Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Interfacial charge separation in Cu_2O/RuO_x as a visible light driven CO_2 reduction catalyst

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EXPERIMENTAL DETAILS

Synthesis

Chemicals for the synthetic part of this work were purchased from commercial suppliers and used without further purification. Chemicals for analytical measurements were purchased in the highest purity available.

Cu_2O films for absorption spectroscopy measurements were prepared using a chemical solution deposition method using $CuSO_4$, $Na_2S_2O_3$ and NaOH reported previously.[1] In a typical film preparation method, cleaned conductive glass (fluorine-doped indium tin oxide (FTO) coated glass) were subjected to successive 20 second immersions into a 1 M NaOH solution and $Na_2S_2O_3$ (0.5 M) – $CuSO_4{\cdot}5H_2O$ (0.08 M) solution mixture at 70 °C, and then left to dry at 70 ºC. The bare Cu_2O film thickness, estimated using cross-sectional FESEM, was found to be *ca.* 100 nm after ten successive immersions.

Cu_2O-RuO_x films were prepared by impregnation method described previously,[2] by dripping small amounts (*approx.* 0.5 mL per 2 cm^2 film area) of 0.05 M aqueous $RuCl_3{\cdot}xH_2O$ over as grown Cu_2O films on FTO coated glass and left dry at 70 ºC. The Cu_2O-RuO_x film had similar morphology to the bare Cu_2O film, and film XRD analysis shows only Cu_2O and FTO peaks (Fig. S1). Both bare Cu_2O and Cu_2O-RuO_x films were annealed at 200 ºC for 1 h, in order to improve its crystallinity before further analysis.

Cu_2O powders used in this study were prepared using solvothermal method reported previously.[3,4] A typical synthesis of cuboid shaped Cu_2O involves the dissolution of $Cu(NO_3)_2{\cdot}2.5H_2O$ in a PTFE lined hydrothermal reactor containing a mixture of ethanol, water (64:36 volume ratio), and formic acid (1.3 M). Deep purple precipitates obtained after 2 hours reaction in 150 °C were washed repeatedly (5-6 times) with copious amount of water (50 mL) and dried at 70 °C overnight. Powder XRD analysis shows only Cu_2O peaks (Fig. S1). Cu_2O-RuO_x junction was prepared by impregnation method using $RuCl_3{\cdot}xH_2O$ in water followed by heat treatment at 200 ºC for 3 h and then washed for a final time and let to dry at 70 °C. The optimum RuO_x loading amount was approximately 0.25 wt% (nominal, based on the initial Cu_2O powder weight).

Materials characterisation

Powder X-Ray Diffraction Data (XRD) was done using Panalytical X'Pert powder diffraction system fitted with X'cellerator scanning linear detector. The incident X-ray is nickel filtered Cu radiation ($CuK_{\alpha1}$: 1.540596 Å, $CuK_{\alpha2}$: 1.544493 Å, $CuK_{\alpha1}/CuK_{\alpha2}$ ratio *ca.* 65/35). The powder XRD measurements were done in 0.0167° steps, 10 s per steps on rotating sample holders at 10 rpm to remove preferred orientation effects. The powder XRD data were fit using Rietveld refinement technique on Bruker AXS Topas 3 platform, taking Cu_2O and RuO_2 reference data from the references.[5,6] The diffraction signal from RuO_x was too weak and could not be reasonably fit. Film XRD was also done using the same diffractometer, using the detector scan mode, with θ fixed to low 5° angle, to minimise the substrate noise contribution. The diffraction signals from the film could not be reasonably fit and only examined qualitatively.

Particle and film morphology was examined using JEOL-7400 high resolution field emission electron microscope operated with LEI or SEI detector mode at 3-5 kV accelerating voltage and 10 mA current 0° stage tilt on gold coated powders. Samples were sputtered with thin layers of gold to improve the image quality.

Elemental analysis and Cu_2O-RuO_x morphology examination were conducted using JEOL-2000-EX-MKII transmission electron microscope (200 kV) fit with Oxford Instrument AN 10000 EDS (Energy Dispersive Spectroscopy) system. Uncoated samples were mounted on holey carbon Au 400 mesh grids (Agar Scientific) to avoid Cu signal contamination from other sources.

