

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

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**We employ transient absorption spectroscopy to record the absorption spectrum of photogenerated charge carriers in  $\text{Cu}_2\text{O}$ . We have found that  $\text{CO}_2$  reduction in  $\text{Cu}_2\text{O}$  is limited by fast electron–hole recombination. The deposition of  $\text{RuO}_x$  nanoparticles on  $\text{Cu}_2\text{O}$  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  $\text{CO}_2$  reduction to  $\text{CO}$ .**

Photochemical reduction of  $\text{CO}_2$  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  $\text{CO}_2$  mitigation.<sup>1</sup> Photoreduction of  $\text{CO}_2$  in heterogeneous systems was first reported using optical excitation of large bandgap semiconductor materials such as  $\text{TiO}_2$ ,  $\text{SrTiO}_3$ ,  $\text{ZnO}$ , or  $\text{SiC}$  with UV light irradiation.<sup>2</sup> 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.  $\text{ZnS}$ ,  $\text{CdS}$ , and  $\text{GaP}$ ), or the functionalization or doping of wide bandgap semiconductors,<sup>3</sup> although overall efficiencies reported for  $\text{CO}_2$  photoreduction remain limited. These low efficiencies have often been attributed to fast charge recombination, requirements of high over-potentials and competition between  $\text{CO}_2$  photoreduction reaction with  $\text{H}_2$  evolution, as well as issues associated with catalyst/co-catalyst degradation or deactivation.<sup>4</sup> Identifying the parameters that

restrain the performance of catalysts towards  $\text{CO}_2$  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  $\text{Fe}_2\text{O}_3$  and other photoanodes for the related reaction of photochemical water-splitting.<sup>5</sup>

Herein, we report the dynamics of charge carriers in  $\text{Cu}_2\text{O}$ . To the best of our knowledge, the absorption spectrum and dynamics of photoexcited electrons in  $\text{Cu}_2\text{O}$  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<sup>6</sup> and degradation of inorganic waste.<sup>7</sup> Since the conduction band of  $\text{Cu}_2\text{O}$  lies above the reduction potential of  $\text{CO}_2$  to  $\text{CO}$ ,<sup>8</sup> it is attracting increasing interest for the photoreduction of  $\text{CO}_2$ .<sup>9</sup> As a p-type semiconductor, interfacial band-bending of  $\text{Cu}_2\text{O}$ , 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 ( $\text{RuO}_x$ ,  $x \leq 2$ ) on top of  $\text{Cu}_2\text{O}$  improves its photocatalytic activity towards  $\text{CO}_2$  reduction.<sup>9b</sup> Herein, we focus on the study of the dynamics of photogenerated electrons in  $\text{Cu}_2\text{O}$  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  $\text{Cu}_2\text{O}$  surface (Fig. 1b). Ruthenium oxide ( $\text{RuO}_x$ ) was selected as the overlayer material because its appropriate work function level can facilitate transfer of holes from  $\text{Cu}_2\text{O}$ , thereby potentially increasing the yield of long-lived electrons in  $\text{Cu}_2\text{O}$  to enable the reduction of  $\text{CO}_2$ .  $\text{RuO}_x$  is also less likely to react with  $\text{Cu}_2\text{O}$  to form an unwanted interfacial layer and

