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In Situ and Ex Situ Observations of the Growth Dynamics of Single Perylene Nanocrystals in Water

Takashi Tachikawa,† Hae-Ryong Chung,‡ Akito Masuhara,‡ Hitoshi Kasai,‡ Hidetoshi Oikawa,*,‡
Hachiro Nakanishi,‡ Mamoru Fujitsuka,† and Tetsuro Majima*,†

The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan, and Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

Received August 5, 2006; E-mail: majima@sanken.osaka-u.ac.jp; oikawah@tagen.tohoku.ac.jp

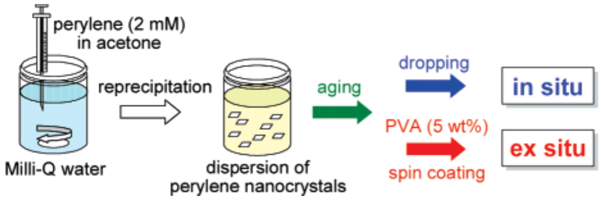
Organic nanocrystals, ranging in crystal size from about tens of nanometers to several hundred nanometers, have attracted great interest in recent years, since they exhibit unique optical and chemical properties which differ from those of isolated molecules and the bulk solid state.[1−8] For example, a blue shift in the absorption and emission peak wavelengths upon decreasing the crystal size was observed for several organic nanocrystals, such as polydiacetylene[2d] and perylene[2c,6] nanocrystals, although the size range for the effect is about 1 order of magnitude larger when compared to semiconductor quantum dots.[9]

We have already demonstrated the use of a "reprecipitation method" for the fabrication of organic and polymer nanocrystals.[2] In this method, a dilute solution of the compound prepared using a water-soluble solvent, i.e., a good solvent, is injected into vigorously stirred water as a poor medium, and the compound is reprecipitated in the form of nanocrystals from an aqueous medium, usually in a stable dispersion (Scheme 1). The size and shape of the resulting nanocrystals can be controlled by varying the reprecipitation and growth conditions, which allows us to deduce the nanocrystallization mechanism.[2b,e] However, the nanocrystallization processes, especially within several hours after reprecipitation, have not yet been clarified for low-molecular-weight aromatic compounds such as perylene and anthracene, due to the instability of the scattered intensity autocorrelation functions in the dynamic light scattering (DLS) measurements.[2e]

Herein, we report our investigation of the growth dynamics of single perylene nanocrystals in water from in situ and ex situ single-particle fluorescence measurements. Single-particle fluorescence spectroscopy has already yielded novel insights into the photophysics and photochemistry of inorganic and organic nanocrystals.[8,10−12] We first examined the spectral characteristics of perylene nanocrystals dispersed in a poly(vinyl alcohol) (PVA) matrix. We then determined the diffusion coefficient (*D*) and diameter (*d*) of individual perylene nanocrystals using an in situ optical imaging technique, and we discuss the growth processes of the perylene nanocrystals in water.

Perylene was used as an active material to prepare nanocrystals using the reprecipitation method.[2a] A suspension of nanocrystals containing PVA (5 wt %) was spin-coated onto a clean glass cover slip. For the in situ observations, a drop of the perylene nanocrystal suspension was sandwiched between a hole-slide glass and a coverslip. The experimental setup is based on using a wide-field fluorescence microscope (Olympus IX71). Light emitted from a continuous-wave Ar ion laser (488 nm, 10 mW, Melles Griot) passing through an objective lens (Olympus, PlanApo, 1.45 NA, 100×) was used to excite the perylene nanocrystal (see Supporting Information for details).[13]

