Energy Transfer in $CuInS_2$ Colloidal Quantum Dot Films through Comparative Photoluminescence Lifetime Investigations

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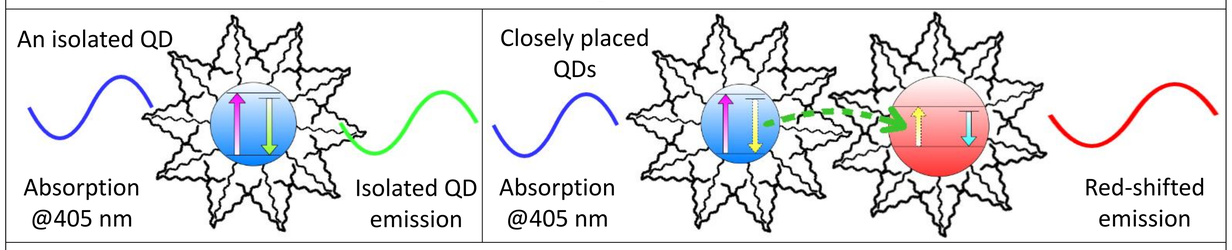
INTRODUCTION

Photoconversion efficiency of solar cells can be improved via energy transfer (ET) by the deposition of quantum dots (QD) as films. Higher energetic smaller QDs within an ensemble transfer the absorbed energy to lower energetic larger QDs more efficiently when deposited as a densely-packed film than in the solution form. The significance of low inter-QD separation in ET for $CuInS_2$ QDs through PL spectroscopy is demonstrated here.

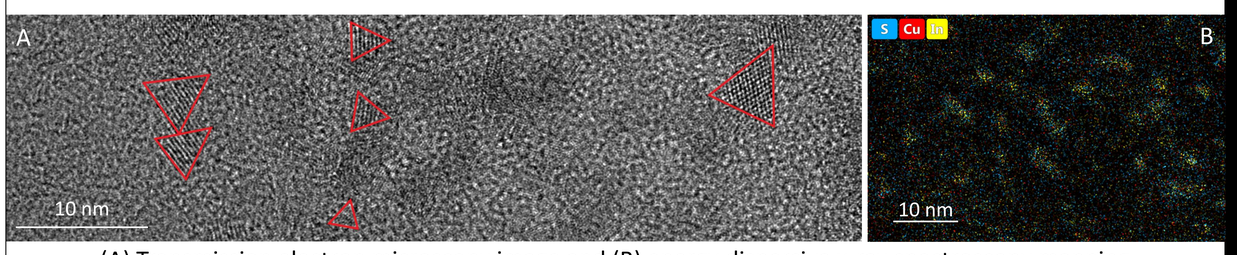


Significance of inter-QD separation in energy transfer

TEM and EDS

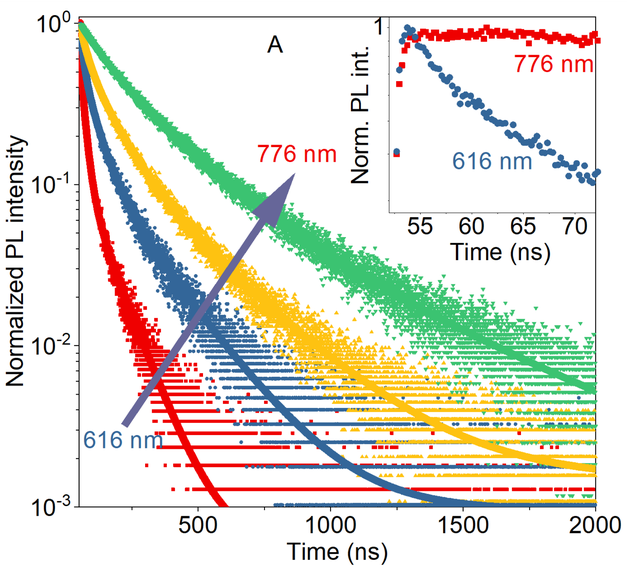
Samples: S_1 (smaller QDs: reaction time 1 min), S_2 (larger QDs : reaction time 15 min), S_3 (S_2 with micelle-encapsulation) solutions and films of all three

