catalysts

# Supplementary Materials

## Co-Encapsulation of Rhenium and Ruthenium Complexes into the Scaffolds of Metal–Organic Framework to Promote $CO_2$ Reduction

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### 1. The composition analysis of a serial of catalysts.

**Table S1.** The summary of feeding quantity and ICP content of Re-Ru@U and the corresponding CO yield.

| Re-Ru@U | Feed quantity (mmol) | | ICP content (wt%) | | CO Yield (μmol/g) |
|---|---|---|---|---|---|
| | Re(4,4`-dcbpy)(CO)$_3$Cl | [Ru(dcbpy)$_3$]$^{2+}$ | Re element | Ru element | |
| **1-1** | 0.008 | $5.8\times10^{-4}$ | 3.80 | 0.091 | 216.3 |
| **2-1** | 0.01 | $5.8\times10^{-4}$ | 2.45 | 0.11 | 1057.2 |
| **3-1** | 0.02 | $5.8\times10^{-4}$ | 2.30 | 0.088 | 537.4 |
| **1-2** | 0.008 | $8.7\times10^{-4}$ | 3.61 | 0.014 | 518.1 |
| **2-2** | 0.01 | $8.7\times10^{-4}$ | 2.69 | 0.17 | 876.1 |
| **3-2** | 0.02 | $8.7\times10^{-4}$ | 2.21 | 0.35 | 410.4 |
| **1-3** | 0.008 | $11.6\times10^{-4}$ | 3.65 | 0.15 | 719.9 |
| **2-3** | 0.01 | $11.6\times10^{-4}$ | 2.54 | 0.39 | 335.0 |
| **3-3** | 0.02 | $11.6\times10^{-4}$ | 2.49 | 0.43 | 282.2 |

