Cu₂O/TiO₂ heterostructures for CO₂ reduction through a direct Z-scheme: Protecting Cu₂O from photocorrosion

Matías E. Aguirre, Ruixin Zhou, Alexis J. Eugene, Marcelo I. Guzman, María A. Grela

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A B S T R A C T
The development of artificial photosynthesis aims to solve the increasing energy demand and associated environmental problems. A model photosynthetic system employing a composite of semiconductors with a Z-scheme can potentially mimic the combined power of photosystems 1 and 2 to transfer electrons. In this work, octahedral cuprous oxide covered with titanium dioxide nanoparticles (Cu₂O/TiO₂) are synthesized by a solvothermal strategy that provides high morphological and crystallographic control. The formation of a p–n heterojunction and characterization of the Type II band alignment of the composite are performed by diffuse reflectance UV-visible (DRUV) spectroscopy, ultraviolet photolocorelectrospectroscopy (UPS), and X-ray photoelectron spectroscopy (XPS). Upon UV-visible irradiation (λ ≥ 305 nm) of the composite in the presence of water vapor as the hole scavenger, the photoreduction of CO₂(g) proceeds selectively to generate CO(g). The production rate of CO by the composite, k[CO] = 2.11 μmol g⁻¹ h⁻¹, is 4-times larger than for pure Cu₂O under identical conditions. Contrasting XPS analyses of Cu₂O and Cu₂O/TiO₂ during photocatalysts operation and the detection of photogenerated hydroxyl radicals (HO•) in the heterostructure at variance with the results obtained for pure Cu₂O are taken as evidences that TiO₂ protects Cu₂O from undergoing photocorrosion. These results provide direct evidence of an efficient Z-scheme as the main mechanism for harvesting energy during CO₂ reduction in the synthesized materials.

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1. Introduction

The design of efficient photocatalysts aimed at the conversion of CO₂ to useful chemicals is a scientific challenge which is driven by the shortage of energy resources and the increased concentration of this greenhouse gas in the atmosphere [1–4]. The high stability of the linear CO₂ molecule makes its reduction difficult and usually demands scarce and expensive species, such as ruthenium or rhenium complexes [4–7]. The use of heterogeneous photocatalytic systems involving TiO₂, ZnO, or ZnS provide a possible, although less efficient alternative for carbon dioxide reduction under UV excitation [8–10]. It should be noticed that none of these semiconductors possesses sufficient potential to mediate the one electron reduction of CO₂ (Equation (1)), since their conduction bands lie below the homogeneous reduction potential of carbon dioxide, E° (CO₂/CO₂⁻) = −1.9 V [11].

\[ \text{CO}_2 + e^- \rightarrow \text{CO}_2^- \]  

Equation (1)

Although adsorption on semiconductor surfaces would certainly bend the linear CO₂ molecule and lower the energy demand for reaction 1, the considerable gap between the CO₂ LUMO and the conduction band (CB) probably prevents direct CO₂ reduction by CB electrons [12]. Thus, the photocatalytic reduction of CO₂ frequently involves the use of sacrificial donors (i.e., alcohols) that generate reactive intermediates (hydroxalkyl radicals) which can accomplish reaction (1). It is also apparent that the low photon intermittency usually employed under practical photocatalytic experiments is against the occurrence of multielectron processes [13], which could by-pass the high energy intermediate CO₂°− [14].

Cuprous oxide (Cu₂O) is an interesting p-semiconductor whose conduction band is much more energetic than the commonly used wide bandgap semiconductors. The bandgap of cuprous oxide is \( E_{\text{gap,2}} \approx \) 2–2.2 eV, while its conduction band is poised at
Scheme 1. Schematic representation of the processes that can take place in a system consisting of two semiconductors in electrical contact under irradiation with photons of suitable energy. (A) Double-charge transfer, and (B) direct Z-scheme mechanism.

\[ E_{CB,2} = -1.4 \text{ eV vs NHE at pH} = 7 \]  [15]. Unfortunately, as commonly found for semiconductors active in the visible region its photo-stability is scarce [16]. However, it can be envisaged that surface modification of Cu2O with a n-type wide bandgap semiconductor such as TiO2 could generate a Type II heterostructure and avoid Cu2O photo-corrosion as discussed below.

Scheme 1 shows the expected energy diagram for the Type II Cu2O/TiO2 heterostructure as discussed below.

