Controlling Optical Properties of ZnO Nanocrystals by Bulkiness of Alkyl Ligands

Yuto Toyota,[a] Shohei Yamashita,[b] Yuki Nagai,[a] Yoshinori Okayasu,[a] Yohei Okada,[c] Yoichi Kobayashi[a,d]
[a]*Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University. E-mail: ykobayas@fc.ritsumei.ac.jp*
[b]*Institute of Global Innovation Research, Tokyo University of Agriculture and Technology.*
[c]*Department of Applied Biological Science, Tokyo University of Agriculture and Technology.*
[d]*PRESTO JST*

Organic ligands on the surface of semiconductor nanocrystals (NCs) are important for the chemical stability and dispersibility of colloidal NCs. Aliphatic ligands are generally used as ligands to enhance the dispersion of NCs, and in terms of electronic interactions, they do not seem to affect the photophysical properties of NCs. On the other hand, insufficient coverage of the surface ligands leads to the formation of structural defects on the NC surface, which have a significant impact on the optoelectrical properties of NCs. Therefore, systematic investigation of the effect of the molecular structures of ligands on the optical properties of NCs is indispensable even in aliphatic ligands. In this study, we synthesized a series of alkylphosphonic-acid-capped zinc oxide (ZnO) NCs (L1S-L3 in Fig. 1a) as a model system and investigated their photophysical properties.

The as-synthesized ZnO NCs have acetic acid as the surface ligand, and then the ligands are replaced with each type of phosphonic acids. Fourier transformed infrared absorption (FT-IR) spectra show that both acetic acid and phosphonic acid were coordinated on the NCs as the ligand. The average diameter of ZnO NCs was 6.45 nm.

The absorption edge of ZnO NCs dispersed in chloroform is 371 nm (3.34 eV), which is slightly larger than the bandgap of bulk ZnO (3.3 eV) due to the quantum size effect.[1] When excited by UV light (350 nm), two emission bands were observed at around 370 and 550 nm. The emission band at the shorter wavelength is ascribed to the band-edge excitonic emission, and that at the longer wavelength is ascribed to the emission from oxygen defects.[2] Structural defects mostly emerge around the surface than inside of NCs. Therefore, it is expected that the bulky ligands increase the number of defects on surface of NCs and the photoluminescence quantum yield (PLQY) increases because the bulky ligands decrease the density of the ligands on the surface of NCs and results in the insufficient surface coverage. The PLQY of L1L-, L2-, and L3-ZnO NCs were 3.5, 4.9, and 4.0%, respectively. The reason why the lower PLQY of ZnO NCs covered with tertiary ligands is probably because L3 is too bulky to be exchanged with acetic acid, which effectively coordinated to the surface of NCs. The larger amount of acetic acid in L3-ZnO is supported by the Fourier-transformed infrared spectroscopy.

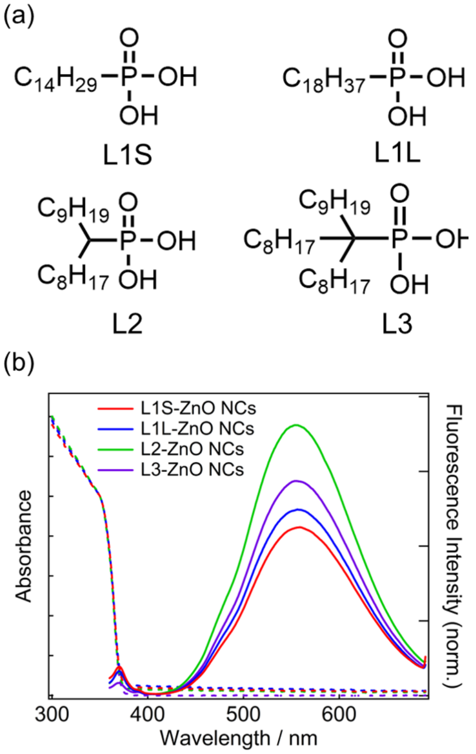

Fig 1. (a) Molecular structures of phosphonate ligands and (b) the absorption and fluorescence spectra of phosphonate-capped ZnO NCs in chloroform (λ_{ex} = 350 nm)

1) V. Srikant, D. R. Clarke, *J. Appl. Phys*. **1998**, *83*, 5447–5451.
2) P.V. Kamat, B. Patrick, *J. Phys. Chem.* **1992**, *96*, 6829–6834.