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Photocatalytic reduction of CO₂ to CO utilizing a stable and efficient hetero-homogeneous hybrid system[†]

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The combination of the conventional inorganic semiconductor CdS and a homogeneous catalyst could reduce CO_2 to CO economically under visible light with high selectivity, stability, and efficiency.

Although carbon dioxide (CO₂) is widely regarded as a greenhouse gas, which results in global warming, it is also one of the most abundant carbon sources for fuels and organic materials.1 The fixation and conversion of CO₂ into chemical fuels or industrial chemicals, which can be used within the current energy and technology infrastructure, is a promising solution from the viewpoint of realizing a sustainable society. However, the conversion process is acceptable only if a renewable and environmentally friendly energy source could be used for this purpose. Photocatalytic reduction of CO2 under solar irradiation (i.e. artificial photosynthesis) is considered to be the most ideal way for the conversion of CO₂. Depending on the number of electrons transferred, the reduction of CO₂ can lead to the formation of different products, such as, carbon monoxide,² formic acid,³ formaldehyde,⁴ methanol,⁴ methane.⁵⁻⁷ Among of them, carbon monoxide (CO), as one of the most important chemical raw materials, has achieved great attentions due to its various industrial applications; for instance, Fischer-Tropsch synthesis.8

Typically, the photocatalytic reduction of CO_2 can be divided into two types: one is homogeneous process and the other is heterogeneous process. In the homogeneous photocatalytic process, metal complex compounds are usually used for absorbing light and reducing CO_2 . The light absorption and catalytic reduction process could be accomplished in a single molecule or two molecules.⁹ Because CO_2 could be coordinated to the metal center of the complex molecules and thus be activated, the homogeneous process often has high quantum efficiencies and selectivities.^{2,10,11} However, despite the difficult separation of the catalysts, the instability of the photosensitizers under long time irradiation¹² strongly limits the application of this method. In the heterogeneous process, semiconductors generally act as the photocatalysts and CO₂ molecules are reduced by the photo-generated electrons on the surface of the semiconductor.^{4,13-16} The semiconductors have better stability than the complex compounds in homogeneous systems and they are easily to be separated from the solvents. Nevertheless, due to the weak adsorption of CO₂ on the surface of semiconductor, the CO₂ molecules could not be well activated and consequently, the quantum yields in heterogeneous system are generally low.^{4,17,18}

Since the homogeneous and heterogeneous processes have high quantum efficiencies and stabilities, respectively, it is reasonable to think that a hybrid of heterogeneous and homogeneous methods may be an ideal pathway with both good stability and high efficiency. Semiconductor linked with ruthenium complex has been reported to be a good photocatalytic system to selectively reduce CO2 into HCOOH.¹⁹ In this system, the semiconductor acts as the photosensitizer to absorb light and the metal complex is used for activating and reducing CO₂. Because the conduction band minimum (CBM) of the semiconductor is more negative than the CO₂ reduction potential in complex, the photo-generated electrons in the semiconductor can easily transfer to the metal complex and then reduce the CO2 molecules. More recently, a cobalt-containing zeolitic imidazolate framework (Co-ZIF-9) cooperating with a rutheniumbased photosensitizer was used for CO₂ conversion.²⁰ But, the ruthenium-based photosensitizers would lose their activities slowly under sustained irradiation. More importantly, triethanolamine (TEOA) was widely used as electron donor in most of previous reports2,19-22 due to its ability of fast consuming of photo-generated holes. However, much attention was paid on the reduction reaction of CO₂, and the oxidation products of TEOA was not investigated which is indeed crucial for cost and energy concerns. If TEOA was excessively oxidized or even

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mineralized into CO_2 , the whole reaction was not economical. Furthermore, no light-energy would be stored in the whole reaction. Therefore, a mild oxidation of TEOA to a more valuable chemical seems an optimal choice. In order to achieve the purpose, both appropriate valence band position and reaction condition are needed.