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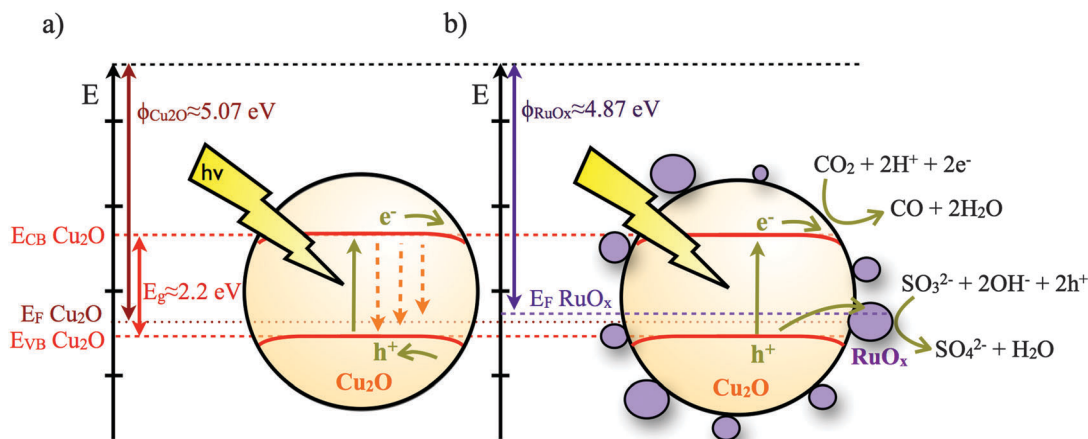


Fig. 1 Schematic of  $\text{Cu}_2\text{O}$  and the  $\text{Cu}_2\text{O}/\text{RuO}_x$  band diagram and electron and hole transfer reactions for the photocatalytic  $\text{CO}_2$  reduction. Energy values were taken from ref. 8b and 12.  $E_{\text{F}}$  stands for Fermi level,  $E_{\text{CB}}$  and  $E_{\text{VB}}$  indicate the energy levels of the conduction band and valence band, respectively.

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

Spectroscopic measurements were performed using  $\text{Cu}_2\text{O}$  films deposited onto FTO glass.  $\text{Cu}_2\text{O}$  cuboid films with a nanoparticle size of *ca.* 100 nm were prepared by a chemical solution method using  $\text{CuSO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{NaOH}$ , as reported previously.<sup>11</sup>  $\text{RuO}_x$  was subsequently deposited in the form of nanoparticles  $<10 \text{ nm}$  on the  $\text{Cu}_2\text{O}$  surface.<sup>13</sup> The  $\text{RuO}_x$  deposition did not alter the bandgap absorption of  $\text{Cu}_2\text{O}$  of approx. 2.2 eV. Only  $\text{Cu}_2\text{O}$  diffraction peaks were detected in  $\text{Cu}_2\text{O}-\text{RuO}_x$  samples, and  $\text{Cu}(\text{I})$  species were confirmed by XPS analysis, albeit coexisting with small amounts of  $\text{Cu}(\text{II})$  (Fig. S4, ESI†). Trace amounts of Ru were detected on the  $\text{Cu}_2\text{O}-\text{RuO}_x$  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  $\text{RuO}_x$ . TAS spectra were recorded after UV excitation (355 nm) of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}/\text{RuO}_x$ , using an experimental setup described previously.<sup>14</sup> 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.<sup>15</sup> Thus, the transient absorption spectrum of  $\text{Cu}_2\text{O}$  films deposited onto the FTO glass was obtained (i) in a  $\text{N}_2$  purged aqueous solution (ii) following the addition of  $\text{Na}_2\text{SO}_3$  as a hole scavenger or (iii)  $\text{AgNO}_3$  as an electron scavenger. Photoexcitation of the  $\text{Cu}_2\text{O}$  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  $<475 \text{ nm}$  and  $>800 \text{ nm}$  (Fig. 2). The signals at wavelengths  $>850 \text{ nm}$  are significantly enhanced by the addition of  $\text{Na}_2\text{SO}_3$  and weakened by the addition of  $\text{AgNO}_3$ . Given that  $\text{Na}_2\text{SO}_3$  can effectively scavenge holes, while  $\text{Ag}^+$  scavenges electrons, we can assign the transient signals above 850 nm to  $\text{Cu}_2\text{O}$  photoexcited electrons. On the other hand, we observed only the signal corresponding to photoexcited holes in  $\text{Cu}_2\text{O}$  at

