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Norio Tagawa [a], Akito Masuhara [a], Hitoshi Kasai [a] [b], Hachiro Nakanishi [a] & Hidetoshi Oikawa [a]

[a] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Aoba-ku Sendai, Miyagi, Japan

[b] PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Saitama, Japan

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Monodispersed and Size-Controlled Diarylethene Nanoparticles Fabricated by the Reprecipitation Method

NORIO TAGAWA,[1] AKITO MASUHARA,[1]
HITOSHI KASAI,[1,2] HACHIRO NAKANISHI,[1] AND
HIDETOSHI OIKAWA[1]

[1]Institute of Multidisciplinary Research for Advanced Materials,
Tohoku University, Aoba-ku Sendai, Miyagi, Japan
[2]PRESTO, Japan Science and Technology Agency (JST), Kawaguchi,
Saitama, Japan

We succeeded in fabrication of monodispersed diarylethene nanoparticles using the reprecipitation method and controlling nanoparticle size in the range of 40 nm to 250 nm by changing concentration of the injected solution and viscosity of good solvent. The obtained nanoparticles exhibited photochromism by alternate irradiation of UV and visible light. In addition, the red-shift of characteristic peak position (around $\lambda = 570$ nm) of closed-DAE nanoparticles was observed with increasing nanoparticle size, which was attributable to the strained molecular structure.

Keywords Diarylethene; organic nanoparticle; photochromism; reprecipitation method

Introduction

Photochromism is a reversible transformation between two forms with different chemical structures induced by photo-irradiation, which may cause various physicochemical properties such as absorption, emission, refractive index, dielectric constant, oxidation-reduction potential and so on [1,2]. Photochromic compounds are usually classified into two types; thermally unstable type (T-type) and thermally stable type (P-type). Azobenzene, spiropyran, and hexaarylbiimidazole [3] belong to T-type. Their photogenerated isomers can return to initial structure at room temperature. The T-type photochromic compounds attract much attention because of their potential applications in photochromic lens, holographic display and so on [1,3]. On the other hand, diarylethene (DAE) and furylfulgide undergo thermally irreversible P-type photochromic reaction. Namely, P-type photochromic compounds can be employed potentially for sustainable application such as optical memory media, switching devices, and light-driven actuators [1,2].

Address correspondence to Akito Masuhara, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku Sendai, Miyagi 980-8577, Japan. Tel. & Fax: 81-22-2175645; E-mail: masuhara@tagen.tohoku.ac.jp

DAE have excellent characteristics among these various photochromic compounds, *e.g.*, thermal stability of both isomers, fatigue resistance, high sensitivity, high response in various states [4]. In order to explore the photochromic properties for bulk to nanometer scale solid-state application, DAE are usually embedded in a solid matrix [5]. DAE exhibits high performance in a solution, not so in a solid state.

On the other hand, organic nanoparticles are particularly interesting, since they can be dispersed in a colloidal aqueous liquid or thin-layer matrix, and can avoid problems of light scattering or shallow light penetration in bulk crystals. A few research groups have reported the fabrication of DAE nanoparticles [6–9]. Sun *et al.* have fabricated DAE nanoparticles, which were H-aggregates on the basis of the blue-shifted absorption peak. Unfortunately, it is much difficult to fabricate monodispersed and size-controlled DAE nanoparticles.

In the present study, we have fabricated successfully DAE nanoparticles using the reprecipitation method [10], and we could control the nanoparticle size by changing reprecipitation conditions. The absorption peak position of DAE nanoparticles with various sizes will be also discussed in detail.

Experimental

Diarylethene (DAE) used was 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene, chemical structure shown in Figure 1(a), which color changes from colorless to blue upon UV irradiation and returns to the colorless by visible light irradiation. DAE was purchased from Tokyo Chemical Industry Co., Ltd., and used without further purification. Tetrahydrofuran (THF), methanol, and ethanol were also purchased from Wako Pure Chemical Industries, Ltd. Water was purified up to 18.2 MΩ cm using Arium 611UV (Sartorius Mechtronics Japan K.K.).

DAE nanoparticles were fabricated by the reprecipitation method as follows. DAE was first dissolved in good solvent such as THF, methanol, and ethanol. The concentrations of DAE solutions were in the range from 0.10 mM to 10 mM. A 200 μL of the solution was injected into vigorously stirred water (10 mL) at room temperature using a microsyringe under UV or visible light irradiation.

The size and shape were evaluated by dynamic light scattering instrument (DLS: Zetasizer Nano series Nano – ZS, Sysmex Co.), and atomic force microscope (AFM: Innova SPM, Nihon Veeco K.K.). Powder X-ray diffraction pattern was measured on a D8 Advance (Bruker AXS K.K.). UV-vis absorption spectra for DAE nanoparticles dispersion liquids were measured with UV-visible spectrometer (V-570DS, JASCO Ltd.). UV irradiation was carried out by using UV lamp (SUV-16, AS ONE corporation).

Results and Discussion

Two kind isomers of diarylethene (DAE) provide various physicochemical properties because of their different π-conjugated open-ring and closed-ring molecular structures. So, we have fabricated DAE nanoparticles from the above-mentioned both isomers.