Herein, we report an economical, stable and efficient hybrid catalytic system for photoreduction of CO_2 , which is obtained by simply mixing CdS nanoparticles (heterogeneous photosensitizer) and $CoCl_2/2, 2'$ -bipyridine (Co-bipy, homogeneous catalyst, $n(bipy)/n(Co^{2+}) = 1$) in an acetonitrile solution. It was found that TEOA was mildly oxidized rather than photo-degraded, and it is estimated that about 43 kJ mol⁻¹ of solar energy are stored in the photocatalytic reaction. Under visible light irradiation, the CO₂ molecules could be selectively reduced into CO with an apparent quantum yield as high as 1.0% at $\lambda = 470$ nm. We believe the use of organic solvent (acetonitrile) and the fast interfacial electron transfer increase the stability of the whole system. Moreover, the ratio of CO and the byproduct H₂ could easily be tuned from 0.7 to 7.0 in this system, which is very helpful for their applications as syngas.

The cadmium sulfide nanoparticles was prepared from sodium sulfide and cadmium sulfate in an aqueous ammonia solution according to the previously reported method.²³ The structure of the synthesized CdS nanocrystals is characterized by X-ray powder diffraction (XRD). The pattern is illustrated in Fig. 1a and it could be indexed as pure zinc blende (cubic) phase of CdS, (JSPDS no. 10-0454) with prominent peaks corresponding to the reflections at (111), (220), and (311) planes, respectively. The broadened peaks indicates the small crystallite size of the as-prepared CdS. When the CdS powder is dispersed in methanol, a yellow dispersion is obtained (inset of Fig. 1b). Fig. 1b shows the UV-vis absorption spectrum of the CdS dispersed in methanol. The most direct way of extracting the optical band gap is to simply determine the wavelength at which the extrapolations of the base line and the absorption edge cross. Using this method, the band gap absorbing edge is about 512 nm. Correspondingly, the band gap of the as-obtained CdS

is estimated to be 2.42 eV, which is consistent with the band gap (2.42 eV) of bulk CdS. The tail absorption in its red region may originate from the scattering of CdS particles. High resolution transmission electron microscopy (HRTEM) image (Fig. S1[†]) shows that the size of CdS nanocrystals ranges from 5 to 8 nm, which is consistent with the XRD result.

In the hybrid system, CdS nanoparticles and Co-bipy complex were all added into the acetonitrile solution. The photocatalytic experiments of CO2 reduction were carried out by using visible light irradiation ($\lambda > 420$ nm) with triethanolamine (TEOA) as electron donor under a pressure of 4 atm. When the photocatalytic process started, large amounts of CO (23 µmol per 3 h) was generated with a small amount of H_2 (3 µmol per 3 h). Studies on the CO/H₂ evolution as a function of irradiation time shows that the relationship between the amount of CO/H₂ produced and the irradiation time is linear (Fig. 2b). The rate of CO and H₂ evolution per gram of CdS was calculated to be 844 and 122 μ mol h⁻¹, respectively. Although photocatalytic reaction rates cannot be accurately compared, the above rates was found to be about 7-fold higher than that in the chemical bonded system.¹⁹ The total amount of CO was 62 µmol after 8 h, thus the corresponding turnover number (TON) was calculated to be 4.1 with respect to the amount of Co²⁺. The measured apparent quantum yield of CO formation at 1 atmosphere was 1.0% under monochromatic irradiation at $\lambda = 470$ nm. Since no activity decreasing was observed within 8 h irradiation, it is indicated that the hybrid system is stable (Fig. 2b). Above results reveal that the hybrid system is an efficient and stable system for photocatalytic CO2 reduction. For comparison, we have done three types of control experiments. When the reaction was performed in dark, no CO or H₂ was detected, which clearly indicated that the production of CO and H₂ depended on the light. When CdS alone was used, large amounts of H_2 (9.5 µmol per 3 h) was produced and only trace amounts of CO was detected. This result suggests that the CdS particles could easily generate H₂ from the oxidative dehydrogenation of TEOA. However, due to the poor adsorption of CO₂ on their surfaces and strongly negative single-electron reduction potential of



Fig. 1 Characterization of the CdS nanocrystals: (a) XRD pattern. (b) UV-vis absorbing spectrum measured under transmission mode. Inset shows the image of the CdS suspension.



