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# Photoactive ZnO materials for solar light induced Cu<sub>x</sub>O-ZnO catalyst preparation

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**Abstract:** In this work, the solar light-induced redox photoactivity of the ZnO semiconductor material was used to prepare at room temperature Cu<sub>x</sub>O-ZnO composite catalysts with a control of the chemical state of the copper oxide phase. Cu<sub>2</sub><sup>(I)</sup>O-ZnO and Cu<sup>(II)</sup>O-ZnO composite catalysts have been prepared by using Cu(acac)<sub>2</sub> in tetrahydrofuran-water and Cu(NO<sub>3</sub>)<sub>2</sub> in water as metallic precursor, respectively. Prior to the implementation of the photon-assisted synthesis method, the most efficient photoactive ZnO material was selected among different ZnO materials prepared by the low temperature polyol method and by the precipitation method with carbonates and carbamates as precipitation agent. The photocatalytic degradation of the 4-chlorophenol compound in water under simulated solar light has been taken as model reaction. The ZnO support materials were characterized by XRD, BET, TGA, SEM and TEM, and the synthesis method was strongly influencing their photoactivity in terms of 4-chlorophenol degradation and of total organic carbon removal. The most photoactive ZnO material has been prepared by precipitation with carbonates and calcined at 300°C, and was taking advantage of a high specific surface area and a small mean crystallite size for achieving a complete 4-chlorophenol mineralization within 70 min of reaction, with a minimum Zn<sup>2+</sup> released to the solution. Beside thermal catalysis applications, this work opened a new route for the facile synthesis of Cu<sub>2</sub>O-ZnO heterojunction photocatalysts, that could take advantage under solar light of the heterojunction built between the *p*-type semi-conductor Cu<sub>2</sub>O with direct visible light band gap and the ZnO semiconductor phase.

**Keywords:** ZnO; photo-oxidation; 4-chlorophenol; Cu<sub>x</sub>O-ZnO catalyst; photodeposition

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## 1. Introduction

Zinc oxide (ZnO) nanostructures are materials with potential applications in many fields of nanotechnology, due to the large variety of nanometric structures or architectures that can be synthesized [1]. Beside numerous applications in optoelectronics, electronics, laser technology, converters and energy generators or as gas sensors [1-6], zinc oxide (ZnO) nanostructures have received special attention for being used directly as (photo)catalyst or as catalyst support.

Indeed, ZnO is a II–VI compound semi-conductor that has emerged as a promising candidate for being used as heterogeneous photocatalyst under near-UV irradiation in environmental applications such as the removal of a large range of organic and inorganic contaminants from environmental water and wastewater, including some of the most toxic and refractory molecules in water like pesticides, herbicides, and dyes [7]. It is characterized by a direct wide band gap close to that of anatase TiO<sub>2</sub> (3.2–3.37 eV), a suitable location of both conduction and valence bands, strong oxidation ability, low cost, abundance and a large exciton binding energy of 60 meV at room temperature [1,8-11] so that exciton emission processes can persist at or even above the room temperature. It has already been reported that the electron lifetime can be significantly higher and that the recombination rate can be lower in ZnO in comparison to TiO<sub>2</sub>, making ZnO attractive and worth to investigate for photocatalytic applications [12]. Further, the photocatalytic activity of ZnO can be enhanced by designing ZnO supported metal nanoparticle photocatalysts, with promising results mainly in the case [13] of Au and Ag [14-19]. In such hybrid metal/ZnO nanostructure, the supported nanoparticles are proposed i) to act as a sink for photoinduced electrons, so that efficient charge separation could be promoted at the semi-conductor/metal interface with efficient interfacial charge transfer, or ii) to induce plasmonic effects either through the direct injection of hot (excited) electrons from the metal to the conduction band of ZnO thanks to intimate electrochemical contact between the plasmonic particle and the semiconductor, or through an near-field enhancement mechanism with overlap between the plasmon wavelength and the photocatalyst absorption.

ZnO nanostructures are also widely studied as catalyst support in several reactions of high fundamental or applicative interest, such as the methanol oxidation [20], the low-temperature methanol synthesis [21,22], the production of hydrogen from methanol by steam reforming, partial oxidation, or a combination thereof [23], the steam reforming of ethanol, the glycerol hydrogenolysis [24], various transesterification reactions [25], or selective hydrogenation reactions [26-30]. The active metals or metal oxides mainly included Cu, Pd, Au, Ag, Co, Ni, Rh, Ir and Pt and were usually stabilized on the ZnO support by ion exchange, wet or incipient wetness impregnation, or (co)-precipitation [31].

The high interest of using zinc oxide as a support result from to its valuable physico-chemical properties. Hydrogenation reactions can take benefit from strong metal-support interactions and from the formation of alloys with the supported metals in reductive atmosphere. This behavior is responsible for the modification of the electronic properties of the supported active metals, which in turn results in

significant activity and selectivity enhancements in many catalytic reactions [32]. Activity improvement can be also associated with the existence of a hydrogen spillover phenomena taking place in the case of zinc oxide supported metal catalysts [33,34].

The most used methods for preparing supported metal catalysts implement consecutive operations, with first the adsorption of the metal precursor on the support. The reduction step consists most of the time in a thermal treatment under hydrogen, or in a chemical reduction in a solvent with *e.g.* hydrazine or sodium borohydrate reactants. The catalysts can suffer from heterogeneous supported nanoparticle size distributions, from unwanted temperature-activated reactions between the support and the metal precursor, and from limitations in terms of metal contents.

It has been demonstrated that the synthesis method is playing a key role in the preparation of ZnO materials with varied bulk and surface physico-chemical properties, and many chemical methods have been reported for synthesizing ZnO nanostructures, including notably mechanico-chemical processes, precipitation, sol-gel, solvothermal and hydro-thermal method, methods using an emulsion or microemulsion environment, sonochemical or microwave-based methods [4-6, 11].

Therefore, the aim of the article is double. First, it aims at selecting an appropriate preparation method for synthesizing photoactive ZnO under solar light. This has been performed by studying the influence of the synthesis method on the ZnO photoactivity, taking the photocatalytic degradation of 4-chlorophenol in water under solar light as model reaction. Further, the solar light-induced redox photoactivity developed by ZnO has been used for preparing at room temperature Cu<sub>x</sub>O-ZnO catalysts, that are catalysts of interest in fundamental and applicative reactions, and that do not require the use of any thermal treatment, or of any gaseous or liquid reductant for controlling the Cu chemical state.

## 2. Materials and Methods

### 2.1 Synthesis of ZnO materials

#### 2.1.1. Polyol method

In the polyol synthesis, 1.5 g of zinc (II) acetate dihydrate (Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O Sigma-Aldrich, ACS reagent, ≥98%) was introduced into 50 ml of propane-1,3-diol solvent (C<sub>3</sub>H<sub>8</sub>O<sub>2</sub>, Sigma-Aldrich, 98%). The obtained mixture was kept under continuous stirring and under reflux at 160°C for 15 min or 60 min. Afterwards, the precipitate obtained was cooled down, centrifuged for 20 min at 3500 rpm, and finally washed and filtrated under vacuum several times with absolute ethanol (Sigma-Aldrich). The synthesized powder was dried at 100°C for 12 h. The samples obtained were labelled as ZnO-P-15 and ZnO-P-60 according to the reflux duration.

### 2.1.2. Precipitation with $\text{Na}_2\text{CO}_3$

In this precipitation synthesis method, 1.75 g of zinc (II) acetate dihydrate and 0.84 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ , Sigma-Aldrich, 99.5%) were dissolved under stirring in 50 ml of distilled water, respectively. Both aqueous solutions were mixed, and the obtained precipitate was aged at room temperature in the mother liquor for 24 h under continuous stirring. The suspension was further centrifuged for 30 min at 3500 rpm, and finally washed and filtrated under vacuum with distilled water. The resulting powder was dried at 100°C for 12 h and subsequently calcined at a temperature of 300°C to 500°C for 2 h with a 10°C/min heating rate, leading to the ZnO-C material series.

### 2.1.3. Precipitation with $\text{NH}_2\text{CO}_2\text{NH}_4$

In that case, 10.98 g of zinc (II) acetate dihydrate and 4.29 g of ammonium carbamate ( $\text{NH}_2\text{CO}_2\text{NH}_4$ , Sigma Aldrich, 99%) were dissolved under stirring in 50 ml of distilled water respectively. Both aqueous solutions were mixed, and the obtained precipitate was aged at room temperature in the mother liquor for 30 min under continuous stirring. The suspension was further centrifuged for 30 min at 3500 rpm, and finally washed and filtrated under vacuum with distilled water. The resulting powder was dried at 100°C for 12 h and subsequently calcined at a temperature of 400°C to 500°C for 2 h with a 10°C/min heating rate, leading *eg.* to the ZnO-c material series.

## 2.2 *Photon-assisted preparation of Cu-ZnO catalysts*

The photon-assisted preparation of Cu-ZnO catalysts was performed by irradiating with solar light a suspension of the ZnO support containing  $\text{Cu}(\text{acac})_2$  or  $\text{Cu}(\text{NO}_3)_2$  as metallic precursors. The irradiation was provided by an Atlas Suntest XLS+ reaction chamber equipped with a Xenon arc lamp adjusted to a 500 W/m<sup>2</sup> irradiance (with a 30 W/m<sup>2</sup> UV-A content) (320-800 nm wavelength range, ICH Q1B guidelines). The amount of copper precursor used was adjusted to target a Cu content of 10 wt.% on the ZnO support.

### 2.2.1. $\text{Cu}(\text{acac})_2$ in THF- $\text{H}_2\text{O}$ solvent

The dissolution of 20.8 mg of copper(II) acetylacetonate (Sigma-Aldrich, 97%) has been achieved for 30 min at 60°C under stirring in tetrahydrofuran (THF, Sigma-Aldrich, 99%) - water mixture with a 2:9 (v/v) ratio, before 45 mg of the ZnO support was dispersed under stirring in 100 mL of copper solution in a beaker-type glass reactor at a 0.21 g/L concentration. The suspension was first stirred in the dark for 0.5 h at 60°C for establishing the ads/des equilibrium, before the photon-assisted synthesis was performed under stirring at 60°C under solar light for 90 min. The synthesis was monitored by UV-vis spectrophotometry by following the disappearance of the absorption peak at  $\lambda = 245$  nm. The samples were washed and filtrated under vacuum several times with distilled water, and finally dried at 100°C for 1 h [13].

