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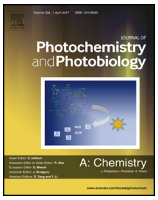

Invited feature article

Effect of solvents on photocatalytic reduction of CO_2 mediated by cobalt complex

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ABSTRACT

Conversion of CO_2 into value-added chemicals by solar energy is one of the most promising pathways to partially address both energy crisis and global warming effect. The properties of reaction medium play a key role in determining the efficiency of CO_2 photoreduction and modulating the distribution of reaction products. Herein, we report the detailed investigation of solvent effects on the performance of photocatalytic CO_2 reduction by means of photo-/electro-chemical and spectroscopy techniques. The relationship between photochemical CO_2 performance and solvent properties (e.g., viscosity, solubility, and electrochemical behaviors) are systematically explored. The active intermediates for CO_2 photoreduction catalysis are examined by UV–vis absorption spectra. Moreover, a possible reaction pathway involving photoexcited charge transfers and intermediate species transformations in various solvents is proposed.

1. Introduction

Photocatalytic reduction of CO_2 by solar resource, a significant half reaction of artificial photosynthesis, has been considered as one promising solution to produce renewable energy and alleviate global warmming [1,2]. Since the pioneer work of photocatalytic reduction of CO_2 in aqueous solution over semiconductor photocatalysts by Inoue et al. a variety of photochemical CO_2 conversion systems have been established and investigated [3]. Among the developed CO_2 reduction systems, gaseous systems for photocatalytic reduction of CO_2 with vaporized H_2O over solid catalysts have been actively studied, which exhibit inspiring achievements [4]. Materials such as TiO_2, $SrTiO_3$, CdS, zeolites, g-C_3N_4 polymers, metal-organicn frameworks (MOF), and covalent organic frameworks (COF) are demonstrated as efficient catalysts for CO_2 photoreduction in liquid reaction mediums [1,5,6]. In the CO_2 reduction systems involving metal based catalysts, the adsorption strength of CO_2^- to the metal species on catalyst surface greatly determines the activity and selectivity of the reaction [5,7]. Of note, the thermodynamically stable linear CO_2 molecules can also be activated by transition-metal catalysts under light irradiation, which coupled to appropriate reductants would efficiently promote the conversion of CO_2. As a demonstration, Lehn's group developed a photochemical CO_2 reduction system containing a catalyst combination of $[Ru(bpy)]_3Cl_2$ (bpy = 2,2′-bipyridine) and $CoCl_2$ to act as a photosensitizer and an electron mediator, respectively, along with TEOA as the electron donor [8].

Cobalt complexes have been widely employed as an efficient homogeneous cocatalysts to mediate CO_2 photoreduction through generating a Co(I) species transition state. The formation of Co-CO_2^- adduct with bent geometry can substantially minimize the activation energy of CO_2 molecules for subsequent conversion reactions. Xu et al. have developed an efficient hybrid CO_2 photoreduction system by mixing CdS nanoparticles and $CoCl_2$/bpy in an acetonitrile solution, which affords a high apparent quantum yield of 1.0% for CO formation under monochromatic irradiation ($\lambda = 470$ nm) [9]. Our previous work revealed that similar reaction mechanism can further be extended to both heterogeneous and homogenous photocatalytic CO_2 reduction systems in acetonitrile solution [10]. Besides, a high-effciency photocatalytic CO_2 reduction system consisting of semiconductor powders and a Ru-based complex is also achieved by Bhatt and coworkers [11]. So far, the reported heterogeneous and homogeneous photocatalytic CO_2 reduction systems are mainly operated in liquid phase (e.g., suspension or solution). Results of these works

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point out that the interaction between CO_2 molecules and metal species on catalysts surface is significantly influenced by reaction medium, especially the reaction solvents.

