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Supercritical fluid crystallization (SCFC) method is proposed for preparing microcrystals of π-conjugated organic compounds as a development of conventional reprecipitation method. In SCFC method, both size and form of titanylphthalocyanine microcrystals could be controlled by changing experimental conditions such as temperature and type of solvent. We have been able to fabricate γ-form of titanylphthalocyanine microcrystals with 50 nm in size, which is expected to be promising material for organic photoconductors.

Keywords: supercritical fluid, microcrystals, reprecipitation, titanylphthalocyanines, organic photoconductor

INTRODUCTION

The properties of phthalocyanines are very interesting in both optics and electronics. In the field of nonlinear optics, phthalocyanines are known to have large $\chi^{(3)}$ and ultrafast optical response in the crystalline state[1]. However, it is almost impossible to make large single crystals of

phthalocyanines, because its solubility is very poor in almost all kinds of solvent. Thus, one of the best way for the application of phthalocyanine crystals would undoubtedly be to make devices with microcrystals. Actually, phthalocyanine microcrystals have been used as materials for organic photoconductor[2]. Size-dependence of inorganic microcrystals with optical properties was investigated mainly for the third-order NLO susceptibility[3]. However, no comprehensive studies have been made so far regarding the relationship between crystal size and the properties of organic microcystals in the contact of optics and electronics. The reason for this being the inability to prepare organic microcrystals with controlled size. Recently, we have established the simple reprecipitation method which is useful for preparation of organic micro and/or nano crystals with controlled size[4-6]. However, the usual reprecipitation method could not be used for making microcrystals of phthalocyanine because of the low solubility. Since, supercritical fluid (SCF) can provide us with high temperature solvent, it is expected to be a powerful technique for making phthalocyanines solutions for the reprecipitation method

In the present study, the size and modification control of titanylphthalocyanine (TiOPc) crystals have been attempted using the reprecipitation method from SCF. Specially, we tried to fabricate γ-form of titanylphthalocyanine microcrystals, which is a hopeful candidate for materials of organic photoconductor (OPC)[2].

EXPERIMENT

The TiOPc used was amorphous particles of approx. 5μm in size. TiOPc microcrystals were fabricated by reprecipitation from the SCF solutions, as shown in fig. 1. This we named as SCF crystallization (SCFC) method. SCF and cooling solvents used in this study were water, methanol , acetone

and mixture of these solvent. Temperature (T_{SCF}) and pressure of SCF in the system were set at 350-670 K and 22 MPa, respectively. T_{SCF} and temperature after cooling (T_{COOL}) was measured by thermocouple.

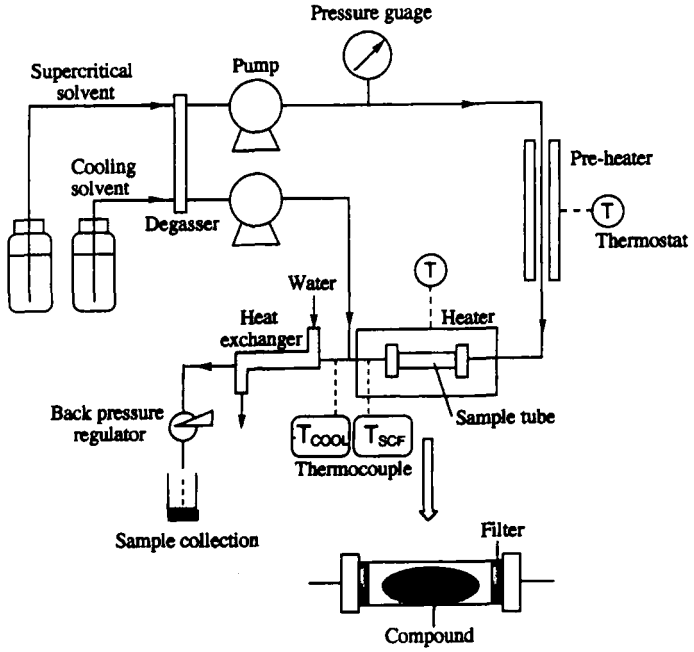

FIGURE 1 Supercritical Fluid Crystallization Method

RESULTS AND DISCUSSION

Supercritical Water System

When water was used as SCF, it was observed that TiOPc started to dissolve in water at about 570K. Control of crystal size and form of TiOPc microcrystals were attempted by changing T_{SCF}, T_{COOL}or cooling solvent. However, in almost all cases, crystal size was several tens of nm, and the form was mainly m-type. Thus, it turned out to be difficult to control the size and the form by supercritical water.

