Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Metal-organic framework (ZIF-67) as efficient cocatalyst for photocatalytic reduction of CO_2: the role of morphology effect

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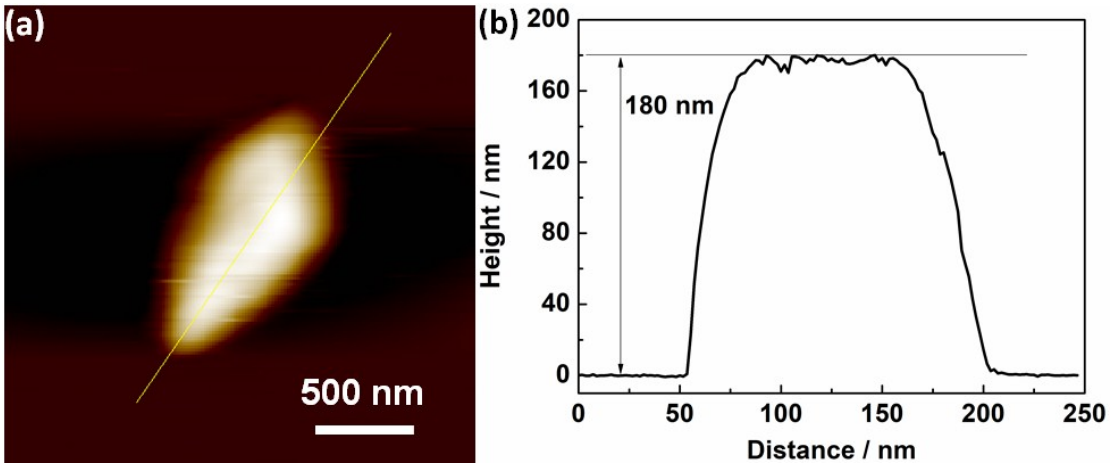

Figure S1. (a) AFM image of ZIF-67_3 and (b) height profile.

