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**Supporting information**

**Interfacial charge separation in Cu$_2$O/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$_2$O films for absorption spectroscopy measurements were prepared using a chemical solution deposition method using CuSO$_4$, Na$_2$S$_2$O$_3$ 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$_2$S$_2$O$_3$ (0.5 M) – CuSO$_4$:5H$_2$O (0.08 M) solution mixture at 70 °C, and then left to dry at 70 °C. The bare Cu$_2$O film thickness, estimated using cross-sectional FESEM, was found to be ca. 100 nm after ten successive immersions.

Cu$_2$O-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$_3$:xH$_2$O over as grown Cu$_2$O films on FTO coated glass and left dry at 70 °C. The Cu$_2$O-RuO$_x$ film had similar morphology to the bare Cu$_2$O film, and film XRD analysis shows only Cu$_2$O and FTO peaks (Fig. S1). Both bare Cu$_2$O and Cu$_2$O-RuO$_x$ films were annealed at 200 ºC for 1 h, in order to improve its crystallinity before further analysis.

Cu$_2$O powders used in this study were prepared using solvothermal method reported previously.$^3$ A typical synthesis of cuboid shaped Cu$_2$O involves the dissolution of Cu(NO$_3$)$_2$:2.5H$_2$O 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$_2$O peaks (Fig. S1). Cu$_2$O-RuO$_x$ junction was prepared by impregnation method using RuCl$_3$:xH$_2$O in water followed by heat treatment at 200 °C 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$_2$O powder weight).

**Materials characterisation**

Powder X-Ray Diffraction Data (XRD) was done using Panalytical X’Pert powder diffraction system fitted with X’celerator 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$_2$O and CuO x-ray reference data from the references.$^5$ 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 0 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$_2$O-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$_2$O and Cu$_2$O-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

CO₂ 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, Cu₂O 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 CO₂ saturated deionised H₂O (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/cm²). 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 H₂, CO₂, O₂ and N₂ 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 CO₂ 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 Cu₂O/RuOₓ photocatalysts was added into 6 mL of CO₂ 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 Cu₂O-RuOₓ was firstly purged with Ar gas for 20 minutes, before introducing ^13CO₂ gas (certified 99% ^13C 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 Cu₂O and Cu₂O-RuOₓ 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$_2$O thin films synthesized using thiosulfate reduction of Cu$^{2+}$ ions on FTO glass, (b) bare Cu$_2$O powder, and (c) Cu$_2$O-RuO$_x$ powder, fitted according to the reference from the crystallographic database.$^{5,6}$
Figure S2: Scanning electron micrographs of (a) bare Cu$_2$O and (b) Cu$_2$O-RuO$_x$ films grown on FTO glass. Transmission electron micrograph of (b-c) bare Cu$_2$O powder and (e-f) Cu$_2$O/RuO$_x$ powder.
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 Cu2O-RuOx sample (Fig. S4 d, arrow) but were absent on bare Cu2O sample (Fig. S4 b).

Figure S3. Typical Energy Dispersive Spectroscopy (EDS) data of bare Cu2O and Cu2O-RuOx powders.

Figure S4. Fitted XPS data showing Cu 2p and Ru 3d regions of bare Cu2O (a-b) and Cu2O-RuOx (c-d) powders, respectively.
CONTROL MEASUREMENTS OF THE PHOTOCATALYTIC ACTIVITY

Figure S5: CO evolution during control experiments with Cu$_2$O – 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$_2$O-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$_2$O-RuO$_x$ in 6 mL of CO$_2$ saturated aqueous solution in the presence of hole scavenger (ca. 0.7 M Na$_2$SO$_3$).
CALCULATION OF THE APPARENT QUANTUM YIELD

Estimation of the initial apparent quantum yield was done using a similar setup as the CO\textsubscript{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 \textit{ca.} 598.5 \mu W cm\textsuperscript{-2}.

The amount CO measured after the first 20 minutes with the Cu\textsubscript{2}O-RuO\textsubscript{x} photocatalyst under 400 nm bandpass filtered light is \textit{ca.} 1.70 \times 10\textsuperscript{-7} mol.

Assuming 2 electrons consumed per CO molecule evolved according to the reaction:
\[
\text{CO}_2 + 2e^- + 2H^+ \rightarrow CO + H_2O
\]

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

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

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

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

ADDITIONAL REFERENCES