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コア-シェル型有機/金属ハイブリッドナノ結晶の作製と光学特性
Preparation of Core-Shell Type Organic/Metal Hybridized Nanocrystals and Their Optical Properties

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Organic nanocrystals (NCs) are in the mesoscopic phase between a single molecule and the corresponding bulk crystals, and are expected to exhibit peculiar optical properties, depending on crystal size and shape. Well-defined, i.e., size- and shape-controlled, organic NCs could be prepared successfully from pai-conjugated organic and polymer compounds by developing the reprecipitation method. Interestingly, organic NCs exhibited the size-dependence of linear optical properties (extinction and fluorescent emission spectra), which is speculated to be caused not by so-called quantum size effect in semiconductor quantum dots by but thermal softening of nanocrystal lattice, due to increase in specific surface area with decreasing crystal size. Namely, the effective pai-conjugation length would decrease, owing to disordered and strained nanocrystal lattice, and then the band gap (or HOMO-LUMO gap) would widen with decreasing crystal size.

In this presentation, recent progress on hybridized organic NCs and ordered array structure of encapsulated organic NCs will be introduced in detail for optically functional materials toward next-generation organic device application. In other word, hybridization is one of the main and important objectives in current material science. Our attention is now focused on core-shell type hybridized organic NCs, which seem to be the best suited nanostructure for the occurrence of novel optoelectronic properties and photonic function induced by core-shell interface interaction. Polydiacetylene (PDA) NCs (core) and Ag nanoparticles (NPs) (shell) hybridized NCs could be fabricated reproducibly by the development of visible-light-driven photocatalytic reduction method. PDA is one of the most promising candidates in organic nonlinear optical (NLO) materials, which shows the large third-order NLO susceptibility and highly speed of optical response in femto-second order. Actually, the value of the susceptibility from PDA NCs (core) has been multiplied evidently, due to the enhancement effect of optically electric field induced by localized surface plasmon resonance from Ag NPs (shell). The present reduction process could proceed easily, being independent of core size and shape, when the redox potential of metal ion (or metal complex) should be located between conduction band and valence band in pai-conjugated polymer such as PDA. So some various hybridized NCs could be produced in the similar manner, for example, rod-like and fibrous PDA NCs, polyalkylthiophene NPs as a core material, and Pt NPs and Au NPs as a shell material. But, the subsequent chemical reduction process was performed at the same time, when Au NPs (shell) is prepared.

On the other hand, it should be necessary to arrange and integrate organic NCs, including hybridized ones, on a substrate so as to receive and transmit input- and output-information signals by electronically and/or optically accessing to organic devices. So, encapsulations of organic NCs, patterned substrate, and tapered cell method have been employed suitably to fabricate and control ordered array structure of organic NCs on a substrate. First, mono-dispersed polystyrene microsphere (PSMS) was used as a model of encapsulated (and hybridized) NCs, and some beautiful ordered array structure could be formed on the patterned substrate by optimizing the size of PSMS and pattern design. Especially, so-called Kagome Structure composed of PSMSs could be fabricated for the first time, which structure is said to provide the confinement effect of light propagation and a kind of photonic crystals. In addition, it has become possible to build-up the order array structure consisted of encapsulated semiconductor NPs and PDA NCs produced by emulsion polymerization process for optoelectronics and photonics devices application.

Finally, the future scope in the relevant fields of optoelectronics and photonics will be discussed in brief.

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