Enhanced Photocatalytic CO_2 Reduction over Co-Doped NH_2-MIL-125(Ti) under Visible Light

Yanghe Fu,[a, b] Huan Yang,[a] Rongfei Du,[a] Gaomei Tu,[a] Chunhui Xu,[a] Fumin Zhang,[a] Maohong Fan[b*] and Weidong Zhu[a*]

[a] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, People's Republic of China.
[b] Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY 82071, USA.

Supporting Information

Table S1. Produced HCOOH in the photocatalytic reduction of CO_2 using TEOA as the sacrificial agent upon visible-light irradiation[a]

Entry	Catalyst	HCOOH ($\mu mol\ g_{cat}^{-1}\ h^{-1}$)
1	NH_2-MIL-125(Ti)	16.3
2[b]	$Co(NO_3)_2{\cdot}6H_2O$ + NH_2-MIL-125(Ti)	15.8
3[c]	CoO + NH_2-MIL-125(Ti)	17.2
4	1 wt.% Co/NH_2-MIL-125(Ti)	38.4

[a] Reaction conditions: 50 mg of photocatalyst, a MeCN/TEOA volume ratio of 5 to 1, and a total solution volume of 60 mL upon visible-light irradiation (800 nm ≥ λ ≥ 420 nm) for 10 h.

[b] With $Co(NO_3)_2{\cdot}6H_2O$ (0.5 mg) and NH_2-MIL-125(Ti) (49.5 mg).

[c] With CoO (0.5 mg) and NH_2-MIL-125(Ti) (49.5 mg).

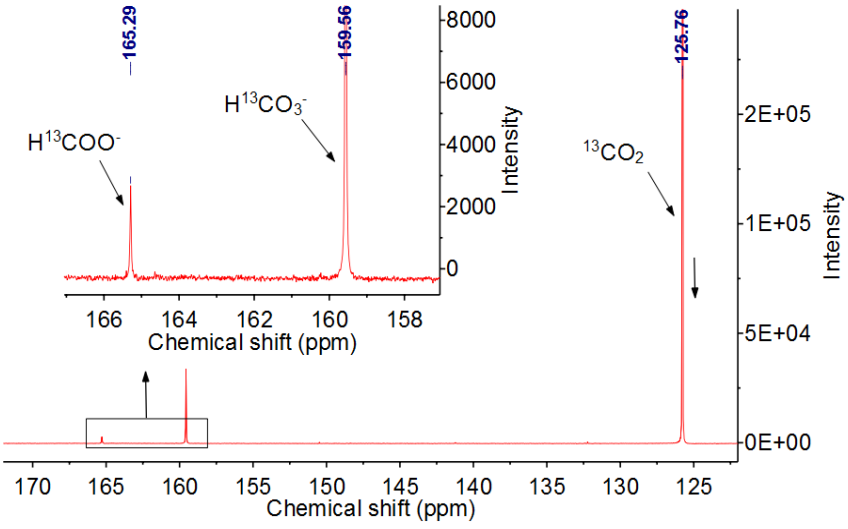

Figure S1. ^{13}C NMR spectrum of the product solution from the photocatalytic reduction of $^{13}CO_2$ over 1.0 wt.% NH_2-MIL-125(Ti) for 20 h upon visible-light irradiation.

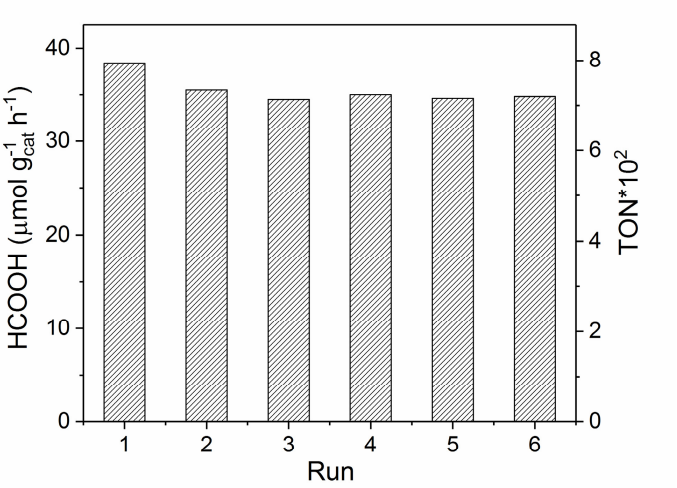

Figure S2. Reusability of 1.0 wt.% Co/NH_2-MIL-125(Ti) in the photocatalytic reduction of CO_2 upon visible-light irradiation. TON (turnover number) was based on HCOOH produced per mole of the Ti species in the catalyst and the reaction of 10 h. Reaction conditions: 50 mg of photocatalyst, a MeCN/TEOA volume ratio of 5 to 1, and a total solution volume of 60 mL upon visible-light irradiation (800 nm $\geqslant \lambda \geqslant$ 420 nm) for 10 h.

