Electronic Supplementary Material (ESI) for Dalton Transactions.

Covalently Linking $CuInS_2$ Quantum Dots with Re Catalyst by Click Reaction for Photocatalytic CO_2 Reduction

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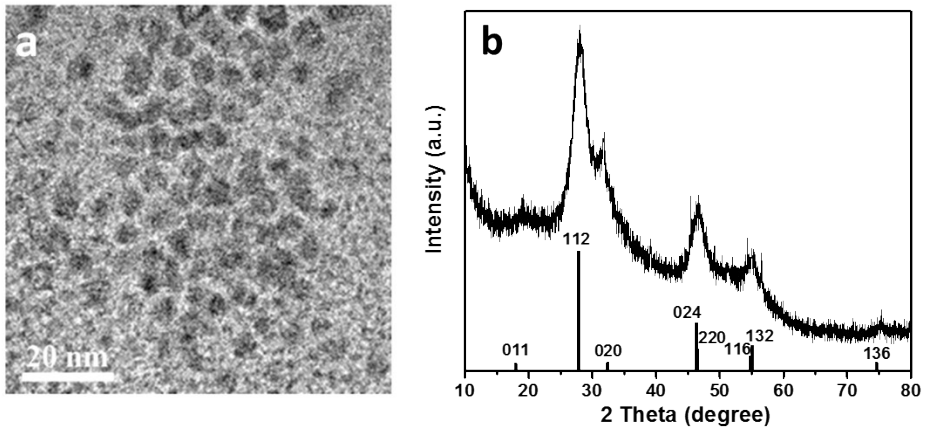

Figure S1. TEM image (a) show that the size of the as-synthesized $CuInS_2$ QDs was around 7 nm and XRD pattern (b) of the as-synthesized $CuInS_2$ QDs can be indexed to tetragonal chalcopyrite structure of $CuInS_2$ (PDF#47-1372).

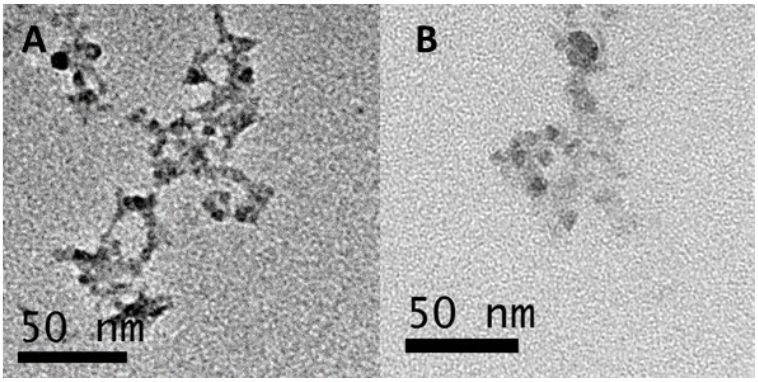

Figure S2. TEM images of MPA capped $CuInS_2$ QDs (A) and $CuInS_2$ QDs-Re hybrid systems (B).

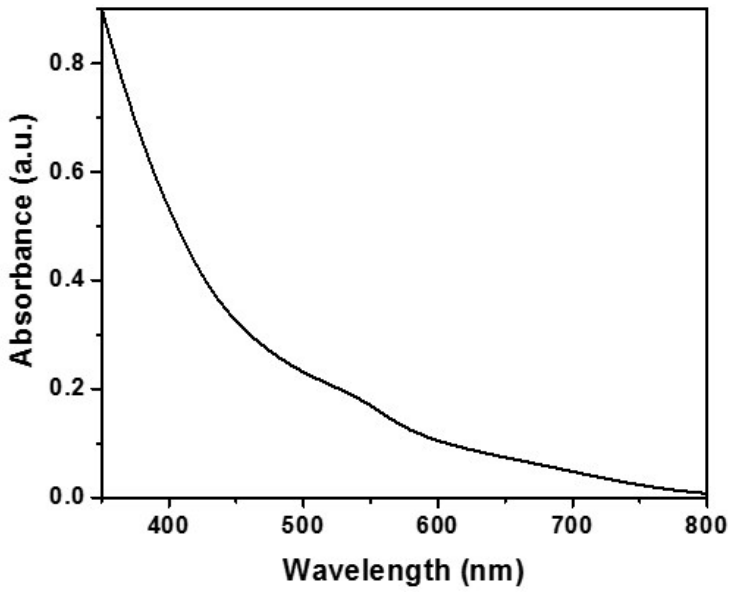

Figure S3. Absorption spectrum of $CuInS_2$ QDs.

