Charge Transfer and Photocatalytic Activity in CuO/TiO₂ Nanoparticle Heterojunctions Synthesised through a Rapid, One-Pot, Microwave Solvothermal Route

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Rapid charge carrier recombination is a major limiting factor over efficiency in many semiconductor photocatalysts. To address this, copper(II) oxide/titanium dioxide (CuO/TiO₂) heterojunctions were synthesised through a novel, rapid solvothermal microwave procedure using a low-cost copper precursor and commercial P25 TiO₂, taking as little as *five minutes* to synthesise well-defined CuO nanoparticles onto the host TiO₂, achieving an intimate contact. The resultant composites encompass pure CuO particles of approximately 6–7 nm diameter, confirmed by means of high resolution transmission electron microscopy and X-ray photoelectron spectroscopy analysis. Photoelectrochemical water splitting was enhanced by nearly 2 times using the junction, whilst \approx 1.6 times enhancement in the photocatalytic mineralisation of a model organic pollutant 2,4-dichlorophenoxyacetic acid (2,4-D) was observed. Furthermore, we studied the initial decomposition mechanism of 2,4-D by means of GC-MS analysis. The increase in catalytic activity, investigated by impedance analysis (Mott–Schottky plots) and photoluminescence spectra, is attributed to photoelectron transfer from the more negative conduction band (CB) of TiO₂ to CuO, leaving the photohole on TiO₂ to take part in oxidation reactions. This strategy allows for in situ charge separation which facilitates superior photocatalytic activity for both pollutant degradation and water splitting.

Introduction

In recent years, semiconductor photocatalysis has shown great potential as a low-cost, environmental friendly and sustainable technology to remove harmful contaminants from water supplies and for renewable energy generation (water splitting into hydrogen fuel).^[1] However, inefficient carrier separation resulting in rapid recombination limits overall efficiencies for both contaminant removal and renewable energy applications.^[2] Heterojunctions based on the combination of narrow bandgap metal oxides and/or co-catalysts with titanium dioxide (TiO₂) have been widely used as composite photocatalysts to alleviate recombination and speed up reaction kinetics, whereby charge carriers are vectorially transferred from one semiconductor to either another semiconductor or co-catalyst in intimate contact.^[3] Importantly, photocatalysis facilitates a cheap and efficient route for pollutant removal from water supplies, which is of utmost importance in developing countries. A further advantage is that through using the environmentally friendly oxidant O₂, photocatalytic reactions can be performed at room temperature through formation of superoxide radicals (oxygen reduction reaction; ORR).^[4] In aqueous solution, valence band holes can oxidise hydroxyl ions to highly reactive hydroxyl radicals, which have been shown to be crucial for degradation of organic contaminants.^[5] P25 TiO₂ is one of the

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 Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201500315. most commonly studied photocatalysts, owing to its low cost, high dispersibility (surface area), appreciable stability in solution and reasonable activity under full arc (visible and UV) light irradiation. As P25 is comprised of \approx 70% anatase and 30% rutile TiO₂ polymorphs, it can itself be regarded as a homojunction with a staggered energy band alignment at the anatase/ rutile interface, therefore, photogenerated electrons will preferentially move to anatase owing to its lower conduction band minimum energy, and holes will move to rutile owing to its higher valence band maximum energy.^[6] To improve the activity further, cheap, earth abundant, non-toxic co-catalysts can be brought in close contact to the TiO₂ surface to aid charge separation.^[7] It is preferable that the method employed to deposit co-catalysts is both cost effective and easy to scale up. For example, photodeposition of Fe^{III} species on TiO₂ was demonstrated to be significantly more effective for both water splitting and pollutant degradation, caused by electron transfer to Fe₂O₃ from TiO₂.^[8] Theoretical calculations revealed that this junction also renders the TiO₂ surface more reactive toward O₂ molecules for the ORR, which is the rate-determining step in photocatalytic environmental purification. However, the low efficiency of photodeposition (less than 50%) limits the overall potential for scale-up, hence a mild, alternative efficient synthetic strategy is required.

Herein, we demonstrate a highly efficient solvothermal microwave precipitation method to fabricate pure CuO/TiO_2 nanocomposite junction photocatalysts, which is performed rapidly under relatively mild conditions and derived from cheap, soluble Cu^{II} salt precursors. Surprisingly, there are fewer reports on the utilisation of CuO as either a photocatalyst or



co-catalyst despite possessing a band-gap in the visible region and being composed of cheap, earth abundant elements. Hashimoto has described the enhanced photocatalytic activity of Cu^{II}-loaded TiO₂ for organic oxidation, caused by electron transfer to CuO forming Cu^I, then reduction of O₂ which regenerates Cu^{II} again.^[9,10] CuO as a co-catalyst has also been proven to improve photocatalytic activity when combined with WO₃ through a similar mechanism.^[11]

