

Supporting Information

Colloidal Nanocrystals of Orthorhombic $\text{Cu}_2\text{ZnGeS}_4$: Phase-Controlled Synthesis, Formation Mechanism and Photocatalytic Behavior

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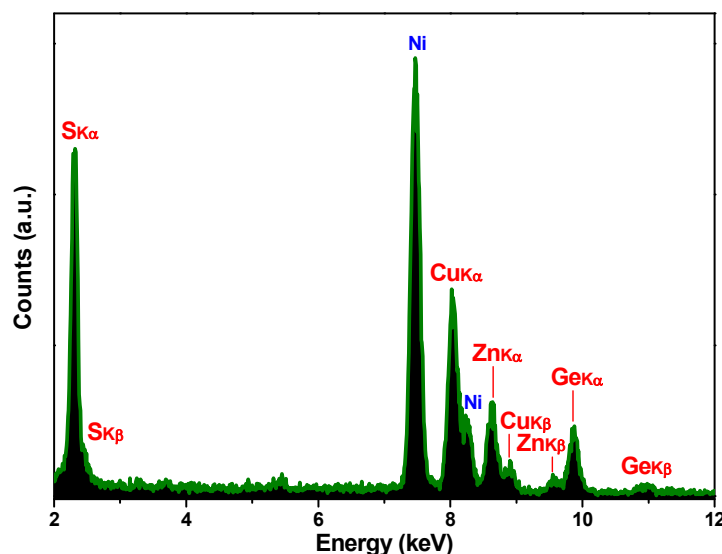


Figure S1. EDX spectrum of orthorhombic $\text{Cu}_2\text{ZnGeS}_4$ (CZGS) nanocrystals. The Ni signals are attributed to the Ni TEM grid.

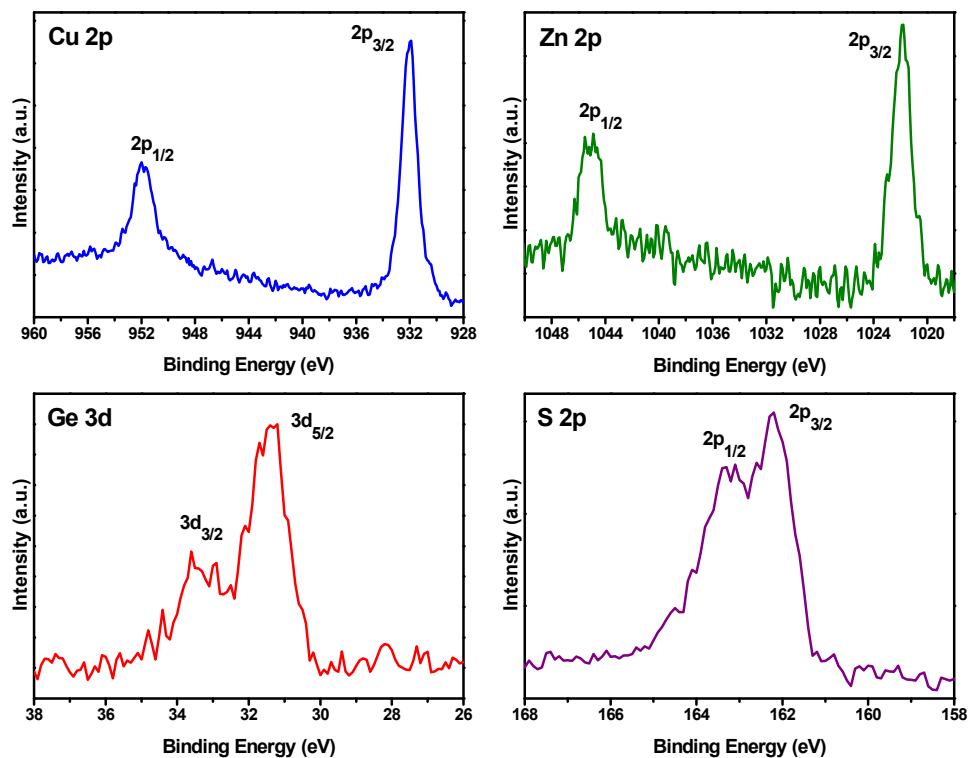


Figure S2. High-resolution XPS analysis of orthorhombic CZGS nanocrystals showing the Cu 2p (blue), Zn 2p (green), Ge 3d (red) and S 2p (purple) spectra.

