Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Efficient and Selective Photocatalytic CO_2 Reduction over Ga Single Atoms Decorated Quantum Dots under Visible Light

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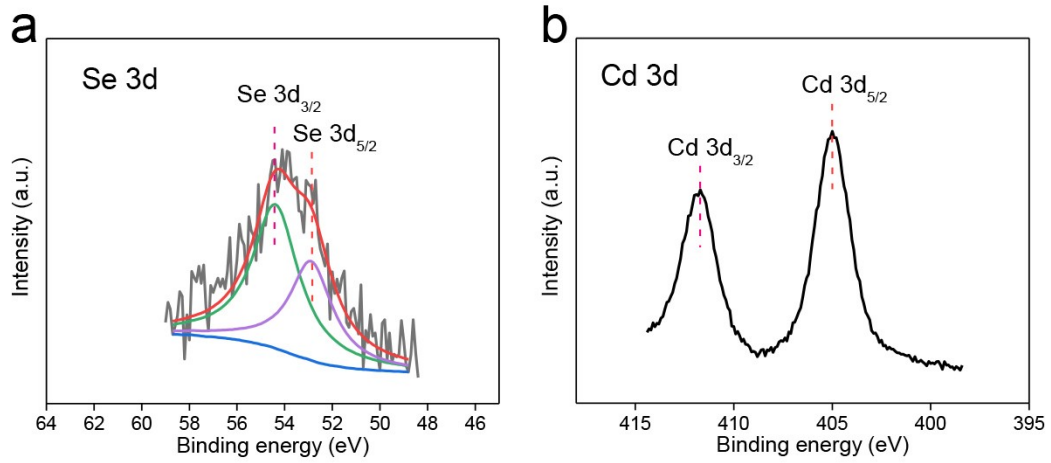

Figure S1. High resolution XPS of CdSe QDs.

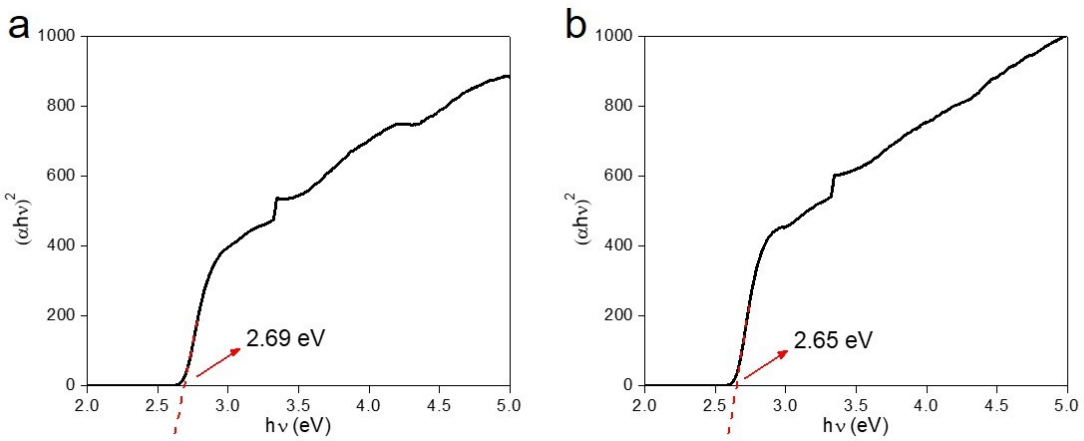

Figure S2. Calculated bandgaps of (a) CdSe QDs and (b) Ga-CdSe QDs.

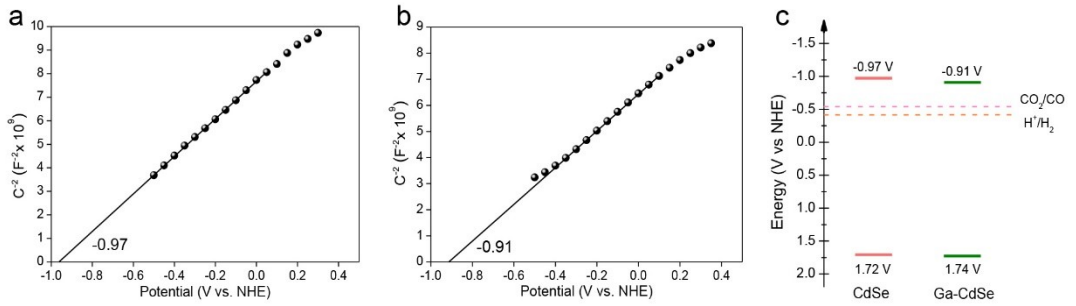

Figure S3. Mott-Schottky plots of (a) CdSe QDs and (b) Ga-CdSe; (c) Band positions of two QDs samples.