Fig. 2 (a) Control experiments after 3 h irradiation. (b) Gas produced as a function of irradiation time for CdS/Co-bipy.

 CO_2 ,²⁴ CdS can hardly reduce CO_2 to CO. When Co-bipy alone was used, no CO or H₂ was produced, indicating that the Cobipy complex itself has no photocatalytic activity.

To verify the source of CO, 13 C labeled experiment was performed by using 13 CO₂ as reactant. The evolution of CO was analyzed by gas chromatography mass spectrometry (GC-MS). Fig. 3 is the mass spectra of CO peak obtained under 12 CO₂ and 13 CO₂, respectively. Under 12 CO₂ (99% abundance), m/z = 28(99% abundance) was assigned to be the molecular ion peak of 12 CO. Under 13 CO₂ (98% abundance), m/z = 29 (98%



Fig. 3 Mass spectrum of CO peak obtained under $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$, respectively.



abundance) was assigned to be molecular ion peak of ¹³CO. The above results approved that the produced CO in our hybrid organic system only comes from the reduction of CO₂.

The effect of bipy and Co^{2+} on photocatalytic reduction of CO_2 was investigated. Fig. 4 shows the ratio of bipy to Co^{2+} affects both CO and H₂ generation. When bipy was absence, large amounts of H₂ was generated while CO evolution was inhibited. After addition of equivalent amounts of bipy, the amount of CO evolution was dramatically increased, while the amount of H₂ evolution was decreased. This can be attributed to the fact that formation of Co(bipy)_x²⁺ can decrease the reduction potential of $\text{Co}^{2+}/\text{Co}^+$. Therefore, the electron-transfer from CdS to Co center was accelerated, which was favorable for CO₂ reduction. When the ratio of bipy to Co^{2+} was increased from 1 to 3, CO generation was decreased slightly which may be due to lack of vacant coordination site for CO₂ binding at the Co center. The highest CO selectivity was obtained when $n(\text{bipy})/n(\text{Co}^{2+}) = 1$.

The influence of CO_2 pressure in our photocatalytic system was also examined. Fig. 5 shows that the production of CO increased with increasing pressure of CO_2 while the production of H_2 decreased. It was reasonably to think that since the reduction reactions of H^+ and CO_2 are competitive in the same system, higher CO_2 concentration in solution is more favorable



Fig. 5 Amount of CO and H_2 as a function of CO₂ pressure.



Scheme 1 Left: photos of the solution before and after irradiation. Right: possible mechanism of photocatalytic CO₂ reduction in the hybrid system. S: solvent or bipy.

for CO₂ reduction. As we know, CO/H₂ mixture can be used to synthesize fuels and other valuable chemicals. Herein, the ratio of CO/H₂ mixture can be easily modulated from 0.7 to 7 by controlling pressure of CO₂, which makes them have potential applications in chemical industry.

A possible mechanism (Scheme 1) of photocatalytic CO₂ reduction in the hybrid system was proposed based on the previous assumption.25 First of all, CdS particles absorb light and generate active electron-hole pair. For the reduction part, the electron reduces Co^{II} to Co^I which is the active intermediate. We observed the evidence of the generation of Co^I (an airsensitive dark blue solution, UV-vis sepectra was shown in Fig. S4[†]) which could also be obtained by chemical reduction of [Co(bipy)₃]²⁺ with Na-Hg.²⁶ Then, CO₂ coordinates to Co¹ through electrophilic attack.²⁵ The subsequent decomposition of Co^{III}-COOH complex forms Co^{III}-CO complex. CO is generated through a ligand-dissociation reaction. Eventually, Co^{III} was reduce to the primary Co^{II} by either electron in CdS or Co^I. For the oxidation part, TEOA was oxidized by the hole in CdS. The primary oxidation product of TEOA was generally considered to be TEOA⁺.²⁷ Through analyzing the solution after irradiation by GC-MS (see Fig. S3[†]), the final oxidation product of TEOA was identified as N,N-bis(2-hydroxyethyl)glycine (Scheme S1B[†]) which is a more valuable chemical than TEOA. This means the oxidation reaction is economically acceptable. Due to the appropriate valence band position of CdS and the absence of water and oxygen, TEOA was mildly oxidized rather than photo-degraded. It is reasonable to speculate that the final oxidation product may originate from further the oxidation of 2-(bis(2-hydroxyethyl)amino)acetaldehyde (A) when it was exposed in air, because the possible mechanism of generation of A from TEOA was proposed in previous report.²⁷ If this is the case, it is estimated that about 43 kJ mol⁻¹ of solar energy are stored in reaction (1) through molecular mechanics calculation (Table S1[†]).