Scheme 1



Perylene nanocrystals have been reported to show size-dependent optical properties.[2c,6] Figure 1A shows the typical fluorescence spectra of single isolated perylene nanocrystals dispersed in a PVA film under ambient conditions. It was expected that only light emissions from the self-trapped excitons, i.e., excimer emission, around 600 nm would be present, because of our detection region (>510 nm).[2c] The emission spectra of individual nanocrystals indicate a red shift in the emission maxima as their intensity increased (see Supporting Information for details). As is well-known, the particle size dependence of emission maxima can be explained in terms of lattice softening, which makes the intermolecular interaction weaker and modifies the energy level of the excimer state in the nanocrystal.[2c,6]

We examined the fluorescence properties as a function of the aging time in water. Figure 1B shows the histograms of the peak energy of the emission spectra observed at different aging times after reprecipitation. The peak energy decreased with increasing aging time, especially within 2 h. It should be noted that the broadening of the energy distribution was significantly reduced by 11 meV at the aging time of 22 h. These experimental results clearly suggest that the crystal size increased with increasing aging time, as expected.

As shown in Figure 1C, we also found two types of fluorescence time trajectories: with a constant intensity and with intensity fluctuations. About 10% of all the perylene nanocrystals show a fluctuation behavior, especially for fluorescent spots with a weak intensity. The observed fluctuation of the fluorescence intensity can be explained in terms of an energy funneling at the trap sites.[8]

We now focused on the growth processes of the perylene nanocrystals in water. Figure 2A shows the in situ fluorescence images observed during the 488-nm excitation for single perylene nanocrystals in water after reprecipitation.[14] We analyzed the trajectories of the single nanocrystals,[15] an example of which is shown in the inset of Figure 2B, and then determined the diameter (d_{SE}) of the perylene nanocrystals on the basis of the Stokes−Einstein relation (Figure 2B).[16] As shown in Figure 2C, both the number and the weight-average diameter (d_W) of the nanocrystals increased with increasing aging time. In particular, a "burst" in the

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† Osaka University.
‡ Tohoku University.

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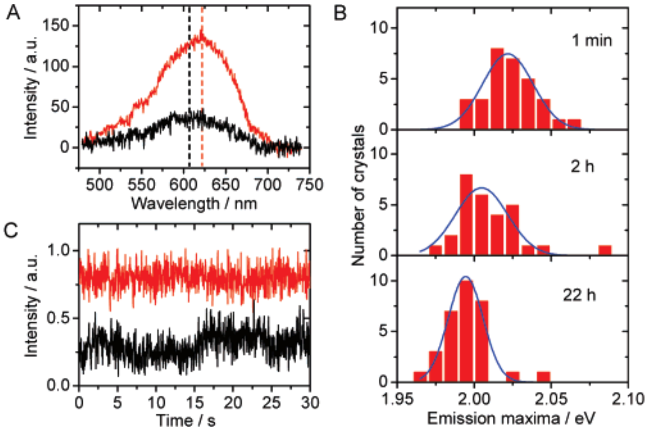

Figure 1. (A) Typical fluorescence spectra observed during the 488-nm excitation for single perylene nanocrystals in a PVA film at 1 h after reprecipitation. Dotted lines indicate the peak wavelength. (B) Histograms of emission maxima of the fluorescence spectra. Solid lines indicate Gaussian distributions fitted with the histograms. (C) Typical trajectories of fluorescence intensity.

