Supporting Information

Construction of Stable Ru-Re Hybrid System Based on Multifunctional MOF-253 for Efficient Photocatalytic CO_2 Reduction

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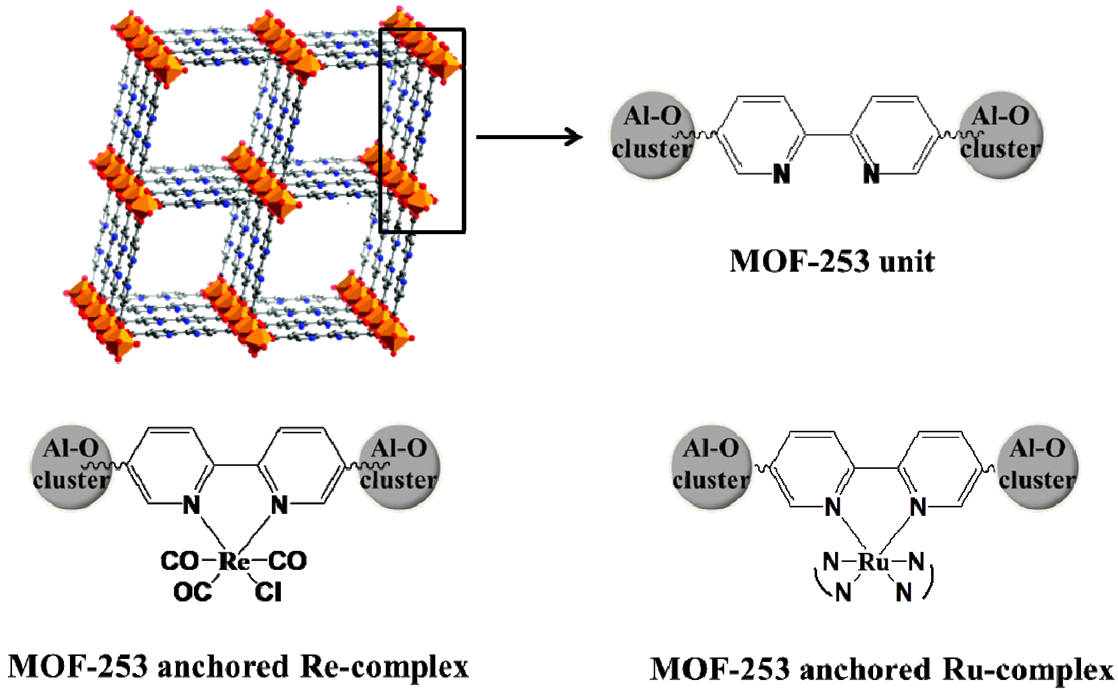
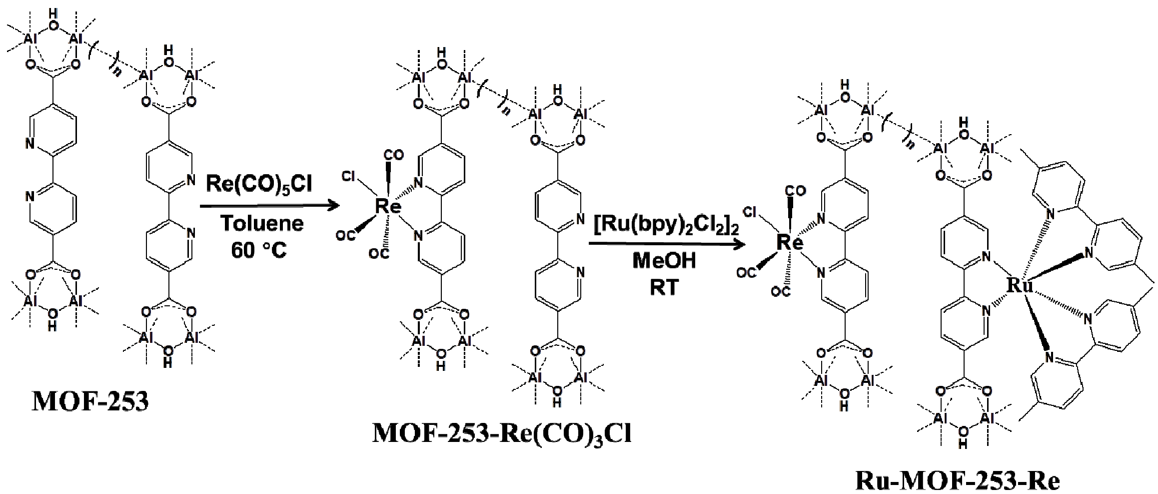
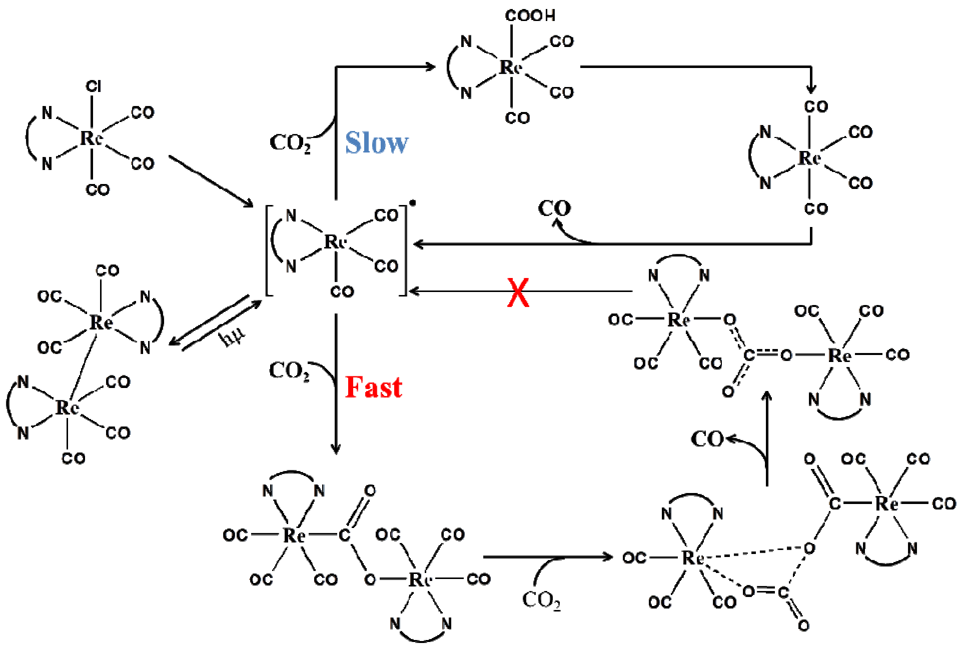