$$CO_2 + \frac{HO}{HO} \xrightarrow{N} OH \xrightarrow{CdS} CO + \frac{HO}{HO} \xrightarrow{O} H + H_2O$$
(1)

The possible mechanism of the oxidation of TEOA is showed in Scheme S1.[†] H_2 originates from reduction of protons by two ways: one is from CdS; one is from the Co-bipy.

The high efficiency and stability of the hybrid system may be due to the following aspects. Firstly, the position of CBM of CdS $(-0.9 \text{ V} \text{ vs. NHE}, \text{pH} = 7)^{28}$ is more negative than the potential of CO_2/CO (-0.53 V vs. NHE, pH = 7), therefore photocatalytic reduction of CO₂ into CO by CdS is thermodynamically feasible. Besides, due to the activation of CO₂ through coordination to Co center, the rate of CO₂ reduction was dramatically increased (Fig. 2a). Secondly, CdS suffers from stability problem when O_2 or H₂O exists.²⁹ And, in aqueous, CdS could generate H₂ at a high rate when using sacrificial agent.^{30,31} In present system, because organic solvent was used and O2 was absent, the stability problem of CdS due to O2 and H2O was avoided. Besides, the photo-generated electrons of CdS can be quickly consumed by Co-bipy, meanwhile the holes can be quickly consumed by TEOA, thus, the fast interfacial electron transfer (IFET) also inhabits the photo-corrosion of CdS. The high stability of CdS in our system was confirmed by the cyclic experiment (Fig. S5[†]), and no activity decrease for CO generation was found after eight cycles. The above aspects result in the high efficiency and stability of the hybrid system.

Conclusions

In summary, a hybrid photocatalytic system has been fabricated to selectively reduce CO₂ to CO under visible light irradiation. Our results suggest that the mixture of metal complex and CdS nanoparticles could offer an economical, efficient and stable system. The measured apparent quantum yield of CO formation at 1 atmosphere was as high as 1.0% under monochromatic irradiation at $\lambda = 470$ nm. We believe that the photocatalytic CO₂ reduction based on CdS in organic phase using the hybrid system could be further extended to couple with a specific oxidation reaction of organic molecules. Therefore, it is helpful for developing a new atomically economical and efficient artificial photosynthesis system.

