Formation of 10 nm-sized Oxo(phtalocyaninato)vanadium(IV) Particles by Femtosecond Laser Ablation in Water

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We have succeeded in preparing oxo(phtalocyaninato)vanadium (IV) (VOPc) nanoparticles dispersed in water by femtosecond laser ablation of its bulk crystals. The mean size of VOPc nanoparticles was 17 ± 7 nm, estimated by a scanning electron microscope (SEM) analysis.

For the past decade, it has been recognized essential and important to establish how to prepare organic nanoparticles as they are very useful as pigments, cosmetics, drugs, and so on. The nanoparticle preparation of metals and semiconductors is very popular, while the difficulty of preparing organic nanoparticles with the size less than 100 nm has been well known. Several approaches have been reported based on vapor deposition[1] under low pressure with inactive gas and reprecipitation.[2–4] Recently, we have applied laser ablation technique to organic nanoparticle preparation.[5–7] Organic microcrystalline powders suspended in a poor solvent are exposed to intense laser pulse, which induces fragmentation of the initial crystals. Consequently, the opaque suspension is converted into a transparent colloidal solution. We demonstrated nanoparticle formation of some aromatic hydrocarbons and phthalocyanines. Phthalocyanine and its metal derivatives are known to possess useful photoconductive and semiconductive properties. In the case of VOPc dispersed in water, nanoparticles with the mean size of about 60 nm were found by irradiation with nanosecond XeF excimer laser (351 nm, 30 ns, 5 Hz).[5] The size was not much varied by changing the poor solvent, excimer laser repetition rate, fluence, and irradiation time.[7] In the present work, we demonstrate the formation of smaller VOPc nanoparticles by using the fundamental beam of a femtosecond laser as an irradiation light source (Figure 1).

VOPc crystalline powders (33 mg) were added into water (50 mL) and sonicated for 15 min. The mixture (3.0 mL) was put into a quartz cuvette of 1 × 1 × 5 cm^3 with 1-cm-optical path length. The crystals were suspended in water by stirring the mixture vigorously and exposed to a regenerated amplified femtosecond Ti:sapphire laser pulse (780 nm, 170 fs FWHM, 10 Hz). The laser beam was focused to the center of the cuvette with a lens ($f = 200$ mm), and the spot area was about 6.7 mm.^{2}

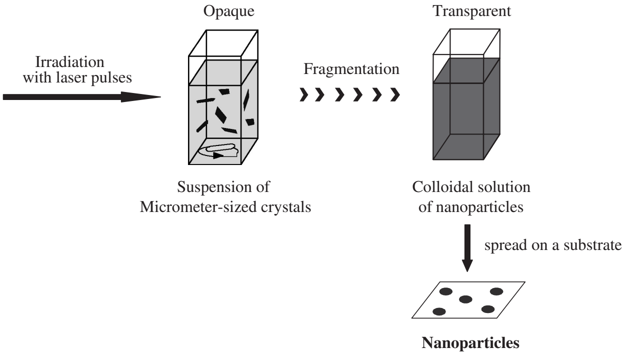

Figure 1. A schematic illustration of laser ablation in water.

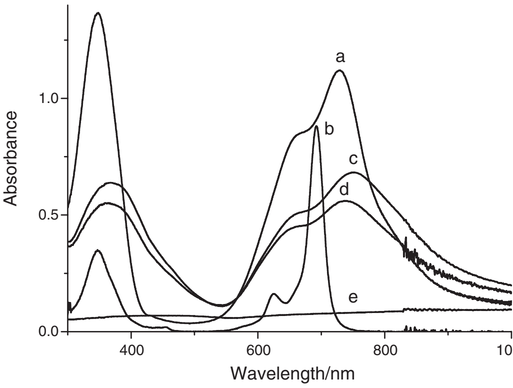

Figure 2. Absorption spectra of VOPc vapor-deposited thin film of phase I after irradiation (a), VOPc in pyridine (b), supernatants of VOPc colloidal solution prepared by nanosecond (48 mJ/cm^2, 10 min) and femtosecond (51 mJ/cm^2, 10 min) laser beam (c, d), respectively, and before irradiation (e).