X-ray photoelectron spectroscopic (XPS) measurements of the Cu_2O and Cu_2O-RuO_x powders were performed using a Kratos Axis Nova X-ray photoelectron spectrometer with a monochromated Al Kα X-ray source. XPS spectra were deconvoluted using CasaXPS v.2.3.16 program (Casa Software Ltd., UK) with a Gaussian/Lorentzian (70/30) product function after subtraction of a Shirley baseline. To estimate the fraction of Cu(II), Cu(I) and Cu(0), shake structures were deconvoluted and their relative area were compared according to reference.[7]

Photocatalytic activity test

CO_2 reduction reaction was carried out in batches using septa-sealed glass chambers (78 mL) fitted with flat borosilicate top window (>90% transmittance for $\lambda \geq 350$ nm). Prior to measurements, Cu_2O powders and glass chamber were treated at 200 °C for 3 hours in a convection oven and under 300 W Xe lamp light source for *ca.* 1 hour to remove traces of organic contaminants. A typical photocatalytic experiment is conducted using 0.5 g of photocatalyst in 3 mL of CO_2 saturated deionised H_2O (Elga Centra). Excess (0.7 M) sodium sulphite was added in each batch as hole scavenger. A 150 W Xe lamp (Newport) was used as a light source (average unfiltered light output *ca.* 0.6 W/cm^2). Light output was measured using Newport 1918-R high performance optical power meter fitted with Newport 918-D calibrated photodetector with integrated attenuator.

Various long pass and bandpass filters (Comar Optics) were applied to estimate internal quantum yield and visible light activity. The reaction product was monitored by periodical sampling of the gas phase from the glass chambers using a gas tight syringe to a gas chromatograph (Varian GC-450) fit with thermal conductivity detector (TCD) connected to (molecular sieve column) to detect H_2, CO_2, O_2 and N_2 and flame ionization detector (FID) connected to CP-SIL 5CB capillary column to detect hydrocarbons. Argon was used as the GC carrier gas. A methaniser was installed to enable the FID to detect CO and CO_2 with 1000× higher sensitivity.

Isotope labelling studies using Gas Chromatography / Mass Spectrometry (GC/MS)

For the isotope-tracer experiment, the same procedure described in photocatalytic activity was used, except that 1 g of Cu_2O/RuO_x photocatalysts was added into 6 mL of CO_2 saturated sodium sulphite solution (0.7 M) due to a larger volume of the septa-sealed reactor (120 mL) used in GC-MS studies. To remove traces of organic contaminants, the photocatalyst and glass chamber were firstly treated at 200°C in the oven during 3 h and then under 300 W Xe lamp for 1 h prior to the measurements. Before each run, the septa-sealed reactor containing Cu_2O-RuO_x was firstly purged with Ar gas for 20 minutes, before introducing $^{13}CO_2$ gas (certified 99% ^{13}C isotope). The reactor was irradiated with a 150 W Xe lamp for 10 minutes, and then 1 mL of the reactor headspace was analyzed by GC/MS (Shimadzu, QP–2010SE) equipped with a molecular sieve 5 Å capillary column. Helium was used as carrier gas.

Transient absorption experiments

Transient absorption decays were recorded from Cu_2O and Cu_2O-RuO_x films, prepared as detailed previously. The microsecond-second transient absorption decays were measured using a Nd:YAG laser (Big Sky Laser Technologies Ultra CFR Nd:YAG laser system, 6 ns pulse width). The third harmonic of the laser, corresponding to 355 nm, at a frequency of 1 Hz, was used as excitation pulse. A liquid light guide with a diameter of 0.5 cm was used to transmit the laser pulse to the sample. The probe light source was a tungsten lamp (Bentham IL1 tungsten lamp), and the probing wavelength was selected by using a monochromator (OBB-2001 dual grating, Photon Technology International) placed prior to the sample. Several high pass and neutral density filters (Comar Instruments) were used to decrease the light arriving to the detector. Transient absorption data was collected with a Si photodiode (Hamamatsu S3071). The information was passed through an amplifier box (Costronics) and recorded using a Tektronics TDS 2012c oscilloscope (microsecond to millisecond timescale) and a National Instruments (NI USB-6211) DAQ card (millisecond to second timescale). The decays observed are the average between 500 and 1000 averages laser pulses. The data was processed using home-built software based on Labview.