### 2.2.2. $\text{Cu}(\text{NO}_3)_2$ in $\text{H}_2\text{O}$ solvent

The protocol was similar to that followed with  $\text{Cu}(\text{acac})_2$ . In this case, the dissolution of 38 mg of  $\text{Cu}(\text{II})$  nitrate trihydrate (Sigma-Aldrich, p.a) has been performed in water at room temperature, before 90 mg of  $\text{ZnO}$  was dispersed under stirring in 100 mL of copper solution in a beaker-type glass reactor at a 0.38 g/L concentration. Prior to irradiation, the suspension was stirred in the dark for 30 min at  $60^\circ\text{C}$  to ensure the establishment of the adsorption/desorption equilibrium, before the photon-assisted synthesis was performed under stirring under solar light for 2 h. The synthesis was monitored by UV-vis spectrophotometry by following the disappearance of the absorption peak at  $\lambda = 800$  nm. The samples were washed and filtrated under vacuum several times with distilled water, and finally dried at  $100^\circ\text{C}$  for 1 h.

### 2.3. Characterisation techniques

The crystallographic structure of the powders has been characterized by X-ray diffraction patterns (XRD) recorded on a D8 Advance Bruker diffractometer in a  $\theta/\theta$  mode and using the  $\text{K}\alpha_1$  radiation of a Cu anticathode ( $\lambda = 1.5406$  Å).

The surface area measurements have been carried out on a Micrometrics Tristar 3000 using  $\text{N}_2$  as adsorbent at  $-196^\circ\text{C}$  with a prior outgassing at  $100^\circ\text{C}$  overnight in order to desorb the impurities or moisture. The Brunauer–Emmett–Teller (BET) specific surface area has been calculated from the  $\text{N}_2$  adsorption isotherm.

Scanning electron microscopy (SEM) was performed in secondary electron mode on a JEOL JSM-6700 F FEG microscope.

Transmission electron microscopy (TEM) was performed using a JEOL 2100F with a point resolution of 0.2 nm. A Mo grid was used for performing EDS analysis of  $\text{Cu-ZnO}$  samples. The interplanar spacings were calculated using ImageJ software.

Thermogravimetric analysis (TGA) was carried out with a 20% (v/v)  $\text{O}_2/\text{N}_2$  mixture at a flow rate of 40 mL/min at a heating rate of  $10^\circ\text{C}/\text{min}$  from  $25^\circ\text{C}$  to  $600^\circ\text{C}$  using a Q 5000 TA Instrument thermoanalyzer.

The copper content in the catalysts was determined by chemical analysis after a microwave-assisted acidic dissolution in aqua regia at  $185^\circ\text{C}$  under autogenic pressure. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out on an Optima 7000 DV spectrometer (Perkin Elmer) at the Analysis Plateform of IPHC-Strasbourg, France.

### 2.4 Evaluation of the photocatalytic efficiency

The experiments were carried out in an Atlas Suntest XLS+ reaction chamber equipped with a Xenon arc lamp adjusted to a  $500\text{ W}/\text{m}^2$  irradiance (with a  $30\text{ W}/\text{m}^2$  UV-A content) (320–800 nm wavelength range, ICH Q1B guidelines). The tests were performed with a reactor volume of 500 mL and a 4 Cl-phenol concentration of

25 mg L<sup>-1</sup>, corresponding to a carbon load of 14.8 ppm. The ZnO catalyst load was 1 g L<sup>-1</sup>. At each time interval, 20 mL of solution has been sampled and then filtered through 0.20 µm porosity filter to remove the photocatalyst powder if any, before the concentration of 4-chlorophenol has been determined by UV-Visible spectrophotometry (Cary 100 scan) by monitoring the disappearance of the main absorption peak at  $\lambda = 224$  nm, and Total Organic Carbon was measured with a Shimadzu TOC-L analyzer to determine the organic carbon load.

A procedure was established for photocatalytically cleaning the ZnO materials under UV-A or solar light prior to the chlorophenol removal, consisting in the continuous stirring of the as-synthesized ZnO catalyst in ultrapure Milli-Q water under either simulated solar light for 2 h or UV-A light for 16 h. UV-A light was provided by blacklight lamps (Philips PL-L 24W/10/4P) emitting at 365 nm with an irradiance of 60 W/m<sup>2</sup>, while the UV-A fraction of the simulated solar light corresponded to a 30 W/m<sup>2</sup> irradiance, as measured using a wide-band RPS900-W rapid portable spectroradiometer from International Light Technology.

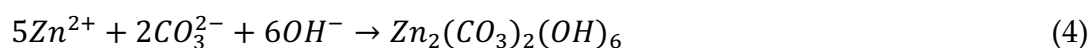
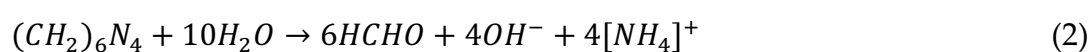
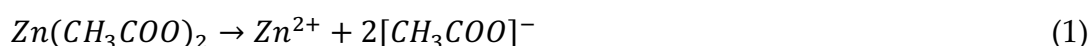
### 3. Results

#### 3.1. Characterization of ZnO materials

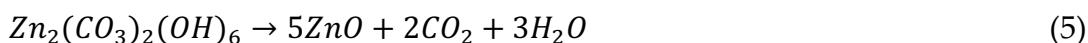
The main physico-chemical properties of the ZnO materials are reported in Table 1. Figure 1A and 1B shows the XRD patterns of the dried ZnO precursors and of the final ZnO materials synthesized *via* the polyol and the precipitation routes.

In the case of the polyol method, the XRD pattern shown in Figure 1a displayed the diffraction peaks characteristic of ZnO crystallized in the hexagonal wurtzite structure and corresponding to the diffraction of the (100), (002), (101), (102), (110), and (103) planes for the most intense peaks (P63mc space group, JCPDS 00-036-1451) [5, 14-16]. As reported for the polyol synthesis, the ZnO material had a good crystallinity without any post-synthesis calcination treatment.

By contrast, the dried material obtained in the case of both precipitation methods consisted in a Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub> zinc carbonate hydroxide, or hydrozincite phase, in the monoclinic structure [17] with the diffraction of the (111), (310), (100), (311), (220) and (021) planes for the most intense peaks (JCPDS 19-1458). Han et al. [18] have proposed that the reactions during the formation of Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub> are likely as follows:

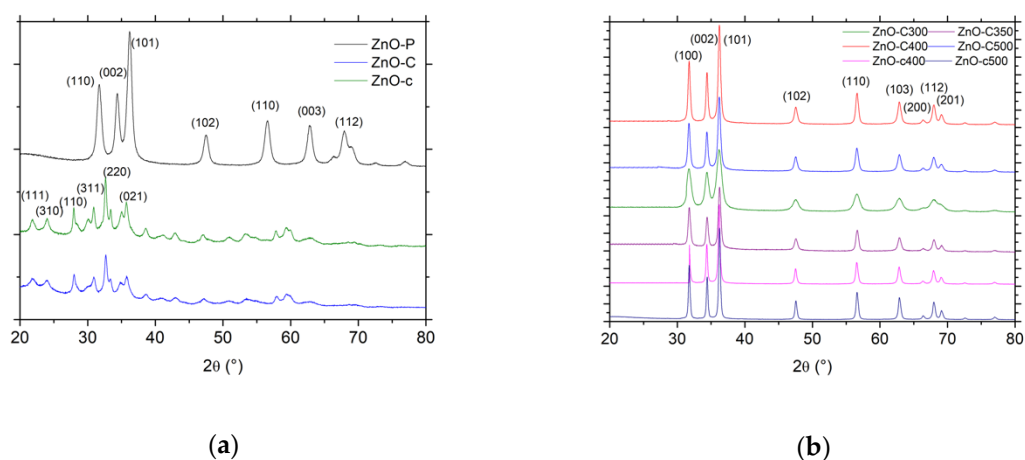


The zinc carbonate hydroxide phase being thermally stable below 200°C, its decomposition into ZnO was evidenced by XRD characterization and TGA analysis in Figure 1b and Figure 2, respectively. After calcination of the zinc carbonate hydroxide at a temperature higher than 300°C, the XRD pattern exhibited the diffraction peaks corresponding to hexagonal ZnO, while, according to the weight loss of  $28\% \pm 1\%$  observed in TGA, the decomposition process can be described as follows, corresponding to a theoretical weight loss of 28,4%:



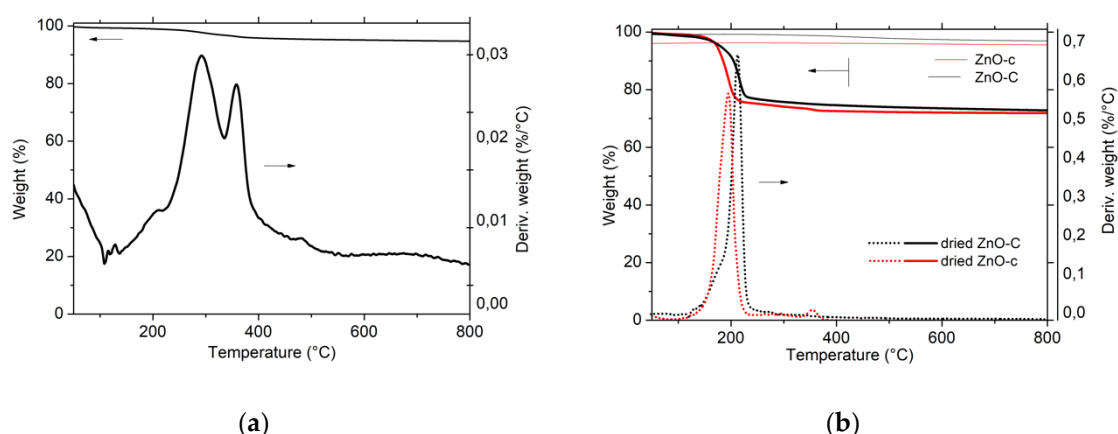
The absence of any weight loss during the TGA of the calcined ZnO materials confirmed the efficiency of the thermal decomposition process. By contrast, a very small weight loss of 6% was observed with ZnO prepared *via* the polyol method, suggesting the residual presence of propane 1-3 diol solvent or acetate species [19].

In agreement with the previous works of Fkiri et al. [14], the ZnO materials synthesized *via* the polyol method displayed a good crystallinity without any post-synthesis heat treatment, and exhibited the smallest average crystallite size of 7 nm and 11 nm, for an aging duration of 15 min and 60 min, respectively. The ZnO materials prepared *via* both precipitation routes had a larger mean crystallite size, as a result of the necessary calcination treatment at temperatures ranging from 300°C to 500°C. The use of carbonates as precipitating agent allowed maintaining a smaller mean crystallite size in the 10-20 nm range, while the mean crystallite size strongly increased to 28-30 nm in the case of the carbamate agent. For a similar calcination temperature, ZnO prepared with carbamates displayed a larger crystallite size than its carbonate counterpart, *eg.* 28 nm *vs.* 20 nm at a temperature of 400°C.



