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Quantitative In Situ Monitoring of Cu-Atom Release by Cu₂O Nanocatalysts under Photocatalytic CO₂ Reduction Conditions: New Insights into the Photocorrosion Mechanism

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Abstract: Cu₂O is among the most promising photocatalysts for CO₂ reduction, however its photocorrosion remains a standalone challenge. Herein, we present an in situ study of the release of Cu ions from Cu₂O nanocatalysts under photocatalytic conditions in the presence of HCO₃ as a catalytic substrate in H₂O. The Cu-oxide nanomaterials were produced by Flame Spray Pyrolysis (FSP) technology. Using Electron Paramagnetic Resonance (EPR) spectroscopy in tandem with analytical Anodic Stripping Voltammetry (ASV), we monitored in situ the Cu²⁺ atom release from the Cu₂O nanoparticles in comparison with CuO nanoparticles under photocatalytic conditions. Our quantitative, kinetic data show that light has detrimental effect on the photocorrosion of Cu₂O and ensuing Cu²⁺ ion release in the H₂O solution, up to 15.7% of its mass. EPR reveals that HCO₃ acts as a ligand of the Cu²⁺ ions, promoting the liberation of {HCO₃-Cu} complexes in solution from Cu₂O, up to 27% of its mass. HCO₃ alone exerted a marginal effect. XRD data show that under prolonged irradiation, part of Cu²⁺ ions can reprecipitate on the Cu₂O surface, creating a passivating CuO layer that stabilizes the Cu₂O from further photocorrosion. Including isopropanol as a hole scavenger has a drastic effect on the photocorrosion of Cu₂O nanoparticles and suppresses the release of Cu²⁺ ions to the solution. Methodwise, the present data exemplify that EPR and ASV can be useful tools to help quantitatively understand the solid–solution interface photocorrosion phenomena for Cu₂O.

Keywords: Cu₂O; CuO; photocorrosion; FSP; EPR; ASV; Cu²⁺ release; CO₂ photocatalysis; HCO₃; surface precipitation



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1. Introduction

The rapid development of human society has led to an increase in energy demands and ensuing environmental deterioration, making the use of new and renewable energy sources imperative. Photocatalysts have become a research hotspot over the last decades. The pioneer work of Fujishima and Honda in 1972 [1] paved the way for light-induced water dissociation by TiO₂ and has ignited numerous studies on photocatalysts, especially TiO₂ [2,3]. Since then, research interest has increased exponentially, combined with the discovery of numerous photocatalysts ranging from metal oxides (e.g., ZnO [4], WO₃ [5], and SnO₂ [6]), non-oxides (e.g., CdS [7], CuInS₂ [8] and ZnS [9]) and metal-free semiconductors (C₃N₄ [10]). Among them, Cu₂O stands out as particularly interesting [11–13] thanks to its highly reducing conduction band edge located at E_{CB} = −1000 mV vs. NHE (pH = 0) [12].

Cu₂O is a promising photocatalyst for CO₂ [14–16] reduction and H₂ production [17,18], i.e., it has a direct band-gap structure with a small energy gap of 2.0–2.2 eV [12], allowing it to absorb efficiently in the visible range of the solar spectrum, maximizing sunlight harvesting. Despite these advantages, photostability issues are among the well-documented drawbacks of Cu₂O [13,19,20]. The so-called photocorrosion phenomenon encodes the key problem, i.e., the photogenerated holes (h⁺) and electrons (e[−]) can be adversely consumed to the self-decomposition of Cu₂O itself [20]. At low degrees of photocorrosion, some Cu¹⁺

atoms of Cu_2O can be either oxidized to Cu^{2+} by the holes (self-photooxidation), or can be reduced to Cu^0 atoms by the electrons (self-photoreduction) [20]. Both self-photooxidation and self-photoreduction are due to the energy positioning of the $\{\text{Cu}^{1+}/\text{Cu}^{2+}\}$ $\{\text{Cu}^{1+}/\text{Cu}^0\}$ redox couples within the band gap of Cu_2O [21] i.e., $E_{1/2}\{\text{Cu}^{1+}/\text{Cu}^{2+}\} = 600$ mV vs. NHE (pH = 0), $E_{1/2}\{\text{Cu}^{1+}/\text{Cu}^0\} = 470$ mV vs. NHE (pH = 0) [12,13]. This phenomenon, even when it does not modify the Cu_2O crystal structure much, limits the electron transfer from the Cu_2O photocatalyst crystal to the surrounding acceptors or donors, which is detrimental to the photocatalytic activity [12,13,19]. It is well anticipated that when photocorrosion accumulates, physical detachment of Cu^{2+} ions can occur, resulting in severe destabilization of the Cu_2O crystal as a whole. Toe et al. revealed that self-photooxidation is the dominant photocorrosion mechanism for Cu_2O [19]. Practically, without the use of a hole scavenger and upon illumination, transformation of Cu_2O to CuO occurs, with no evidence of Cu^0 formation regardless of the presence of an electron scavenger. Moreover, in [19], XRD and SEM images confirm the growth of CuO on the surface of Cu_2O .