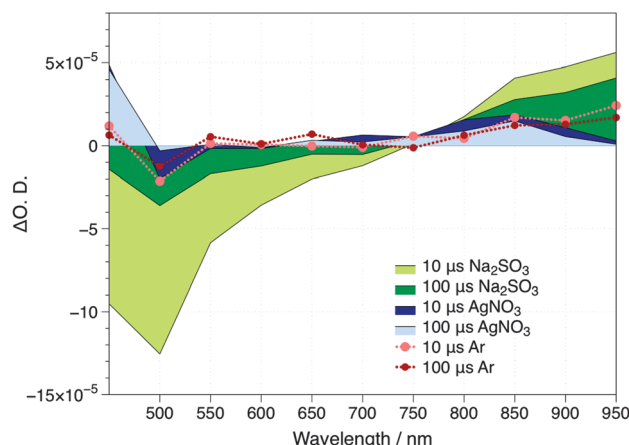


Fig. 2 Transient absorption spectrum of  $\text{Cu}_2\text{O}$  recorded under  $\text{N}_2$ , in the presence of a 0.1 M  $\text{Na}_2\text{SO}_3$  and 0.01 M  $\text{AgNO}_3$  aqueous solutions. The samples were excited at  $\lambda_{\text{ex}} = 355 \text{ nm}$ , with a laser intensity of  $\sim 1.2 \text{ mJ cm}^{-2}$ .

wavelengths  $<475 \text{ nm}$  when using  $\text{AgNO}_3$  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  $\text{Cu}_2\text{O}$  are already present in the 10  $\mu\text{s}$  timescale, our measurements indicate that electron–hole scavenging by the relevant chemicals are very fast ( $<10 \mu\text{s}$ ), 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.<sup>4b,16</sup> Thus, transient absorption spectroscopy experiments were also employed to assay the effect of  $\text{RuO}_x$  deposition on the  $\text{Cu}_2\text{O}$  charge carrier dynamics. Typical kinetic data of the photoinduced electron absorption signals taken at 950 nm are



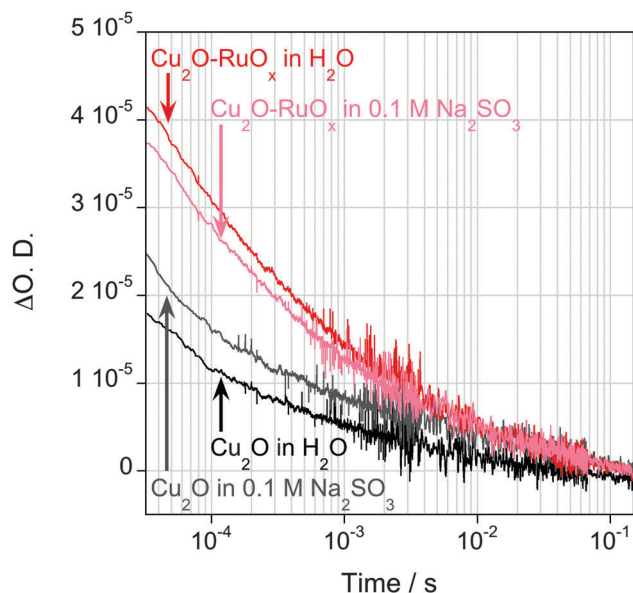


Fig. 3 TAS decays of photo-excited electrons of  $\text{Cu}_2\text{O}$  films (black trace) and  $\text{Cu}_2\text{O-RuO}_x$  films (red trace) in  $\text{N}_2$  purged water, and in the presence of a  $\text{N}_2$  purged 0.1 M  $\text{Na}_2\text{SO}_3$  aqueous solution ( $\text{Cu}_2\text{O}$  films: grey trace,  $\text{Cu}_2\text{O-RuO}_x$  films: pink trace). Data obtained at  $\lambda_{\text{probe}} = 950$  nm with an excitation intensity of  $1.6 \text{ mJ cm}^{-2}$  at  $\lambda_{\text{ex}} = 355$  nm.

