catalysts

MDPI

Supplementary Materials

Crystalline ZnO photocatalysts prepared at ambient temperature: Influence of morphology on *p*-nitrophenol degradation in water

Julien Mahy [1,*,∞], Louise Lejeune [1,∞], Tommy Haynes [1], Nathalie Body [1], Simon De Kreijger [1], Benjamin Elias [1], Raphael Henrique Marques Marcilli [2], Charles-André Fustin [2] and Sophie Hermans [1,*]

1 Molecular Chemistry, Materials and Catalysis (MOST), Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Bâtiment Lavoisier. Pl. Louis Pasteur, 1, 1348 Louvain La Neuve, Belgium; l.lejeune@student.uclouvain.be (L.L.), tommy.haynes@uclouvain.be (T.H.), nathalie.body@uclouvain.be (N.B.), simon.dekreijger@uclouvain.be (S. K.), benjamin.elias@uclouvain.be (B. E.)

2 Bio and Soft Matter Division (BSMA), Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Place Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium; raphael.marques@uclouvain.be (R.H.M.M.); charles-andre.fustin@uclouvain.be (C.-A.F.)

* Correspondence: julien.mahy@uclouvain.be (J.G.M.), sophie.hermans@uclouvain.be (S.H.); Tel.: +32 10 47 28 10

∞ These two authors participated equally to the research.

1. XRD patterns

Figure S1 presents the XRD patterns of sample Z1 before and after washing, the peaks between 5 and 27° correspond to the contamination that is removed after washing.

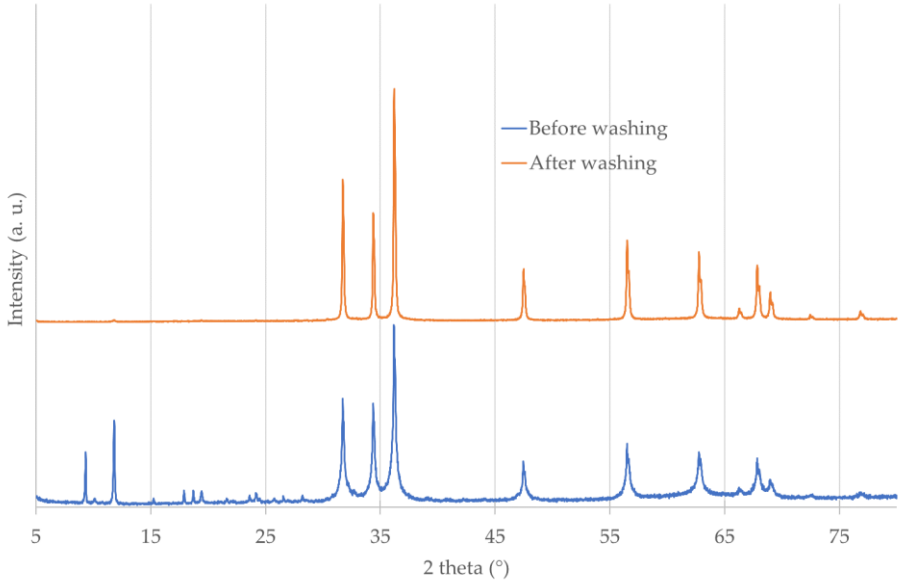

Figure S1. XRD diffraction patterns obtained for a ZnO sample (Z1) before and after washing.

2. XPS

Zn *2p*, O *1s*, N *1s*, and C *1s* XPS spectra are presented in Figure S2 for Z19 ZnO sample shown as example. Indeed, all the samples presented similar XPS spectra.

On the Zn *2p* spectra (Figure S2a), one peak is observed at 1021 eV which corresponds to Zn^{2+} linked to O [1]. So it corresponds to the expected ZnO [1]**.** The quantification gives 31 at.% for Zn.

For the O *1s* spectra (Figure S2b), there is a peak at 530.1 eV corresponding to Zn-O bonds in ZnO [1]**.** The shoulder at higher binding energy in the O *1s* peak is hardly exploitable because of the presence of a non-negligible amount of oxygen involved in the common carbonaceous contamination (Figure S2d) [2]. The quantification gives 47 at.% for O.

For the N *1s* spectra (Figure S2c), one peak is observed around 399 eV with a quantification of 0.4 at.%. According to literature, a N *1s* peak around 399 eV may correspond to the formation of oxynitride ($ZnO_{1-x}N_x$) due to substitution of O atoms of ZnO by nitrogen [3,4].

