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ORIGINAL CONTRIBUTION

Preparation and characterization of copper(II) tetrasulfonated phthalocyanine nanoparticles formed by laser ablation in poor solvents

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Abstract Laser irradiation of copper(II) tetrasulfonated phthalocyanine (CuTsPc) microcrystals in poor organic solvents such as methanol, 2-methyl-2-propanol, ethanol, tetrahydrofuran, and acetone has produced CuTsPc nanoparticles with 15–112 nm in diameter. Field emission scanning electron microscopy (FESEM) images have shown the formation of CuTsPc nanoparticles in poor organic solvents used in this work. The mean diameters of CuTsPc nanoparticles obtained from transmission electron microscopy (TEM) images in methanol, 2-methyl-2-propanol, ethanol, tetrahydrofuran, and acetone were determined to be 26, 36, 35, 86, and 78 nm, respectively. A correlation between the size of CuTsPc nanoparticles and a solvent polarity could be found in this work.

Keywords Nanoparticle · Laser ablation · Solvent polarity · Absorption spectroscopy · Scanning electron microscopy

Introduction

Organic nanoparticles have attracted keen interest in the past several years [1–10]. Phthalocyanines are a class of organic versatile synthetic dyes with planar electron-rich aromatic macrocycles, high extinction coefficients in the red/near-infrared region, and exhibiting a wide range of application in material science, industries, and medicine [2, 3]. Metal phthalocyanine molecules also show similarity in structure and properties with biological molecular chlorophyll and hemoglobin [4]. Owing to their intriguing high stability, photophysical and photoconductive properties, and many other desirable features, this class of functional molecules has been studied extensively as sensitizers for photovoltaic devices, optical limiters, catalysts for photodegradation of pollutants, and in other fields [5, 6]. Interestingly, size reduction of these metal phthalocyanine nanoparticles enhance their properties. This is because the Q-band absorption spectra of phthalocyanines in solid state strongly depends on mutual molecular orientation and intermolecular distance; thus, spectroscopic analysis is useful for elucidating the morphological and electronic properties of formed nanoparticles [5, 7].

Oikawa et al. [8] have prepared microcrystals of perylene and polydiacetylene by reprecipitation. This reprecipitation method has been widely employed to prepare organic nanoparticles for various organic compounds. This technique is based on the addition of a solution of the organic molecule to a poor solvent, and then nanometer-sized particles can be collected and observed [8, 9]. Despite the simplicity of the method, it is fraught with difficulties. For instance, organic solvents or surfactants are often used to control the particle size, and the obtained size distributions are relatively broad, which is in stark contrast to those for well-controlled semiconductors or metal nanoparticles. Kasai et al. [10] achieved size control by choosing suitable solutions and adjusting the concentration and temperature of the solution; however, the obtained sizes are still to be undesired.

Recently, Masuhara et al. [12, 13] have applied a laser ablation technique for the preparation of organic nanoparticles and then concluded that by optimizing optical

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parameters and chemical conditions such as laser wavelength, fluence, pulse width, solvent, concentration, and temperature, the phase and size of organic nanoparticles can be controlled using this laser ablation technique in poor solvents [10–13].

In this work, we report the preparation of copper(II) tetrasulfonated phthalocyanine (CuTsPc) nanoparticles of different sizes in various organic solvents by a laser ablation technique. We have tried to correlate the size of the produced nanoparticles with some solvent parameters. Thus, to propose a general trend for parameters such as solvent polarity, solvent diffusivity, and dielectric constant, we used methanol, ethanol, 2-methyl-2-propanol, acetone, and tetrahydrofuran as poor organic solvents. The size and characterization of the formed CuTsPc nanoparticles was investigated in detail by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) observations.

Experimental

CuTsPc was purchased from Aldrich-sigma (Tokyo, Japan) and used without further purification. Methanol, ethanol, tetrahydrofuran, 2-methyl-2-propanol (Wako, Osaka, Japan), and acetone (Dotite, Kumamoto, Japan) were used as poor organic solvents and used as received. CuTsPc crystalline powders (0.5 mg) were introduced in a quartz cell of $1\times1\times5$ cm^3 with 1-cm optical path length. The CuTsPc suspension (3 mL) was contained in the above cell and stirred during irradiation. The nanoparticles of CuTsPc were prepared by the laser ablation method similar to [13]. A Nd:YAG laser system (Spectron Laser SL402, 355-nm wavelength, 10-Hz repetition rate, 10-ns full width at half-maximum) was used as a light source.

