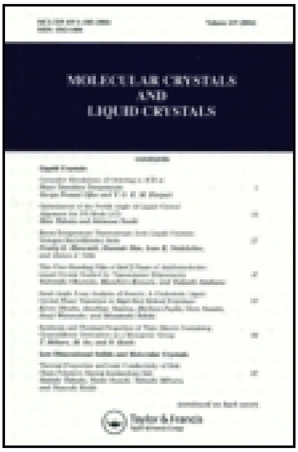

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Nanocrystallization Process of Diarylethene

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Nanocrystallization Process of Diarylethene

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We have clarified nanocrystallization process of diarylethene in the reprecipitation method using a derivative, cis-1,2-cyano-1,2-bis(2,4,5,-trimethyl-3-thienyl)ethene (CMTE) as a typical example of diarylethene. The crystal growth was investigated by the time-dependence measurement of crystal size with dynamic light scattering (DLS). Nanocrystallization process could be explained by the cluster-model.

Keywords Diarylethene; nanocrystallization; nanocrystals; organic nanocrystal; photochromism; reprecipitation method

Introduction

Photochromism is a reversible photoisomerization induced by alternate UV and visible light irradiation [1,2]. Among various photochromic compounds, diarylethene has received much attention in the field of optical devices because of their excellent properties and functions, e.g., high sensitivity, thermal stability, fatigue resistance and optical response in bulk crystal state [3,4].

Although a large number of researches for diarylethene were reported so far, only a few groups have fabricated diarylethene nanoparticles [5–8]. Organic nanoparticles may promote deep light penetration and low light scattering, and can be assembled into thin film or ordered structure, because they can be obtained as a colloidal dispersion liquid by the reprecipitation method [9,10] or by laser ablation method [11]. Moreover, organic nanoparticles are expected to exhibit distinctive optoelectronic and photonic behaviors associated with size-dependence. With this background, in the previous study, we reported first the fabrication of diarylethene

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Address correspondence to Norio Tagawa, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku Sendai, Miyagi 980-8577, Japan. Tel. & Fax: +81-22-217-5645; E-mail: tagawa@mail.tagen.tohoku.ac.jp derivative nanocrystals, which means nanoparticles having high-crystallinity, by improving the reprecipitation method [12].

In the present study, we have analyzed nanocrystallization process of diarylethene in the reprecipitation method, which could be followed with dynamic light scattering (DLS) measurement, and nanocrystallization mechanism will be discussed.

Experimental

Diarylethene used was cis-1,2-cyano-1,2-bis(2,4,5,-trimethyl-3-thienyl)ethene (CMTE) as shown in Figure 1a, which was purchased and used without further purification. Water was purified up to 18.2 MΩ cm using Arium 611UV (Sartorius Mechtronics Japan K.K.).

CMTE nanocrystals were fabricated by the reprecipitation method as follows [10]. CMTE was first dissolved in acetone. The concentration of CMTE solution was adjusted to 2.0 mM. A 200 μL of CMTE solution was injected into vigorously stirred water (10 mL) using a microsyringe.

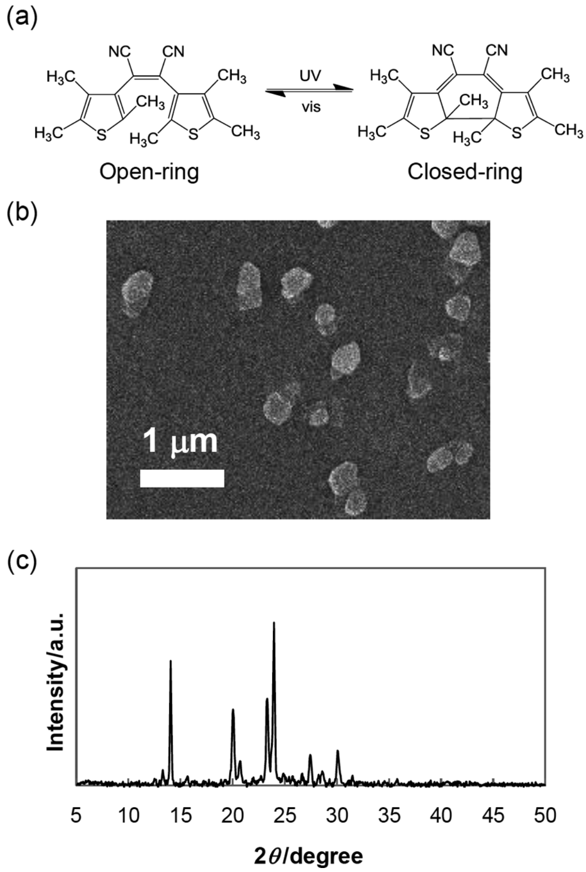

Figure 1. (a) Chemical structures of CMTE: open-ring and closed-ring structure. (b) SEM image and (c) powder XRD pattern of CMTE nanocrystals prepared by the reprecipitation method.

The size and shape were evaluated by dynamic light scattering instrument (DLS: Zetasizer Nano-ZS, Malvern Instruments Ltd.) and scanning electron microscope (SEM: JSM-67000 F, JEOL). Powder X-ray diffraction (XRD) pattern was measured with D8 Advance (Bruker AXS K.K.). UV-vis absorption spectra for CMTE nanocrystal were measured with UV-vis diffuse reflectance spectrometer (V-570DS, JASCO Ltd.). Photo-cyclization reaction was induced by UV irradiation with handy lamp (SUV-16, AS ONE Co.). All experiments were carried out at room temperature.

