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Relationship between the Surface Morphology and Optical Property of Organic Nanocrystals

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We studied the relationship between the surface morphology and optical property of 9,10-bis(4-(N-carbazolyl)phenyl)anthracene (BCPA) nanocrystals having a small nanoparticle on their surface using an atomic force microscope (AFM) followed by density functional theory (DFT) calculations and optical spectroscopy. The estimated mean unit size of the small particles on the nanocrystal's surface in lateral terms was smaller than 20 nm, consisting of several thousand BCPA molecules. The fine structure observed in the emission spectrum of e-BCPA would be assigned to the vibronic transitions of BCPA molecules.

Keywords Organic nanocrystal; surface morphology; optical property; emission with vibronic structure

1. Introduction

The morphology of nanosized inorganic particles is strongly related to their electronic structure [1–5]. Compared with inorganics, little research has been conducted on the effects of morphology on the optical properties of organic nanocrystals, due to the limitation of fabrication methods. To date, only a few studies have investigated the size-dependence of optical and electronic properties in organic nanocrystals using spectroscopic techniques such as single-nanoparticle spectroscopy [6].

Previously we reported the first surface structure effect on the optical properties of organic nanocrystals with 9,10-bis(4-(N-carbazolyl)phenyl)anthracene (BCPA) [7]. BCPA nanocrystals with different surface morphology were achieved by employing the 'emulsion' [8] and 'reprecipitation' [9] methods. Although the emission spectra of BCPA nanocrystals were found to be strongly affected by the surface characteristics, the characterization of the surface, especially in term of the very small particles covering it, was not well performed. In

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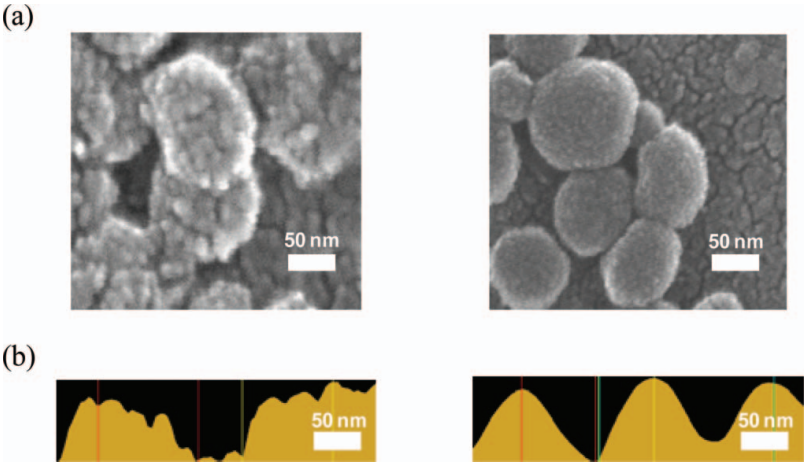

Figure 1. (a) Scanning electron microscopy (SEM) images of e-BCPA (left) and r-BCP (right), (b) cross-sectional atomic force microscopy (AFM) images of e-BCPA (left) and r-BCP (right).

this study, we studied the small particles on the BCPA nanocrystals in more detail using an atomic force microscope (AFM) followed by density functional theory (DFT) calculations and optical spectroscopy.

2. Experimental

The organic nanocrystals, e-BCPA (using the emulsion method) [8] and r-BCPA (using the reprecipitation method) [9] were fabricated according to our previously reported methods. The distribution of the particle sizes of each nanocrystal was measured by dynamic light scattering (DLS) (ALV-GmbH, ALV-5000). The surface morphologies of the samples were investigated by scanning electron microscopy (SEM) using a Jeol JSM-6700F and also examined by AFM using a Seiko SPI-3800N in tapping mode. The DFT calculations were carried out by the hybrid B3LYP functional using a 6-31G basis set. The photoluminescence (PL) excitation and emission spectra of samples were obtained by using a Hitachi F-2500 fluorescence spectrometer at room temperature.

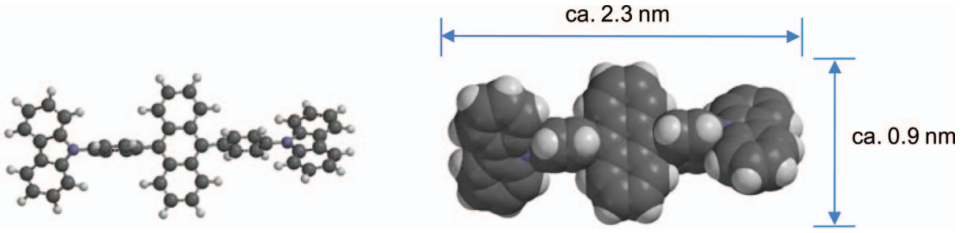

Figure 2. Optimized molecular structure of BCPA from the DFT calculations at the B3LYP/6-31G level of theory (left), and corresponding space-filling model (right).