Absorption spectra of the supernatants prior to irradiation and the colloidal solutions were measured with a spectrophotometer (Shimadzu, MPS-2000). Morphological characterization of CuTsPc nanoparticles on platinum-coated substrates was carried out with a FESEM (Hitachi, S-3500N). CuTsPc nanoparticles with various sizes were observed by AFM (Digital Instruments, Nanoscope III); their samples were prepared by dropping 2 mL of the nanoparticle–solvent dispersion onto glass substrates. The substrate was immediately placed in a vacuum oven and the solvents evaporated under reduced pressure (7–10 mbar) at room temperature. For TEM (JEOL JEM-3010 VII) studies, approximately 10 μL of freshly prepared nanoparticle suspension of each solvent was dropped onto a coated copper grid, which was later on carbon-coated. The solvents were evaporated under reduced pressure at room temperature in an incubator for 3 days. The resulting samples were used for the measurement of TEM images.

Results and discussion

Initially before laser irradiation, CuTsPc crystals sank to the bottom of the quartz cell and after 30-min sonication, a faint color change was noticed in methanol and ethanol, whereas no change was observed for other solvents. This fact indicates that organic solvents used in this work are poor solvents for CuTsPc. One major challenge using metal phthalocyanines is their relative low solubility in polar and non-polar solvents. In other to broaden the range of suitable solvents, they require chemical modification. The most frequent chemical modifications to render them soluble in aqueous media are sulfonations or carboxylations on the peripheral benzene rings. However, these modified species tend to aggregate. In the case of phthalocyanines, the driving force for aggregation is π–π^* interaction between macrocycles which promotes ring stacking along the axis perpendicular to the plane of the macrocycle and makes the material insoluble in common organic solvents [14].

Exposing all of the organic solvents containing CuTsPc crystals to laser pulses during stirring, the solution became suspension and the color of the solution became blue. Figure 1 shows typical absorption spectra of CuTsPc suspension in methanol by laser irradiation at a fluence of 20 mJ/cm^2. The absorption bands around 280–345 and 600–680 nm in Fig. 1 can be assigned to the Soret band and Q-band of CuTsPc, respectively. With increasing irradiation time, absorbance of absorption bands increased and the color of the suspensions and the degree of scattering of CuTsPc crystals became darker and lower, respectively. This change reveals that nanoparticles of CuTsPc are formed in methanol. Moreover, absorption spectral pattern of CuTsPc suspension in all organic solvents by irradiation at a fluence of 20 mJ/cm^2 for 80 min is summarized in Fig. 2; the result of spectral change is dependent on the kind of solvent used in this work. This change also reveals that nanoparticles are formed in all poor solvents used in this work. As shown in Fig. 2a, the absorption spectrum of CuTsPc for tetrahydrofuran (THF) is significantly different from that for other solvents. Two main absorption maxima at 600 and 680 nm were observed in THF. This fact suggests that CuTsPc nanoparticles formed in THF are present in the form of monomeric species and that no aggregated species such as a dimer is formed under the present conditions. The absorption bands around 280–345 and 600–680 nm are assigned to the Soret band and Q-band, respectively. These transitions originate from the molecular orbitals within the 18 π-electrons system and from overlapping on the central metal [14–18]. The Q-band in aqueous solution and in all the used solvents split into two with contributions from both monomer and aggregate absorption. The latter can be attributed to the absorption by dimers or larger aggregates [18]. The degree of phthalocy-