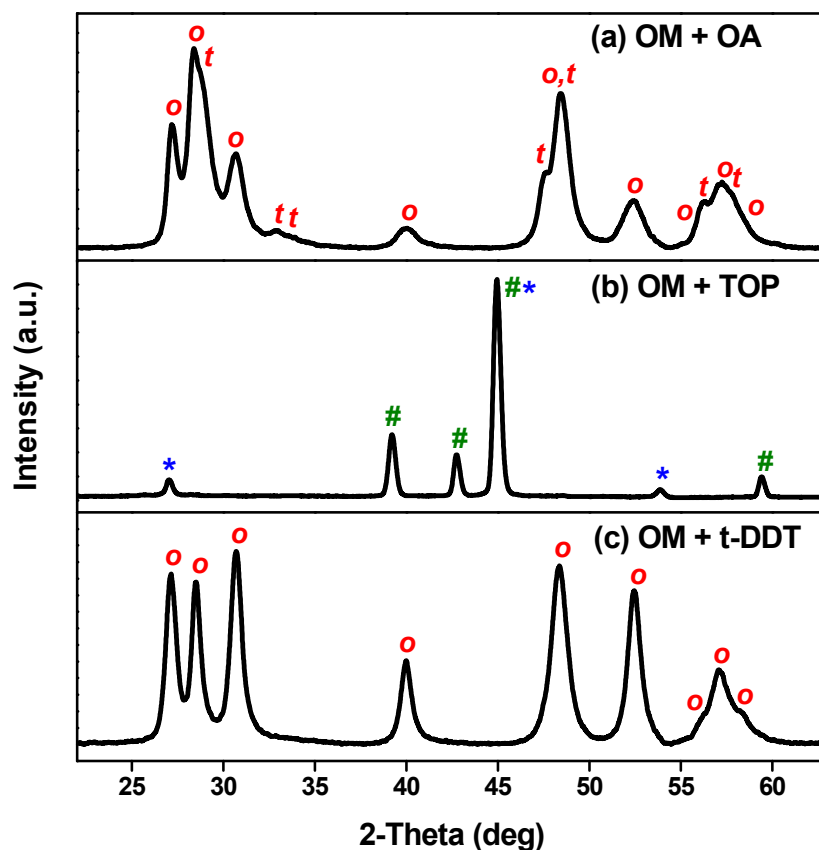


Figure S3. XRD pattern of the nanocrystals obtained when oleylamine (OM) is paired with (a) oleic acid (OA), (b) trioctylphosphine (TOP), and (c) *tert*-dodecanethiol (t-DDT). The solvent mixtures were prepared using 9:1 v/v ratio (e.g. 9 mL OM + 1 mL t-DDT). The peaks marked with red *t* and red *o* are attributed to the presence of tetragonal-phase (JCPDS #25-0327) and orthorhombic-phase (JCPDS #26-0572) CZGS, respectively. A blue asterisk is used to denote the presence of Ge (JCPDS #04-0545) whereas a green hash sign is used to mark the presence of Cu₃Ge (JCPDS #06-0693).