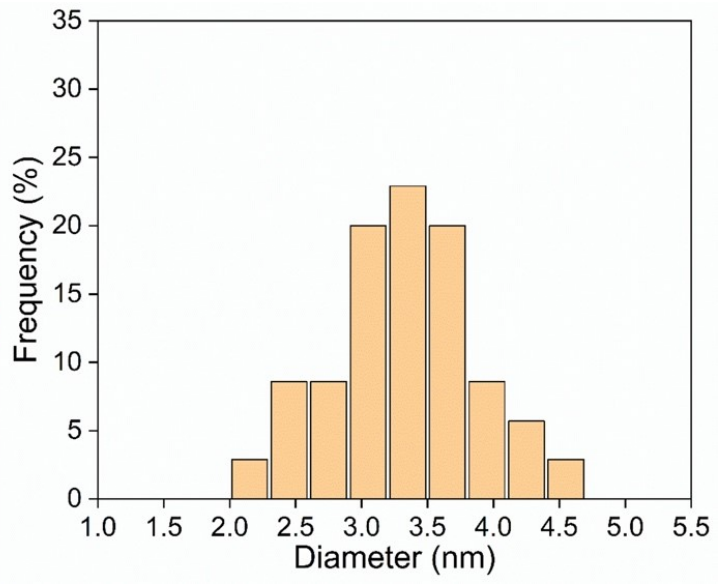

Figure S4. Size distribution of CdSe QDs.

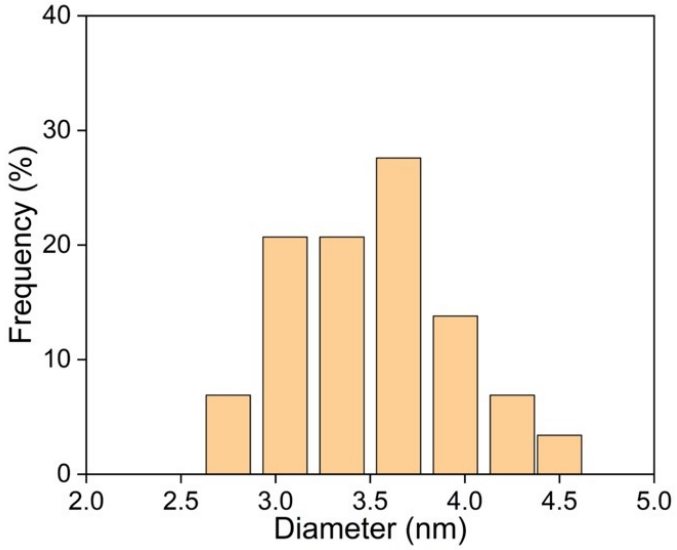

Figure S5. Size distribution of Ga-CdSe QDs.

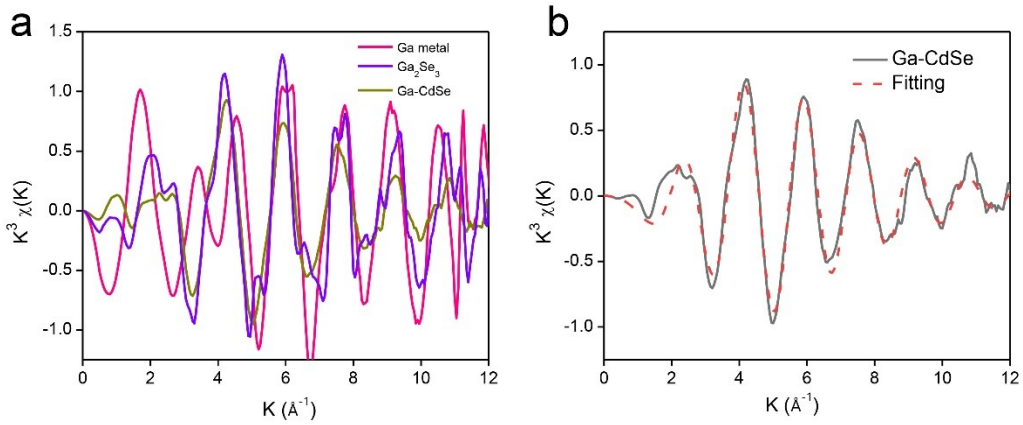

Figure S6. (a) EXAFS k space experimental results of Ga metal, Ga_2Se_3 and Ga-CdSe QDs; (b) fitting curve of Ga-CdSe QDs.

