be-

cause it is difficult to control the sizes of organic nanoparticles prepared by reprecipitation method, one of the research aims is to resolve this key problem in the investigation and application of organic nanoparticles. In this work, perylene nanoparticles with different sizes were prepared by reprecipitation method, and it was shown that the growth of the nanoparticles could be slowed down effectively by the addition of both cationic and anionic surfactants. At the same time the energy level diagram of perylene molecule and nanoparticle, which will contribute to the basic researches of organic nanocrystals was proposed.

## Experimental

The perylene powder (>99%) used was purchased from Acros. Perylene nanoparticles were prepared by the above-mentioned reprecipitation method.<sup>7</sup> Pure water (18.2 M $\Omega$ ·cm) was used as a nonsolvent. To prepare perylene nanoparticles, a certain amount of acetone solution of perylene (1 mmol/L) was injected into 10 mL of water under stirring. The nanoparticles were obtained as yellow dispersion in water. Cetyl trimethyl ammonium bromide and sodium dodecyl sulfonate solutions (1.0 mmol/L) were also used as nonsolvents instead of pure water to investigate the effect of surfactant on the growth of perylene nanoparticles. UV-visible spectra were taken on a Shimadzu UV-1601 PC spectrophotometer. A JEOL JEM-200CX transmission electron microscope (TEM) was used to observe the morphologies of nanoparticles. For electron diffraction experiments,

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perylene nanoparticles were embedded in the pores of solidified monolithic silica gel glasses prepared by acidic hydrolysis of  $\text{Si}(\text{OEt})_4$ .<sup>13,14</sup>

## Results and discussion

### *Fabrication of the perylene nanoparticles*

The sizes of the nanoparticles prepared increase with the enhancing amount of perylene solution injected. Table 1 shows the relationship between the injected amount of perylene solution and the sizes of the obtained perylene nanoparticles. It was seen that when 100  $\mu\text{L}$  of perylene acetone solution was injected into 10 mL of pure water, the size of the resulting nanoparticle is about 10 nm. When 400  $\mu\text{L}$  of solution was injected into 10 mL of pure water, the size of the resulting nanoparticles is about 20 nm. However, the sizes of the perylene nanoparticles in water increased rapidly with the increase of aging time. For example, in the above-mentioned perylene nanoparticle dispersions, the sizes of perylene nanoparticles grew to 60 nm and 250 nm, respectively, after two days' aging. Shown in Fig. 1 are the TEM micrographs of the 20 nm and 60 nm perylene nanoparticles.

**Table 1** Relationship between the sizes of perylene nanoparticles and their preparing conditions

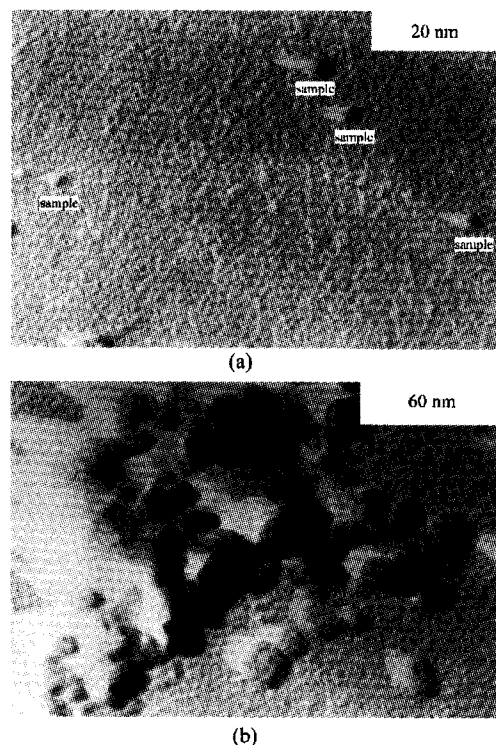
Aging time (h)	Size of the perylene nanoparticles (nm)	
	Solution injected (100 $\mu\text{L}$ )	Solution injected (400 $\mu\text{L}$ )
0	10	20
2	30	110
4	40	180
8	50	220
12	60	240
48	60	250