Nevertheless, the ambiguity over the positions of the conduction and valence band positions in CuO has perhaps limited its investigation for photocatalytic applications. Furthermore, there are very few reports of the synthesis of robust junctions using microwave precipitation, which is somewhat surprising given the potential advantage of utilising this technique, which include high-speed, efficiency and excellent yield.^[12] Indeed, if the microwave-assisted reaction is performed in a closed vessel under high pressure and stirring, more energy input at the same temperature coupled with a huge acceleration in reaction time can be achieved, and, therefore, a reaction which under conventional hydrothermal or solvothermal conditions would take several hours, can be completed in as little as a few minutes. The reported CuO/TiO₂ composites were characterised fully by means of XRD, UV/vis, X-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM), which altogether revealed copper species present as pure Cu^{II}, that is, CuO in the composites. The loading of CuO on TiO₂ was optimised and investigated for photocurrent generation and degradation of a model herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) under full arc solar irradiation. 2,4-D is a member of the highly toxic phenoxy family of herbicides and pesticides which were widely used in many developing countries and applied through spraying onto open crop fields for effective weed control, resulting in contaminated river and groundwater supplies. Importantly, the initial photocatalytic degradation mechanism of 2,4-D was elucidated by means of a gas chromatographymass spectrometry (GC-MS) study of the degradation intermediates and the effect of different radicals on its degradation were probed. The mechanism of improved photocatalytic activity for CuO/TiO₂ was probed using photoluminescence spectroscopy and Mott-Schottky analysis to determine band offsets and, therefore, possible charge carrier migration pathways in CuO/TiO₂.

Experimental Section

A microwave solvothermal method was used to fabricate CuO and CuO/TiO₂ composite photocatalysts. In a typical experiment, 0.3 g of commercial P25 (Degussa, composed of about 70 % anatase and 30 % rutile) with a surface area of about 49 $m^2 g^{-1}$ was added to 60 mL absolute ethanol (99.99%, VWR) under vigorous stirring to form slurry. To this, the appropriate amount percentage weight of copper(II) acetate monohydrate [(Cu(CO₂CH₃)₂·H₂O), (98%, VWR)] (e.g. 1 wt %) was added under stirring. The solution was transferred to a Teflon hydrothermal reactor equipped with a magnetic stirrer bar and temperature probe. The solution was subjected to microwave heating (400 W) at 150 °C for a hold time of 5 min at a ramp rate of 10 °Cmin⁻¹. The obtained slurry was filtered using

centrifugation (3000 rpm, 30 min) and washed several times with ethanol and dried at $100\,^{\circ}$ C for 24 h. The exact amount (i.e. the efficiency) of CuO loading was determined by energy-dispersive X-ray spectroscopy (EDS) analysis.

Characterisation

X-ray diffraction (XRD) was performed using a Bruker D4 diffractometer in reflection geometry using Cu-K_{α} radiation ($\lambda =$ 1.54054 Å, 40 kV, 30 mA). UV/vis absorption spectra were collected using a Shimadzu UV/vis 2550 spectrophotometer equipped with an integrating sphere. Reflectance measurements were performed on powdered samples, using a standard barium sulphate powder as a reference. The reflection measurements were then converted to absorption spectra using the Kubelka-Mulk transformation. The morphologies of the products were characterised by HRTEM (JEOL-2010F) coupled with an EDS detector (Oxford Instruments). Highresolution XPS was performed using a Thermo Scientific K-alpha photoelectron spectrometer using monochromatic Al-K_a radiation; peak positions were calibrated to carbon (284.5 eV) and plotted using the CasaXPS software. Specific surface area measurements were taken using the BET method (N₂ absorption, TriStar 3000, Micromeritics). Photoluminescence (PL) spectra were conducted using a Renishaw 1000 Raman system using a $\lambda = 325$ nm laser at room temperature.

Photocatalysis measurements

The photocatalytic activity of the TiO₂-based composites was firstly investigated by measuring the photodegradation of 2,4-D, which was monitored using UV/vis spectroscopy for decomposition and total organic carbon (TOC) analysis for mineralisation, in an identical procedure to that published previously.^[8] In a typical measurement, 10 mg of photocatalyst was suspended in 100 mL of a 50 ppm aqueous solution of 2,4-D in deionised water. The suspension was sonicated then stirred in the dark for 2 h to achieve the equilibrium adsorption. The suspension was then illuminated with a full arc 300 W Xenon lamp. The concentration change of 2,4-D was monitored by measuring the UV/vis absorption spectra of the suspension at regular 30 min intervals, using a Shimadzu UV/visible 2550 spectrophotometer. Owing to the very small particle size of CuO, for each measurement the suspension was filtered three times using a filter syringe to remove the insoluble photocatalyst before UV/vis measurements. The TOC was measured at the same time intervals using a Shimadzu TOC-L analyser to confirm the degree of mineralisation. GC-MS analysis of the intermediates formed during the mineralisation of 2,4-D was obtained using a Shimadzu GC-MS 2010 equipped with a silica capillary column by injecting \approx 0.1 µl of a 500 ppm initial concentration of 2,4-D in water.

Photocurrent studies were performed to further test the photocatalytic activity of the composite junction. In a typical run, 15 mg of photocatalyst and 10 μ L of Nafion solution (5 wt %) were dispersed in a 1 mL water/isopropanol mixed solvent (3:1 v/v) followed by 30 min ultrasound sonication to form a homogeneous colloid suspension. For the measurements, 100 μ L of the catalyst colloid was deposited onto fluorine-doped tin oxide (FTO) conductive glass (TEC 15, 35 Ω , \approx 1 cm²) by spin-coating at 500 rpm for 30 s to form a working electrode. A platinum mesh was used as a counter electrode whilst an Ag/AgCl electrode was employed as the reference electrode in a three electrode photoelectrochemical cell. The electrolyte was 0.5 m Na₂SO₄ (pH 6.5) aqueous solution



degassed with argon for 30 min. Mott–Schottky (impedance) plots were obtained at a frequency of 1 kHz in the dark with an AC amplitude of 5 mV. Equation (1) was used to determine flat band potential ($V_{\rm fb}$).