Simultaneous excitation of the individual components of the composite leads to an electron-hole pair in each photocatalytic center. Different mechanisms can be envisaged to rationalize the charge transfer across the interface in p-n heterojunctions. Scheme 1A represents a double-charge transfer mechanism, in which the Cu2O electrons move to the TiO2 center and TiO2 holes migrate to Cu2O [18,19]. Alternatively, Scheme 1B involves a direct Z-scheme mechanism [20–23] where the TiO2 electrons are used to scavenge Cu2O holes. The double-charge transfer mechanism favors charge separation, at the expense of a decrease in the potential energy of electrons and holes. Moreover, it generates an excess of holes in Cu2O that could lead to its photocorrosion in absence of a suitable electron donor. Instead, under the Z-scheme mechanism the electron transfer across the interface could provide a way for preserving Cu2O photo-stability while maintaining a high reduction potential. Both, mechanisms A and B (Scheme 1), have been previously invoked to explain the higher efficiency of the heterostructures in comparison to the individual counterparts; however, the factors favoring one of the two mechanisms remain elusive.

In this work, we synthesize and fully characterize a type II heterostructure based on p-type octahedral Cu2O and n-type TiO2 nanoparticles. The synthesized material shows an enhanced efficiency for CO2 photoreduction in comparison to the individual materials. Based on comparative X-ray photoelectron spectroscopy (XPS) studies of Cu2O and Cu2O/TiO2 heterostructures under ultraviolet irradiation, we provide direct experimental evidence in favor of the Z-scheme mechanism.

2. Experimental

2.1. Chemicals and materials

Copper(II) chloride dihydrate (CuCl2·2H2O, 99.4% assay, J. T. Baker), polyvinylpyrrolidone (PVP, average MW = 29000 from Aldrich), sodium hydroxide (NaOH, 99.3% assay, VWR), L-ascorbic acid (99.7% assay, Sigma-Aldrich), ethanol (absolute for analysis, 99.9% assay, EMD Chemicals) and titanium(IV) butoxide (97.0% assay, Sigma-Aldrich) were used as received. Carbon dioxide (CO2, UHP) and carbon monoxide (CO, CP) were purchased from Scott Gross. All procedures employed ultrapure water (18.2 MΩ cm, ELGA PURELAB flex, Veolia).

2.2. Synthesis of Cu2O octahedra

Cu2O synthesis closely follows a previous published procedure [24]. In a typical experiment, 6.68 g of PVP were dissolved in an aqueous solution of CuCl2·2H2O (0.01 mol L−1, 100 mL) at 55 °C. Then, 10.0 mL of NaOH aqueous solution (2.0 mol L−1) was added dropwise into the above transparent light green solution. During this process, the solution color changes from blue-green to dark brown. The reaction mixture was stirred for 0.5 h, keeping the temperature at 55 °C. Afterwards, 10 mL of an aqueous ascorbic acid solution (0.6 mol L−1) was added dropwise and the mixture was aged for 3 h under constant stirring and strict temperature control (55 °C). This last stage gradually produces a red suspension. The resulting precipitate was collected by centrifugation and washed consecutively with 10 mL of deionized water and absolute ethanol (5 times). Finally, the solid was dried under vacuum at 60 °C for 5 h for further use and characterization.

When mentioned a thermal treatment was applied to the as-synthesized solid. Briefly, the solid was resuspended in absolute ethanol, transferred to 200 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h in a programmable oven. An initial ramp of 1 °C min−1 was used to achieve the final temperature.

2.3. Preparation of TiO2/Cu2O

The modification of Cu2O octahedra was performed following the procedure developed by Liu et al. [25]. Briefly, 186 mg of Cu2O were resuspended in 65 mL of absolute ethanol with the aid of ultrasonication for 30 min, and the suspension was cooled at 0 °C. At this temperature, 1.3 mL of titanium (IV) butoxide ethanolic solution (0.1 mol L−1) were added dropwise into the Cu2O suspension and stirred for 1 h at 0 °C. Afterwards, 6.5 mL of a water:ethanol solution (volume ratio 1:4) were added dropwise to the mixture under vigorous stirring for another hour. The reaction mixture was diluted with 98 mL of absolute ethanol, transferred to 200 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h in a programmable oven. An initial ramp of 1 °C min−1 was used to achieve the final temperature. The amount of Cu2O and TiO2 precursors used in this approach guarantee a nominal proportion of 0.05:0.95 of TiO2/Cu2O in weight. The product was collected by centrifugation and washed consecutively with 10 mL of deionized water and absolute ethanol (5 times). Finally, the solid was dried in vacuum at 60 °C for 5 h for further use and characterization.

