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A study of the formation and embedding of perylene nanocrystals

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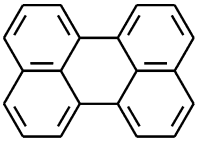
Abstract

This paper reports parameters germane to growing and controlling the size of perylene nanocrystals, as well as to embedding these nanocrystals in suitable media. The perylene nanocrystals obtained in this study were of the α form and produced J-aggregates having a stacking angle about 40.7°. Investigation of the spectral properties of these nanocrystals revealed a size-dependent blue shift in their absorption spectra, which makes them potentially useful in optics.

Keywords: Perylene; Nanocrystals; Crystal growth; Embedding; J-aggregate; Size-dependency

1. Introduction

For more than 30 years, studies involving nanocrystals of metals, inorganic semiconductors, metal oxides and ceramics have been of considerable interest because these substrates afford interesting optical, optoelectronic, electronic, magnetic, mechanical, and other properties [1–5]. With regard to organic substrates, the size-dependent properties of organic nanocrystals fabricated by reprecipitation have been studied, and it was found that they had potential usage in optics [6–8]. In other studies concerning the properties of organic nanocrystals, it was shown that further advances in the commercial utility of organic nanocrystals would require an improved understanding of the crystal growth controlling process and the matrices that serve as hosts for nanocrystals [9–11]. In view of the paucity of research pertaining to the growth and embedding of organic nanocrystals, we elected to study the aggregation of perylene nanocrystals and to define the parameters associated with controlling nanocrystal size. The fluorescence perylene dye used in this study is structure **1**.



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2. Experimental

Perylene powder (99 + %) was obtained from Acros Organics Company and perylene nanocrystals were prepared by a reprecipitation method [7].

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Pure water (18.2 MΩ·cm) was used in crystal growth experiments. In this regard, an acetone solution of perylene (~1 mmol/l) was injected into 10 ml water. This afforded a yellow dispersion of nanocrystals in water, which had the appearance of a true solution. Aqueous solutions of cetyl trimethyl ammonium bromide (1.0 mmol/l) and sodium dodecyl sulfonate (1.0 mmol/l) were used in lieu of pure water to investigate the influence of surfactants on the aggregation of perylene nanocrystals. The critical micelle concentrations for these surfactants were 0.92 and 1.0 mmol/l, respectively.

Solidified monolithic silica gel glasses were prepared by acidic hydrolysis of $Si(OEt)_4$, followed by slow (over ~2 weeks) condensation polymerization at room temperature [12,13]. Perylene was added prior to gelation, to give nanocrystals embedded in the pores of SiO_2 gel.

Absorbance measurements were performed on a Shimadzu UV-1601 PC UV–visible spectrophotometer. A JEM-200CX transmission electron microscope (TEM) was used to examine the sizes and shapes of nanocrystals. Select area electron diffraction was carried out with the aid of the TEM to study the structures of the nanocrystals produced.

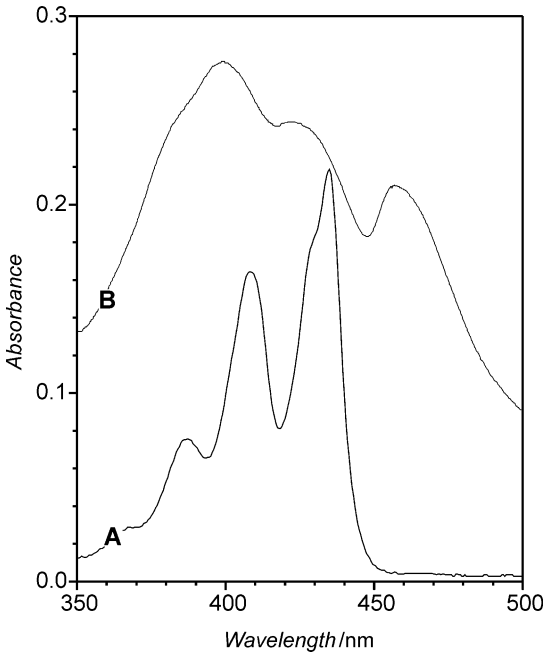

Fig. 1. The absorption spectra of perylene in acetone (A) and perylene nanocrystal dispersion (B).