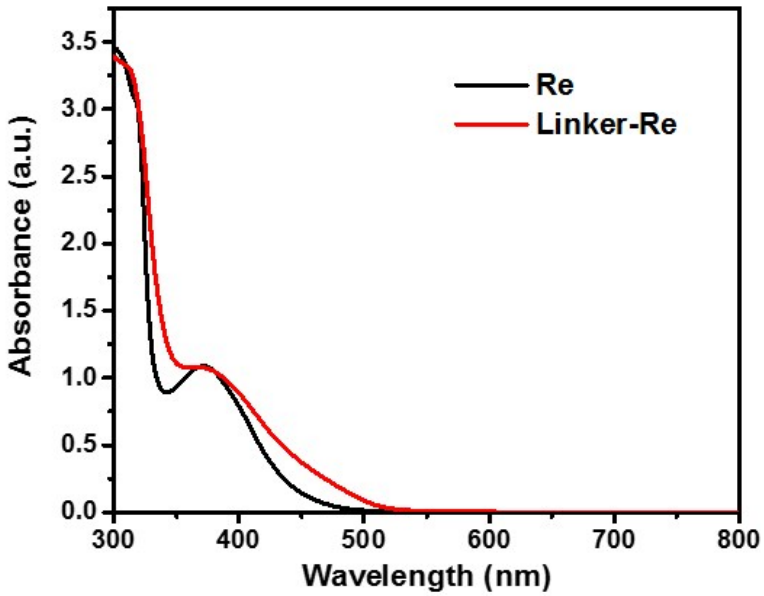

Figure S4. UV-Vis absorption spectra of the Re catalyst and the Re catalyst bound with linker.

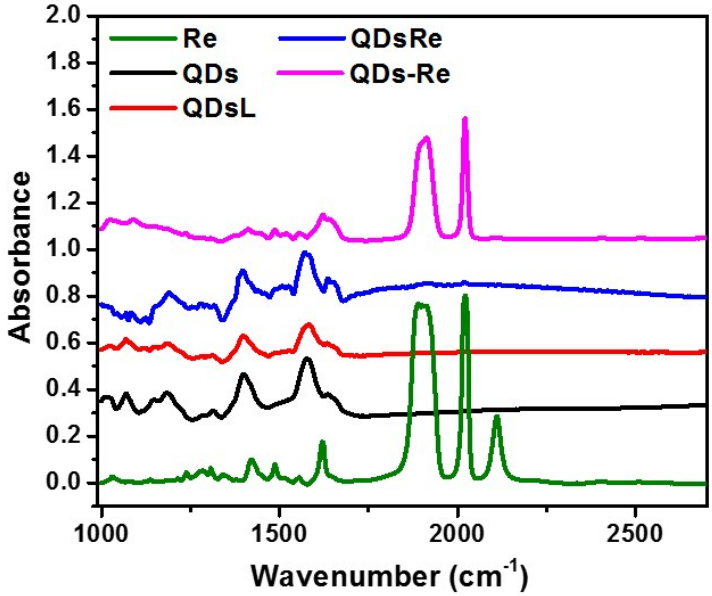

Figure S5. FTIR spectra of $CuInS_2$ QDs, Re catalyst, $CuInS_2$ QDs binding with linker (QDsL), $CuInS_2$ QDs and Re catalyst without linker (QDsRe) and $CuInS_2$ QDs-Re hybrid systems.