In this context, the study of the photocorrosion effects of Cu_2O under light plus CO_2 is particularly appealing, i.e., since there is a thrust in the use of Cu_2O as a CO_2 -reduction photocatalyst. To this end, most of the previous studies have mainly used photoelectrochemical tools to study the photocorrosion of Cu_2O [22,23]. Complementary information on the fate of the Cu_2O structure can be monitored with XRD [19], XPS [23] and Raman spectroscopy [24] to name a few methods. Herein, we introduce a methodology for in situ monitoring of the release of Cu^{2+} ions from Cu_2O under photocatalytic CO_2 -reduction conditions. The method is based on in tandem use of a high analytical sensitivity method, Anodic Stripping Voltammetry (ASV) [25] and Electron Paramagnetic Resonance (EPR) spectroscopy [26]. EPR spectroscopy has been proven a valuable tool for the study of Cu^{2+} ions at the oxide–solution interface. Examples include monitoring of Cu^{2+} species in Spinel-Type Oxide $\text{Mg}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$ [27], Fe-doped copper oxide nanoparticles [28], Cu^{2+} on Al_2O_3 [29] and mononuclear Cu complexes immobilized on SiO_2 [30]. We have demonstrated that EPR can provide detailed information on Cu^{2+} surface coordination, i.e., such as distances between neighboring Cu sites [30,31]. Thus, EPR can provide quantitative coordination information on the Cu^{2+} interaction with surfaces. Herein, we used EPR as a state-of-the-art tool to monitor in situ the formation of Cu^{2+} ions by Cu_2O nanoparticles under photocorrosion scenarios/conditions. In addition, we used electroanalytical Anodic Stripping Voltammetry for precise analytical determination of Cu^{2+} ions released in solution [32]. Recently, we demonstrated that ASV can be used as a very sensitive analytical tool to detect trace levels (part-per-billion, ppb) of cadmium (Cd^{2+}) ions released during the photocorrosion of CdS quantum dots [33]. Thus, herein, our methodology was based on the combined use of EPR and ASV to monitor the formation of Cu^{2+} ions at the Cu_2O and their release in the reaction solution phase.

The Cu_2O nanocatalysts used herein were synthesized using Flame Spray Pyrolysis (FSP) technology [34,35]. Previously, synthesis of CuO has been achieved by FSP by Waser et al. [36]. However, thus far, synthesis of high-purity Cu_2O by FSP has not been achieved. Zhu et al. reported the successful existence of a Cu_2O fraction in their CuO particles made by FSP synthesis [37]. Athanassiou et al. used a modified FSP reactor operating under highly reducing conditions to produce carbon-coated metallic copper nanoparticles [38]. Herein, in addition to Cu_2O , we also synthesized CuO nanoparticles using Flame Spray Pyrolysis (FSP) as reference materials to study the Cu^{2+} -release dynamics under the photocatalytic CO_2 -reduction process.

The specific aims of the present research were: [i] to monitor quantitatively the kinetics of Cu^{2+} ions release in solution, using EPR and ASV under photocorrosion conditions of Cu_2O vs. CuO photocatalysts. [ii] To clarify the role of HCO_3^- as substrate. [iii] To understand the role of photoinduced holes in the observed photocorrosion process.

2. Materials and Methods

2.1. Flame Spray Pyrolysis (FSP) Synthesis of CuO and Cu₂O Nanoparticles

A conventional FSP process was used for the synthesis of CuO, as described in detail in previous works [39–41]. A precursor solution of 0.25 M was prepared by dissolving Copper (II) Nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ 99–104%, Sigma-Aldrich (Saint Louis, MO, USA)) in a 1:1 (by volume) mixture of acetonitrile ($\geq 99.9\%$, Supelco (Bellefonte, Pennsylvania, USA)) and ethylene glycol ($\geq 99\%$, Supelco (Bellefonte, PA, USA)). This precursor solution (P) was fed at a rate of $P = 5 \text{ mL min}^{-1}$ to our system and atomized to fine droplets using an oxygen dispersion flow of $D = 5 \text{ L min}^{-1}$ at a pressure drop of 1.5 bar. The spray was ignited and sustained by an oxygen/methane pilot flame of O_2/CH_4 : 4/2 L min^{-1} . For the particle collection, an additional 10 L min^{-1} O_2 sheath was used, and the produced particles were deposited on a glass microfiber filter (Hahnemühle GF 6 257) with the assistance of a vacuum pump (BUSCH V40).

The synthesis of high-purity Cu₂O nanoparticles required a more-demanding FSP-setup with control of the combustion-atmosphere surrounding the spray nozzle (see Figure 1a). We used a cylindrical metal chamber consisting of two concentric tubes, a sinter metal tube (outer tube) and a porous metal tube (inner tube) to isolate the flame compartment from the surrounding atmosphere. The porous walls of the inner tube allow the radial inflow of an inert mixing gas, in our case, N_2 , to exclude O_2 . Moreover, to provide an additional O_2 -excluding source and aid the particle collection, a 10 L min^{-1} N_2 sheath was used. Once again, a 0.25 M precursor solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ dissolved in a 1:1 mixture of acetonitrile and ethylene glycol was sprayed into our system with a P/D ratio of 3/3. A series of N_2 radial inflows were tested in the range 0 to 30 L min^{-1} , resulting in progressively higher Cu₂O-phase percentages. In all cases, in addition to the radial N_2 , a N_2 sheath gas was fixed at 10 L min^{-1} , except in the case of pristine CuO, where we used a 10 L min^{-1} O_2 sheath. The produced materials, listed in Table 1, are codenamed as Cu-xN, where x = the radial N_2 -inflow in L/min^{-1} . In Table 1, we list the most pertinent materials with the Cu-20N to contain the higher Cu₂O fraction ($>95\%$). Higher radial N_2 inflows resulted in the deterioration of particle crystallinity and are not discussed herein.

