

## Supporting Information

### CdS/NH<sub>2</sub>-UiO-66 Hybrid Membrane Reactors for Efficient Photocatalytic Conversion of CO<sub>2</sub>

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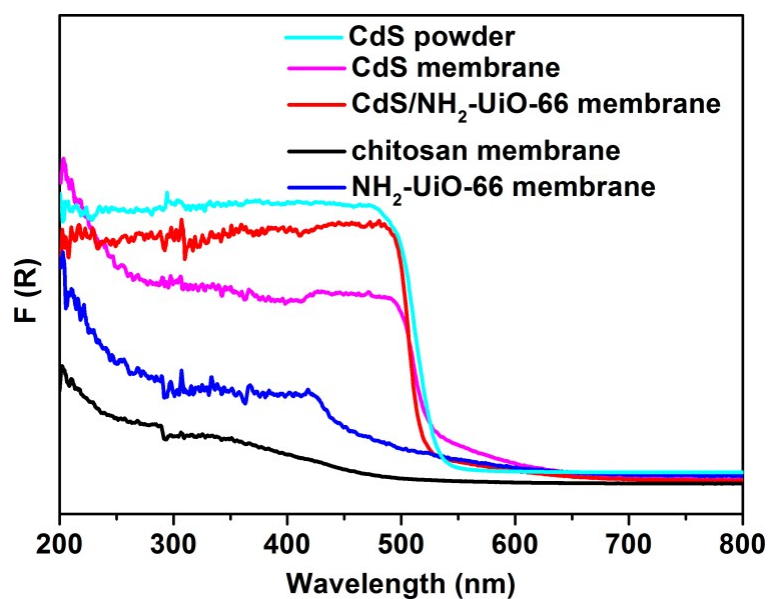


Fig. S1. UV-vis absorption spectra of the prepared samples.