Scheme S1 Structure of MOF-253 viewed from b axis (from reference 1), structures of MOR-253 supported Re and Ru complex.



Scheme S2 Synthetic procedures for MOF-253-Re$(CO)_3$Cl and Ru-MOF-253-Re.



Scheme S3 Mechanism for photocatalytic CO_2 reduction over [Re(N,N')$(CO)_3$X] under visible light.

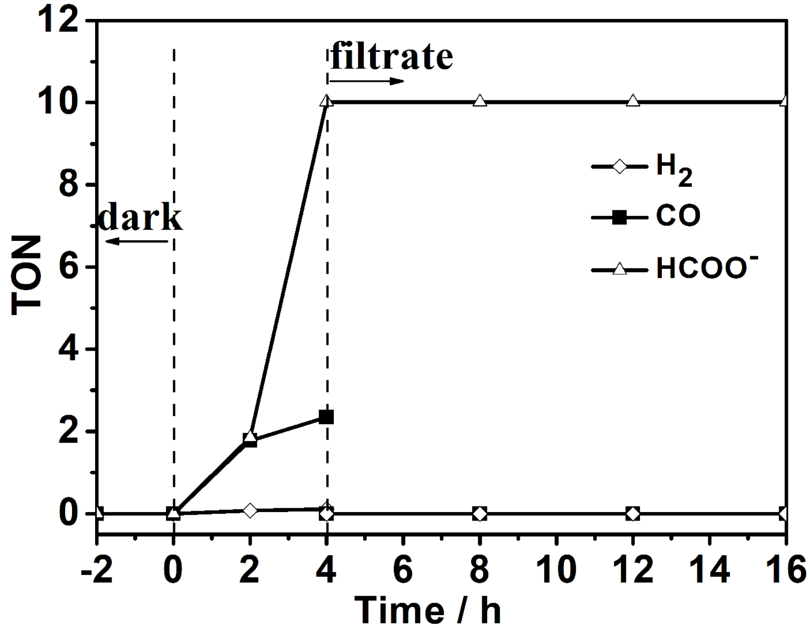


Figure S1 The TON of products formed over MOF-253-Re$(CO)_3$Cl after 4 h reaction and filtrate solution for another 12 h.

