Interfacial charge separation in Cu$_2$O/RuO$_x$ as a visible light driven CO$_2$ reduction catalyst†

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We employ transient absorption spectroscopy to record the absorption spectrum of photogenerated charge carriers in Cu$_2$O. We have found that CO$_2$ reduction in Cu$_2$O is limited by fast electron–hole recombination. The deposition of RuO$_x$ nanoparticles on Cu$_2$O results in a twofold increased yield of long-lived electrons, indicating partially reduced electron–hole recombination losses. This observation correlates with an approximately sixfold increase in the yield of CO$_2$ reduction to CO.

Photochemical reduction of CO$_2$ has the potential to convert this greenhouse gas into clean fuels or value-added chemicals. As such, it can contribute significantly to both renewable energy generation and CO$_2$ mitigation. 1 Photoreduction of CO$_2$ in heterogeneous systems was first reported using optical excitation of large bandgap semiconductor materials such as TiO$_2$, SrTiO$_3$, ZnO, or SiC with UV light irradiation. 2 Since this initial study, many reports have focused on the development of materials with improved light absorption properties in the visible region, such as narrow bandgap non-metal oxide semiconductors (e.g. ZnS, CdS, and GaP), or the functionalization or doping of wide bandgap semiconductors, 3 although overall efficiencies reported for CO$_2$ photoreduction remain limited. These low efficiencies have often been attributed to fast charge recombination, requirements of high over-potentials and competition between CO$_2$ photoreduction reaction with H$_2$ evolution, as well as issues associated with catalyst/co-catalyst degradation or deactivation. 4 Identifying the parameters that restrain the performance of catalysts towards CO$_2$ reduction and designing a system capable of overcoming these limitations is therefore a key challenge. In this context, transient absorption spectroscopy (TAS) is a technique that allows the assessment of competing kinetic processes in a semiconductor, namely charge separation and recombination, by monitoring the dynamics of charge carriers. We have, for example previously reported the signals corresponding to electrons and holes in Fe$_2$O$_3$ and other photoanodes for the related reaction of photochemical water-splitting. 5

Herein, we report the dynamics of charge carriers in Cu$_2$O. To the best of our knowledge, the absorption spectrum and dynamics of photoexcited electrons in Cu$_2$O have not been identified. This narrow bandgap (ca. 2.2 eV) p-type semiconductor has been shown to be photocatalytically active for reduction of water 6 and degradation of inorganic waste. 7 Since the conduction band of Cu$_2$O lies above the reduction potential of CO$_2$ to CO, 8 it is attracting increasing interest for the photoreduction of CO$_2$. 9 As a p-type semiconductor, interfacial band-bending of Cu$_2$O, where present, is likely to favour interfacial reduction reactions but hinder oxidation reactions by presenting an energetic barrier for holes to approach the semiconductor surface. These surface reduction/oxidation reactions will be in kinetic competition with electron–hole recombination loss pathways (Fig. 1a). We have recently reported that the deposition of a charge acceptor (RuO$_x$, x ≤ 2) on top of Cu$_2$O improves its photocatalytic activity towards CO$_2$ reduction. 9b Herein, we focus on the study of the dynamics of photogenerated electrons in Cu$_2$O when forming an inorganic heterojunction with a material capable of (1) increasing the accessibility of photogenerated holes to the electrolyte, (2) having appropriate reaction sites to drive photo-oxidation reactions and (3) reducing the electron–hole recombination reaction on the Cu$_2$O surface (Fig. 1b). Ruthenium oxide (RuO$_x$) was selected as the overlayer material because its appropriate work function level can facilitate transfer of holes from Cu$_2$O, thereby potentially increasing the yield of long-lived electrons in Cu$_2$O to enable the reduction of CO$_2$. RuO$_x$ is also less likely to react with Cu$_2$O to form an unwanted interfacial layer and

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has been shown to have the ability to oxidize many hole scavengers, including water.10

Spectroscopic measurements were performed using Cu_2O films deposited onto FTO glass. Cu_2O cuboid films with a nanoparticle size of ca. 100 nm were prepared by a chemical solution method using CuSO_4, Na_2S_2O_3 and NaOH, as reported previously.11 RuO_x was subsequently deposited in the form of nanoparticles <10 nm on the Cu_2O surface.13 The RuO_x deposition did not alter the bandgap absorption of Cu_2O of approx. 2.2 eV. Only Cu_2O diffraction peaks were detected in Cu_2O–RuO_x heterojunction by elemental analysis during TEM and XPS investigations, but not X-ray diffraction due to the low loading amount and small crystallite size of RuO_x. TAS spectra were recorded after UV excitation (355 nm) of Cu_2O and Cu_2O/RuO_x, using an experimental setup described previously.14 Details of synthetic procedures, material characterisation and experimental setup for transient absorption measurements can be found in the ESI† (Fig. S1–S4).