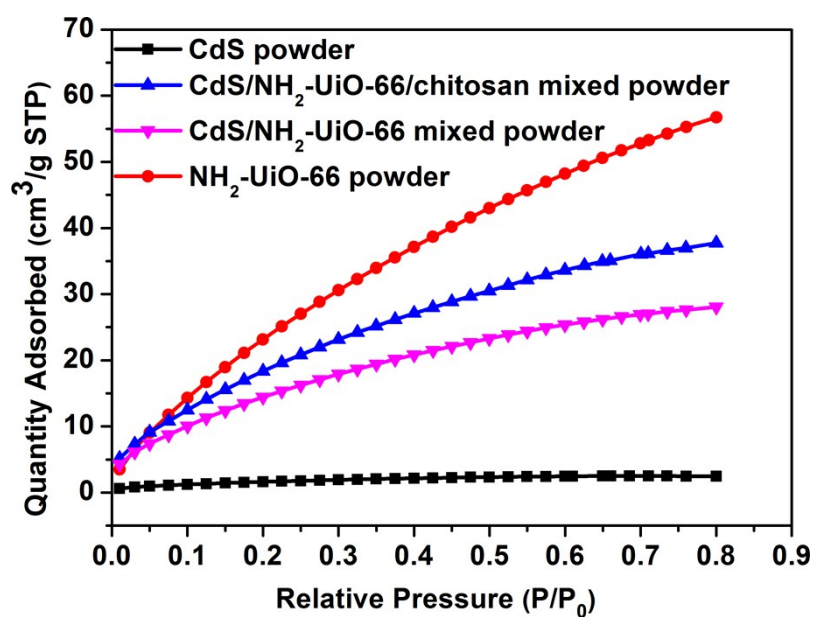


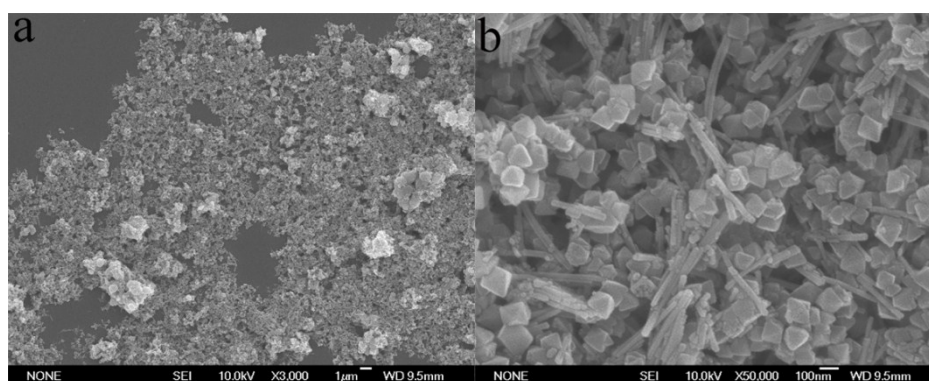
Fig. S2. CO<sub>2</sub> adsorption isotherms (1atm, 298 K) of the samples.

**Table S1** Comparison of the reaction conditions and performances with other catalysts for photocatalytic CO<sub>2</sub> reaction.

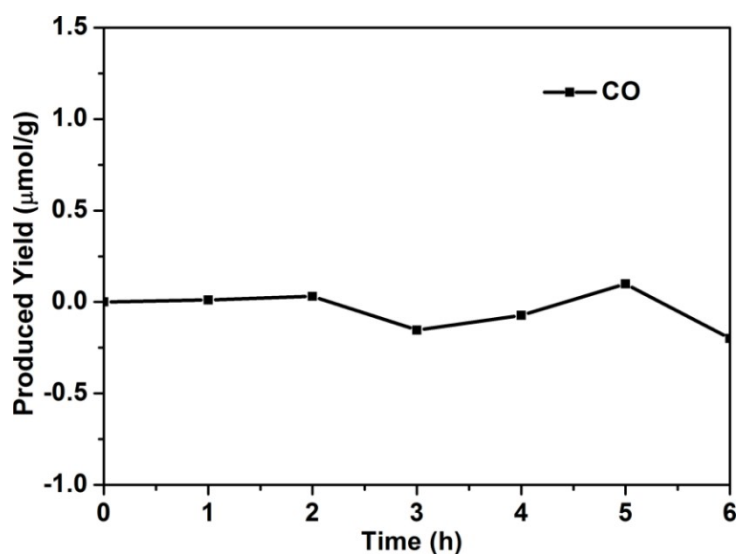
| Catalyst                                         | Light source           | Reduction medium                                                                   | Products | Activity&<br>Sel. <sub>co</sub> (%)                 | Reference                               |
|--------------------------------------------------|------------------------|------------------------------------------------------------------------------------|----------|-----------------------------------------------------|-----------------------------------------|
| CdS/NH <sub>2</sub> -<br>UiO-66<br>membrane      | 300 W lamp             | Saturated CO <sub>2</sub><br>inmixture of water,<br>MeCN, TEOA and<br>bpy, 1atm    | CO       | 87.0 μmol·g <sup>-1</sup> ·h <sup>-1</sup> ,<br>99% | This work                               |
| ZnO/Ag <sub>0.5</sub> Cu <sub>0.5</sub> /<br>CdS | 450 W lamp             | Saturated CO <sub>2</sub> in<br>water, NaHCO <sub>3</sub> and<br>2-propanol, 1 atm | CO       | 327 μmol·g <sup>-1</sup> ·h <sup>-1</sup> ,<br>63%  | Rao al. (ref. <sup>1</sup> )            |
| CdS                                              | 300W Xenon<br>arc lamp | Saturated CO <sub>2</sub> in<br>water and 2-propanol<br>, 1 atm                    | CO       | 0.11 μmol·g <sup>-1</sup> ·h <sup>-1</sup> ,<br>24% | Yoneyama et<br>al. (ref. <sup>2</sup> ) |