### 2. PXRD, IR spectra and X-ray photoelectron spectra (XPS).

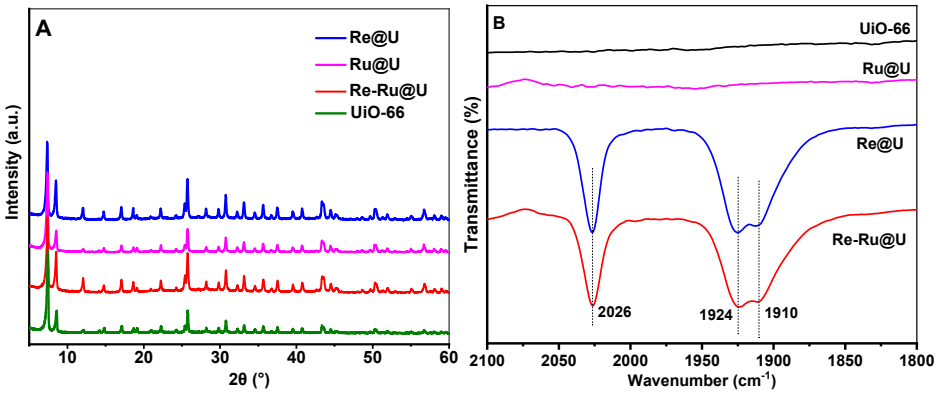


**Figure S1.** (A) PXRD and (B) IR spectra of $ReC_2$, $RuC_6$, Re-Ru@U, Re@U, Ru@U and UiO-66.

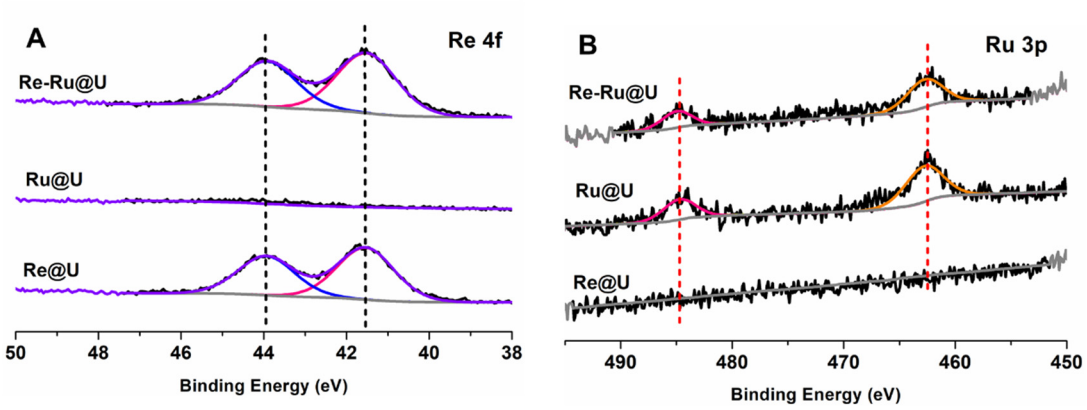


**Figure S2.** XPS binding energy of (A) Re 4f and (B) Ru 3p in samples of Re@U, Ru@U and Re-Ru@U.

### 3. The $^1$H NMR spectra of the digested Re-Ru@U, Re@U and Ru@U.

All of the $^1$H NMR data were collected on Bruker AVANCE III 400 (400 MHz). For digestion, Samples were immersed in 400 μL $D_2O$ solution with 1M $NH_4HCO_3$ at room temperature and sonicated for 30 min to achieve clear solution. 20 μL of DMSO-$d^6$ as internal standard were added and sonicated for 15 min.

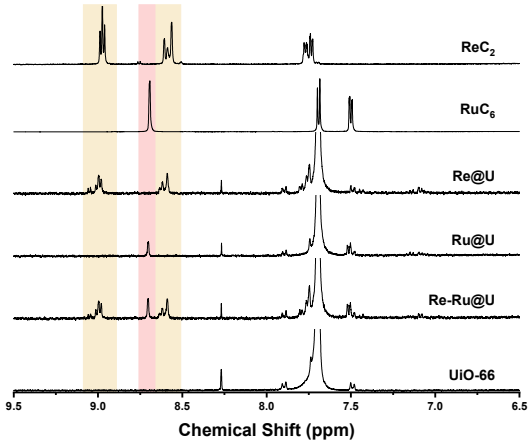


**Figure S3.** $^1$H NMR ($D_2O$-DMSO-$d^6$) spectra of pristine $ReC_2$ and $RuC_6$ complexes and the digested samples of Re-Ru@U, Re@U, Ru@U and UiO-66.

### 4. $N_2$ adsorption-desorption isotherms.

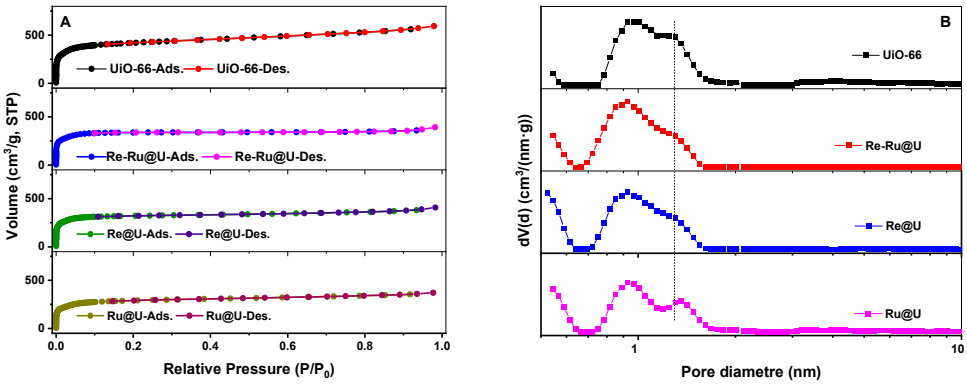


**Figure S4.** (A) 77K $N_2$ adsorption and desorption isothermal curves and (B) cumulative pore size profiles for different assembled catalysts.

**Table S2.** BET surface areas and pore volumes.

| Samples | Surface area $^{BET}$ ($m^2/g$) | $V^{DFT}$ ($cm^3/g$) |
|---|---|---|
| UiO-66 | 1696 | 0.877 |
| URu | 1161 | 0.5743 |
| URe | 1233 | 0.589 |
| UReRu | 1390 | 0.5564 |

## 5. $^{13}CO_2$ isotopic labeling experiment

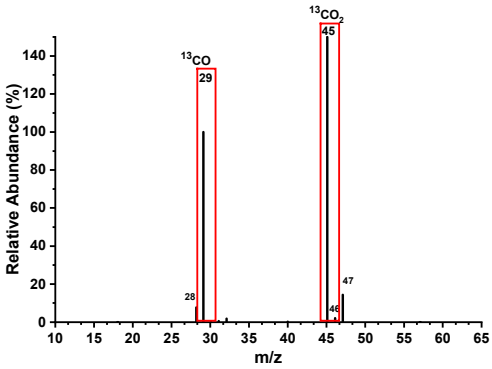


**Figure S5.** The product analysis by GC/MS chromatograms for photocatalytic $CO_2$ reduction in $^{13}CO_2$-saturated DMA-TEOA (v/v=9:1) solution containing 1 mg catalyst and 28 mg BIH.

