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Construction of Supported Ru Complex on Bifunctional MOF-253 for Photocatalytic CO_2 Reduction under Visible Light

Dengrong Sun, Yanhong Gao, Jinlong Fu, Zhaohui Li *

Research Institute of Photocatalysis, State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou, 350002, P. R. China

* Author to whom all correspondences should be addressed.
E-mail: zhaohuili1969@yahoo.com

Experimental

General. 2,2'-bipyridine-5,5'-dicarboxylic acid (dcbpy), $[Ru(CO)_3Cl_2]_2$ and $Ru(bpy)_2Cl_2 \cdot 2H_2O$ were obtained from J & K Chemical Technology. All the syntheses were performed with a Schlenk line in dark with flasks and tubes wrapped in aluminum foil. All solvents were distilled prior to use. Al(OH)(dcbpy) (MOF-253) and $[Ru(CO)_2Cl_2]_n$ were synthesized following the previous literatures.[1]

Synthesis of MOF-253-$Ru(CO)_2Cl_2$ The obtained MOF-253 was firstly was de-solvated under vacuum at 200°C for 12 h before the synthesis. The de-solvated MOF-253 (0.4323 g, 1.5 mmol) and $[Ru(CO)_3Cl_2]_2$ (0.1152 g, 0.225 mmol) were refluxed in anhydrous methanol (60 ml) with stirring for 12 h under inner condition. After the reaction, the resultant powder was filtered, washed with methanol and dried at 60 ºC under vacuum to give rise to the greenish yellow solid (0.2793 g, 89% yield). The obtained products was denoted as MOF-253-$Ru(CO)_2Cl_2$.

Synthesis of $Ru(bpy)_2Cl_2$ sensitized MOF-253-$Ru(CO)_2Cl_2$ Different amount of $Ru(bpy)_2Cl_2$ (0.0012g, 2.3μmol) was dissolved in a minimum amount of methanol. MOF-253-$Ru(CO)_2Cl_2$ (50 mg) was added to the above solution and the resulted suspension was incubated at room temperature for 12 h. The resultant product was washed with methanol for several times and dried at 60 ºC under vacuum to obtain gray powder.

Synthesis of homogeneous [Ru(5,5'-dcbpy)$(CO)_2Cl_2$ 5, 5'-dcbpy (1.3624 g, 5.58 mmol) and $[Ru(CO)_2Cl_2]_n$ (1.2720 g, 5.58 mmol) were added into a solution containing degassed H_2O (50 ml) and HCl (25 ml). The as-obtained solution was refluxed for 8 h. After the reaction, the resultant precipitate was filtered and washed with water, diethyl ether and hexane respectively and dried under vacuum to obtain the greenish yellow solid product (1.8540 g, 70% yield). ^{1}HNMR (400 MHz, d_6-DMSO) δ 9.92 (s, 1H), 9.32 (s, 1H), 8.99 (d, 1H), 8.94 (d, 1H), 8.82 (dd, 1H), 8.69 (dd, 1H).

Characterizations

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer with Cu K_α radiation. The accelerating voltage and the applied current were 40 KV and 40 mA, respectively. Data were recorded at a scan rate of 0.02° 2θ s^{-1} in the 2θ range from 5° to 40°. The IR experiments were carried out on a Nicolet 670 FT-IR spectrometer. ^{1}H NMR spectra were obtained on a 400 MHz Bruker AVANCE III 400 system (400MHz). The amount of Ru was determined by an Inductively Coupled Optical Emission Spectrometer (ICP-OES) on Optima 8000 (PerkinElmer).