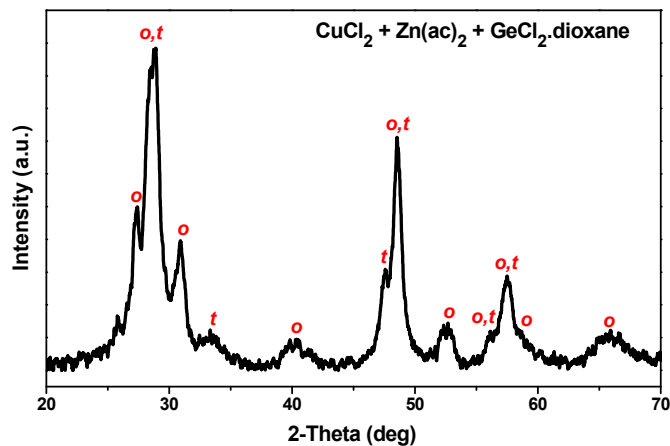


Figure S4. XRD pattern of the nanocrystals obtained when CuCl_2 was used as the Cu precursor instead of $\text{Cu}(\text{dte})_2$. The peaks marked with red *t* and red *o* are attributed to the presence of tetragonal (JCPDS #25-0327) and orthorhombic (JCPDS #26-0572) CZGS, respectively.

