Characterization of Copper Phthalocyanine Nanoparticles Formed by Laser Ablation in Poor Solvents

Kwati Leonard, Myint Thein Tun, and Junichi Kurawaki*
Department of Chemistry and Bioscience, Faculty of Science, Kagoshima University, 1-21-35 Korimoto, Kagoshima 890-0065, Japan

Tsuyoshi Akiyama and Sunao Yamada
Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

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Laser irradiation of Copper phthalocyanine tetrasulfonate (CuPcTs) microcrystals in some poor solvents has produced CuPcTs nanoparticles with 15-112 nm in diameter. Field emission scanning electron microscopy (FESEM) images have shown densely packed nanoparticles of CuPcTs formed in methanol and acetone. The mean diameter of CuPcTs nanoparticles obtained from TEM images in methanol, 2-methyl-2-propanol, ethanol, tetrahydrofuran, and acetone were determined to be 26, 36, 35, 86, and 78 nm, respectively. The size and surface morphology of CuPcTs nanoparticles have been correlated with solvent parameters such as polarity and thermal diffusivity.

Keywords: Laser ablation; Nanoparticle; Solvent polarity; Absorption spectroscopy; Scanning electron microscopy

I. 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 macro cycles, high extinction coefficients in the red/near infrared region and exhibiting a wide range of application in materials 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, photo physical, and photo-conductive properties, and many other desirable features, this class of functional molecules have been studied extensively as sensitizers for photovoltaic devices, optical limiters, catalysts for photo degradation 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 morphological and electronic properties of formed nanoparticles [5, 7].

Several approaches have been reported for organic nanoparticle preparation, even though most of the methods are still to be desired. Nakanishi et al. [8] prepared microcrystals of perylene and polydiacetylene by recrystallization. This method has been widely employed to prepare organic nanoparticles for various organic compounds. This technique is based on adding a solution of the organic molecule a poor solvent and nanometer sized particles are 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] equally achieved size control by choosing suitable solutions and adjusting the concentration and temperature of the solution, however the obtained sizes are still to be desired. Masuhara et al. [12, 13] have concluded that by optimizing optical parameters and chemical conditions such as laser wavelength, fluence, pulse width, solvent, concentration and temperature, 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 CuPcTs nanoparticle of different sizes in some kinds of organic solvents by a laser ablation technique. We have tried to correlate the size, growth and orientation of the produced nanoparticles with some solvent parameters. Thus experimentally proposing a generally trend for parameters such as solvent polarity, solvent diffusivity, and dielectric constant. Methanol, ethanol, 2-methyl-2-propanol, acetone and tetrahydrofuran were used as solvents. The morphology of the formed nanoparticles was examined in detail by TEM, AFM, FT-IR, and FESEM observations.

II. EXPERIMENTAL

Copper phthalocyanine tetrasulfonate (CuPcTs) was purchased from Aldrich and used without further purification. Methanol (Wako), ethanol (Wako), tetrahydrofuran (Wako), acetone (Dotite), and 2-methyl-2-propanol (Wako) were used as poor organic solvents and used without further purification. CuPcTs crystalline powders (0.5 mg) were introduced in a quartz cell of 1 × 5 cm3 with 1 cm optical path length. The CuPcTs suspension (3 mL) was contained in the above cell and stirred during irradiation. Copper phthalocyanine tetrasulfonate (CuPcTs) nanoparticles were prepared by laser ablation method similar to ref. [13]. A Nd:YAG laser system (Spectron SL-403G, 355 nm wavelength, 10 Hz repetition rate, 10 ns fwhm) was used as a light source. Irradiation was conducted at a laser fluence of 20 mJ/cm2 for respective time intervals.

*Corresponding author: kurawaki@sci.kagoshima-u.ac.jp
Absorption spectra of the supernatants prior to irradiation and the colloidal solutions were measured with a spectrophotometer (Shimadzu, MPS-2000). Morphological characterization of CuPcTs nanoparticles on platinum coated substrates was carried out with a field emission scanning electron microscopy (FESEM) (Hitachi, S-3500N). CuPcTs nanoparticles with various sizes were observed by atomic force microscopy (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 transmission electron microscopy (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 three days. The resulting samples were used for the measurement of TEM images.