|                                                         |                                  |                                                                                                   |                                         |                                                                                                                                                                                              |                                      |
|---------------------------------------------------------|----------------------------------|---------------------------------------------------------------------------------------------------|-----------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|
| CdS/Co-ZIF-9                                            | 300W Xenon arc lamp              | Saturated CO <sub>2</sub> in mixture of water, MeCN, TEOA and bpy, 1 atm                          | CO                                      | 1301.5 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ,<br>58%                                                                                                                          | Wang et al. (ref. <sup>3</sup> )     |
| CdS/BCN                                                 | 300W Xenon arc lamp              | Saturated CO <sub>2</sub> in mixture of water, MeCN, TEOA and bpy, CoCl <sub>2</sub>              | CO                                      | 128 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ,<br>79%                                                                                                                             | Wang et al. (ref. <sup>4</sup> )     |
| CODH/CdS                                                | 250W tungsten halogen bulb       | 2-(N-morpholino)ethanesulfonic acid, additional ascorbate, KI, TEOA, 1 atm CO <sub>2</sub>        | CO                                      | 60 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$                                                                                                                                       | Armstrong et al (ref. <sup>5</sup> ) |
| NH <sub>2</sub> -UiO-66                                 | 500W Xenon arc lamp              | TEOA, MeCN, high purity CO <sub>2</sub> gas (1atm)                                                | HCOOH                                   | CO: 40 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ;                                                                                                                                 | Li et al (ref. <sup>6</sup> )        |
| CdS/g-C <sub>3</sub> N <sub>4</sub>                     | 250W lamp (UV light irradiation) | Saturated CO <sub>2</sub> in methanol, 1 atm                                                      | methyl formate                          | 1352.07 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ,<br>$1\cdot\text{h}^{-1}$ ,                                                                                                     | Yin et al. (ref. <sup>7</sup> )      |
| CdS /rGO/TiO <sub>2</sub>                               | 300 W Xenon arc lamp             | Saturated CO <sub>2</sub> in 0.4 mL of deionized water                                            | CH <sub>4</sub> , O <sub>2</sub>        | 0.12 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ,                                                                                                                                   | Zou et al. (ref. <sup>8</sup> )      |
| CdS/CdV <sub>2</sub> O <sub>6</sub>                     | 300 W Xenon arc lamp             | high purity CO <sub>2</sub> gas, 0.1 M Na <sub>2</sub> S and 0.5 M Na <sub>2</sub> S <sub>3</sub> | CH <sub>4</sub>                         | 2.98 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ,                                                                                                                                   | He et al. (ref. <sup>9</sup> )       |
| CdS@CeO <sub>2</sub>                                    | 300 W Xenon arc lamp             | high purity CO <sub>2</sub> gas                                                                   | CH <sub>4</sub> ,<br>CH <sub>3</sub> OH | CH <sub>4</sub> : 2.98 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ,<br>$1\cdot\text{h}^{-1}$ ,<br><br>CH <sub>3</sub> OH: 137.5 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ | He et al. (ref. <sup>10</sup> )      |
| Fe <sub>2</sub> V <sub>4</sub> O <sub>13</sub> /RGO/CdS | 300 W Xenon arc lamp             | deionized water, high purity CO <sub>2</sub> gas                                                  | CH <sub>4</sub> , O <sub>2</sub>        | CH <sub>4</sub> : 1.57 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ,<br>$1\cdot\text{h}^{-1}$ ,                                                                                      | Zou et al. (ref. <sup>11</sup> )     |