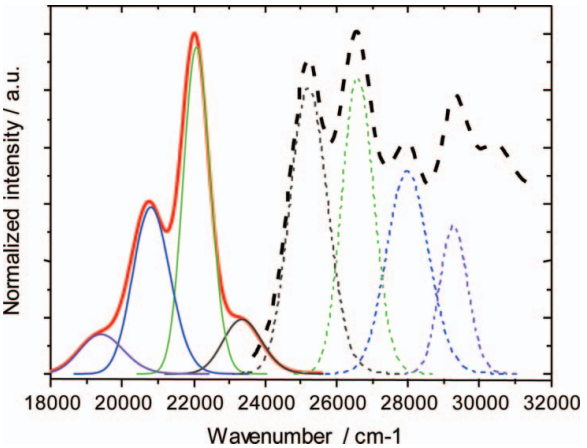

Figure 3. Room temperature photoluminescence (PL) emission spectrum of e-BCPA (solid line, λ_{ex} = 290 nm) nanocrystals dispersed in water and PL excitation spectrum of molecular BCPA (dotted line, λ_{ex} = 435 nm) in *o*-dichlorobenzene at room temperature with the waveform analysis results.

3. Result and Discussion

The particle sizes obtained by the 'emulsion' and the 'reprecipitation' methods were approximately 120 nm of e-BCPA and 110 nm of r-BCPA, respectively, the sizes of which were estimated by DLS measurements. As shown in Fig. 1, the difference in surface roughness of both e-BCPA and r-BCPA was confirmed by SEM. Although e-BCPA had a rough uneven surface morphology, the surface of r-BCPA was smooth. The estimated mean unit size of the small particles on the nanocrystal's surface was smaller than 20 nm in lateral terms, as demonstrated by the AFM image. Judging from the size of the BCPA molecular dimensions calculated using the DFT methods, the unit size 20 nm cube of the small particles on the nanocrystal surface consists of several thousand BCPA molecules (Fig. 2).

As shown in Fig. 3, the energy differences between each vibrational signal in the emission spectrum of e-BCPA, showing a fine structure, were exactly the same as that of the excitation for the BCPA molecules. This indicated that the fine structure in the emission spectrum of e-BCPA was originated from a molecular character of BCPA.

Thus, we demonstrated the first direct observation of the very small organic particles on the organic nanocrystals. Although the fine structure in the photoluminescence spectrum of e-BCPA would be due to vibronic transitions of BCPA molecules, it is unclear whether the other morphological factor of the small particles influenced the fine structure. Further research relating to the very small particles on the nanocrystal surface is presently in progress.

4. Conclusions

The relationship between the surface morphology and the optical property of BCPA nanocrystals with a small nanoparticle on their surface was investigated using AFM, DFT calculations, and the optical spectroscopy. The estimated mean unit size of the small particles on the e-BCPA nanocrystal's surface was smaller than 20 nm in lateral terms, consisting of several thousand BCPA molecules. The fine structure observed in the emission spectrum of e-BCPA would be assigned to the vibronic transitions of BCPA molecules.

References

[1] Hafnor, J. (2006). *Laser Focus World*, *42*, 99.
[2] Yoshikawa, H., Hosokawa, C., Ito, S., & Masuhara, H. (2005). *Hyomen Kagaku*, 26681.
[3] Norman Jr., T. J., Grant, C. D., & Zhang J. Z. (2006). In: *Nanoparticle Assemblies and Superstructures*, Kotov, N. A. (Ed.), CRC Press, LLC, Boca Raton.
[4] Frenzel, J., Joswig, J-. O., Sarkar, P., Seifert, G., & Springborg, M. (2005). *Eur. J.* Inorg. Chem., *18*, 3585.
[5] El-Shall, M. S. (2005). *J. Saudi Chem. Soc.*, *9*, 91.
[6] Masuhara, H., Nakanishi, H., & Sasaki, K. (Eds.), (2003). *Single Organic Nanoparticles*, Springer, Berlin.
[7] Kwon, E., Chung, H.-R., Araki, Y., Kasai, H., Oikawa, H., Ito, O., & Nakanishi, H. (2007). *Chem. Phys. Lett.*, *441*, 106.
[8] Kwon, E., Oikawa, H., Kasai, H., & Nakanishi, H. (2007). *Cryst. Growth Des.*, *7*, 600.
[9] Kasai, H., Nalwa, H. S., Oikawa, H., Okada, S., Matsuda, H., Minami, N., Kakuta, A., Ono, K., Mukoh, A., & Nakanishi, H. (1992). *Jpn. J. Appl. Phys.*, *41*, L1132.