Pure TiO2 was obtained using the same solvothermal procedure described above, in absence of Cu2O crystals.

2.4. Catalyst characterization

The crystalline properties of the as-prepared samples were analyzed via powder X-ray diffraction (XRD). The analysis was carried out on an X’Pert PRO (PANalytical) powder X-ray diffractometer, with Cu Kα (1.54 Å) as the incident radiation and operated at an accelerating voltage of 40 kV with a current intensity of 40 mA.

The morphology of the samples was observed by scanning electron microscopy (SEM) using a Hitachi S-4300 instrument with an accelerating voltage of 25 kV. A ca. 10 µL drop of colloidal suspension in ethanol (10 mg mL−1) was put on a SEM grid and dried under a red light lamp. The phase distribution in the Au-metallized samples, was analyzed by Energy-Dispersive X-ray Spectroscopy (EDS) using a Jeol JSM-6460LV scanning electron microscope, operating at 15 kV coupled to a EDS probe Genesis XM4-Sys 60. X-ray photoelectron spectroscopy (XPS) measurements of the powdered samples were conducted using a PHI VersaProbe II spectrometer with an Al
K-α anode (1486.6 eV photon energy, 86.6 W). Ultraviolet photoelectron spectroscopy (UPS) studies were carried out by using a PHI 5600 system with He (10.2 eV) as monochromatic light source with a polarization potential (bias) of −5.0 eV. All values determined from UPS analysis are referred to vacuum. The diffuse reflectance UV-visible (DRUV) spectra of the powered samples were obtained with an Evolution 220, ISA-220 accessory, Thermo Scientific UV−vis spectrophotometer using a built-in 10 mm silicon photodiode with a 60 mm Spectralon sphere. The ISA-220 accessory was used in a configuration to register the diffuse reflectance spectrum of dry solid powders as a Kubelka−Munk function against the certified Spectralon standard [14].

2.5. Photocatalytic studies

The photocatalytic experiments were performed in a 135 cm³ customized quartz photoreactor with flat circular windows (diameter = 5.08 cm). Based on the elemental distribution obtained by SEM-EDS analysis [see Supporting Information, S1], 3 mL of suspensions of appropriate concentrations to deposit 30 mg of Cu₂O/TiO₂, 28.4 mg of Cu₂O, or 1.6 mg TiO₂ were uniformly deposited in one of the reactor windows, and left to dry overnight. The reactor was then filled with 1 atm CO₂(g) saturated with water vapor by sparging the gas during 20 min (0.5 L min⁻¹) through a gas wash bottle. The reactor sealed with septa was kept in the dark for 1 h before irradiation to ensure a homogenous internal atmosphere. UV-visible irradiation was performed with a collimated 1 kW high-pressure Hg (Xe) arc lamp provided with a water filter and a cut-off filter at λ ≥ 305 nm (Newport) previously described [14]. The intensity of the lamp was measured in the interval 305 < λ ≤ 665 nm with a calibrated radiometer (Ocean Optics). Gas aliquots of 0.5 cm³ were taken from the reactor at different irradiation times for analysis by gas chromatography (SRI 8610C, Multiple Gas #3 GC) equipped with two columns (a silica gel HaySep D as column 1 and a Molec-Sieve 13X as column 2), a thermal conductivity detector (TCD), and a flame ionization (FID) detector interfaced to a methanizer. The irradiation of the photocatalyst and quantification of produced CO(g) were performed at room temperature (20°C). Additionally, the reaction products were identified by FTIR spectroscopy using a 2.4 m path length infrared gas cell with ZnSe windows (PIKE) thermostatted at 100°C mounted in an iZ10 FTIR module connected to an infrared microscope (Thermo Scientific Nicolet iN10) [26]. Furthermore, photocatalyst alteration during irradiation was monitored by XPS using a Thermo-Scientific K-Alpha X-ray Photoelectron Spectrometer with an Al K-α anode (1486.6 eV photon energy, 300 W).