The influence of solvent on chemical equilibrium has long been investigated, and can be mainly measurened by dielectric constants [12]. It is well known that the first step in CO_2 conversion involves the formation of a "CO_2^-" intermediate, which requires a high reaction potential (e.g., −2.2 V *vs.* SCE, in DMF solution) [13–15]. Previous studies demonstrate that the properties of used solvent can obviously decrease the energy barrier during CO_2 activation. For instance, using 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF_4) as solvent, the generation of CO_2^- anion only necessitates a much lower overpotential of 0.17 V due to the complex effect of EMIM [15]. Besides, it is also reported that the selectivity of CO_2 reduction is mainly depended on the adsorption of CO_2^- on catalyst surface, which is also largely affected the nature of reaction solvent. In low polar solvents, the formed CO_2^- may be adsorbed strongly to the active surface sites of photocatalyst by carbon atom of the anion. In this case, carbon monoxide and formate are usually the main products. Alternatively, the CO_2^- anion is prone to be stabilized by the solvent molecules with high dielectric constant, resulting in weakened interaction with photocatalyst, and thus generating formate as the product [16]. Additionally, the solvent-dependent, charge-transfer equilibrium between active radicals is explored as well in organic synthesis [12]. On the other hand, the CO_2^- anion would form a M-CO_2^- (M = metal) intermediate as the first reaction step in metal-containing CO_2 reduction systems, and the properties of reaction solvent are considered to be of crucial importance to the generation and stabilization of M-CO_2^- adducts [17].

Based on the above considerations, we are interested in conducting an intensive study on the influences of solvent molecules to CO_2 activation and conversion through the formation of M-CO_2^- adduct, which is of particular importance but rarely reported. Herein, we demonstrate the detailed investigation of solvent effects on the performance of photocatalytic CO_2 reduction by means of photo-/electro-chemical and spectroscopy techniques. The relationship between photochemical CO_2 performance and solvent properties (e.g., viscosity, solubility, and electrochemical behaviors) are systematically investigated. The active intermediates for CO_2 photoreduction catalysis are examined by UV–vis absorption spectra. Moreover, a possible reaction pathway involving photoexcited charge transfers and intermediate species transformations in various solvents is proposed.

2. Experimental section

2.1. Chemicals

All the chemicals were purchased from China Sinopharm Chemical reagent Co. Ltd and without further purification. Cadmium sulfide (CdS) is of high purity (99.999%), and other chemicals including N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofufan (THF), acetonitrile (AN), triethanolamine(TEOA), cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$) and 2,2-bipyridine (bpy) are of reagent grade. The used water used is ultrapure with resistivity of *ca.*18 MΩ cm.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-ray diffractometer (Cu $K_{\alpha1}$ irradiation, $\lambda = 1.5406$ Å). Absorption spectra were obtained on an UV–vis spectrophotometer (Varian Cary 50 Conc). The metal-solvent and metal-ligand-solvent were directly mixed before measurement. Detection of Co^I transition was conducted in a sealed container adaptable for record equipment, and exposed light irradiation for 10 min before test.

2.3. Electrochemical measurements

Electrochemical measurements were conducted with a CHI 660E workstation in a conventional three electrode cell, using a Pt plate as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The photoelectrode was immersed in a 0.1 M KCl aqueous solution. The photoelectrodes were prepared by a typical coating method: the aqueous slurries of CdS were quantificationally coated on ITO glass substrates[18]. The films on ITO glass substrate were dried in air and annealed at 100 °C for 1 h as the final photoelectrodes. The electrolyte solution (*ca.* 60 m1), saturated with N_2 or CO_2 respectively and stirred by a magnetic stirrer, contained the same ingredients as photocatalytic reduction system in each solvent. The cell was then sealed and, at the same time, the three electrodes were immersed into the electrolyte because they were fixed on the cover of the cell. The electrolysis cell was placed into a constant temperature water bath of 20 °C. Time dependent photocurrent curves were measured at −1.2 V with amperometric i-t curve method; and the electrocatalytic behavior were test from 0 to −1.8 V with cyclic voltammetry model.

2.4. Photocatalysis test

All experiments were performed in a Schlenk flask (80 ml) under an atmosphere pressure of CO_2 (1 atm) [19]. In the Schlenk flask, CdS (50 mg), bpy(15 mg), $CoCl_2{\cdot}6H_2O$ (10 μmol) were added in the mixture of solvent (5 ml) and triethanolamine (TEOA, 1 ml). TEOA was used as the sacrificial agent. The system was subjected to vacuum degassing and backfilling with pure CO_2 gas. This process was repeated three times and after the last cycle the flask was back filled with CO_2. Then the system was irradiated with two counter non-focus 50 W white LED light source under vigorous stirring at 20 °C controlled by a water-cooling system. The produced gases (CO, H_2) were detected by a gas chromatography (Agilent 7890, Agilent Technologies) equipped with a packed column (TDX–1 mesh 42/10). Ar was used as the carrier gas.