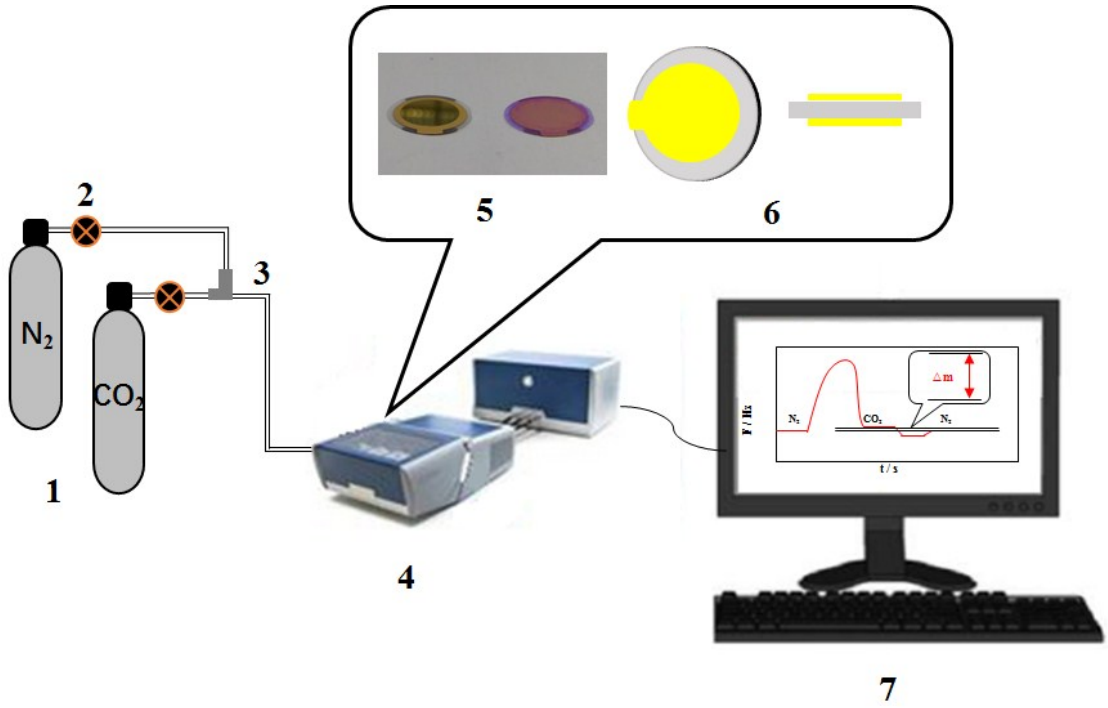

Figure S2. Schematic drawing of in-situ quartz-crystal microbalance setups coupled with high-temperature chamber for CO_2 adsorption. (1) gas supply (N_2 and CO_2); (2) gas flow controller; (3) three-way valve gas distributor; (4) QCM with high temperature chamber; (5) QCM sensor with and without ZIF-67 coating; (6) QCM sensor: top view(lift), and cross section(right); (7) computer.

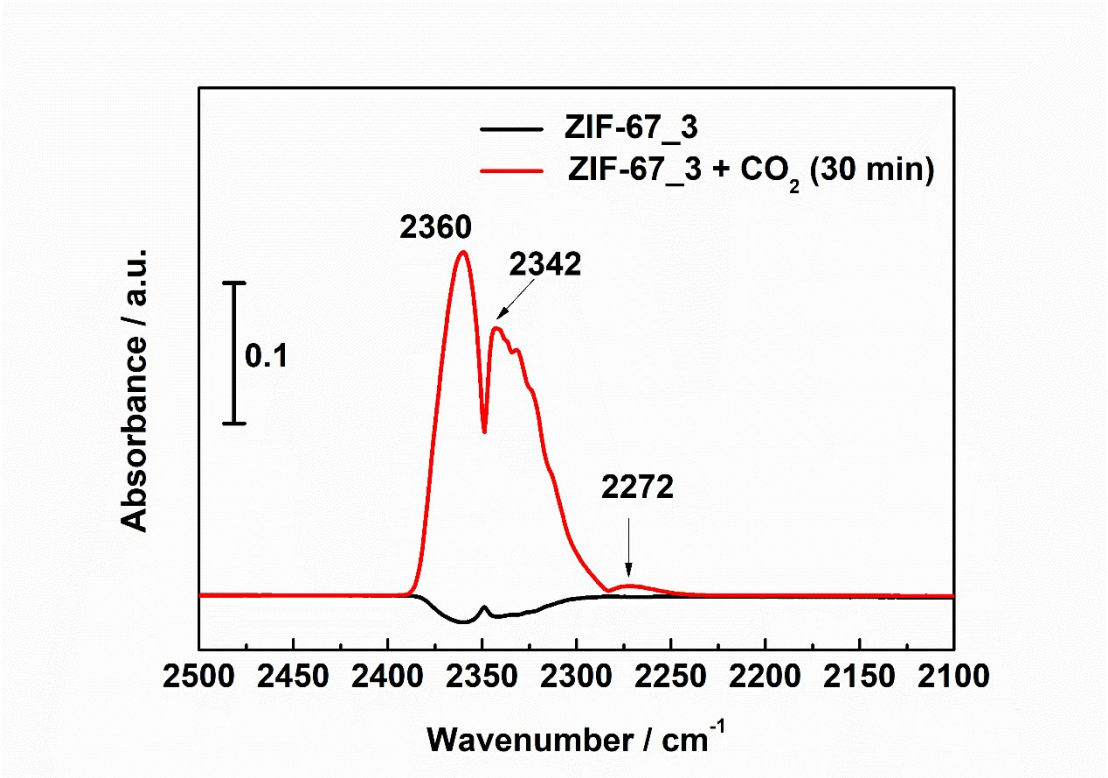

Figure S3. In-situ FTIR spectra recorded with ZIF-67_3 sample with and without CO_2. The solution was continuously bubbled with CO_2 during the measurement. Therefore, the band at 2360 cm^{-1} and 2342 cm^{-1} can be attributed to the R branch and P branch of the antisymmetric of CO_2 stretching vibrations, respectively.

