Supporting Information

Photochemical reduction of CO_2 into CO coupling with triethanolamine decomposition

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Experimental section

Chemicals

Triethanolamine (TEOA, GR) was purchased from Aladdin (Shanghai, China). Deuterium oxide (D_2O) was purchased from Shanghai Macklin Biochemical Co., Ltd. High purity CO_2 (99.99%) and N_2 (99.99%) gas was purchased from Huizhou Kaimeite Gas Co., Ltd. $^{13}CO_2$ gas was purchased from Innochem Technology Co., Ltd. All materials in this work were used as received without further purification.

Photochemical CO_2 reduction performance measurements

Photochemical CO_2 reduction performance were investigated in a 250 mL custom-built cell (efficient irradiation area about 12.5 cm^2) with different volume ratio of TEOA and H_2O. The light source was a 300 W Xenon lamp. In a typical experiment, 95 mL deionized water was added into the photoreaction cell, and then 5 mL TEOA was injected into the deionized water under the magnetic stirring condition. Prior to light irradiation, the mixture solution was degassed by bubbling high purity CO_2 gas for 30 min to remove the oxygen. The gaseous products were detected using on-line gas chromatography (GC) (Shimadzu, GC-2014C). The mixture solution after photochemical CO_2 reduction reaction was freeze-dried for 48 h to remove water, while the achieved residual substance was used for subsequent characterization.

The apparent quantum yield (AQY) was performed with a 300 W Xe lamp irradiation equipped with various band-pass filters (254, 275, 295, 313, 350, 365 and 380 nm). And the photon flux of the incident light was quantified by a Ray virtual radiation actinometer. The AQY was calculated according to equation 1:

$$AQE\ [\%] = n_{CO} / n_p \times 100\% \quad (1)$$

Where the n_{CO} represents the mole number of CO generation, and the n_p represents the number of incident photons.