3. Results and disscussion

Results of photocatalytic CO_2 reduction performance in different reaction solvents are listed in Table 1. With acetonitrile (AN) as the reaction solvent under visible light irradiation for 2 h (Entry 1, Table 1), the CO_2 reduction system exhibits a high photocatalytic activity, generating 42.6 μmol of CO production and 7.4 μmol of H_2 evolution. When DMF is used as the reaction solvent, the formation of CO is diminished to 29.4 μmol (Entry 2, Table 1), but with comparable CO selectivity relative to that in AN. The generation and selectivity of CO in DMSO solvent is much

Table 1
Photocatalytic CO_2 reduction performance with various solvents as the reaction medium.[a]

Entry	Solvent	Viscosity (cp)	Solubility (mol/L)	CO [μmol]	H_2 [μmol]	Sel.[b] [%]
1	AN	0.37	0.28	42.6	7.4	85.2
2	DMF	0.92	0.20	29.4	4.8	86.0
3	DMSO	2.24	0.14	8.9	8.0	52.7
4	THF	0.55	0.21	24.7	2.6	90.5
5	H_2O	1	0.03	0.23	1.9	10.8

[a] All the reactions were perfomed under 1 atm and at 20 °C.
[b] Sel. = mol CO/mol (H_2 + CO) × 100.

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inferior among the examined aprotic solvents (Entry 3, Table 1), mainly because of the low CO_2 solubility and the high viscosity hindering the reaction kinetics. Although the CO_2 solubility in THF is similar to that in DMF, the archived CO evolution is only moderate (Entry 4, Table 1), but the selectivity of CO (90.5%) is the highest. This high CO selectivity should be intimately related with the high coordination ability of THF to Co-bpy complex [20]. Once using H_2O as a classic protic solvent, only a tiny amount of CO and H_2 is produced (Entry 5, Table 1), indicating that aprotic solvents are more favorable for CO_2 reduction in the developed reaction system. Besides, it is worth mentioning that trace amount of formic acid was detected when AN or H_2O was employed as the reaction solvent. The distribution of reaction products is consistent with the results of reported works [21–24]. All these results suggest that the CO_2 solubility and the metal-coordinating capabilities of reaction solvents impressively affect the performance of photocatalytic CO_2 reduction. From Table 1, it is concluded that the order of CO production is in good accordance with CO_2 solubility in solvents, and no obvious correlation with solvent viscosity is observed.

The above conclusions are also supported by the time courses of products in different solvents. As shown in Fig. 1, the reaction rate of CO_2 reduction catalysis is largely determined by the properties of used solvents. When the reaction is performed with AN as the solvent, the catalytic system manifests the highest production of CO and H_2. After reaction for about 2 h, the generation of CO is almost unchanged, due mainly to the consumption of electron donor TEOA in the system. Using H_2O as the reaction solvent, the production of CO is negligible, but the evolution rate of H_2 is nearly maintains at constant. This observation is reasonable as the presence of plentiful protons facilitates H_2 generation. These findings further demonstrate that the solubility of CO_2 in the solvent greatly influences the performance of CO_2 photoreduction.