The absorption spectrum of charge carriers in a semiconductor can be characterized by TAS, by employing relevant fast hole and electron scavengers.15 Thus, the transient absorption spectrum of Cu_2O films deposited onto the FTO glass was obtained (i) in a N_2 purged aqueous solution (ii) following the addition of Na_2SO_3 as a hole scavenger or (iii) AgNO_3 as an electron scavenger. Photoexcitation of the Cu_2O semiconductor in the absence of charge carrier scavengers results in the appearance of a ground state bleach signal between 475 and 750 nm and two positive photoinduced absorption peaks at wavelengths <475 nm and >800 nm (Fig. 2). The signals at wavelengths >850 nm are significantly enhanced by the addition of Na_2SO_3 and weakened by the addition of AgNO_3. Given that Na_2SO_3 can effectively scavenge holes, while Ag^+ scavenge electrons, we can assign the transient signals above 850 nm to Cu_2O photoexcited electrons. On the other hand, we observed only the signal corresponding to photoexcited holes in Cu_2O at wavelengths <475 nm when using AgNO_3 as an electron scavenger. Thus, the direct probing of holes under the current experimental photocatalytic conditions is hindered by the partial overlap with the bleach signal of the ground state and cannot be directly monitored. Since these signals corresponding to photoexcited electrons and holes in the Cu_2O are already present in the 10 µs timescale, our measurements indicate that electron–hole scavenging by the relevant chemicals are very fast (<10 µs), beyond the instrument’s limit of response.

The formation of inorganic heterojunctions or the addition of sacrificial agents which are able to scavenge charge carriers have been reported to improve the performance of the photocatalytic systems for organic waste decomposition or water splitting reactions by decreasing the recombination of photogenerated electrons and holes in a semiconductor.16 Thus, transient absorption spectroscopy experiments were also employed to assay the effect of RuO_x deposition on the Cu_2O charge carrier dynamics. Typical kinetic data of the photoinduced electron absorption signals taken at 950 nm are

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**Fig. 1** Schematic of Cu_2O and the Cu_2O/RuO_x band diagram and electron and hole transfer reactions for the photocatalytic CO_2 reduction. Energy values were taken from ref. 8b and 12. \( E_F \) stands for Fermi level, \( E_{CB} \) and \( E_{VB} \) indicate the energy levels of the conduction band and valence band, respectively.

**Fig. 2** Transient absorption spectrum of Cu_2O recorded under N_2, in the presence of a 0.1 M Na_2SO_3 and 0.01 M AgNO_3 aqueous solutions. The samples were excited at \( \lambda_{ex} = 355 \text{ nm} \), with a laser intensity of \( \sim 1.2 \text{ mJ cm}^{-2} \).
plotted in Fig. 3, showing the decay dynamics on the micro- to second timescales. We note that we only observed significant long-lived signal amplitudes with relatively intense excitation densities, indicative of the presence of significantly fast (\(<10 \text{ ms})\) electron–hole recombination in these films. The presence of Na2SO3 resulted in an increase in the amplitude of this Cu2O electron signal (Fig. 2), although this effect is relatively minor, indicative of inefficient hole scavenging/fast recombination, and consistent with the expected band bending impeding access of photogenerated holes to the Cu2O surface (Fig. 1a). The deposition of RuOx on the Cu2O surface results in a significant increase in the amplitude of the long-lived electron signal, independent of the presence of Na2SO3, and indicative of a more efficient reduction in fast electron–hole recombination losses. These results qualitatively suggest that RuOx deposition results in a significant increase in the yield of long-lived (\(>100 \text{ ms}\)) Cu2O electrons. This is attributed to a reduction in fast electron–hole recombination losses due to formation of the inorganic junction, most probably due to hole transfer from Cu2O to RuOx, thereby increasing the spatial separation of electrons and holes and facilitating the photoreduction reaction by holes. The lack of absorption of RuOx in the near IR region of the spectrum indicates that the increase in absorbance observed at 950 nm is not due to the reduction of RuOx by Cu2O photexcited electrons, and therefore confirms our peak assignation.\(^\text{17}\) We want to note that a Cu2O-Al2O3-TiO2-RuOx heterojunction for H\(^+\) reduction, where the Cu2O and RuOx interfaces are connected through an interfacial (AZO-TiO2) layer, has been reported by Tilley et al.\(^\text{16d}\) Contrary to our approach, where RuOx accepts the holes from Cu2O, charge separation in Cu2O–AZO–TiO2–RuOx takes place through electron transfer from Cu2O to RuOx. We believe that, while in the Cu2O–AZO–TiO2–RuOx there is a favorable downhill electron transfer cascade from Cu2O to RuOx, the AZO–TiO2 layer blocks the hole transfer to RuOx.

