

Piezo-enhanced photocatalytic diclofenac mineralization over ZnO

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Supplementary Material

S1. Materials and methods

During experiments, reagents of analytical grade purity and bi-distilled water passed through a MilliQ apparatus were used, unless differently specified. For HPLC analyses, HPLC-grade acetonitrile and water were purchased from Honeywell.

S1.1 Tested photocatalysts

Different photocatalytic materials were compared. In particular, a commercial ZnO sample from Sigma-Aldrich, labelled as *ZnO_1*, and a lab-made ZnO sample synthesized according to a recently reported ultrasound-assisted procedure [1], named *ZnO_2* in the following. In brief, 100 mL of a 0.2 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution was mixed with 100 mL of 0.5 M KOH solution in a 300 mL beaker. The mixture was sonicated for 30 min in adiabatic conditions using a Thermo-Fischer Q700 ultrasonic processor, working at 20 kHz and equipped with a 13-mm Ti-6Al-4 V horn. The resulting precipitate was collected via centrifugation and washed with water by centrifugation-resuspension cycles until neutral pH was reached. The powder was then dried in oven at 70 °C and calcined in 9 NL/h O_2 flow and at 400 °C, using a 2 °C min^{-1} heating rate and 1 h at stationary temperature. Moreover, a commercial TiO_2 sample (Kronos 1077), named *TiO_{2_ref}* in the following, was adopted as benchmark.

S1.2 Samples characterization

Phase composition was determined by powder X-ray diffraction, using a PANalytical X'Pert PRO diffractometer working with Cu $K\alpha$ radiation and at 40 kV \times 40 mA nominal X-ray power. The average crystallite size was estimated according to the Scherrer equation.

Specific surface area (SSA) values were measured according to the Brunauer-Emmett-Teller (BET) method, by analyzing nitrogen adsorption-desorption isotherms recorded at subcritical conditions on a Coulter SA3100 instrument.

The sample morphology was investigated by scanning electron microscopy (SEM), performed on a Zeiss LEO 1525 field emission microscope, equipped with an Inlens detector, upon metallization with chromium, and by high resolution transmission electron microscopy (HRTEM), performed on a Jeol JEM 3010-UHR instrument (LaB₆ filament, acceleration voltage 300 kV). Before TEM analysis, samples were dry dispersed onto Cu grids coated with lacey carbon film and images were digitally acquired by means of a Gatan Ultrascan 1000 camera.

The band gap values of the samples were determined by analyzing diffuse reflectance spectra (DRS), acquired on a UV-vis spectrophotometer (UV-2600 Shimadzu) equipped with an integrating sphere.

S1.3 Degradation test setup and procedure

Three different types of tests were performed: sonocatalytic tests (indicated with the suffix *_US*) were performed using sonication in the presence of the photocatalyst without light irradiation; photocatalytic tests involved UV light irradiation in the presence of the photocatalyst (labelled with a suffix *_UV*); sonophotocatalytic degradation tests (named with the suffix *_UV-US*) were instead performed using simultaneously sonication and light irradiation in the presence of the photocatalyst.

The experiments were conducted in either ultrapure water or simulated drinking water, prepared according to Annex B2 of the second protocol of the French Norm NF P41-650 regarding the specification for water filter pitchers (Tab.S1).

Table S1: Electrolyte contents of the simulated drinking water.

species	concentration (mg L ⁻¹)
Ca ²⁺	44.5
Na ⁺	45.7
Mg ²⁺	9.3
Cl ⁻	78.7
SO ₄ ²⁻	36.5
HCO ₃ ²⁻	121.2

Dark adsorption experiments were also carried out for all the photocatalysts: adsorption-desorption equilibrium was reached after 30 min, resulting in 12.2% and 14.1% DCF adsorption in ultrapure water for ZnO_1 and ZnO_2, respectively; a slightly lower adsorption was observed in simulated tap water (10.7 and 9.9% for ZnO_1 and ZnO_2, respectively).