For the C *1s* region (Figure S2d), the signal can be decomposed in three different peaks: (i) one at 284.8 eV corresponding to C-(C,H) bondings, (ii) another at 286.3 eV corresponding to C-O bondings, and (iii) a third at 288.5 eV corresponding to O=C-O bondings. The quantification gives the following repartition: (i)15.4, (ii) 2.0, and (iii) 4.2 at.% respectively.

The ratio Zn/O is close to 1 (0.85) if the amount of O linked to C is removed (47% minus 10.4% equals 36.6%).

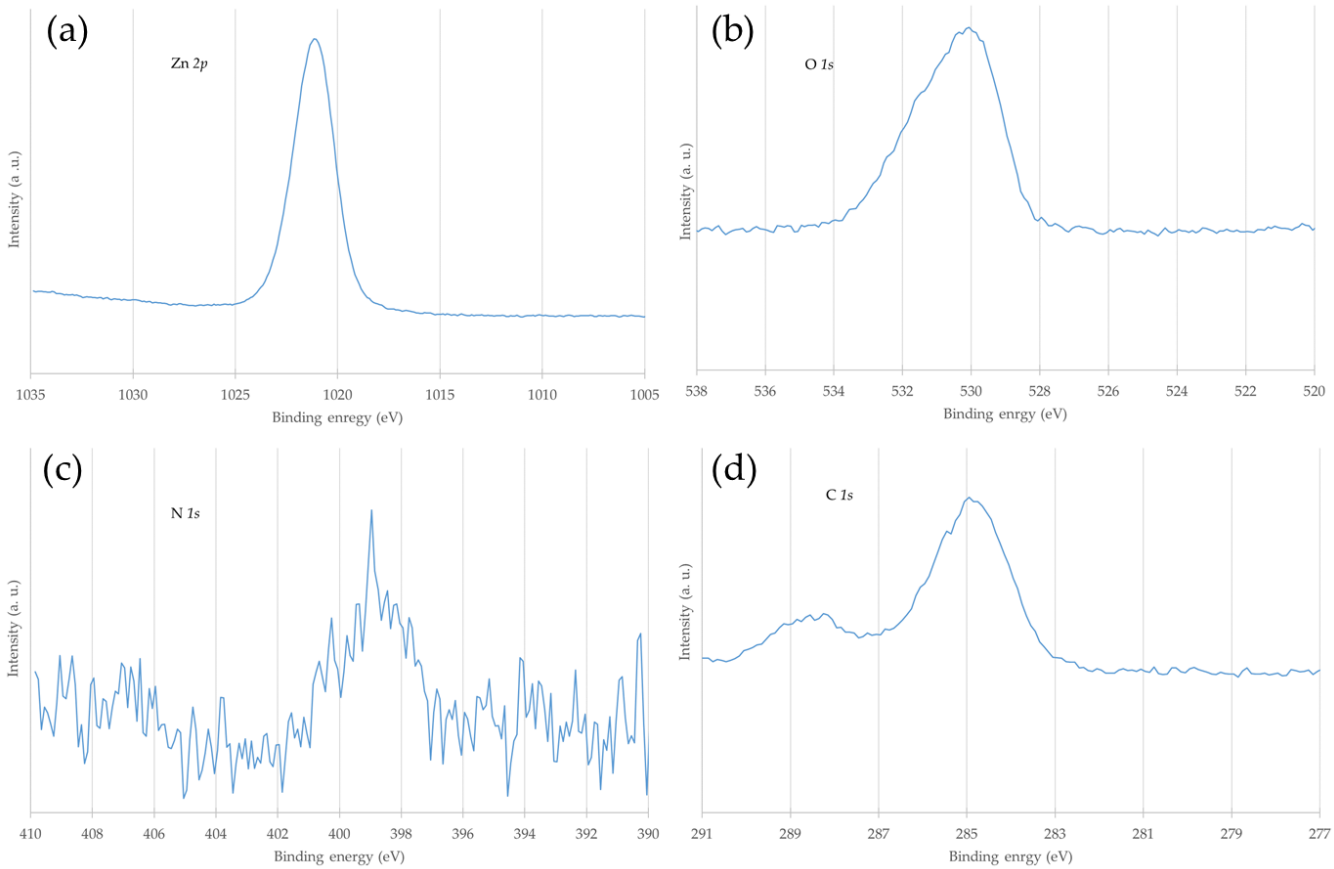

Figure S2. XPS spectra of Z19 ZnO sample: (a) Zn *2p* region, (b) O *1s* region, (c) N *1s* region and (d) C *1s* region.