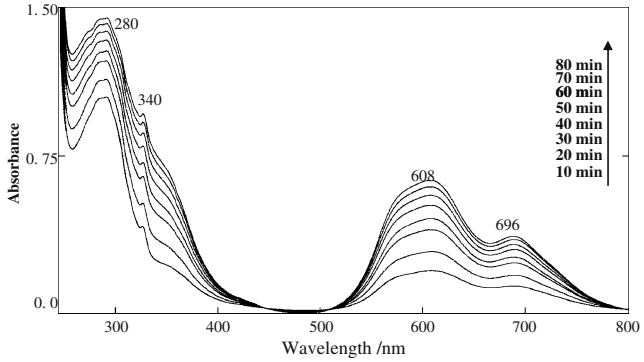

Fig. 1 Irradiation time dependence of absorption spectra of CuTsPc nanoparticle solutions in methanol with a laser fluence of 20 mJ/cm^2 at 355-nm excitation. The total irradiation periods are shown in the figure

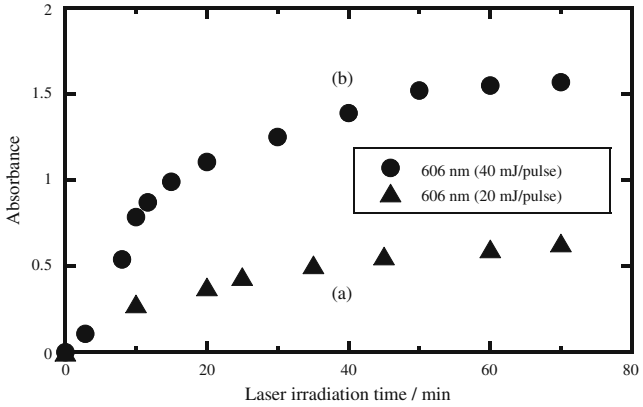

Fig. 3 Temporal profiles of 606-nm absorbance of CuTsPc colloidal solutions in methanol by irradiated at a fluence of 20 (**a**) and 40 mJ/cm^2 (**b**)

anine aggregation depends on the metallic cation, and in aqueous solution, it is observed that the dimerization constant for CuTsPc is higher compared to other metal-lophthalocyanine tetrasulfonates [14].

The laser fluence dependence for nanoparticle formation was assessed by monitoring the Q-band intensity of the absorption spectra after specific irradiation time. The absorbance at 686 nm after 10-min irradiation was plotted as a function of the laser fluence (data not shown). This result indicated that the absorbance increase only above 20 mJ/pulse, thus indicating that CuTsPc nanoparticle formation has a threshold laser fluence which does not depend on the total photon number but on the excitation photon density, as reported by Tamaki et al. [13]. The absorbance profiles at 606-nm absorbance of CuTsPc in methanol by irradiating at a fluence of 20 and 40 mJ/cm^2 are shown in Fig. 3. The formation rate of CuTsPc nanoparticles at 40 mJ/cm^2 is faster than that at 20 mJ/cm^2. This result also means that the nanoparticle formation requires a high photon density as in laser ablation of organic materials and indicates that CuTsPc can be dispersed in poor solvents as nanoparticles.

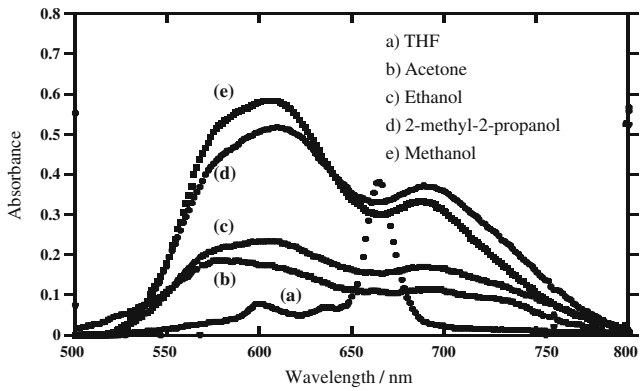

Fig. 2 Absorption spectra of CuTsPc nanoparticles formed in THF (**a**), methanol (**b**), 2-methyl-2-propanol (**c**), ethanol (**d**), and acetone (**e**) by laser irradiation at a fluence of 20 mJ/cm^2 for 80 min