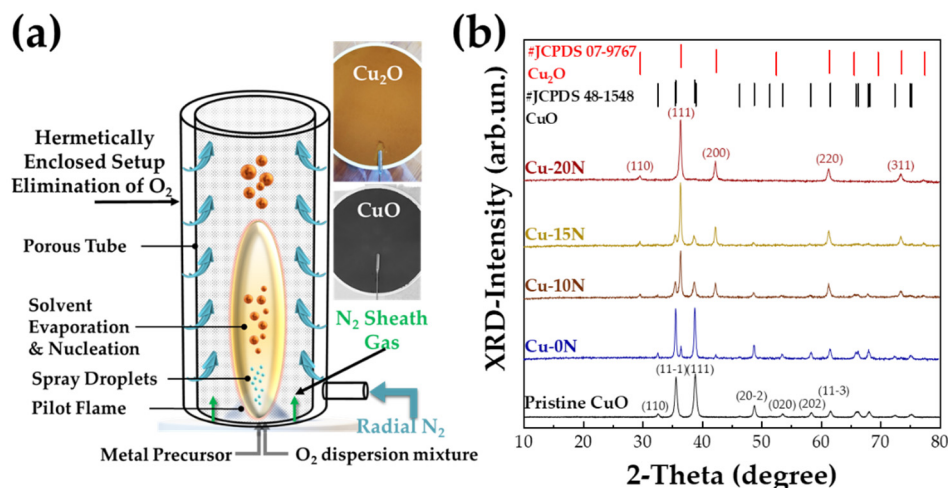


Figure 1. (a) Anoxic FSP reactor set-up used for the synthesis of CuO, Cu₂O nanomaterials. The photos are the as-produced CuO and Cu₂O powders on the FSP filter; (b) XRD patterns of our Cu-oxide nanomaterials.

Table 1. Structural characteristics of the FSP-made Cu-oxide nanomaterials.

	Radial N ₂ (L min ^{−1})	CuO (%)	Cu ₂ O (%)	d _{XRD} CuO (nm)	d _{XRD} Cu ₂ O (nm)
Pristine CuO	-	100 ± 1	-	20 ± 1	-
Cu-0N	0	90 ± 2	10 ± 2	29 ± 1	34 ± 1
Cu-10N	10	60 ± 2	40 ± 2	21 ± 1	30 ± 1
Cu-15N	15	40 ± 3	60 ± 2	22 ± 1	31 ± 1
Cu-20N (Cu ₂ O)	20	5 ± 3	95 ± 2	-	25 ± 1

2.2. Characterization of Materials

Powder X-Ray Diffraction (pXRD): The as-prepared nanomaterials were characterized using a powder X-ray diffractometer (Bruker D8 Advanced using CuK α radiation = 1.5405 Å) with a scanning step of 0.03° at a rate of 2 s per step and 2-theta (θ) angle ranging from 10–80° at current 40 mA and voltage 40 kV. The average crystal size was calculated by using the Scherrer Equation (1) [42]:

$$d_{XRD} = \frac{k\lambda}{\beta(\cos\theta)} \quad (1)$$

where, d_{XRD} is the crystallite size (nm), k is a shape constant (in this case 0.9), λ is the wavelength of CuK α radiation, β is the full width at half maximum and θ is the peak-diffraction angle. To determine the percentage of CuO/Cu₂O crystal phase in each Cu-based nanomaterial, we used Profex, which is a graphical user interface for Rietveld refinement [43].

2.3. Electron Paramagnetic Resonance Spectroscopy (EPR)

EPR spectra were recorded at 77 K using a Bruker ER200D spectrometer equipped with an Agilent 5310 A frequency counter operating at X-band (~9.6 GHz) with a modulation amplitude of 10 G peak to peak. The spectrometer is controlled with a custom-made software based on LabView. To obtain an adequate signal-to-noise ratio, each spectrum is an average of 5–10 scans. Theoretical analysis of the Cu²⁺ EPR signals was performed using a spin Hamiltonian and can be simulated using EasySpin MATLAB toolbox [44] assuming a spin system with $S = 1/2$ and $I = 3/2$ for ^{63,65}Cu²⁺.