UV-vis diffuse-reflectance spectrometry (UV-vis DRS) were obtained on a UV-visible spectrophotometer (Cary 500 Scan Spectrophotometers, Varian). $BaSO_4$ was used as a reflectance standard in the UV□visible diffuse reflectance experiment. N_2 adsorption/desorption isotherms was carried out at 77 K on ASAP2020 apparatus (Micromeritics Instrument Corp., USA). The samples were degassed in vacuum at 200 °C for 12h and then measured at 77 K. The X-ray absorption fine structure (XAFS) spectra were collected in Shanghai Synchrotron Radiation Facility (SSRF) with a Si (311) double-crystal monochromator in fluorescence mode. The source of BL14W1 is a 38-pole wiggler device with maximum magnetic field 1.2 T and magnet period 80 mm. The storage ring was operated at 3.5 GeV with injection currents of 100 mA. Ru K-edge XAFS spectra were collected with a Si (311) double-crystal monochromator in fluorescence mode (-200~800 eV, energy of Ru K-edge is set to zero) and analyzed with ATHENA and ARTEMIS using IFEFFIT.

Photocatalytic CO_2 reduction

Before the photocatalytic reaction, photocatalyst (5 mg) was degassed and purged with CO_2. A mixture of MeCN and TEOA (6 mL, MeCN/TEOA is 10/1) degassed by CO_2 to remove dissolved O_2 was injected into the reaction tube. The reaction tube was then further purged with CO_2 to ensure the absence of O_2 in the system. The reaction was carried out under the irradiation of Xe lamp with a UV-cut filter to remove all wavelengths lower than 420 nm and an IR-cut filter to remove all wavelengths longer than 800 nm. After reaction, the produced $HCOO^-$ was detected by ion chromatography (881 Compact IC pro, Metrosep) with Metrosep A supp 5 250/4.0 column. The column temperature was maintained at 303 K. A mixture of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ was used as eluent. The gaseous products were analyzed by GC-TCD (Shimadzu GC-2014) with a TDX-01 packed column.

Reference

1. (a) E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long, O. M. Yaghi, *J. Am. Chem. Soc.* **2010**, 132, 14382-14384; (b) P. A. Anderson, G. B. Deacon, K. H. Haarmann, F. R. Keene, T. J. Meyer, D. A. Reitsma, B. W. Skelton, G. F. Strouse, N. C. Thomas, J. A. Treadway, A. H. White, Inorg. Chem. **1995**, 34, 6145-6157.

Fig. S1 N_2 adsorption/desorption isotherms (77 K) of prepared samples.

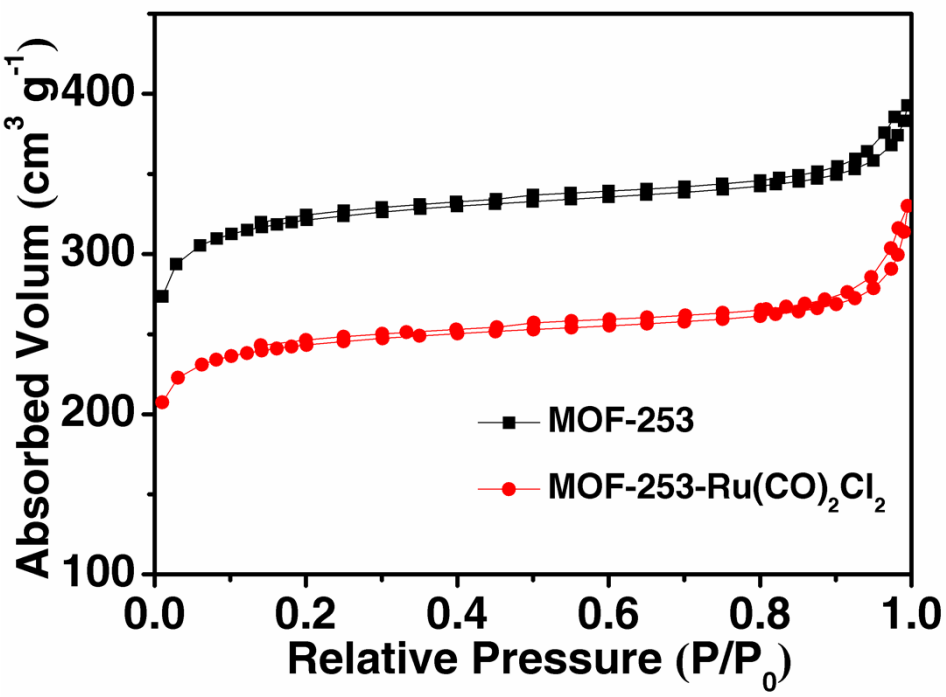

Fig. S2 Powder XRD patterns for MOF-253-$Ru(CO)_2Cl_2$ (a) before and (b) after catalytic reaction.