**Figure 1.** XRD patterns of (a) the dried materials and (b) the calcined materials. JCPDS card No. 00-036-1451 and No. 19-1458 for ZnO and the zinc carbonate hydroxide phases, respectively.





**Figure 2.** TGA of the materials after the drying step synthesized by (a) the polyol method, (b) the carbonate-derived precipitation method and the carbamate-derived precipitation method. The weight loss observed with the ZnO-C and ZnO-c materials after calcination at 300°C and 400°C, respectively, was reported.

**Table 1.** Main physico-chemical properties of ZnO materials.

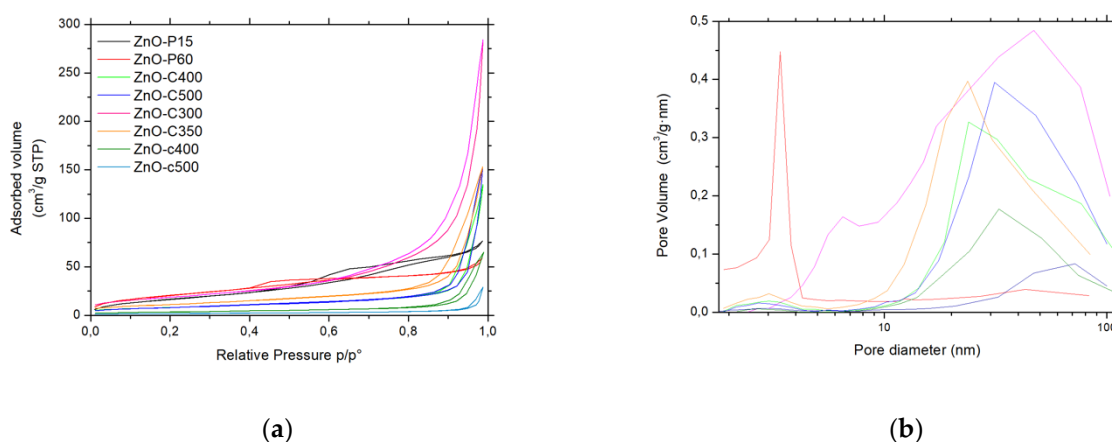
Sample	Mean crystallite size (nm) <sup>a</sup>	BET surface area (m <sup>2</sup> /g) <sup>b</sup>	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
ZnO-P-15	7	78	0.13	5
ZnO-P-60	11	66	0.09	6
ZnO-C-300	10	68	0.45	21
ZnO-C-350	22	41	0.24	21
ZnO-C-400	20	29	0.21	27
ZnO-C-500	18	29	0.24	30
ZnO-c-400	28	12	0.10	30
ZnO-c-500	30	6	0.05	28
Cu <sub>2</sub> O-ZnO	13	95	0.68	26
CuO-ZnO	20	33	0.24	29

<sup>a</sup> derived from XRD pattern, as the mean size of the coherently-diffracting domains, derived from the Scherrer equation using the classical assumption of spherical crystallites. The full-width at half-maximum of the diffraction peaks of ZnO (102), (110), and (103) planes was used for the estimation.

Figure 3a shows the N<sub>2</sub> adsorption–desorption isotherms of the ZnO materials. The ZnO-P materials displayed IV-type isotherms, characteristic of mainly mesoporous solids with a mainly H2-type hysteresis corresponding to

interconnected mesopores with non-uniform shape or size [14]. For ZnO obtained by precipitation, the isotherms turned to be preferentially of type II with H3-type hysteresis. This suggested that the porosity mainly resulted from macropores (or large mesopores) and is characteristic of aggregates or agglomerates of nanoparticles forming slit shaped pores with non-uniform size and/or shape. This was in agreement with the corresponding pore size distributions shown in Figure 3b, that evidenced clearly the influence of the synthesis method on the mean pore size.

The specific surface area of the ZnO materials was ranging from 6 m<sup>2</sup>/g to 78 m<sup>2</sup>/g without any microporous contribution. Among the different materials, the ZnO-P and ZnO-C-300 samples had the highest specific surface areas, within the 66–78 m<sup>2</sup>/g range, in agreement with their smallest mean crystallite sizes of 7–11 nm. The increase in the calcination temperature for carbonate-derived ZnO materials from 300°C to 500°C led to a progressive decrease in the surface area from 68 m<sup>2</sup>/g to 29 m<sup>2</sup>/g, as a result of the slight increase in the mean crystallite size. It is worth noting that the carbamate-derived ZnO samples calcined at 400°C and 500°C displayed a lower surface area than their carbonate-derived counterparts, at 12 m<sup>2</sup>/g and 6 m<sup>2</sup>/g respectively, in agreement with a larger mean crystallite size.

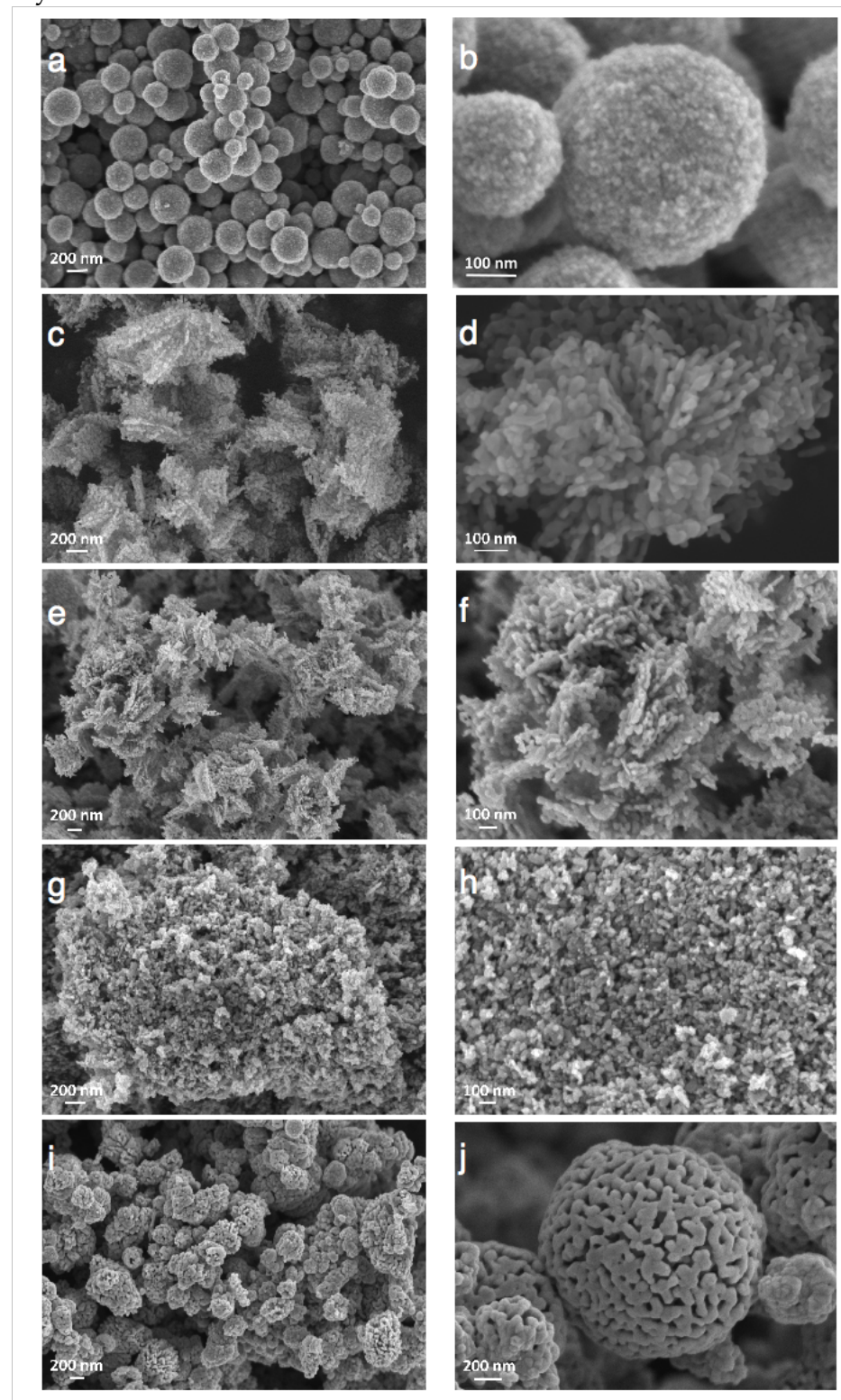


**Figure 3.** (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore size distributions of ZnO materials.

The synthesis method had no influence on the band gap of the ZnO materials, graphically estimated at 3.1 eV *via* the Tauc plot derived from the UV–vis diffuse reflectance analysis, in agreement with the literature (Figure S1b) [14,35]. Therefore, the ZnO materials will be activated by incident photons with wavelengths within the UV-A range, whether the photocatalytic tests are performed under solar light or pure UV-A light.

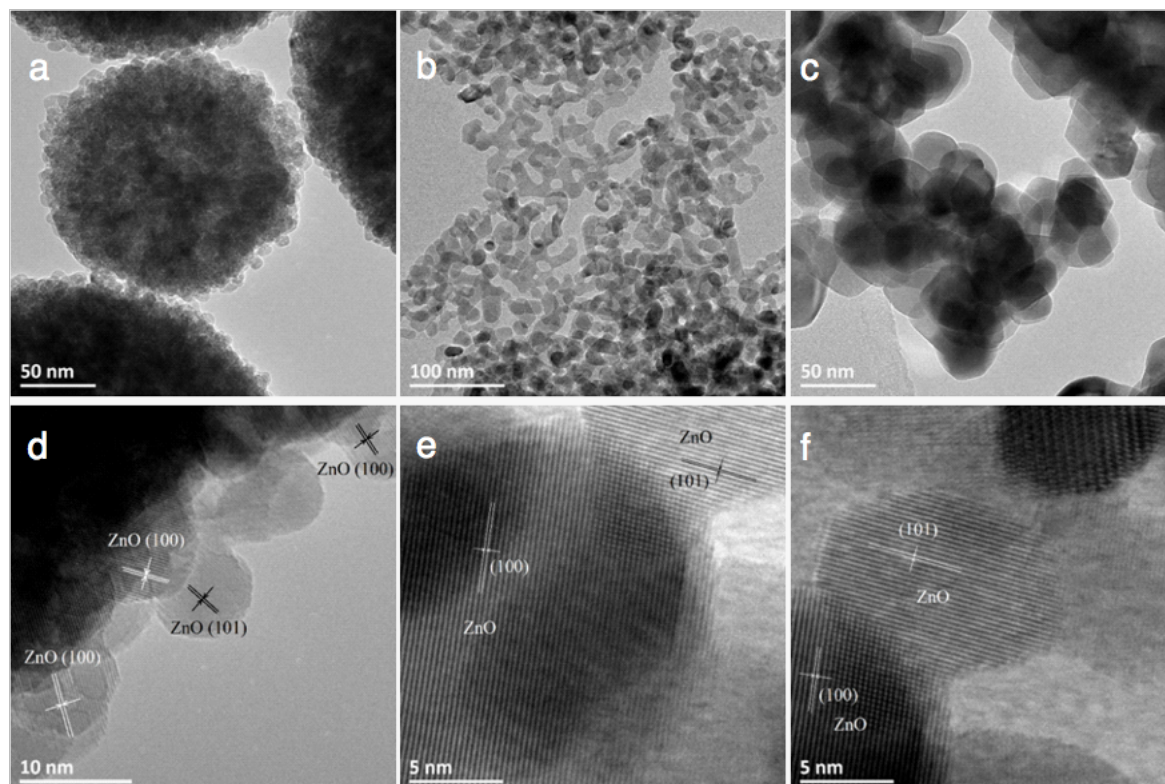
Figure 4 depicts a selection of SEM images of the ZnO materials and evidenced that the synthesis method and the nature of the precipitating agent strongly influenced the morphology of the ZnO material. ZnO from polyol synthesis was composed of (100–200 nm) large spherical aggregates of small-size ZnO particles

with an average crystallite size around 10 nm, in agreement with that derived from the XRD patterns. The aging duration had no influence on the general morphology of the ZnO-P materials. The interplanar spacing of 0.28 and 0.25 nm shown in Figure 5 was consistent with the (100) and (101) plane of hexagonal (wurtzite) ZnO crystallites.