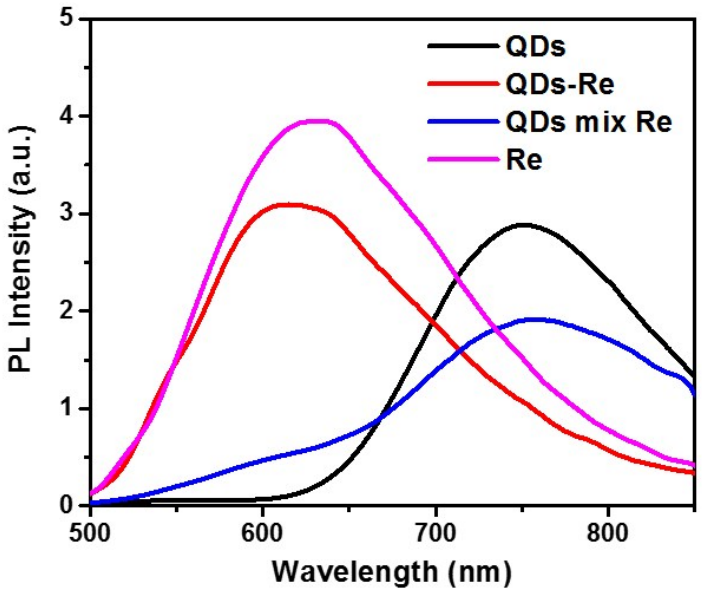

Figure S6. Fluorescence spectra of $CuInS_2$ QDs, Re catalyst, $CuInS_2$ QDs-Re hybrid system and mixed solution of $CuInS_2$ QDs and Re catalyst in DMSO upon excitation at 470 nm. The concentration of QDs in all samples (excluding for the sample of Re catalyst) was 0.5 mM, and the concentration of Re catalyst in all samples (excluding for the sample of QDs) was 0.2 mM.

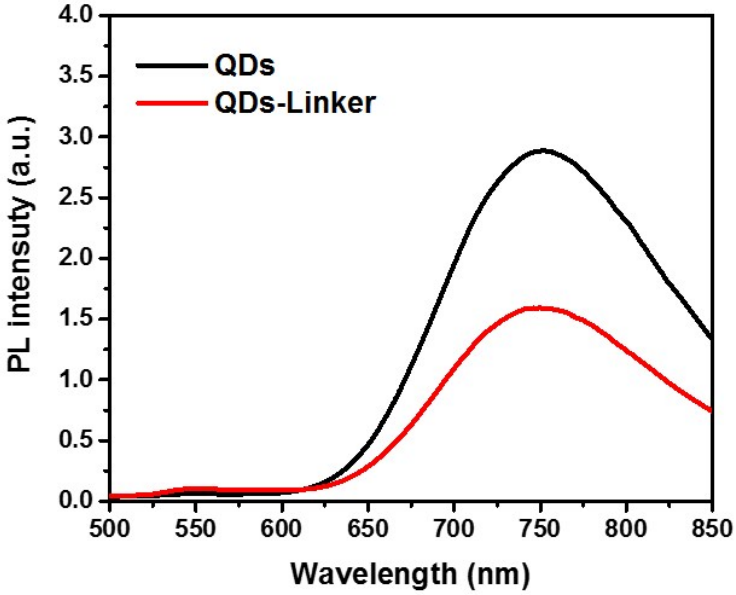

Figure S7. Fluorescence spectra of bare $CuInS_2$ QDs and $CuInS_2$ QDs with linker upon excitation at 470 nm.

