Synthesis of Zn-doped $CuGaS_2$ Nano-discs for Photocatalytic Hydrogen Evolution

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Semiconductor nanocrystals have been extensively studied for applications in LEDs, solar cells, and photocatalysis due to their tunable optical properties. Cu-based I–III–VI semiconductor nanocrystals have been reported to exhibit excellent visible-light absorption. It was reported that tuning the morphologies of $CuGaS_2$ enhanced their photocatalytic activity for hydrogen evolution.[1] This paper reports the preparation of heavy-metal-free Zn-doped $CuGaS_2$ (Zn-CGS) nanocrystals with a disc shape. The morphology of the obtained Zn-CGS nano-discs (NDs) was modified by changing the Zn fraction in the resulting NDs.

Zn-CGS NDs were synthesized using a heating-up method. The precursors of CuI, $Ga(acac)_3$, $Zn(OAc)_2$, and thioacetamide were suspended in oleylamine (OLA)-dodecanethiol (DDT) mixture solution and then heat-treated at 350 ºC for 10 min under an N_2 atmosphere. The optical properties of resulting NDs were controlled by varying the precursor ratio, (Cu+Ga)/(Cu+Ga+Zn) (= x).

Disk-shaped nanoparticles were formed regardless of the precursor ratio. The NDs prepared with x = 0.7 had 16.7 nm in the average diameter with a narrower size distribution, forming a hexagonal-shaped array (Fig. 1a). The absorption onset of Zn-CGS NDs were red-shifted from 470 nm to 550 nm with an increase in the x value (Fig. 1a), indicating a decrease in the bandgap from 2.61 eV to 2.25 eV. The electronic energy structure was determined using the photoemission yield spectroscopy in air (PYSA). As shown in Fig. 1b, the conduction band minimum (CBM) was changed from −2.76 eV to −3.07 eV with an increase in the x value, while the valence band maximum (VBM) was almost constant at about −5.34 eV. We will further discuss the photocatalytic performance for H_2 evolution and the growth mechanism of NDs.

1) Liu Z, et al. *Nanoscale*, **2019**, 11(1): 158-169.

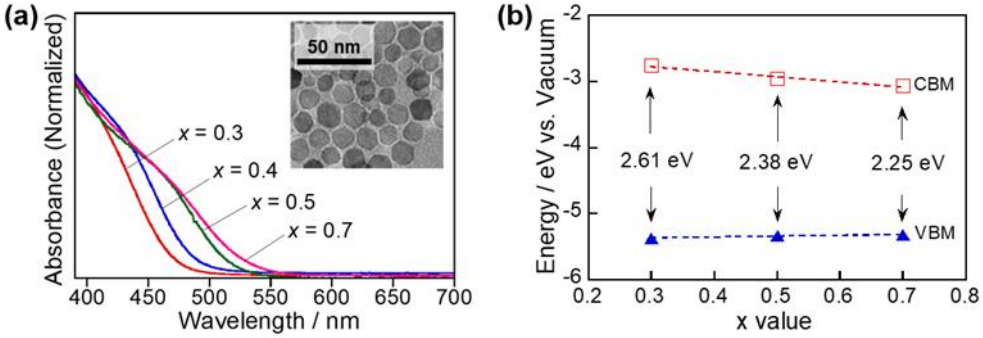

Fig. 1 (a) UV-vis absorption spectra of Zn-CGS NDs prepared with different metal fractions. (Inset) A TEM image of Zn-CGS NDs with x = 0.7. (b) Composition-dependent energy levels of Zn-CGS NDs.