The formation of hydroxyl radicals (HO·) on the surface of irradiated Cu₂O/TiO₂ was quantified using the coumarin fluorescence method with a Lumina Fluorescence Spectrometer (Thermo Scientific) using excitation at λexc = 332 nm. While coumarin is a poorly fluorescent molecule, it is an excellent probe to quantify [HO·] trapped in the produced 7-hydroxycoumarin. 7-Hydroxycoumarin has a characteristic fluorescent signal at λem = 456 nm [27], which is proportional to the formed [HO·] [28]. The experimental procedure followed the same steps of the photoreduction experiments, except that 30 mg of coumarin ([Alfa Aesar, 98.0%]) were deposited on top of the 30 mg of nanocomposite thin film for a 1:1 mass ratio [20]. Each data point corresponds to individual irradiation experiments at times of 0, 1, 2, and 3 h. Controls in the dark and with the individual components were also performed. Samples were extracted with 51 mL of water [20], centrifuged at 4400 rpm for 5 min, and forced through a filter (Acrodisc 0.2 μm pore size; Pall Corp.) to quantify by standard addition the 7-hydroxycoumarin (Acros, 98.5%) produced.

3. Results and discussion

3.1. Selection of Cu₂O shape and composite architecture

By modifying the reaction conditions, i.e., the relative amount between the capping agent and Cu₂O precursors, the shape of Cu₂O crystals can be easily modified from cubic to octahedra. This issue has attracted the attention of many researchers, who concluded that octahedral Cu₂O with exposed (111) facets exhibited much higher photocatalytic activity than the cubic structure [29–31]. It is apparent that crystalline (111) facets containing active Cu atoms can increase the interaction with donors and acceptors [24,32]. Guided by these conditions, we choose Cu₂O octahedral as the starting point to design the composite [33,34]. Also, since the hybrid composite would allow free access of the acceptor and donor to both surfaces, we regulated the content of the semiconductor precursors taking into account the individual size and surface area in order to warrant nearly all of TiO₂ nanoparticles cover the surface of Cu₂O and the amount of free TiO₂ nanoparticles is depreciable as verified by SEM analysis. The actual proportion by weight in the composite was estimated by SEM-EDS analysis to be 0.053:0.947 of TiO₂:Cu₂O, in very good agreement with the nominal proportion (See Fig. S1).

3.2. XRD and SEM analysis of crystal structure and morphology

Fig. 1 shows the X-ray diffraction patterns of the synthesized Cu₂O octahedra, TiO₂ and Cu₂O/TiO₂. For both Cu₂O and Cu₂O/TiO₂, all the peaks belong to the face-centered cubic Cu₂O phase (PDF Card No. 05-0667) and no diffraction peaks of CuO or metallic Cu could be detected. The strong and sharp peaks attributable to Cu₂O indicate a high degree of crystallinity. A low-intensity diffraction peak at θ = 25.08° is present in the Cu₂O/TiO₂ diffraction pattern, and ascribed to the (100) plane of anatase, as shown in the inset of Fig. 1.

The XRD pattern of pure TiO₂(Fig. 1), obtained in a parallel synthesis is in agreement with the report for anatase (JCPDS 21–1272). SEM measurements, Fig. 2(a, b), show that after solvothermal treatment of the titanium(IV) butoxide ethanolic solution in the presence of Cu₂O octahedral particles, fine TiO₂ nanoparticles cover Cu₂O (Fig. 2(c, d)). It is also apparent that Cu₂O morphology is not
altered by the thermal treatment, thus, the difference observed in the photocatalytic activity of the composite presented below cannot be attributed to changes in the surface chemistry of Cu$_2$O particles, but rather to the presence of TiO$_2$. Distribution phase was confirmed by EDS (Fig. S1).

### 3.3. Surface characterization by XPS analysis

Fig. 3a shows the XPS survey spectrum for Cu$_2$O/TiO$_2$ composites, which demonstrates the existence of Cu, Ti and O in the sample. The C 1s peak, associated to the widespread presence of carbon in the environment is also clearly observed. Fig. 3b compares the high resolution XPS spectrum in the region of Cu 2p$_{3/2}$ for pure Cu$_2$O and Cu$_2$O/TiO$_2$ composite. The same deconvolution procedure was applied throughout the analysis of the peaks and basically involves the subtraction of a Shirley-type baseline and the use of Voigt-type functions to reproduce the spectra. For Cu$_2$O the main peak is centered at 932.01 eV and is readily assigned to Cu(I) [35], while the shake-up satellite peaks with higher binding energy (933.98, 942.46, 943.98 eV) confirm the presence of an unfilled Cu 3d shell corresponding to Cu(II) species at the Cu$_2$O surface. This observation has been commonly attributed to the oxidation of Cu(I) during sample preparation for analysis [36]. For the Cu$_2$O/TiO$_2$ composites, the position of the peaks is similar (See Fig. 3b) but the relative area Cu(I):Cu(II) obtained through the deconvolution of Cu 2P$_{3/2}$ spectrum changes from 0.75:0.25 (for pure Cu$_2$O) to 0.65:0.35 (in Cu$_2$O/TiO$_2$ composites). The previous information together with the results from XRD diffractograms suggests that a minimum fraction of surface copper changes its electronic state during the solvothermal treatment.