Degradation experiments were performed using the batch configuration reported in Fig. S1. In a typical experiment, 600 mL of a 25 ppm sodium diclofenac solution in either ultrapure or simulated drinking water was treated. Tests were carried out at spontaneous pH, which depends on the type of water used (5.5 for the ultrapure water and 7.5 for the simulated drinking water). In all tests, a 0.1 g L⁻¹ photocatalyst was added. The experiments were performed under constant magnetic stirring to improve the mixing and the catalyst suspension. In tests under light irradiation, the light source was a 500 W halide lamp emitting in the UV-A (320–400 nm) with an effective power density of irradiation of 37 W m⁻². A 20 kHz ultrasonic processor (VibraCell VCX 500, Sonics and Materials) was located on the top of the reactor and the US probe

(136 mm) was immersed into the sodium diclofenac solution. The 13 mm tip of the US-probe was composed by a titanium alloy (Ti-6Al-4V). A pulsed sonication was adopted (5 s on/5 s off). The ultrasound output power, as determined by calorimetric calibration, was 23 W. Sodium diclofenac degradation was monitored for 6 h, withdrawing aliquots every 15 min in the first hour and every 30 min in the subsequent five hours. Samples were filtered with 0.22 μm nylon filters and were analysed using high performance liquid chromatography (HPLC by Agilent 1100 Series) equipped with a C18 Supelco column (25 cm x 4 mm, 5 μm), a 20 μL autosampler and a UV detector. The chromatographic separation of the mixture was accomplished with 1 mL min^{-1} eluent flow rate by injecting 20 μL samples. The eluent used was composed by 60 % acetonitrile, 40 % water and 0.1 % formic acid. The mineralisation of the mixture was determined by a total organic carbon (TOC) analyser (TOC-L CSH/CSN, Shimadzu) in the case of ultrapure water tests. The estimated standard deviation of DCF conversion and mineralization degree, estimated by repeated tests, were 1.4% and 1%, respectively.

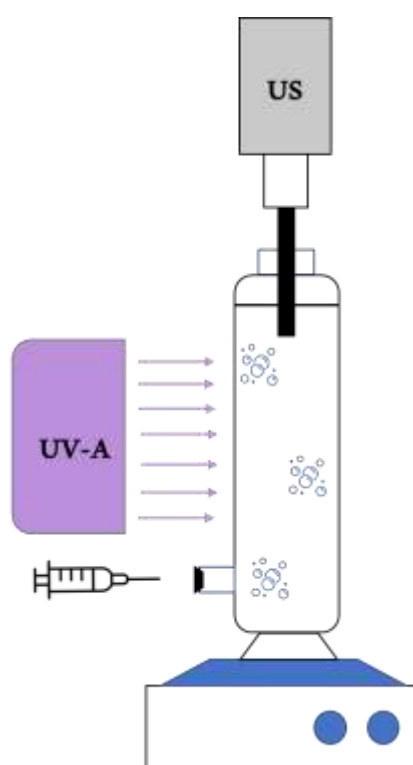


Figure S1: Experimental setup for the degradation of diclofenac.

UPLC-MS analyses were carried out in order to monitor and identify the transformation products (TPs) during degradation tests. For this scope, a LCQ Fleet ion trap mass spectrometer equipped with a UPLC UltiMate 3000 system containing a UV detector was used. A Zorbax RX-C18 (4.6x150 mm-3.5 μm) was employed for the chromatographic separation at a flow rate of 1 mL/min and at a temperature of 30°C. The mobile phase was solvent A (0.1% formic acid in water) 40% and solvent B (0.1% formic acid in acetonitrile) 60%. The injection volume was 20 μL and the detection wavelength was 278 nm. The mass spectrometer was operated with electrospray ionization (ESI) in both positive and negative ion mode. The MS interface conditions for sample acquisition were the following: heater temperature 80 °C, sheath gas flow rate (arb) 20, auxiliary gas flow rate (arb) 10, sweep gas flow rate (arb) 0, spray voltage negative mode 4.50 kV, capillary temperature 275 °C, capillary voltage negative mode -5 V, tube lens negative mode -85.60 V, spray voltage positive mode 4.00 kV, capillary voltage positive mode 15.00 V, tube lens positive mode 65.00

V, m/z range 50–500. For the analyses aliquots of each solution were withdrawn at time intervals, filtered (nylon 0.22 μm) and analysed as described.