3. JMP

Figures S3, S4 and Table S1 correspond to the JMP analysis including the parameters (stirring * reaction time) and (reaction time * reaction time) in addition to those taken into account in the analysis presented in the main article (section 2.1.3.).

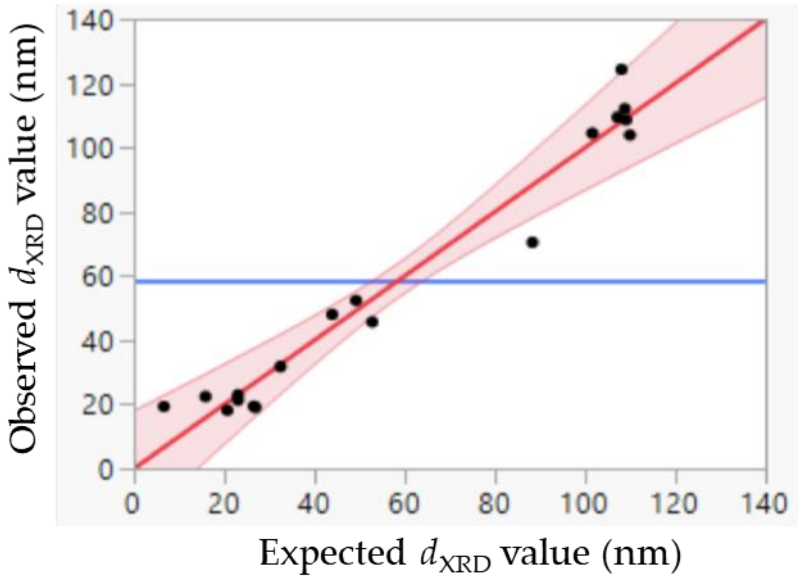

Figure S3. Observed d_{XRD} values in function of expected d_{XRD} by the built model. The red area and the blue line represent respectively the confidence interval and the mean value of the d_{XRD}.

Table S1. Analysis of variance report.

Source	Degree of freedom	Sum of the squares	Mean square	F ratio	Prob.>F
Model	7	26,787.35	3,826.76	36.4561	<0.0001
Error	10	1.049	104.97	-	-
Corrected total	17	27,837.04	-	-	-

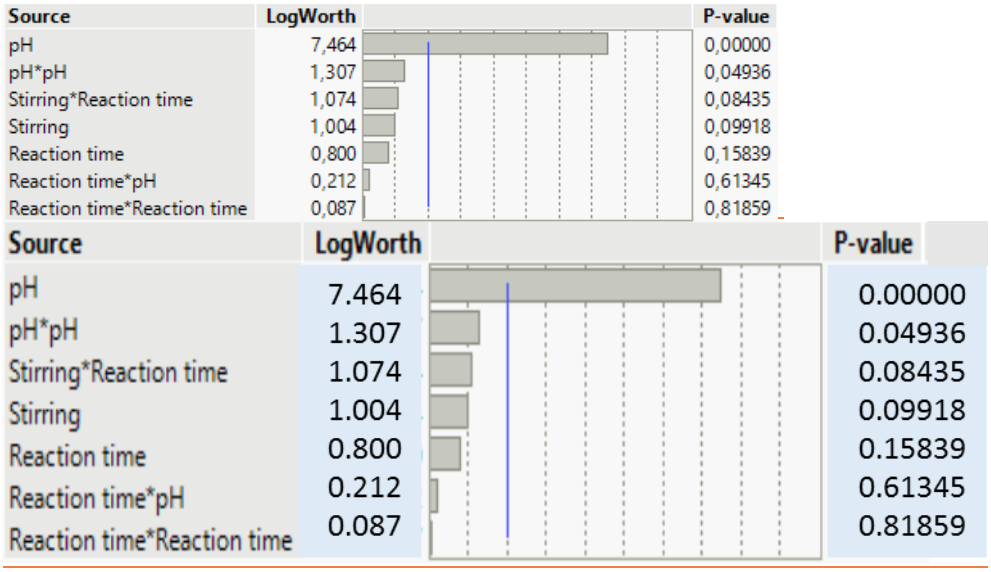

Figure S4. Effects summary. the blue line represents the LogWorth reference equal to 2.

4. Photolysis activity of PNP alone

Figure S5 shows the PNP absorption spectra for PNP respectively: not irradiated, irradiated with UV-A light during 7h non filtered, same but filtered with the same syringe filter as used for the catalysts, and filtered followed by the addition of a drop of HNO_3 (1 mol.L^{-1}).