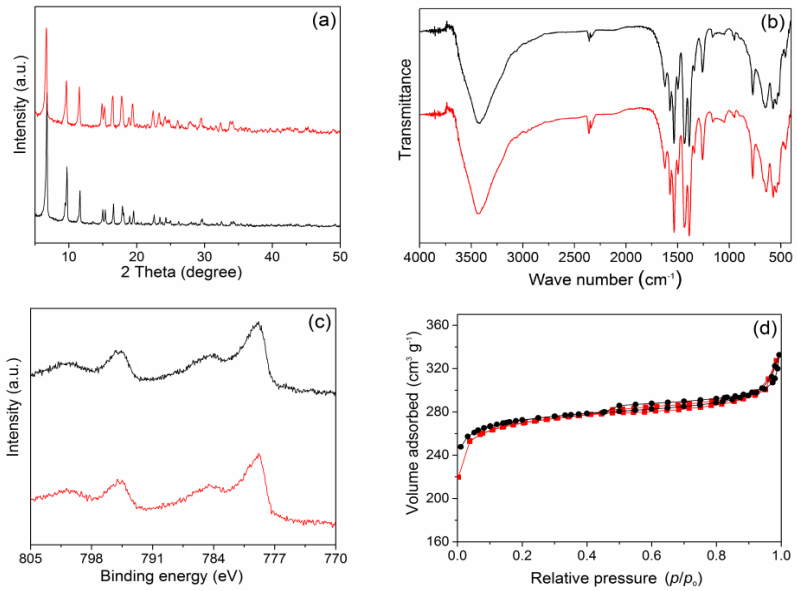

Figure S3. XRD patterns (a), IR spectra (b), N_2 adsorption-desorption isotherms at -196 °C (c), and high-resolution XPS spectra (d) of the fresh (black) and used (red) 1.0 wt.% Co/NH_2-MIL-125(Ti) after the irradiation of visible light.

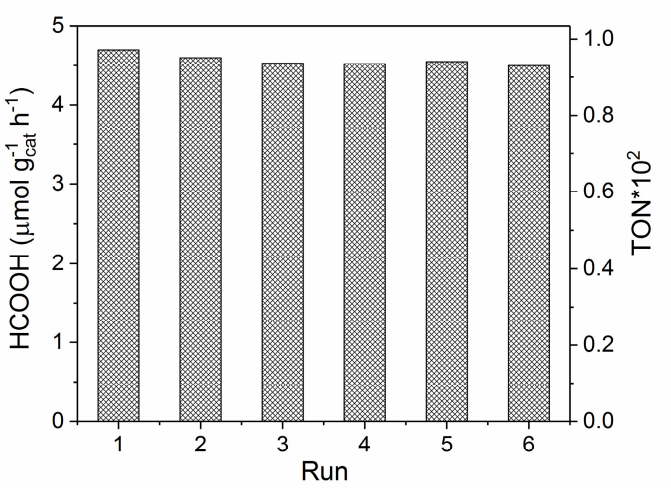

Figure S4. Reusability of 1.0 wt.% Co/NH_2-MIL-125(Ti) in the photocatalytic reduction of CO_2 upon UV-light irradiation. TON (turnover number) was based on HCOOH produced per mole of the Ti species in the catalyst and the reaction of 10 h. Reaction conditions: 50 mg of photocatalyst, a MeCN/TEOA volume ratio of 5 to 1, and a total solution volume of 30 mL upon UV-light irradiation (four 4 W UV lamps with a wavelength centered at 365 nm used as an irradiation source) for 10 h.