**Figure 4.** SEM of ZnO materials synthesized through the polyol method (ZnO-P-60) (a,b), the precipitation with carbonates: ZnO-C300 (c,d), ZnO-C400 (e,f), ZnO-C500 (g,h) and the precipitation with carbamates: ZnO-c400 (i) and ZnO-c500 (j).

TEM images of ZnO synthesized *via* the different methods are shown in Figure 5. Whatever the synthesis method, they evidenced interplanar spacings of 0.28 nm and 0.25 nm consistent with the (100) and (101) planes of the hexagonal wurtzite ZnO phase [JCPDS No. 00-036-1451] and confirmed the general morphology of the wurzite ZnO materials previously observed in SEM images, with crystallite sizes in agreement with those derived from the XRD patterns.



**Figure 5.** TEM images of ZnO materials synthesized through (a,d) the polyol method (ZnO-P-60), (b,e) the precipitation with carbonates (ZnO-C300) and (c,f) the precipitation with carbamates (ZnO-c400), evidencing the general morphology of the materials and interplanar spacings of 0.28 nm and 0.25 nm consistent with the (100) and (101) planes of hexagonal wurtzite ZnO crystallites.

### 3.2. Photocatalytic activity of ZnO

#### 3.2.1. Influence of a photocatalytic pre-cleaning step

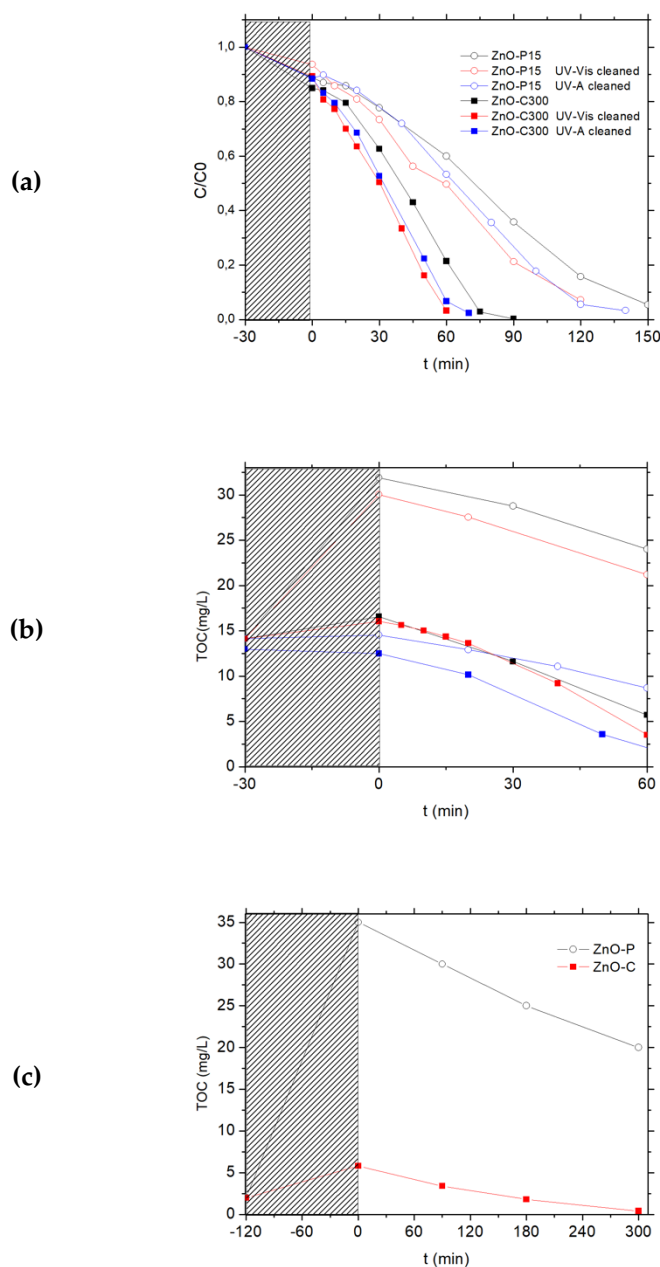
The photocatalytic activity of the as-synthesized ZnO materials was first evaluated in water under solar light using 4-Cl-phenol as test molecule. Two catalysts prepared *via* the polyol method and the carbonate-through precipitation method have been selected for studying the influence of a photocatalytic pre-cleaning step, *ie.* the dried ZnO-P-15 (sample not subjected to any calcination treatment) and the calcined ZnO-C-300 sample, respectively (Figure 6).



First, no detectable degradation of chlorophenol has been observed for 3 h under solar light, demonstrating that the chlorophenol photolysis can be neglected, as evidenced also by Eslami et al. and Gaya et al. [36,37].

As depicted in Figure 6a, the pollutant concentration evolution with the time under irradiation showed that both ZnO catalysts were able to oxidize the phenolic compound until its complete degradation, achieved within 90 min and 150 min of reaction on ZnO-P-15 and ZnO-C-300. By contrast, a TOC release to the aqueous solution has been evidenced during the adsorption period in the dark for both uncleaned ZnO catalysts, before the TOC removal was observed with a kinetic rate constant  $k'_{\text{TOC}}$  of 0.13 ppm/min and 0.18 ppm/min for ZnO-P-15 and ZnO-C-300 catalysts, respectively (Figure 6b). This TOC release was notably very pronounced in the case of ZnO synthesized *via* the polyol route, for which no thermal treatment was applied, with a TOC overshoot of 15 ppm at the beginning of the reaction attributed to the release to water of some organic residues from the synthesis, while only 4 ppm of extra TOC was released with the calcined ZnO-C-300 catalyst. This difference in terms of TOC release was in agreement with the higher weight loss recorded on the ZnO-P material and that resulted from the combustion of carbon residues from the synthesis, in comparison to that observed on the calcined ZnO materials.

The catalyst behavior was strongly affected by applying a photocatalytic cleaning step prior to the chlorophenol removal. This cleaning step consisted in submitting an aqueous suspension of the as-synthesized ZnO catalyst either to simulated solar light (2 h, 25 W/m<sup>2</sup> UV-A irradiance) or to UV-A light (16 h, 60 W/m<sup>2</sup> irradiance). Figure 6c shows in the case of UV-A that those carbonated species can be mineralized during the photocatalytic pre-cleaning step of the as-synthesized materials. The volcano-like TOC profile observed has been attributed to the release and the subsequent mineralization of carbon-containing residues coming from the precursors used in the ZnO synthesis, and that remained adsorbed at the catalyst surface or trapped in the bulk of the ZnO crystallites. It confirmed that ZnO synthesized *via* the polyol method contained larger amounts of carbonated residues than its counterparts obtained *via* the precipitation approach. They were potentially blocking the ZnO active sites, being consequently in competition with the chlorophenol pollutant for the oxidative species, or acting as recombination centers in the ZnO crystallite bulk for the photogenerated charge carriers.



**Figure 6.** Influence of the photocatalytic pre-cleaning step on (a) the relative 4-Cl-phenol concentration and (b) the TOC concentration evolution upon photocatalysis with ZnO materials. (c) Evolution of the TOC concentration during the photocatalytic pre-cleaning step of the as-synthesized ZnO-P and ZnO-C materials under UV-A light in ultrapure Milli-Q water.

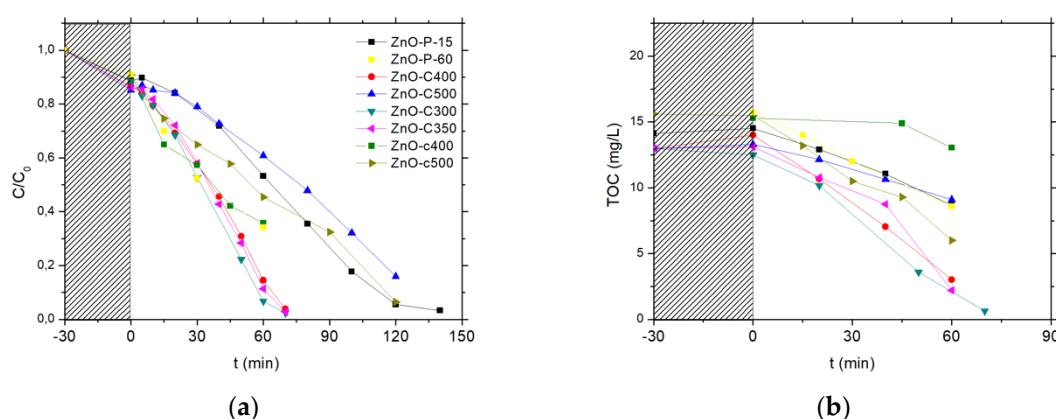
Performing the cleaning procedure under solar light or UV-A light allowed the degradation rates obtained with the ZnO materials to be improved, as it can be observed in Figures 6a and 6b. Both ZnO catalysts cleaned under solar light or UV-A displayed a faster disappearance of chlorophenol than their uncleaned counterparts. It should be noted that performing the pre-cleaning step for 2 h with a  $25 \text{ W/m}^2$  UV-A irradiance (*ie.* solar light as incident light) allowed already a significant enhancement of the kinetic rate constant for the chlorophenol

degradation to be obtained, while by contrast the initial TOC release was only slightly improved. The TOC overshoot was totally suppressed only when the pre-cleaning step was performed under UV-A light for 16 h ( $60 \text{ W/m}^2$  irradiance).

