Example

Fine Synthesis of Groups 11–13–16 Semiconductor Quantum Dots and Their Potential Applications

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Colloidal semiconductor quantum dots (QDs) are a new class of photoluminescent materials exhibiting intense monochromatic emission characteristics originating from band-edge transitions. Since 1993, cadmium chalcogenide QDs have been the focus of development. However, recent applications in display devices require cadmium-free QDs. Ternary nanoparticles composed of group 11, 13, and 16 elements are candidates for cadmium-free QDs and are represented by $CuInS_2$ and $AgInS_2$. Unfortunately, the QDs of this category exhibit spectrally broad photoluminescence (PL) derived from the electronic transitions via defect levels, and the band-edge emissions have not been observed until recently. In 2018, we reported the spectrally narrow band-edge emission in the yellow region (580 nm) by coating $AgInS_2$ QDs with a gallium sulfide (GaS_y) shell.[1]

The blue-shift emission was attempted by partly replacing indium with gallium to increase the bandgap of the core semiconductors. Consequently, the narrowband emissions have been realized between green and yellow according to the $AgInS_2$–$AgGaS_2$ alloy phase composition (Fig. 1).[2] Typically, the synthesis of quaternary materials is not as easy as that of binary materials due to the difference in the reactivity between metal precursors. This work attempted to solve this problem by separating the reactions, i.e., nucleation of Ag_2S and subsequent conversion to $Ag(In_{1-x}Ga_x)S_2$, which increased product yield significantly. Due to the well-controlled synthesis, the compositional uniformity of the $Ag(In_{1-x}Ga_x)S_2$ core QDs was improved, and the full width at half maximum of the PL spectra after the GaS_y shell coating was 30 nm, a record-narrow value as Cd-free QDs.

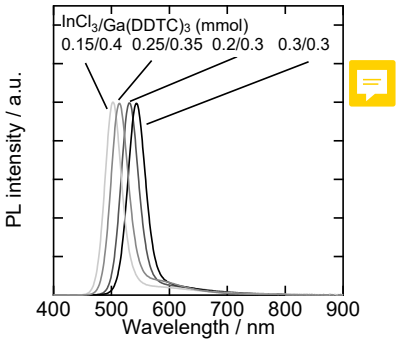

Fig. 1. PL spectra of $Ag(In_xGa_{1-x})S_2/GaS_y$ core/shell QDs with different In/Ga ratio.

The durability of the $AgInS_2/GaS_y$ and $Ag(In_{1-x}Ga_x)S_2/GaS_y$ core/shell QDs is lower than that of Cd-based QDs protected by ZnS. Whereas the chemical stability of ZnS is favorable, overcoating by ZnS shell spoils the band-edge PL from $AgInS_2/GaS_y$ core/shell QDs. Therefore, we attempted durability enhancement by embedding the core/shell QDs into a matrix of GaS_y (Fig. 2). The GaS_y matrix was generated by a sol–gel method using a gallium complex and thioacetamide as gallium and sulfur sources. A pale-orange powder exhibiting bright yellow photoluminescence was obtained, which has higher durability against light and heat. Increasing chemical stability is crucial for using these QDs in wavelength conversion and electroluminescence.

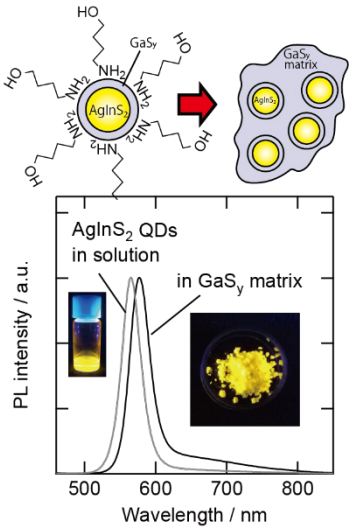

Fig. 2. Incorporation of $AgInS_2/GaS_y$ core/shell QDs into GaS_y matrix.

References

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2) W. Hoisang, T. Uematsu, T. Torimoto, S. Kuwabata, *Inorg. Chem.*, **2021**, *60*, 13101-13109.