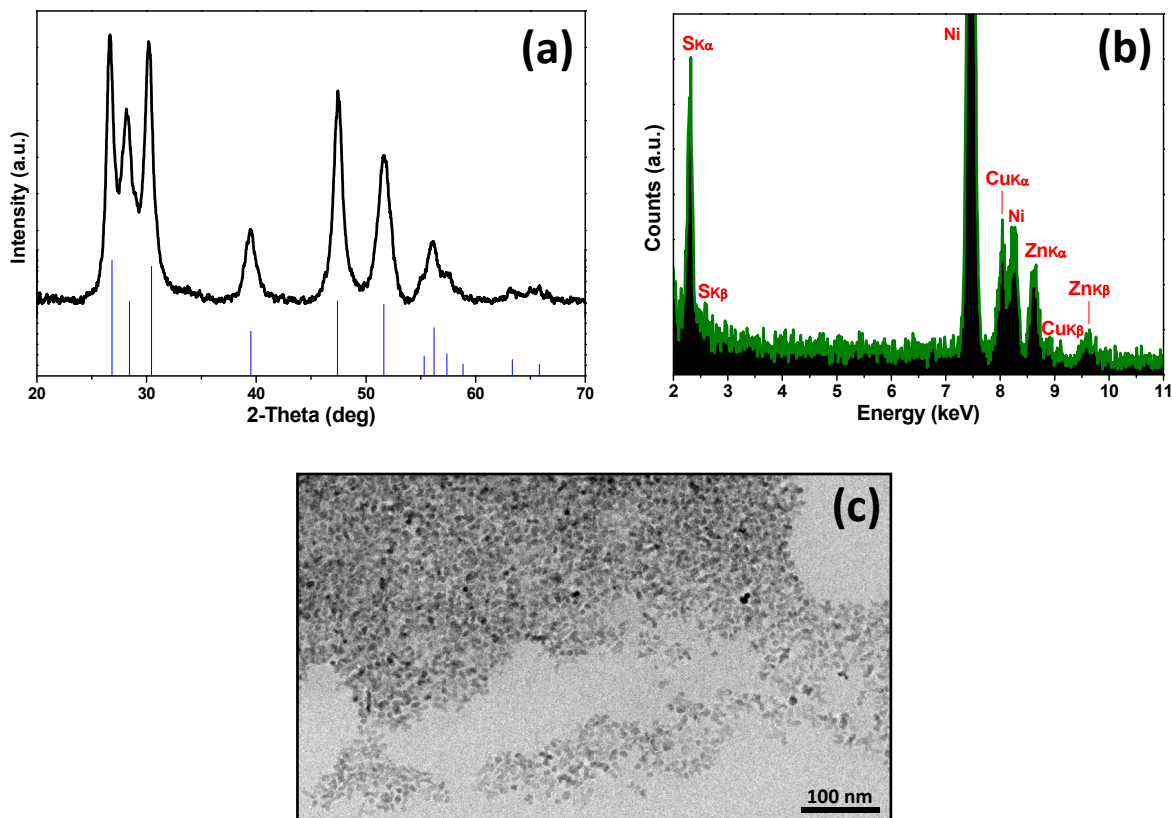


Figure S5. (a) XRD pattern, (b) EDX spectrum and (c) TEM image of the material obtained at 100 °C. The blue pattern in (a) is from the standard JCPDS file for wurtzite ZnS (JCPDS #75-1547). The Ni signals in (b) are attributed to the Ni TEM grid.

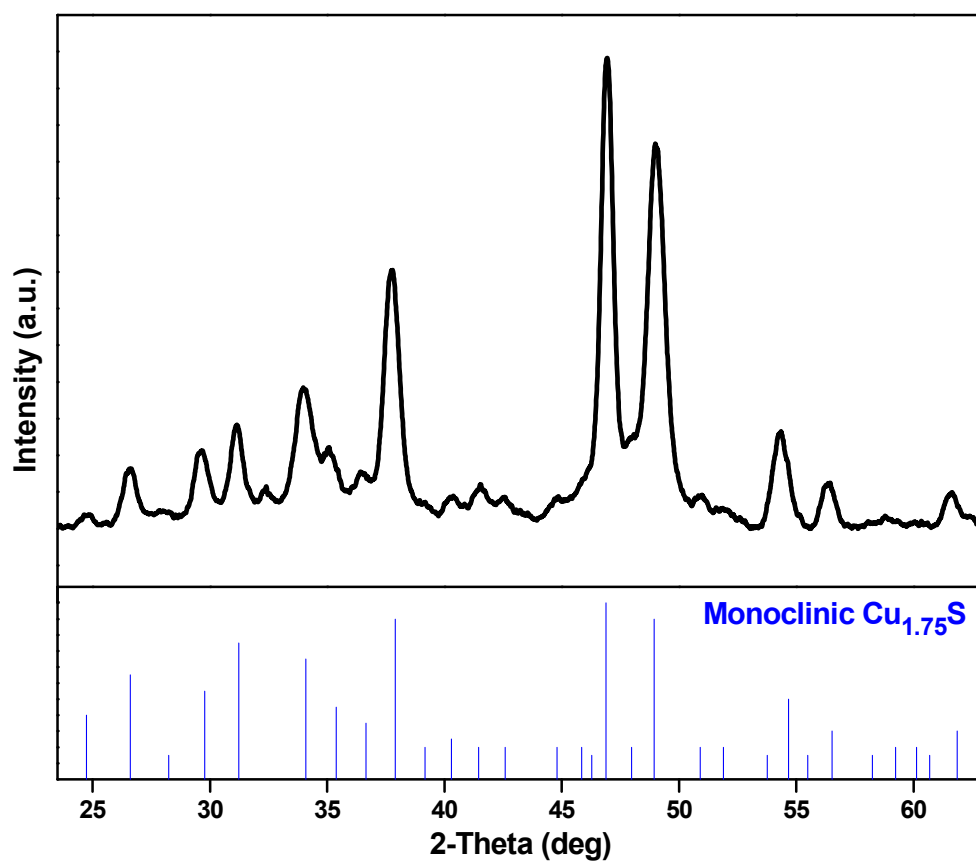


Figure S6. XRD pattern of the material obtained when $\text{Cu}(\text{dtc})_2$ is heated solely in OM:t-DDT (9:1, v:v) at 100 °C. The blue pattern at the bottom is from the standard JCPDS file for monoclinic $\text{Cu}_{1.75}\text{S}$ (JCPDS #23-0958).