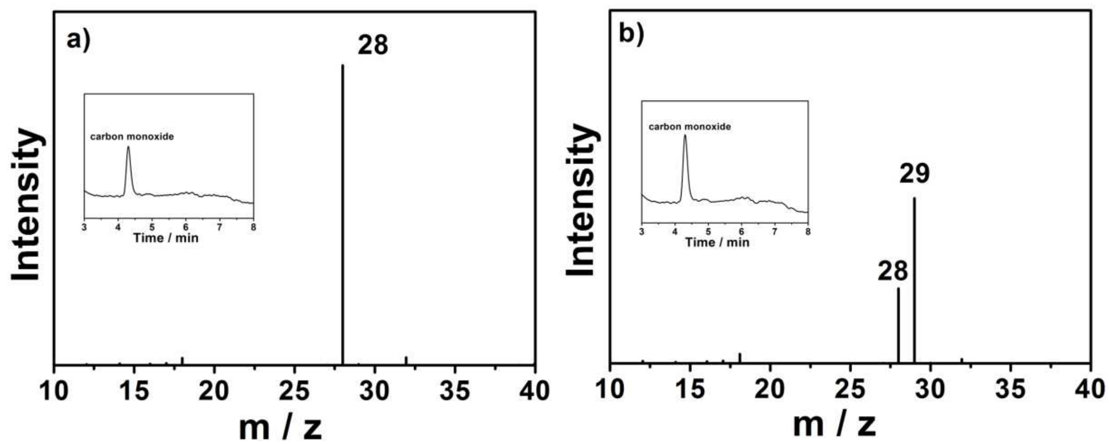


Figure S2 The GC-MS spectra for the CO obtained from the reaction with $^{12}CO_2$ (a) and $^{13}CO_2$ (b) in mixture of DMF-d_7/TEOA/H_2O (5/1/0.2) under visible light.

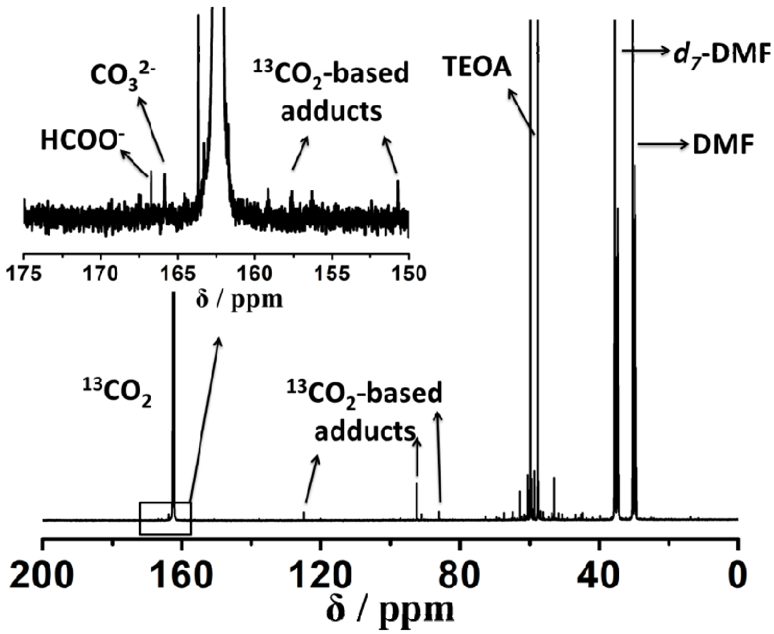


Figure S3 The ^{13}C NMR spectrum for the product obtained from the reaction with $^{13}CO_2$ in mixture of DMF-*d*7/TEOA/H_2O (5/1/0.2) under visible light.

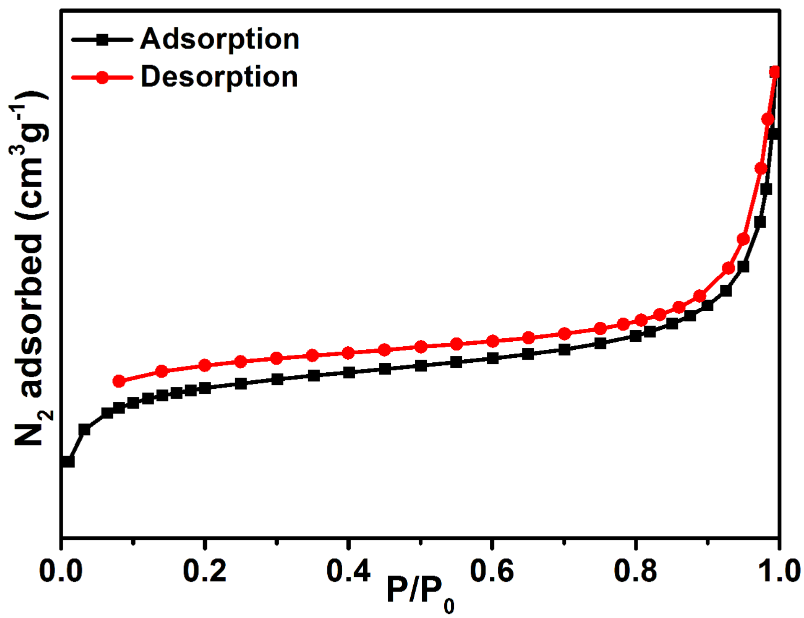


Figure S4 N_2 adsorption/desorption isotherms (77 K) of Ru-MOF-253-Re.