The high resolution XPS spectrum of Ti 2p in Cu$_2$O/TiO$_2$ can be adjusted with great accuracy with two Voigt-type functions centered in 458.31 and 464.19 eV that can be assigned to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively for Ti(IV) [37] in agreement with the results...
obtained for pure TiO₂ (Fig. S2). The deconvolution peaks of the O 1 s spectrum for the Cu₂O/TiO₂ requires a greater number of components than for Cu₂O and in particular, three curves centered in 530.01, 532.08 and 533.63 eV are necessary. The two last components could be assigned to hydroxyl groups and water molecules adsorbed on the TiO₂ surface [38,39]. It should be noticed that the hydroxylation and the presence of adsorbed water molecules benefits CO₂ photoreduction [20] (See Fig. S3, for details).

3.4. Optical properties and energy bands alignments at the heterojunction

Assessing the bands edge positions of Cu₂O and TiO₂ and the band alignment is important to understand the electron transfer process at the heterojunction and to determine the reactions that are thermodynamically feasible. The combined information from DRUV, UPS and XPS spectroscopies was used to determine electronic band alignments and the construction of the band energy diagram as discussed below.

DRUV spectra of Cu₂O, pure TiO₂, and Cu₂O/TiO₂ are shown in Fig. 4a. The absorption edges for pure Cu₂O and TiO₂ samples were approximately 600 and 390 nm, respectively. Analysis of Tauc plots indicates that the optical bandgaps are \( E_{\text{opt}}(\text{Cu}_2\text{O}) = 2.03 \text{ eV} \), (as a direct semiconductor) and \( E_{\text{opt}}(\text{TiO}_2) = 3.16 \text{ eV} \), (as an indirect semiconductor) [40] (Fig. S4). These figures agree with the previously reported values for Cu₂O [41] and TiO₂ [10].

Fig. 4b shows the UPS spectra of Cu₂O, TiO₂ and Cu₂O/TiO₂. By applying the method of linear approximation to the UPS spectra, the work function and the corresponding energy of the Fermi level of Cu₂O were estimated to be 4.70 and −4.70 eV, respectively. Similarly, the valence band maximum was calculated to be −5.20 eV. Considering the average bandgap energy value (2.03 eV for Cu₂O) obtained from the Tauc plots (Fig. S4, Supporting Information), the minimum of the conduction band is located at −3.17 eV. The quantities previously determined are referred to the vacuum level. Therefore, according to the relationship between the potential of the normal hydrogen electrode (NHE), \( E_p \), and the energy of the vacuum \( E_{\text{vac}} \) \( E_{\text{vac}} - E_p = -4.44 \) (at 298 K), the conduction and valence bands of Cu₂O are poised at −1.27 and 0.76 eV, respectively. Similarly, following this procedure for TiO₂, the estimated Fermi level \( E_F \), CB and VB vs NHE are −0.38, −0.57 and 2.59 eV, respectively (Fig. S5, Supporting Information).

After contact, the Fermi level of Cu₂O and TiO₂ equilibrates due to the formation of a \( p-n \) heterojunction at the interface of the
Cu2O/TiO2 composite [42]. This process alters the band positions, as observed by XPS. Fig. S5 in the Supporting Information provides the XPS spectra. The band alignment at the interface of Cu2O/TiO2 was determined following the method of Kraut [43]. To accurately determine the valence band offset, ΔEVBO, the energy difference between the core level (ECL) and the valence band maximum (EVM) in the pure materials, as well as the energy difference between the core levels at the interface of the heterostructure (ΔECL) are needed. Eqs. (2) and (3) are used to calculate ΔEVBO and ΔECL, respectively:

$$\Delta E_{\text{VBO}} = (E_{\text{Cu}^0} - E_{\text{VBM}}) - (E_{\text{TiO}_2} - E_{\text{VBM}}) + \Delta E_{\text{CL}}$$  \hspace{1cm} (2)$$

$$\Delta E_{\text{CL}} = (E_{\text{Cu}^0} + E_{\text{TiO}_2}) - E_{\text{Cu}^0/\text{TiO}_2}$$  \hspace{1cm} (3)$$