To confirm the fragmentation of CuTsPc crystals and morphology of CuTsPc nanoparticles, FESEM, TEM, and AFM images of formed CuTsPc nanoparticles formed in poor organic solvents were also investigated. Figure 4a, b shows typical FESEM images of CuTsPc nanoparticles in methanol and ethanol, respectively. These images show densely and almost uniformly packed nanoparticles and nanospheroids which agglomerate on the substrate after evaporation of the solvents. Moreover, the images after 80-min irradiation (Fig. 4a, b) show the agglomeration states of CuTsPc nanoparticles because the number of nanoparticles by laser ablation increases sufficiently. Also, we confirmed that at the early stage of laser irradiation, CuTsPc particles are formed as a single nanoparticle from the images. The diameters of CuTsPc nanoparticles formed in each solvent by laser irradiation could be determined based on the TEM images, as shown in Fig. 4c, d; the results for all poor solvents used in this work are shown in Fig. 5. It is worth noting that the particles are sufficiently small and size distributions are almost uniform in all solvents. Moreover, the roughness of CuTsPc nanoparticles in each solvent on quartz plate was also estimated from AFM images, as shown in Fig. 4e, f. The results almost confirm the uniform and porous structure of CuTsPc nanoparticles by laser ablation, as evidenced from AFM and FESEM images for each solvent.

The nanoparticle formation process is somewhat complicated and strongly influenced by dynamic factors such as solvent polarity, viscosity, solvent diffusivity, dielectric constant, and the relative solubility of CuTsPc in the solvents. It has been reported that the exposure of phthalocyanine thin film to solvent such as aliphatic alcohols induces molecular rearrangement through electronic interaction between solvent and phthalocyanine molecules, and these interactions play an important role in

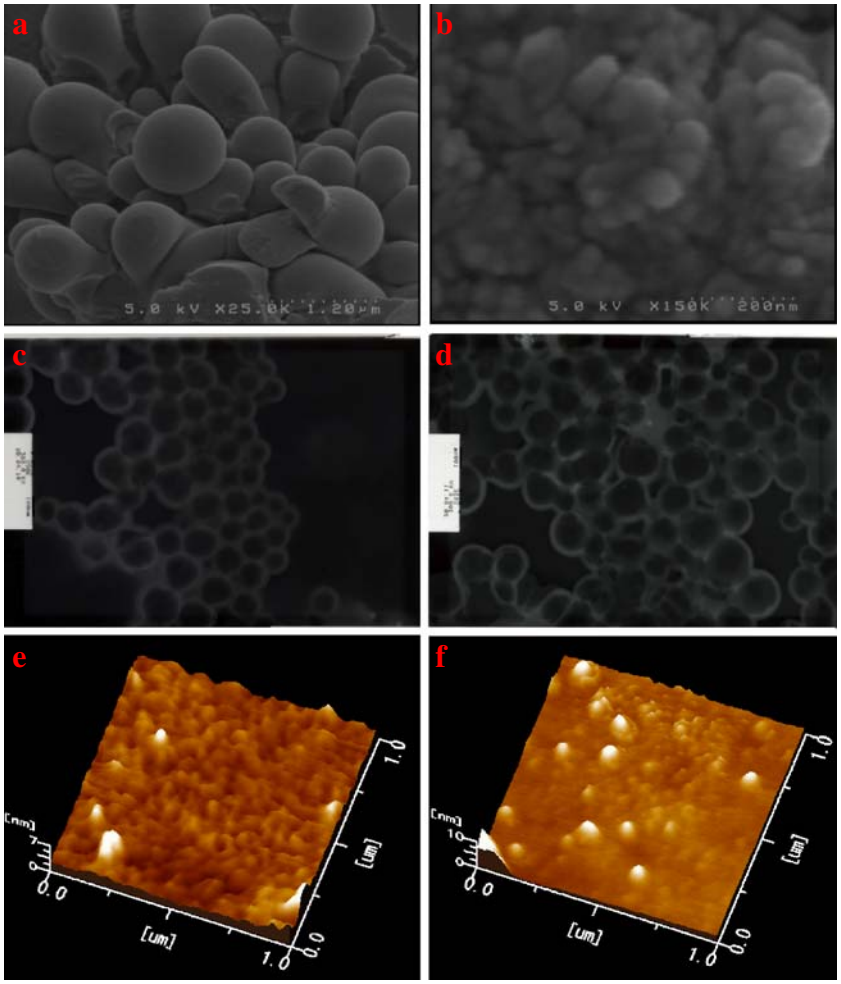

Fig. 4 **a**, **b** FESEM images of CuTsPc nanoparticles formed in methanol (**a**), ethanol (**b**). **c**, **d** TEM images CuTsPc nanoparticles formed in acetone (**c**) and THF (**d**). **e**, **f** AFM images of CuTsPc nanoparticles formed in methanol (**e**), 2-methyl-2-propanol (**f**) (laser fluence, 20 mJ/cm^2; irradiation time, 80 min)