S2. Photocatalysts characterization

Table S2: Physicochemical parameters of the investigated photocatalysts.

sample	crystal phase	crystallite size (nm)	SSA (m^2g^{-1})	band gap (eV)
ZnO_1	wurtzite	43	10.8	3.25
ZnO_2	wurtzite	20	12.0	3.20
TiO₂_ref	anatase	130	11.0	3.15

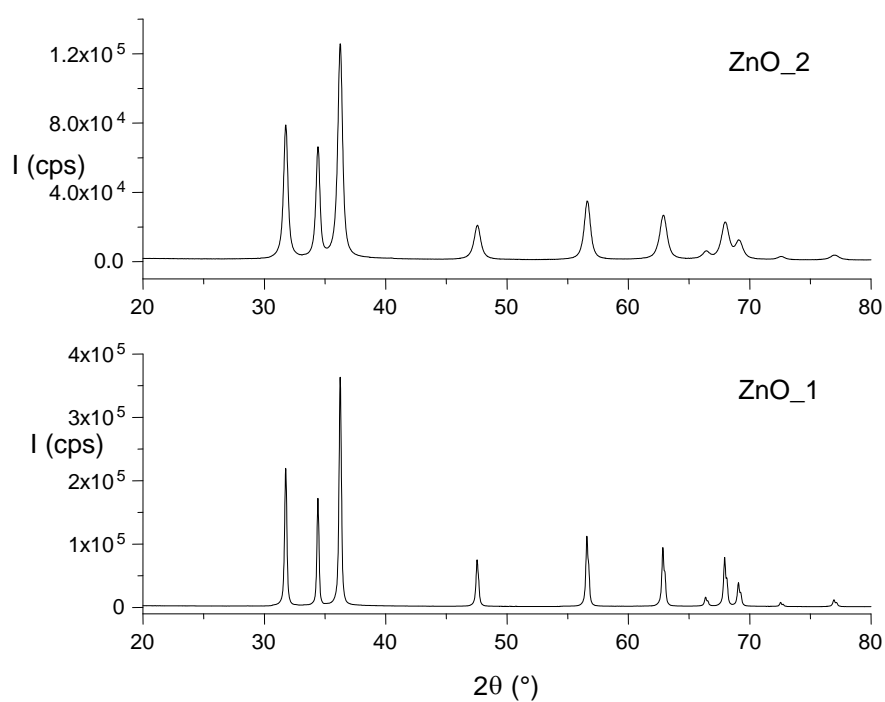


Figure S2: Powder XRD patterns of ZnO₁ and ZnO₂.

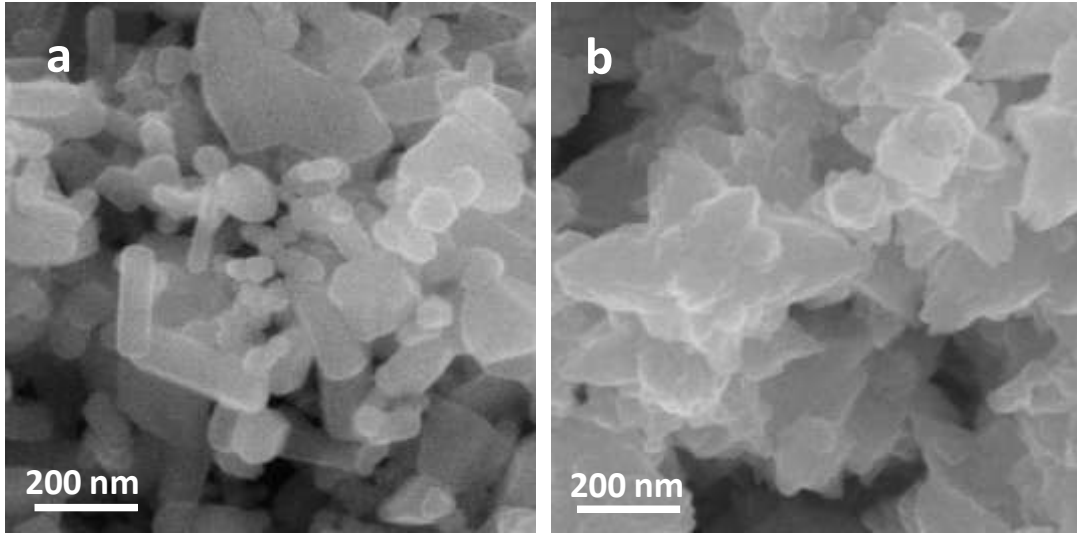


Figure S3: SEM images of (a) ZnO_1 and (b) ZnO_2.