2.4. Analytical Cu²⁺ Leaching Study by Anodic Stripping Voltammetry (ASV)

The concentration of Cu²⁺ in aqueous solution was determined by Anodic Stripping Voltammetry (ASV) using a Metrohm 797 VA computrace stand equipped with a Metrohm multimode electrode (MME). More specifically, a conventional three-electrode arrangement was used comprising Hanging Mercury Drop Electrode (HMDE) as the working electrode, Platinum rod (Pt) as the auxiliary electrode and Ag/AgCl (3 mol L^{−1} KCl) as the reference electrode. Cu standard solutions used for the quantification of our unknown samples were prepared by dissolving Cu(NO₃)₂ • 3H₂O in ultrapure triple-distilled (3d) water obtained from a Millipore-Q water purification system (USA) with a resistivity of >18 M Ω cm and diluting to obtain the desired Cu concentrations. The measurements were carried out at a volume of 10 mL of 0.1 M KNO₃ and 3 d water of pH:4 adjusted with HNO₃ to ensure the maximum presence of Cu²⁺ ions based on the theoretical copper speciation for hydroxo complexes in pure water [45]. The instrumental settings were as follows: mercury drop size 0.4 mm and scan rate 20 mV s^{−1}. Moreover, a deposition potential of −0.6 V versus Ag/AgCl (+0.2 V versus SHE at 25 °C) was used and the deposition time was carried out for 90 s. The reported data represent an average of three independent experimental repetitions.

3. Results

Figure 1a shows the FSP reactor set-up and photos of as-produced pure CuO and Cu₂O powders on the FSP filter. The black color is typical for CuO, while the red-brown color of Cu₂O originates from its band gap $E_g = 2.0\text{--}2.2\text{ eV}$ [12]. Figure 1b shows the XRD patterns of Cu materials, also listed in Table 1. The characteristic peaks at 35.6° , 38.8° and 48.8° correspond to the planes (11-1), (111) and (20-2) of CuO (JCPDS card no. 48-1548) while the peaks at 29.6° , 36.4° and 42.3° are characteristic of the planes (110), (111) and (200) of Cu₂O (JCPDS card no. 07-9767).

The XRD data in Figure 1 show that increasing N₂ inflow, promoted the formation of Cu₂O at the expense of the originally predominating CuO phase. The XRD-estimated particle diameters values (d_{XRD}) of the CuO and Cu₂O phases as well as their respective phase percentages are listed in Table 1. We see that Cu-20N is a Cu₂O material with at least 95% and a minor fraction of CuO. Based on several trials, we conclude that a small percentage (2–5%) of CuO was formed upon exposure of the originally pure Cu₂O to atmospheric O₂ during the particle handling. Once formed, this CuO did not further increase. Thus, the Cu₂O/CuO phase compositions listed in Table 1 represent stable compositions of FSP-made nanomaterials.

To underscore the Cu₂O-formation process, we note that in FSP, the gas atmosphere where the particle formation takes place, is of key importance [34,46]. Under an oxygen-rich atmosphere, i.e., such as ambient air inflow with 20% O₂, the produced materials are highly stable and fully oxidized ceramic powders [47]. In the present case of Cu oxide formation, this FSP protocol results in the formation of pristine CuO, see Figure 1. Decreasing the oxygen concentrations in the FSP reactor by the N₂ sheath and mostly by the radial N₂ inflow, see Figure 1a, resulted in the promotion of stable, reduced metal oxide (Cu₂O) whose lattice is formed by Cu¹⁺ ions. In our case, the use of N₂ in our FSP reactor played a dual role: first, the exclusion of oxygen and second, the reduction of oxygen partial pressure inside the reactor, resulting in the progressive formation of Cu₂O. We should note here that the formation of metallic Cu⁰ was not observed, which led us to conclude that this modified FSP setup allows meticulous exploration of the formation of suboxides rather than metallic particles.

3.1. Cu²⁺ Ion Release under CO₂-Photoreduction Conditions

The Role of pH: First, we examined the chemical stability, without light, by monitoring the Cu ions' release from CuO and Cu₂O in H₂O under different pH values. Figure 2a presents results based on ASV determination of Cu²⁺ ions in solution after 3 h of exposure. This time scale (3 h) is typical time span for photocatalytic experiments. As we see in Figure 2a, under acidic pH (pH:2), both CuO and Cu₂O materials were 100% dissolved after 3 h. On the contrary, increasing the pH towards more alkaline values, Cu²⁺ release decreased rapidly, with a threshold pH > 7, where the Cu²⁺ release was <5% at 3 h. Notice that the CuO phase exhibited better chemical stability than Cu₂O. Even at neutral pH, Cu₂O was more unstable, having a dissolution of 7%, which is 3.5-fold higher vs. the corresponding leaching of CuO (better viewed at the zoomed Figure 2a inset).

The Role of Light-Photons: Based on these results, a series of Xenon-lamp illuminations were performed under a slightly alkaline pH (pH:8), often used in CO₂ photocatalysis in HCO₃[−]/H₂O systems [12,14], and both CuO and Cu₂O are relatively stable, with Cu²⁺ release of 0.6% and 3.5%, respectively (Figure 2a). As seen in Figure 2b, under full-Xenon spectrum illumination, $h\nu > 200\text{ nm}$, CuO showed ~1.5% light-induced Cu²⁺ release, that is a +1% increase vs. no light. Elimination of UV photons by filtration $h\nu > 340\text{ nm}$ resulted in a lower Cu²⁺ release by CuO, i.e., by ~1% (Figure 2b). Overall, the data in Figure 2a show that the damage of light on the CuO nanoparticles was limited.