phase transformation and size reduction [19–22]. Owing to solvent-induced molecular mobility, dipole–dipole interaction seems to contribute to the adsorption of solvent onto nanoparticle surface, and molecular solubility which dissolves molecules to form nanoparticles may be probably important.

We found a correlation between the size of formed CuTsPc nanoparticles in each solvent and a solvent parameter such as a solvent polarity. A plot data of CuTsPc nanoparticle size versus the solvent polarity of the solvents is shown in Fig. 6; almost linear relationship can be observed. It can be shown that the diameter size of CuTsPc nanoparticles produced by nanosecond laser ablation increases with decreasing solvent polarity of poor solvents. The present result may suggest that particle formation and its growth are influenced by the solvent polarity. After a particle with small size by the laser ablation generates, nucleation with another particle and its growth process occurs and then the particle size becomes big. In the case of poor solvents with low polarity, the lowered polarity may decrease the solubility of small aggregates and grown particles in the systems or may provide a repulsive force between particles, resulting in the formation of nanoparticles with large size. Although more detailed experimental and theoretical studies are needed, the solvent polarity of poor solvents in the present experiments may be a key factor for the size of formed CuTsPc nanoparticles.

Moreover, Hosokawa et al. [23] proposed and confirmed a photothermal ablation mechanism for CuPc thin films with femtosecond, picosecond, and nanosecond excitation. Their unique etch profiles could be interpreted in terms of rapid temperature elevation, since the relaxation dynamics from electronically excited states to vibrationally excited states was clarified directly by ultrafast pump-probe experiment. In the nanosecond laser ablation proposed by them, photothermal conversion and morphological change take place simultaneously during pulse excitation. The photothermal conversion process also can be considered to be due to sequential and cyclic multiphotonic absorption [23, 24]. In both processes, chromophore can absorb while the nanosecond excitation laser is irradiated. But in the latter process, the chromophore absorbs photons competitively with the ground-state chromophores. The surface layer after receiving excitation energy becomes hot and

