

FIBER GROWTH OF COPPER PHTHALOCYANINE NANOPARTICLES FABRICATED BY NS-LASER IRRADIATION IN ORGANIC SOLVENTS

Ryo Kihara,¹ Miki Higaki,¹ Tsuyoshi Kawai,² Tsuyoshi Asahi¹

¹Graduate School of Science and Engineering, Ehime University, 3 Bunkyo, Matsuyama, Ehime, Japan

²Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma, Nara, Japan

E-mail: e862001u@mails.cc.ehime-u.ac.jp

Laser fragmentation in liquids is one of the modern techniques to prepare organic nanoparticles colloid. So far, we had reported in preparation of various organic nanoparticles by nanosecond laser irradiation to microcrystals in water. [1] Here, we succeeded in the fabrication of hexadecafluorophthalocyanine copper (F-CuPc) nanofibers in ethanol, as shown in Figure 2(a). Due to investigate the nanofibers formation, we examined the morphology and crystal structure of F-CuPc nanoparticles in ethanol at different storage times after laser irradiation. A mixture (6.3×10^{-3} wt %) of F-CuPc powder and ethanol was exposed with nanosecond Nd³⁺ YAG laser pluses (532-nm wavelength, 8-ns FWHM, 10 Hz repetition) at the laser fluence of 140 mJ/cm² for 10 min, and nanospheres having a mean diameter of 25 nm were obtained. From SEM observation, number of nanosphere decreased with an increase of storage time of the colloid, and nanorods having length of 80 nm were generated in 6 hours. The length of nanorods became longer with keeping of the width for 2 weeks. Figure 2(b) shows clear fringes parallel to long axis of nanofiber with fringe spacing of 1.3 nm, which indicated the single crystalline nature of the nanofibers. On the other hands, the absorption spectra of the F-CuPc colloid changed in 2 weeks (Figure 3). The spectrum just after laser irradiation was characterized to α -phase CuPc, while the spectral shape 2 weeks later was in good agreement with that of β -phase CuPc. [2] At 6 hours, the absorption spectrum was that of the mixture of α -phase and β -phase CuPc. These results suggest that α -phase F-CuPc nanospheres formed by laser irradiation will aggregate one-dimensionally and grow into a nanofiber accompanying with crystalline phase transition to β -phase in the nanostructure, as illustrated in Figure 4.

We also examined storage temperature and solvent dependence for size of β -phase nanofibers. Mean sizes of nanofibers prepared under different conditions were summarized in Table, which indicates that the size could be controlled by storage temperature and poor solvent.

Table. Mean size of F-CuPc nanofibers in several preparation conditions

solvent	Temperature(°C)	Length (nm)	Aspect ratio
Ethanol	22	353	7.9
	60	408	15
2-propanol	22	113	7.0
Ethyl acetate		429	15



Figure 1 . F-CuPc

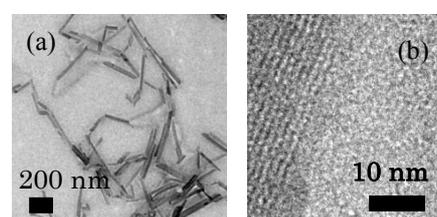


Figure 2 . (a)TEM and (b)HRTEM image of F-CuPc nanofibers

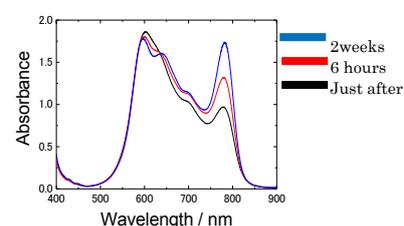


Figure 3 . Absorption spectra of F-CuPc colloids

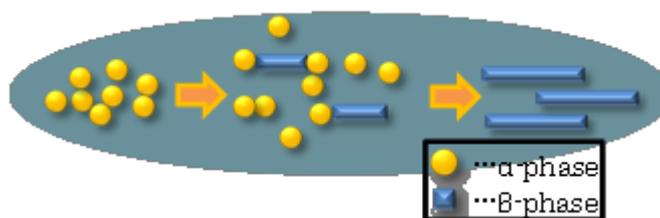


Figure 4. Illustration of F-CuPc nanofibers formation

[1] T. Asahi, T.Sugiyama, H.Masuhara; Acc.Chem.Res., **2008**, 41,1790-1798

[2] S.Karan, B.Mallik, J. Phys. Chem. C, **2007**, 111, 7352–7365.