### *Spectra character of the nanoparticles*

Absorption spectra of perylene solution and its nanoparticles with different sizes are given in Fig. 2. Fig. 2(a) shows the absorption spectrum of dilute perylene solution ( $10^{-6}$  mol/L). Figs. 2(b)—2(e) give the absorption spectra of the nanoparticles of 250 nm, 60 nm, 20 nm and 10 nm, respectively. It can be seen that the absorption peaks of the perylene nanoparticles, no matter what sizes they are, shift to the longer wavelength

compared with the absorption peaks of perylene solution, indicating that *J*-aggregates have formed in the perylene nanoparticles.

The energy level diagram of perylene molecule and perylene nanoparticle is proposed in Scheme 1. Under the irradiation of UV light, electrons of perylene molecules were excited from ground state ( $S_0$ ) to excited state ( $S_1$ ). The transitions to different vibration bands of  $S_1$  were observed at 434 nm, 406 nm and 384 nm. In

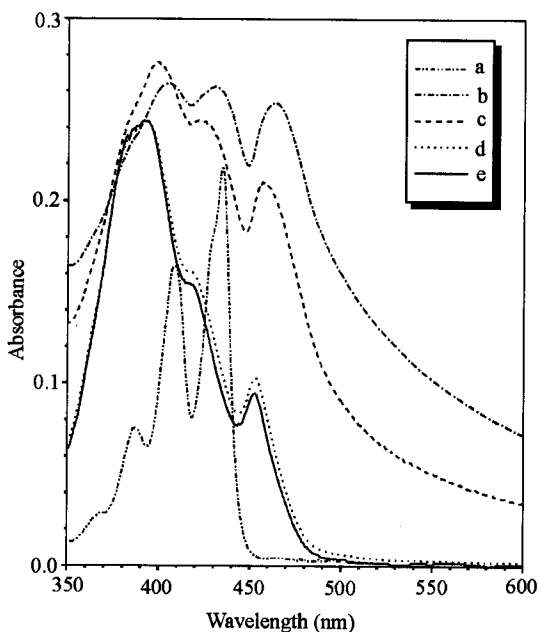
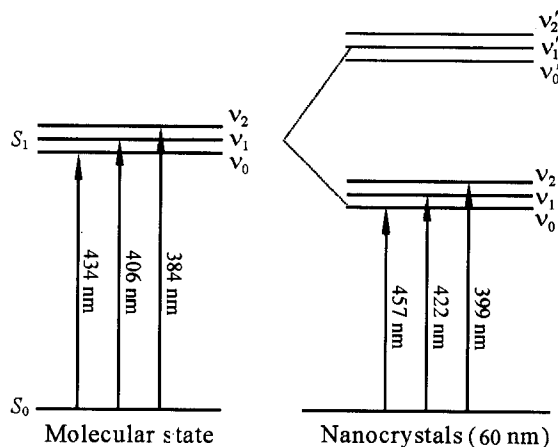


**Fig. 1** TEM micrographs of perylene nanoparticles of (a) 20 nm and (b) 60 nm.

the nanoparticles, the formation of *J*-aggregates resulted in the splitting of energy level of the molecules. According to the transition selection rule, only the transition to the lowered level is allowed. Therefore, all the three peaks experience red-shifts. As the sizes of the nanoparticles increased, the interactions between the molecules in the nanoparticles became stronger. This would result in greater splitting of the energy level, thus the absorption shifts to longer wavelength gradually with the increased sizes. From Fig. 2, it could also be seen that when the sizes of nanoparticles decreased (from 250 nm to 10 nm), the absorption peak shifts to the shorter wavelength region (from 464 nm to 453 nm), showing that similar to inorganic nanoparticles, size-dependent

optical property can also be observed for the perylene nanoparticles. The reason of the blue shift is that micro-crystallization causes lattice softening, and the coulombic interaction energies between molecules become weaker, leading to wider band gaps.<sup>6</sup>

