Letter

Effect of PVA on the growth and the optical properties of perylene nanocrystals

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Poly(vinyl alcohol) (PVA) was added to a water suspension of perylene nanocrystals prepared through the reprecipitation method. The growth of the nanocrystals can be sustained by the protecting effect of PVA. At the same time, the monomer emission of perylene nanocrystals is enhanced and the lifetime of the excited state is prolonged after the addition of PVA, owing to the interaction between perylene nanocrystals and PVA molecules.

In recent years, interest has been rapidly growing in research on nanocrystals. Due to quantum size and surface enhancement effects, nanocrystals have unique optical and electronic properties, allowing them to be used as new optically functional materials. Although current studies in such fields mainly focus on semiconductor, metal and other inorganic nanocrystals,[1,2] some scientists have reported results on organic nanocrystals.[3–8] Through the reprecipitation method, aqueous dispersions of nanocrystals of organic compounds, such as perylene and diacetylene, have been prepared and some interesting phenomena have been observed, such as red-shifting of the absorption maximum with increasing size of nanocrystals.

Although the reprecipitation method is considered a versatile and easy way to fabricate organic nanocrystals, it is difficult to form stable nanocrystal dispersions. In the process of reprecipitation, the nanoparticles grow with time, from tens of nanometers to hundreds of nanometers, and finally large particles are formed, depositing out of the solution. Under such circumstances, the optical spectra reported by Nakanishi *et al.* were actually obtained during this dynamic process and are related to the approximate size of the nanocrystals at every stage.[3,4] In this study, to improve the reprecipitation method and to form a stable dispersion of nanocrystals, we used a water soluble polymer, poly(vinyl alcohol) (PVA), as a protective or stabilizing colloid to obtain a stable hydrosol of the nanocrystals. It is found that the optical properties of the dispersion can be modulated by the amount of PVA added.

A series of perylene nanocrystals from tens to hundreds of nanometers were prepared in this experiment. SEM photographs of perylene nanocrystals with sizes of 50 and 200 nm stabilized by PVA are displayed in Fig. 1. The size and the distribution of the perylene nanocrystals were also confirmed by dynamic light scattering (DLS). It can be seen that as the size of the nanoparticles increases, the shape of the perylene nanocrystals changes from spherical to cubic or rectangular with sharp and distinct edges, indicating the formation of a crystalline material. Under the protection of PVA, the nanocrystals are clearly well separated and no aggregation is found, indicating effective capping of PVA on the nanoparticle surfaces. This stabilizing effect is also verified by the absorption spectral measurements. After the addition of PVA, the absorption spectra of the perylene nanocrystals show no changes with time. This means that there is no growth of the nanocrystals.[3–5] Therefore, dispersions of perylene nanocrystals with different sizes can be obtained by adding PVA at different aging times.

Similar to the function of gelatin in the controlled precipitation process,[9] the absorption of PVA on precipitated perylene nanocrystals is controlled by hydrophobic interactions. Upon adsorption, the PVA molecules rearrange their

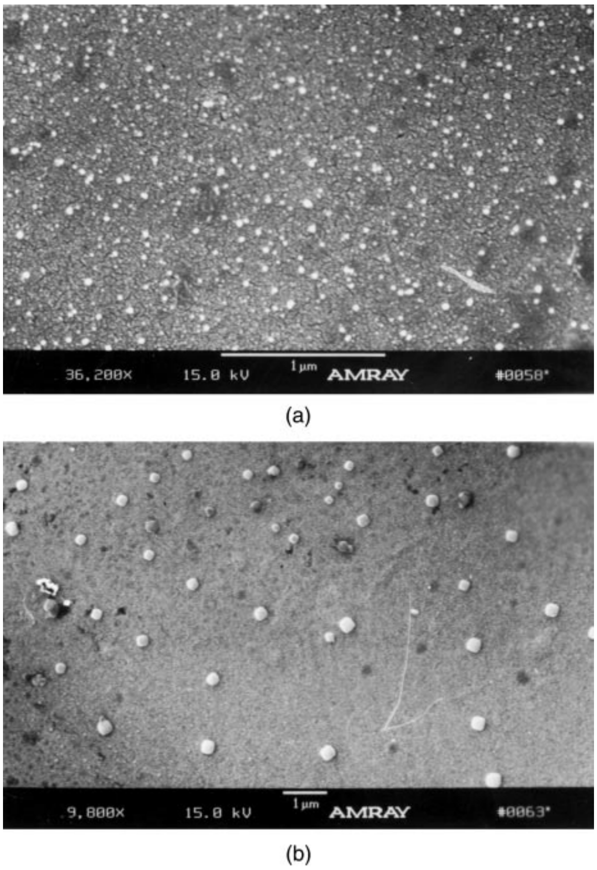

Fig. 1 SEM photographs of PVA-capped perylene nanocrystals of different sizes: (a) 50, (b) 200 nm. The concentration of the PVA–water solution used in the preparation was 0.02 g ml^{-1}.