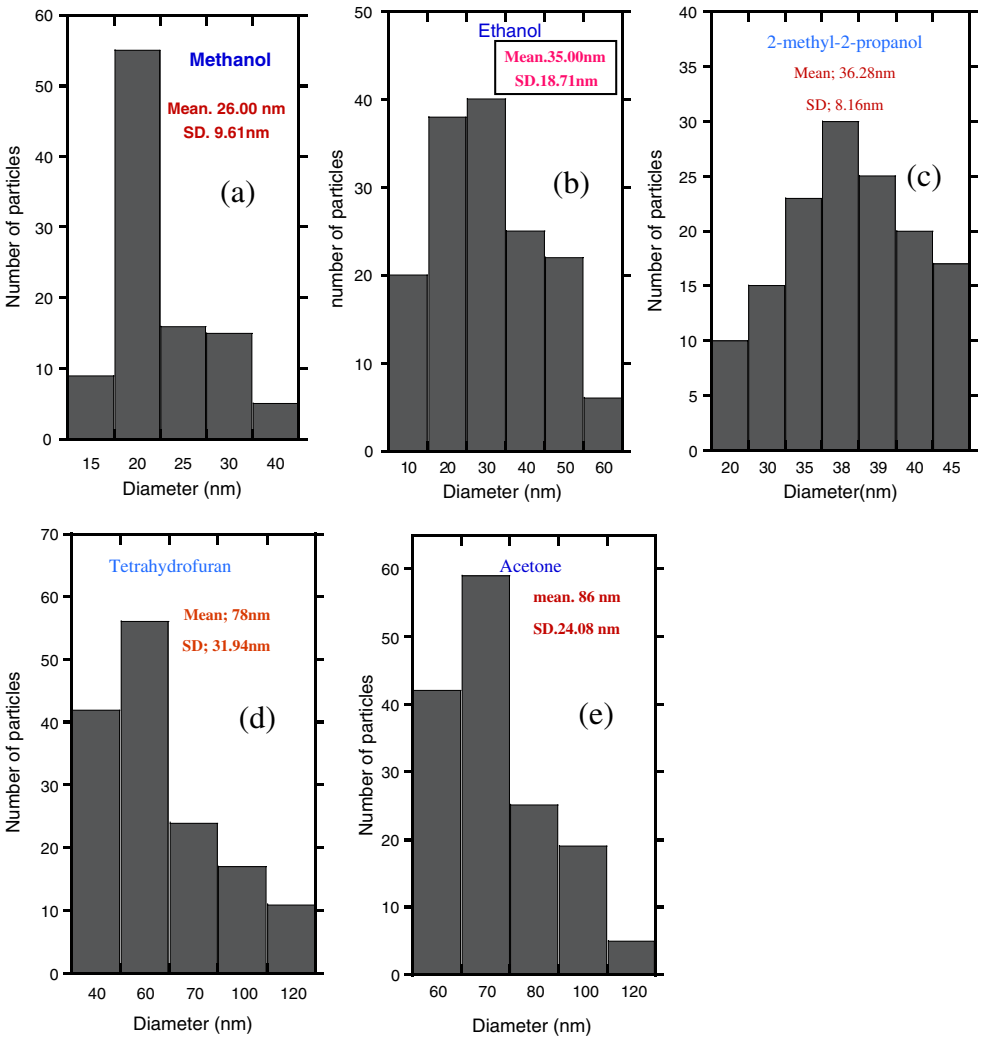

Fig. 5 Histograms of diameters of CuTsPc nanoparticles produced by laser irradiation at a fluence of 20 mJ/cm^2 for 80 min. Solvents used are methanol (**a**), ethanol (**b**), 2-methyl-2-propanol (**c**), THF (**d**), and acetone (**e**). The mean diameter size and the standard deviation (*SD*) of nanoparticles formed by laser irradiation are given in the figures

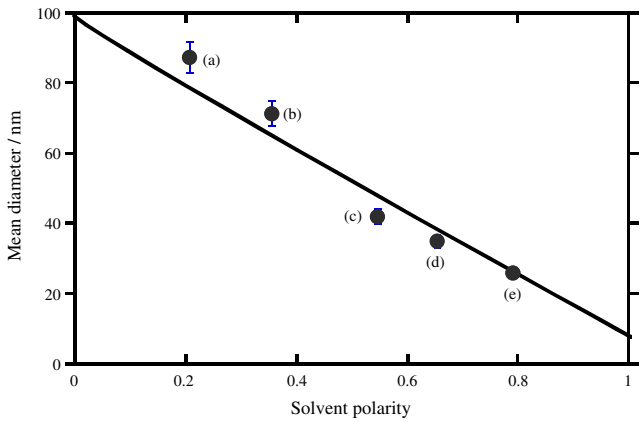

Fig. 6 Correlation of the mean diameter with solvent polarity of organic solvents for CuTsPc nanoparticles by laser irradiation at a fluence of 20 mJ/cm^2 for 80 min. Solvents used are THF (**a**), acetone (**b**), 2-methyl-2-propanol (**c**), ethanol (**d**), and methanol (**e**)

undergoes active molecular motion, cluster formation, and fragmentation. The behavior continues with pulse excitation. During the formation process, we can think that only the photo-excited surface layer may be fragmented into nanometer-sized particles, and this surface fragmentation may occur on every laser excitation. Detailed theoretical studies for the laser ablation mechanism and the correlation between the particle size and the solvent polarity are now in progress.

Conclusions

In conclusion, we have investigated nanoparticle formation by laser ablation of CuTsPc crystalline powders in some poor organic solvents. The formation processes of CuTsPc nanoparticles can be characterized by spectroscopic and microscopic techniques; the results indicate that the size distribution of the CuTsPc nanoparticles are narrow and dependent on the kind of solvent used in this work. The

sizes of CuTsPc nanoparticles formed are dependent on the kind of poor solvents used in the present work, and a correlation between the size of CuTsPc nanoparticles and the solvent polarity can be found.

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