3. Results and discussion

3.1. Aggregation and growth parameters of perylene nanocrystals

Representative absorption spectra of the dispersion of perylene nanocrystals in water are shown in Fig. 1. Curve A is the absorption spectrum of a dilute (1.0×10^{-6} mol/l) perylene solution, while curve B is the absorption spectrum obtained in water after 4 h. The appearance of the peak at a longer wavelength (curve B) indicates that the perylene nanocrystals are mainly J-aggregates.

The relationship between wavelength changes following crystal growth and the associated stacking angles was determined using Eq. (1) [14].

$$\Delta\nu = h^{-1}\frac{<m^2>}{r^3}(1-3\cos^2\alpha) \quad (1)$$

where $\Delta\nu$ is the spectral shift associated with the formation of aggregates from the monomeric species, h is Planck's constant, r is the distance between molecular centers, α is the stacking angle that defines the angle between the transition dipole and the molecular axis of aggregates, and $<m^2>$ is the transition dipole moment of monomeric species. The quantity $<m^2>$ can be determined from Eq. (2).

$$< m^2 >= 9.185\times10^{-39}\int_{\lambda_1}^{\lambda_2}\varepsilon(\mathrm{d}\lambda/\lambda) \quad (2)$$

Here, λ_1 and λ_2 are the limits of a well-defined absorption band. By using $\lambda_1 = 418$ nm and $\lambda_2 = 450$ nm for the spectrum of monomeric perylene, we obtained a value of 1925 $(\mathrm{mol/l})^{-1}\,\mathrm{cm}^{-1}$ for $<m^2>$. Knowing that $r = 0.35$ nm [15] and $\Delta\nu = -1499$ cm^{-1}, we obtained a value of 40.7° for α.

The perylene concentration in the initial acetone solution, the amount of perylene solution injected into water, the aging time of perylene nanocrystal dispersions, and the presence or absence of surfactant played important roles in controlling the perylene particle size distribution. Changes in the perylene concentration in the initial acetone solution

and the ratio between solution and water both brought changes in the perylene concentration of its nanocrystal dispersion. For example, the size of nanocrystals increased with increasing perylene concentration, as would be expected. We could obtain nanocrystals with different size by changing the concentration of nanocrystal dispersions. Table 1 shows the relationship between the injected amount of perylene solution (~1 mmol/l) and the size of perylene nanocrystals obtained. When 100 μl of the acetone solution of perylene was added to 10 ml of pure water, 10 nm crystals were initially produced. The data also show that the size of the nanocrystals increased with aging time and the volume of acetone solution employed. Fig. 2 shows the TEM micrographs of the 60 and 250 nm perylene nanocrystals produced after a 2-day aging period.

Table 1
The effects of perylene quantity and aging time on the size of perylene nanocrystals

Perylene solution (μl)	Aging time (h)	Size of nanocrystals (nm)
100	0	~10
100	48	~60
400	0	~20
400	48	~250