Table S1. Structural parameters calculated by the fit of the inverse Fourier transformed EXAFS oscillations. *N,* σ^2, ΔE referred to the coordination number, Debye-Waller factor, and potential shift, respectively.

Sample	Shell	*N*	σ^2 ($\times 10^{-3}$) ($Å^2$)	ΔE (eV)	R-factor
Ga-CdSe	Ga-Se	3.3	4.6	-2.8	0.0038

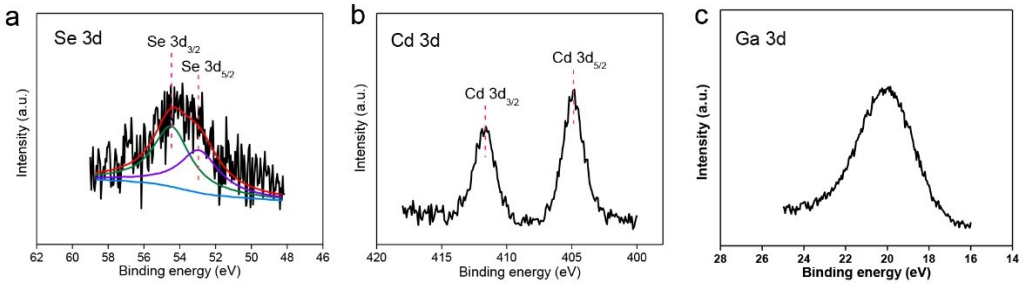

Figure S7. High resolution XPS of Ga-CdSe QDs.

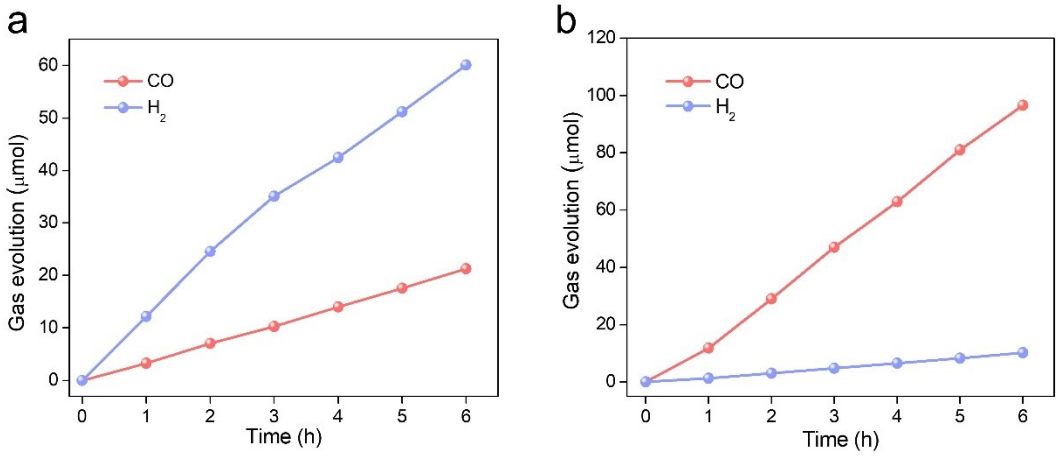

Figure S8. Time dependent yields of CO and H_2 products over (a) CdSe QDs and (b) Ga-CdSe QDs in photocatalytic CO_2 reduction.

Table S2. The comparison of photocatalytic CO_2 reduction performance over different reported QDs photocatalysts.