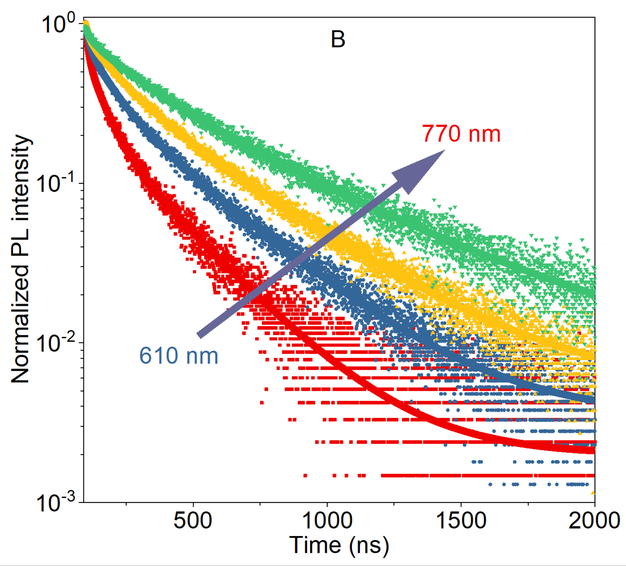
Results of TEM on S_2: **Pyramidal, chalcopyrite** $CuInS_2$ QDs[1]; **Inhomogeneous QD size distribution**: QD sizes 2 nm - 5 nm



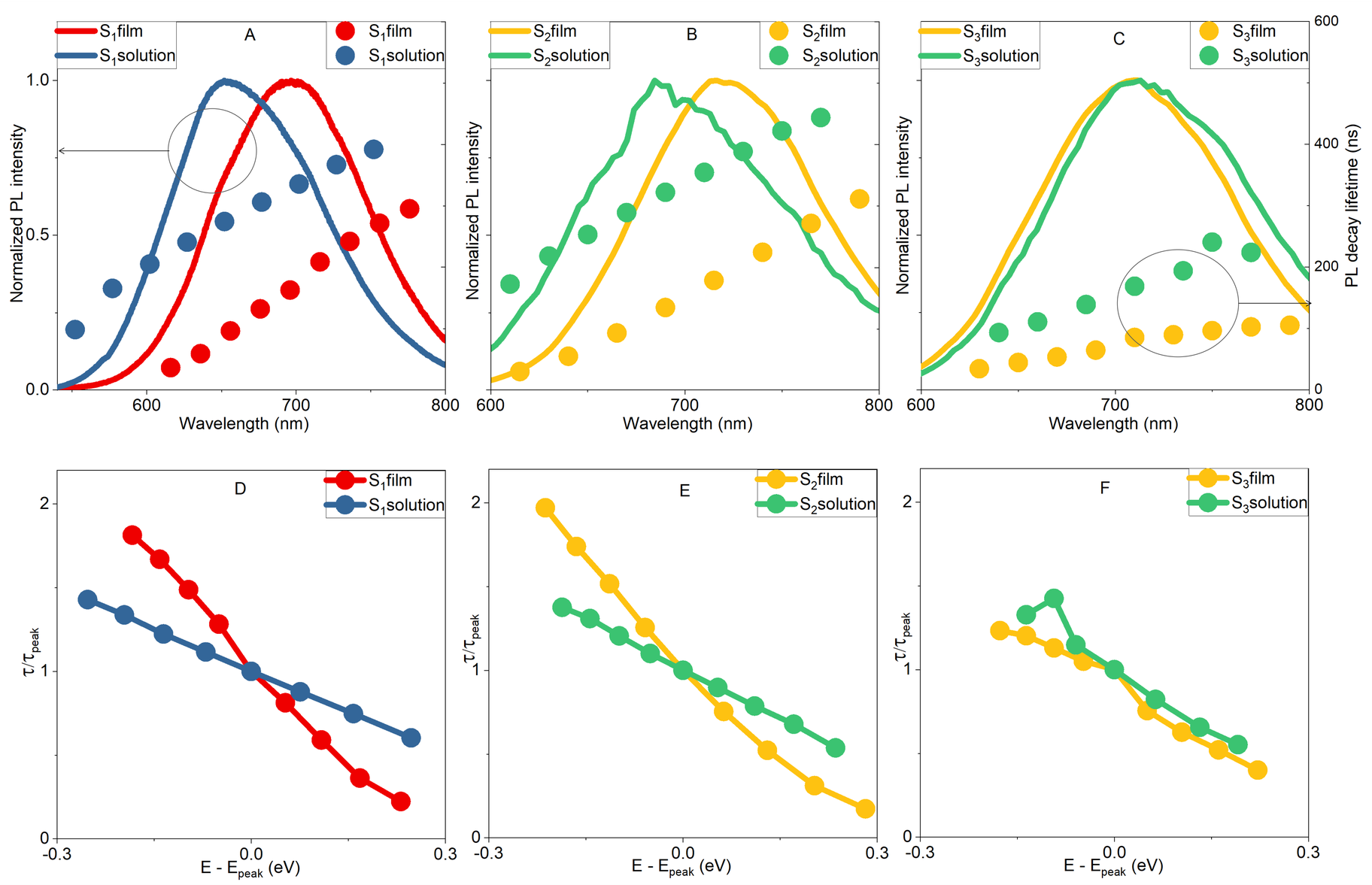
(A) Transmission electron microscopy image and (B) energy dispersive x-ray spectroscopy mapping