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon_r e N_A} \left(V - V_{\rm fb} - \frac{k_{\rm B} T}{e} \right) \tag{1}$$

Here $N_{\rm A}$ is the carrier density, ε_0 is the permittivity in vacuum; ε_r is the relative permittivity; *V* is the applied potential and *T* is the absolute temperature. Value *e* is the electronic charge, and $k_{\rm B}$ is the Boltzmann constant. Hence a plot of $1/C^2$ versus potential (*V*) will yield a line, which when extrapolated to the *x*-axis, will correspond to the flat-band potential of the semiconductor.^[13] Potentials were referenced to the reversible hydrogen electrode (RHE) using the Nernst equation [Eq. (2)]:

$$E_{\rm RHE} = E^{0}_{\rm Ag/AgCl} + E_{\rm Ag/AgCl} + 0.059 \,\text{pH}$$

$$E^{0}_{\rm Ag/AgCl} = 0.1976 \text{ at } 25 \,^{\circ}\text{C}. \tag{2}$$

Results and Discussion

Microwave solvothermal treatment of the preformed P25 TiO_2 particles with copper(II) acetate at a temperature of 150°C in ethanol solvent at a holding time of 5 min resulted in lightbrown coloured fine particles after filtration and washing in ethanol. A typical X-ray diffraction pattern of the largest loading of Cu (20 wt% Cu) on P25 TiO_2 is shown in Figure 1b, together with the XRD pattern of untreated P25 powder. For



Figure 1. XRD patterns of a) CuO nanoparticles, b) 20% CuO/P25 and P25.

20 wt% Cu loading all of the XRD peaks can be indexed to both anatase and rutile forms of TiO₂, with no obvious peaks that could be ascribed to copper species, possibly due to the low nominal loading or high dispersion over TiO₂. In the absence of P25, copper(II) acetate was dissolved in ethanol and heated to 150 °C. The resultant dark brown solid was washed and dried in an identical manner used for synthesis of the Cu/ TiO₂ composites. The XRD pattern of this material (Figure 1 a) revealed the formation of pure CuO (Tenorite, JCPDS 48–1548), indicating that the TiO₂ does not catalyse the production of copper(II) oxide species in this system. Thus microwave treatment appears to be an effective preparative route to synthesise CuO particles very rapidly.

Raman spectroscopy was also utilised to identify the species present in the composites. Figure S1 shows the Raman spectra recorded at a laser wavelength of 514.5 nm for CuO/P25, pristine P25 TiO₂ and CuO powder synthesised by microwave solvothermal treatment. As the anatase and rutile polymorphs belong to different space groups ($I4_1/amd$, Z=4 for anatase, $P4_2/mnm$, Z=2 for rutile), the peaks centred at 142 (E_q), 197 (E_g), 394(B_{1g}), 517 (A_{1g}) and 640 cm⁻¹ (E_g) were attributed to the anatase phase, whilst low intensity peak broadening at 445 and 610 cm^{-1} was attributed to the E_g and A_{1g} vibrational modes of the rutile phase.^[14] The CuO particles exhibited the characteristic Raman scattering pattern attributed to CuO in the literature; ^[15] the broad peak corresponding to the A_{α} mode was found at 282 cm^{-1} , with the B_{q} vibration contributing to the peaks observed at 335 and 620 cm⁻¹. No other peaks were identified from the Raman pattern which provides further evidence that the sample is pure CuO. Likewise, for the 5% CuO/ P25 sample, broad peaks for CuO were observed at 280 and 618 cm^{-1} , with the high intensity peak at 149 cm^{-1} originating from the anatase phase of TiO₂.

The UV/vis absorption spectra of pristine P25 and various CuO/TiO₂ with different CuO loadings (Figure 2) revealed the expected band-gap TiO₂ absorption at 3.2 eV, however, increasing the CuO loading resulted in a slight red-shift and an increased visible absorption was observed ($\lambda > 400$ nm), which was not surprising given the dark brown appearance of pure CuO. Indeed from the absorption spectrum of pure CuO (Supporting Information Figure S2), a band-gap absorption of ≈ 1.3 eV and strong visible light absorption was exhibited, as expected for CuO according to literature reports.^[16]



Figure 2. UV/vis absorption spectra of CuO/P25 composites.

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Figure 3. XPS Spectra of a) Cu2p regions in CuO and CuO/P25 and b) Ti2p region in CuO/P25.

X-ray photoelectron spectroscopy was utilised to ascertain the exact chemical valence state of the copper species present in the samples. Figure 3a shows the XPS spectra of both pure CuO and 20 wt% CuO/P25 synthesised by microwave solvothermal synthesis. In both cases, copper species is present as Cu^{II} as both samples exhibit characteristic peaks for Cu2p_{3/2} at 934.2 eV and Cu2p_{1/2} at 954 eV.^[17] The shake-up satellite peaks characteristic of the presence of Cu^{II} are clearly observed between 940–945 eV and 963 eV. In comparison, but as expected, the microwave solvothermal synthesis method did not alter the chemical state of titanium in the CuO/P25 composite, evidenced by the characteristic Ti2p_{3/2} peak at 458.7 eV, associated with the presence of Ti⁴⁺ (Figure 3b).^[18] XPS, therefore, provides additional evidence for the formation of pure Cu^{II} species in the junctions.