Photocatalysts	light source	photocatalytic activity	references
Ga-CdSe QDs	300 W Xe lamp, $\lambda > 400$ nm	CO evolution rate: 16.1 μmol h^{-1} H_2 evolution rate: 1.7 μmol h^{-1}	This work
ZnSe QDs/ NiCycP	AM 1.5G	CO evolution rate: ca. 0.25 μmol h^{-1} H_2 evolution rate: ca. 0.55 μmol h^{-1}	Chem. Sci. 2018, 9, 2501–2509
CdS QDs/ $[Ni(terpyS)_2]^{2+}$	AM 1.5G	CO evolution rate: 0.415 μmol h^{-1} H_2 evolution rate: 0.312 μmol h^{-1}	J. Am. Chem. Soc. 2017, 139, 7217−7223
g-C_3N_4–$CsPbBr_3$ QDs	300 W Xe lamp, $\lambda > 420$ nm	CO evolution rate: 1.19 μmol h^{-1}	Angew. Chem. Int. Ed. 2018, 57, 13570 –13574
CdSe QDs	Blue LED-photoreactor (λ_{max} = 450 nm)	CO evolution rate: 1.81 μmol h^{-1} H_2 evolution rate: 0.10 μmol h^{-1}	ChemSusChem. 2019, 12,4617 – 4622
CdS QDs/ Co_2L	300 W Xe lamp, $\lambda > 420$ nm	CO evolution rate: 0.288 μmol h^{-1} H_2 evolution rate: 0.007 μmol h^{-1} CH_4 evolution rate: 0.008 μmol h^{-1}	ACS Catal. 2018, 8, 12, 11815–11821
$CsPbBr_3$ QDs/ GO	100 W Xe lamp with an AM 1.5G filter	CO evolution rate: 0.02 μmol h^{-1} H_2 evolution rate: trace CH_4 evolution rate: 0.01 μmol h^{-1}	J. Am. Chem. Soc. 2017, 139, 5660−5663

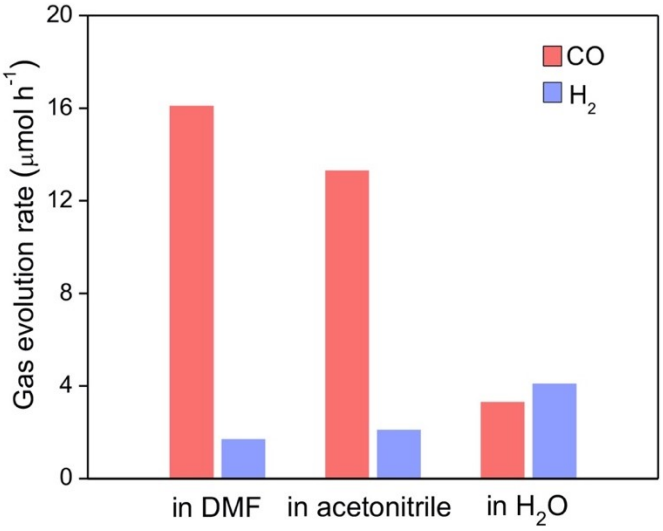

Figure S9. Photocatalytic CO_2 reduction performances of Ga-CdSe QDs in different solvents.

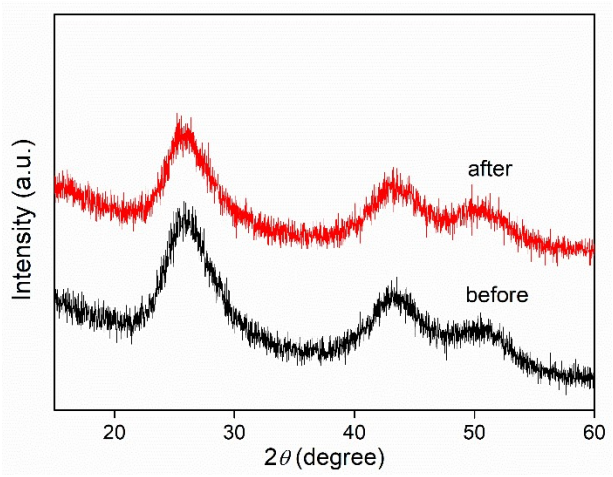

Figure S10. XRD pattern of Ga-CdSe QDs before and after photocatalytic reaction.

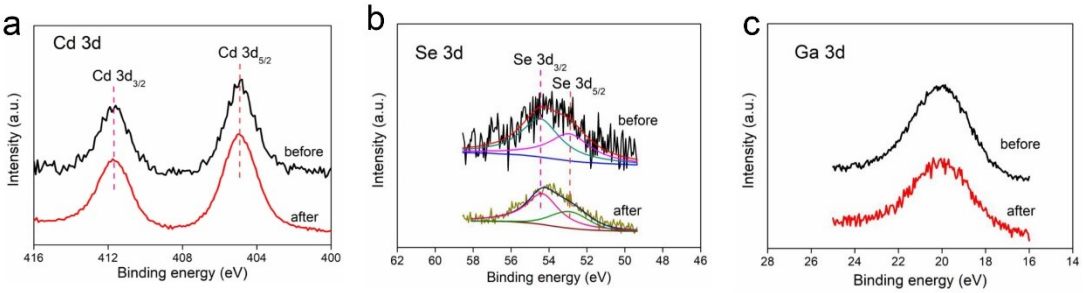

Figure S11. XPS spectra of Ga-CdSe QDs before and after photocatalytic reaction.