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 ( $< 10 \text{ }\mu\text{s}$ ) electron-hole recombination in these films. The presence of  $\text{Na}_2\text{SO}_3$  resulted in an increase in the amplitude of this  $\text{Cu}_2\text{O}$  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  $\text{Cu}_2\text{O}$  surface (Fig. 1a). The deposition of  $\text{RuO}_x$  on the  $\text{Cu}_2\text{O}$  surface results in a significant increase in the amplitude of the long-lived electron signal, independent of the presence of  $\text{Na}_2\text{SO}_3$ , and indicative of a more efficient reduction in fast electron-hole recombination losses. These results qualitatively suggest that  $\text{RuO}_x$  deposition results in a significant increase in the yield of long-lived ( $> 100 \text{ }\mu\text{s}$ )  $\text{Cu}_2\text{O}$  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  $\text{Cu}_2\text{O}$  to  $\text{RuO}_x$ , thereby increasing the spatial separation of electrons and holes and facilitating the photo-oxidation reaction by holes. The lack of absorption of  $\text{RuO}_x$  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  $\text{RuO}_x$  by  $\text{Cu}_2\text{O}$  photoexcited electrons, and therefore confirms our peak assignment.<sup>17</sup> We want to note that a  $\text{Cu}_2\text{O-Al:ZnO-TiO}_2\text{-RuO}_x$  heterojunction for  $\text{H}^+$  reduction, where the  $\text{Cu}_2\text{O}$  and  $\text{RuO}_x$  interfaces are connected through an interfacial ( $\text{AZO-TiO}_2$ ) layer, has been reported by Tilley *et al.*<sup>6d</sup> Contrary to our approach, where  $\text{RuO}_x$  accepts the holes from  $\text{Cu}_2\text{O}$ , charge separation in  $\text{Cu}_2\text{O-AZO-TiO}_2\text{-RuO}_x$  takes place through

electron transfer from  $\text{Cu}_2\text{O}$  to  $\text{RuO}_x$ . We believe that, while in the  $\text{Cu}_2\text{O-AZO-TiO}_2\text{-RuO}_x$  there is a favorable downhill electron transfer cascade from  $\text{Cu}_2\text{O}$  to  $\text{RuO}_x$ , the  $\text{AZO-TiO}_2$  layer blocks the hole transfer to  $\text{RuO}_x$ .

The effect of enhanced charge separation by the  $\text{Cu}_2\text{O-RuO}_x$  junction strategy on  $\text{CO}_2$  photoreduction was tested using analogous bare  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O-RuO}_x$  nanoparticulate suspensions in  $\text{CO}_2$ -saturated deionised  $\text{H}_2\text{O}$  in the presence of a  $\text{Na}_2\text{SO}_3$  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  $\lambda \geq 420 \text{ nm}$ ,<sup>9b</sup> the coupling of  $\text{Cu}_2\text{O}$  with  $\text{RuO}_x$  results in a nearly sixfold increase of the initial rate of  $\text{CO}$  production, from  $0.16 \text{ }\mu\text{mol g}^{-1}$  on bare  $\text{Cu}_2\text{O}$  to around  $0.88 \text{ }\mu\text{mol g}^{-1}$  on the  $\text{Cu}_2\text{O-RuO}_x$  junction after 1 h irradiation using a 150 W Xe lamp. Trace amounts of methanol ( $0.01 \text{ }\mu\text{mol g}^{-1} \text{ h}^{-1}$ ) and methane ( $< 0.001 \text{ }\mu\text{mol g}^{-1} \text{ h}^{-1}$ ) were also observed in the  $\text{Cu}_2\text{O-RuO}_x$  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.*  $600 \pm 40 \text{ }\mu\text{W cm}^{-2}$ ). The apparent initial quantum yield for  $\text{CO}$  generation (20 min) for the  $\text{Cu}_2\text{O-RuO}_x$  heterojunction was determined to be *ca.* 1.6%. It is also noted that the  $\text{CO}$  evolution rate is reduced after the first hour. These results can be explained in terms of the instability of  $\text{Cu}_2\text{O}$  towards the presence of increasing amounts of  $\text{SO}_4^{2-}$  formed upon scavenging the holes by  $\text{Na}_2\text{SO}_3$ .<sup>18</sup> Another possible explanation for non-linear  $\text{CO}$  evolution could be the strong interaction between  $\text{CO}$  and  $\text{Cu}_2\text{O}$ , which will result in lowered catalytic activity over time.<sup>19</sup> Studies to address this instability by using alternative hole scavengers and further modifying material protection layers are ongoing.