The as-synthesised particles were analysed by TEM imaging. The TEM image of pristine P25 TiO_2 is shown in the Supporting Information, Figure S3, which exhibits particles of approximately 20–60 nm in diameter. In contrast, the TEM images of both 5% and 20% CuO/P25 are shown in Figure 4a and b respectively. One can still distinguish the larger P25 TiO_2 as straightedged particles, however, there appears to be clusters of smaller particles randomly positioned on the TiO_2 facets. EDS analysis revealed these particles to consist of copper species, whilst the HRTEM image of the sample synthesised by microwave solvothermal treatment in the absence of P25 resulted in

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Figure 4. TEM images of a) 5% CuO/P25 and b) 10% CuO/P25, c) HRTEM of CuO nanoparticles synthesised by microwave solvothermal treatment, d) HRTEM of 20% CuO/P25.

5-10 nm diameter CuO particles (Figure 5c). The particle size distribution (see Figure S4, Supporting Information) indicated that a mean particle size of between 6-7 nm could be synthesised under these microwave conditions. The size and morphology are in stark contrast to CuO particles synthesised under microwave conditions using copper(II) acetate precursor with and without urea, reported recently, which exhibited a flowerlike morphology consisting of \approx 500 nm diameter structures.^[19] In the present work, it is proposed that CuO formation is most likely attributable to the decomposition of in situ formed Cu(OH)₂ during hydrolysis or its reaction with ethanol solvent. From this sample, the lattice spacing which corresponds to the [111] 0.23 nm interplanar spacing of CuO was detected. The HRTEM of the 20% CuO/P25 junction revealed lattice spacings of 0.35 nm for anatase [101] and 0.32 nm for rutile [110] planes respectively. Additionally, the CuO [110] lattice fringe was observed at 0.27 nm for a single CuO particle which is shown on the surface of a TiO₂ particle. Thus a robust, intimate contact is formed between the two individual materials, which is beneficial for charge transfer. Notably, owing to the high energy of HRTEM, some beam damage was observed which led to distortion of the edges of the nanoparticles at this high magnification. To check the distribution of CuO species on TiO₂, EDS mapping was performed on several samples (see Supporting Information, Figure S5). Somewhat surprisingly, the EDS map indicates that the loading efficiency of microwave synthesis is close to 100% in these composites, for example, the 10 wt% nominal copper loaded sample resulted in an actual loading amount of Cu species as high as 9.7%. Similarly, for the 5 wt% Cu loading, an actual loading of 4.4% Cu species was observed. The distribution also appeared to be quite





Figure 5. a) Typical degradation of 2,4-D over 1% CuO/P25 followed by UV/vis spectroscopy, b) degradation of 2,4-D over various CuO/P25 junction composites, c) TOC removal over CuO/P25 junction composites, d) degradation rates of the CuO/P25 composites, revealing 5% CuO/P25 to be the most active sample.

homogeneous over the sample, which indicates the advantage of microwave synthesis for rapid and efficient nanoparticle synthesis compared to other methods of co-catalyst deposition, such as photodeposition or impregnation.

Photocatalytic testing

The application of these CuO/TiO₂ heterojunction composites for photocatalytic removal of toxic herbicides was evaluated by the photo-mineralisation of 2,4-D, which was monitored by UV/vis absorption spectroscopy and TOC analysis. Similar to our previous report, zero degradation of a 50 ppm solution of 2,4-D in deionised water was observed after irradiation with a full-arc 300 W solar lamp at room temperature in the absence of photocatalyst.^[8] To assess the activity of bare CuO toward 2,4-D degradation, 10 mg of CuO was dispersed into a 50 ppm 2,4-D aqueous solution and irradiated with a full arc 300 W Xe light source for 4 h, which resulted in zero degradation of the pollutant over this time frame, likely, in part, to be attributable to the band positions of CuO, which are not sufficiently aligned for oxidation reactions or the one electron reduction of O₂.^[20] However, the pristine P25 showed appreciable activity, with an approximate 80% removal efficiency over the four hour period according to the UV/vis spectrum. A typical UV/vis spectrum observed during the degradation of 2,4-D is shown in Figure 5a. Upon introducing CuO onto P25 TiO₂, a notable enhancement in 2,4-D removal was observed for the majority of samples. For low CuO loadings, that is, 0.5% and 1%, a little enhancement in degradation over P25 was observed;

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however, the largest increase was exhibited by the 5% and 10% CuO/P25 samples. In fact the rate constant for the best performing sample (5% CuO/ TiO₂) was calculated to be 2.077 min⁻¹, approximately 1.6 times that of pristine P25 whose rate constant was 1.324 min⁻¹, whereas the rate constant for the 10% CuO/TiO₂ composite was a little lower at 1.547 min^{-1} . In all cases the degradation profile represents first-order kinetics. To ensure that 2,4-D was mineralised in this process instead of being incompletely decomposed to other products, the total organic carbon (TOC) analysis was measured for all of the samples. The results obtained were in good agreement with the degradation results observed in the UV/vis spectra, with the 5% CuO/TiO2 representing the best performing sample. Furthermore, as the TOC value reached zero after a period of \approx 120 min illu-

mination (for the 5% CuO/P25 sample), we can indeed conclude that 2,4-D was mineralised in this process. Hence the optimum CuO loading on P25 was found to be 5% CuO, closely followed by 10% CuO, 1% CuO, 0.5% and lastly, 20% CuO, the latter of which had a detrimental effect compared to pristine P25.