X-RAY DIFFRACTION DATA

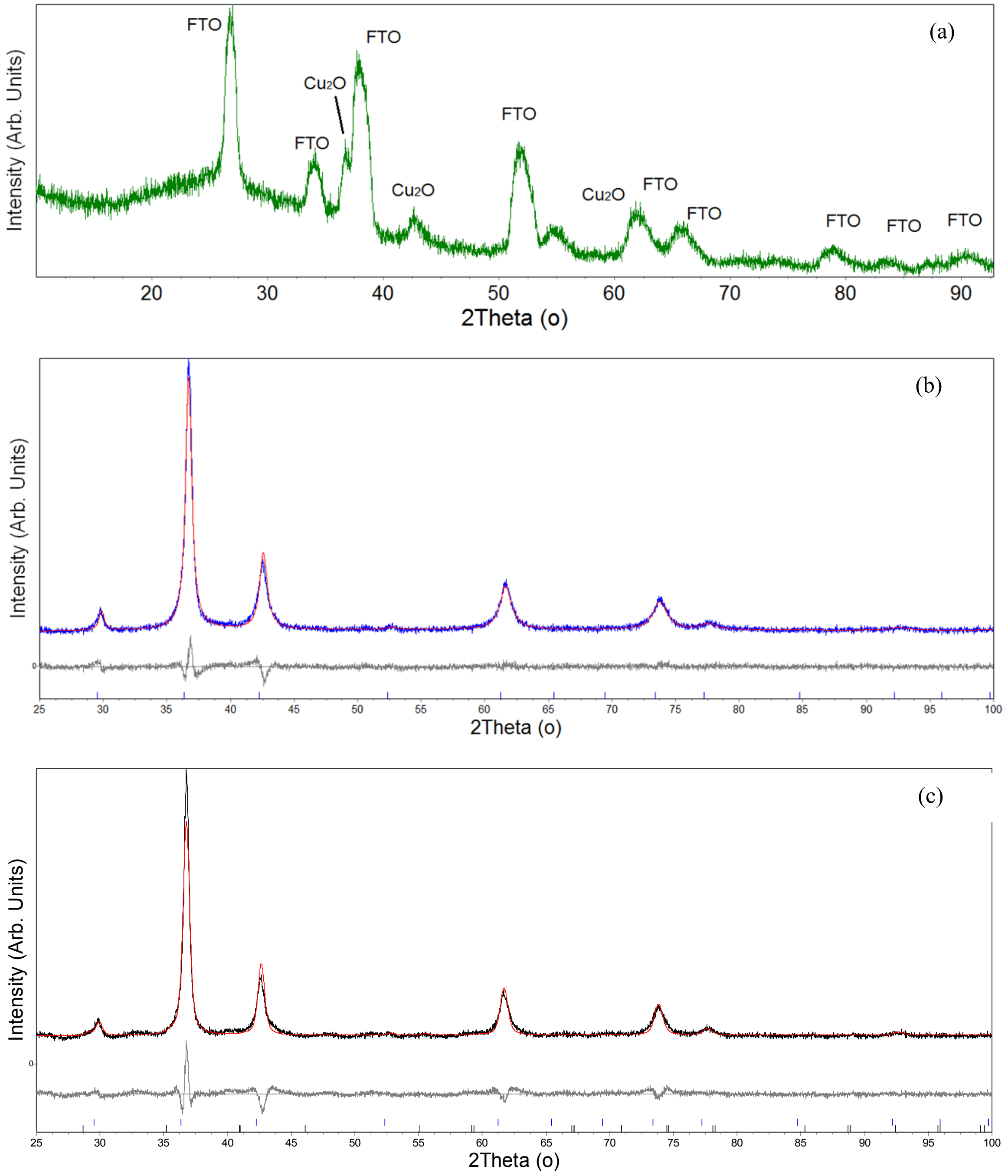

Figure S1: X-ray diffraction (XRD) of (a) Cu_2O thin films synthesized using thiosulfate reduction of Cu^{2+} ions on FTO glass, (b) bare Cu_2O powder, and (c) Cu_2O-RuO_x powder, fitted according to the reference from the crystallographic database.[5,6]