Figures 1(b) and 1(c) show the AFM images of DAE nanoparticles fabricated from open-ring and closed-ring isomers. Size distributions were also confirmed by DLS in Figure 1(d). The obtained DAE nanoparticles prepared from open-ring

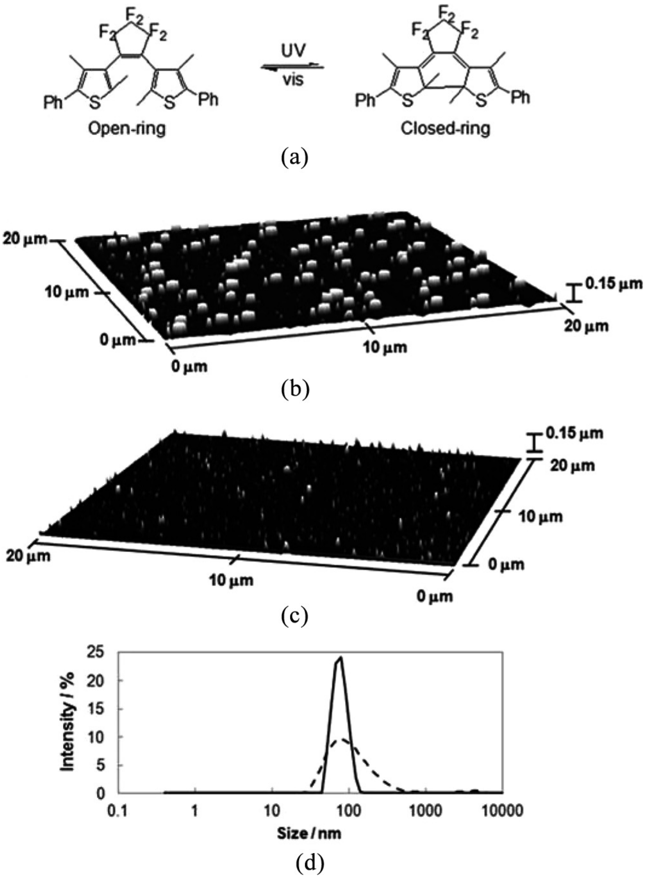


Figure 1. (a) Chemical structure of used diarylethene (DAE): open-ring and closed-ring structure. AFM images of DAE nanoparticles prepared by reprecipitation method, (b) from open-ring DAE produced by visible light irradiation, (c) from closed-ring DAE formed under UV light irradiation. (d) Size distributions of DAE nanoparticles fabricated from open-DAE (dotted line) and closed-DAE (solid line) by DLS measurement.

isomer took various sizes. That is, the size distribution was broad. On the other hand, the nanoparticles obtained from closed-ring isomers were almost monodispersed sizes. These facts suggested that the different steric molecular structures of two isomers affected their morphology such as size, shape, and monodispersity. The closed-ring isomer has relatively planar structure, two thiophene rings are bonded directly on one planar. Namely, we could successfully fabricate monodispersed DAE nanoparticles from closed-ring isomer, compared with open-ring isomer, having flexible structure. Herein after, we would focus on the fabrication of DAE nanoparticles from closed-ring isomer in the present article.

We could control the nanoparticle size by changing concentration of the injected solution and a kind good solvent. Figure 2 indicates the relationship between concentration of the injected solution and DAE nanoparticle size. The concentration of the injected solution was changed from 0.10 to 10 mM. The nanoparticle size increased with concentration of the injected solution [10]. THF, methanol, and

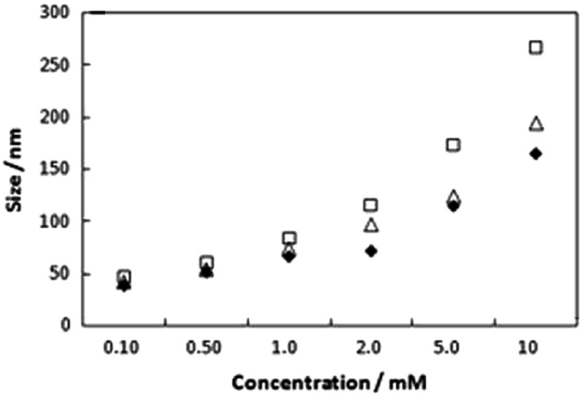


Figure 2. Relationship between concentration of the injected solutions and DAE nanoparticle sizes. The three kinds of good solvents were used: □, ethanol ($\eta = 1.2\,\mathrm{mPa\cdot s}$), △, methanol ($\eta = 0.61\,\mathrm{mPa\cdot s}$), and ◆, tetrahydrofuran ($\eta = 0.49\,\mathrm{mPa\cdot s}$).

ethanol were used as a good solvent. In comparison with the DAE nanoparticle size at the same concentration, the nanoparticle size increased with viscosity of good solvent. This tendency remarkable at concentrated region, and the largest size in DAE nanoparticles could be observed when used ethanol solution. On the other hand, the smallest one was obtained from THF solution, as shown in Figure 2. That is to say, the nanoparticle size depended on not only the concentration of the injected solution but also the viscosity of good solvent. Actually, we could control the monodispersed DAE nanoparticle size with the range of 40 nm to 250 nm.