As can be seen from Figure S3, with the introduction of CO_2, a band at 2272 cm^{-1} was observed, which can be assigned to asymmetric stretching vibrations of CO_2 molecule adsorbed on Co^{2+}.

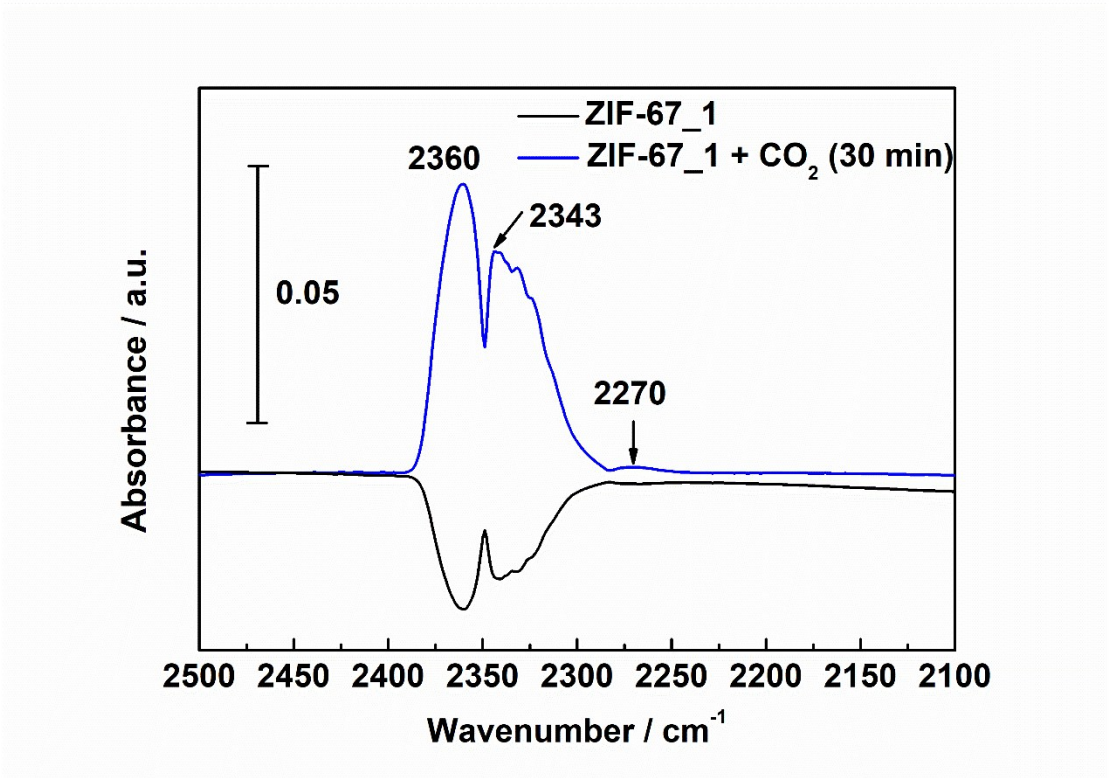

Figure S4. In-situ FTIR spectra recorded with ZIF-67_1 sample with and without CO_2. The solution was continuously bubbled with CO_2 during the measurement. Therefore, the band at 2360 cm^{-1} and 2343 cm^{-1} can be attributed to the R branch and P branch of the antisymmetric of CO_2 stretching vibrations, respectively.

As can be seen from Figure S4, with the introduction of CO_2, a band at 2270 cm^{-1} was observed, which can be assigned to asymmetric stretching vibrations of CO_2 molecule adsorbed on Co^{2+}.