SPECTROSCOPIC RESULTS





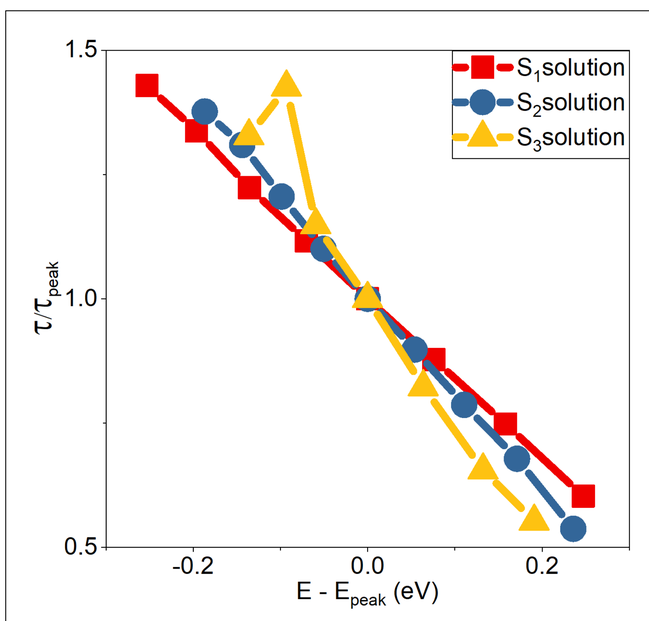
(A) Shorter and more spectrally dependent PL decays of S_1 film, (Inset) first 30 ns show rise time of the longest PL decay compared with the shortest decay; (B) longer and less spectrally dependent PL decays of S_2 solution



(Top) Steady-state PL spectra (continuous curves) and PL decay lifetimes (solid circles); (Bottom) spectral dependence: PL decay lifetimes normalized with the peak PL decay lifetime against energy shift from the peak PL energy. Data for each film is compared with the corresponding solution. (A) and (D) S_1, (B) and (E) S_2, and (C) and (F) S_3