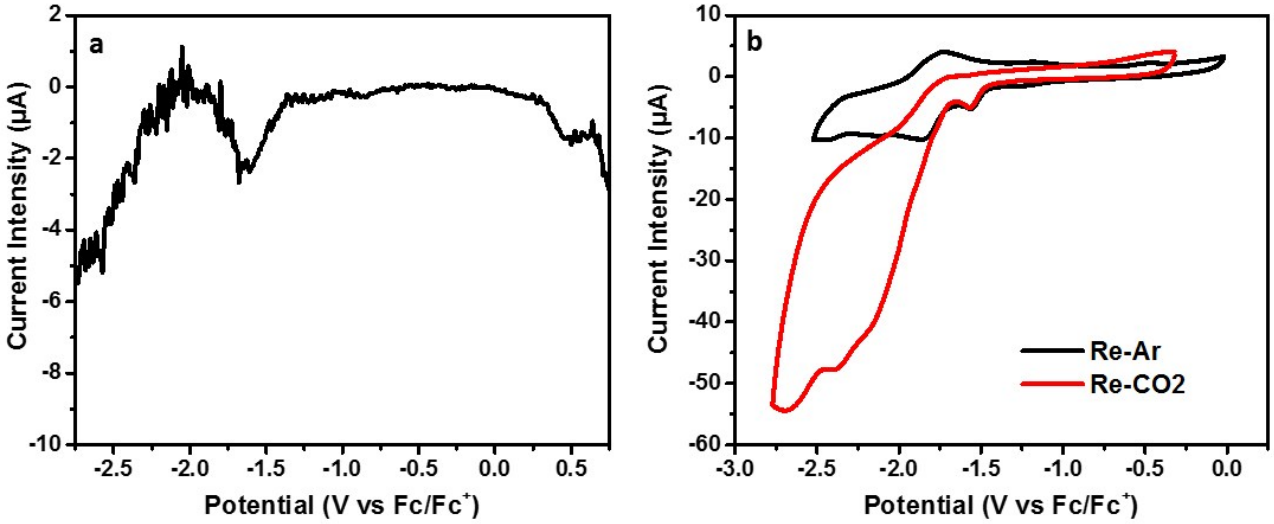

Figure S8. DPV spectrum of 1 mM $CuInS_2$ QDs with 50 mM tetrabutylammonium hexafluorophosphate in THF and CV spectra of 1 mM Re catalyst with 50 mM tetrabutylammonium hexafluorophosphate in DMSO under Ar and CO_2.

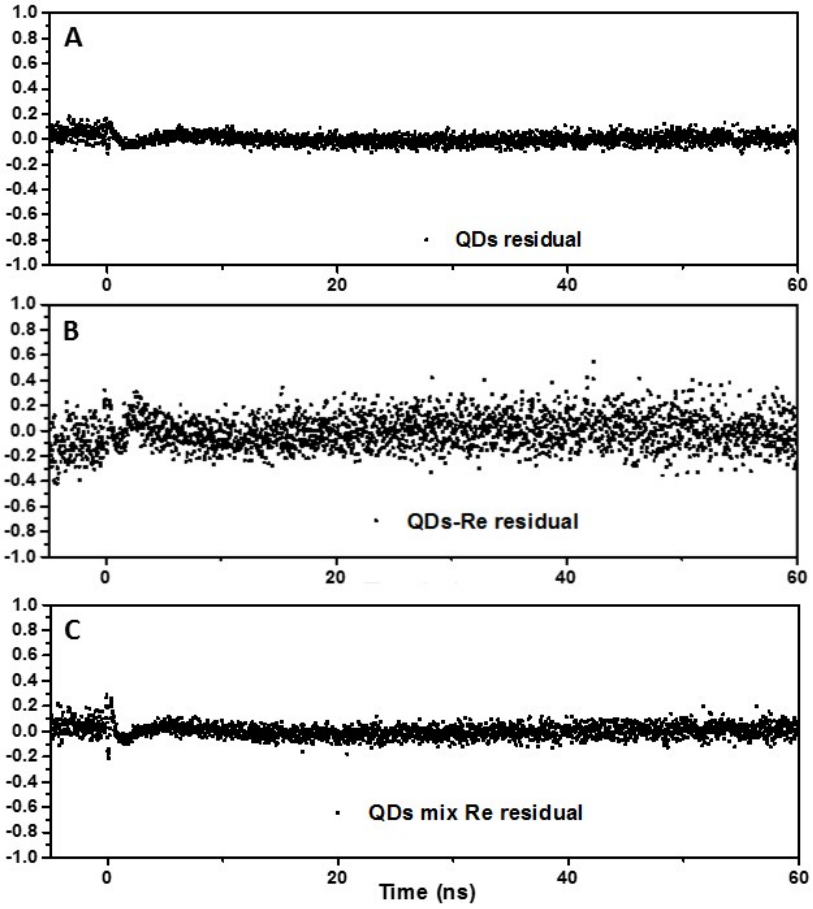

Figure S9. Residual plots of fitting from TCSPC measurements, in which (A) is for the pure QDs, (B) is for the QDs-Re hybrid system and (C) is for the mixed sample of QDs and Re catalyst.