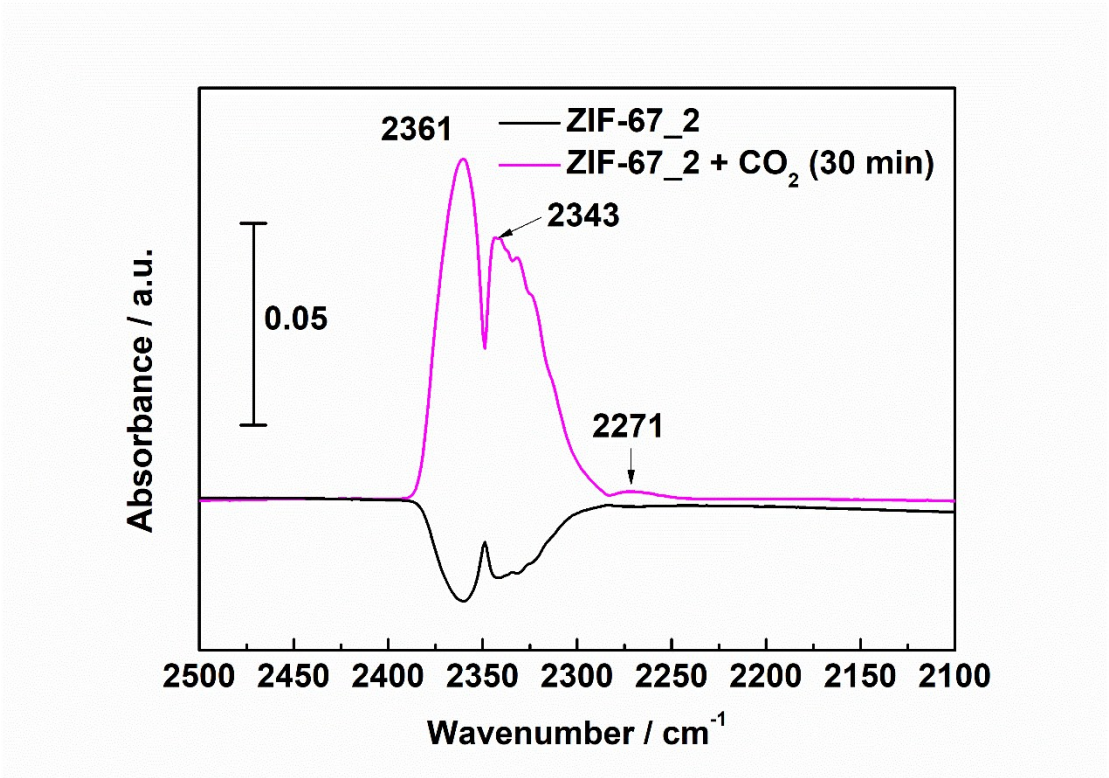

Figure S5. In-situ FTIR spectra recorded with ZIF-67_2 sample with and without CO_2. The solution was continuously bubbled with CO_2 during the measurement. Therefore, the band at 2361 cm^{-1} and 2343 cm^{-1} can be attributed to the R branch and P branch of the antisymmetric of CO_2 stretching vibrations, respectively.

As can be seen from Figure S5, with the introduction of CO_2, a band at 2271 cm^{-1} was observed, which can be assigned to asymmetric stretching vibrations of CO_2 molecule adsorbed on Co^{2+}.