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conformation, thus orienting the polar hydroxyl groups towards the water phase, whereas the non-polar carbon chain domains are closely bound to the surface of the nanocrystals. The absorption layer can provide excellent steric stabilization, leading to stable dispersions of the nanocrystals. Since PVA has superior solidifying properties, a dispersion of perylene nanocrystals stabilized by PVA can be readily transformed into a dry powder by techniques such as spray drying, and they can also be deposited as perylene nanocrystal/PVA composite films on solid substrates by using casting or spin-coating methods.

As PVA can bind onto the surface of the perylene nanocrystals, the interactions between PVA and the nanocrystals might have some influence on the optical properties of perylene nanocrystals. To test this assumption, different amounts of PVA were added to water dispersions of perylene nanocrystals of the same size and the resulting dispersions were characterized by their fluorescence spectra (see Fig. 2). The peaks around 440 and 475 nm are assigned to the emission of perylene monomer, since they appear at the same positions as in the emission spectrum of a dilute perylene solution. The strong peak at longer wavelength may stem from molecular association and, after analysis, is shown to include two emissions; that centered at 560 nm is attributed to E-type excimer emission[10,11] and the other at 540 nm may be due to Y-type excimers.[12,13] In perylene nanocrystals, although perylene molecules are in pairs, some have a non-ideal dimer packing configuration. After being excited, they might form excimers and undergo a slight excimer-like configurational change, leading to the Y-type excimer emission at about 540 nm with about a 2.5 ns decay time. Other perylene dimers have the ideal sandwich configuration with the two molecular planes placed exactly opposite to each other. The emission of these excimers is around 560 nm with about a 10 ns decay time. As can be seen from Fig. 2, in which all the spectra are normalized to the peak of the excimer emission, the relative intensity of perylene monomer emission is enhanced with increasing concentration of PVA in the dispersions. This kind of luminescence change cannot be explained by a surface modification effect, as is observed with inorganic nanoparticles such as PbS or ZnO.[14,15] In the case of inorganic nanoparticles, the luminescence mainly originates from electron–hole pairs trapped on the surface; the polymer capped on the surfaces of nanoparticles can passivate or chemically modify the surfaces, thus changing the electron–hole trapping state and leading to changes in the luminescence. For perylene nanocrystals, the luminescence changes chiefly result from the dislocated perylene monomers. In our experiment, the nanocrystals are prepared through the reprecipitation method, which is based on the different solubility of perylene in two different solvents. In the dispersions, the nanocrystals are actually in a dynamic state, which results from the equilibrium between precipitation and dissolution. Hence, at the periphery of the nanocrystals, perylene molecules usually dislocate from the lattice, forming free monomers and leading to monomer emission. It is well known that organic molecules such as perylene and pyrene show strong emissions that are easily affected by molecular quenching induced by collisions between molecules, allowing them to be used as probes for their surroundings.[16,17] When the concentration of PVA in the dispersion increases, the non-polarity of the nanocrystal surroundings is strengthened, since more PVA molecules are present in the dispersion to wrap the surface of the nanocrystals with their hydrophobic groups. Thus, the dislocated perylene molecules are more likely to be bound to PVA hydrophobic chains due to the strong hydrophobic interactions between them. The movements and configuration changes of those perylene molecules wrapped by PVA chains will be constrained. Hence, the collisions between molecules, which can induce fluorescence quenching, are eliminated and the fluorescence intensity is enhanced.