No visible light driven activity ($\lambda > 420 \text{ nm}$) was observed for any of the composites, which demonstrates that excitation in CuO is not responsible for photocatalytic activity. Furthermore, it is likely that the poorer activity of 20% CuO/TiO₂ is owed to screening of photons by highly absorbing CuO, which competes with TiO₂ for light absorption. The active species involved in the photocatalytic mineralisation of 2,4-D over CuO/ TiO₂ were investigated. Isopropanol was utilised as an hydroxyl radical (OH') scavenger, EDTA as a hole scavenger, and potassium iodide as both hole and OH' scavengers. The system was also purged with argon gas to investigate the absence of superoxide radicals on the mineralisation mechanism. No degradation of the organic was observed in the presence of the hole scavenger, whereas a 25% removal was obtained in the absence of O_2^- and $\approx 75\%$ removal using OH scavenger, compared to CuO/P25 (see Figure S6), somewhat similar to the results obtained by Pignatello using methanol as the OH' scavenger.^[21] Addition of both hole and hydroxyl radical scavengers together resulted in no decomposition, indicating the decomposition of 2,4-D is dominated by a hole mechanism. In fact, it has been reported that the photocatalytic degradation of 2,4-D is 70% governed by OH and 30% by direct oxidation by photoholes.^[22]



To clarify the reasons for the enhanced photoactivity of the heterojunctions, the surface areas of the photo-deposited CuO/TiO₂ samples were measured using a surface area analyser using the BET method (Table S1, Supporting information). A typical N₂ adsorption-desorption isotherm for 5% Cu/P25 is shown in Figure S7, Supporting Information. For pure CuO particles, the surface area obtained was 77 m²g⁻¹, much higher than pristine P25 (49 m^2g^{-1}). However, there appears to be almost negligible variation in surface area for the CuO/TiO₂ composites indicating that microwave treatment did not adversely affect the surface area of P25, nor increase the surface area which could have resulted in better activity for 2,4-D degradation. The stability of a photocatalyst is critically important to lower overall manufacturing costs and would be more beneficial to the environment. To assess the stability of these composites for sequential photocatalytic mineralisation of 2,4-D, 5 cycles of repeated testing using the same photocatalyst sample was conducted (see Supporting Information Figure S8). It is notable that no significant decrease in activity was observed during this repeated testing which is testament to the appreciable stability of these robust composites, which could allow for their utilisation in commercial devices for photocatalytic water treatment. Only a slight decrease in activity was observed after the fifth cycle. Furthermore, post degradation XPS analysis of the sample revealed very little difference according to the Cu2p spectrum (Figure S9, Supporting Information), apart from a slight broadening of the Cu2p_{3/2} signal at 934.2 eV.

To investigate the initial decomposition pathway of the model contaminant 2,4-D, we utilised GC-MS to analyse the degradation products at each stage of the photocatalytic mineralisation process. To improve the sensitivity of the GC-MS technique, a 500 ppm aqueous solution of 2,4-D was used, together with 100 mg of P25 photocatalyst. Direct liquid injection of a 0.1 µl aqueous sample of 2,4-D in the absence of photocatalyst or light irradiation resulted in the expected peak at $m/z^+ = 221$, corresponding to the molecular ion of 2,4-D. After 30 min illumination, a peak at $m/z^+ = 164$ was observed, indicating production of 2,4-dichlorophenol species ($M_w =$ 164 g mol⁻¹). A further peak was observed after 60 min at $m/z^+ = 178$, corresponding to either of the dihydroxy-substituted dichlorobenzenes; 3,5-dichlorocatechol or 4,6-dichlororesorcinol. After 120 min degradation, the only observed product was dihydroxychlorobenzene, followed by trihydroxybenzene after 150 min. This indicates that each chlorine atom is substituted for an OH moiety during the degradation process. It has previously been shown using liquid chromatography, that the first step in the photocatalytic degradation of 2,4-D is the oneelectron oxidation of the carboxylic acid group followed by hydrolysis to yield 2,4-dichlorophenol and glycoxylic acid, which occurs most efficiently at pH 3.^[21] Initial cleavage of the carboxylic acid moiety of 2,4-D was also confirmed by Djebbar et al.^[22] using P25 TiO₂ photocatalyst and GC-MS measurements, however, the major final reaction product measured in their system was 2-chloro-1,4-benzoquinone.

Further illumination of the solution did not yield conclusive results from our GC-MS analysis; however, it is likely that fur-

ther degradation to water and CO_2 eventually takes place.^[23] The initial decomposition pathway, therefore, involves cleavage of the carboxylic acid moiety through its replacement with OH. This is followed by addition of OH at the adjacent carbon, followed by sequential substitution of the remaining chlorine atoms by OH groups. Scheme 1 illustrates the major intermediates detected by GC-MS analysis.



Scheme 1. Intermediates detected using GC-MS during the photocatalytic mineralisation of 2,4-D over P25 TiO_2 .