Characterizations

The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-

FTIR) was recorded on a Fourier transform infrared spectrometer (Niclet iS50). The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy were acquired on Bruker Avance III 600 MHz spectrometer. High resolution mass spectra (MS) were recorded using a Q Exactive mass spectrometer (Thermo Fisher Scientific, USA). The ultraviolet-visible (UV-vis) absorption spectrum was performed on lambda 950 UV/VIS spectrometer (Perkin Elmer, USA).
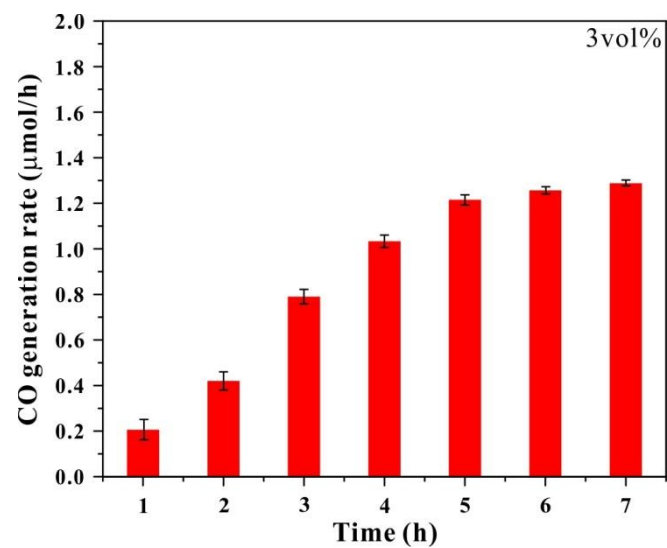
Figure S1 The time-depended performance of photochemical CO_2 reduction in 3vol% TEOA aqueous solution under light irradiation. The error bars represent the standard deviation of three separate measurements.
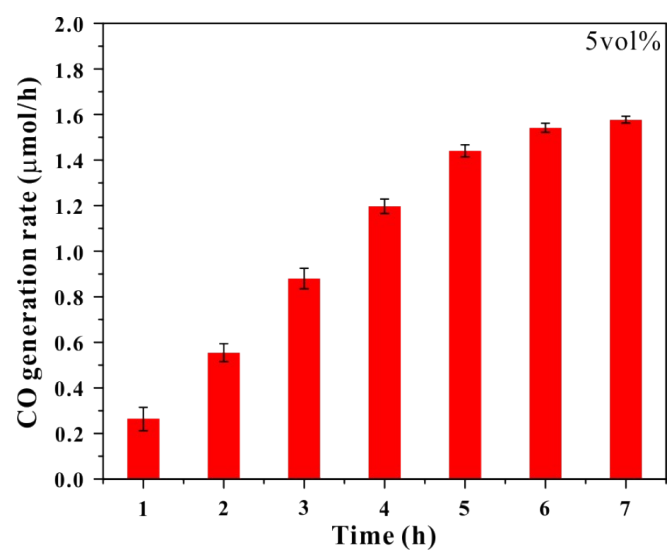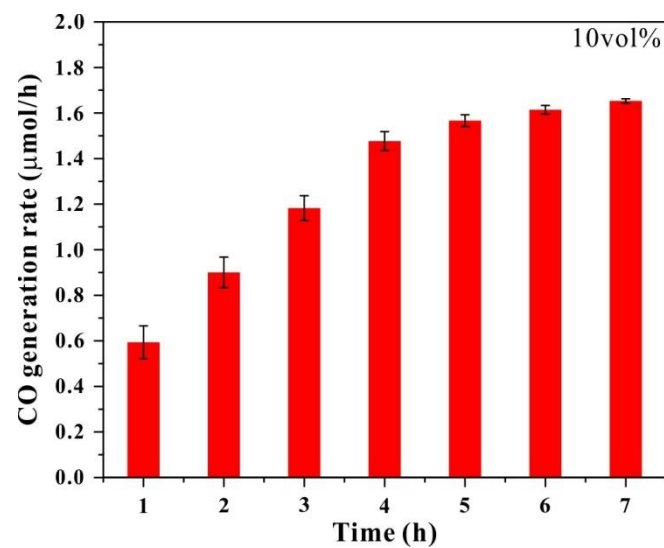
Figure S2 The time-depended performance of photochemical CO_2 reduction in 5vol% TEOA aqueous solution under light irradiation. The error bars represent the standard deviation of three separate measurements.
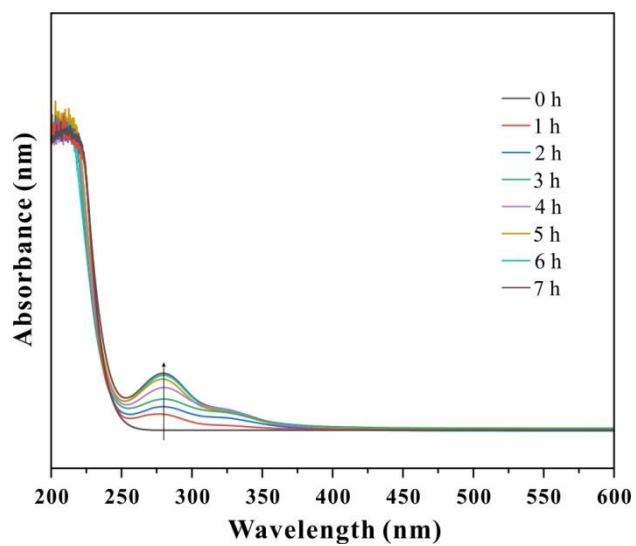
Figure S3 The time-depended performance of photochemical CO_2 reduction in 10vol% TEOA aqueous solution under light irradiation. The error bars represent the standard deviation of three separate measurements.

Figure S4 The UV-vis absorption spectra of 5vol% TEOA aqueous solution during photochemical CO_2 reduction with different irradiation time.

Table S1 The photochemical reaction under different sets of conditions.

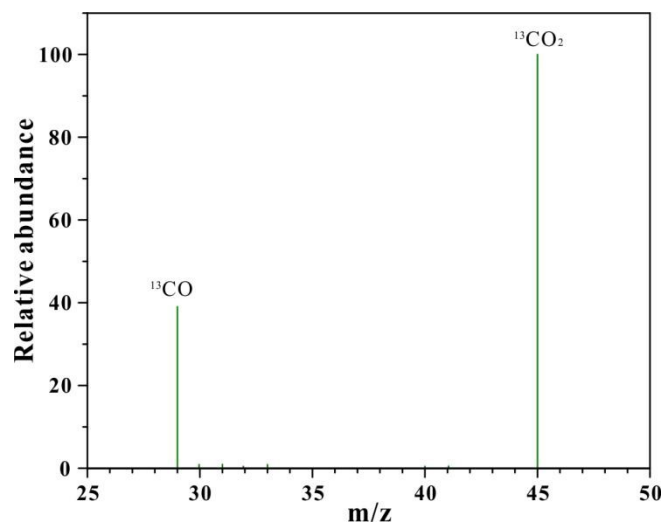| Entry	Gas	Ligth condition	TEOA volume percentage	CO generation rate (μmol/h)
1	CO_2	Full spectrum	3vol%	1.29
2	CO_2	Full spectrum	5vol%	1.58
3	CO_2	Full spectrum	10vol%	1.65
4	CO_2	visible light（$\lambda \geq 420$ nm）	5vol%	−
5	N_2	Full spectrum	5vol%	−

Figure S5 Mass spectra via gas chromatography of the generated gas from 5vol% TEOA aqueous solution under 1 atm $^{13}CO_2$ within 10 h irradiation.

