PREPARATION AND CHARACTERIZATION OF ORGANIC MICROCRYSTALS FOR PHOTONICS

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Microcrystals of π -conjugated organic compounds, the size of which ranges from several tens nm to μm , have been prepared by simple reprecipitation from the solution, and their interesting optical properties such as size-dependent absorption and fluorescence, and nonlinear optical responses have been demonstrated.

1. Introduction

Microcrystals, differing from both bulk crystals and isolated atoms and molecules, would have peculiar physical and chemical properties. Preparation of microcrystals of π -conjugated organic compounds, however, have been little investigated except for the evaporation method in an inert gas [1,2] and the crystal growth in a porous polymer film [3]. The former method is not applicable for thermally unstable compounds, and in the case of the latter method, observation of crystal size is not possible. Recently we have found that organic microcrystals can easily be obtained by simple reprecipitation method from solution at moderate temperature [4], and show interesting optical properties for photonics. Here, some typical results will be introduced.

2. Method

Compounds investigated so-far were chromophers with particular relevance to nonlinear optics, including solid-state polymerizable diacetylenes (Fig.1).

Microcrystals of several tens nm to $1\mu\text{m}$ in size were successfully prepared by dispersing solutions of organics into vigorously stirred non-solvents [4], or salting-out from solutions [5] at ambient temperatures (Fig. 2) : In a typical experiment, 50 μl of ethanol or acetone solution (ca. 10^{-2} M) was dispersed into 10 ml of stirred water at room temperature, and the dispersion was kept until it became a dispersion of reprecipitated microcrystals.

Fig. 1 π -conjugated compounds used for the preparation of microcrystals.

3. Polydiacetylene (PDA) microcrystals

Microcrystals of diacetylene monomers could be polymerized to give microcrystals of the conjugated polymers (Fig. 1). Interestingly, the molecular weight of poly-4BCMU from microcrystals became greater than that from large bulk crystals, suggesting that single chain of conjugated polymer is elongated from one end to the other end of the microcrystals. In fact, among the microcrystals, the three-times larger preparation method of microcrystals ones attained three-times greater molecular weight (Fig. 3).

PDAs are known to have strong excitonic

Fig. 2 Experimental set-up of the preparation method of microcrystals

absorption at the longer wavelength edge. In the case of polymerization of DCHD microcrystals, where no phase transition from the monomer crystal to the polymer crystal occurs, the absorption maximum stayed at the same wavelength until the complete conversion to the polymer. Thus the size dependence of excitonic absorption could be investigated. It turned out that the absorption maximum takes place blue shift with decreasing size, even in the size range of several tens nm (Fig. 4 and 5).

In the polymerization of 14,8-ADA which has rather loose crystalline lattice, polymerization behaviours including ultimate conversion varied with the crystal size [6].

Water dispersion of poly-DCHD and poly-14,8-ADA microcrystals were very stable, whereas that of poly-4BCMU, without surfactants, was so unstable as to cause precipitation of aggregated microcrystals.

Fig. 3 Scanning electron micrographs of poly-4BCMU microcrystals with average size of (a) 1 μ m and (b) 300nm. The molecular weights were found to be 1.6 and 0.55 million, respectively.

Fig. 4 Scanning electron micrographs of DCHD microcrystals; The averaged size of (a), (b), and (c) is 70, 100, and 150 nm, respectively.

Fig. 5 Size-dependent absorption spectra of poly-DCHD

4. Perylene microcrystals

In the case of perylene microcrystal as well, the free exciton absorption peaks were found to shift to the higher energy side with decreasing crystal size in the range from 50 nm to 200 nm (Fig. 6 and 7). In addition, the peaks became sharper with decreasing size (Fig. 6) [7].

Fig. 6 Absorption spectra of water dispersion of perylene microcrystals with different sizes: A, 50nm; B, 200nm; C, more than 1 μ m.

Fig. 7 Relationship between the excitonic absorption and the crystal size of perylene microcrystals.

Fig. 8 Emission spectra of perylene crystals with different sizes: A, 50 nm; B, 200 nm; C, bulk crystals.

Emission also varied with crystal size (Fig. 8). Those from the free exciton state shifted to the higher energy side with decreasing size, though the shift was rather small compared with that of absorption. It should be noted that strong fluorescence from the free exciton state was observed even at room temperature for the microcrystals. Bulk crystals at room temperature give fluorescence only from the self-trapped exciton state.

Table 1 summarizes the data of size-dependent energy shift of absorption spectra, including those of semiconductors. It is so interesting to know that organic microcrystals, at the free standing state as dispersed in amorphous media, take place the same extent of higher energy shift with decreasing, even though the size range is almost one order of magnitude larger than that of semiconductors. This finding requires new theory of quantum confinement, that is to say, completely different from that so-far used for semiconductors.

Table 1. The size-dependency of peak position of excitonic absorption of various microcrystals.