The appearance of PVA on the perylene nanocrystals can also affect the decay time of their excited state. Fig. 3(a) displays the decay profiles of the emission of the perylene nanocrystals at 560 nm under different PVA concentrations. The fitting results of these profiles are shown in Fig. 3(b), from which it can be seen that with increased PVA concentration,

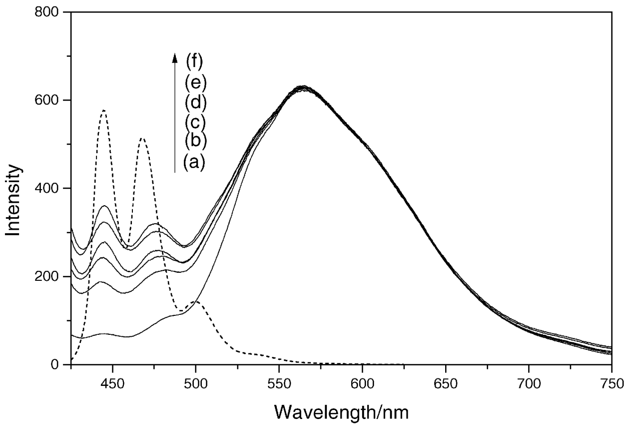

Fig. 2 Fluorescence emission spectra of perylene nanocrystals dispersed in aqueous solutions with different concentrations of PVA (g l^{-1}): (a) 0, (b) 0.003, (c) 0.008, (d) 0.02, (e) 0.04 and (f) 0.05 (the size of the perylene nanocrystals is about 100 nm in all the dispersions). Dotted line: emission spectrum of perylene–acetone solution (7 × 10^{-6}mol l^{-1}).

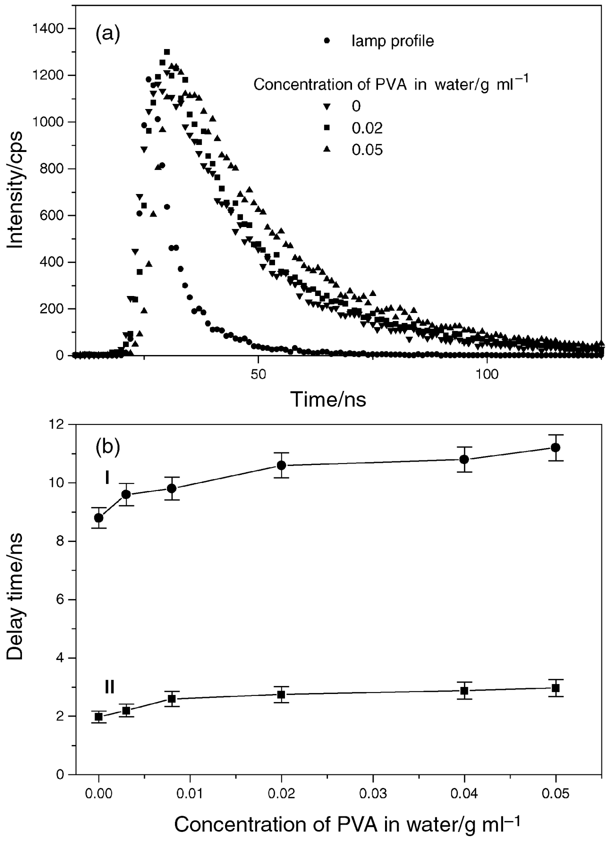

Fig. 3 (a) Decay profiles of the fluorescence emission of perylene nanocrystals dispersed in aqueous solution with different concentrations of PVA. (b) Change in the decay time of the E-excimer and Y-excimer emission with changing PVA concentration: (I) E-excimer emission (II) Y-excimer emission. [For a clear comparison, some of the decay profiles are not shown in (a); however, the fitting results of all the decay profiles are given in (b).]

the decay time of the E-excimer emission changes from 9 to 11 ns. At the same time, the decay time of the Y-excimer emission is prolonged for more than 1 ns. These kinds of lifetime changes with different PVA concentrations may stem from the binding of PVA on nanocrystals. In the dispersion without PVA, nanocrystals are in the process of precipitating and dissolving. Actually, perylene molecules, especially those near the periphery, are in a dynamic state. So the excimer formed in this region is unstable. Although the dimers in the inner part of the nanocrystals may be more stable, being less affected by their surroundings, they are not readily subject to excitation because the scattering of the crystal lattice weakens the intensity of the incident light. Thus, the excimer emissions mainly come from molecules near the periphery and the emission lifetime might be affected by the surroundings. When PVA is added into the solution, it can be adsorbed on the surface of the particles, insulating the particles from their surroundings. The dissolution and precipitation processes are restrained, stabilizing the nanocrystals. As a result, the excimer has a longer decay time since fewer paired perylene molecules will decompose in the stabilized nanocrystals. Another aspect that may affect the decay time is fluorescence quenching induced by collisions. In water suspension, the tiny particles undergo random Brownian movements and collisions between them frequently occur, inducing fluorescence quenching. But with the protecting PVA, the quenching effect is eliminated because the outer polymer layer prevents perylene molecules of the nanocrystals from colliding. In our experiment, when the amount of PVA added is increased, the nanocrystals are more heavily coated and the excited state becomes more stable, resulting in longer decay times.