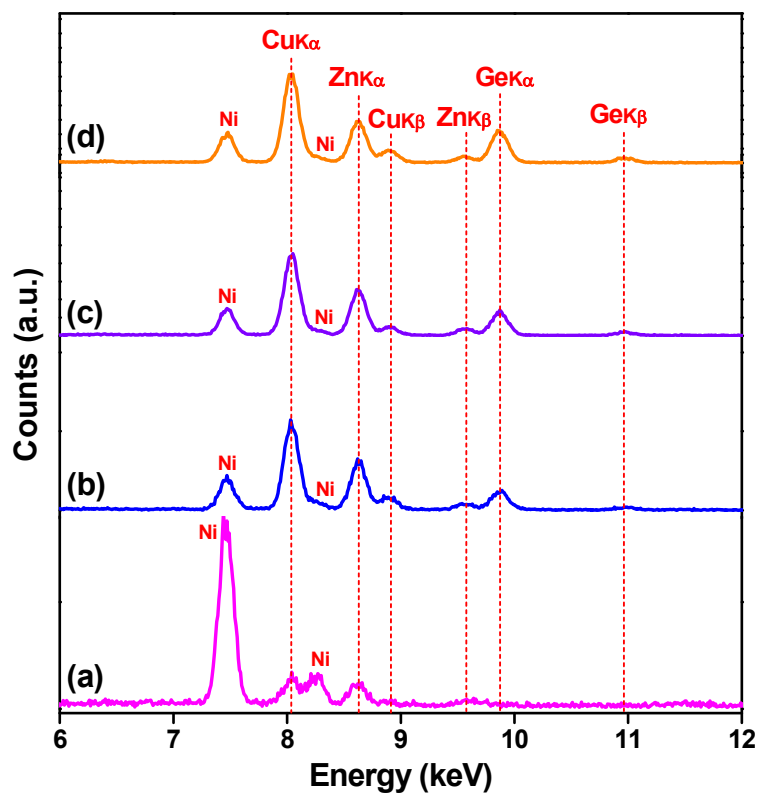


Figure S7. EDX spectra of the nanocrystals that form at different stages of the reaction: (a) 100 °C; (b) 200 °C; (c) 300 °C, 0 min; (d) 300 °C, 60 min. The Ni signals are attributed to the Ni TEM grid.

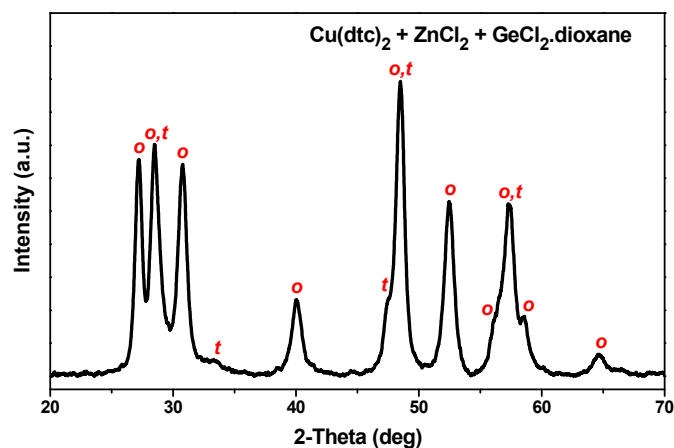


Figure S8. XRD pattern of the nanocrystals obtained when ZnCl_2 was used as the Zn precursor instead of $\text{Zn}(\text{ac})_2$. The peaks marked with red *t* and red *o* are attributed to the presence of tetragonal (JCPDS #25-0327) and orthorhombic (JCPDS #26-0572) CZGS, respectively.

