

The interplay between magnetism and structure in Co/Fe-CdSe Diluted Magnetic Quantum Dots

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SI. 1 Preparation of dithiocarbazate acid (DTC complex)

The DTC complex is prepared by stirring 10 mL of hydrazine hydrate [(N₂H₄.xH₂O), Sigma-Aldrich] with 15 mL carbon disulphide [(CS₂), Sigma-Aldrich 99%] in a canonical flask using an ice bath. A 5 mL of 0.5 M sodium hydroxide [(NaOH), Sigma-Aldrich 97%] is added. To ensure the solubility of the CS₂ into the N₂H₄, a suitable amount of methanol is added. The stirring process lasts for about 2 h until the solution turns into a yellow color, declaring the formation of sodium dithiocarbazate (CH₃NaN₂S₂). At the last stage, we add a few drops of glacial acetic acid [(CH₃CO₂H), Sigma-Aldrich] until a white powder of dithiocarbazate acid (DTC complex) is precipitated. The powder is filtered and washed several times with deionized water, then dried at 80 °C.

SI. 2 The optical absorption of DMQDs during the early stages of growth

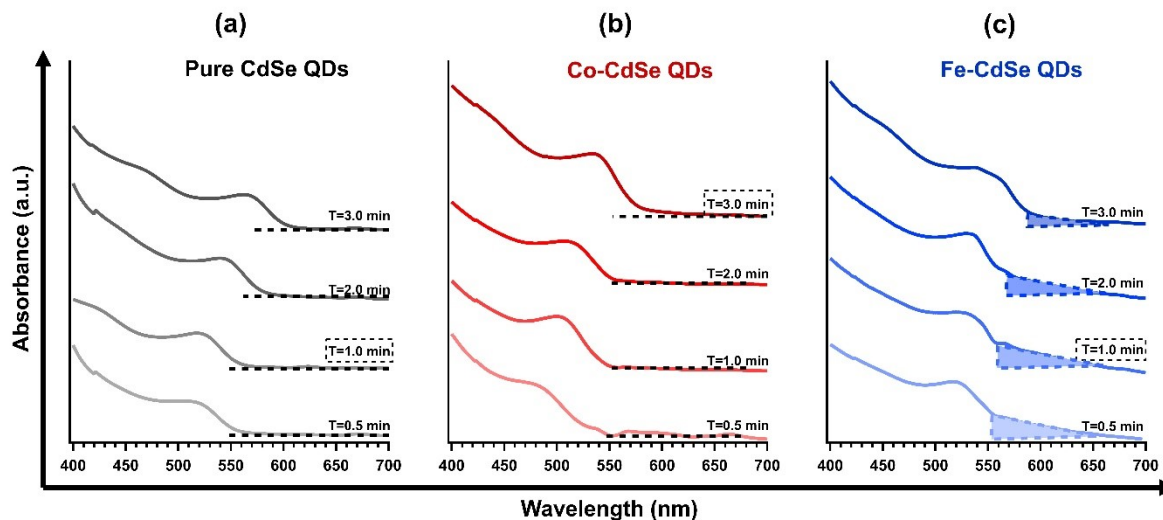


Figure SI-1: Optical absorption spectra for: (a) pure, (b) Co-doped, and (c) Fe-doped CdSe QDs at the early growth stages.

Focusing on the early stages of the growth process for pure and Co/Fe-doped CdSe QDs, we can see that by comparison; the Fe-doped CdSe QDs are showing some optical transition in the wavelength region of 650 – 570 nm, i.e. 1.90 – 2.18 eV, see the shaded triangles in Figure SI-1. These optical transitions are not observed in pure or the Co-doped CdSe QDs. Thus, they most probably belong to the FeSe optical transition [1]. The intensity of these transitions decreases with growth time since the main CdSe QDs band gaps are shifting towards longer wavelengths and/or the possibility that the FeSe structure is only evolving inside the core of the CdSe QDs. More explanations can be found in the original article text.

SI. 3 The proof of the DTC decomposition at the early stages of growth

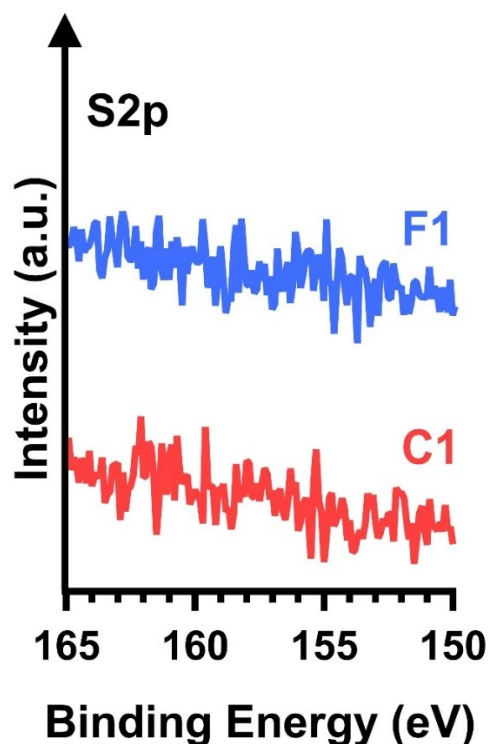


Figure SI-2: XPS spectra of S2p core levels for small-size Co/Fe-doped CdSe QD samples, i.e., C1 and F1, respectively.

To ensure the inclusion of only the transition metal ions during the doping process without the inclusion of the dithiocarbazate (DTC, $\text{CH}_3\text{N}_2\text{S}_2$) salt, we measured the S2p core level for both doped systems at the early stage of the growth process, see Figure SI-2. There is no emission from S2p core levels of the DSC salt in small-size Co/Fe-doped CdSe QD samples, i.e., C1 and F1, respectively. This further proves the successful doping process using the Co/Fe-DTC salts in the organometallic method.

[1] Hou, B.; Benito-Alifonso, D.; Webster, R.F.; Cherns, D.; Galan, M.C.; Fermín, D.J. Synthetic Mechanism Studies of Iron Selenides: An Emerging Class of Materials for Electrocatalysis. *Catalysts* 2021, 11, 681. <https://doi.org/10.3390/catal11060681>