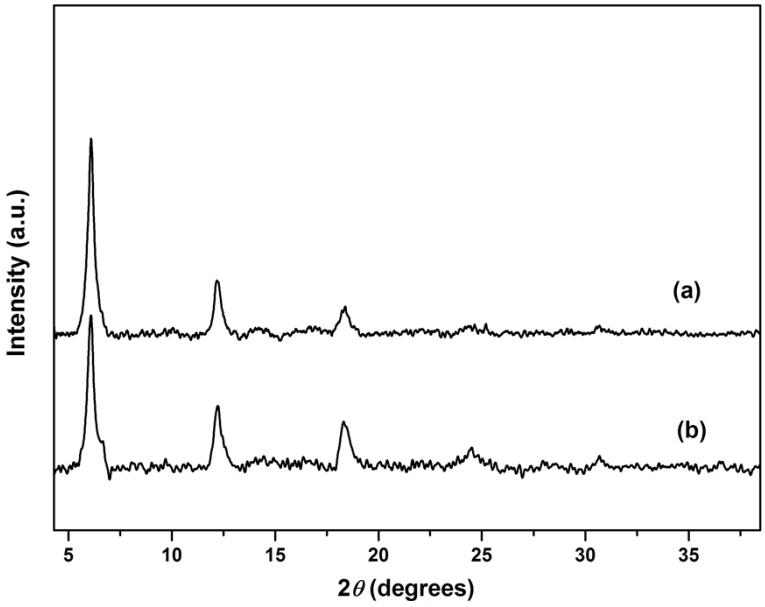

Fig. S3 The ^{13}C NMR spectrum for the product obtained from the reaction with $^{13}CO_2$ in mixture of CD_3CN/TEOA (5:1 v/v) under visible light.