The electrochemical behaviors of CO_2 reduction are then inspected by cyclic voltammetry (CV). In these tests, the processes of CO_2 reduction can be monitored indirectly, which involves the initial reduction of Co^{II} complexes and their subsequent reaction with CO_2 to form Co-CO_2 intermediates. The thus formed Co^{I} complexes are important redox active catalysts [8,9]. In the tests, the reduction potential of CO_2 is approaching to the thermodynamic value. The obtained CV curves are shown in Fig. 2. In the absence of CO_2, the obtained redox potential ($E^{00} = -0.7$ V) in AN, DMF, and DMSO (Fig. 2a–c) is attributed to the conversion of Co^{II} complex to Co^{I} counterpart [25]. In this stage, the low valent Co intermediates are stabilized by pyridine ligand through weak coordination [26], promoting the activation of CO_2 molecules *via* nucleophilic attack. The activity of CO_2 conversion reaction is determined not only by the energy barrier of forming the corresponding intermediates, but also by the solubility of CO_2 in the reaction solvent. No obvious signal is observed in THF solution (Fig. 2d), possibly because of the generation of a light blue precipitate as shown in Fig. S2. In H_2O (Fig. 2e), one couple of redox peaks are detected ($E^{00} = -0.4$ V, and $E^{00} = -1.2$ V), which is different from that observed in organic solvents (Fig. 2a–c). This finding may be caused by the protonation of Co^{I} to produce Co^{I}-H complex, subsequently decreasing the reduction potential [27]. When CO_2 is introduced (Fig. 2a–c), the corresponding peaks observed in N_2 shift toward anodic position with the potential of about 500 mV, and the intensities of peak are enhanced considerably. The markedly increased current densities indicate that the reaction systems experience electrocatalytic CO_2 reduction reactions with high efficiency. With CO_2 being introduced into THF, the shape of the CV is almost unchanged compared with that in N_2 saturated solution, consistent with the results in UV–vis measurements. This phenomenon is mainly resulted from the coordination of cobalt species with oxygen atom of the solvent molecule, and thus hindering the formation of M-CO_2^- and the charge transfers afterwards. Besides, when the CO_2 reduction reaction is conducted in H_2O, an obvious reduction peak ($E^{00} = -0.4$ V) is detected as well. This result further suggests the proton-coupled CO_2 reduction mechanism.

During the processes of photocatalytic reactions, electron-hole paires and some labile intermediates are formed upon light irradiation [28]. The typical role of electron migration in organic electrolytes could be reflected by transient photocurrent response under light illumination. The photocurrent responses of the CO_2 reduction systems with different solvents as the electrolytes are displayed in Fig. S3. The photocurrent intensity indicates the transfer kinetics of charge carriers. The trend of photocurrent density is in good agreement with the order of CO_2 photoreduction activity in organic solvents as shown in Fig. 1. The observed photocurrent generation in H_2O in mainly attributed to H_2 evolution reaction. These results reveal that the transportation of photo-induced charges of CO_2 conversion photocatalysis can be accelerated by selecting appropriate solvent as the reaction medium.

Absorption spectroscopy is employed to characterize the interaction of solute-solvent in CO_2 reduction system. The UV–vis absorption spectra of solute molecules are influenced by solvent molecules around and other environments. In order to minimize the interferences caused by the surrounding factors, the UV–vis absorption spectra are collected in solution by directly dissolving Co^{2+} ($CoCl_2$) in various solvents. As shown in Fig. 3, the UV–vis absorption spectra obtained in all the organic solution generally exhibit two absorption bands (line a–d). The absorption

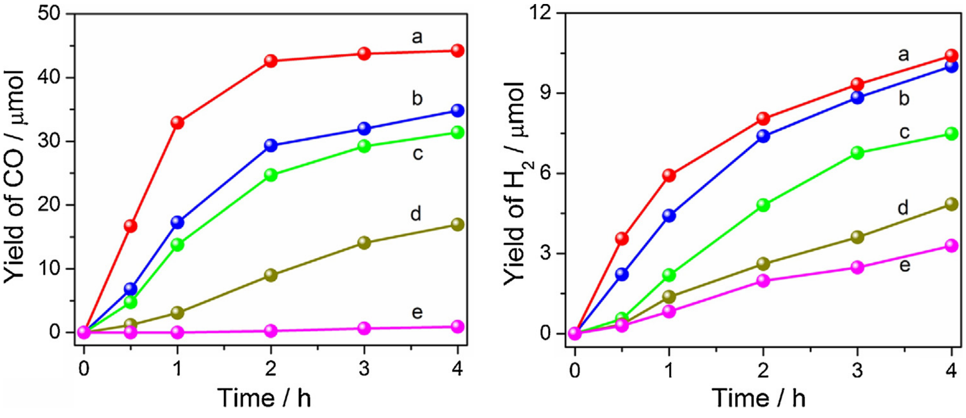

Fig. 1. Production of CO and H_2 in different solvents: (a) AN, (b) DMF, (c) THF, (d) DMSO, and (e) H_2O.