**Scheme 1** Energy level diagram of perylene molecule and the perylene nanoparticle (60 nm)



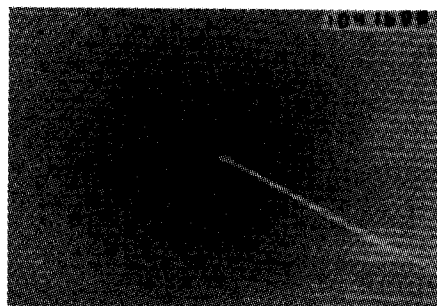
**Fig. 2** Absorption spectra of (a) dilute perylene solution and its nanoparticles of different size: (b) 250 nm, (c) 60 nm, (d) 20 nm and (e) 10 nm.

#### *Electron diffraction patterns of the nanoparticles embedded in silica glass*

The SiO<sub>2</sub> gel glass doped with perylene nanoparticles is porous, yellow and transparent. When the SiO<sub>2</sub>

gel glass in which the perylene nanoparticles were doped was immersed in leaching solvent such as ethanol,<sup>13</sup> no detectable leakage of perylene could be observed from the doped glass by UV-visible measurements. This indicates that perylene nanoparticles have been successfully embedded.

After embedded into the silica gel glass, the structures of perylene nanoparticles were studied by electron diffraction. Electron diffraction patterns of all the prepared nanoparticles show regular diffraction spots, indicating that the ones obtained are in crystallite states. Fig. 3 shows the electron diffraction pattern of the 60 nm nanoparticles embedded in silica gel glass.

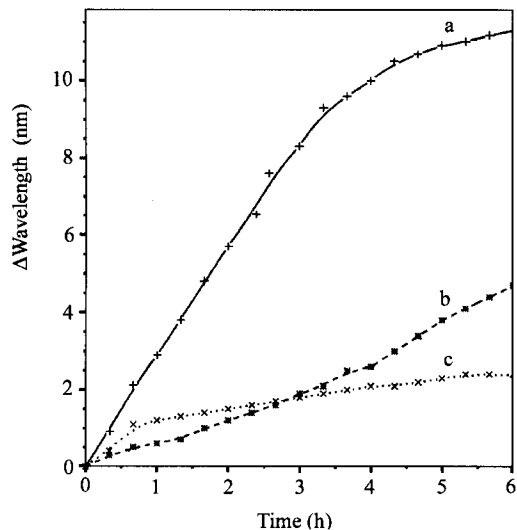


**Fig. 3** Electron diffraction pattern of perylene nanoparticle embedded in SiO<sub>2</sub> gel glass.

#### *Stabilization of the nanoparticles during aging process*

The growth rate of nanoparticles can be slowed down by the addition of surfactants. Here cationic surfactant (C<sub>16</sub>H<sub>33</sub>(CH<sub>3</sub>)<sub>3</sub>NBr) or anionic surfactant (C<sub>12</sub>H<sub>25</sub>SO<sub>3</sub>Na) solution was employed as a nonsolvent to prepare perylene nanoparticle dispersions in stead of pure water. It has been shown that the absorption wavelength of the nanoparticles is related to their sizes (see Fig. 2). Moreover, the UV-visible spectral studies indicate that the addition of surfactants do not affect the optical properties of the nanoparticles. And the change of absorption peak position can be used as a measure of nanoparticle sizes. Fig. 4 shows the relationship between the changes of absorption peak position and the aging time of perylene nanoparticles. Distinctly, when cationic surfactant (C<sub>16</sub>H<sub>33</sub>(CH<sub>3</sub>)<sub>3</sub>NBr) (curve c) was used as a nonsolvent in stead of pure water (curve a), the growth rate of perylene nanoparticles was slowed down remarkably. When anionic surfactant (C<sub>12</sub>H<sub>25</sub>SO<sub>3</sub>Na) (curve b) was used as nonsolvent, the growth