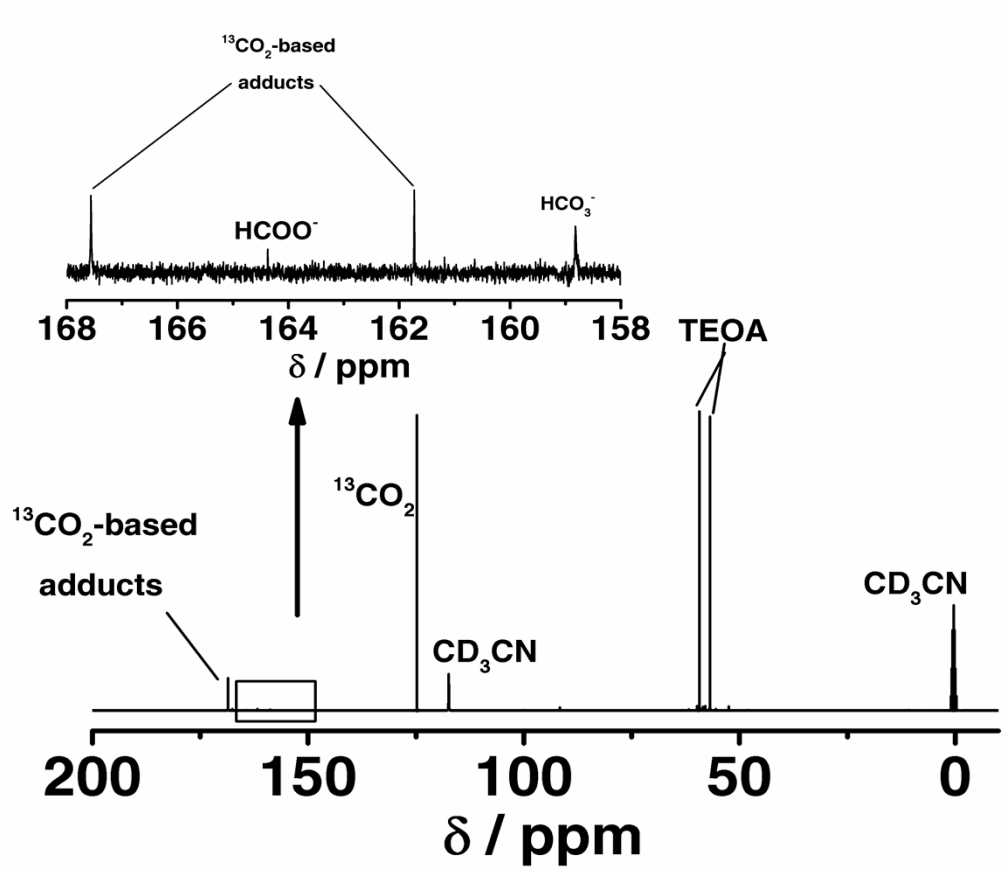

Fig. S4 The GC-MS spectra for the product obtained from the reaction with (a) $^{13}CO_2$ and (b) $^{12}CO_2$ in mixture of CD_3CN/TEOA (5:1 v/v) under visible light.