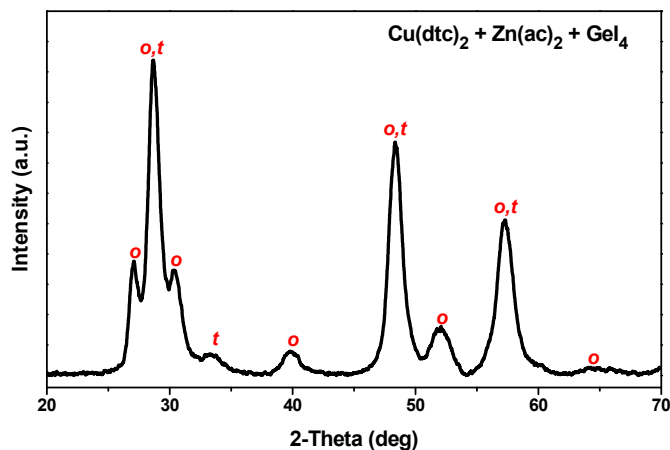


Figure S9. XRD pattern of the nanocrystals obtained when GeI_4 was used as the Ge precursor instead of $\text{GeCl}_2 \cdot \text{dioxane}$. The peaks marked with red *t* and red *o* are attributed to the presence of tetragonal (JCPDS #25-0327) and orthorhombic (JCPDS #26-0572) CZGS, respectively.

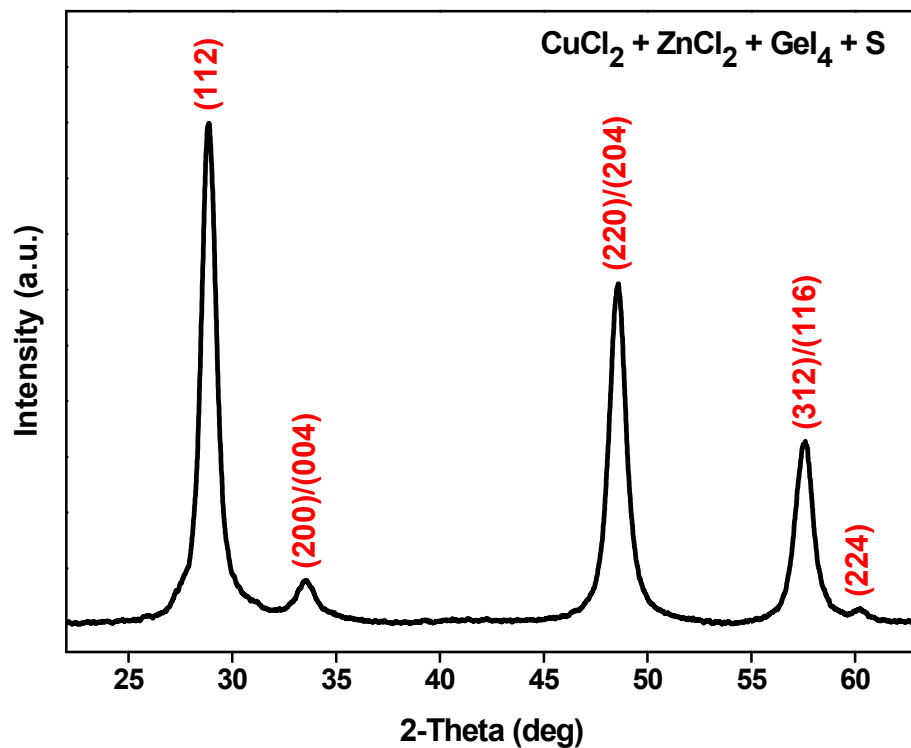


Figure S10. XRD pattern of the nanocrystals obtained when the precursors used are CuCl_2 , ZnCl_2 , GeI_4 and S . The solvent used is OM. All the diffraction peaks can be indexed according to the standard diffraction pattern of tetragonal CZGS (JCPDS #25-0327).

