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

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Ernest Pastor,[a] Federico M. Pesci,[a] Anna Reynal,*[a] Albertus D. Handoko,‡[b] Mingjia Guo,[b] Xiaoqiang An,[b] Alexander J. Cowan,§[a] David R. Klug,[a] James R. Durrant[a] and Junwang Tang*[b]

We employ transient absorption spectroscopy to record the absorption spectrum of photogenerated charge carriers in Cu_2O. We have found that CO_2 reduction in Cu_2O is limited by fast electron–hole recombination. The deposition of RuO_x nanoparticles on Cu_2O 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_2O_3 and other photoanodes for the related reaction of photochemical water-splitting.[5]

Herein, we report the dynamics of charge carriers in Cu_2O. To the best of our knowledge, the absorption spectrum and dynamics of photoexcited electrons in Cu_2O 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_2O 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_2O, 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, $x \leq 2$) on top of Cu_2O improves its photocatalytic activity towards CO_2 reduction.[9b] Herein, we focus on the study of the dynamics of photogenerated electrons in Cu_2O 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_2O 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_2O, thereby potentially increasing the yield of long-lived electrons in Cu_2O to enable the reduction of CO_2. RuO_x is also less likely to react with Cu_2O to form an unwanted interfacial layer and

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[a] *Department of Chemistry, Imperial College London, Exhibition Road, SW7 2AZ, London, UK. E-mail: a.reynal@imperial.ac.uk*

[b] *Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, UK. E-mail: junwang.tang@ucl.ac.uk*

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‡ Present address: Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore.

§ Present address: Stephenson Institute for Renewable Energy, Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK.

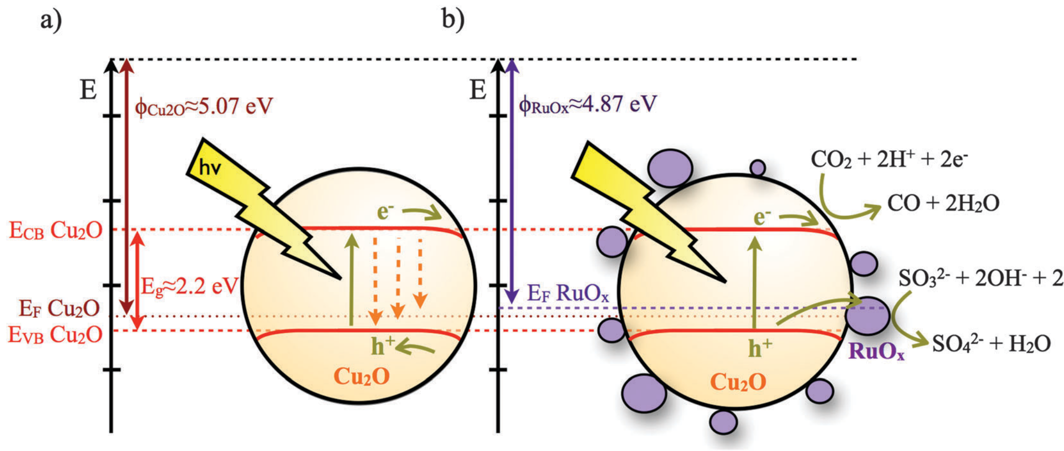

Fig. 1 Schematic of Cu_2O and the Cu_2O/RuO_x band diagram and electron and hole transfer reactions for the photocatalytic CO_2 reduction. Energy values were taken from ref. 8*b* and 12. E_F stands for Fermi level, E_{CB} and E_{VB} indicate the energy levels of the conduction band and valence band,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

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 samples, and Cu(I) species were confirmed by XPS analysis, albeit coexisting with small amounts of Cu(II) (Fig. S4, ESI†). Trace amounts of Ru were detected on the 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^+ scavenges 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.