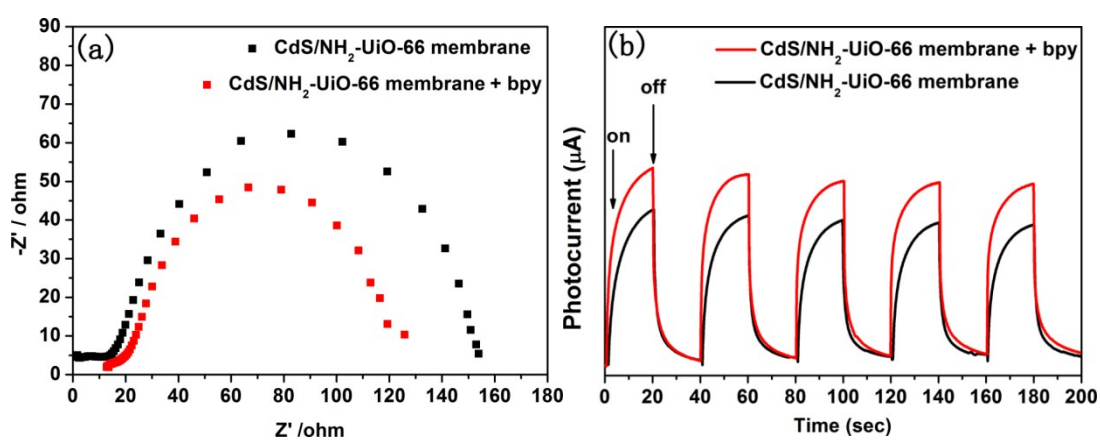
|                                                                  |                            |                                                     |                                  |                                                                                                                                 |                                       |
|------------------------------------------------------------------|----------------------------|-----------------------------------------------------|----------------------------------|---------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|
| CdS/ZnS                                                          | UV 8 W Hg<br>lamp (254 nm) | 0.2 M NaOH solution,<br>purity CO <sub>2</sub> gas  | CH <sub>4</sub> , H <sub>2</sub> | CH <sub>4</sub> : 0.69 μmol·g <sup>-1</sup> ·h <sup>-1</sup> ,<br><br>H <sub>2</sub> : 11 μmol·g <sup>-1</sup> ·h <sup>-1</sup> | Praus et al.<br>(ref. <sup>12</sup> ) |
| CdS/ZnS                                                          | UV 8 W Hg<br>lamp (365 nm) | 0.2 M NaOH solution,<br>purity CO <sub>2</sub> gas  | CO, H <sub>2</sub>               | CO: 0.03 μmol·g <sup>-1</sup> ·h <sup>-1</sup> ,<br><br>H <sub>2</sub> : 0.34 μmol·g <sup>-1</sup> ·h <sup>-1</sup>             | Praus et al.<br>(ref. <sup>12</sup> ) |
| Bi <sub>2</sub> S <sub>3</sub> /CdS                              | 500 W Xenon<br>arc lamp    | deionized water, high<br>purity CO <sub>2</sub> gas | CH <sub>3</sub> OH               | CH <sub>3</sub> OH: 122.6<br>μmol·g <sup>-1</sup> ·h <sup>-1</sup>                                                              | Li et al. (ref. <sup>13</sup> )       |
| Cd <sub>0.2</sub> Zn <sub>0.8</sub> S@<br>UiO-66-NH <sub>2</sub> | 300 W Xenon<br>arc lamp    | 0.5 M NaOH,<br>purity CO <sub>2</sub> gas           | CH <sub>3</sub> OH               | CH <sub>3</sub> OH: 6.8<br>μmol·g <sup>-1</sup> ·h <sup>-1</sup>                                                                | Wang et al<br>(ref. <sup>14</sup> )   |



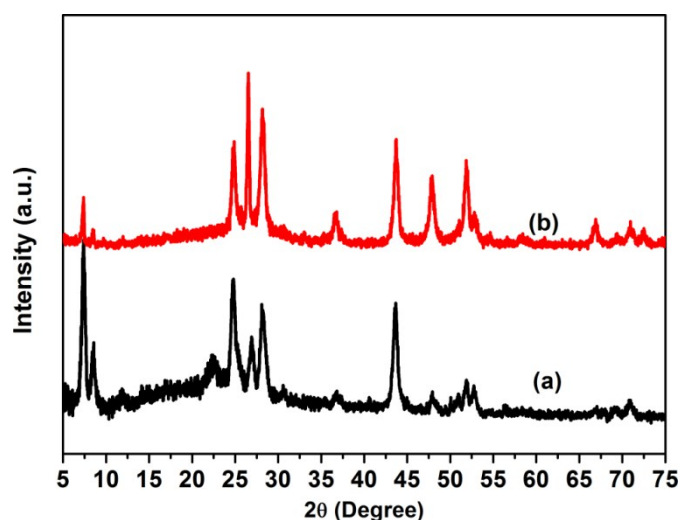
**Fig. S3.** SEM images of CdS/NH<sub>2</sub>-UiO-66 mixed powder.