The conduction band offset, ΔECBO, can be readily obtained from the bandgap energies (EBG) of the pure materials and ΔEVBO:

$$\Delta E_{\text{CB0}} = E_{\text{BEG}} - E_{\text{TiO}_2} + \Delta E_{\text{VBO}}$$  \hspace{1cm} (4)$$

Combining the information gathered during XPS and DRUV analyses reveals that for the nanocomposite ΔEVBO = 1.93 eV and ΔECBO = 0.81 eV (Fig. 5). The energy difference between the conduction and valence bands for the materials in the composite are about 0.11 eV higher than the values before contact. From the previous observation and the onset value of the composite (Fig. 4b), the valence band maximum of Cu2O in the composite is calculated to lie at 0.62 eV (vs NHE). The last figure is useful to calculate the apparent bandgap of Cu2O in the composite, which together with ΔEVBO and ΔECBO is needed to estimate the minimum of the conduction band of Cu2O in the composite to be −1.39 eV (vs NHE) and the valence band maximum and conduction band minimum of TiO2, which are depicted at 2.55 and −0.58 eV in Fig. 5, respectively [20].

Fig. 5 shows the energy diagram indicating the formation of a Type II (staggered) band heterostructure, whose highly energetic conduction band favors the reduction of CO2 through photogenerated electrons. We assume that the assignment of the composite bands corresponds to values that are far from the Cu2O/TiO2 interface. Taking into account this observation, and considering that the energy differences between CB and EF for TiO2 as well as from VB and EF for Cu2O do not remain constant before and after contact, we showed in Fig. 5 the associated band benders [44–46].

The energy difference between the valence band maximum of Cu2O and the conduction band minimum of TiO2 can be estimated as 1.33 and 1.2 eV for the separated semiconductors and the composite, respectively. This change indicates that under UV-visible irradiation, the electron transfer from the conduction band of TiO2 to the valence band of Cu2O (direct Z-scheme) could be favored due to the increased overlap of energy levels involved upon p-n heterojunction formation.

3.5. Photocatalytic CO2 reduction

Irradiation of the composite with λ ≥ 305 nm results in the selective formation of CO, (and O2). The time series for CO evolution from the irradiated composite is shown in Fig. 6 together with the results obtained under similar conditions for pure Cu2O and TiO2. Control experiments for Cu2O/TiO2 showed that no CO evolved in the dark or when the irradiation was carried out in the absence of CO2 under 1 atm argon (Fig. S6).

It is apparent from the results in Fig. 6 that the formation of the p-n heterojunction improves the CO2 reduction efficiency. Considering the same initial stage of irradiation, the CO evolution rates were calculated to be 2.11 and 0.55 μmol gcat⁻¹ h⁻¹ for Cu2O/TiO2 and Cu2O, respectively, which represents a 4-times enhancement for the composite. The ratio from the areas for the convolution of the irradiance of the lamp with the DRUV spectra of 1) Cu2O/TiO2 and 2) Cu2O in the interval 305 ≤ λ ≤ 665 nm indicates the nanocomposite absorbs ca. 2-times more photons than Cu2O per unit mass under the experimental conditions in Fig. 6. Thus, only a 50% of the enhanced photocatalytic activity can be explained to arise from an increment in the oscillator strength (or the resulting increase of the integrated absorption per unit mass). Therefore, the synergistic effect from the materials in the nanocomposite is proposed to provide the remaining 50% photocatalytic enhancement.

