# Effect on Nanocrystal Surface on Photochromism of Cu-Doped ZnS Nanocrystals

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Doping of metal ions to semiconductors is an effective way to modify the electrical, optical, and magnetic properties of semiconductor nanocrystals (NCs). For example, the introduction of transition-metal dopants such as Cu and Mn ions forms midgap states between the valence and conduction bands of host semiconductor NCs, which largely alter optoelectrical properties of NCs. Recently, our group reported that hydrophilic Cu-doped ZnS NCs exhibit relatively fast T-type photochromism, which is brought by hole trapping in the Cu level and interparticle electron hopping.[1] The NCs show more efficient photosensitivity than other inorganic photochromic materials and exhibit temperature-insensitive color fading at around room temperature.[2] In addition, Cu-doped ZnS NCs are composed of earth-abundant atoms and are easy to synthesize in large quantities. Therefore, this material is promising for large-scale industrial applications. For industrial use such as paint materials, however, solubility in organic solvents is strongly desired. In this study, we synthesized organic solvent-soluble Cu-doped ZnS NCs and investigated the photochromic properties.

Hydrophobic Cu-doped ZnS NCs were synthesized by the hot-injection method using oleylamine (OLA) as surface ligand. The color of Cu-doped ZnS NCs in chloroform reversibly changes from pale yellow to dark brown by UV light irradiation. A broad absorption band is observed in the visible light region (Fig. 1 (a)). Because the observed absorption spectra are very similar to that of phidrophic Cu-doped ZnS NCs, it suggests that the origin of coloration is the same mechanism as the previous study: the electronic transition from the valence band to the $Cu^{2+}$ level (Fig. 1 (b)).[1] It takes several minutes in the color fading reaction, and it is relatively longer than the hydrophilic Cu-doped ZnS NCs in the previous report.

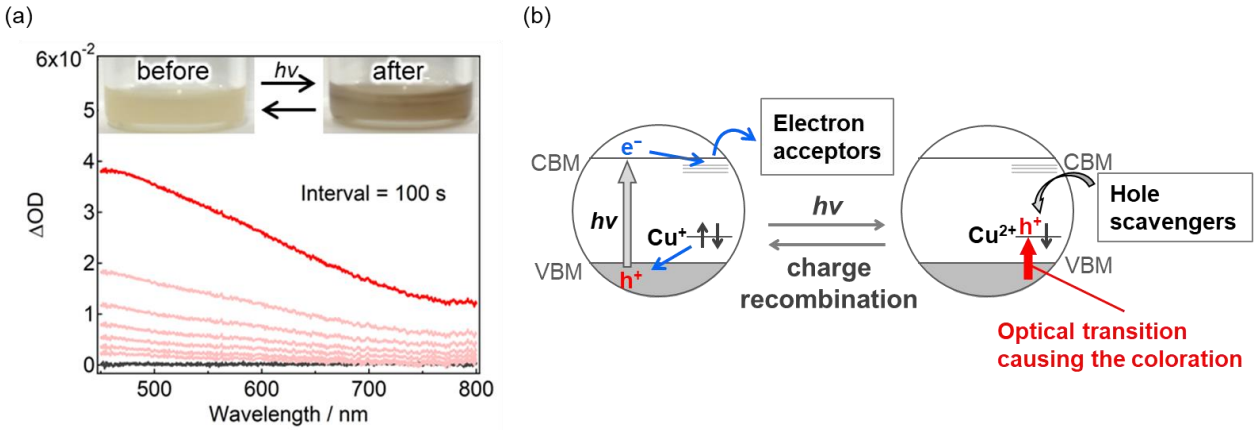


Fig. 1 (a) Photographs and time evolution of the differential absorption spectrum of the Cu-doped ZnS NCs in chloroform after continuous-wave UV irradiation (365 nm, 150 mW $cm^{-2}$) for 30 s and (b) plausible coloration scheme of Cu-doped ZnS NCs in organic solvents after 365 nm UV irradiation.

1) Y. Han, M. Hamada, I.Y. Chang, K. Hyeon-Deuk, Y. Kobori, Y. Kobayashi, *J. Am. Chem. Soc.* **2021**, *143*, 2239.
2) Y. Sanada, D. Yoshioka, Y. Kobayashi, *J. Phys. Chem. Lett.* **2021**, *12*, 8129.