Photoelectrochemical testing of the composites was performed to verify the mechanism of charge transfer in the heterojunctions. Photoelectrodes were synthesised by spin-coating the colloidal photocatalysts, which were suspended in a Nafion/isopropanol solvent onto FTO-coated glass substrates. They were subsequently dried at 200 °C to remove organic species. Figure 6a shows the current-voltage curves of 5% CuO/P25 and bare P25 in 0.5 м Na₂SO₄ electrolyte (pH 6.5) under both light and dark conditions. The photocurrent of 5% CuO/P25 under full arc 150 W illumination is $\approx 30 \ \mu A \ cm^{-2}$ (at 1 V versus Ag/AgCl) which is over two times higher than that of P25 (\approx 12 μ A cm⁻²), which is in reasonable agreement with the increased activity (almost 1.6 times) observed for photocatalytic degradation of 2,4-D, compared to P25. Dark current was negligible for both samples. The onset potential of CuO/ P25 appears slightly shifted toward more positive potentials, indicating that the photo-generated electrons in TiO₂ are rapidly trapped by CuO, (see Figure 7a, inset ii). One can, therefore, qualitatively reason that the conduction band of CuO is more positive than that of anatase TiO₂. Furthermore, the stability of 5% CuO/P25 was found to be excellent over the 1 hour test period; the transient photocurrent was recorded at a fixed potential of 0.5 V (versus Ag/AgCl) in the same electrolyte (Figure 7a, inset i). Initially the photocurrent transient exhibited a sharp decrease, owing to fast recombination at the start of the experiment, however, for the P25 sample, a gradual decrease in photocurrent was observed, which we attribute to recombination rather than photocorrosion. We used photoluminescence spectroscopy (PL) to investigate the feasibility of charge transfer in the CuO/P25 system. PL spectra has been used extensively to reveal the efficiency of charge carrier trapping, transfer, and separation and to investigate the fate of photogenerated electrons and holes in semiconductors, because the PL emission results from the recombination of free charge carriers.^[24] Figure 6b shows the PL spectra of P25 and







Figure 6. a) *I–V* curves for P25 and 5% CuO/P25 in Na₂SO₄ electrolyte (pH 6.5), insets show i) the transient photocurrent measured at 0.5 V versus Ag/AgCl and ii) enlarged section of the *I–V* curve showing onset region; b) Photoluminescence spectra of P25 and 5% CuO/P25 recorded at room temperature using a 325 nm Raman PL laser.

5% CuO/P25 recorded at room temperature under 325 nm UV excitation. A broad peak centred at 525 nm was observed for pristine P25, whilst strikingly, a very broad emission at much lower intensity was exhibited by CuO/P25. Furthermore, this emission spectrum appears to have red-shifted and is centred at approximately 575 nm. Owing to its low intensity we were not able to accurately fit the spectrum to a model; however, the CuO/P25 exhibits \approx 85% reduction in luminescence, which one can ascribe to efficient rectifying charge transfer between the two materials despite possessing a similar band-gap absorption (from the UV/vis spectra).

Further experiments were undertaken to clarify the most likely direction for charge transfer in the CuO/P25 heterojunction. To do this, one must first rationalise the relative band positions of the two materials, CuO, and the majority phase in P25, anatase TiO₂. One method to experimentally determine the conduction and valence band positions of semiconductors is through the interpretation of impedance (Mott–Schottky) plots. Notably, however, the absolute values obtained by this technique to determine band positions of semiconductors can be strongly affected by particle size, inhomogeneity, surface defects, vacancies, and measurement temperature, to name just a few factors,^[25,26] but the method can be used to give an



Figure 7. Mott–Schottky plots for a) CuO, b) anatase TiO_2 ; c) mechanism of charge transfer in CuO/TiO₂ heterojunctions.

approximation of the valence and conduction band levels in both p- and n-type semiconductors if other techniques are not available.

From the Mott–Schottky plots we can estimate the flat-band position ($E_{\rm fb}$), which is generally considered to be close to the valence band position for p-type semiconductors and located approximately 0.3 V below the conduction band for n-type semiconductors.^[27,28] Consequently, using the same experimental procedure described earlier for the fabrication of P25 and CuO/P25 electrodes, CuO nanoparticles, which were synthesised by microwave solvothermal treatment in the absence of P25, were formed into a working electrode after spin coating. A pure anatase TiO₂ electrode was formed in a similar manner. From the Mott–Schottky plot (Figure 7 a), CuO exhibited the characteristic p-type semiconductor direction of slope, which when extrapolated to the *x*-axis yielded a flat-band position of + 0.51 V versus Ag/AgCl. On the other hand, pure anatase TiO₂



displayed typical n-type behaviour and the slope is in the opposing direction to that of CuO (Figure 7b). The value for $E_{\rm fb}$ for anatase was determined to be -0.52 V (versus Ag/AgCl). Consequently, the position of the valence band of CuO was calculated to be +1.4 V (versus RHE) and its conduction band located at +0.1 V (versus RHE); the latter value derived from the band-gap absorption of CuO, which is approximately 1.3 eV, and is in good agreement with reported values.^[29,30] For TiO_2 , the conduction band is located at approximately -0.24 V (versus RHE) and the valence band at +2.96 V (versus RHE), in good agreement with the literature.^[31] The difference in conduction band energies of the two materials suggests that electron transfer from TiO_2 to CuO is feasible given the $\approx\!0.34\,V$ offset which could provide sufficient driving force for charge separation. This is further evidenced by the fact that pure CuO exhibits zero activity for the organic decomposition, and thus photocatalytic oxidation by CuO does not occur. Hashimoto et al.^[10] have proposed that loading of Cu^{II} on TiO₂ results in the in situ formation of Cu^I species, caused by electron transfer from TiO₂. In air, Cu¹ species can reduce O_2 , whilst becoming oxidised itself back to Cu^{II}. This multi-step reduction process is initiated with a two electron reduction to peroxide [Eq. (3)] and the following possible four-electron reductions [Eqs. (4) and (5)].