PL AND TRPL CHARACTERISTICS OF S_1, S_2, AND S_3

- **Excitation:** 405 nm 50 ps pulse laser (picoquant) for all samples
- **PL:** broad – FWHM: about 305 meV
- **Redshift in PL**: PL of S_1 and S_2 films 120 meV and 75 meV redshifted from PL of S_1 and S_2 solutions, respectively; no redshift of film PL from solution PL in S_3
- **PL lifetimes (τ)**: S_1 and S_2 solutions - approximately 300 ns, films - 170 ns; S_3 solution - 160 ns, film - 90 ns.
- **Spectral dependence**: τ/τ_{peak} for all solutions changes by 3X over their spectral range; S_1 and S_2 films - 10X change; S_3 film - 3X change; all solutions have an identical spectral dependence
- **Rise time:** S_1 film - small rise time of 0.5 ns at the red end of the PL spectrum



Spectral dependence of all solutions

PL DECAY RATES IN SOLUTIONS AND FILMS[5]

$$k_{sol} = k_{rad}(E) + k_{non\text{-}rad}$$
$$k_{film} = k_{rad}(E) + k_{non\text{-}rad} + k_{ET} + k'_{non\text{-}rad}$$

Intrinsic decay rates (radiative and non-radiative)

Additional terms - ET and non-radiative recombination in films

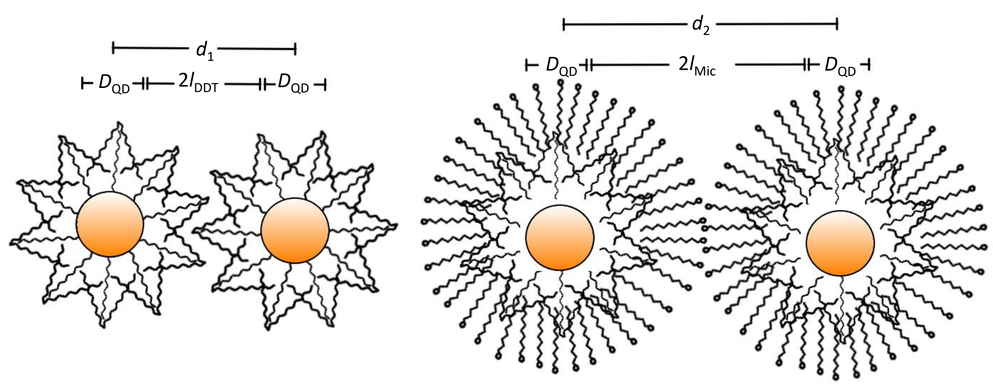
INTER-QD SEPARATION

Absorbance peak - QD diameter calibration curve[2]: QD diameter (D_{QD}) = **2.5 nm**

2X DDT length ($2l_{DDT}$) = **3.5 nm**[3]; 2X DDT + micelles length ($2l_{Mic}$) = **6.2 nm**[4]

$d_1 = D_{QD} + 2l_{DDT}$ — S_1 and S_2 films : d_1 = **6 nm**

$d_2 = D_{QD} + 2l_{Mic}$ — S_3 film: d_2 = **8.7 nm**



Inter-QD distance for DDT-capped and micelle-capped samples adapted from [3].

MIXED QD ENSEMBLE

PL and trPL of S_1 mixed with large QDs as solution and film

CONCLUSIONS

- Heterogeneous $CuInS_2$ QD-size distribution drop-cast: **densely packed QD films formed**
- PL and trPL characteristics of S_1 and S_2 films strikingly distinct from those of the corresponding solutions: **film deposition affects emission**
- PL redshift, PL decay lifetime shortening, and stronger spectral dependence of PL decay lifetime for S_1 and S_2 films from their solutions: **spectroscopic signatures of ET** as in the CdTe QD system[6]
- **PL rise time** observed in the lowest energy decay of film S_1: **higher energy QDs transfer their energy to lower energy QDs**
- No evidences of ET observed in film S_3: **micelle encapsulation increases the inter-QD separation and makes ET inefficient**
- **The significance of low inter-QD separation in ET demonstrated for $CuInS_2$ QDs through PL spectroscopy**

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