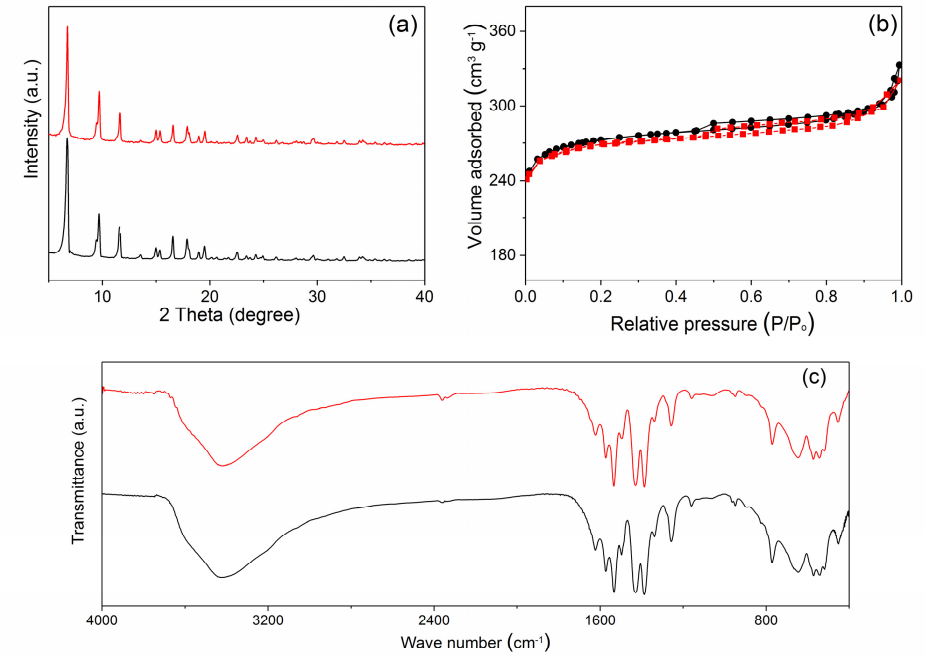

Figure S5. XRD patterns (a), N_2 adsorption-desorption isotherms at -196 °C (b), and FT-IR spectra (c) of the fresh (black) and used (red) 1.0 wt.% Co/NH_2-MIL-125(Ti) after the irradiation of UV light.

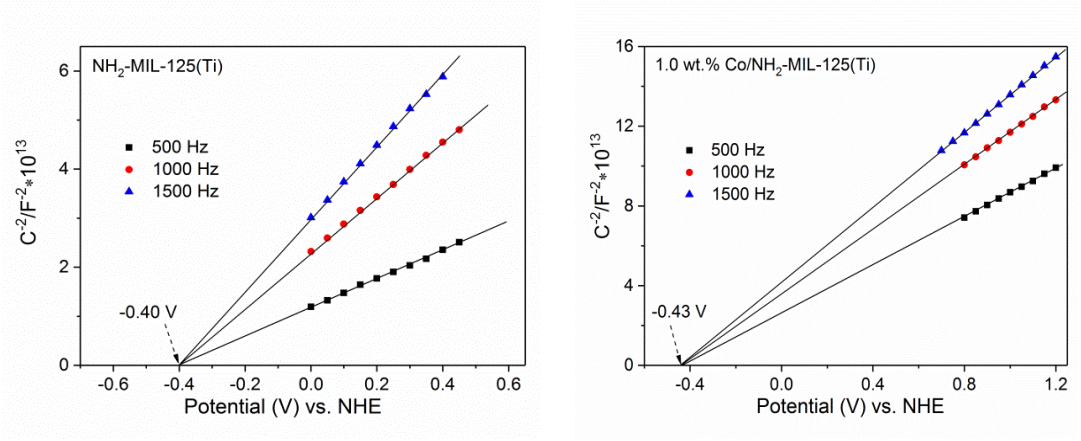

Figure S6. Mott-Schottky plots of NH_2-MIL-125(Ti) (left) and 1.0 wt.% Co/NH_2-MIL-125(Ti) (right) measured at different frequencies.

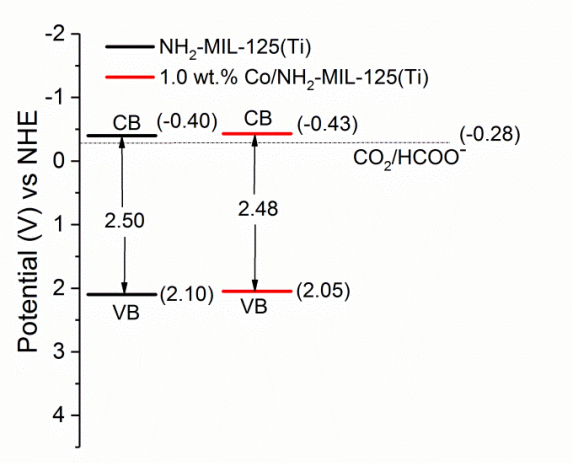

Figure S7. Calculated band positions for NH_2-MIL-125(Ti) and 1.0 wt.% Co/NH_2-MIL-125(Ti).

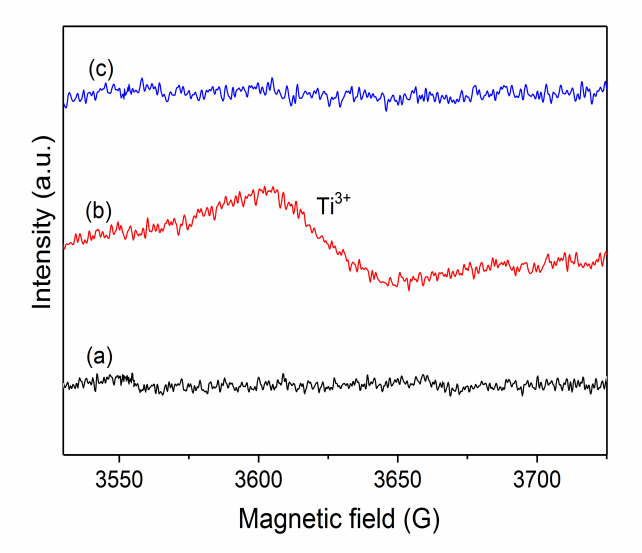

Figure S8. ESR spectra of 1.0 wt.% Co/NH_2-MIL-125(Ti) with TEOA in the dark (a), upon visible-light irradiation for 1 min in N_2 (b), and after the introduction of CO_2 without visible-light irradiation (c).