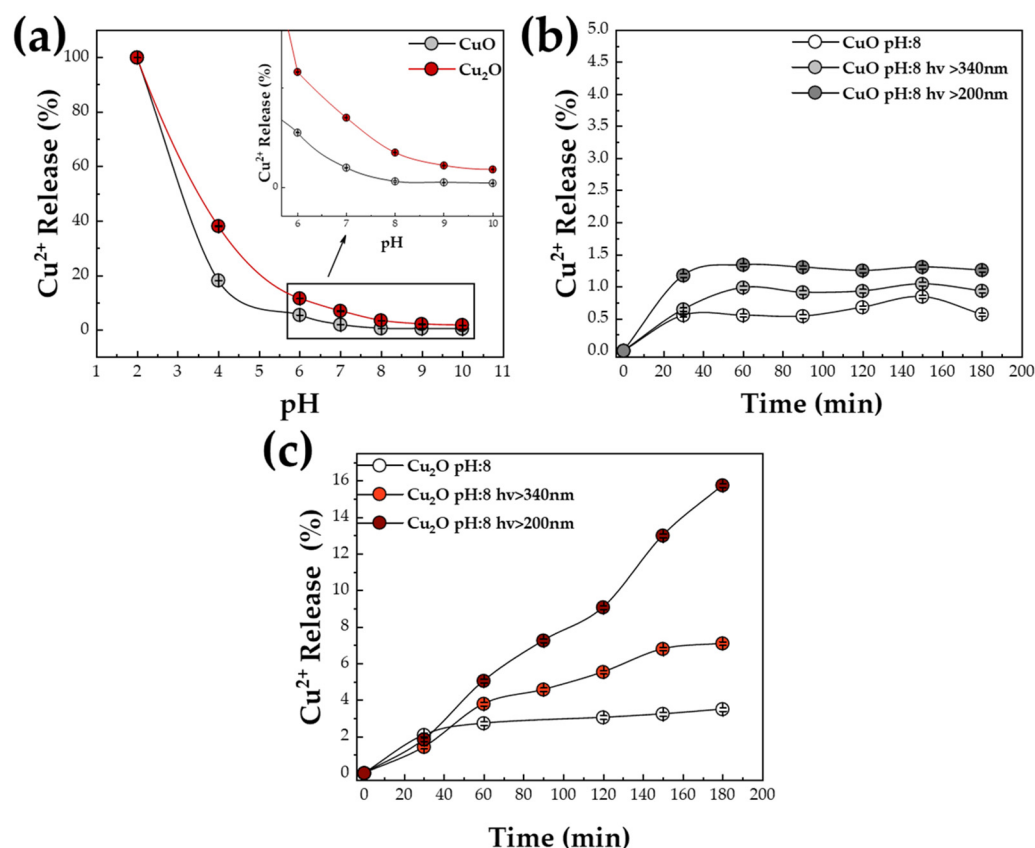


Figure 2. Release of Cu^{2+} atoms in solution, determined by ASV. The percentages show the fraction of Cu ions released vs. the Cu ion content of the added Cu oxide, in each experiment. (a) Release of Cu^{2+} ions by CuO and Cu_2O (material Cu-20N) dissolution versus pH values, from highly acidic (pH:2) to slightly basic (pH:10), for an incubation time of 3 h. (b,c) Release of Cu^{2+} ions by CuO and Cu_2O (material Cu-20N) in H_2O pH:8, under the effect of Xenon-light photons ($h\nu > 200\text{ nm}$ and $h\nu > 340\text{ nm}$).

On the contrary, light photons exerted a severe effect on Cu^{2+} leaching by the Cu_2O nanophase (material Cu-20N) (Figure 2c). Full-Xenon illumination, $h\nu > 200\text{ nm}$, resulted in dissolution higher than >15% of the Cu_2O matrices, releasing the Cu^{2+} ions in the aqueous solution. Thus, $h\nu > 200\text{ nm}$ photons enhanced the Cu release by 500%, i.e., from ~3% in the dark to ~15%. Filtering out the UV photons, $h\nu > 340\text{ nm}$, resulted in a significant drop of Cu^{2+} ions release to 7% (Figure 2c), which is about 200% versus no light. Overall, the data in Figure 2b,c reveal that [i] Cu_2O is far more prone, about 10 fold, to Cu^{2+} release in solution than CuO. [ii] This is a direct manifestation of photocorrosion. That is to say, photocorrosion starts as an oxidation event inside the Cu_2O crystal, as evidenced by many previous data [19,20], and, in the following, the present data show that photocorrosion persists until the physical detachment of the Cu ions from the particle matrix. As we show hereafter, photoinduced holes are the origin of the Cu^{1+} to Cu^{2+} oxidation.

The effect of photon wavelength can be understood as follows: the band gap of Cu_2O particles near 2.1 eV entails that photons with $\lambda \leq 580\text{ nm}$, i.e., visible and UV photons, can photoexcite it, creating holes and electrons. This includes 200 nm photons, i.e., $h\nu \sim 6\text{ eV}$, which excite highly energetic “deep” holes with energies well below the valence band top. Similarly, electrons well above the conduction-band edge can be excited. The data in Figure 2c, with $h\nu > 200\text{ nm}$, indicate that the high energetic holes dramatically boost the Cu^{2+} release. This results in a significant 15% of the Cu_2O mass to literally deteriorate. In the same context, allowing $h\nu > 340\text{ nm}$ contains photons with energy $\leq 3.4\text{ eV}$ that can also photoexcite “deep” holes, though with less energy than the 200 nm photons. Thus, the $h\nu > 340\text{ nm}$ results in about half of the Cu^{2+} release by the Cu_2O particles.