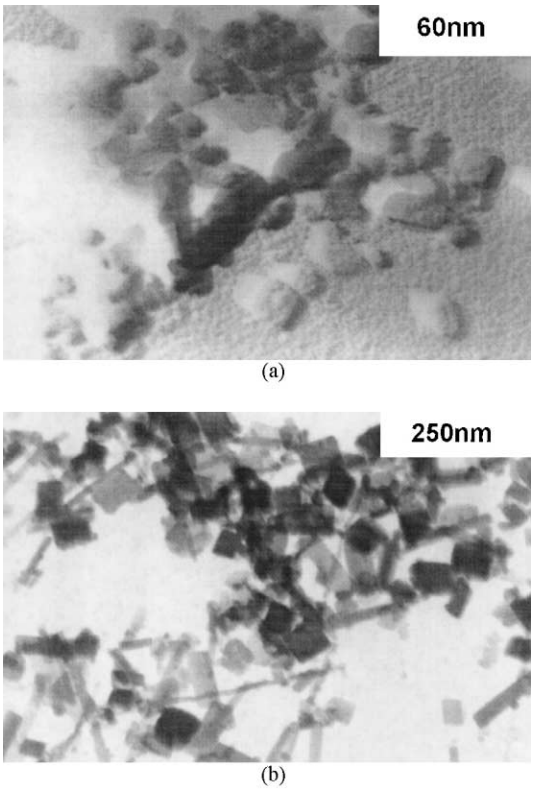

Fig. 2. TEM micrographs of perylene nanocrystals of different sizes: 60 nm (a) and 250 nm (b).

The surfactant influenced the growth rate of nanocrystals. When a solution containing the cationic surfactant $C_{16}H_{33}(CH_3)_3NBr$ or the anionic surfactant $C_{12}H_{25}SO_3Na$ solution was used instead of pure water, we found that both surfactants decreased the growth rate of perylene nanocrystals (Fig. 3). Since increasing nanocrystal size causes spectral shifts to longer wavelengths, we used changes in the absorption peak position as a measure of nanocrystal size. Fig. 3 shows the changes in absorption peak position as a function of perylene nanocrystal aging time. Distinctly, when

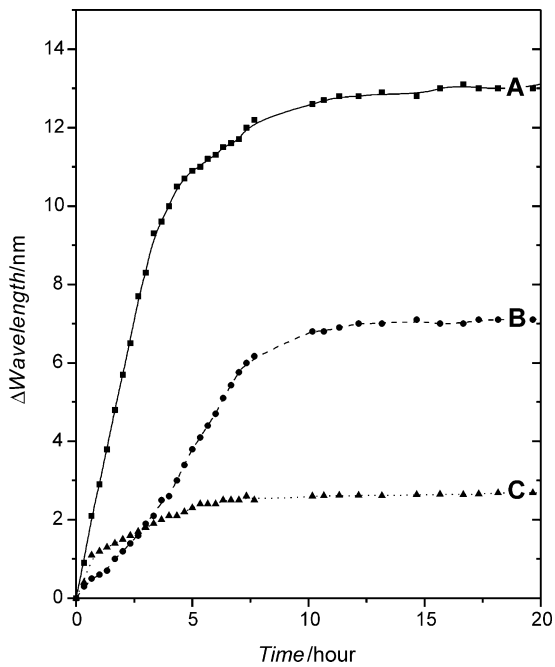

Fig. 3. Changes in λ_{max} with aging time in different media: pure water (A); aq. sodium dodecyl sulfonate solution (B); aq. cetyl trimethyl ammonium bromide solution (C).

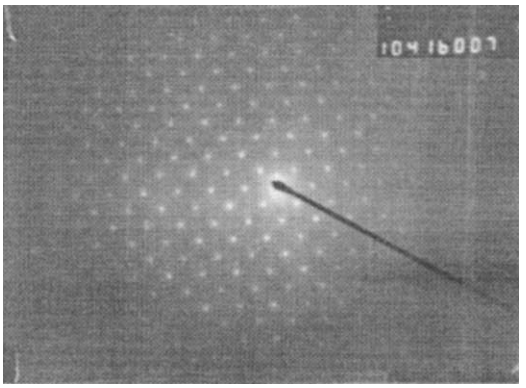

Fig. 4. The electron diffraction pattern of perylene nanocrystals embedded in SiO_2 gel.