**Fig. S4.** Time-production plot of CO produced from the CdS/NH<sub>2</sub>-UiO-66 membrane using N<sub>2</sub> instead of CO<sub>2</sub>. Reaction conditions: solvent - 18 ml, MeCN : H<sub>2</sub>O: TEOA = 3:2:1; bpy: 10mg; N<sub>2</sub>-1 atm; 760 nm  $\geq \lambda \geq$  400 nm; room temperature; 6 h.



**Fig. S5.** (a) EIS Nyquist plots of the photocatalysts and (b) Transient photocurrent responses under visible light irradiation (760 nm  $\geq \lambda \geq$  400 nm) of samples.



**Fig. S6.** PXRD patterns of CdS/NH<sub>2</sub>-UiO-66 membrane (a) before and (b) after the photocatalytic reaction.

## References

- [1] S. R. Lingampalli, M. M. Ayyub, G. Magesh and C. N. R. Rao, *Chem. Phys. Lett.*, 2018, **691**, 28-32.
- [2] B. J. Liu, T. Torimoto and H. Yoneyama, *J. Photo. Photobio. A*, 1998, **113**, 93-97.
- [3] S. B. Wang and X. C. Wang, *Appl. Catal. B-Environ.*, 2015, **162**, 494-500.
- [4] M. Zhou, S. B. Wang, P. J. Yang, C. J. Huang and X. C. Wang, *ACS Catal.*, 2018, **8**, 4928-4936.
- [5] Yatendra S. Chaudhary, Thomas W. Woolerton, Christopher S. Allen, Jamie H. Warner, Elizabeth Pierce, Stephen W. Ragsdale and Fraser A. Armstrong, *Chem. Commun.*, 2012, **48**, 58-60.
- [6] D. Sun, Y. Fu, W. Liu, L. Ye, D. Wang, L. Yang, X. Fu and Z. Li, *Chem. Eur. J.*, 2013, **19**, 14279-14285.
- [7] X. X. Yang, W. Y. Xin, X. H. Yin and X. Shao, *Chem. Phys. Lett.*, 2016, **651**, 127-132.
- [8] L. B. Kuai, Y. Zhou, W. G. Tu, P. Li, H. J. Li, M. Xiao and Z. G. Zou, *RSC Adv.*, 2015, **5**, 88409-88413.
- [9] S. Ijaz, M. F. Ehsan, M. N. Ashiq, N. Karamt, M. Najam-ul-Haq and T. He, *Mater. Design*, 2016, **107**, 178-186.
- [10] S. Ijaz, M. F. Ehsan, M. N. Ashiq, N. Karamt and T. He, *Appl. Sur. Sci.*, 2016, **390**, 550-559.
- [11] P. Li, Y. Zhou, H. J. Li, Q. F. Xu, X. G. Meng, X. Y. Wang, M. Xiao and Z. G. Zou, *Chem.*

*Commun.*, 2015, **51**, 800-803.

[12] P. Praus, M. Edelmannová, N. Ambrosová, I. Troppová, D. Fridrichová, G. Słowik and J. Ryzkowski, *J. Nanosci. Nanotechnol.*, 2017, **17**, 4041-4047.

[13] X. Li, J. T. Chen, H. L. Li, J. T. Li, Y. T. Xu, Y. T. Liu and J. R. Zhou, *J. NAT. Gas. Chem.*, 2011, **20**, 413-417.

[14] Y. Su, Z. Zhang, H. Liu and Y. Wang, *Appl. Catal. B-Environ.*, 2017, **200**, 448-457.