ELECTRON MICROSCOPY IMAGES (SEM AND TEM)

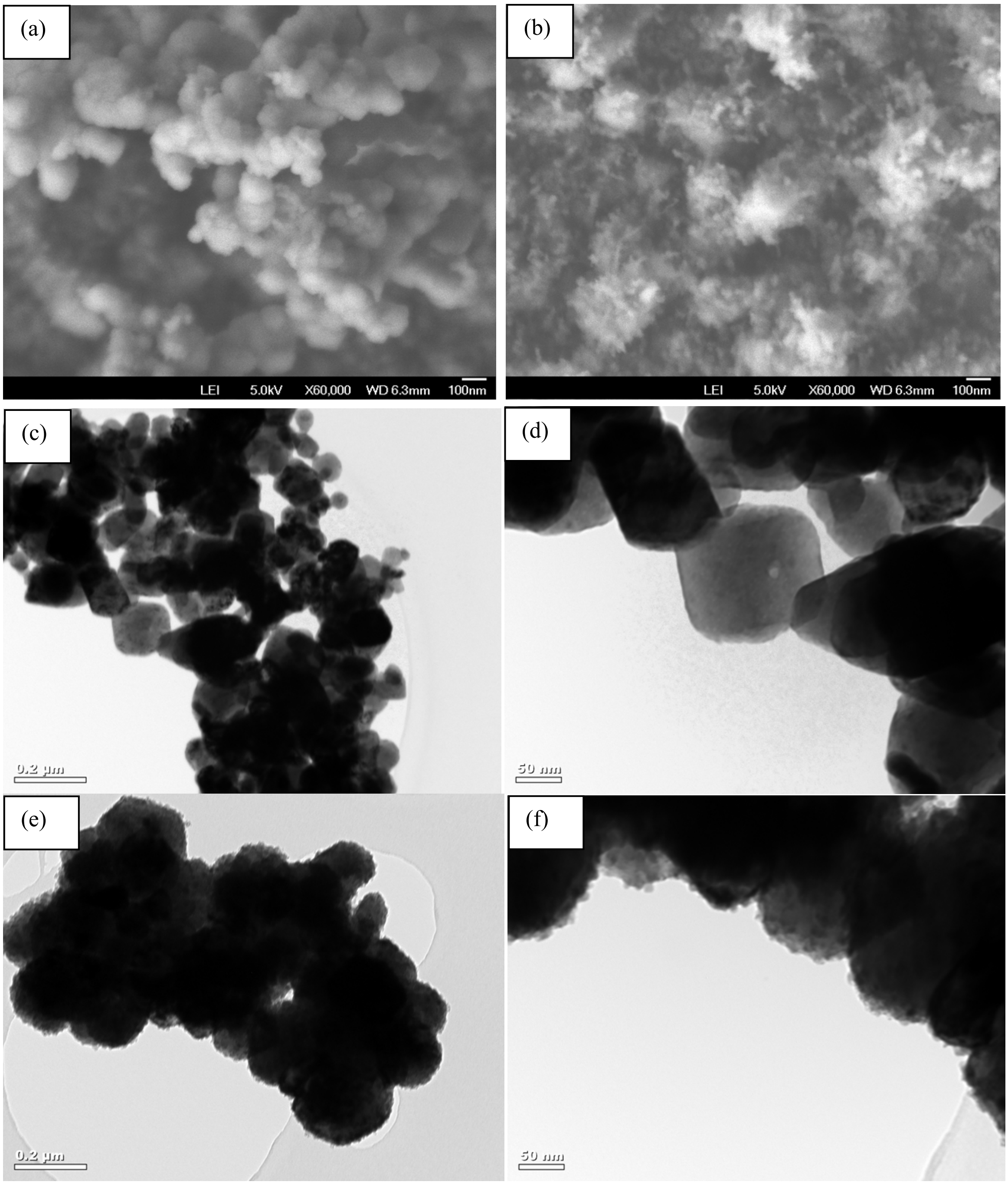

Figure S2: Scanning electron micrographs of (a) bare Cu_2O and (b) Cu_2O-RuO_x films grown on FTO glass. Transmission electron micrograph