Figure 3 demonstrates the image of the proposed formation process of DAE nanoparticles. The formation process is as follows: the injected solution is first divided into a number of droplets, under shear field by mechanical stirring (I), and then nano-emulsions are formed (a). Since good solvent is gradually diffused and dissolved into water, the concentration in nano-emulsions would reach supersaturated (II). Subsequently, nuclei are formed and nanoparticles start to grow inside the individual droplets (b).

When the concentration of the injected solution is high, the amount of DAE molecule in one droplet would be also large, which would provides large-sized nanoparticle. On the other hand, if the size of the droplet increases, the amount of DAE molecule becomes large at the same concentration of the injected solution. Probably, the size droplet becomes large at high viscosity of the used good solvent under the

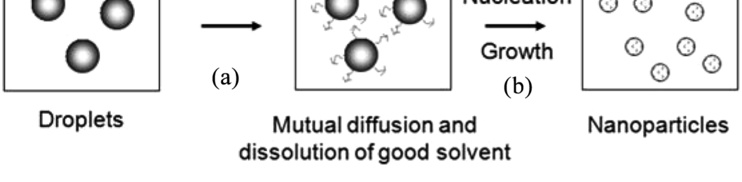
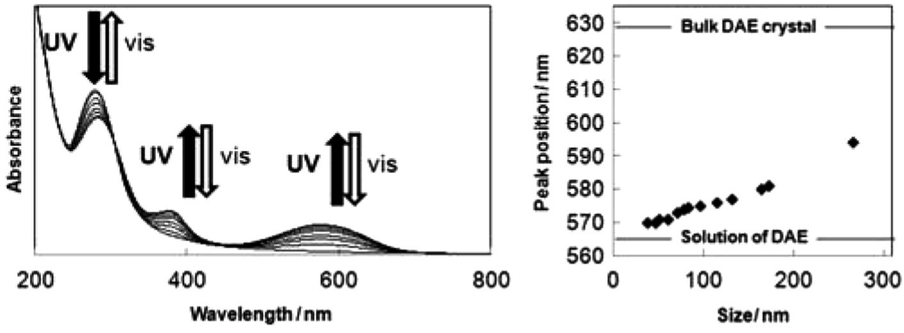


Figure 3. Proposed formation process of DAE nanoparticles.



(a) (b)

Figure 4. (a) UV-vis absorption spectral changes of DAE nanoparticles (size: 132 nm) dispersed in an aqueous liquid with UV or visible light irradiation. (b) Dependence of characteristic absorption peak positions for DAE nanoparticles on size. The two lines are, respectively, the absorption peaks of bulk DAE crystals ($\lambda = 630$ nm) and DAE solution ($\lambda = 562$ nm).

same concentration. Thus, the dependence on viscosity as shown in Figure 2 could be explained by the above discussion.

Figure 4(a) exhibits the UV-vis absorption spectral changes for DAE nanoparticles dispersed in water during UV or visible light irradiation process, which could represent finely photochromism behaviors of DAE nanoparticles. It was found that the characteristic peak (around $\lambda = 570$ nm) of closed-DAE nanoparticles was shifted. The plots of the DAE nanoparticle size vs. the characteristic peak position is shown in Figure 4(b). With increasing nanoparticle size, the peak position was red-shifted within in the range of peak position between bulk DAE state (630 nm) [11] and DAE solution state (562 nm) [12].

The present shift of peak positions is not likely to H-aggregates inside DAE nanoparticles, because the absorption peak position for H-aggregates is usually blue-shifted, compared with that of the solution state [6]. On the other hand, Kobatake *et al.* reported the red-shift of the similar DAE derivative in bulk crystal state, which was attributed to the planar structure of molecule strained in crystal lattice [13].

Perhaps, it seems that the red-shift of characteristic peak position of closed-DAE nanoparticles was also due to the planar structure of closed-DAE nanoparticles. The strain can be easily released, when DAE nanoparticle is small, owing to large specific surface area. As a result, DAE molecule becomes non-planar structure in the nanoparticles, which is the similar to the solution state.

The broad diffraction pattern measured with powder XRD measurement may support the above discussion. In a word, the present DAE nanoparticles are semicrystalline state, not rigid in the bulk state. The strain, DAE molecule may undergo in the nanoparticles, is considered to be changeable with nanoparticles size, and then the characteristic peak position may reflect such the state.

Conclusions

In conclusion, we have succeeded in fabricating monodispersed diarylethene (DAE) nanoparticles using the reprecipitation method and controlling the nanoparticle size in the range of 40 nm to 250 nm. The obtained DAE nanoparticles exhibited cleanly photochromism by alternate irradiation of UV and visible light. In addition, the red-shift of characteristic peak position (around $\lambda = 570$ nm) of closed-DAE nanoparticles was observed with increasing nanoparticle size, which was attributable to the strained and planar molecular structure. The inner structure and the detail photochromism of DAE nanoparticles are currently under investigation.

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