### 3.2.2. Photocatalytic activity of ZnO materials

Figure 7 shows the evolution with time under irradiation of the 4-Cl-Phenol and TOC concentrations observed on the different ZnO catalysts after the photocatalytic cleaning step under UV-A light has been applied for 2 h. Table 2 shows the corresponding kinetic rate constants for both the 4-Cl-Phenol and the TOC removal.

Whatever the cleaned material tested, no significant TOC release has been observed at the beginning of the test, confirming the efficiency of the photocatalytic pre-cleaning step. Globally, the ZnO-C materials prepared by precipitation with carbonates displayed the highest activity for both the removal of 4 Cl-phenol and that of TOC when compared to their counterparts prepared *via* the polyol method or using the carbamates as precipitation agent. Among the carbonate-through precipitation ZnO series, the highest kinetic rate constants of  $k'_{\text{Phenol}} = 0.21 \text{ mg/L/min}$  and  $k'_{\text{TOC}} = 0.18 \text{ mg/L/min}$  have been obtained with the ZnO-C-300 catalyst, for which the complete mineralization of the pollutant has been achieved within 70 min of irradiation. This activity fairly improves the results found in the literature for the removal of 4-chloro-phenol with ZnO catalyst under UVA irradiation [36]. Gaya et al. reached the complete 4-Cl-Phenol depletion in 3 h using  $2 \text{ g/L}$  of ZnO.



**Figure 7.** Relative 4-Cl-Phenol concentration (a) and TOC concentration (b) evolution upon photocatalysis on UV-A light cleaned ZnO materials.

ZnO obtained by the polyol and the carbamate precipitation methods exhibited reduced kinetic constant rates for phenol disappearance and TOC removal, in some cases even two orders of magnitude smaller than that obtained with the most active ZnO. Further, among the ZnO materials prepared with carbonates, ZnO calcined at the highest temperature of  $500^\circ\text{C}$  displayed significantly lower activity compared to that shown by its counterparts calcined in the  $300\text{--}400^\circ\text{C}$  range.

We may propose that the ZnO-C-300 photocatalyst takes advantage of a higher specific surface area as well as of a large pore volume and a large mean pore size, that facilitate the access of the 4-chlorophenol reactant and of the reaction intermediates to the ZnO surface sites. By contrast, the high surface area ZnO obtained by the polyol method probably suffered from a very low pore volume and a small mean pore size, while the low surface area of the ZnO-c material prepared with carbamate was assumed to be detrimental to the removal efficiency.

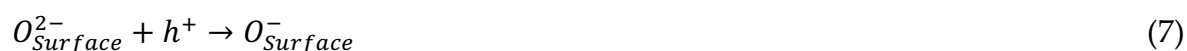
**Table 2.** Pseudo first-order kinetic rate constant of 4-Cl-Phenol removal and zero order rate constant of TOC removal obtained on UV-A light cleaned ZnO catalysts (with the corresponding linear regression coefficients)

Catalyst	$k'_{\text{TOC}} (\text{mg/Lmin})/R^2$	$k'_{\text{Phenol}} (\text{min}^{-1})/R^2$
ZnO-P15	0.097/0.99	0.008/0.98
ZnO-P60	0.130/0.88	0.011/0.94
ZnO-C300	0.180/0.99	0.210/0.99
ZnO-C350	0.173/0.90	0.017/0.99
ZnO-C400	0.180/0.99	0.014/0.99
ZnO-C500	0.071/0.99	0.007/0.97
ZnO-c400	0.030/0.89	0.010/0.93
ZnO-c500	0.153/0.98	0.007/0.98

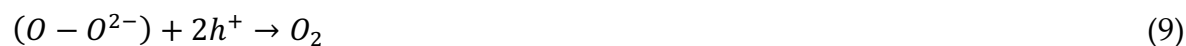
As far as ZnO is concerned, surface photocorrosion remains one of its main drawbacks for being used in water treatment. Photocorrosion consists in the dissolution of the ZnO surface with release of  $\text{Zn}^{2+}$  to the reaction media, so that the catalyst suffers from deactivation with time under irradiation as well as from intrinsic limitation in terms of reusability. The surface corrosion of ZnO is considered to be induced by the photogenerated holes ( $h^+$ ) and the overall reaction of the ZnO surface dissolution can be expressed as follow:



According to previous works, the overall surface photocorrosion process consists in two low-rate steps followed by two high-rate steps as follows [38,39] :



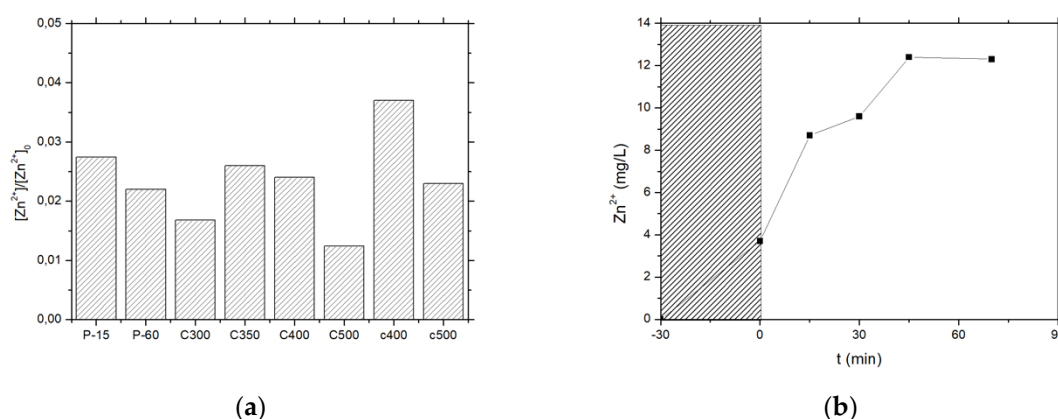




Therefore, it was of high interest to evaluate the influence of the synthesis method on the stability of the ZnO photocatalysts in terms of  $Zn^{2+}$  release to the media, expressed as the percentage of  $Zn^{2+}$  released from the ZnO catalysts into the water (Figure 8). In a first approximation, the materials with a higher activity exhibited a higher stability, with a lower release of  $Zn^{2+}$  cation to the solution being observed for the most active catalysts and globally a lower release for the ZnO material series prepared by precipitation with carbonates, *eg.* a 0,016 fraction in the case of the most active catalyst ZnO-C-300.

The ZnO-C-500 material displayed a better stability than its counterparts calcined at 300°C, but was suffering from a largely lower activity under UV-A light. Therefore, based on the kinetic rate constants derived from both the chlorophenol disappearance and the TOC evolution curves, as well as on the level of  $Zn^{2+}$  release to the media, this fast screening allowed selecting the ZnO-C-300 material obtained *via* the precipitation method with carbonates and calcined at 300°C, for implementing subsequently the solar light photon-assisted preparation of the Cu-ZnO hybrid catalysts in the next section.

However, we would like to point out that the surface photocorrosion of ZnO materials remained a key-issue for using such materials as photocatalysts in water treatment. Indeed, a strong loss of activity has been observed when performing sequential runs on the ZnO-C-300 photocatalyst. Using the TOC conversion achieved after 75 min of test as indicator (*ie.* the duration necessary for achieving full TOC conversion in the run#1), Table 3 evidences that the surface photocorrosion was accompanied by an important loss of activity with sequential runs.



**Figure 8.** Fraction of  $Zn^{2+}$  released into the water (a) at the end of the photocatalytic run with ZnO materials and (b) as a function of time under irradiation in the case of the ZnO-C-400 catalyst.

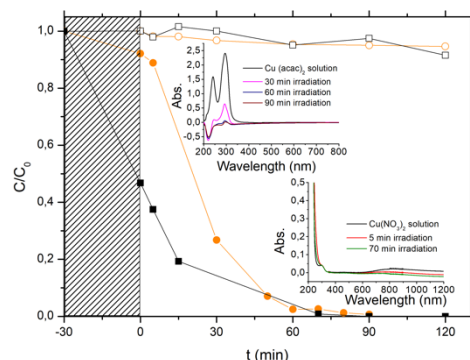
**Table 3.** TOC conversion after several sequential photocatalytic runs with the ZnO-C300 catalyst.

Run	X <sub>TOC</sub> (%)
First	100
Second	88
Third	61

### 3.3. Preparation of Cu-ZnO catalysts by the photon-assisted synthesis method

The photon-assisted preparation of the Cu-ZnO catalysts has been performed using the ZnO-C-300 material as semi-conductor support, since the first part of this work evidenced that it displayed the highest photoactivity in terms of removal of both chlorophenol and TOC, and showed also a high photo-stability in water. The photon-assisted synthesis method takes advantage of the redox photo-activity of the ZnO semiconductor under solar light for allowing the reduction of the metal ions adsorbed at the host surface by the photogenerated electrons from the conduction band of the irradiated semi-conductor. Both Cu(acac)<sub>2</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> metallic precursors were used, and Figure 9 depicts the disappearance curves of both precursors during the photon-assisted synthesis in the presence of the ZnO-C-300 catalyst, derived from the time-evolution of the UV-vis absorbance spectra.

First, photolysis of the copper precursors could be neglected under solar light in our experimental conditions, since no changes of the UV-vis spectra was observed whatever the precursor used (not shown). The evolution with time of the C/C<sub>0</sub> relative concentrations evidenced that the photodeposition occurred on the ZnO support, and further that the copper precursor nature influenced the kinetics of the photodeposition process at the surface of the irradiated ZnO support. However, it has to be noticed that the time-monitoring of the photo-deposition process was more difficult using the nitrate precursor than its acetylacetonate counterpart. Indeed, the ability of semi-conductor photocatalysis to perform nitrate reduction and nitrate oxidation in water led to produce first nitrite as initial intermediate (very unstable and easily oxidized back to nitrate) and further higher oxidation state products such as ammonia. The UV-vis signature of those N-compounds is known to overlap around similar absorption wavelengths, so that the photodeposition was monitored in a first approximation by following the disappearance of the low intensity absorption peak at  $\lambda = 800$  nm related to the Cu<sup>2+</sup> concentration, which resulted in a less accurate time-monitoring. However, ICP-OES analysis revealed that the Cu-ZnO catalyst had a Cu content of 9.7 wt.%, in good agreement with the targeted theoretical amount of 10 wt.%. By contrast, only a Cu content of 7 wt.% was obtained in the case of the Cu(acac)<sub>2</sub> precursor. This difference has been attributed to a possible release of non-steadily anchored Cu species during the washing of the Cu-ZnO materials directly after the photon-assisted synthesis.