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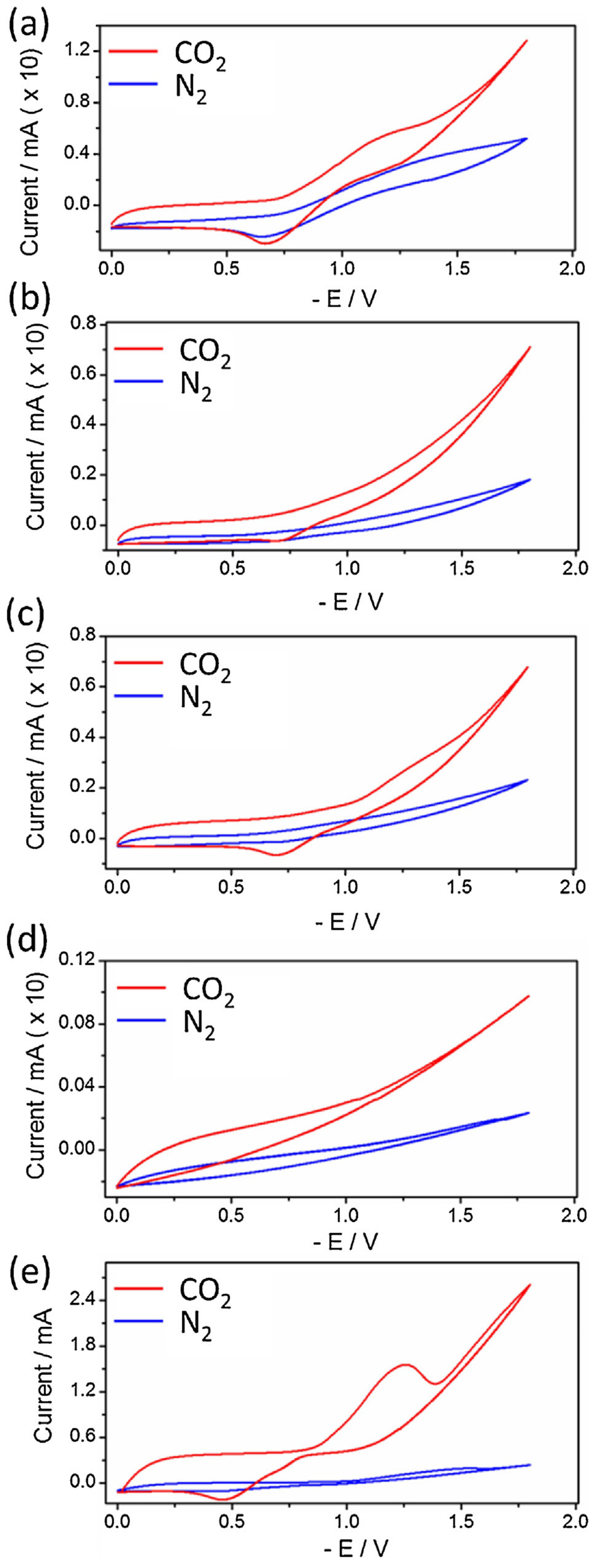

Fig. 2. Cyclic voltammograms of CdS/ITO electrodes in various electrolyte: (a) AN, (b) DMF, (c) DMSO, (d) THF, and (e) H_2O.

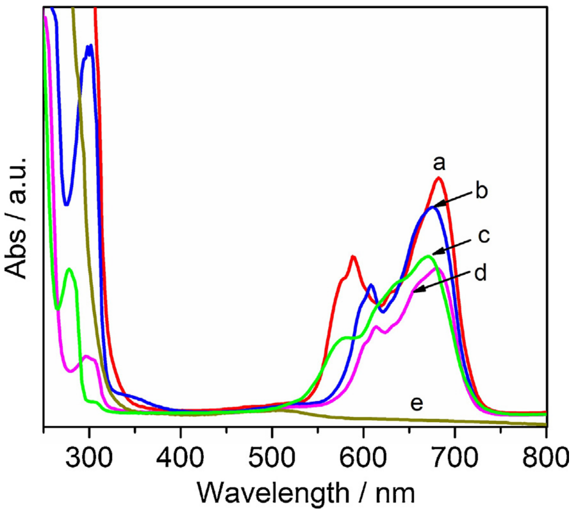

Fig. 3. UV–vis absorption spectra of Co^{2+}-solvent interaction recorded in different solvents: (a) AN, (b) DMF, (c) DMSO, (d) THF, and (e) H_2O.