The Role of HCO_3^- : As mentioned previously [48,49], Cu_2O is identified as a promising CO_2 photocatalyst. In aqueous-phase photocatalytic processes, carbonate species are pertinent. Herein, we tested the role of HCO_3^- as a photocatalytic substrate that prevails in the pH range 6.5–10.5 in H_2O systems [50]. We used 30 mM HCO_3^- , which is an average amount used in CO_2 -photocatalytic experiments [51,52]. Control data show that HCO_3^- with no illumination had an insignificant effect on Cu^{2+} release (Figure 3a) from CuO . Similarly, the Cu^{2+} release data in Figure 3a show that during underexposure of CuO in HCO_3^- plus light, Cu-atom release was extremely low, i.e., 0.75% without irradiation and ~1% with $h\nu > 200$ nm. This confirms the stability of CuO under light and as well as light + HCO_3^- .

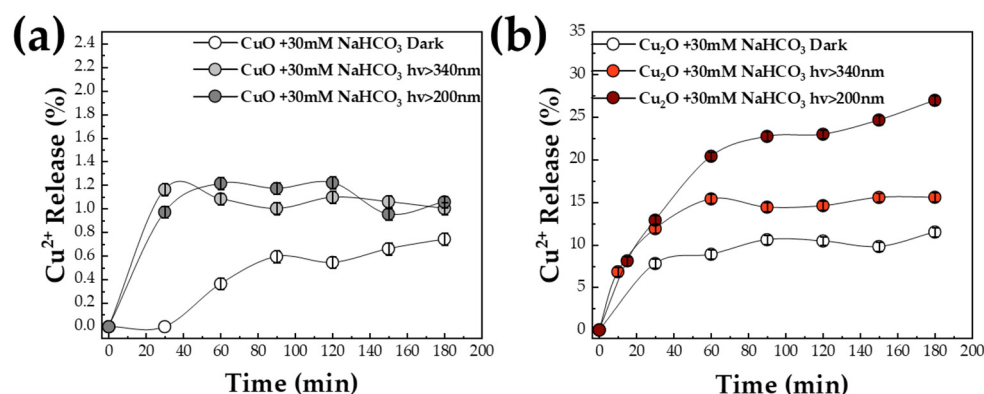


Figure 3. Release of Cu^{2+} ions in solution, in the presence of 30 mM NaHCO_3 , determined by ASV. (a) % of Cu^{2+} -ions release by CuO versus time, in H_2O pH 8, in the dark or under illumination. (b) % of Cu^{2+} -ions release by Cu_2O (material Cu-20N) in H_2O pH:8 versus time, in dark or under illumination ($h\nu > 200$ nm and $h\nu > 340$ nm).

In the case of Cu_2O , the presence of HCO_3^- alone with no light (Figure 3b) caused a Cu-atom release ~11%. This is higher than the Cu^{2+} release by Cu_2O with no HCO_3^- , i.e., 3.5% (compare Figure 3b vs. Figure 2c). This reveals a direct chemical, not photochemical effect of HCO_3^- on the Cu_2O atoms. As we show hereafter by EPR data, HCO_3^- extracts Cu^{2+} ions from the Cu_2O particles via formation of Cu-HCO_3 complexes.

As seen in Figure 3b, under light photons, the HCO_3^- severely intensifies the Cu^{2+} release, which reached ~27% of its mass (Figure 3b) under $h\nu > 200$ nm. Filtering off UV photons (Figure 3b), $h\nu > 340$ nm, resulted in ~15% Cu^{2+} release. These results clearly reveal that carbonate, i.e., HCO_3^- exerts a deteriorating effect in two ways: [i] In the dark, HCO_3^- is able to drive detachment of some Cu atoms from the Cu_2O particles. [ii] Under illumination, the photocorrosive Cu release is exacerbated by the presence of carbonates.

3.2. EPR Spectroscopy

Figure 4a shows X-band EPR spectra for Cu^{2+} ions released by Cu_2O particles under Xenon light irradiation, either in the presence or absence of HCO_3 . All spectra displayed in Figure 4a are typical for mononuclear Cu^{2+} (electron spin $S = 1/2$, nuclear spin $I = 3/2$) [30,53]. The well-resolved hyperfine lines of Cu^{2+} EPR spectra correspond to isolated Cu^{2+} ions in solution. All EPR spectra can be simulated, assuming a spin system with $S = 1/2$, $I = 3/2$, i.e., for Cu^{2+} , see dotted lines in Figure 4a with Cu^{2+} Spin Hamiltonian parameters (tensors g and A), listed in Table 2. In Figure 4b, we represent a so-called Peisach–Blumberg plot [54] for Cu^{2+} species using the $g_{//}$ and $A_{//}$ from Table 2. Peisach and Blumberg developed a method which correlates EPR parameters ($g_{//}$, $A_{//}$) with the number and type of ligand donor atoms in Cu^{2+} complexes. Previously, we showed that this method may be used to precisely detect the coordination of Cu^{2+} ions on metal oxides' surfaces and to distinguish the form of Cu atoms in solution [30,31].