$$2 Cu^{I} + O_{2} + 2 H^{+} \rightarrow 2 Cu^{II} + H_{2}O_{2}$$
(3)

$$3 Cu' + O_2 + 4 H^+ \rightarrow 2 Cu'' + Cu''' + 2 H_2 O$$
(4)

$$4 Cu^{I} + O_{2} + 4 H^{+} \rightarrow 4 Cu^{II} + 2 H_{2}O$$
(5)

As the reduction potential of O_2/H_2O_2 is 0.7 V versus NHE, this pathway could be viable for our CuO/TiO₂ junction.^[32]

Recently, a slightly different mechanism was reported for CuO/TiO₂ junctions tested for H₂ evolution from water whereby the authors observed significantly higher activity from 1.7% CuO loaded TiO₂ compared to the unmodified material, owing to the insitu reduction of CuO to Cu species, which acts as a co-catalyst for H₂ production.^[33] However, in the absence of a strong hole scavenger such a mechanism would be unlikely to occur in our junctions. Previously, Cu¹ and Cu⁰ species were photo-deposited onto TiO₂ to yield Cu₂O/TiO₂/Cu triple junctions that exhibited improved removal of the toxic organic pollutant 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) from water.^[34] However, using this photo-reduction method it is extremely difficult to control the selectivity and dispersibility of Cu and Cu₂O over the host photocatalyst. A slightly different mechanism for increased photocatalytic activity for CuO/TiO₂ heterojunctions studied for methylene blue decolourisation has been put forward. Here, EPR spectroscopy revealed the presence of highly dispersed CuO clusters and substitutional Cu²⁺ sites in low weight percentage loadings of CuO in TiO₂ (Ti-O-Cu linkages), whilst larger loadings resulted in CuO acting as a recombination centre.^[35] However, our mechanism is different. We propose that the mechanism for the enhanced activity for CuO/TiO₂ junctions is a multi-step process: upon full-arc illumination there is light absorption and charge-carrier generation in TiO₂, followed by in situ rectifying electron transfer to the conduction band of CuO. Photo-excited holes in TiO₂ may then migrate to the surface for the expected oxidation reactions. In fact, as P25 is composed of anatase and rutile, the complete CuO/P25 composite could be considered a triple junction, however, the question over the direction of charge transfer between anatase and rutile phases is currently a topic of much debate.^[6] Furthermore, we noticed there is no photocatalytic oxidation performed by CuO, which we will now discuss. Firstly, as its valence band position is not well aligned for oxidation reactions and thus exhibits no overpotential (driving force), photocatalytic oxidation is not kinetically nor thermodynamically feasible on the CuO surface. Secondly, and in contrast, the surface of TiO₂ has been demonstrated to be extremely active for both photocatalytic oxidation reactions and surface induced hydrophilicity, whereas crucially, CuO is inactive for both processes.^[36] This hydrophilicity is considered to be induced by structural changes at the surface, that is, through the diffusion of photogenerated holes to the surface of metal oxides (TiO₂) before being trapped at surface lattice oxygen atoms, followed by the dissociative adsorption of a water molecule at these defect sites. It is more likely, therefore, that the photohole diffuses to the TiO₂ surface rather than into CuO upon UV excitation, which rationalises the charge transfer pathway depicted in Figure 7 c and the lack of photocatalytic activity exhibited by CuO alone. This also agrees with our observation upon which the photocatalytic decomposition of 2,4-D is governed by a hole-dominated process.

Conclusions

To the best of our knowledge, we demonstrate for the first time that mild modification of high surface area TiO₂ photocatalysts with robust metal oxide redox co-catalysts using microwave co-precipitation is a promising strategy, which facilitates high loading efficiencies and results in the significant enhancement in photocatalytic activity for water splitting and degradation of toxic organic pollutants. This technique could be easily scaled up, for example, by using continuous flow technology to rapidly synthesise large amounts of material for commercial applications instead of the current batch method described here. It was found that 5% CuO/P25 exhibited a near 1.6 times enhancement in mineralisation of a model organic pollutant, 2,4-D, compared to the benchmark photocatalyst P25 TiO₂. Furthermore, the photocurrent was found to be enhanced by nearly 2 times and the CuO/P25 junction exhibited appreciable stability during both long-term water splitting and organic degradation reactions. As our junctions do not increase the visible light absorption of P25, their function is purely for charge separation and transfer. We have also monitored the photocatalytic mineralisation of 2,4-D and elucidated the intermediates formed using GC-MS, which is important for studies investigating the removal of persistent organic waste matter from water supplies. Finally, the mechanism for this enhancement in efficiency was determined and discussed based upon Mott-Schottky plots, photocurrent measurement and photoluminescence spectroscopy, which revealed that the



most likely path of charge transfer in the CuO/P25 junctions is attributed to electron transfer from TiO_2 to CuO, followed by hole transfer to the TiO_2 surface. Further theoretical work is currently underway to investigate the effect of CuO loading on the surface characteristics of TiO_2 .

