Controllable Plasmonic Properties of Cu-Ge-S Multinary Quantum Dots with Ag^+ Doping

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Keywords: Semiconductor, Quantum dot, Cu-Ag-Ge-S

Semiconductor quantum dots (QDs) have attracted much attention for solar light conversion systems due to the tunability of optical properties and electronic structure with particle size and composition. Conventional binary QDs such as CdSe and PbS contain highly toxic elements, limiting their practical application. Thus, environmentally friendly multinary QDs composed of less toxic elements have been intensively investigated. Previous studies have highlighted I-IV-VI group QDs such as Ag_8GeS_6,[1] Cu_2SnS_3,[2] and Cu_2GeS_3[3] as promising alternatives due to their low cost, low toxicity, and potential electronic properties. In this work, we report a novel solution-phase synthesis of Ag^+-doped Cu-Ge-S (Cu-Ag-Ge-S) QDs and their tunable optical properties in the near-IR region.

Cu-Ag-Ge-S QDs were synthesized by reacting metal precursors of $(Ge(gly)_2(H_2O)_2$, $Cu(DDTC)_2$, and AgDDTC with thiourea in a mixture solution of oleylamine and 1-dodecanethiol at 150°C for 20 min. The optical properties of resulting Cu-Ag-Ge-S QDs were controlled by varying the precursor ratio Cu/(Cu+Ag) (= x).

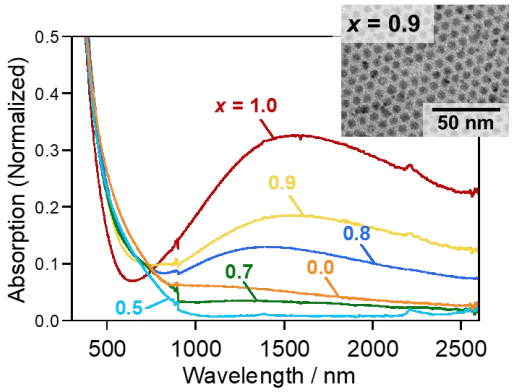

Fig. 1 Absorption spectra of Cu-Ag-Ge-S QDs prepared with different Cu/(Cu+Ag) (= x) ratios.

Spherical particles were formed regardless of the precursor ratio. Notably, the QDs prepared with x = 0.9 had 6.4 nm in the average diameter with a very narrow size distribution, forming a two-dimensional hexagonal array (Fig. 1). The absorption onset of QDs were red-shifted from 620 nm to 1100 nm with a decrease in the x value (Fig. 1), indicating a decrease in the bandgap from 2.02 eV to 1.13 eV. Furthermore, a broad peak assignable to the localized surface plasmon resonance (LSPR) was observed around 1500 nm for QDs with x > 0.7. The LSPR peak intensity decreased with decreasing x value, probably due to the decrease of carrier density originating from Cu-related defect sites.

1) D. I. Bletskan, *et al., Semicond Phys. Quant.*, **20**, 19 (2017).
2) X. Liu, *et al., Chem. Mater.*, **27**, 1342 (2015).
3) Q. Chen, *et al., Jpn. J. Appl. Phys.*, **57**, 08RC20 (2018).