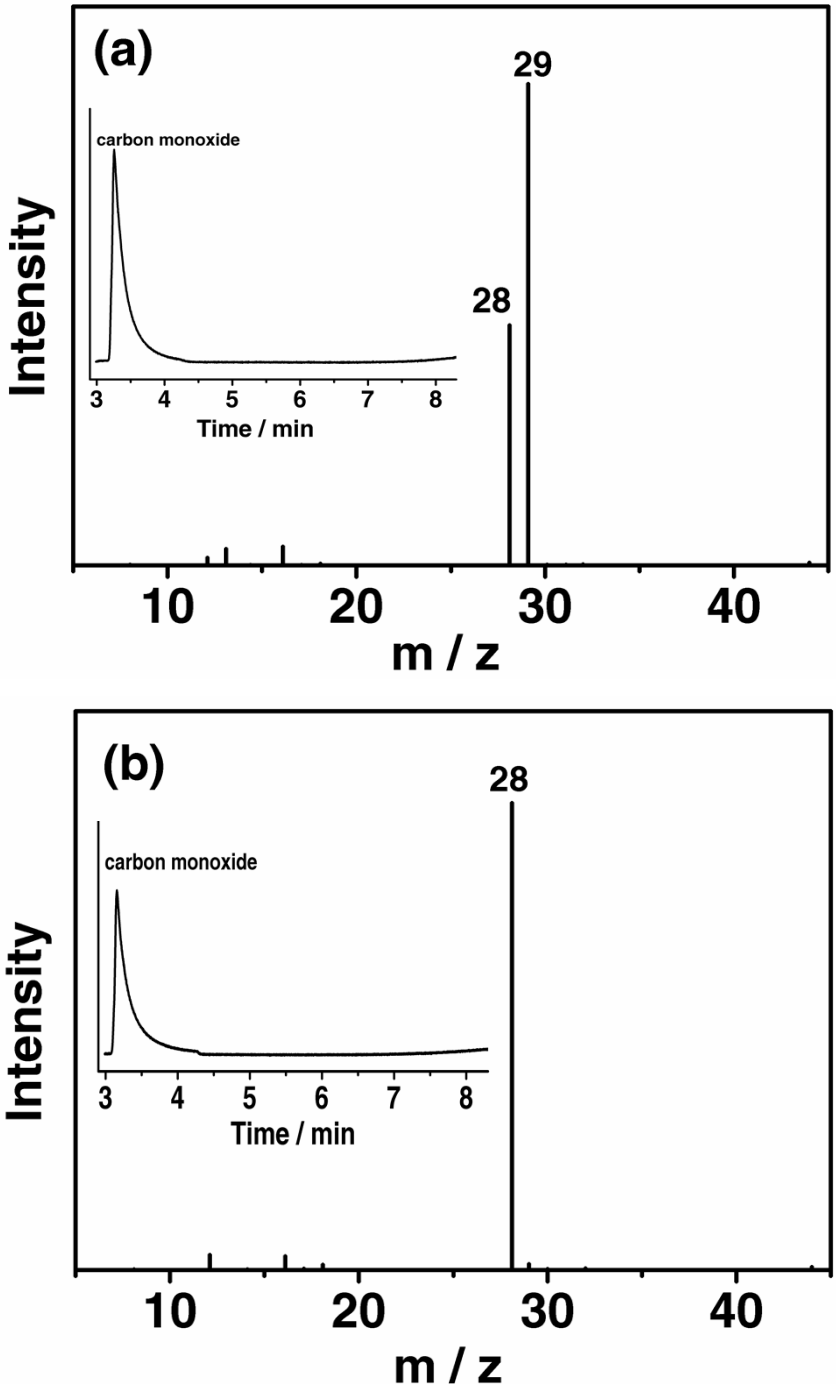

Fig. S5 IR spectra of MOF-253-Ru$(CO)_2Cl_2$ samples recorded (a) before and (b) after catalytic reaction.

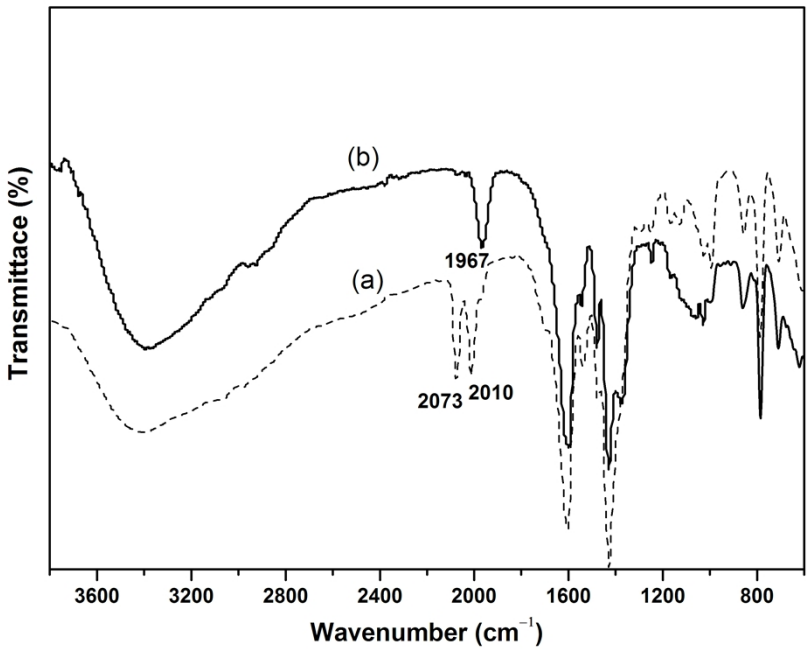

Table S1 Products obtained under different conditions.

	MOF-253-Ru$(CO)_2Cl_2$ irradiated for 4 h			filtrate irradiated for another 4 h		
	CO	H_2	$HCOO^-$	CO	H_2	$HCOO^-$
The amount of products/μmol	1.61	0.04	0.38	0.1	0	0.02

Table S2 Amount of products formed over $Ru(bpy)_2Cl_2$ and MOF-253 supported $Ru(bpy)_2Cl_2$.

Photocatalyst	Reaction time /h	The amount of products/μmol		
		$HCOO^-$	CO	H_2
Homogeneous $Ru(bpy)_2Cl_2$	8	0.27	0.18	0
MOF-253-$Ru(bpy)_2Cl_2$	8	0.46	0.21	0.07