**Figure 9.** Disappearance curves of (■) the  $\text{Cu}(\text{NO}_3)_2$  and (●) the  $\text{Cu}(\text{acac})_3$  precursors during the photon-assisted synthesis in the presence of the ZnO-C-300 catalyst. Blank photolysis experiments in the absence of ZnO photocatalyst for (□)  $\text{Cu}(\text{NO}_3)_2$  and (◊)  $\text{Cu}(\text{acac})_3$  precursors. Insert: Time-evolution of the UV-vis absorbance spectra for both precursors (selected analysis times are reported for not overloading the UV-vis absorbance graphs).

### 3.4. Characterization of Cu-ZnO catalysts

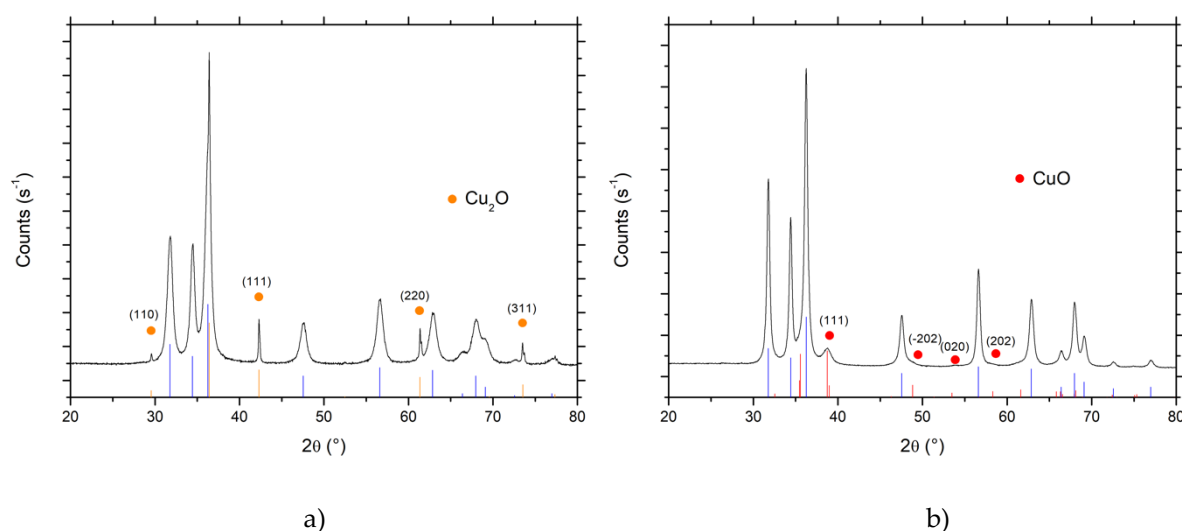
Figure 10 shows the XRD patterns of both Cu-ZnO catalysts. In the case of the  $\text{Cu}(\text{acac})_3$  precursor, besides the diffraction peaks of ZnO crystallized in the hexagonal wurtzite structure, additional diffraction peaks have been observed at  $29.6^\circ$ ,  $42.2^\circ$ ,  $61.3^\circ$  and  $73.4^\circ$ , and attributed to the diffraction of (110), (111), (220) and (311) planes of cubic  $\text{Cu}^{(I)}_2\text{O}$  nanoparticles with an average crystallite size of 65 nm (JCPDS Card 00-005-0667). By contrast, in the case of  $\text{Cu}(\text{NO}_3)_2$  precursor, additional diffraction peaks and shoulders have been recorded at  $2\theta = 38.8^\circ$ ,  $54.0^\circ$  and  $58.0^\circ$ , and attributed to the diffraction of (111), (020) and (202) planes of monoclinic  $\text{Cu}^{(II)}\text{O}$  nanoparticles with an average crystallite size of 10 nm (JCPDS Card 01-089-5895). Very interestingly, the choice of the photon-assisted synthesis/deposition parameters allowed to selectively drive the oxidation state of the Cu nanoparticles synthesized on the ZnO support towards either cuprous or cupric oxides, so that the prepared catalysts could be considered as  $\text{Cu}^{(I)}_2\text{O}$ -ZnO or  $\text{Cu}^{(II)}\text{O}$ -ZnO. This suggests the possibility of controlling the oxidation state of the Cu nanoparticles in the Cu-ZnO while implementing a preparation procedure at room temperature without applying any final thermal treatment.

In the case of the Cu nitrate precursor, the reduction of adsorbed  $\text{Cu}^{2+}$  ions by the photogenerated electrons would give first  $\text{Cu}^0$ , that might be further re-oxidized by the  $\text{OH}^\bullet$  radicals formed *via* the oxidation of adsorbed water by the photogenerated holes from the valence band, or directly by the holes.  $\text{Cu}^0$  was also suggested to undergo reoxidation by  $\text{O}_2$  into  $\text{Cu}^{2+}$  [40], the  $\text{Cu}^{2+}/\text{Cu}^0$  couple being then considered to act as an electron mediator from the conduction band to  $\text{O}_2$ . In the case of the acetylacetonate precursor, the direct  $\text{Cu}(\text{acac})_3$  reduction into  $\text{Cu}^0$  was reported to be strongly unfavored compared to that of  $\text{Cu}^{2+}$  [40]. By contrast, the

adsorbed acetylacetonate precursor was proposed to be first oxidized by  $\text{OH}^\circ$  radicals formed *via* the oxidation of adsorbed water by the photogenerated holes from the valence band, or directly by the holes. Subsequently, the ligand oxidation would generate adsorbed  $\text{Cu}^{2+}$  ions that can be subsequently reduced by the photogenerated electrons.

Further complementary works are actually being performed for understanding the mechanisms involved in the selective formation of  $\text{Cu}^{2+}$  or  $\text{Cu}^+$  species at the surface of the ZnO support and for shedding light on the main synthesis parameters enabling to drive the oxidation state of the Cu within the Cu-ZnO material.

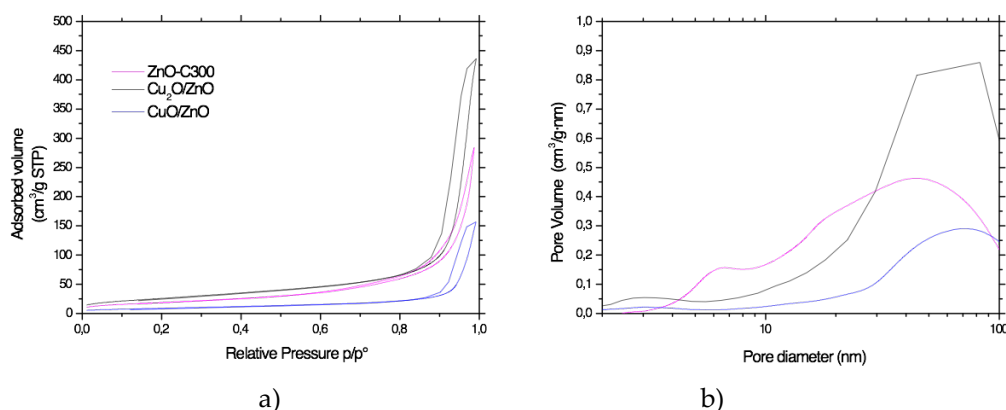
We have to note that performing the photodeposition process on the ZnO support led to an increase in the mean crystallite size of the semi-conductor support from 10 nm to 20 nm in the case of the copper nitrate precursor. By contrast, no significant change was observed in the case of the acetylacetonate precursor, with a mean crystallite size of 13 nm being obtained.



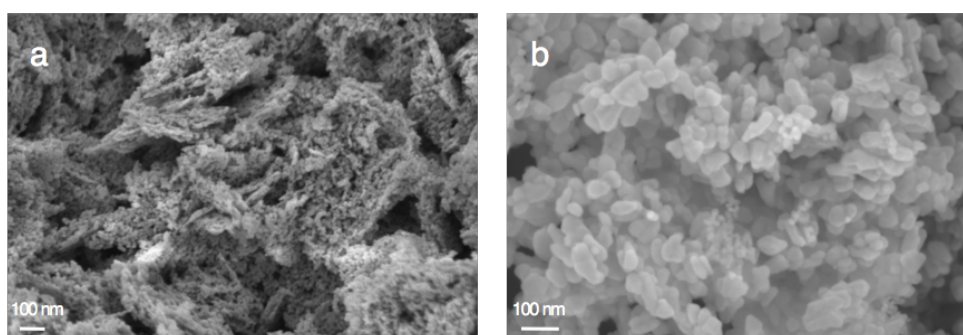
**Figure 10.** XRD patterns of the  $\text{Cu}_x\text{O}$ -ZnO materials synthesized by photodeposition using (a)  $\text{Cu}(\text{acac})_2$  and (b)  $\text{Cu}(\text{NO}_3)_2$  as metallic precursor. Main reflexes from JCPDS cards No 01-089-5895 and 00-005-0667 for CuO and  $\text{Cu}_2\text{O}$  phases, respectively. The main reflexes from JCPDS card No 00-036-1451 for the ZnO support are shown in blue.

The main physico-chemical properties of the  $\text{Cu}_x\text{O}$ /ZnO materials are reported in Table 1. It evidenced that the synthesis of the CuO-ZnO and  $\text{Cu}_2\text{O}$ -ZnO composite materials by photodeposition resulted in specific surface area and pore volume changes, and the composite materials displayed specific surface areas of  $33 \text{ m}^2/\text{g}$  and  $95 \text{ m}^2/\text{g}$ , respectively, with pore volumes of  $0.24 \text{ cm}^3/\text{g}$  and  $0.68 \text{ cm}^3/\text{g}$ . Figure 11 shows that the photon-assisted synthesis of  $\text{Cu}_x\text{O}$  did not modify both isotherm and hysteresis types, of type II and H3, respectively, while it slightly influenced the pore size distribution profiles. In addition, the SEM images shown in Figure 12 indicate that the overall

morphology of the ZnO-based materials has not been modified by the photon-assisted synthesis process.



**Figure 11.** (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore size distributions of both Cu<sub>x</sub>O-ZnO catalysts and bare ZnO material as reference.



