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Simple Chemical Approaches for Luminescent Si Nanostructures

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Abstract – The potential use in optics application of luminescent silicon nanostructures will be discussed in this presentation. Si is the cornerstone for current microelectronics and at the same time shows a high chemical affinity for carbon, oxygen, and nitrogen for covalent linkages, thereby producing a wide variety of its organic derivatives hybridized at the molecular level. This promises that the organic modified Si nanostructures can behave like organic molecules, and therefore, have a high degree of potential for working as light emitting soft nanomaterials. The precise control of organic shells on molecular density leads to appearance of unique optical property based on the quantum confinement effect. This presentation demonstrates our recent studies on solution synthesis, internal core structures, and optical properties of organically modified nanostructures.

Bulk silicon provides a platform for large-scale integrated circuits, but shows significantly poorer optical performance because of its indirect bandgap character. Modifying the structure of Si such that its three-dimensional physical size does not exceed 5 nm for crystalline nanoparticles produces a remarkable change in its optical transition. The effect of quantum confinement imposed upon the charge carriers is postulated to increase the bandgap from 1.1 eV for bulk to about 3.3 eV, and it improves the PL quantum yield. Such luminescent Si nanoparticles have been synthesized by a range of different methods including the gas and solution phase decomposition of silanes or organosilanes, the electrochemical etching of Si wafers, laser ablation, and solution reduction of $SiCl_4$. Modification of the nanoparticles with organic monolayers allows the control of surface polarity. For example, hydrophobic termination has a potential to be fully miscible with conducting polymer for optelectronic applications, while some of hydrophilic surfaces have opened an avenue for fluorescent labels in bioimaging and medical diagnostics.

The method shown in Figure 1 is the unique synthetic route for organically modified nanoparticles, because it allows the simultaneous achievement of nanoparticle synthesis and subsequent organic modification in a single action by performing laser ablation of target Si in reactive molecules, e.g., an unsaturated hydrocarbon. As illustrated, the focused laser beam irradiation produces Si vapors. Due to the rapid quenching by surrounding molecules, the vapors condense to form nanoparticles. In the absence of water and oxygen molecules, surfaces of the nanoparticles remain covered with silicon-centered radicals, and react with the surrounding molecules to give a covalent linkage of carbon-silicon. Accordingly, a liquid like sample was obtained because of organic modification. An analysis using ^{1}H and ^{13}C NMR confirmed the successful reaction between the nanoparticle surface and the reactant under irradiation of laser. FTIR spectrum showed a high molecular density in the organic shell, preventing the surface of crystalline core from oxidation. In the Raman spectrum, a maximum of the vibration band is found at around 511 cm^{-1}, due to the reduced physical size of the nanoparticles. In addition to this macroscopic observation, the nanoscopic analysis using TEM confirmed that the core of the sample is composed of single-crystalline diamond lattice structure. Overall, the sample contained a number of crystalline nanoparticles with sizes range from 1 to 10 nm in diameter. Optical absorbance and emission spectra of the sample are shown in Figure 1. The absorption edge of the sample is blueshifted by about 0.2 eV compared with that of bulk silicon due to size reduction of the nanoparticles. The PL spectrum corrected with 266 nm excitation shows fairly broad peak, with a 107 nm of FWHM, at the wavelength ranging from 300 to 650 nm. Next, we developed a solution route to synthesis of nanoparticles that emit the light selectively in the near-UV (300-380 nm) region. To achieve this, a microemulsion synthesis approach is employed. In this presentation, the unique optical properties from silicon nanostructures will be discussed.

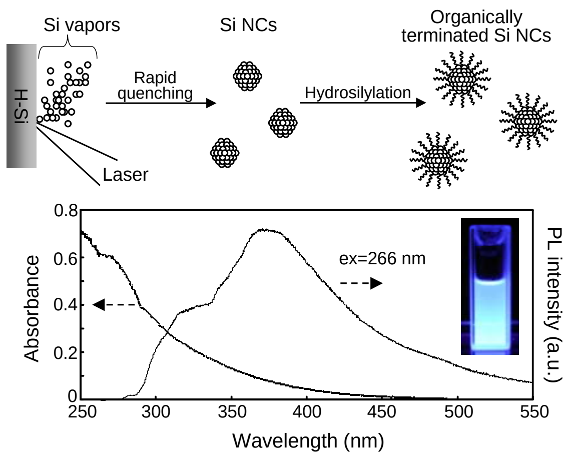

Figure 1. Illustration for laser chamical synthesis method for organically functionalized Si nanoparticles, and the optical absorbance and PL spectra of the Si nanoparticle prepared in 1-octene.