Table S2. The results of AQY measurements under AM 1.5G solar simulator light source with different wavelengths in 5vol% TEOA aqueous solution.

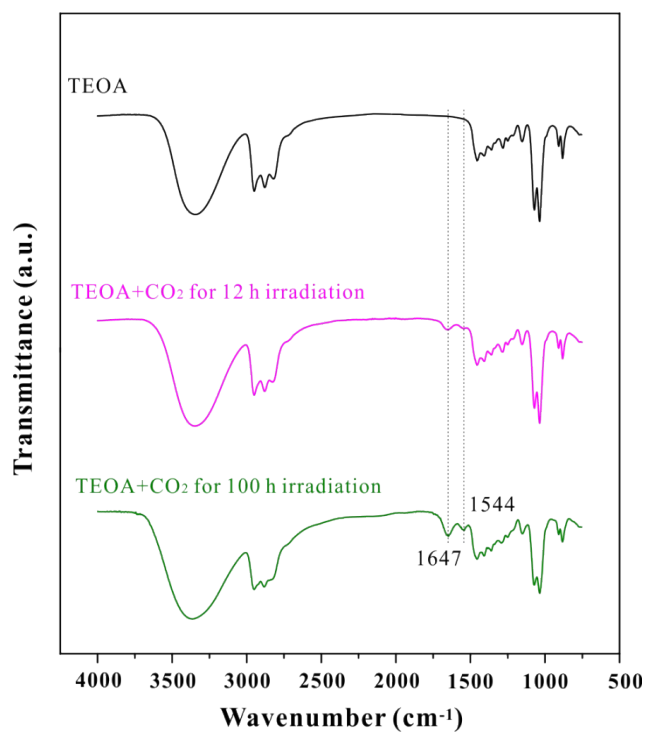| Wavelength (nm)	N_a (μmol h^{-1})	Activity (μmol h^{-1}) CO	AQY of CO_2 (%)
254	66.24	0.113	0.086
275	64.81	0.039	0.030
295	57.65	0.051	0.044
313	67.68	0.015	0.011
350	324.03	0.050	0.008
365	381.62	0.074	0.010
380	237.67	0.080	0.017