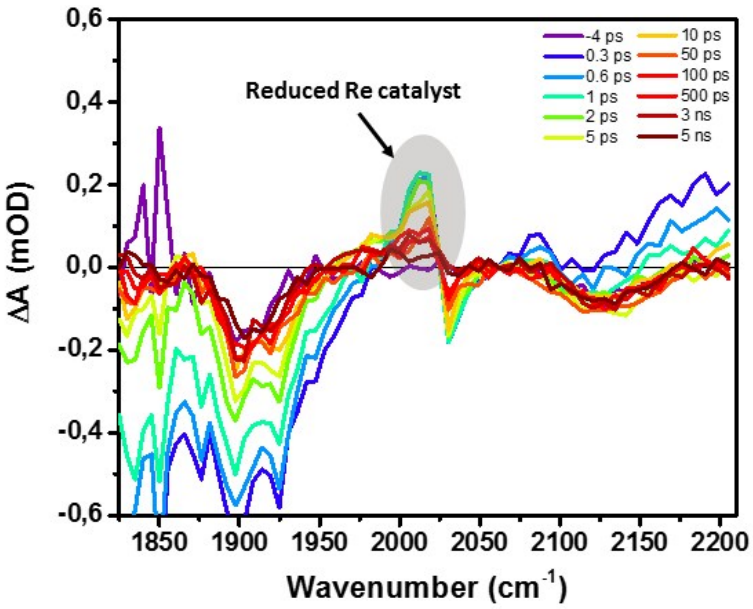

Figure S10. fs-TRIR spectra for the $CuInS_2$ QDs-Re hybrid system in DMSO after 520 nm excitation.

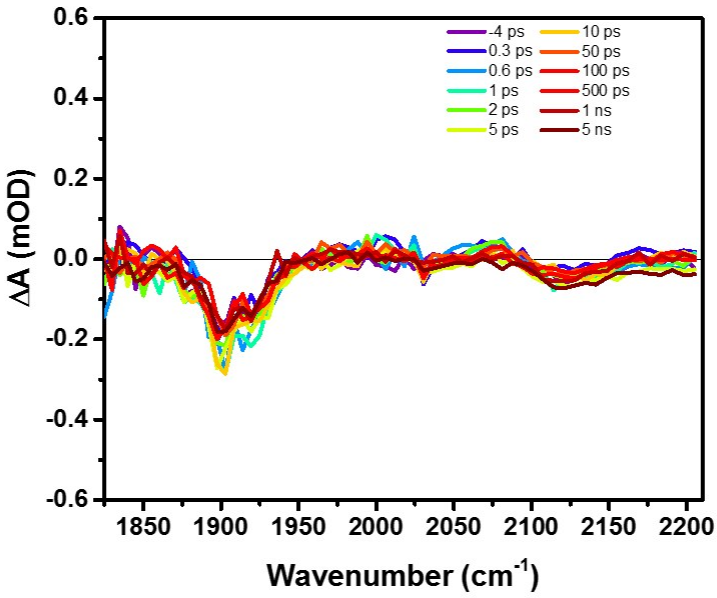

Figure S11. fs-TRIR spectra for Re catalyst in DMSO after 520 nm excitation, showing that there is no signal from the reduced catalyst from direct excitation. Note that the catalyst absorbance is negligible at 520 nm (cf. Figure S4), which explains the small signals seen.