rate could be also slowed down. When the surfactant was used, it shielded perylene molecules and formed a protective layer surrounding them. Therefore, it became more difficult for perylene nanoparticles to agglomerate and form larger nanoparticles in surfactant solution than in water. Thus the growth rate was slowed down in surfactant solutions. It has been proved that there was nearly no charge on the surface of perylene nanoparticles by zeta-potential measurements. So, it is reasonable for the nanoparticles to be covered by both the cationic surfactant and anionic surfactants, thus slowing down the growth rate of nanoparticles. When a surfactant containing longer alkyl chain was used, the surfactant molecules wrapped around the perylene nanoparticles could bring larger steric effect than that for the surfactants containing shorter alkyl chain.<sup>15</sup> Therefore, the growth rate of perylene nanoparticles decreased more effectively by  $C_{16}H_{33}(CH_3)_3NBr$  (curve c) than by  $C_{12}H_{25}SO_3Na$ . A further study about the influence of alkyl chain is being carried out. Anyway, it is possible to select a suitable surfactant to control the growth rate of perylene nanoparticles and obtain nanoparticles with required size.



**Fig. 4** Changes in wavelength of absorption peak with aging time in different nonsolvents: (a) water, (b) sodium dodecyl sulfonate solution and (c) cetyl trimethyl ammonium bromide solution.

## Conclusion

In summary, perylene nanoparticles with different size has been prepared by reprecipitation method. Perylene nanoparticles showed size-dependent property in absorption spectra. The addition of surfactants can stabilize the growth of the nanoparticles and thus the optical properties. Such a study will provide useful information for the preparation of organic nanoparticulate materials with adjustable optical properties.

## References

- 1 Kubo, R. *J. Phys. Soc. Jpn.* **1962**, *17*, 975.
- 2 Sundaram, M.; Chalmers, S. A.; Hopkins, P. F.; Gosard, A. C. *Science* **1991**, *254*, 1326.
- 3 Banin, U.; Cao, Y.-W.; Katz, D.; Millo, O. *Nature* **1999**, *400*, 542.
- 4 Cao, Y.-W.; Banin, U. *J. Am. Chem. Soc.* **2000**, *122*, 9692.
- 5 Alivisatos, A. P. *Science* **1996**, *271*, 933.
- 6 Kasai, H.; Kamatani, H.; Okada, S.; Oikawa, H.; Matsuda, H.; Nakanishi, H. *Jpn. J. Appl. Phys.* **1996**, *35*, L221.
- 7 Kasai, H.; Naiwa, H. S.; Okada, S.; Matsuda, H.; Oikawa, H.; Minami, N.; Kakuta, A.; Ono, K.; Mukoh, A.; Nakanishi, H. *Jpn. J. Appl. Phys.* **1992**, *31*, L1132.
- 8 Katagi, H.; Kasai, H.; Okada, S.; Oikawa, H.; Matsuda, H.; Nakanishi, H. *J. Macromol. Sci.-Pure Appl. Chem.* **1997**, *A34*, 2013.
- 9 Fu, H.-B.; Ji, X.-H.; Yao, J.-N. *Chem. Lett.* **1999**, *9*, 967.
- 10 Fu, H.-B.; Ji, X.-H.; Zhang, X.-H.; Wu, S.-K.; Yao, J.-N. *J. Colloid Inter. Sci.* **1999**, *220*, 177.
- 11 Fu, H.-B.; Wang, Y.-Q.; Yao, J.-N. *Chem. Phys. Lett.* **2000**, *322*, 327.
- 12 Fu, H.-B.; Yao, J.-N. *J. Am. Chem. Soc.* **2001**, *123*, 1434.
- 13 Avnir, D.; Levy, D.; Reisfeld, R. *J. Phys. Chem.* **1984**, *88*, 5956.
- 14 Ibanez, A.; Maximov, S.; Guiu, A.; Chaillout, C.; Baldeck, P. L. *Adv. Mater.* **1998**, *10*, 1540.
- 15 Eicke, H.-F.; Parfitt, G. D. *Interfacial Phenomena in Aqueous Media*, Marcel Dekker, New York, **1987**.