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Keywords: copper · oxidation · photocatalyst semiconductor · titania

- S. J. A. Moniz, R. Quesada-Cabrera, C. S. Blackman, J. Tang, P. Southern, P. M. Weaver, C. J. Carmalt, J. Mater. Chem. A 2014, 2, 2922.
- [2] H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu, X. Wang, Chem. Soc. Rev. 2014, 43, 5234.
- [3] S. J. A. Moniz, S. A. Shevlin, D. Martin, Z. Guo, J. Tang, *Energy Environ. Sci.* 2015, 8, 731–759.
- [4] J. Tang, Z. Zou, J. Ye, Angew. Chem. Int. Ed. 2004, 43, 4463; Angew. Chem. 2004, 116, 4563.
- [5] M. N. Chong, B. Jin, C. W. K. Chow, C. Saint, Water Res. 2010, 44, 2997.
- [6] D. O. Scanlon, C. W. Dunnill, J. Buckeridge, S. A. Shevlin, A. J. Logsdail, S. M. Woodley, C. R. A. Catlow, M. J. Powell, R. G. Palgrave, I. P. Parkin, G. W. Watson, T. W. Keal, P. Sherwood, A. Walsh, A. A. Sokol, *Nat. Mater.* 2013, *12*, 798.
- [7] S. Neubert, P. Pulisova, C. Wiktor, P. Weide, B. Mei, D. A. Guschin, R. A. Fischer, M. Muhler, R. Beranek, *Catal. Today* 2014, 230, 97.
- [8] S. J. A. Moniz, S. A. Shevlin, X. An, Z.-X. Guo, J. Tang, Chem. Eur. J. 2014, 20, 15571.
- [9] X. Qiu, M. Miyauchi, K. Sunada, M. Minoshima, Y. L. Min Liu, D. Li, Y. Shimodaira, Y. Hosogi, Y. Kuroda, K. Hashimoto, ACS Nano 2012, 6, 1609.
- [10] H. Irie, K. Kamiya, T. Shibanuma, S. Miura, D. A. Tryk, T. Yokoyama, K. Hashimoto, J. Phys. Chem. C 2009, 113, 10761.

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- [11] T. Arai, M. Horiguchi, M. Yanagida, T. Gunji, H. Sugihara, K. Sayama, J. Phys. Chem. C 2009, 113, 6602.
- [12] L. Pan, X. Liu, Z. Sun, C. Q. Sun, J. Mater. Chem. A 2013, 1, 8299.
- [13] K. Gelderman, L. Lee, S. Donne, J. Chem. Educ. 2007, 84, 685.
- [14] X. Chen, Y.-B. Lou, A. C. S. Samia, C. Burda, J. L. Gole, Adv. Funct. Mater. 2005, 15, 41.
- [15] W. Wang, Q. Zhou, X. Fei, Y. He, P. Zhang, G. Zhang, L. Peng, W. Xie, *CrystEngComm* **2010**, *12*, 2232.
- [16] H. S. Park, C. Lee, E. Reisner, *Phys. Chem. Chem. Phys.* 2014, *16*, 22462.
 [17] S. Poulston, P. M. Parlett, P. Stone, M. Bowker, *Surf. Interface Anal.* 1996,
- 24, 811.
- [18] B. Erdem, R. Hunsicker, G. Simmons, Langmuir 2001, 17, 2664.
- [19] G. Qiu, S. Dharmarathna, Y. Zhang, N. Opembe, H. Huang, S. L. Suib, J. Phys. Chem. C 2012, 116, 468.
- [20] H. Chen, Y. Xu, RSC Adv. 2015, 5, 8108.
- [21] Y. Sun, J. J. Pignatello, Environ. Sci. Technol. 1995, 29, 2065.
- [22] K. Djebbar, A. Zertal, T. Sehili, Environ. Technol. 2006, 27, 1191.
- [23] Y. Yu, J. Ma, Y. Hou, J. Environ. Sci. 2006, 18, 1043.
- [24] Q. Xiang, J. Yu, M. Jaroniec, J. Phys. Chem. C 2011, 115, 7355.
- [25] J. W. Ondersma, T. W. Hamann, Energy Environ. Sci. 2012, 5, 9476.
- [26] R. Beranek, Adv. Phys. Chem. 2011, 786759.
- [27] W. Chun, A. Ishikawa, H. Fujisawa, T. Takata, J. Kondo, M. Hara, M. Kawai, Y. Matsumoto, K. Domen, J. Phys. Chem. B 2003, 107, 1798.
- [28] S. J. A. Moniz, J. Zhu, J. Tang, Adv. Energy Mater. 2014, 4, 201301590.
- [29] Q. Huang, F. Kang, H. Liu, Q. Li, X. Xiao, J. Mater. Chem. A 2013, 1, 2418.
- [30] F. P. Koffyberg, F. A. Benko, J. Appl. Phys. 1982, 53, 1173.
- [31] S. Ho-Kimura, S. J. A. Moniz, A. D. Handoko, J. Tang, J. Mater. Chem. A 2014, 2, 3948.
- [32] H. Yu, H. Irie, Y. Shimodaira, Y. Hosogi, Y. Kuroda, M. Miyauchi, K. Hashimoto, J. Phys. Chem. C 2010, 114, 16481.
- [33] G. Moon, J. Joo, I. Lee, Y. Yin, Nanoscale 2014, 6, 12002.
- [34] X. An, H. Liu, J. Qu, S. J. A. Moniz, J. Tang, New J. Chem. 2015, 39, 314.
- [35] G. Li, N. Dimitrijevic, L. Chen, J. Phys. Chem. C 2008, 112, 19040.
- [36] M. Miyauchi, A. Nakajima, T. Watanabe, K. Hashimoto, Chem. Mater. 2002, 14, 2812.

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