Figure S6 The ATR-FTIR observation of pure TEOA, TEOA after 12 or 100 h irradiation under CO_2 bubbling condition. The TEOA after photochemical reaction in 5vol% TEOA aqueous solution is achieved by freeze-drying for 48 h to remove residual water.
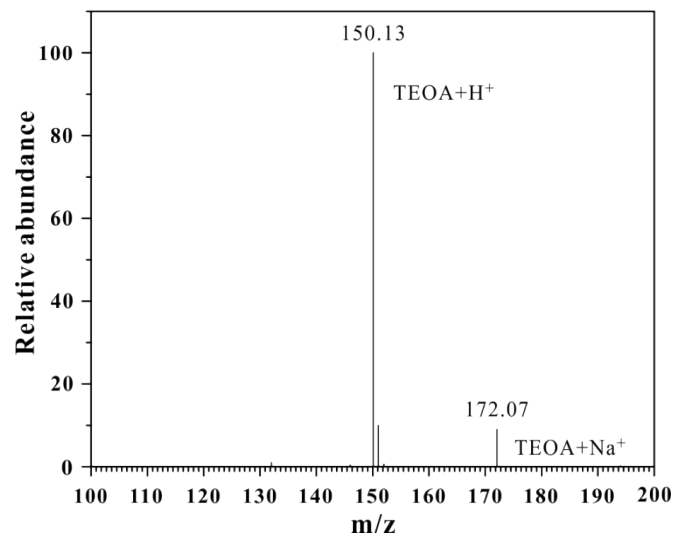
Figure S7 Mass spectra via liquid chromatography of pure TEOA. The solution consists of 100 µL pure TEOA and 1.9 mL deionized water.
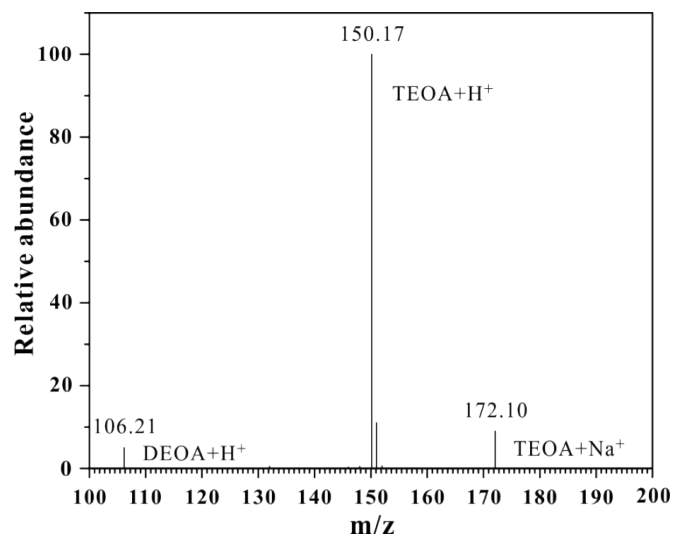
Figure S8 Mass spectra via liquid chromatography of TEOA after 12 h irradiation under CO_2 bubbling condition. The solution consists of 100 μL TEOA and 1.9 mL deionized water. The TEOA after photochemical reaction in 5vol% TEOA aqueous solution is achieved by freeze-drying for 48 h to remove residual water.
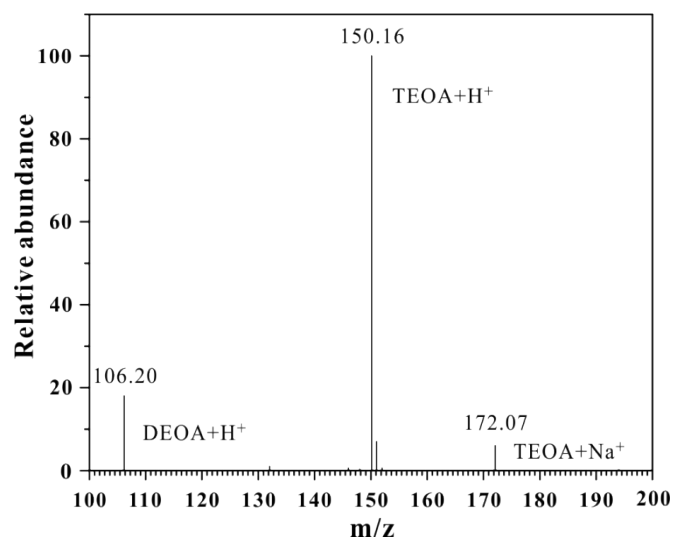
Figure S9 Mass spectra via liquid chromatography of TEOA after 100 h irradiation under CO_2 bubbling condition. The solution consists of 100 µL TEOA and 1.9 mL deionized water. The TEOA after photochemical reaction in 5vol% TEOA aqueous solution is achieved by freeze-drying for 48 h to remove residual water.
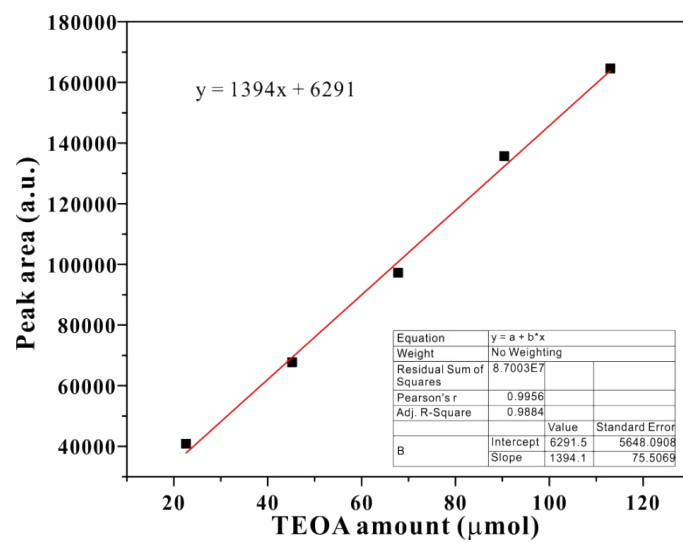
Figure S10 Standard curve of TEOA for ^{1}H NMR analysis.