Table S1 Some Examples of Mononuclear and Supramolecular Re-Based Photocatalyst for the CO_2 Reduction and Their Turnover Numbers.[a]

Entry	Catalyst	Donor	TON[b] / Time (h)	Ref
1	$Re(dcbpy)(CO)_3Cl$	TEOA	9.4 / 4	This Work
2	Ru-MOF-253-Re	TEOA	28.8 /4	This Work
3	$[Re(dmb)(CO)P(OEt)_3)]^+$	TEOA	4.1 / 17	2
4	$[Re(bpy)(CO)P(OEt)_3)]^+$	TEOA	5.9 / 13	2
5	$[Re(bpy)(CO)(P(O\text{-}i\text{-}Pr)_3)]^+$	TEOA	6.2 / 13	2
6	*fac*-$[Re(bipy)(CO)_3(PPh_3)]^+$	TEOA	12 / 20	3
7	$Re(dcbpy)(CO)_3Cl\text{-}D\text{-}SiO_2$	TEOA	8.8 / 4	4
8[c]	*fac*-$[Re(bpy)(CO)_3(PPh_3)]^+(OTf)^-$/Bp-PMO	TEOA	2.2 / 24	5
9	$Re(bpy)(CO)_3Cl$-POP	TEOA	5 / 20	6
10	UiO-67-$Re(bpy)(CO)_3Cl$	TEA	10.9 / 20	7
11	$[Rubpy_2(MebpyCH_2CH_2bpyMe)Re(CO)_3Cl]Cl_2\cdot 8H_2O$	Sodium Ascorbate	26.2 / 24	8
12[d]	$[Re(bpy)(CO)_2(PPh_3)_2]^+$	BNAH	16.5 / 6	9
13	K41C_$ReC_{ys}Ru_{NH}$	BNAH	15.6 / 15	10
14[e]	$[Ru(BL_2)Re(CO)_2\{P(p\text{-}F\text{-}C_6H_4)_3\}_2]^{3+}$	BNAH	212 / 20	11
15[f]	$[Ru(dmb)_2(bpy\text{-}CH_2\text{-}CH_2\text{-}bpy)Re(CO)_3Cl]Cl_2\cdot 5H_2O$	$BI(CO_2H)H$	130 / 6	12

16	$[Cl(CO)_3Re(mfibpy)Ru(dmb)_2](PF_6)_2$	BNAH	28 / 18.5	13
17	$[(dmb)_2Ru(bpyCH_2\text{-}CH_2\text{-}CH_2bpy)Re(CO)_3Cl](PF_6)_2$	BNAH	170 / 16	13
18	$[(CH_3CN)(CO)_3Re(bpy(CH_2)_{14}bpy)Re(CO)_3(CH_3CN)](PF_6)_2$	BNAH	103 / 18	14
19[e]	$[(CH_3CN)(CO)_3Re(bpy(CH_2)_2bpy)Re(CO)_3(CH_3CN)](PF_6)_2$	BNAH	192 / 18	14
20	$[(dmb)_2Ru(bpyCH_2\text{-}CH_2bpy)Re(CO)_2\{POEt)_3\}_2](PF_6)_3$	BNAH	27 / 20	15
21	$[(dmb)_2Ru(bpyCH_2\text{-}CH_2bpy)Re(CO)_2\{P(p\text{-}FPh)_3\}_2](PF_6)_3$	BNAH	207 / 20	15
22	$[(5dmb)_2Os(bpyCH_2\text{-}CH_2bpy)Re(CO)_2\{P(p-F\text{-}C_6H_4)_3\}_2](PF_6)_3$	BIH	762/ 20	16
23	$[(5dmb)_2Os(bpyCH_2\text{-}CH_2bpy)Re(CO)_2\{P(p\text{-}Cl\text{-}C_6H_4)_3\}_2](PF_6)_3$	BIH	1138 / 20	16

[a] Abbreviations used: TEOA =triethanolamine, TEA=triethylamine,BNAH=1-benzyl-1,4-dihydronicotinamide, BI(CO_2H)H = 2-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)benzoic, BIH =1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]-imidazole, dcbpy = 2,2'-bipyridine-5,5'-dicarboxylic acid, bpy = 2,2'-bipyridine, dmb = 2,2'-bipyridine-5,5'-dimethyl, OTf = CF_3SO_3, BL_2 = 4-methyl-2-(5-(2-(5-(4-methylpyridin-2-yl)pyridin-3-yl)ethyl)pyridin-3-yl)pyridine. [b] TON is the turnover number for production of CO and HCOOH molecules per catalyst site. [c]Catalyst was deactivated after 5h. [d]λ_{ex}> 500 nm. [e] $[Ru(dmb)_3]^{2+}$ as photosensitizer. [f]λ_{ex}> 500 nm, with NaOH (0.1 M) added.

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