of (b-c) bare Cu_2O powder and (e-f) Cu_2O/RuO_x powder.

ELEMENTAL ANALYSIS

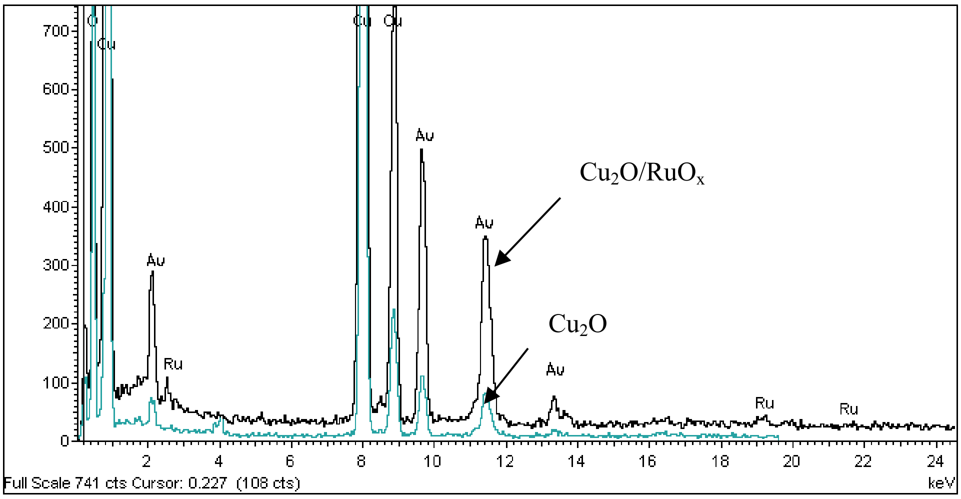

Figure S3. Typical Energy Dispersive Spectroscopy (EDS) data of bare Cu_2O and Cu_2O/RuO_x powders.