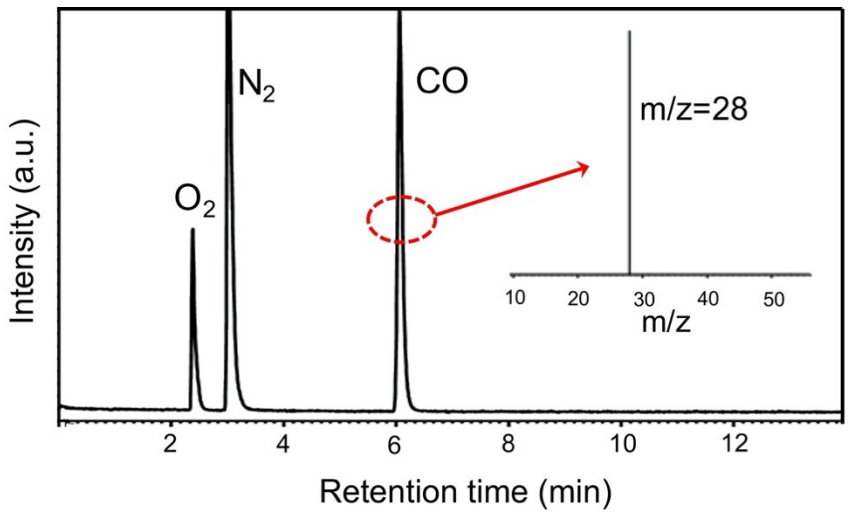

Figure S12. GC-MS of ^{12}CO generated in the photocatalytic reduction of $^{12}CO_2$ over Ga-CdSe QDs.

Table S3. Fitting data of the decay curves.

Samples	a_1	t_1	a_2	t_2	$T_{average}$ (ns)
CdSe QDs	17074	0.7	868	8.1	3.4
Ga-CdSe QDs	489518	0.3	2060	3.2	0.4

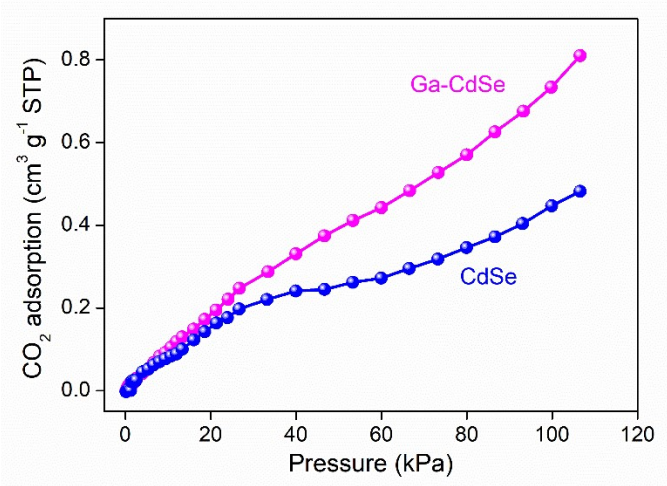

Figure S13. CO_2 adsorption ability of CdSe QDs and Ga-CdSe QDs.

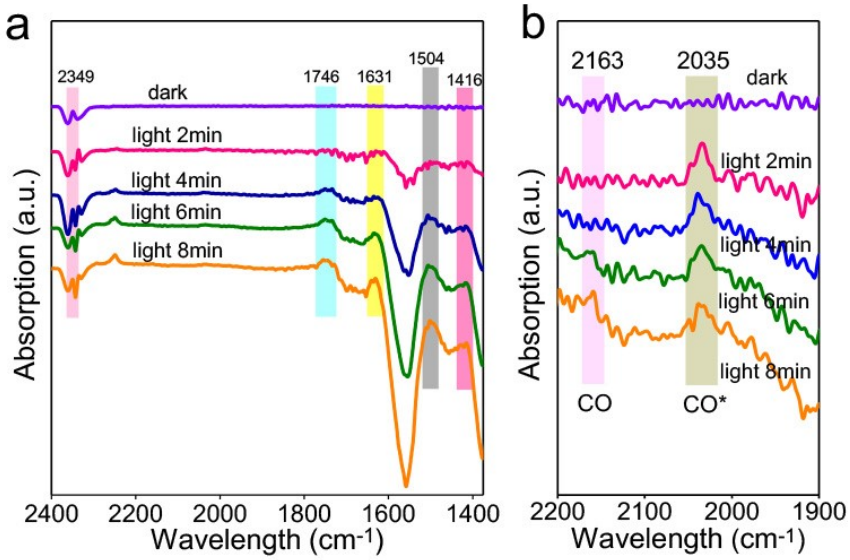

Figure S14. In-situ FTIR spectra of CdSe QDs in photocatalytic CO_2 reduction.