Supercritical Methanol System

In this system, different size and forms of TiOPc microcrystals were successfully fabricated by changing the cooling solvent type, as shown in fig. 2. In particular, it is interesting that formation of helicoid-like microcrystals using methanol as cooling solvent was observed by SEM photographs (fig. 2b). However, we could not do enough experiments so as to establish clear relationship between T_{SCF} and crystal size or form, because decomposition of methanol as SCF was occurring at more than 570 K and solubility of TiOPc to methanol was very low (about 0.05 g/l).

(a) (b)

FIGURE 2 SEM photograph of TiOPc microcrystals fabricated in supercrical methanol system at 520K by using different cooling solvent: (a) water and (b) methanol .

Supercritical Acetone System

Because acetone as SCF started to dissolve TiOPc at higher than 470 K, and was stable at high temperature, experiments in wide temperature range could be done, as shown in Table. Composition of cooling solvent and T_{SCF} had large influence to crystal size and form in this system. As a result, we were able to prepare γ-form TiOPc microcrystals with 50 nm in size by SCFC method, which should be of much promise for OPC.

TABLE Crystal Size and Crystal Form of TiOPc Microcrystals

Run	Cooling solvent	T_{SCF} / K	T_{COOL} / K	Crystal size / nm (Shape)	Crystal form
A1	Acetone	620	410	5000 (Square)	β
A2	Acetone	520	370	500 (Square)	β
A3	Acetone-Water (75 : 25)	620	380	50 (Spherical) 5000 (Rodlike, Square)	β
A4	Acetone-Water (75 : 25)	520	350	50 (Spherical) 250 (Ellipsoidal)	γ,β
A5	Acetone-Water (50 : 50)	620	370	50 (Spherical) 150 (Ellipsoidal)	γ , m, β
A6	Acetone-Water (50 : 50)	520	340	50 (Spherical)	γ
A7	Acetone-Water (25 : 75)	620	360	50 (Spherical)	α, γ, (m, β)
A8	Acetone-Water (25 : 75)	520	340	50 (Spherical)	α, γ, (m, β)
A9	Water	620	360	50 (Spherical)	α
A10	Water	520	340	30 (Spherical)	α

Maps of crystal size and form of TiOPc microcrystals, depending on T_{SCF} and ratio of acetone to water in cooling solvent (R_A) in supercritical acetone system are summarized in figure 3. The crystal size became smaller when R_A was decreasing or T_{SCF} was set to be lower. As for modification of the microcrystals, R_A had larger influence rather than T_{SCF}. In the case of using just acetone as cooling solvent (R_A = 100), 500 nm-microcrystals with stable β type were prepared. On the other hand, when cooling solvent was water (R_A = 0), crystal size was small (30-50 nm) and the crystal form was inclined to be metastable α type. Thus, because the affinity of TiOPc to acetone was estimated to be larger than that to water, many nuclei were quickly generated in the case of R_A = 0. And then, metastable TiOPc microcrystals with 30 nm in size was formed.

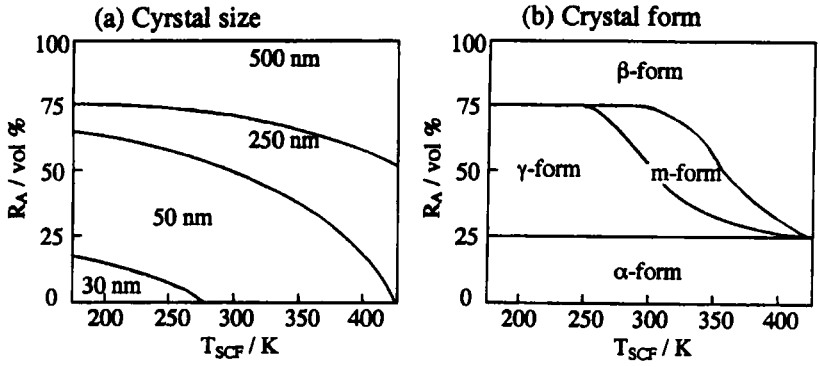

FIGURE 3 Maps of (a) crystal size and (b) crystal form of TiOPc microcrystals, depending on T_{SCF} and R_A in supercritical acetone system.

In conclusion, it has been clearly shown that the reprecipitation method from SCF solutions, especially from acetone, is effective for the control of the crystal size (in the range from 30 to 500 nm) and the modification [among α, m, the most unstable γ, β (the most stable)] of TiOPc microcrystals.

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