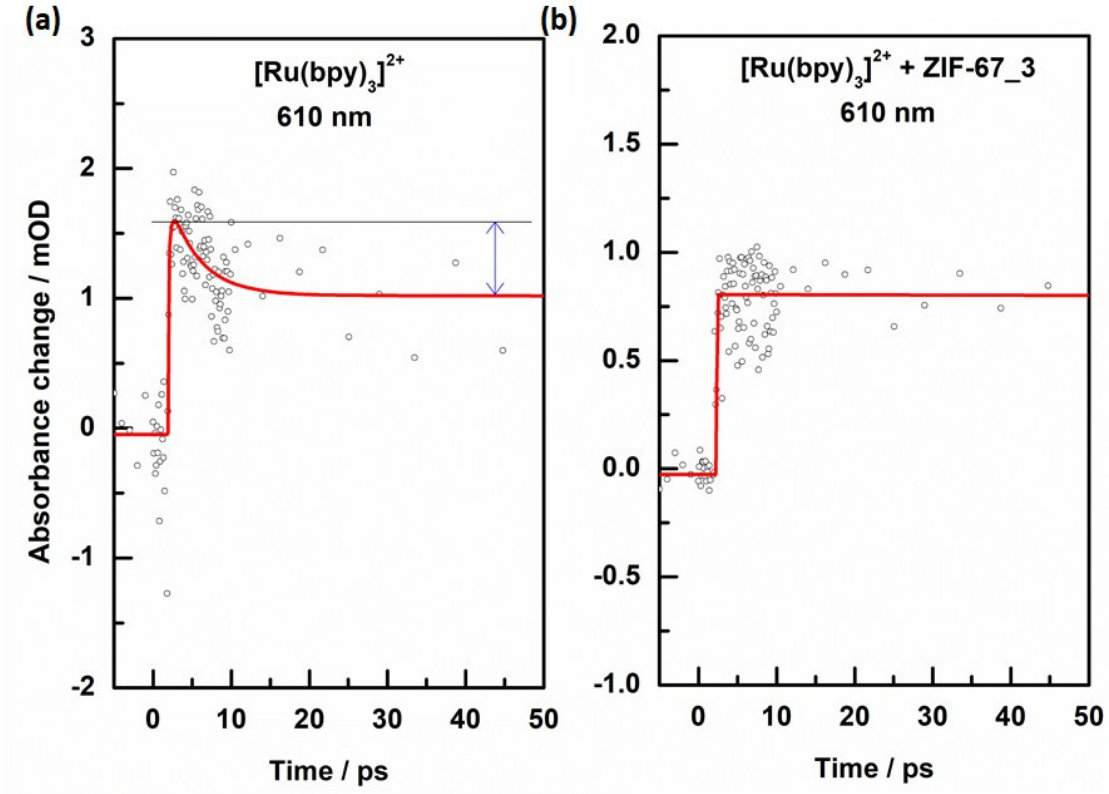

Figure S6. Transient kinetics monitored at 610 nm for $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ +ZIF-67_3.