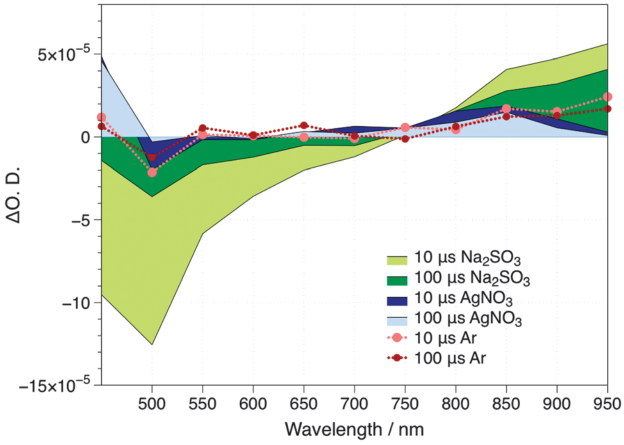

Fig. 2 Transient absorption spectrum of Cu_2O recorded under N_2, in the presence of a 0.1 M Na_2SO_3 and 0.01 M $AgNO_3$ aqueous solutions. The samples were excited at λ_{ex} = 355 nm, with a laser intensity of ∼1.2 mJ cm^{-2}.

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.[4b,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

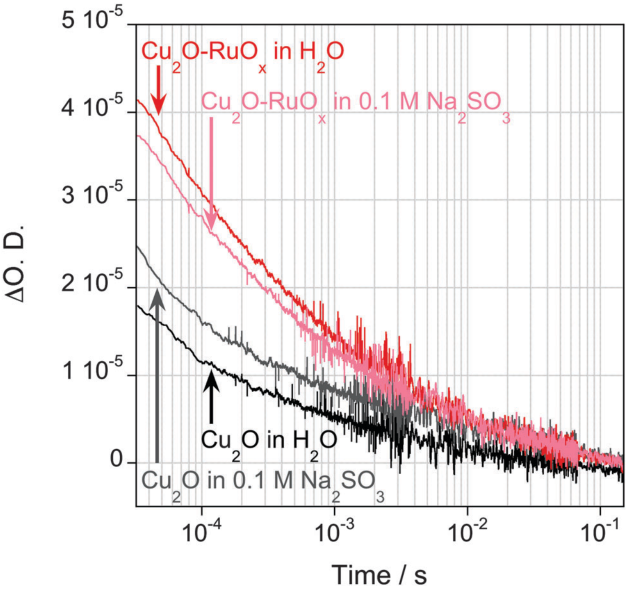

Fig. 3 TAS decays of photo-excited electrons of Cu_2O films (black trace) and Cu_2O–RuO_x films (red trace) in N_2 purged water, and in the presence of a N_2 purged 0.1 M Na_2SO_3 aqueous solution (Cu_2O films: grey trace, Cu_2O–RuO_x films: pink trace). Data obtained at λ_{probe} = 950 nm with an excitation intensity of 1.6 mJ cm^{-2} at λ_{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 μs) electron–hole recombination in these films. The presence of Na_2SO_3 resulted in an increase in the amplitude of this Cu_2O 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 Cu_2O surface (Fig. 1a). The deposition of RuO_x on the Cu_2O surface results in a significant increase in the amplitude of the long-lived electron signal, independent of the presence of Na_2SO_3, and indicative of a more efficient reduction in fast electron–hole recombination losses. These results qualitatively suggest that RuO_x deposition results in a significant increase in the yield of long-lived (>100 μs) Cu_2O 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 Cu_2O to RuO_x, thereby increasing the spatial separation of electrons and holes and facilitating the photo-oxidation reaction by holes. The lack of absorption of RuO 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 RuO_x by Cu_2O photoexcited electrons, and therefore confirms our peak assignation.[17] We want to note that a Cu_2O–Al:ZnO–TiO_2–RuO_x heterojunction for H^+ reduction, where the Cu_2O and RuO_x interfaces are connected through an interfacial (AZO–TiO_2) layer, has been reported by Tilley *et al.*[6d] Contrary to our approach, where RuO_x accepts the holes from Cu_2O, charge separation in Cu_2O–AZO–TiO_2–RuO_x takes place through electron transfer from Cu_2O to RuO_x. We believe that, while in the Cu_2O–AZO–TiO_2–RuO_x there is a favorable downhill electron transfer cascade from Cu_2O to RuO_x, the AZO–TiO_2 layer blocks the hole transfer to RuO_x.