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Notes and references

- 1 S. C. Roy, O. K. Varghese, M. Paulose and C. A. Grimes, *ACS Nano*, 2010, **4**, 1259–1278.
- 2 S. Sato, T. Morikawa, T. Kajino and O. Ishitani, *Angew. Chem., Int. Ed.*, 2013, **52**, 988–992.
- 3 Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu and Z. Li, *Angew. Chem., Int. Ed.*, 2012, **51**, 3364–3367.
- 4 T. Inoue, A. Fujishima, S. Konishi and K. Honda, *Nature*, 1979, 277, 637–638.
- 5 S. C. Yan, S. X. Ouyang, J. Gao, M. Yang, J. Y. Feng, X. X. Fan,
 L. J. Wan, Z. S. Li, J. H. Ye, Y. Zhou and Z. G. Zou, *Angew. Chem., Int. Ed.*, 2010, 49, 6400–6404.
- 6 Q. Liu, Y. Zhou, J. Kou, X. Chen, Z. Tian, J. Gao, S. Yan and Z. Zou, J. Am. Chem. Soc., 2010, 132, 14385–14387.
- 7 E. E. Barton, D. M. Rampulla and A. B. Bocarsly, *J. Am. Chem. Soc.*, 2008, **130**, 6342–6344.
- 8 A. Y. Khodakov, W. Chu and P. Fongarland, *Chem. Rev.*, 2007, **107**, 1692–1744.
- 9 A. J. Morris, G. J. Meyer and E. Fujita, *Acc. Chem. Res.*, 2009, **42**, 1983–1994.
- 10 J. Hawecker, J.-M. Lehn and R. Ziessel, *Helv. Chim. Acta*, 1986, **69**, 1990–2012.
- 11 H. Takeda, K. Koike, H. Inoue and O. Ishitani, *J. Am. Chem. Soc.*, 2008, **130**, 2023–2031.
- 12 J. Lin, Z. Ding, Y. Hou and X. Wang, *Sci. Rep.*, 2013, **3**, 1056–1061.
- 13 S.-I. In, D. D. Vaughn and R. E. Schaak, Angew. Chem., Int. Ed., 2012, 51, 3915–3918.
- 14 W. Hou, W. H. Hung, P. Pavaskar, A. Goeppert, M. Aykol and S. B. Cronin, ACS Catal., 2011, 1, 929–936.
- 15 N. M. Dimitrijevic, B. K. Vijayan, O. G. Poluektov, T. Rajh,
 K. A. Gray, H. He and P. Zapol, *J. Am. Chem. Soc.*, 2011,
 133, 3964–3971.

- 16 O. K. Varghese, M. Paulose, T. J. LaTempa and C. A. Grimes, *Nano Lett.*, 2009, 9, 731–737.
- 17 N. Zhang, S. Ouyang, P. Li, Y. Zhang, G. Xi, T. Kako and J. Ye, *Chem. Commun.*, 2011, **47**, 2041–2043.
- 18 S. N. Habisreutinger, L. Schmidt-Mende and J. K. Stolarczyk, Angew. Chem., Int. Ed., 2013, **52**, 7372–7408.
- 19 S. Sato, T. Morikawa, S. Saeki, T. Kajino and T. Motohiro, *Angew. Chem., Int. Ed.*, 2010, **49**, 5101–5105.
- 20 S. Wang, W. Yao, J. Lin, Z. Ding and X. Wang, *Angew. Chem., Int. Ed.*, 2014, **53**, 1167.
- 21 J. Lin, Z. Pan and X. Wang, ACS Sustainable Chem. Eng., 2013,
 2, 353–358.
- 22 Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu and Z. Li, *Angew. Chem.*, 2012, **124**, 3420–3423.
- 23 A. Reinheimer, R. van Eldik and H. Kisch, *J. Phys. Chem. B*, 2000, **104**, 1014–1024.
- 24 W. Koppenol and J. Rush, *J. Phys. Chem.*, 1987, **91**, 4429–4430.
- 25 R. Ziessel, J. Hawecker and J.-M. Lehn, *Helv. Chim. Acta*, 1986, **69**, 1065–1084.
- 26 B. Martin, W. McWhinnie and G. Waind, J. Inorg. Nucl. Chem., 1961, 23, 207–223.
- 27 K. Kalyanasundaram, J. Kiwi and M. Grätzel, *Helv. Chim. Acta*, 1978, **61**, 2720–2730.
- 28 M. F. Finlayson, B. L. Wheeler, N. Kakuta, K. H. Park, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber and J. M. White, *J. Phys. Chem.*, 1985, **89**, 5676–5681.
- 29 L. Spanhel, M. Haase, H. Weller and A. Henglein, J. Am. Chem. Soc., 1987, **109**, 5649–5655.
- 30 Y. Zhang, Y. Tang, X. Liu, Z. Dong, H. H. Hng, Z. Chen, T. C. Sum and X. Chen, *Small*, 2013, 9, 996–1002.
- 31 H. Tong, N. Umezawa, J. Ye and T. Ohno, *Energy Environ. Sci.*, 2011, 4, 1684–1689.