In this experiment, a soluble polymer, poly(vinyl alcohol) (PVA), was used to stabilize water dispersions of perylene nanocrystals. Perylene nanocrystals show three emissions, from perylene monomers, Y-excimers and E-excimers. With increasing amounts of PVA added, the intensity of the monomer emission is enhanced and the decay time of the excited states becomes longer owing to the prevention of dissolution and molecular collisions by PVA. The surface binding of PVA not only affects the stability properties but also plays a very important role in controlling the optical properties of perylene nanocrystals. In addition, it provides a feasible way to transfer the nanoparticles into powders *via* spray drying or into thin films *via* casting or spin-coating methods.

Experimental

The nanocrystals of perylene were prepared as follows: 400 μl of perylene–acetone solution (7.0×10^{-4} mol l^{-1}) was injected into 10 ml of water. Since perylene does not dissolve in water, it precipitated from the solution as a result of "salting out". After vigorous stirring, a yellow dispersion formed. At different stages of the nanocrystal growth, PVA was added into the dispersions, forming stable suspensions of perylene nanocrystals with different sizes. The water used in this experiment was purified by a Milli-Q Plus water purification system and had a resistivity of 18.2 MΩ.

The fluorescence spectra of perylene nanocrystals were recorded with a F-4500 Hitachi fluorescence spectrophotometer. The sizes and shapes of the nanocrystals were observed using a field emission scanning electron microscope (AMRAY, 1910FE). The size and distribution of nanocrystals dispersed in water were also investigated by the dynamic lights scattering (DLS) technique using a Zetplus BI-9000 (Brookhaven Instruments Corporation). The decay times of excited states were measured with a Hitachi NAES-1100 spectrometer using single photon counting techniques.

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References

1 A. P. Alivisatos, *Science*, 1996, **271**, 933.
2 A. Henglein, A. Kumar, E. Jananta and H. Weller, *Chem. Rev.*, 1989, **89**, 1861.
3 H. Kasai, H. S. Nalwa, H. Oikawa, S. Okada, H. Matsuda, N. Minami, A. Kakuta, K. Ono, A. Mukoh and H. Nakanishi, *Jpn. J. Appl. Phys.*, 1992, **31**, L1132.
4 H. Kasai, H. Kamatani, S. Okada, H. Oikawa, H. Matsuda and H. Nakanishi, *Jpn. J. Appl. Phys.*, 1996, **35**, L221.
5 H. Karagi, H. Kasai, S. Okada, H. Oikawa, H. Matsuda and H. Nakanishi, *Pure Appl. Chem.*, 1997, **A34**, 2013.
6 Y. Shen, D. Jakubczyk, F. Xu, J. Swiakiewicz and P. N. Prasad, *Appl. Phys. Lett.*, 2000, **76**, 1.
7 Y. Shen, J. Swiakiewicz, J. Winiarz, P. Markowicz and P. N. Prasad, *Appl. Phys. Lett.*, 2000, **77**, 2946.
8 A. Ibanez, S. Maximov, A. Guiu, C. Chaillout and P. L. Baldeck, *Adv. Mater.*, 1998, **10**, 1540.
9 H. Auweter, V. Andre, D. Horn and E. Luddecke, *J. Dispersion Sci. Technol.*, 1998, **19**, 163.
10 A. G. Bitukhnovsky, M. I. Sluch, J. G. Warren and M. C. Petty, *Chem. Phys. Lett.*, 1991, **184**, 235.
11 J. G. Warren, J. P. Cresswell, M. C. Petty, J. P. Lloyd, A. Bitukhnovsky and M. I. Sluch, *Thin Solid Films*, 1989, **179**, 515.
12 D. Weiss, R. Kietzmann, J. Mahrt, B. Tufts, W. Storck and F. Willig, *J. Phys. Chem.*, 1992, **96**, 5320.
13 T. X. Wu, D. W. Brown and K. Lindenberg, *J. Lumin.*, 1990, **45**, 245.
14 M. Gao, Y. Yang, B. Yang and J. Shen, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 4121.
15 L. Guo and S. Yang, *Appl. Phys. Lett.*, 2000, **76**, 2901.
16 E. Araujo, Y. Rharbi, X. Huang and M. A. Winnik, *Langmuir*, 2000, **16**, 8664.
17 S. N. Daniel, E. D. Niemeyer and F. V. Bright, *Macromolecules*, 1999, **32**, 8084.