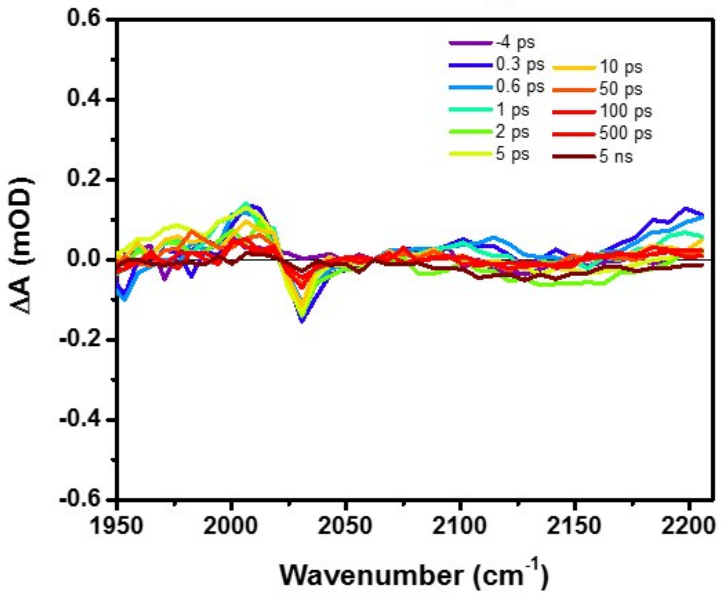

Figure S12. fs-TRIR spectra for mixed sample of $CuInS_2$ QDs and Re catalyst after 520 nm excitation.

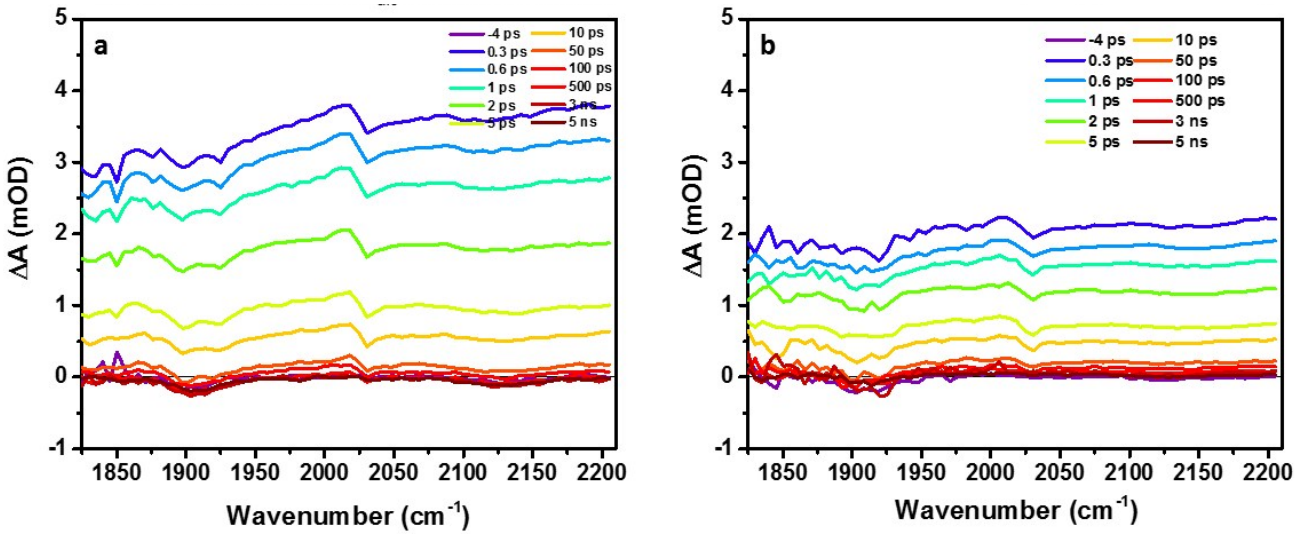

Figure S13. Raw data of fs-TRIR measurements of $CuInS_2$ QDs-Re hybrid systems (a) and mixed sample of $CuInS_2$ QDs and Re catalyst (b) after 520 nm excitation.