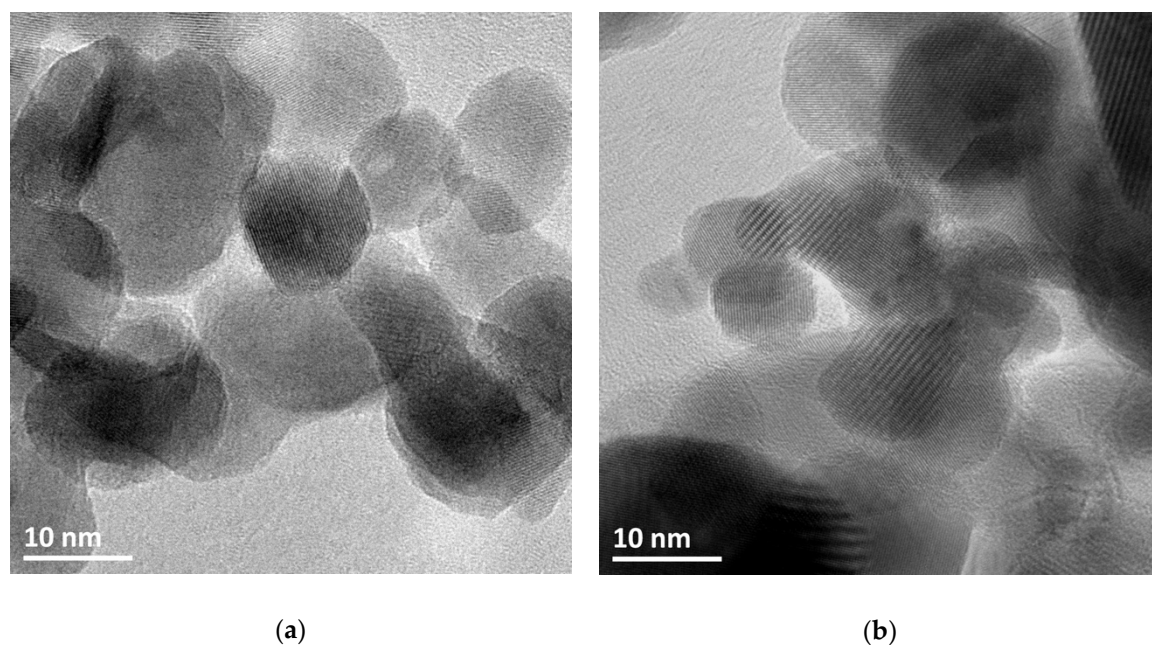
**Figure 12.** SEM images of Cu<sub>2</sub>O-ZnO (a) and CuO-ZnO (b) catalysts.

Figure 13 shows the TEM images of the Cu-ZnO materials obtained by the photon-assisted synthesis method with both copper precursors. Unfortunately, the similarities of the interplanar spacings corresponding to the main planes of the ZnO material and of both Cu<sup>(II)</sup>O and Cu<sub>2</sub><sup>(I)</sup>O crystallites did not allow to identify and to locate specifically the different phases within the Cu-ZnO materials that consisted in very entangled oxide crystallites in close contact. Indeed, the (101) and (100) planes of ZnO have interplanar distances of 0.25 nm and 0.28 nm [JCPDS No.00-036-1451], while the (111) and (002) planes of the Cu<sup>(II)</sup>O phase have 0.23 nm and 0.25 nm interplanar distance respectively [JCPDS No. 01-089-5895] [41], and the (111) planes of the Cu<sub>2</sub><sup>(I)</sup>O crystallites have an interplanar distance of 0.25 nm [JCPDS No. 00-005-0667] [42]. However, the presence of copper has been confirmed by performing overall EDS analysis on both samples, with a Cu content of 7.4 wt.% and 9.5 wt.% for the CuO-ZnO and the Cu<sub>2</sub>O-ZnO materials, respectively, in good agreement with the ICP-OES data.

It is worth noting that whatever the copper precursor, the prepared material can be considered as a Cu-ZnO composite catalyst since both Cu<sub>2</sub>O and CuO crystallites do not exhibit significantly smaller mean sizes than the ZnO crystallites, rather than

as a ZnO supported Cu catalyst, that would usually consist in smaller size Cu-based nanoparticles dispersed on the ZnO support. Considering the exclusive presence of one single chemical state for the crystalline Cu-based crystallites in the samples as shown by XRD - keeping in mind the detection limit of the XRD measurement -, the Cu-ZnO materials can thus be considered as Cu<sup>(II)</sup>O-ZnO and Cu<sub>2</sub><sup>(I)</sup>O-ZnO composite catalysts, although the assignment of both transition metal oxide phases to specific crystallites in TEM images was not possible.

In addition, we cannot rule out that in addition to larger crystallites, some Cu species might remain highly dispersed on ZnO, thanks to a strong interaction between Cu and the amphoteric ZnO material, that seems to protect the Cu nanoparticles from sintering, consequently providing enhanced interphase contact [43].



**Figure 13.** TEM images of the Cu-ZnO materials synthesized by photodeposition using (a) Cu(acac)<sub>2</sub> and (b) Cu(NO<sub>3</sub>)<sub>2</sub> as metallic precursor. An example of STEM imaging is shown as Figure S2.

## 5. Conclusions

Cu<sub>x</sub>O-ZnO composite catalysts with a control of the chemical state of the copper oxide phase have been prepared at room temperature using the solar light-induced redox photoactivity of the ZnO semiconductor support. The preparation of Cu<sub>2</sub><sup>(I)</sup>O-ZnO and Cu<sup>(II)</sup>O-ZnO composite catalysts has been achieved by using Cu(acac)<sub>2</sub> in THF-water and Cu(NO<sub>3</sub>)<sub>2</sub> in water as metallic precursor, respectively.

The photoactive ZnO host material has been prepared through the precipitation method with carbonate as precipitation agent, and its superior activity compared to



ZnO synthesized by other methods has been evaluated by taking the photocatalytic degradation of the 4-chlorophenol compound in water under simulated solar light as model reaction.

Works are ongoing for understanding the key-parameters driving the selective synthesis of the  $\text{Cu}_x\text{O}$  phase within the ZnO-based catalysts. The activity of  $\text{Cu}_x\text{O}$ -ZnO catalysts will be investigated in high interest reactions in the field of biomass conversion. Beside thermal catalysis applications, this work opened a new route for the facile synthesis of  $\text{Cu}_2\text{O}$ -ZnO heterojunction photocatalysts, that could take advantage under solar light of the heterojunction built between the *p*-type semiconductor  $\text{Cu}_2\text{O}$  with direct band gap of about 2.17 eV and the ZnO semiconductor phase.

**Author Contributions:** Experimental works, M.B. and P.G.M.; Data analysis, M.B., P.G.M., A.R. and N.K.; Writing-Original Draft Preparation, P.G.M. and N.K.; Visualization, P.G.M. and M.B.; Supervision, N.K. and A.R.; Project Administration, N.K.; Funding Acquisition, M.B., N.K. and A.R.

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**Conflicts of Interest:** The authors declare no conflict of interest.



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## References

- Kołodziejczak-Radzimska, A.; Jesionowski, T. Zinc Oxide From Synthesis to Application: A Review. *Materials* **2014**, *7*, DOI doi: 10.3390/ma7042833.
- Segets, D.; Gradl, J.; Taylor, R.K.; Vassilev, V.; Peukert, W. Analysis of Optical Absorbance Spectra for the Determination of ZnO Nanoparticle Size Distribution, Solubility, and Surface Energy. *ACS Nano* **2009**, *3*, 1703-1710, DOI doi: 10.1021/nn900223b.
- Chaari, M.; Matoussi, A. Electrical conduction and dielectric studies of ZnO pellets. *Physica B: Condensed Matter* **2012**, *407*, 3441-3447, DOI <https://doi.org/10.1016/j.physb.2012.04.056>.
- Bacaksiz, E.; Parlak, M.; Tomakin, M.; Özçelik, A.; Karakız, M.; Altunbaş, M. The effects of zinc nitrate, zinc acetate and zinc chloride precursors on investigation of structural and optical properties of ZnO thin films. *Journal of Alloys and Compounds* **2008**, *466*, 447-450, DOI <https://doi.org/10.1016/j.jallcom.2007.11.061>.
- Wang, Z.L. Splendid One-Dimensional Nanostructures of Zinc Oxide: A New Nanomaterial Family for Nanotechnology. *ACS Nano* **2008**, *2*, 1987-1992, DOI: 10.1021/nn800631r
- Wang, J.; Cao, J.; Fang, B.; Lu, P.; Deng, S.; Wang, H. Synthesis and characterization of multipod, flower-like, and shuttle-like ZnO frameworks in ionic liquids. *Mater Lett* **2005**, *59*, 1405-1408, DOI <https://doi.org/10.1017/S1431927606060430>
- Sudha, D.; Sivakumar, P. Review on the photocatalytic activity of various composite catalysts. *Chemical Engineering and Processing: Process Intensification* **2015**, *97*, 112-133, DOI <https://doi.org/10.1016/j.cep.2015.08.006>.