## 6. The characterization of recycled samples.

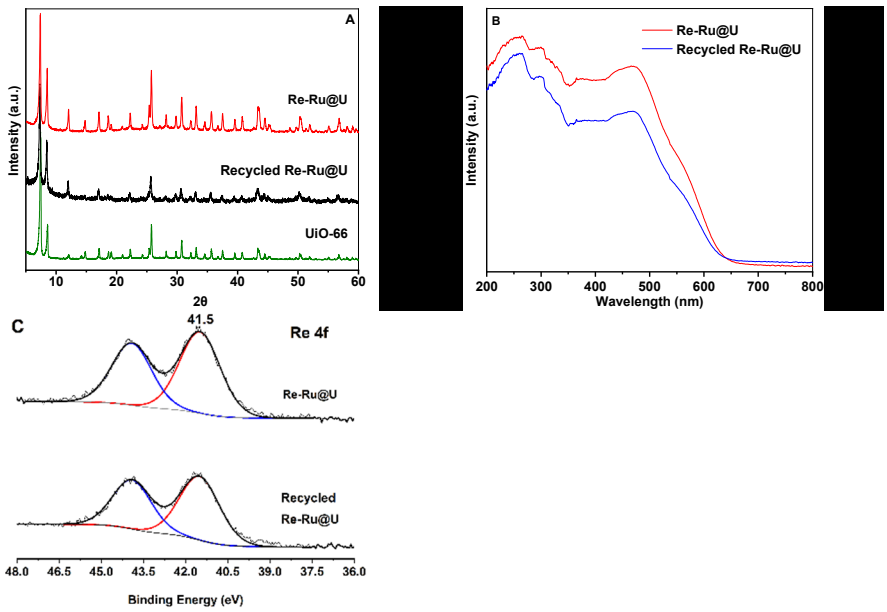


**Figure S6.** (A) XRD patterns, (B)UV-Vis spectra and (C) Re 4f XPS spectra of Re-Ru@U and recycled Re-Ru@U samples.

## 7. Performance comparison of Re-Ru@U with that of a hybrid catalyst.

**Table S3.** $CO_2$ conversion performances of Re and Ru complexes incorporated into different MOFs.

| Sample | Ru/Re (molar ratio) | Solvent | λ (nm) | Sacrificial agent | $H_2$ | CO | HCOO- | Ref. |
|---|---|---|---|---|---|---|---|---|
| **Ru-MOF-253-Re** | **0.31** | DMF/$H_2O$ | 400~800 | 4.5 mmol TEOA | TON(4h)=1.0 | TON(4 h)=5.4 | TON(4 h)=23.4 | 1 |
| **$Ru_{0.04}$-$Re_{0.04}$-BPy-PMO** | **0.84** | DMF | 420 nm | 301 mmol TEOA 1.4 mmol BIH | TON(24h)=1.7 | TON(12 h)=15 | \ | 2 |
| **ReRu-66** | **2.7** | ACN | 450 nm | 1.5 mmol TEOA | \ | TON(1.5 h)=16 | \ | 3 |
| | | ACN | 450 nm | 1.5 mmol BIH | \ | TON(5 h)=419 | \ | |
| **Zr-MBA-Ru/Re-MOF** | **3.9** | ACN-$H_2O$ | > 400 nm | 1.5 mmol TEOA 9.33 μM BANH | 55.6 μmol/g | TON(48h)=57 | $CH_4$=345.8μmol/g | 4 |
| **ReRu-MIL** | **7.9** | ACN | 450 nm | 1.5 mmol TEOA | \ | TON(24 h)=9.2 | \ | 5 |
| | | ACN | 450 nm | 1.5 mmol BIH | \ | TON(24 h)=344 | \ | |
| **Re-Ru@U** | **0.08** | DMA | > 420 nm | 3.7 mmol TEOA 0.12 mmol BIH | \ | TON(12 h)=15 | \ | This work |

## References


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3. Stanley, P.M.; Haimerl, J.; Thomas, C.; Urstoeger, A.; Schuster, M.; Shustova, N. B.; Casini, A.; Rieger, B.; Warnan, J.; Fischer, R.A. Host-Guest Interactions in a Metal-Organic Framework Isoreticular Series for Molecular Photocatalytic $CO_2$ Reduction. *Angew. Chem. Int. Ed .Engl.* **2021,** *60*, 17854-17860.
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