After irradiation of VOPc suspended in water at a fluence of 51 mJ/cm^2 for 10 min, the solution became transparent and blue. In order to prove that the colloidal solution was prepared by laser ablation, we examined the absorption spectra. The spectrum of the supernatant after standing the solution for 1 h is shown in Figure 2. The standing period was necessary to exclude the contribution of non-fragmented large crystals from the supernatant. Indeed, without laser excitation the initial micrometer-sized VOPc crystals sank to the bottom of water in a few tens of min after stopping the stirring, and its supernatant was almost colorless. The spectra can be compared with those of a VOPc vapor-deposited thin film (a),[8] of VOPc molecules dissolved in pyridine (b),[8] and of a supernatant without laser irradiation (e) in Figure 2. The flat spectrum (e) is ascribed mainly to scattering by large VOPc crystals suspended in the colorless supernatants. The absorption spectrum of the colloidal solution (d) is nearly the same to that prepared by nanosecond laser at a fluence of 48 mJ/cm^2 for 10 min (c)[5] and is closer to that of thin film (a) than to that of pyridine solution (b). Judging from these results we conclude that femtosecond laser ablation of micrometer-sized VOPc crystals is responsible for the nanoparticle formation in water.

For characterizing VOPc nanoparticles, a scanning electron microscope (SEM) analysis was performed with FEI Strata DB 235-31. A drop of the supernatant dispersing VOPc particles was dried on a silicon substrate, of which surface was modified

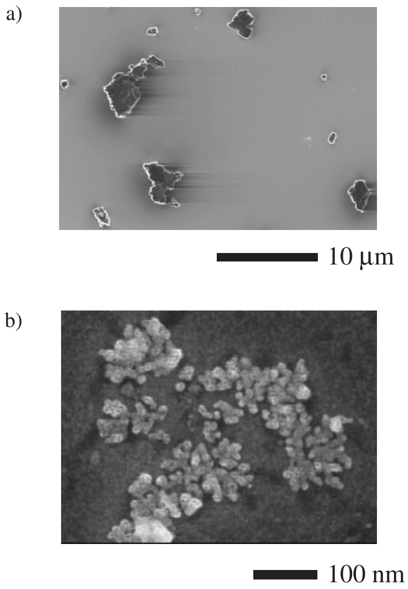

Figure 3. SEM images of initial VOPc crystals (a), VOPc nanoparticles formed by laser irradiation at the fluence of 51 mJ/cm^2 for 10 min (b).

into a hydrophobic one using standard cleaning process. SEM images of initial VOPc crystals and prepared nanoparticles are shown in Figure 3. It is confirmed that the initial crystal size dispersed in water was in a micrometer-order. The size distribution of 181 VOPc nanoparticles after femtosecond laser irradiation is summarized as a histogram in Figure 4. Because their shape was not always spherical, the longest part was defined as their size. The size was estimated to be 17 ± 7 nm, which is much smaller than the nanoparticles by using nanosecond laser irradiation (60 nm).[5]

It has been reported that some organic nanoparticles show the interesting size dependence of absorption spectra.[3,4,10–13] In our results of VOPc, the absorption spectrum peak of nanoparticles with a mean size of 17 nm is blue-shifted compared to that of the 60 nm-sized one as shown in Figure 2. This result is consistent with the previously reported size effect for other compounds.

Recently we have examined the pulse width effect on the etching profiles in laser ablation of CuPc thin film.[14–16] On the basis of time-resolved spectroscopic imaging in studies, we have concluded that temperature elevation rate in pulse laser excitation strongly affect to resultant surface morphology of the films. Namely, for femtosecond excitation photothermal conversion process should take place in a 10 ps time scale, while that in nanosecond laser excitation continues during the pulse duration of a few 10 ns. We consider that the difference in the rate of photothermal conversion process determine the size of nanoparticles, although the mechanism has not been clear yet.

In conclusion, it is clearly demonstrated that femtosecond laser irradiation of VOPc crystals in water gave nanoparticles with smaller size and narrower distribution compared with that by nanosecond laser excitation. The size is smaller than pigments prepared with mechanical grinding methods, and the present laser ablation method can be applied to a variety of organic pigments. Furthermore, nanoparticle formation process can be controlled precisely by pulse width, wavelength repetition rate, fluence, and so on.

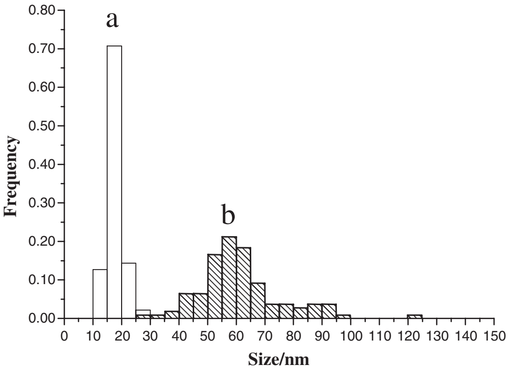

Figure 4. Histograms of the size of VOPc nanoparticles formed by femto second laser (a) and nanosecond laser[5] (b) irradiations. The femtosecond laser irradiation condition is the same to that in Figure 3.

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