The effect of enhanced charge separation by the Cu2O–RuOx junction strategy on CO\(_2\) photoreduction was tested using analogous bare Cu2O and Cu2O–RuOx nanoparticulate suspensions in CO\(_2\)-saturated deionised H\(_2\)O in the presence of a Na2SO3 hole scavenger upon irradiating under the full arc of a 150 W Xe lamp (Fig. 4). In agreement with the results observed upon irradiating the samples with visible light (\(\lambda \geq 420 \text{ nm}\)),\(^\text{16}\) the coupling of Cu2O with RuOx results in a nearly sixfold increase of the initial rate of CO production, from 0.16 \(\mu\)mol g\(^{-1}\) on bare Cu2O to around 0.88 \(\mu\)mol g\(^{-1}\) on the Cu2O–RuOx junction after 1 h irradiation using a 150 W Xe lamp. Trace amounts of methanol (0.01 \(\mu\)mol g\(^{-1}\) h\(^{-1}\)) and methane (\(<0.001 \mu\)mol g\(^{-1}\) h\(^{-1}\)) were also observed in the Cu2O–RuOx sample during the reaction. Quantum yield measurements were carried out using a near monochromatic visible light 400 nm bandpass filter (\(\Delta \lambda < 10 \text{ nm}\), filtered light output ca. 600 ± 40 \(\mu\)W cm\(^{-2}\)). The apparent initial quantum yield for CO generation (20 min) for the Cu2O–RuOx heterojunction was determined to be ca. 1.6%. It is also noted that the CO evolution rate is reduced after the first hour. These results can be explained in terms of the instability of Cu2O towards the presence of increasing amounts of SO\(_4^{2-}\) formed upon scavenging the holes by Na2SO3.\(^\text{18}\) Another possible explanation for non-linear CO evolution could be the strong interaction between CO and Cu2O, which will result in lowered catalytic activity over time.\(^\text{19}\) Studies to address this instability by using alternative hole scavengers and further modifying material protection layers are ongoing.

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**Fig. 3** TAS decays of photo-excited electrons of Cu2O films (black trace) and Cu2O–RuOx films (red trace) in N\(_2\) purged water, and in the presence of a N\(_2\) purged 0.1 M Na2SO3 aqueous solution (Cu2O films: grey trace, Cu2O–RuOx films: pink trace). Data obtained at \(\lambda_{\text{probe}} = 950 \text{ nm}\) with an excitation intensity of 1.6 mJ cm\(^{-2}\) at \(\lambda_{\text{exc}} = 355 \text{ nm}\).

**Fig. 4** CO\(_2\) reduction to CO on bare and heterojunction based Cu2O core photocatalysts under full arc 150 W Xe lamp irradiation. Photoreduction reactions were undertaken in 3 mL of CO\(_2\) saturated H\(_2\)O in the presence of a hole scavenger (ca. 0.7 M Na2SO3).
RuO$_2$ has been reported to be able to either reduce or oxidize water$^{6d,20}$ but is unable to reduce CO$_2$ due to its work function being more positive than the $E_{\text{red}}$(CO$_2$/CO) reduction potential. We did not observe any water oxidation and oxygen evolution upon the addition of RuO$_2$, as holes are preferentially scavenged by Na$_2$SO$_3$. Thus, the increase in the CO$_2$ photoreduction yield is consistent with the efficient charge separation due to the inorganic heterojunction, where holes are transferred to RuO$_2$ and CO$_2$ reduction takes place at the surface of Cu$_2$O.

In order to provide evidence that the formation of CO is due to the photoreduction of CO$_2$ by Cu$_2$O, three different control experiments were carried out: (1) traces of organic contaminants were removed by treating the aqueous suspension system under strong light irradiation without CO$_2$ until there was no increase in the CO or CO$_2$ amount as detected by gas chromatography before the photocatalytic measurements. (2) Control experiments under similar conditions but in the absence of photocatalyst, CO$_2$ or light, and irradiating the Cu$_2$O with longer wavelength light ($\lambda > 668$ nm, much lower than Cu$_2$O bandgap requirement) demonstrated that surface carbon gasification is not a major contributing factor [Fig. S5, ESI†]. (3) Gas chromatography – Mass spectrometry isotope labelling analysis showed the sole formation of $^{13}$CO ($m/z$ 29) [Fig. S6, ESI†]. These results strongly indicate that the CO observed by GC is due to photochemical reduction of CO$_2$ rather than from the reduction of organic contaminants present on the surface of Cu$_2$O–RuO$_2$.

### Conclusions

In summary, we have assigned the transient absorption spectrum of Cu$_2$O photoexcited electrons to appear at wavelength $\lambda > 800$ nm, and holes at $\lambda < 475$ nm. In bare Cu$_2$O films, the major loss pathway limiting their photocatalytic activity is the fast electron–hole recombination. Our results demonstrate that the Cu$_2$O–RuO$_2$ heterojunction strategy is effective in partially suppressing this electron–hole recombination loss through the transfer of photogenerated holes from Cu$_2$O to RuO$_2$. This is shown by a significant increase in the yield of long-lived Cu$_2$O electrons as observed by transient absorption spectroscopy. This electron yield and a lifetime increase is translated into a sixfold photocatalytic reaction increase by Cu$_2$O–RuO$_2$ coupling in favour of CO$_2$ reduction.

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### Notes and references