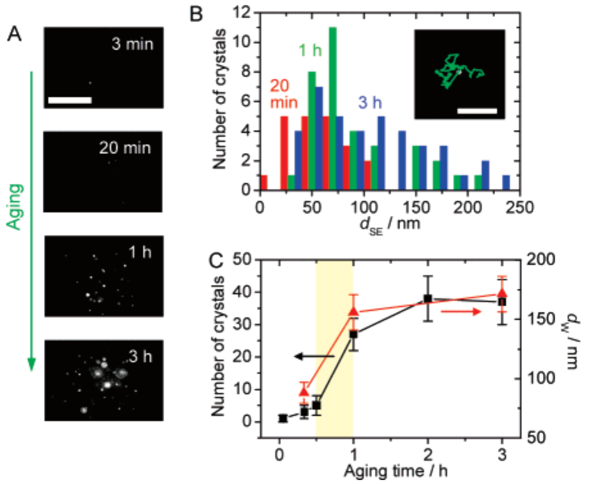

Figure 2. (A) Fluorescence images observed for single nanoperylene crystals in water after reprecipitation (scale bar is 50 μm). (B) Size distribution of perylene nanocrystals in water observed at different aging times. Inset shows the trajectory of the nanocrystal movement (scale bar is 10 μm). (C) Aging time dependence of the number and the weight-average diameter (d_W) of perylene nanocrystals in water.

number and size of the nanocrystals occurred 1 h after the reprecipitation.

Considering the crystallization processes of perylene in water, after reprecipitation, the clusters are probably formed from fine droplets via mutual diffusion of the good solvent and water.[2e] The dissolved molecules can quickly make contact with the water phase and rapidly form clusters. The clusters then aggregate to form the initial nanoparticles, such as amorphous nanoparticles of perylene,[6] within 30 min after reprecipitation. We believe that the metastable intermediates, such as the clusters and initial nanoparticles, are relevant for the early stages of nucleation and growth of the organic nanocrystals. Most initial nanoparticles grow or aggregate to form the seed nanocrystals within 30 min to 1 h after reprecipitation. This growth process is confirmed by the fact that significant increases in the number and size of the perylene nanocrystals in water were observed 1 h after reprecipitation. At this stage, the seed nanocrystals coexist with the growing nanocrystals, resulting in the broad distribution of the emission maxima and size of the nanocrystals, as shown in Figures 1B and 2B, respectively. The crystal size determined by in situ single-particle fluorescence measurements is quite consistent with those obtained from the DLS and scanning electron microscopy (SEM) measurements.[2e] Eventually, the seed nanocrystals grow to produce large nanocrystals of >100 nm and almost the same α-form crystal structure as the perylene bulk crystals.[2e,17]

In conclusion, we directly observed the growth processes of fluorescent perylene nanocrystals, which are fabricated by the reprecipitation method, using in situ and ex-situ single-particle fluorescence spectroscopies. Our method can provide further insight into the crystallization mechanism of organic nanocrystals. In the future, the influences of fundamental factors, such as temperature and the physical properties of good solvents, on the growth processes of organic nanocrystals will be carefully studied at the single-particle level.

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Supporting Information Available: Experimental details and individual emission spectra (PDF); movies showing the diffusion of the perylene nanocrystals in water observed 30 min and 1 h after reprecipitation (AVI). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Small nanocrystals ($d < 30$ nm) were only slightly observed in water because of their fast diffusion.
(15) (a) The two-dimensional mean-square displacement, $\langle r(\tau)^2\rangle$, in the image plane is defined by[15b] $\langle r(\tau)^2\rangle = \langle [x(t+\tau) - x(t)]^2 + [y(t+\tau) - y(t)]^2\rangle$, where x and y are the time-dependent coordinates of the center of the fluorescence spot, τ is the so-called lag time, and the angular brackets indicate an average over many starting times. The lag time τ is the time elapsed from the arbitrary repeated time of beginning the monitoring of particle displacements. Unconstrained Brownian motion follows the familiar relation for diffusion in two dimensions: $\langle r^2\rangle = 4Dt$. (b) Crocker, J. C.; Grier, D. G. *J. Colloid Interface Sci.* **1996**, *179*, 298−310.
(16) Simple Brownian movement with D is given by the Stokes−Einstein equation, $d_{SE} = kT/3\pi\eta_0 D$, where d_{SE} is the diameter of the nanocrystal, k is Boltzmann's constant, T is the absolute temperature, and η_0 is the viscosity. The D value was obtained from the slope at the time region, in which fluorescent areas in pixel units are almost constant, since the nanocrystals undergo three-dimensional diffusion in water. See Supporting Information for details.
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