	Compound	Crystal Size	$\lambda_{\max}$ of Excitonic Abs. nm (cm ⁻¹)	Energy Shift from Bulk Crystal $\Delta E/\text{cm}^{-1}$	Meas. Temp.	
Inorganics	CuCl	Bulk	386 (25900)	0	77 K	A.Nakamura, Hyomen (Surface) Vol.30, 330 (1992).
		3.3 nm	384 (26000)	100		
		2.1 nm	382 (26200)	300		
	CdSe	Bulk	674 (14800)	0	2 K	
		12 nm	664 (15100)	300		
		1.8 nm	507 (19700)	4900		
Organics	NTCDA/PTCDA (Super lattice)	Bulk	560 (17860)	0	R.T.	F. F. So et al, Appl. Phys. Lett., 56, 674 (1990).
		4 nm	558 (17900)	40		
		1 nm	555 (19000)	160		
	PPy/PBT (Polymer Super lattice)	Bulk	(P. L.) (16130)	0	R.T.	T. Shimidzu et al, J.Appl. Phys., 74, 1283 (1993).
		9 nm	(P. L.) (16210)	80		
		3 nm	(P. L.) (16390)	260		
	Perylene	Bulk	480 (20800)	0	R.T.	This work
		200 nm	470 (21300)	500		
		50 nm	450 (22200)	1400		
	PDA (DCHD)	Bulk	665 (15000)	0	R.T.	This work
		150 nm	652 (15300)	300		
		50 nm	635 (15700)	700		

5. Nonlinear optical response of organic microcrystals

One of the important characteristics of microcrystal dispersion is that it provides us both high performance as single crystalline materials and low scattering loss as almost isomorphous materials, as well as easy fabricatabilities. Taking these advantages, optical Kerr shutter response of both PDAs and J-aggregated merocyanine microcrystals dispersed in water were examined. The $\chi^{(3)}$ values normalized by concentration (1 M) were approximately 10^{-9} esu, of which order is found to be very large even in this nonresonant wavelength region (Table 2) [8].

Four-wave mixing experiments of vanadylphthalocyanine revealed that the microcrystal dispersion shows completely different behaviours from the solution: that is, no slow response and saturable absorption appeared in contrast to the superposed slow response and induced absorption of the solution.

Table 2. The Kerr shutter response of microcrystal dispersions

Microcrystals	c / M	Crystal size / nm	T at 813 nm / %	T at 1064 nm / %	$\chi^{(3)}$ / esu	$\chi^{(3)} c^{-1}$ / esuM ⁻¹
J-aggregated MeSe-C18	2.0×10^{-4}	20	44	69	0.20×10^{-12}	1.0×10^{-9}
	6.2×10^{-4}	20	7.9	25	1.1×10^{-12}	1.8×10^{-9}
PDA(14-8ADA)	1.0×10^{-3}	300	43	>90	0.86×10^{-12}	0.86×10^{-9}
PDA(DCHD)	2.3×10^{-3}	70	1.6	17	1.4×10^{-12}	0.61×10^{-9}
	2.3×10^{-3}	100	1.6	17	2.2×10^{-12}	0.93×10^{-9}
	1.6×10^{-3}	150	0.03	16	1.6×10^{-12}	1.0×10^{-9}

6. Conclusion

The microcrystal dispersion in liquid could easily be converted into the dispersion of well defined microcrystals in polymer thin film. Thus, microcrystallization was demonstrated to be one of potential materialization techniques of organic chromophers.

References

- 1) H. Toyotama, Kinouzairyou (Functional Materials), 6, 44 (1987).
- 2) K. Yase, T. Inoue, M. Okada, T. Funada, and J. Hirano, Hyomenkagaku (Surface Science), 8, 434 (1987).
- 3) K. Mizuno and A. Matsui, Mol. Cryst. Liq. Cryst., 218, 49 (1992).
- 4) H. Kasai, H. S. Nalwa, H. Oikawa, S. Okada, H. Matsuda, N. Minami, A. Kakuta, K. Ono, A. Mukoh, and H. Nakanishi, Jpn. J. Appl. Phys., 31, L1132 (1992).
- 5) H. Kamatani, H. Kasai, S. Okada, H. Matsuda, H. Oikawa, M. Minami, A. Kakuta, K. Ono, A. Mukoh, and H. Nakanishi, Mol. Cryst. Liq. Cryst., 252, 233 (1994).
- 6) R. Iida, H. Kamatani, H. Kasai, S. Okada, H. Oikawa, H. Matsuda, A. Kakuta, and H. Nakanishi, Mol. Cryst. Liq. Cryst., 267, 95 (1995).
- 7) H. Kasai, H. Kamatani, S. Okada, H. Oikawa, H. Matsuda, and H. Nakanishi, Jpn. J. Appl. Phys., 35, L221 (1996).
- 8) H. Kasai, H. Kanbara, R. Iida, S. Okada, H. Matsuda, H. Oikawa, and H. Nakanishi, Jpn. J. Appl. Phys., 34, L1208 (1995).