The ratio of quantum efficiencies for CO production, ΦCO, for Cu2O/TiO2 and Cu2O can be easily calculated from the established relationships between the initial reaction rates (R0,CO) and the absorbed photon fluxes I0, which was established above,

$$\frac{\Phi_{\text{CO}}^{\text{Cu}2\text{O}/\text{TiO}_2}}{\Phi_{\text{CO}}^{\text{Cu}_2\text{O}}} = \frac{\frac{R_{\text{0,CO}}^{\text{Cu}2\text{O}/\text{TiO}_2}}{I_{\text{0}}^{\text{Cu}2\text{O}/\text{TiO}_2}}}{\frac{R_{\text{0,CO}}^{\text{Cu}_2\text{O}}}{I_{\text{0}}^{\text{Cu}_2\text{O}}}} = \frac{R_{\text{0,CO}}^{\text{Cu}2\text{O}/\text{TiO}_2}}{R_{\text{0,CO}}^{\text{Cu}_2\text{O}}} \times \frac{I_{\text{0}}^{\text{Cu}_2\text{O}}}{I_{\text{0}}^{\text{Cu}2\text{O}/\text{TiO}_2}} = 4 \times \frac{1}{2} = 2$$  \hspace{1cm} (5)$$

Therefore, the relative quantum efficiencies in Eq. (5) clearly demonstrate that Cu2O/TiO2 has an enhanced photocatalytic activity over Cu2O.
Another point of interest is that the evolution of CO decreases with the irradiation time. This is a characteristic of many photocatalytic processes [10] and, in particular, has been observed for the photocatalytic CO₂ reduction over α-Fe₂O₃/Cu₂O [20], and over pure Cu₂O and Cu₂O/RuOₓ systems [47]. The actual reason for this behavior is not well understood but possible causes for the non-linear time profile are commonly ascribed to the strong interaction between Cu₂O and CO, or the formation of O₂, which competes with carbon dioxide reduction [47]. To get more insight, we investigate the rate of CO evolution in repeated 1 h irradiation cycles. After each run, the reactor was thoroughly evacuated and re-loaded with the same amount of CO₂ and H₂O before irradiation. Fig. 7 shows that after 4 cycles, CO yields slightly diminish, in sharp contrast with the results obtained under continuous irradiation. These experiments indicate that the inhibition observed in Fig. 6 is not irreversible, and the catalyst may be recycled without significant loss of efficiency, if the products are periodically removed.

3.6. Analysis of the reaction mechanism

As discussed above, two different schemes commonly referred as (A) double-charge transfer and (B) direct Z-scheme mechanisms are often proposed to explain the electron transfer processes across the interface in p–n heterojunctions after the simultaneous excitation of the centers of Type II heterostructures [19,48]. To determine which of these two mechanisms is operative, the photocatalyst was separated from the reactor and analyzed by XPS after different photons doses to monitor the possible change in the copper oxidation state during the irradiation experiments. The most relevant results are summarized in Table 1, which details are provided in Fig. S7.

XPS and XRD analysis allow us to discard the possible photoreduction of Cu(I) [30,46] during the irradiation experiments for Cu₂O and Cu₂O/TiO₂ composite as no Cu(0) could be observed. On the other hand, as shown in Table 1, XPS analysis of pure Cu₂O shows a relative increment of the contribution of Cu(II) in the Cu 2P₃/₂ in relation to the Cu(I) content. Cu₂O photocorrosion might have been anticipated since Cu₂O irradiation generates a highly reductive conduction band electron, E_Cₑ = −1.27 eV, but a valence band hole with insufficient energy to oxidize water [11] (Scheme 2a).

This key point is also demonstrated during experiments presented below that have quantified the production of HO* radicals.

By contrast, in the Cu₂O/TiO₂ composite, the ratio Cu(II)/Cu(I) keeps constant along the entire photocatalytic reaction. To account for these results, we proposed that UV-visible irradiation induces the formation of an electron/hole pair in each photocatalytic center, Eq. (6):

\[
\text{Cu}_2\text{O}/\text{TiO}_2 + h\nu_{\text{UV-visible}} \rightarrow \text{Cu}_2\text{O} \left( e_{\text{CB}}, h_{\text{VB}} \right)/\text{TiO}_2 \left( e_{\text{CB}}, h_{\text{VB}} \right)
\]

and after carrier generation, the electrons in the conduction band of TiO₂ are transferred to Cu₂O (see Scheme 2b):

\[
\text{Cu}_2\text{O} \left( e_{\text{CB}}, h_{\text{VB}} \right)/\text{TiO}_2 \left( e_{\text{CB}}, h_{\text{VB}} \right) \rightarrow \text{Cu}_2\text{O} \left( e_{\text{CB}} \right)/\text{TiO}_2 \left( h_{\text{VB}} \right) + \text{heat}
\]

and the TiO₂ holes localize on surface oxygen, forming (Ti³⁺_surf and (Ti⁴⁺O⁶⁻)_surf paramagnetic species, respectively. By these processes, we achieved a heterostructure with strongly reductive electrons,Cu₂O(e_{CB}), and oxidative holes, TiO₂(h_{VB}), able to oxidize water. Water oxidation by TiO₂ is not only thermodynamically allowed but also kinetically feasible as revealed by EPR experiments, which indicate that surface trapped holes react with adsorbed molecules even at the extremely low temperatures used in the EPR studies [49].