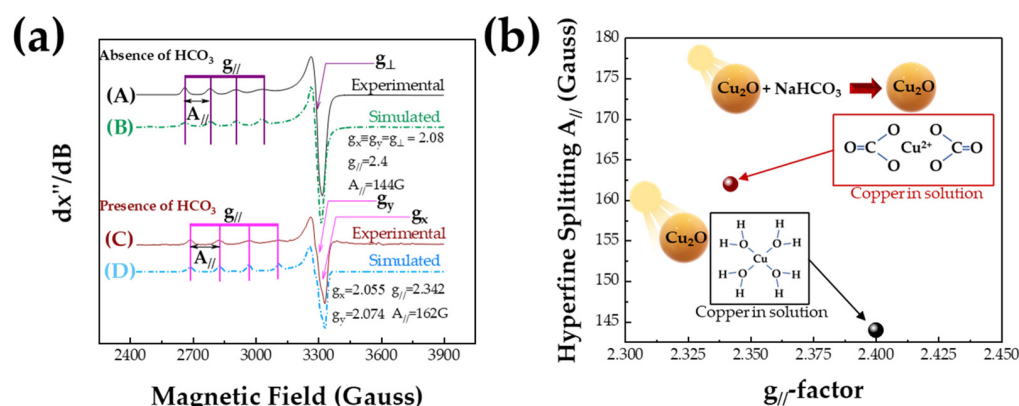


Figure 4. (a) 77K-EPR spectra for Cu²⁺ ions release from irradiated Cu₂O particles in the absence of the presence of 30 mM NaHCO₃. The same samples as those used in Figures 2 and 3 and were used. (Solid lines: experimental EPR spectra, dotted lines: theoretical simulations of Cu²⁺-EPR using the Spin Hamiltonian parameter listed in Table 2). (b) The relation between g_∥ and A_∥ parameters for Cu²⁺ ions in the presence and absence of HCO₃⁻.

The structural significance of the EPR spectral features can be understood by comparison of the g_∥ and A_∥ parameters with the literature data according to the method established by Peisach and Blumberg. These data indicate that: (a) In the absence of carbonates, the Cu²⁺ ions are released from illuminated Cu₂O as aqua-coordinated ions in solution. (b) In the presence of HCO₃⁻ as a photocatalytic substrate, copper ions are released in the form of Cu(HCO₃)₂ complexes in the aqueous solution. In all cases, the Cu²⁺ ions are coordinated by O atoms in an octahedral symmetry with the ground-state orbital of the Cu-unpaired electron to be d_{x²-y²} [55,56].

Table 2. Spin Hamiltonian EPR parameters used to simulate the Cu²⁺-EPR spectra for the atoms released from Cu₂O nanomaterials.

	g [g _x , g _y , g _z]	A _z = A _∥ /Gauss	Reference
Cu ²⁺ from Cu ₂ O + hν (Xenon > 200 nm)	g _x = g _y = g _⊥ = 2.08 g _z = g _∥ = 2.4	144	This work
Cu ²⁺ from Cu ₂ O + hν (Xenon > 200 nm) + NaHCO ₃	g _x = 2.055 g _y = 2.074 g _z = g _∥ = 2.342	162	This work
Cu ²⁺ + H ₂ O (pH:2)	g _x = 2.078 g _y = 2.078 g _z = g _∥ = 2.42	126	[29]
(Cu ²⁺ in zeolites) Cu-CHA hydrated	g _x = g _y = g _⊥ = 2.07 g _z = g _∥ = 2.394	157	[57]
(Cu ²⁺ in zeolites) Cu-MOR hydrated	g _x = g _y = g _⊥ = 2.08 g _z = g _∥ = 2.4	154	[57]

4. Discussion

The present data show that in the presence of HCO₃⁻, the Cu₂O photocorrosion is severely accentuated. Even in the dark, bicarbonate should be viewed as a highly active coordinating agent that can bind on the Cu₂O surface and promote the release of Cu(HCO₃)₂ complexes in aqueous solution. Additionally, light photons can promote the formation of Cu²⁺ via self-oxidation.

The Role of Hole Scavenger: The data in Figures 2 and 3 clearly exemplify the photocorrosion phenomena that prevail in Cu₂O. As mentioned by Toe [19,20], photoinduced holes should be considered as the key reactive species that promote the Cu²⁺ release from

photo-cited Cu_2O . In Figure 5, we examine the role of hole scavenger using isopropanol as a standard hole scavenger.