bands located at around 300 nm are attributed to the metal-to-ligand charge transition (MLCT) band. The absorption bands positioned at 550–750 nm is due to the d–d transition in CoL_4 tetrahedral complexes [29]. These results indicate the strong interaction between the ligand and metal cation in the CO_2 systems when organic solvents are used as the reaction medium. However, only a weak absorption peak (*ca.* 480 nm) is observed when the Co^{2+} is dissolved in H_2O [30]. These changes are mainly induced by the alternation of the chemical nature of solvent molecules, such as the charge transfers between solvent and solute, solvent dependent aggregation and complexation.

Fig. 4 displays the UV–vis absorption spectra of the reaction mixture with the presence of bpy. As can be seen, after the introduction of bpy, the absorption position around 300 nm experiences an obvious red-shift, highlighting the enhanced MLCT process. While the absorption intensity at 550–750 nm is weakened, which indicats that the cobalt center is favored to coordinate with bpy, rather than the solvent molecules. It should be noted that the tertiary amine TEOA may also contribute to the solvent effect in photocatalytic CO_2 reduction systems by serving as a ligand to coordinate with cobalt center. Reults of UV–vis absorption characterizations demonstrate that the ligand (e.g., bpy) in CO_2 reduction system can alter the charge distribution of

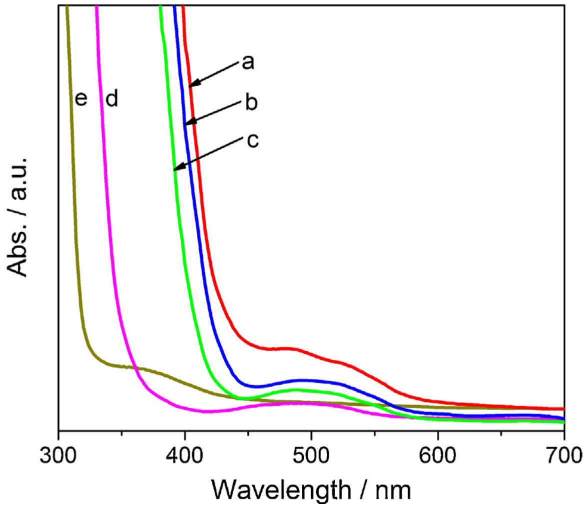

Fig. 4. UV–vis absorption spectra of $Co(bpy)_nCl_2$ in different solution: (a) AN, (b) DMF, (c) DMSO, (d) H_2O, and (e) THF.

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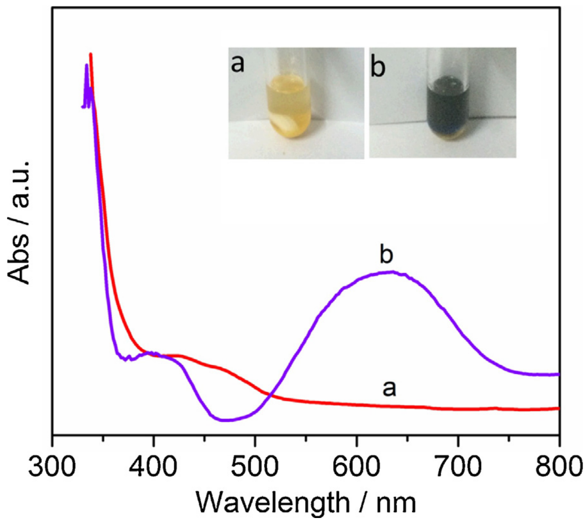
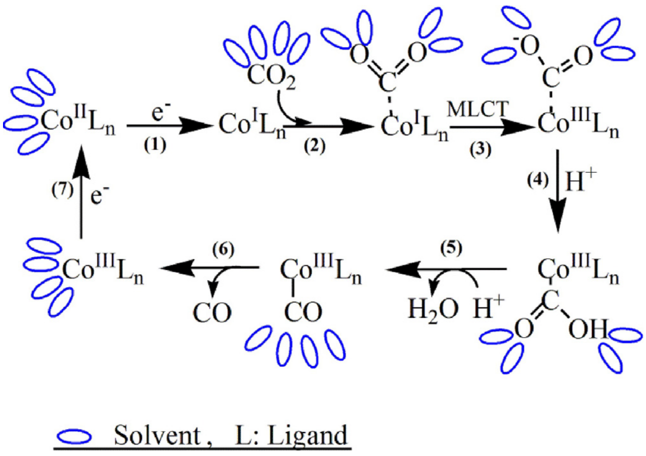