\[
\text{TiO}_2 \left( h_{\text{VB}} \right) + \text{H}_2\text{O} \rightarrow \text{HO}^+ + \text{H}^+
\]

The fluorescence spectra for the production of 7-hydroxycoumarin during irradiation of Cu₂O/TiO₂ is presented in Fig. S8 (Supplementary Information). The characteristic fluorescence peak at λ_em = 456 nm matches the reported spectrum of 7-hydroxycoumarin [28], which implies that only this species is produced [27]. Importantly, no peak for 7-hydroxycoumarin production was observed during 1) a dark control with Cu₂O/TiO₂, or 2) irradiated Cu₂O. These controls strongly support the assignment of HO*, an important intermediate for O₂ production, as a unique product from the photoactivity of the nanocomposite. The linear relationship between fluorescence intensity and irradiation time (Fig. S8) indicates a constant production rate for 7-hydroxycoumarin. Consequently, the production of HO* displayed in the inset of Fig. S8 (Supplementary Information) is
quantified by standard addition of 7-hydroxycoumarin to the samples. From the slope of the inset in Fig. 5B (Supplementary Information), the production rate of HO· is 0.22 (±0.03) μmol g_{cat}^{-1} h^{-1}. Comparatively, after 3 h of irradiation, the rate of production of CO is 5-times larger. By correcting the previous rates in a per photon basis using the stoichiometric consumptions of 2 e−, 2 h+ and 1 H_2O for CO and HO· species produced, respectively, indicates that 40% of the theoretical amount of HO· is trapped by 7-hydroxycoumarin. The previous observation is not surprising for HO·, a high reactivity and short lived species with a lifetime τ ~ 1 ns [28].

In the presence of CO₂, additional evidence of water oxidation by CuO₂/TiO₂ nanostuctures, comes from the analysis of the ratio between CO and O₂ yields. After 1 h of irradiation, we determined CO/μmol g_{cat}^{-1} h^{-1} = 1.69 ± 0.12 and O₂/μmol g_{cat}^{-1} h^{-1} = 0.83 ± 0.06, which gives CO/O₂ = 1.69:0.83 = 2.03, in close agreement with the expected reaction stoichiometry.

According to the Z-scheme, the anodic reaction takes place in the CuO₂ surface. In this regard, it is interesting to notice that the one electron homogeneous reduction potential for the mono-electronic reduction of CO₂ (Eq. (1)), is more negative than the conduction band level of CuO₂ (E_{CB}(CuO₂) = −1.39 eV). Thus, in order to make the CO₂ reduction thermodynamically feasible, some stabilization must be invoked [50,51]. Alternatively, rapid hole scavenging by adsorbed molecular water could lead to electron accumulation in CuO₂, and reduce CO₂ by a two-electron process,

\[ 2e^{-}_{CB,CuO_{2}} + CO_{2} + 2H^{+} \rightarrow CO + H_{2}O \] (9)

with lower energy demand (E^*(CO₂/CO) = −0.53 V) [52], avoiding the formation of the high energy intermediate, CO₂−. However, current evidence does not allow distinguishing between the two possibilities.

4. Conclusion

A CuO₂/TiO₂ photocatalyst with high morphologic and crystallographic quality was synthetized by a simple solvothermal method. The new material shows a 4-times enhancement for the photoreduction of CO₂ induced by UV-visible irradiation in comparison to pure CuO₂. Detailed analyses of the photocatalysts by XPS spectroscopy under operation, as well as the formation of HO· radicals in the CuO₂/TiO₂ system, at variance with the results for pure CuO₂, unequivocally prove a Z-scheme mechanism. The results obtained are of practical interest for photocatalysis and are also relevant for the understanding of photoinduced interfacial charge-transfer processes at the p-n heterojunction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, at the online version, at http://dx.doi.org/10.1016/j.apcatb.2017.05.058.

References