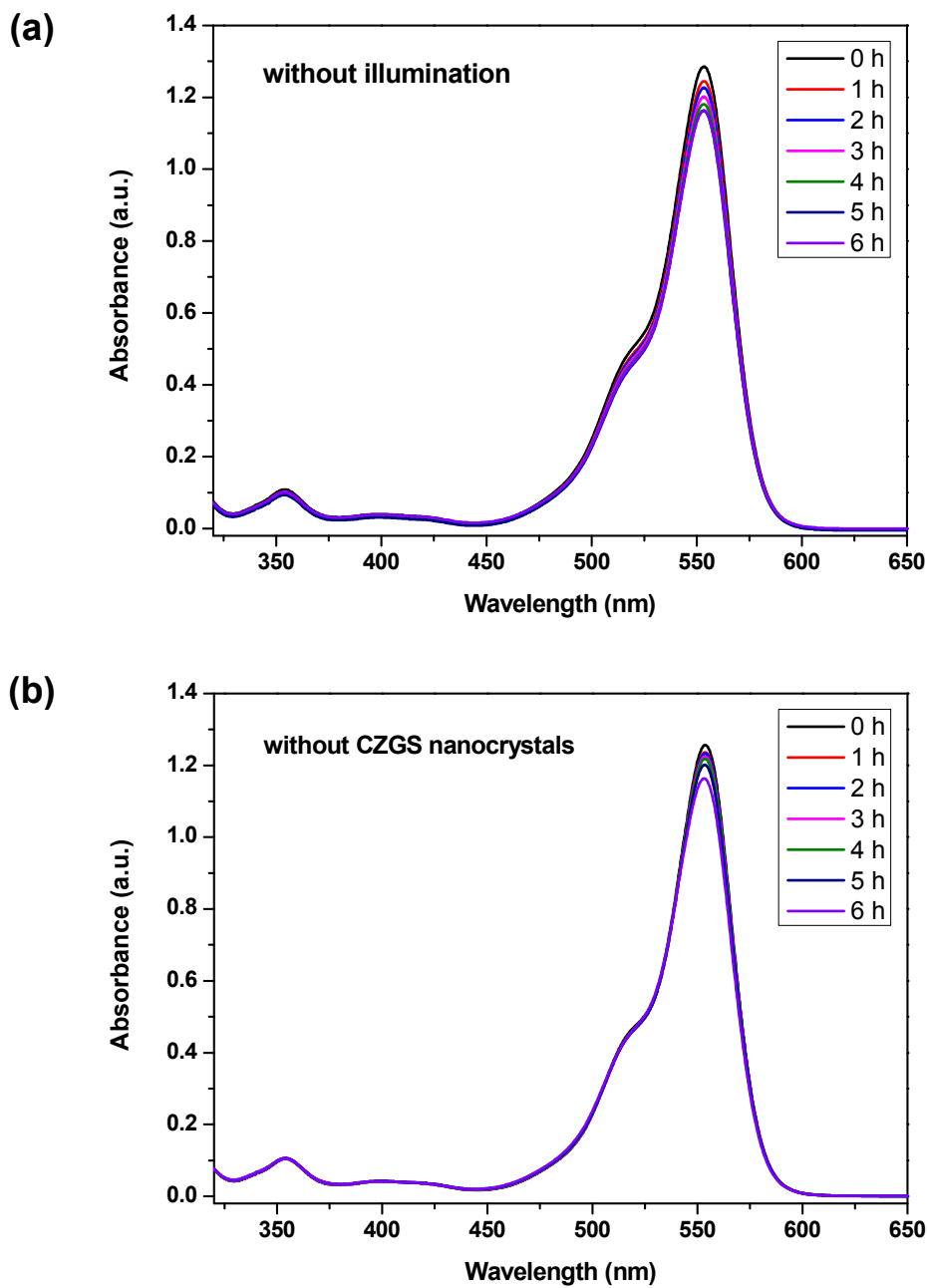


Figure S11. Temporal evolution of the absorption spectra of an aqueous RhB solution (a) in the presence of orthorhombic CZGS nanocrystals without illumination (performed in the dark) and (b) in the absence of orthorhombic CZGS nanocrystals with visible-light illumination.