Table S4. The adsorption energy of CO_2 on the surface of CdSe and Ga-CdSe systems.

Configuration	Site	E_{ads}
CdSe	Cd	-0.29 eV
Ga-CdSe	Ga	-1.47 eV

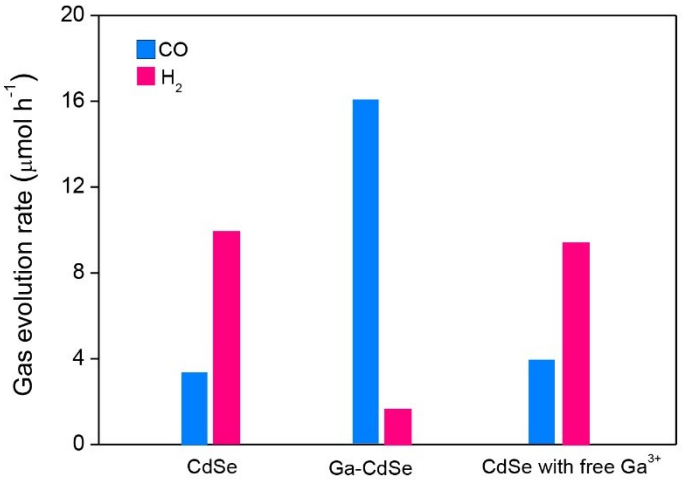

Figure S15. Photocatalytic CO_2 reduction performances of CdSe QDs, Ga-CdSe QDs, and CdSe QDs with free Ga^{3+}. The amount of Ga in CdSe QDs was determined by ICP method, which was measured to be 0.17 wt%. The added amount of free Ga^{3+} is the same with the amount of Ga in Ga-CdSe QDs.

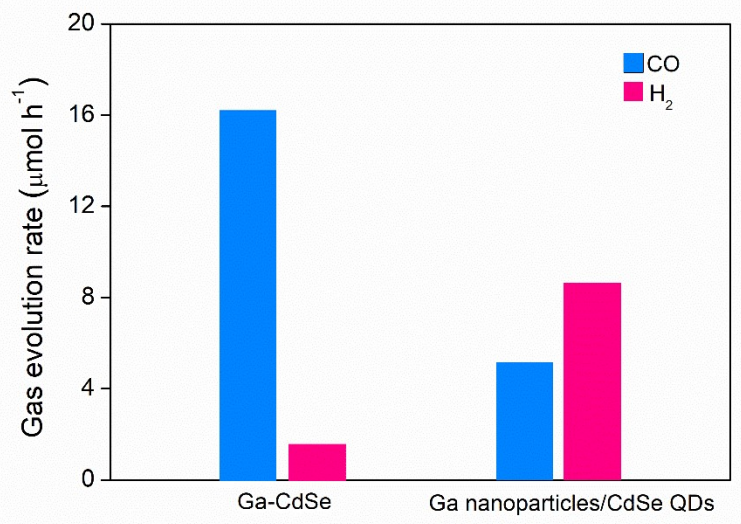

Figure S16. Photocatalytic CO_2 reduction performances of Ga-CdSe QDs and Ga nanoparticles/CdSe QDs composite.

Ga nanoparticles are prepared according to the reported method (J. Am. Chem. Soc. 2022, 144, 6779–6790). Briefly, 0.1ml liquid commercial Ga (Adamas corporation) was added into 14ml ethanol and sonicated by sonication for 15 minutes. Then, Ga nanoparticles colloidal ethanol solution was obtained. Ga nanoparticles/CdSe QDs composite was prepared by mixing CdSe QDs with certain amount of Ga nanoparticles in ethanol solution under stirring, and then was obtained by centrifugation. The added amount of Ga nanoparticles is the same with the amount of Ga in Ga-CdSe QDs.