8. Anderson Janotti and Chris G Van, de Walle Fundamentals of zinc oxide as a semiconductor. *Reports on Progress in Physics* **2009**, 72, 126501, DOI <https://doi.org/10.1088/0034-4885/72/12/126501>
9. Reynolds, D.C.; Look, D.C.; Jogai, B.; Litton, C.W.; Cantwell, G.; Harsch, W.C. Valence-band ordering in ZnO. *Phys Rev B* **1999**, 60, 2340-2344 DOI <https://doi.org/10.1103/PhysRevB.60.2340>
10. Chen, Y.; Bagnall, D.M.; Koh, H.; Park, K.; Hiraga, K.; Zhu, Z.; Yao, T. Plasma assisted molecular beam epitaxy of ZnO on c-plane sapphire: Growth and characterization. *J Appl Phys* **1998**, 84, 3912-3918, DOI <https://doi.org/10.1063/1.368595>
11. Udom, I.; Ram, M.K.; Stefanakos, E.K.; Hepp, A.F.; Goswami, D.Y. One dimensional-ZnO nanostructures: Synthesis, properties and environmental applications. *Materials Science in Semiconductor Processing* **2013**, 16, 2070-2083, DOI <https://doi.org/10.1016/j.mssp.2013.06.017>.
12. Hernández-Carrillo, M.A.; Torres-Ricárdez, R.; García-Mendoza, M.F.; Ramírez-Morales, E.; Rojas-Blanco, L.; Díaz-Flores, L.L.; Sepúlveda-Palacios, G.E.; Paraguay-Delgado, F.; Pérez-Hernández, G. Eu-modified ZnO nanoparticles for applications in photocatalysis. *Catalysis Today* **2018**, DOI <https://doi.org/10.1016/j.cattod.2018.04.060>.
13. Machín, A.; Cotto, M.; Duconge, J.; Arango, J.C.; Morant, C.; Pinilla, S.; Soto-Vázquez, L.; Resto, E.; Márquez, F. Hydrogen production via water splitting using different Au@ZnO catalysts under UV-vis irradiation. *Journal of Photochemistry and Photobiology A: Chemistry* **2018**, 353, 385-394, DOI <https://doi.org/10.1016/j.jphotochem.2017.11.050>.
14. Fkiri, A.; Santacruz, M.R.; Mezni, A.; Smiri, L.-.; Keller, V.; Keller, N. One-pot synthesis of lightly doped Zn<sub>1-x</sub>Cu<sub>x</sub>O and Au-Zn<sub>1-x</sub>Cu<sub>x</sub>O with solar light photocatalytic activity in liquid phase. *Environ Sci Pollut Res* **2017**, 24, 15622-15633 DOI <https://doi.org/10.1007/s11356-017-9067-5>
15. Liu, Y.; Zhong, M.; Shan, G.; Li, Y.; Huang, B.; Yang, G. Biocompatible ZnO/Au Nanocomposites for Ultrasensitive DNA Detection Using Resonance Raman Scattering. *J Phys Chem B* **2008**, 112, 6484-6489 DOI: 10.1021/jp710399d
16. Udawatte, N.; Lee, M.; Kim, J.; Lee, D. Well-Defined Au/ZnO Nanoparticle Composites Exhibiting Enhanced Photocatalytic Activities. *ACS Appl Mater Interfaces* **2011**, 3, 4531-4538 DOI: 10.1021/am201221x
17. Li, H.; Liu, E.; Chan, F.Y.F.; Lu, Z.; Chen, R. Fabrication of ordered flower-like ZnO nanostructures by a microwave and ultrasonic combined technique and their enhanced photocatalytic activity. *Materials Letters* **2011**, 65, 3440-3443, DOI <https://doi.org/10.1016/j.matlet.2011.07.049>.
18. Li, P.; Wei, Z.; Wu, T.; Peng, Q.; Li, Y. Au@ZnO Hybrid Nanopyramids and Their Photocatalytic Properties. *J Am Chem Soc* **2011**, 133, 5660-5663, DOI: 10.1021/ja111102u
19. Chen, P.; Lee, G.; Anandan, S.; Wu, J.J. Synthesis of ZnO and Au tethered ZnO pyramid-like microflower for photocatalytic degradation of orange II. *Materials Science and Engineering: B* **2012**, 177, 190-196, DOI <https://doi.org/10.1016/j.mseb.2011.12.001>.
20. Sun, Q.; Men, Y.; Wang, J.; Chai, S.; Song, Q. Support effect of Ag/ZnO catalysts for partial oxidation of methanol. *Inorganic Chemistry Communications* **2018**, 92, 51-54, DOI <https://doi.org/10.1016/j.inoche.2018.04.001>.
21. Grunwaldt, J.-.; Molenbroek, A.M.; Topsøe, N.-.; Topsøe, H.; Clausen, B.S. In Situ Investigations of Structural Changes in Cu/ZnO Catalysts. *Journal of Catalysis* **2000**, 194, 452-460, DOI <https://doi.org/10.1006/jcat.2000.2930>.
22. Ichikawa, M. Catalysis by Supported Metal Crystallites from Carbonyl Clusters. I. Catalytic Methanol Synthesis under Mild Conditions over Supported Rhodium, Platinum, and Iridium Crystallites Prepared from Rh, Pt, and Ir Carbonyl Cluster Compounds Deposited on ZnO and MgO. *Bull Chem Soc Jpn* **1978**, 51, 2268-2272, DOI <https://doi.org/10.1246/bcsj.51.2268>
23. Cubeiro, M.L.; Fierro, J.L.G. Selective Production of Hydrogen by Partial Oxidation of Methanol over ZnO-Supported Palladium Catalysts. *Journal of Catalysis* **1998**, 179, 150-162, DOI <https://doi.org/10.1006/jcat.1998.2184>.
24. Zheng, L.; Li, X.; Du, W.; Shi, D.; Ning, W.; Lu, X.; Hou, Z. Metal-organic framework derived Cu/ZnO catalysts for continuous hydrogenolysis of glycerol. *Applied Catalysis B: Environmental* **2017**, 203, 146-153, DOI <https://doi.org/10.1016/j.apcatb.2016.10.011>.



25. Alba-Rubio, A.C.; Santamaría-González, J.; Mérida-Robles, J.M.; Moreno-Tost, R.; Martín-Alonso, D.; Jiménez-López, A.; Maireles-Torres, P. Heterogeneous transesterification processes by using CaO supported on zinc oxide as basic catalysts. *Catalysis Today* **2010**, *149*, 281-287, DOI <https://doi.org/10.1016/j.cattod.2009.06.024>.
26. Zhu, Y.; Kong, X.; Zheng, H.; Ding, G.; Zhu, Y.; Li, Y. Efficient synthesis of 2,5-dihydroxymethylfuran and 2,5-dimethylfuran from 5-hydroxymethylfurfural using mineral-derived Cu catalysts as versatile catalysts. *Catal Sci Technol* **2015**, *5*, 4208-4217, DOI [10.1039/C5CY00700C](https://doi.org/10.1039/C5CY00700C)
27. Llorca, J.; de la Piscina, P.R.; Dalmon, J.; Sales, J.; Homs, N. CO-free hydrogen from steam-reforming of bioethanol over ZnO-supported cobalt catalysts: Effect of the metallic precursor. *Applied Catalysis B: Environmental* **2003**, *43*, 355-369, DOI [https://doi.org/10.1016/S0926-3373\(02\)00326-0](https://doi.org/10.1016/S0926-3373(02)00326-0).
28. Homs, N.; Llorca, J.; de la Piscina, P.R. Low-temperature steam-reforming of ethanol over ZnO-supported Ni and Cu catalysts: The effect of nickel and copper addition to ZnO-supported cobalt-based catalysts. *Catalysis Today* **2006**, *116*, 361-366, DOI <https://doi.org/10.1016/j.cattod.2006.05.081>.
29. Ammari, F.; Lamotte, J.; Touroude, R. An emergent catalytic material: Pt/ZnO catalyst for selective hydrogenation of crotonaldehyde. *Journal of Catalysis* **2004**, *221*, 32-42, DOI [https://doi.org/10.1016/S0021-9517\(03\)00290-2](https://doi.org/10.1016/S0021-9517(03)00290-2).
30. Spencer, M.S. The role of zinc oxide in Cu/ZnO catalysts for methanol synthesis and the water gas shift reaction. *Topics in Catalysis* **1999**, *8*, 259, DOI: [10.1021/jp990375a](https://doi.org/10.1021/jp990375a)
31. Pinna, F. Supported metal catalysts preparation. *Catalysis Today* **1998**, *41*, 129-137, DOI [https://doi.org/10.1016/S0920-5861\(98\)00043-1](https://doi.org/10.1016/S0920-5861(98)00043-1).
32. Liu, X.; Liu, M.H.; Luo, Y.C.; Mou, C.Y.; Lin, S.D.; Cheng, H.; Chen, J.M.; Lee, J.F.; Lin, T.S. Strong Metal-Support Interactions between Gold Nanoparticles and ZnO Nanorods in CO Oxidation. *Journal of the American Chemical Society* **2012**, *134* (24), 10251, DOI <https://pubs.acs.org/doi/abs/10.1021/ja3033235>
33. Le Valant, A.; Comminges, C.; Tisseraud, C.; Canaff, C.; Pinard, L.; Pouilloux, Y. The Cu-ZnO synergy in methanol synthesis from CO<sub>2</sub>, Part 1: Origin of active site explained by experimental studies and a sphere contact quantification model on Cu + ZnO mechanical mixtures, *Journal of Catalysis* **2015**, *324*, 41, DOI <https://doi.org/10.1016/j.jcat.2015.01.021>
34. Collins, S.S.E.; Cittadini, M.; Pecharrómán, C.; Martucci, A.; Mulvaney, P. Hydrogen Spillover between Single Gold Nanorods and Metal Oxide Supports: A Surface Plasmon Spectroscopy Study. *ACS Nano* **2015**, *9*(8), 7846, DOI <https://pubs.acs.org/doi/abs/10.1021/acs.nano.5b02970>
35. Lee, K.M.; Lai, C.W.; Ngai, K.S.; Juan, J.C. Recent developments of zinc oxide based photocatalyst in water treatment technology: A review. *Water Research* **2016**, *88*, 428-448, DOI <https://doi.org/10.1016/j.watres.2015.09.045>.
36. Gaya, U.I.; Abdullah, A.H.; Zainal, Z.; Hussein, M.Z. Photocatalytic treatment of 4-chlorophenol in aqueous ZnO suspensions: Intermediates, influence of dosage and inorganic anions. *Journal of Hazardous Materials* **2009**, *168*, 57-63, DOI <https://doi.org/10.1016/j.jhazmat.2009.01.130>.
37. Eslami, A.; Hashemi, M.; Ghanbari, F. Degradation of 4-chlorophenol using catalyzed peroxy monosulfate with nano-MnO<sub>2</sub>/UV irradiation: Toxicity assessment and evaluation for industrial wastewater treatment. *Journal of Cleaner Production* **2018**, *195*, 1389-1397, DOI <https://doi.org/10.1016/j.jclepro.2018.05.137>.
38. Ma, X.; Li, H.; Liu, T.; Du, S.; Qiang, Q.; Wang, Y.; Yin, S.; Sato, T. Comparison of photocatalytic reaction-induced selective corrosion with photocorrosion: Impact on morphology and stability of Ag-ZnO. *Applied Catalysis B: Environmental* **2017**, *201*, 348-358, DOI <https://doi.org/10.1016/j.apcatb.2016.08.029>.
39. Han, C.; Yang, M.; Weng, B.; Xu, Y. Improving the photocatalytic activity and anti-photocorrosion of semiconductor ZnO by coupling with versatile carbon. *Phys Chem Chem Phys* **2014**, *16*, 16891-16903, DOI [10.1039/C4CP02189D](https://doi.org/10.1039/C4CP02189D)
40. Naya, S.I.; Tanaka, M.; Kimura, K.; Tada, H. Visible-Light-Driven Copper Acetylacetonate Decomposition by BiVO<sub>4</sub>. *Langmuir* (2011) *27*:10334-10339, DOI: [10.1021/la2016935](https://doi.org/10.1021/la2016935)
41. Liu, Y.; Zhong, L.; Peng, Z.; Song, Y.; Chen, W. Field emission properties of one-dimensional single CuO nanoneedle by in situ microscopy. *J Mat Sci* **2010**, *45*, 3791-3796, DOI <https://doi.org/10.1007/s10853-010-4433-4>

42. Kim, M.H.; Lim, B.; Lee, E.; Xia, Y. Polyol synthesis of Cu<sub>2</sub>O nanoparticles: use of chloride to promote the formation of a cubic morphology. *J Mater Chem* **2008**, *18*, 4069-4073, DOI: 10.1039/b805913f
43. Chen, S.; Wojcieszak, R.; Dumeignil, F.; Marceau, E.; Royer, S. How Catalysts and Experimental Conditions Determine the Selective Hydroconversion of Furfural and 5-Hydroxymethylfurfural. *Chem. Rev.* DOI: 10.1021/acs.chemrev.8b00134