Results and Discussion

There are two forms of CMTE isomers, open-ring and closed-ring, which exhibit different physicochemical properties. In general, photo-cyclization reaction of diarylethene is in the equilibrium between two isomers, which means that open-ring isomer is not completely converted into closed-isomer. So, we have fabricated CMTE nanocrystals from only open-ring isomer.

Figure 1b shows the SEM image of CMTE nanocrystals fabricated by the reprecipitation method. The resulting CMTE nanocrystals were stably dispersed in water medium without adding a surfactant. In addition, powder XRD pattern exhibits the sharp diffraction peaks in Figure 1c, which indicates that the CMTE nanocrystals have high degree of crystallinity.

Figure 2 displays the plots of CMTE nanocrystal size measured with DLS *vs.* time. The crystal growth of perylene nanocrystals in the reprecipitation process has been already analyzed semi-quantitatively within the framework of Rayleigh's scattering theory, i.e., so-called "cluster-model" [13,14]. According to cluster-model, the crystal size of grown perylene nanocrystals with the elapsed time, t, was given by

$$D(t) = D(\infty)[1 - \exp(-\alpha N t)]^{\frac{1}{3}}, \tag{1}$$

where $D(t)$ and $D(\infty)$ are, respectively, the crystal size at $t = t$ and $t = \infty$, α is the crystal growth rate constant, and N is the number of scattering body that is assumed to be constant through the crystal growing process [14].

Equation (1) was fitted to the experimental data as shown in Figure 2, and the correlation coefficient was 0.968. The fitted line was able to reproduce well the

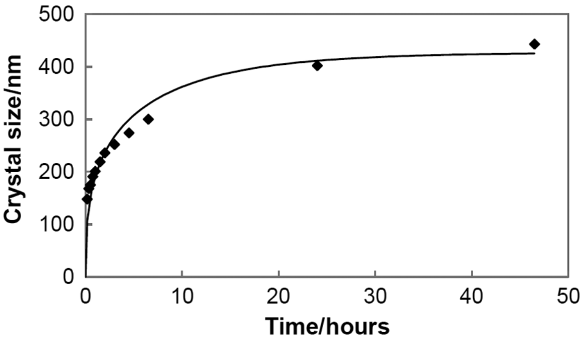

Figure 2. Plots of CMTE nanocrystal size measured with DLS *vs.* time. The solid line is the fitted one with Equation (1).

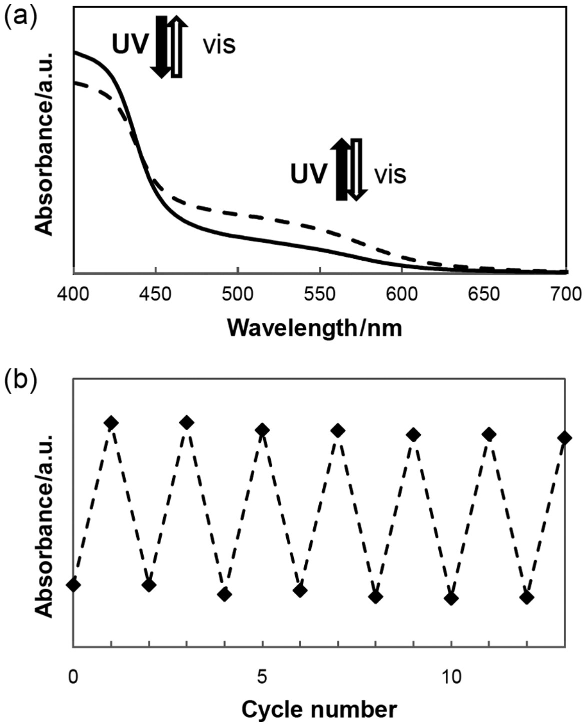

Figure 3. (a) UV-vis absorption spectral changes of CMTE nanocrystals with alternate UV and visible light irradiation, (b) absorbance at $\lambda = 580\,\text{nm}$ with cycle number.

experimental data. This fact suggests that nanocrystallization of CMTE can be described by a "cluster-model" [14], which is one of the proposed models for nanocrystallization process in the reprecipitation method [10,15]. The cluster-model is explained as follows: the injected CMTE solution becomes ultrafine droplets dispersed in an aqueous medium. The solvent in the droplets is smoothly dissolved into water, and the clusters consisted of CMTE molecules are formed, which are too small to scatter the light. The nuclei are generated by thermal collision between clusters, and crystal growth proceeds through the aggregation of clusters to nuclei. As a result, CMTE nanocrystals are formed.

We have also confirmed photochromism of CMTE nanocrystals by alternate irradiation of UV and visible light. During UV light irradiation ($\lambda = 254\,\text{nm}$), the yellow CMTE nanocrystals turned to red, and absorption spectrum changed as shown in Figure 3a. The red color returned again to yellow when irradiated with visible light ($\lambda > 420\,\text{nm}$), and spectrum was also restored. These changes were repeated several times as presented in Figure 3b, which indicates that CMTE nanocrystals actually exhibited photochromism.

Conclusions

In conclusion, we have clarified nanocrystallization process of CMTE in the reprecipitation method through the time-dependence of crystal size measurement with dynamic light scattering. Nanocrystallization process could be explained successfully by the so called cluster-model. The elucidation of nanocrystallization process will progress researches for diarylethene in nano-scale.

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