Visualizing core-shell structure of heavily doped silicon quantum dots by electron microscope using atomically thin support film

Sugimoto, H.[1], Sakiyama, M.[1] and Fujii, M.[1]

[1] Kobe University, Japan

Recent progress in the optoelectronic and biophotonic applications of colloidal quantum dots (QDs) is largely ascribed to the successful formation of the stable Type-I core/shell structure such as CdSe/ZnS and PbSe/CdSe QDs. The core/shell structure extends the freedom of design of the energy state structure and improves the electrical and optical properties. In contrast to Cd and Pb-chalcogenide QDs, the formation of a core/shell structure has not been successful in silicon (Si) QDs despite their importance in biophotonics. This is mainly due to the lack of proper semiconductor materials for the shell. As a result, organic ligands are directly attached on Si QD surface and the ligands play a role of a wide energy gap shell.
Recently, we proposed a new class of colloidal Si QD having a heavily boron (B) and phosphorus (P) codoped shell.[1,2] Figure 1 shows the photograph and transmission electron microscope (TEM) image of colloidal Si QDs. Thanks to the shell with a negative surface potential, the Si QDs are dispersible in water and alcohol without any organic functionalization processes. The all-inorganic Si QDs exhibit many superior properties such as size-tunable photoluminescence in a wide wavelength range (700-1450 nm) and are attracting attention as a new environmentally friendly nanomaterial for biophotonics.
The structure of the core/shell Si QDs has been investigated by various state of the art analytical methods such as atom probe tomography, scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), etc. Although all the data suggest the formation of a heavily B and P codoped (> 1 at.%) shell, it has not been directly visualized. In this work, we present the methodology to visualize the shell by TEM and to fully clarify the structure. To achieve this, we employ a graphene oxide support film, which has good affinity with a hydrophilic Si QDs and provides a much better contrast than a conventional amorphous carbon support film. Figure 2 shows the high-resolution TEM image of a codoped Si QD on graphene support film. We observe the crystalline Si core and amorphous shell ~1 nm in thickness. The STEM-EELS mapping reveals that the shell is composed of B, Si and P, which is consistent with the XPS data. The Raman spectroscopy suggests that the shell consists of B, B-P, and B-Si-P clusters. We investigate the relation between the shell thickness and the dopant concentration. It is shown that the shell thickness can be controlled by the dopant concentration.

References: [1] H. Sugimoto et al., Nanoscale, 6, 122 (2014)

[2] Y. Hori, et al., Nano Letters, 16, 2615 (2016)

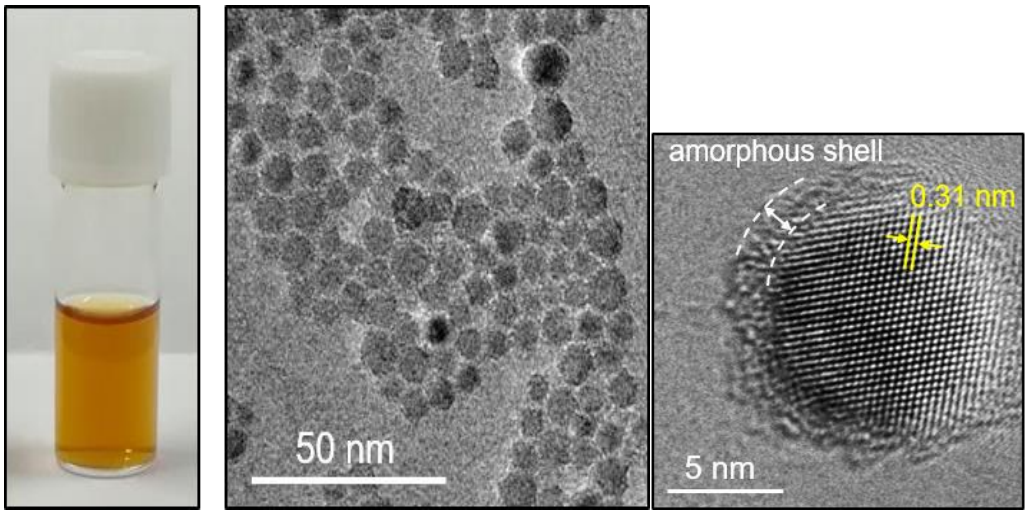

Figure 2. High-resolution TEM image of a codoped Si QD on graphene oxide film.