## Supporting Information

## Highly Efficient Proton-Assisted Photocatalytic CO2 Reduction over 3-

## Mercaptopropionic Acid-Capped CdS Quantum Dots

Duc-Trung Nguyen, Anis Chouat, and Trong-On Do\*

Department of Chemical Engineering, Laval University, Québec, G1V 0A6, Canada

\*Corresponding author

Email address: <a href="mailto:trong-on.do@gch.ulaval.ca">trong-on.do@gch.ulaval.ca</a>



**Magnetic Stirrer** 

Fig. S1. Schematic illustration of the photoreactor for photocatalytic CO<sub>2</sub> reduction [1]



**Fig. S2**. Pictorial images of aqueous CdS-xA QDs. Excepting that CdS-0A is insoluble in water, other CdS-xA QDs (x = 1-4) exhibit good solubility and stability in water



Fig. S3. The TEM images of CdS-1A quantum dots (a-b) and CdS-0A quantum dots (c-d)



Fig. S4. The XRD spectra of CdS-0A and CdS-1A quantum dot (\* indicate the presence of

chracteristic Cd(OH)<sub>2</sub> peaks)



Fig. S5. The survey XPS spectra of CdS-1A quantum dot

26.78

20.87

17.11

11.94

23.30



Fig. S6. The optimization of CdS-0.5A concentration for the photocatalytic CO<sub>2</sub> reduction



Fig. S7. The optimization of CdS-1A concentration for the photocatalytic CO<sub>2</sub> reduction



Fig. S8. The optimization of CdS-2A concentration for the photocatalytic CO<sub>2</sub> reduction

Entry	$\mathbf{H}_2$	СО
1	No	No
2	No	No
3	No	No
4	H <sub>2</sub> (trace)	No

Table S1. Control experiments for the photocatalytic  $CO_2$  reduction

 $^{1}$  without photocatalyst;  $^{2}$  in the dark;  $^{3}$  without TEA;  $^{4}$  using Ar instead of CO<sub>2</sub>

Table S2. The comparison in the Apparent Quantum Yield of CdS-1A in the photocatalytic  $CO_2$ 

Catalyst	Light source	Co-catalyst	Sacrificial agent	AQE (%)	Ref.
CdS-1A	150 W Xe lamp	No	TEA	4.17% (420 nm) 0.32% (460 nm)	This work
N-doped graphene/CdS hollow sphere	350 W Xe lamp,	No	H <sub>2</sub> O	0.9% (420 nm)	[2]
tetra-coordinated Co(II) modified CdS	300W Xe lamp	_	Na <sub>2</sub> SO <sub>3</sub>	2.2% (420 nm)	[3]
Au <sub>(25</sub> )@CdS HMCHPs	300W Xe lamp	Co(bpy) <sub>3</sub> <sup>2+</sup>	TEOA	0.61% (420 nm)	[4]
CdS-WO <sub>3</sub>	300W Xe lamp	No	No	0.4% (420 nm)	[5]
Co-ZIF- 9/[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> .6 H <sub>2</sub> O	500W Xe lamp	Co-ZIF-9	TEOA	1.48% (420 nm)	[6]
rGO-MoS <sub>2</sub>	300 W Xe lamp, AM 1.5 G, 1 Sun	No	H <sub>2</sub> O	0.3% (523 nm)	[7]
Co-ZIF-9/CdS	300W Xe lamp	Co-ZIF-9	TEOA	1.93 % (420 nm)	[8]
g-C <sub>3</sub> N <sub>4</sub> /Co-ZIF-9	Xe lamp (intensity not available)	Co-ZIF-9	TEOA	0.9% (420 nm)	[9]

reduction with the reported photocatalyst in the literature

Ru complex/C <sub>3</sub> N <sub>4</sub>	400W Hg lamp	Ru complex	TEOA	5.7 % (400 nm)	[10]
Carbon layer coated Cu <sub>2</sub> O	300W Xe lamp	No	H <sub>2</sub> O	2.07 % (400 nm)	[11]
Polymeric carbon nitride/ZnIn <sub>2</sub> S <sub>4</sub>	300W Xe lamp	Co(bpy) <sub>3</sub> <sup>2+</sup>	TEOA	2.4% (420 nm)	[12]
Ni metal-organic framework (MOF) monolayers	5W white LED light	-	TEOA	2.2 % (420 nm)	[13]
Cu <sub>2</sub> O/WO <sub>3</sub> -001	400W Xe lamp	-	H <sub>2</sub> O	0.503 % (420 nm)	[14]
Triazine-based conjugated microporous polymers	300W Xe lamp	Co(bpy) <sub>3</sub> <sup>2+</sup>	TEOA	1.75 % (405 nm)	[15]
Mixed MPA,MUA- capped CdS QDs	LED (λ = 400 nm)	No	TEOA	HCOOH: 23.2 % (400 nm) CO: 0.4 % (400 nm) CH4: 0.2 % (400 nm)	[16]



Fig. S9. The FTIR spectra of CdS-1A QDs before (line a) and after 4 cycles test (line b)



**Fig. S10**. (a) The photocatalytic activity of CdS-1A after ligand stripping by treating CdS-1A with HCl 1M at pH=4 at different durations of time (0, 16, and 48 hours), and (b) their corresponding FTIR spectra



**Fig. S11**. The comparison between the photocatalytic activity of CdS QDs synthesized by the aqueous synthesis (CdS-1A) and hot-injection method (CdS-1LE)



**Fig. S12.** (a) The color of CdS-1A QDs in 9/1 v/v DMSO/TEA at three different intervals during the photocatalytic CO<sub>2</sub> reduction, and (b) its corresponding PL spectra (*Interval 1*: before solar-light irradiation, no CO<sub>2</sub> purging; *Interval 2*: solar-light irradiation for 2 hours, with saturated CO<sub>2</sub> solution; *Interval 3*: solar-light irradiation off, with desaturated CO<sub>2</sub> solution).

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