Synthesis and Optical Properties of ZnTe/ZnS Core-Shell Nanocrystals

Sota Tokuoka,[a] Daisuke Yoshioka,[a] Yoshinori Okayasu,[a] Yuki Nagai,[a] Yoichi Kobayashi[a,b]
[e]*Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University. E-mail:*
ykobayas@fc.ritsumei.ac.jp
[b]*PRESTO JST*

ZnTe is a visible-light-responsive semiconductor with a direct transition band gap of 2.26 eV. Because of this feature, it is expected to be used for green LEDs and solar cells. In general, semiconductor nanocrystals (NCs) are expected to improve luminescence quantum yield and high reactivity as photocatalysts compared to the bulk state. However, ZnTe NCs are easily decomposed by light irradiation, which has been a serious challenge in their application. Although covering ZnS layers around ZnTe NCs to confine excitons has been reported as a useful method to improve the photostability,[1] the detail such as excitation dynamics is unclear. In this study, we synthesized ZnTe/ZnS core-shell NCs and compared the stability and excited-state dynamics with those of ZnTe NCs. Understanding the excited-state dynamics will provide additional insight into their use as photofunctional materials.

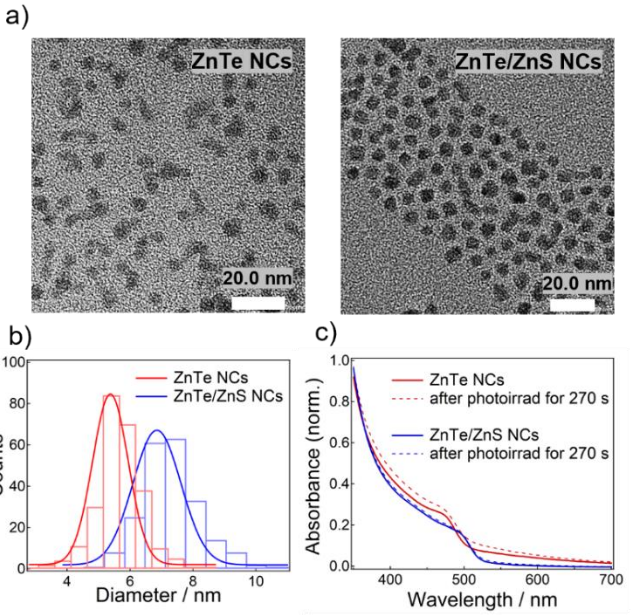

Fig. 1 a) TEM images of ZnTe and ZnTe/ZnS NCs. b) Particle size distribution of ZnTe and ZnTe/ZnS NCs. c) Absorption changes of ZnTe/ZnS and ZnTe NCs under light irradiation (360 nm, 72 mW/cm^2)

ZnTe NCs were synthesized by hot injection using oleic acid as ligands.[2] The ZnS shell was grown on the ZnTe core using the successive ionic layer adsorption and reaction (SILAR) method in octadecene. ZnTe NCs and ZnTe/ZnS NCs were characterized by X-ray diffraction (XRD) measurements, X-ray fluorescence analysis, and transmission electron microscopy. The crystal structure of the ZnTe NCs was zincblende and the average particle diameter was 5.4 nm (Fig. 1a,b). The average diameter increases to 6.9 nm by the shell growth process. Because the length of the monolayer of ZnS shell is estimated to be 0.32 nm from the crystal structure, the change of the diameter from 5.3 to 6.9 nm by the shell growth process indicates that the 2.5 monolayers of ZnS were grown on the surface of ZnTe NCs. Furthermore, the absorption spectrum of ZnTe/ZnS NCs exhibited red-shifted band-edge absorption compared to ZnTe NCs (Fig. 1c, solid lines), which indicates that the bandgap was decreased due to the quantum size effect, i.e. the increase in the particle size by shell formation.

Air- and photo-stability of the NCs in hexane were evaluated from the UV-Vis spectral changes. Both in the air-saturated solution in the dark and in the N$_2$-atmosphere solution under UV light (365 nm, 72 mW cm^{-2}), the spectral change of ZnTe/ZnS NCs was small compared to that of ZnTe NCs (Fig. 1c). This result shows that the formation of ZnS layer enhanced the air- and photo-stability. In addition, transient absorption spectroscopy was conducted to compare the excited state dynamics. A positive broad signal, which may originate from surface defects, was observed in both samples. This signal intensity was weaker in the ZnTe/ZnS NCs, which suggests that some surface defects on the ZnTe core were removed by the ZnS layer formation.

1) C. Lincheneau et al., *J. Mater. Chem. C,* **2014**, *2*, 2877.

2) J. Zhang et al., *J. Phys. Chem. C,* **2008**, *112*, 5454.