Fig. 5. UV–vis absorption spectra of the $Co(bpy)_n^+$ intermediates formed in the CO_2 reduction system with acetonitrile as the reaction solvent (a) before and (b) after light irradiation. Inserts are the corresponding photographs [9].

metal center, and eventually affect CO_2 adsorption and the catalytic performance of CO_2 reduction system.

To investigate the experiences of Co^{II} during CO_2 photoreduction processes, after photocatalysis the reaction solution is measured by UV–vis absorption spectroscopy. As shown in Fig. 5, using AN as the solvent, the color of reaction mixture is changed from orange to dark blue color upon light irradiation for about 10 min. This observation is accompanied by the formation of a new absorption band (*ca.* 500–700 nm) in the UV–vis absorption spectrum, together with the blue shift of the initial absorption bands at *ca.* 300 nm. The broad absorption band is attributed to the intramolecular charge-transfer from metal center to pyridinium moiety. Similar results are also detected when using other solvents as the reaction medium (Fig. S4), mainly because of the generation of a reducing Co^I-complex during photocatalytic CO_2 reduction reaction. The findings of UV–vis absorption measurements further indicate that the photochemical CO_2 conversion reaction is triggered by light irradiation. Interestingly, the color change of reaction mixture is also found when N_2 is used as the gas feedstock instead of CO_2 (Fig. S5), suggesting that the Co^I-complex can form as long as the process is operated in anaerobic condition.

Based on the results of CO_2 reduction evaluation and photo-/electro-chemcial characterizations, a possible mechanism is proposed as illustrated in Scheme 1. Under light irradiation, semiconductor photocatalyst is excited and liberates electrons from valence band to conduction band [31]. The photogenerated electrons are then departed from the surface of photocatalyst and grasped easily by Co (II) ion, thus generating the active intermediate of Co^I complex [8]. Meanwhile, H_2 evolution reaction through combination of Co^I intermediate with protons to form Co^{III}-hydride is probably similar to the CO_2 conversion [27]. The cobalt ion allows a strong interaction with CO_2 to form a metal carbonate. After the production of metal carbonate, the negative charge of the oxygen atom of CO_2 increased as a result of back-donation from an occupied metal orbital to an unoccupied CO_2 π^* orbital. Meanwhile the protonation is promoted and thus providing oxygen atom from activated CO_2 molecules by a proton to yield the reduction product CO [32]. During the processes, the properties of reaction solvent critically affect the generation and stability of active species through solvation. In view of the interaction between cobalt ion and solvent, the process of charge transfer between the metal ion and coordinated CO_2 is inevitably influenced by the nature of reaction solvent. As demonstrated from Scheme 1, a general explanation of solvent effects on photocatalytic CO_2 reduction is that the photoexicetd electrons are apt to be localized at oxygen atoms or carbon atoms of the metal-CO_2 carbonate, which is determined by the interaction between solvent and CO_2 molecules.



Scheme 1. Diagram of solvent effect on photocatalytic CO_2 reduction system.

In conclusion, we have demonstrated a detailed study of solvent effects on photocatalytic CO_2 reduction catalysis mediated by cobalt complex. The properties of solvent play a crucial role in determining the activity and selectivity of CO_2 photoreduction. Moreover, electrochemical and photochemical measurements are proved to be of useful tools to provide new insights into the solvent effect in photocatalytic CO_2 reduction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2017.09.019.

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