III. RESULTS AND DISCUSSION

Initially before laser irradiation, CuPcTs 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 observe for other solvents. This fact indicates that the mentioned solvents are poor solvents for CuPcTs. One major challenge using metal phthalocyanines is their relative low solubility in polar and non polar solvents. In order to broaden the range of suitable solvents, they require chemical modification. The most frequent chemical modification to render them soluble in aqueous media are sulfonations or carboxylations on the peripheral benzene rings. However these modified species tend to aggregate. In case of phthalocyanines, the driving force for aggregation is the π-π* interaction between macro cycles which promote ring stacking along the axis perpendicular to the plan of the macro cycle and makes the material insoluble in common organic solvents [14]. Exposing all the solutions to laser pulses while stirring, the suspensions become transparent and blue. With increasing irradiation time, the color of the suspensions and the degree of scattering of CuPcTs crystals become deeper and lower. This change reveals that nanoparticles are formed in all solvents used in the present work.

Figures 1(a) and (b) show absorption spectra of CuPcTs nanoparticles formed by laser irradiation for two solvents. As shown in Fig. 2, absorption spectral pattern of CuPcTs suspension is dependent on the kind of solvent used in this work. It is clear from Fig. 1 that absorption spectra increases with increasing laser irradiation time. The absorption bands around 280-345 nm and 600-680 nm are assigned to the Soret band and Q-band, respectively. These transitions originate from the molecular orbital’s within the 18 π-electrons system and from overlapping on the central metal [14-18]. The Q-band in aqueous solution (not shown) and in all the used solvents is split into two with contributions from both monomer and aggregate absorption. The later can be attributed to absorption by dimmers or higher aggregates [18]. It has been known that the dimerization constant for CuPcTs is higher compared with that of other metallophthalocyanine derivatives [14]. The laser fluence dependence for nanoparticles formation was assessed by monitoring the Q-band intensity of the spectra (in THF) after specific irradiation time. The absorbance at 668 nm after 10 minutes irradiation is plotted as a function of the laser fluence (data not shown). As shown in Fig. 3, it is clear that the absorbance increase only above 20 mJ/pulse thus indicating that CuPcTs nanoparticles formation has a threshold laser fluence which does not depend on total photon number but on excitation photon density as reported by Tamaki et al. [13]. To confirm the fragmen-
The nanoparticle formation process is somewhat complicated and strongly influenced by dynamic factors such as solvent polarity, viscosity coefficient, solvent diffusivity, dielectric constant and the relative solubility of CuPcTs 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 phase transformation and size reduction [22]. Owing to solvent-induced molecular mobility, dipole-dipole interaction seem to contribute to adsorption of solvent onto nanoparticle surface, and molecular solubility is probably important once dissolve molecules form nanoparticles.

We attempted to correlate the size of the CuPcTs nanoparticles with various physical properties of the solvents such as polarity and thermal diffusivity. A plot data of CuPcTs nanoparticle size versus the solvent polarity of the solvents is shown in Fig. 6. A linear relationship can be observed within experimental error. With increasing polarity of poor solvents, the size of CuPcTs nanoparticles is decreasing. Therefore, it can be concluded that the size of CuPcTs nanoparticles produced by nanosecond laser ablation decreases as solvent polarity increases.

Masuhara 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 relax-

FIG. 3: Temporal profiles of 680 nm-absorbance of CuPcTs in methanol at 20 and 40 mJ/cm².

FIG. 4: FESEM images of CuPcTs nanoparticles in (a) methanol, (b) acetone, and (c) ethanol formed by laser irradiation at the fluence of 20 mJ/cm² for 80 min.

FIG. 5: Histograms of diameters of CuPcTs nanoparticles formed with the mean and standard deviation (SD) of the diameters.

FIG. 6: Correlation of diameter size with solvent polarity for CuPcTs nanoparticles produced by nanosecond laser ablation. (a) THF, (b) acetone, (c) 2-methyl-2-propanol. (d) ethanol, and (e) methanol.
FIG. 7: Relationship of diameter size with thermal diffusivity for CuPcTs nanoparticles formed by nanosecond laser ablation.

IV. CONCLUSIONS

We have investigated nanoparticle formation by laser ablation of CuPcTs crystalline powders in some organic solvents. The formation processes of CuPcTs nanoparticles can be characterized by spectroscopic studies; the results indicate that size distribution of the CuPcTs nanoparticles are narrow and are dependent on the kind of solvent used in this work. The sizes of CuPcTs nanoparticles formed in some organic solvents are different with each other on the basis of absorption spectra and SEM images. The thermal diffusivity of the solvents and some characteristics of the nanoparticles suggest that the rate of heat transfer from photo-excited CuPcTs to the surrounding solvent during nanoparticle formation may influence size and orientation of nanoparticles. Judging from our results, it can be concluded that we can control sizes and morphologies of organic nanoparticles by changing laser fluence, solvent and irradiation time.

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