

Blue-Shifted Photoluminescence of MEHPPV Nanoparticles Fabricated by a Novel Visible-Laser Solution-Droplet Processing

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Liquid-phase laser processing, where the laser-irradiated target material is immersed in water for cooling, has been reported as a promising processing technique for thermally fragile organic materials. Although nanometer-sized particles have been reported to be obtained with the liquid-phase laser processing, the physical property did not change because quantum-mechanical size effect does not exhibit itself in the zero-radius Frenkel excitons. In the present study, we step further to use solution droplets as a target material, where organic molecules are dispersed in an organic solvent and, therefore, expected to easily alter the conformation and the energy upon laser irradiation [1]. Small volume organic solvent is quickly evaporated upon laser irradiation, letting the bare organic molecule placed in water and rapidly cooled. To prevent the chemical decomposition of the target π -conjugated molecule, the specimen was resonantly irradiated by a ns-pulse green laser, not by a conventional UV laser.

When the solid state spin-coat film of MEH-PPV was used as a irradiation target immersed in water, resulting MEH-PPV particles showed similar photoluminescence (PL) like the PL of the spin-coat film and PL of the chloroform solution, including the 0-1, 0-2, 0-3 vibrational transitions: this indicates that the energy levels were not modified from the spin-coat film. In comparison, when tiny droplets of MEH-PPV chloroform solution (orange color) were suspended in water, laser irradiation gave rise to yellow MEH-PPV particles which showed 550 nm and 530 nm PL (type B), blue-shifted from the spin-coat film PL 580 nm (type A), suggesting a successful phase transition of MEH-PPV polymer conformation. When these yellow MEH-PPV particles were dissolved in chloroform and irradiated again by a green laser, the resulting particles showed the identical type B PL. The unidirectional phase transition from type A to type B suggests that the type B ground state has lower energy than type A, which is consistent with the blue-shifted PL of type B, providing that the excited state energy is similar between the two states. Thermal annealing up to 200°C of type A state did not give rise to type B state, which indicates that the activation potential between the two states is higher than the thermal energy at 200°C, and that only the proposed solution-phase laser processing enables the system to cross over this potential.

[1] K. Takada, A. Tomioka, J. Phys.: Conf. Ser. **358**, 112012 (2012).

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