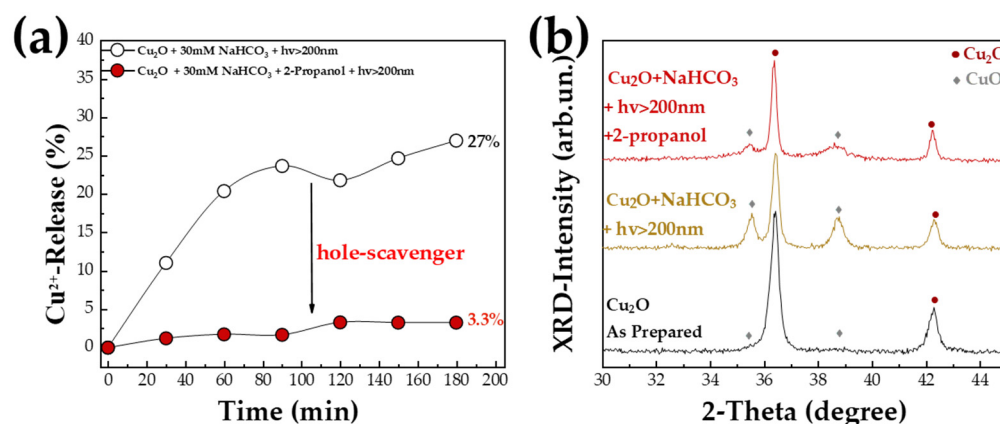


Figure 5. (a) % of Cu^{2+} -ions release by Cu_2O (material Cu-20N) versus irradiation time ($\text{hv} > 200\text{ nm}$) in H_2O pH 8, in the presence of NaHCO_3 or NaHCO_3 plus 2-propanol. (b) XRD patterns by Cu_2O (material Cu-20N) after 3 h irradiation in presence of NaHCO_3 or NaHCO_3 plus 2-propanol.

In the presence of 2-propanol plus NaHCO_3 , a significant suppression of the photocorrosion is observed, as evidenced by the decrease from 27% to 3% of Cu^{2+} -ion release (Figure 5a). This provides clear evidence that scavenging of the photoinduced holes, provides significant protection against photocorrosion of Cu_2O under realistic CO_2 -photocatalytic conditions. This is a very encouraging result, showing a route to address the Cu_2O photocorrosion problem.

To further understand the process, we examined by XRD the Cu_2O particles after 3 h photocatalytic exposure (Figure 5b). As seen in Figure 5b, in the presence of NaHCO_3 , after 3 h of irradiation (Xenon, $\text{hv} > 200\text{ nm}$) the initial Cu_2O -crystal phase composition is changed from $>95\%$ Cu_2O (see Table 3) to 60% CuO. We underline that the particles collected after 3 h photocorrosion represent only the fraction that is not dissolved to Cu^{2+} ions. Thus, the photocorrosion of Cu_2O in the presence of NaHCO_3 has two consequences: [i] Part of the Cu_2O particle is dissolved towards Cu^{2+} ions. [ii] The remaining Cu-oxide particle phase is altered from Cu_2O to CuO. Importantly, in the presence of 2-propanol, the Cu^{2+} -release and XRD data show that [i] Practically minimal Cu^{2+} -ions release occurs. That is the Cu-oxide particles remain mostly intact. [ii] The crystal composition is modified, i.e., according to Table 3, the Cu-oxide particles consist of 25% CuO, i.e., the initial 95% Cu_2O has been retained to 75%. We consider that the formed 25% CuO forms a protective layer around the Cu_2O , and this inhibits the Cu^{2+} -ion release.

Table 3. XRD analysis of Cu_2O particles before and after the photocatalytic/photocorrosion process.

Material	CuO (%)	Cu_2O (%)	d_{XRD} CuO (nm)	d_{XRD} Cu_2O (nm)
Cu_2O (Cu-20N)	5 ± 3	95 ± 3	-	25 ± 1
$\text{Cu}_2\text{O} + 30\text{ mM NaHCO}_3 + \text{hv} > 200\text{ nm}$	60 ± 3	40 ± 3	17 ± 1	26 ± 1
$\text{Cu}_2\text{O} + 30\text{ mM NaHCO}_3 + \text{hv} > 200\text{ nm} + 2\text{-propanol}$	25 ± 3	75 ± 3	8 ± 1	33 ± 1

5. Conclusions

Using EPR spectroscopy in tandem with ASV, the in situ study of the release of Cu ions from Cu_2O nanocatalyst under photocatalytic conditions provides new insight into the role of HCO_3^- as a catalytic substrate. Light and HCO_3^- have detrimental effects on the photocorrosion of Cu_2O and the ensuing Cu^{2+} -ion release in the H_2O solution. EPR reveals that HCO_3^- acts as ligand of the Cu^{2+} ions, promoting the liberation of $\{\text{HCO}_3^--\text{Cu}\}$

complexes in solution from Cu_2O , up to 27% of its mass. Even in the dark, bicarbonate acts as a highly active coordinating agent that can bind on Cu_2O surface and promote the release of $\text{Cu}(\text{HCO}_3^-)_2$ complexes in aqueous solution. On top of this, light photons can promote the formation of Cu^{2+} via self-oxidation. XRD data show that under prolonged irradiation, part of Cu^{2+} ions can re-precipitate on the Cu_2O surface, creating a passivating CuO layer that stabilizes the $\text{CuO-Cu}_2\text{O}$ from further photocorrosion. Moreover, including isopropanol as a hole scavenger has a drastic impact on the photo-oxidation of Cu_2O to CuO as well as suppresses the release of Cu^{2+} ions. Method-wise, the present data exemplify that EPR and ASV can be useful tools to quantitatively understand the solid–solution interface photocorrosion phenomena for Cu_2O .

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