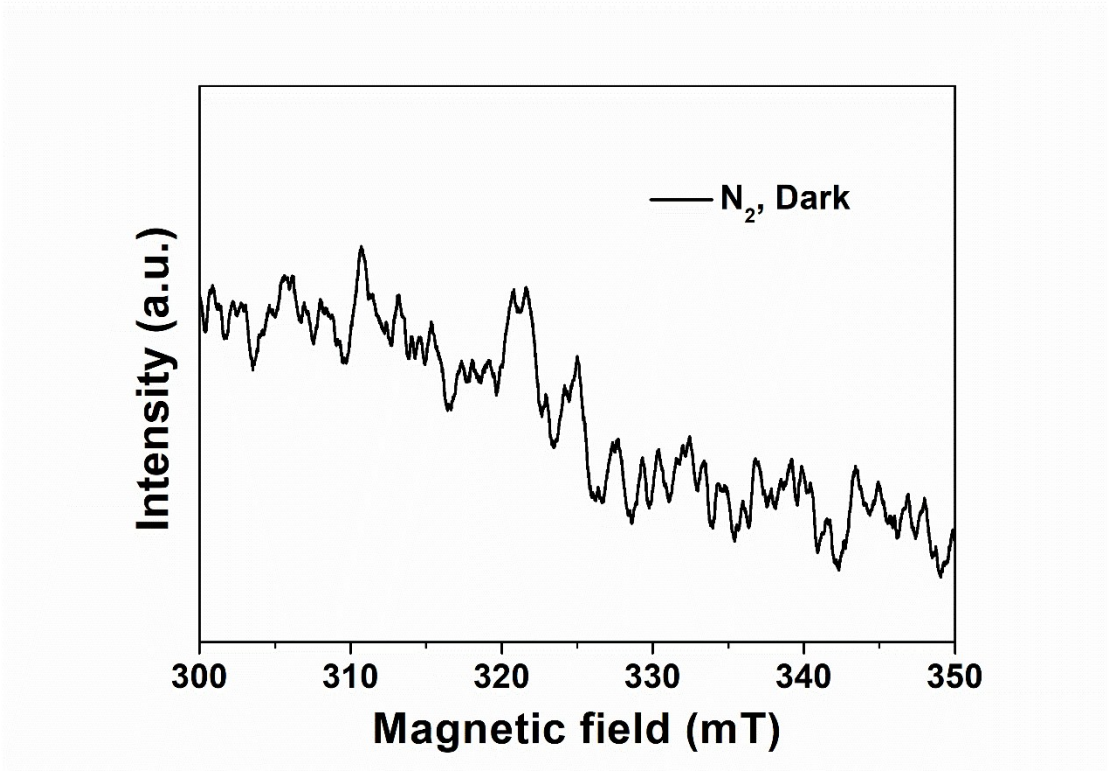

Figure S7. ESR signal of $[Ru(bpy)_3]^{2+}$ + ZIF-67_3 recorded at 150 K in N_2 without light.

Table S1. Vibrational frequencies of MIM, and the as-synthesized ZIF-67 materials together with their corresponding band assignments.

Nr.	Band position / cm^{-1}		Assignment
	MIM	ZIF-67_1-3	
1	680, 741, 754	687,754	$\gamma_{imidazole\ ring}$
2	900-1350	900-1350	$\beta_{imidazole\ ring}$
3	1372	1382	$\upsilon_{sym}CH_3$
4	1457	1481	$\upsilon_{assym}CH_3$
5	1350-1500	1350-1500	$\upsilon_{imidazole\ ring}$
6	1594	1562	
7	1844	/	υ_{N-H}

Table S2. BET surface area and microporous volume of ZIF-67 of different morphology.

Sample	S_{BET} / m^2g^{-1}	V_{pore} / cm^3g^{-1}	V_{micro} / cm^3g^{-1}
ZIF-67_1	1698.877	0.6924	0.581
ZIF-67_2	835.704	0.3863	0.288
ZIF-67_3	16.245	0.05079	0

Table S3. Reported MOF materials for converting CO_2 to CO under visible light irradiation.

MOFs	Condition				Product CO[μmol]	TON	Ref.
	Quantity	Light [nm]	Solvent (Sacrificial agent)	Time [h]			
Co-ZIF-9	0.8 μmol	λ>420	MeCN/H_2O (TEOA)	0.5	41.8	52.2	[1]
ZIF-67	0.45 μmol	λ>420	MeCN/H_2O (TEOA)	0.5	37.4	112	[2]
Co-ZIF-9	4 μmol	λ>420	MeCN/H_2O (TEOA)	1	50.4	12.6	[3]
MOF-1		410	MeCN/H_2O (TEA)	6	/	6.44	[3b]
UiO-66/ carbon nitride	0.1 g	400 < λ < 800	MeCN/H_2O (TEA)	6	59.4	/	[4]
MOF 4	1-2 μmol	λ>300	MeCN (TEA)	6	/	5	[5]
ZIF-67_3 (ZIF-L)	4.4 μmol	λ>400	MeCN/H_2O (TEOA)	3.8	15.57	3.5	This work
MOF-525-Co	2 mg	400 < λ < 800	MeCN (TEOA)	6	2.25	/	[6]
CPO-27-Mg/TiO_2	10 mg	365	water vapor	10	409		[7]
Ag⊂Re3-MOF	0.5-8 μmol	400 < λ < 700	MeCN (TEA)	50	/	2.8	[8]
Re-MOF-(NH_2)(X%)	5 mg	400 < λ < 700	TEA	6	33	/	[9]

References

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