XPS ANALYSIS

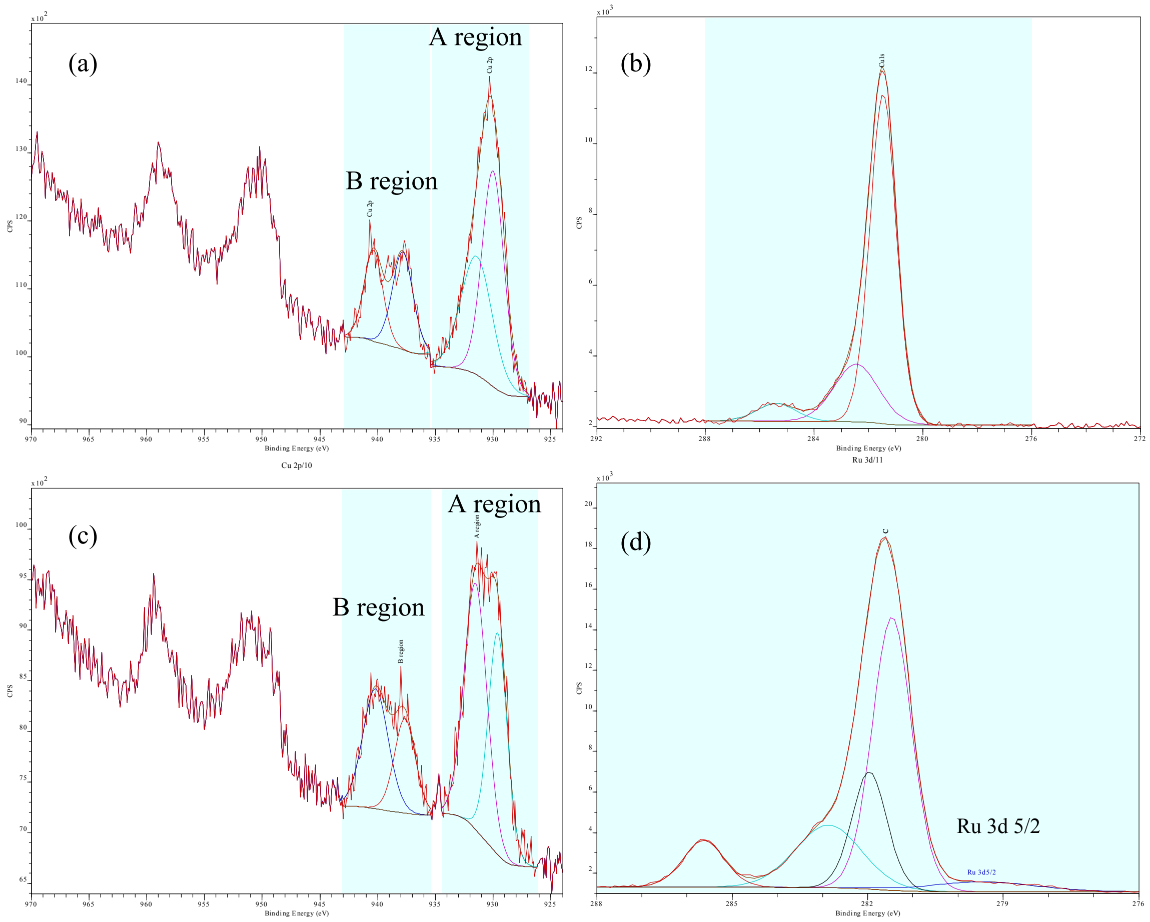

Figure S4. Fitted XPS data showing Cu 2p and Ru 3d regions of bare Cu_2O (a-b) and Cu_2O-RuO_x (c-d) powders, respectively. The region B of the Cu 2p shake up structure (Figs. S4 a and c) indicates presence of Cu(II), estimated to be *ca.* 30% of the surface when calculated according to ref [6]. The weak spectrum of Ru 3d 5/2 was only observed on Cu_2O-RuO_x sample (Fig. S4 d, arrow) but were absent on bare Cu_2O sample (Fig. S4 b).

CONTROL MEASUREMENTS OF THE PHOTOCATALYTIC ACTIVITY

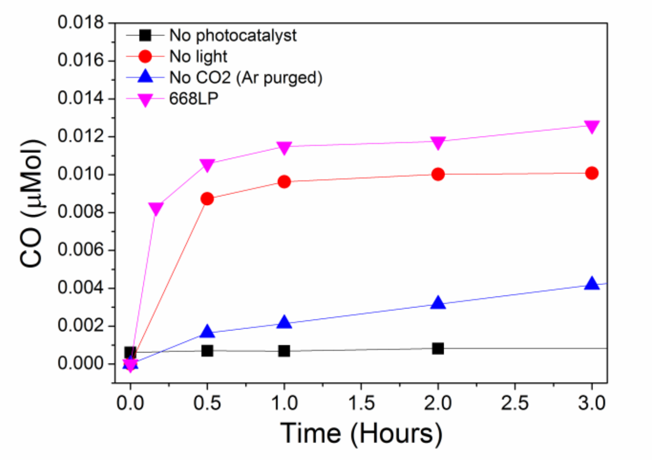

Figure S5: CO evolution during control experiments with Cu_2O – RuO_x samples: without photocatalyst (black squares), without light (red circles), without CO_2 (blue triangles) and while irradiating with longer wavelengths than the Cu2O bandgap (668 nm longpass filter) (purple triangles).