using cation surfactant ($C_{16}H_{33}(CH_3)_3NBr$) (curve C) as nonsolvent instead of water (curve A), the growth rate of perylene nanocrystals slowed down, remarkably. When using anion surfactant ($C_{12}H_{25}SO_3Na$) (curve B) as nonsolvent, the growth rate also slowed down comparing with using water (curve A). It can be seen that the anionic surfactant quenched nanocrystal growth to a slightly lesser degree than the cationic surfactant (curve B vs. C). However, these results also indicate that there is virtually no charge on the surface of perylene molecules, as both surfactant types reduce the nanocrystal growth rate. We believe that surfactant micelles form around the small perylene nanocrystals, interfering with the aggregation process that occurs in surfactant-free systems. The nonpolar perylene molecules partition to the hydrophobic interiors of surfactant micelles. The hydrophilic exteriors would create an even stronger oleophobic barrier for perylene molecules to cross during agglomeration/crystallization than present in surfactant-free systems. It is also possible that the longer alkyl chain in the cationic surfactant contributed to the larger decrease in nanocrystal growth rate versus the anionic surfactant. Nevertheless, it is apparent that the use of suitable surfactants can control perylene nanocrystal growth rate and particle size. Studies involving the impact of surfactant concentration on (a) equilibration growth rate and (b) equilibrium particle size comprise the logical next steps in this investigation.

3.2. Embedding and structure analysis of perylene nanocrystals

SiO_2 gel glass doped with perylene nanocrystals is porous, yellow and transparent. It is also clear that perylene nanocrystals can be effectively embedded in SiO_2 gel, as immersing the doped gel glass in ethanol gave no detectable removal of perylene dye [12]. To further investigate the structure of the perylene nanocrystals we obtained, we recorded their electron diffraction pattern [16] with the aid of a TEM (cf. Fig. 4). Following this experiment, we calculated d_I, a and $h_ik_il_i$ values for each point in the diffraction pattern. The results showed that the embedded perylene nanocrystals were of the α form [15].

3.3. Spectra character of perylene nanocrystals

The absorption spectra of nanocrystals of different sizes are illustrated in Fig. 5. Curves A, B, C and D are the absorption spectra of perylene nanocrystals that have an average size of 250, 60, 20 and 10 nm,

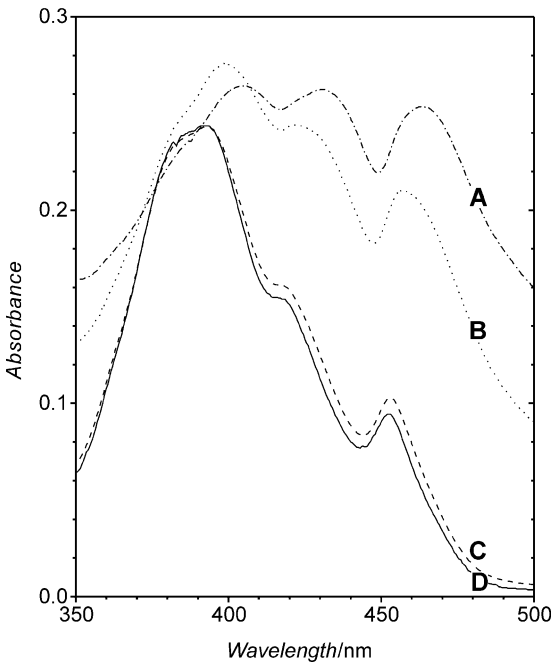

Fig. 5. Absorption spectra of perylene nanocrystals of different sizes: 250 nm (A); 60 nm (B); 20 nm (C); 10 nm (D).

respectively. It can be seen that decreasing the size of nanocrystals from 250 to 10 nm (A→D) caused absorption peak shifts from 463.5 to 452.5 nm. The blue shift arises from microcrystallization, which in turn causes lattice softening. Therefore, the coulombic interaction energies between molecules are smaller, leading to wider band gaps [6].

4. Conclusions

It has been found that perylene nanocrystals are J-aggregates and that perylene concentration, crystal-growth aging time, and the presence or absence of a surfactant influence nanocrystal size. We also found that perylene nanocrystals exhibit size-dependent absorption spectra and that they can be embedded in SiO_2 gel for various end-use applications.

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