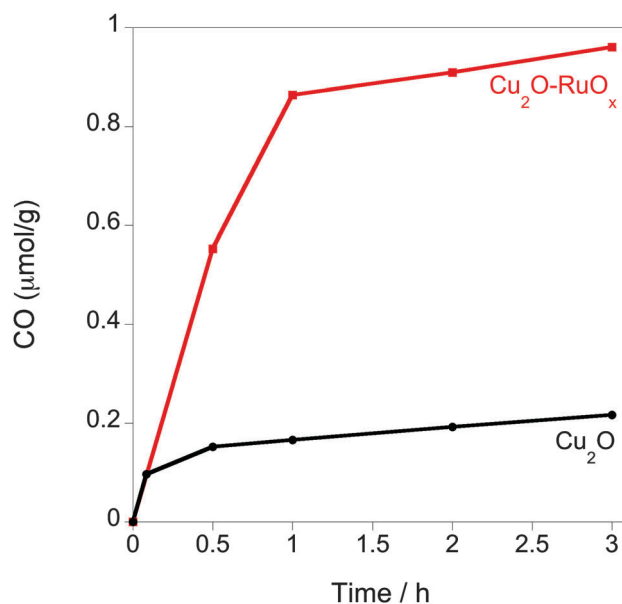


Fig. 4  $\text{CO}_2$  reduction to  $\text{CO}$  on bare and heterojunction based  $\text{Cu}_2\text{O}$  core photocatalysts under full arc 150 W Xe lamp irradiation. Photoreduction reactions were undertaken in 3 mL of  $\text{CO}_2$  saturated  $\text{H}_2\text{O}$  in the presence of a hole scavenger (*ca.* 0.7 M  $\text{Na}_2\text{SO}_3$ ).



$\text{RuO}_x$  has been reported to be able to either reduce or oxidize water,<sup>6d,20</sup> but is unable to reduce  $\text{CO}_2$  due to its work function being more positive than the  $E_{\text{red}}(\text{CO}_2/\text{CO})$  reduction potential. We did not observe any water oxidation and oxygen evolution upon the addition of  $\text{RuO}_x$ , as holes are preferentially scavenged by  $\text{Na}_2\text{SO}_3$ . Thus, the increase in the  $\text{CO}_2$  photoreduction yield is consistent with the efficient charge separation due to the inorganic heterojunction, where holes are transferred to  $\text{RuO}_x$  and  $\text{CO}_2$  reduction takes place at the surface of  $\text{Cu}_2\text{O}$ .

In order to provide evidence that the formation of CO is due to the photoreduction of  $\text{CO}_2$  by  $\text{Cu}_2\text{O}$ , 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  $\text{CO}_2$  until there was no increase in the CO or  $\text{CO}_2$  amount as detected by gas chromatography before the photocatalytic measurements. (2) Control experiments under similar conditions but in the absence of photocatalyst,  $\text{CO}_2$  or light, and irradiating the  $\text{Cu}_2\text{O}$  with longer wavelength light ( $\lambda > 668$  nm, much lower than  $\text{Cu}_2\text{O}$  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  $^{13}\text{CO}$  ( $m/z$  29) (Fig. S6, ESI†). These results strongly indicate that the CO observed by GC is due to photochemical reduction of  $\text{CO}_2$  rather than from the reduction of organic contaminants present on the surface of  $\text{Cu}_2\text{O}$ – $\text{RuO}_x$ .

## Conclusions

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

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