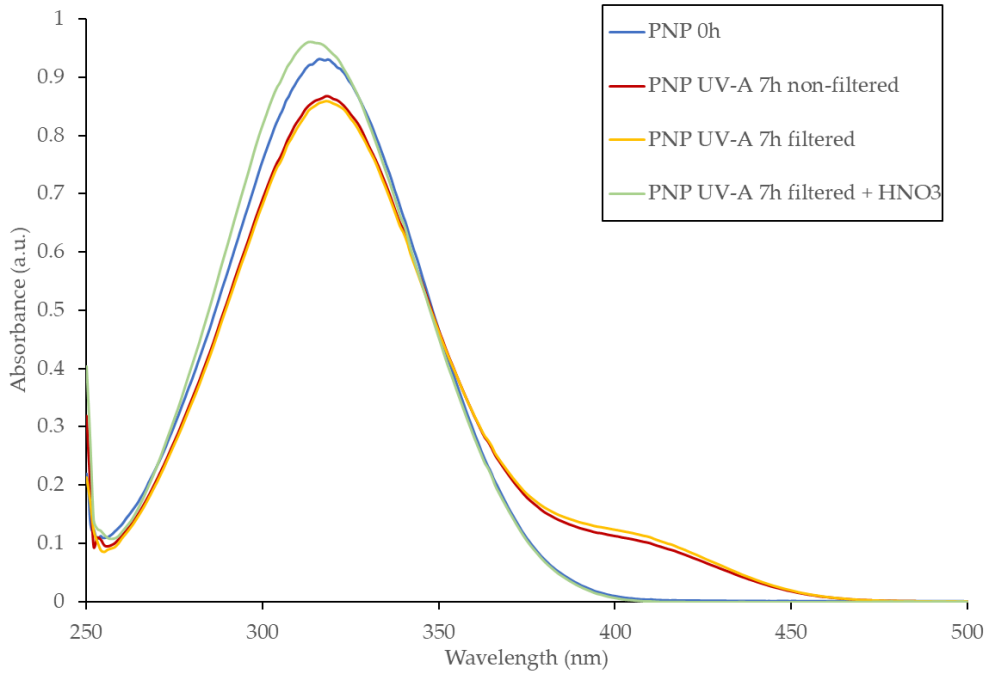

Figure S5. Evolution of the absorbance of PNP between 250 and 500 nm for pure PNP (blue line), after 7h of UV-A irradiation not filtered (red line), filtered (yellow line) and with a drop of HNO_3 (green line) in order to evaluate the effects of these parameters on the PNP absorbance before performing the photocatalytic experiments.

5. XRD pattern after recycling experiments

Figure S6 presents the XRD pattern of Z19 sample after three successive photocatalytic experiments. The crystallinity was constant compared to the initial XRD pattern (Figure 6).

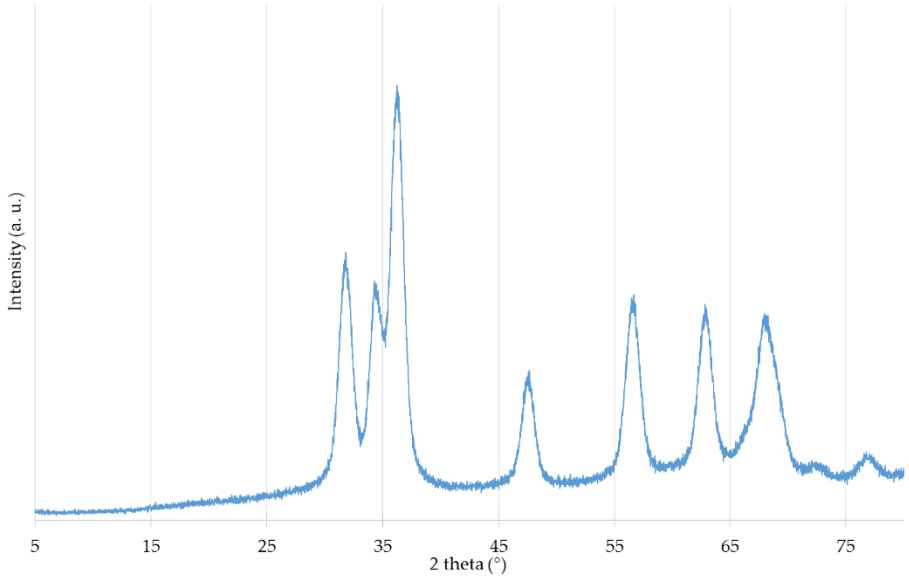

Figure S6. XRD pattern of Z19 sample after three successive photocatalytic experiments in PNP degradation.

References

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