GC/MS LABELLING STUDIES

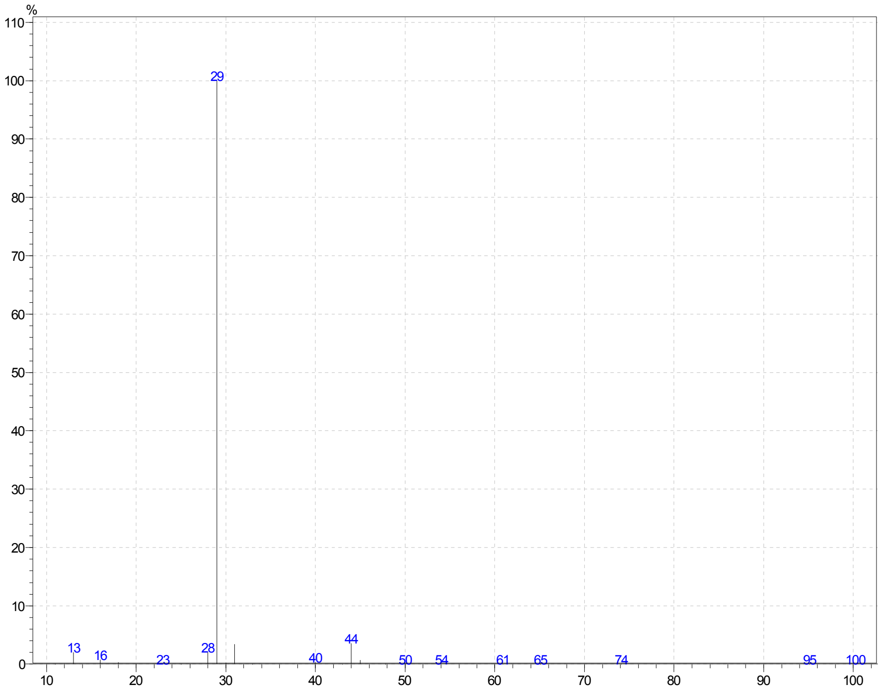

Figure S6. GC/MS analysis of the ^{13}CO (m/z 29) produced by Cu_2O-RuO_x under full arc 150 W Xe lamp after 10 minutes of reaction. Photoreduction products were analysed from the headspace (1 mL) of a photoreactor containing 1g of Cu_2O-RuO_x in 6 mL of CO_2 saturated aqueous solution in the presence of hole scavenger (*ca.* 0.7 M Na_2SO_3).

CALCULATION OF THE APPARENT QUANTUM YIELD

Estimation of the initial apparent quantum yield was done using a similar setup as the CO_2 photo reduction experiment with an additional 400 nm bandpass filter. The amount of light arriving to the photocatalyst was estimated by measuring filtered light after passing flat borosilicate glass and 3 mL of water (to reflect actual experimental conditions). This estimation excludes the amount of light reflected or passed through the photocatalyst during stirring, which could not be measured using the current setup; therefore the results underestimate the actual quantum yield.

The spatial average of light power density at 400 nm (at 10 different points) measured after the 400 nm bandpass filter, flat borosilicate glass, and 3 mL water was *ca.* 598.5 µW cm^{-2}.

The amount CO measured after the first 20 minutes with the Cu_2O-RuO_x photocatalyst under 400 nm bandpass filtered light is *ca.* 1.70×10^{-7} mol.

Assuming 2 electrons consumed per CO molecule evolved according to the reaction:

$$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O$$

The apparent quantum yield can then be estimated by the yield of CO following the equation:

$$AQY\% = \frac{\text{Number of reacted electron}}{\text{Number of incident photon}}$$

$$AQY\% = \frac{[\mathrm{CO}] \times 2 \times N_A}{H \times \mathrm{A} \times \frac{\lambda}{\mathrm{hc}} \times t}$$

Where:
[CO] is the CO amount (mol) after 20 minutes
N_A is the Avogadro's number (mol^{-1})
H is the apparent light input at the photocatalyst (W m^{-2})
A is the base reactor area (m^2)
h is the Planck's constant (J s)
c is the speed of light (m s^{-1})
λ is the light wavelength (m)
t is the time (s)

ADDITIONAL REFERENCES

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