The effect of enhanced charge separation by the Cu_2O–RuO_x junction strategy on CO_2 photoreduction was tested using analogous bare Cu_2O and Cu_2O–RuO_x nanoparticulate suspensions in CO_2-saturated deionised H_2O in the presence of a Na_2SO_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 $\lambda \geq 420$ nm,[9b] the coupling of Cu_2O with RuO_x results in a nearly sixfold increase of the initial rate of CO production, from 0.16 μmol g^{-1} on bare Cu_2O to around 0.88 μmol g^{-1} on the Cu_2O–RuO_x junction after 1 h irradiation using a 150 W Xe lamp. Trace amounts of methanol (0.01 μmol g^{-1} h^{-1}) and methane (<0.001 μmol g^{-1} h^{-1}) were also observed in the Cu_2O–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 nm, filtered light output *ca.* 600 ± 40 μW cm^{-2}). The apparent initial quantum yield for CO generation (20 min) for the Cu_2O–RuO_x 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 Cu_2O towards the presence of increasing amounts of SO_4^{2-} formed upon scavenging the holes by Na_2SO_3.[18] Another possible explanation for non-linear CO evolution could be the strong interaction between CO and Cu_2O, which will result in lowered catalytic activity over time.[19] Studies to address this instability by using alternative hole scavengers and further modifying material protection layers are ongoing.

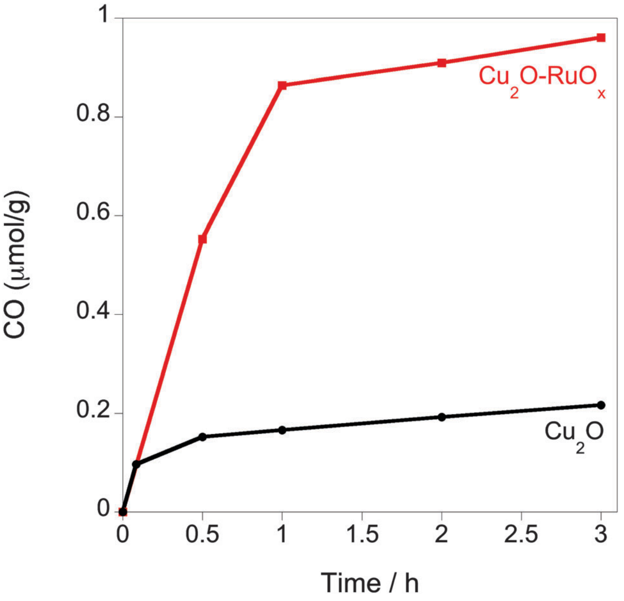

Fig. 4 CO_2 reduction to CO on bare and heterojunction based Cu_2O core photocatalysts under full arc 150 W Xe lamp irradiation. Photoreduction reactions were undertaken in 3 mL of CO_2 saturated H_2O in the presence of a hole scavenger (*ca.* 0.7 M Na_2SO_3).

RuO_x 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 $E_{red}(CO_2/CO)$ reduction potential. We did not observe any water oxidation and oxygen evolution upon the addition of RuO_x, as holes are preferentially scavenged by Na_2SO_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_x and CO_2 reduction takes place at the surface of Cu_2O.

In order to provide evidence that the formation of CO is due to the photoreduction of CO_2 by Cu_2O, 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_2O with longer wavelength light ($\lambda >$ 668 nm, much lower than Cu_2O 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 $Cu_2O–RuO_x$.

Conclusions

In summary, we have assigned the transient absorption spectrum of Cu_2O photoexcited electrons to appear at wavelength $\lambda > 800$ nm, and holes at $\lambda < 475$ nm. In bare Cu_2O films, the major loss pathway limiting their photocatalytic activity is the fast electron–hole recombination. Our results demonstrate that the $Cu_2O–RuO_x$ heterojunction strategy is effective in partially suppressing this electron–hole recombination loss through the transfer of photogenerated holes from Cu_2O to RuO_x. This is shown by a significant increase in the yield of long-lived Cu_2O electrons as observed by transient absorption spectroscopy. This electron yield and a lifetime increase is translated into a sixfold photocatalytic reaction increase by $Cu_2O–RuO_x$ coupling in favour of CO_2 reduction.

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