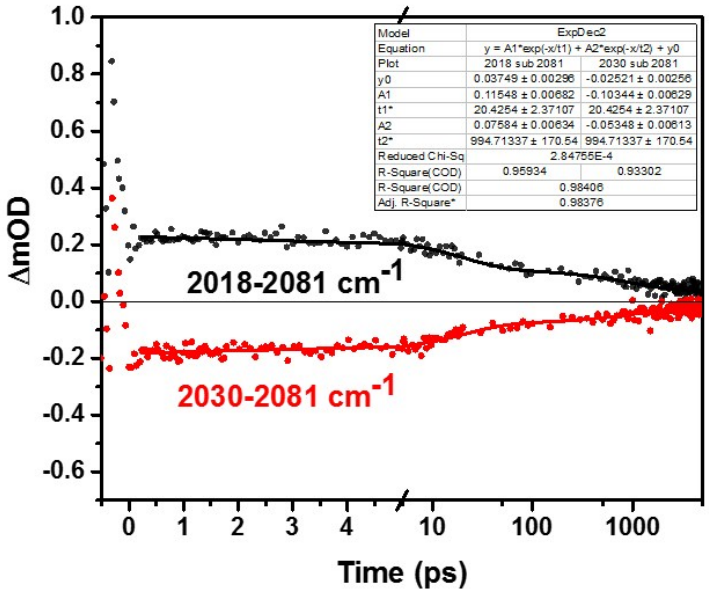

Figure S14. TRIR single point kinetic traces for the decay of the reduced catalyst (black dots, 2018 cm^{-1}) and the depletion and reformation of the ground state bands (red dots, 2030 cm^{-1}) of QDs-Re hybrid system. 2081 cm^{-1} represented the electrons in the conduction band of QDs.

Table S1. Calculated lifetime of reduced catalyst from TRIR measurement of QDs-Re hybrid system by fitting globally to a biexponential model.

Component	Lifetime	Weight		Average Weight
		2018 – 2081 cm^{-1}	2030 – 2081 cm^{-1}	
τ_1	(2.0 ± 0.24) ×10 ps	(1.2 ± 0.07) $\times 10^{-1}$ (50%)	(-1.0 ± 0.06) $\times 10^{-1}$ (57%)	54%
τ_2	(9.9 ± 1.7) × 10^2 ps	(7.6 ± 0.63) $\times 10^{-2}$ (33%)	(-5.3 ± 0.61) $\times 10^{-2}$ (29%)	31%
τ_3	>5 ns	(3.7 ± 0.30) $\times 10^{-2}$ (16%)	(-2.5 ± 0.26) $\times 10^{-2}$ (14%)	15%

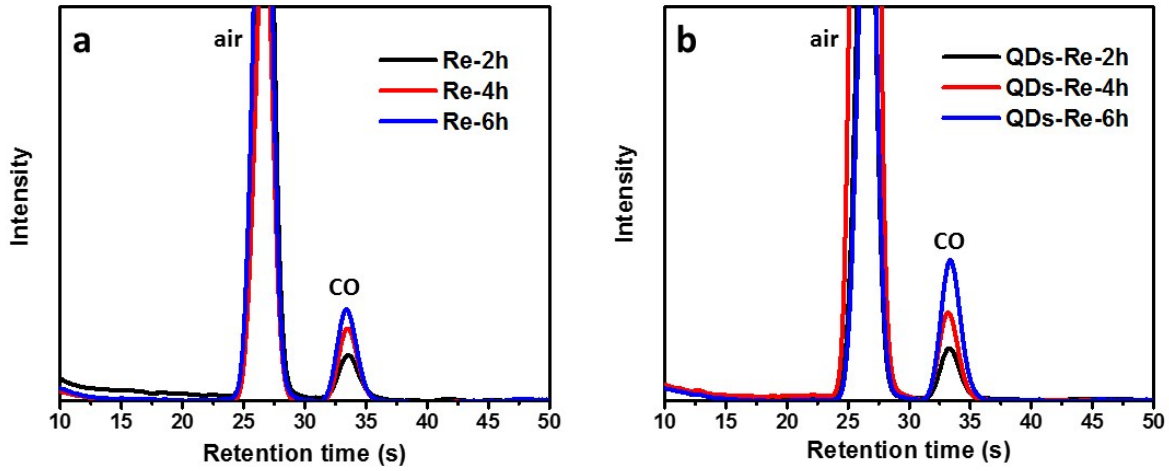

Figure S15. GC traces of produced CO by Re catalyst (a) and $CuInS_2$ QDs-Re hybrid systems (b).