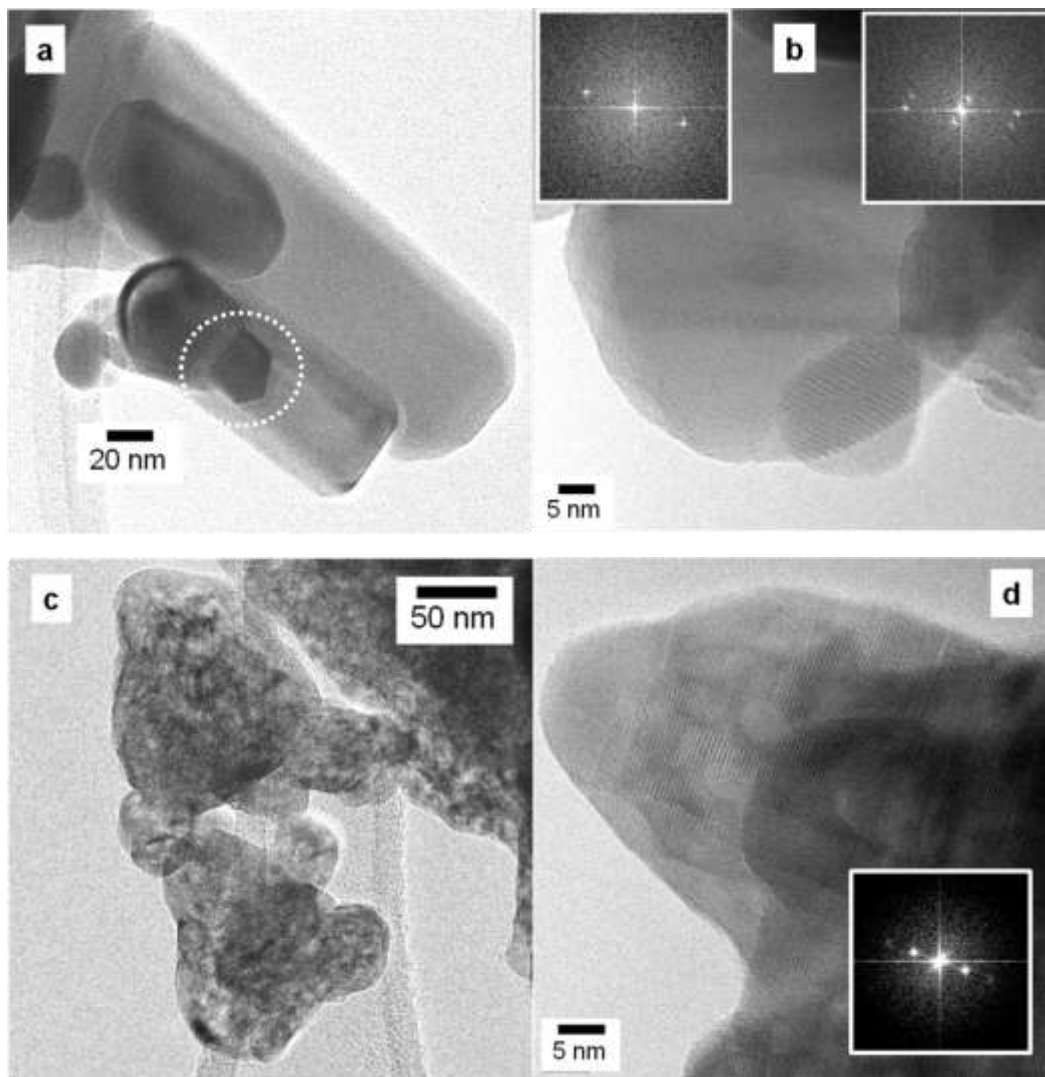


Figura S4: HRTEM images of ZnO_1 (a, b) and ZnO_2 (c, d). Inset: Fast Fourier Transform (FFT) elaboration of the direct images, highlighting the interplanar distances. In the case of ZnO_1, the most frequently evidenced family of planes belong to (101) planes of zincite (inter-planar distance = 0.24(7) nm) as from ICDD 36-1451. On the contrary, the pattern observed for ZnO_2 belongs only to Moiré's or thickness fringes.

S5. Degradation tests

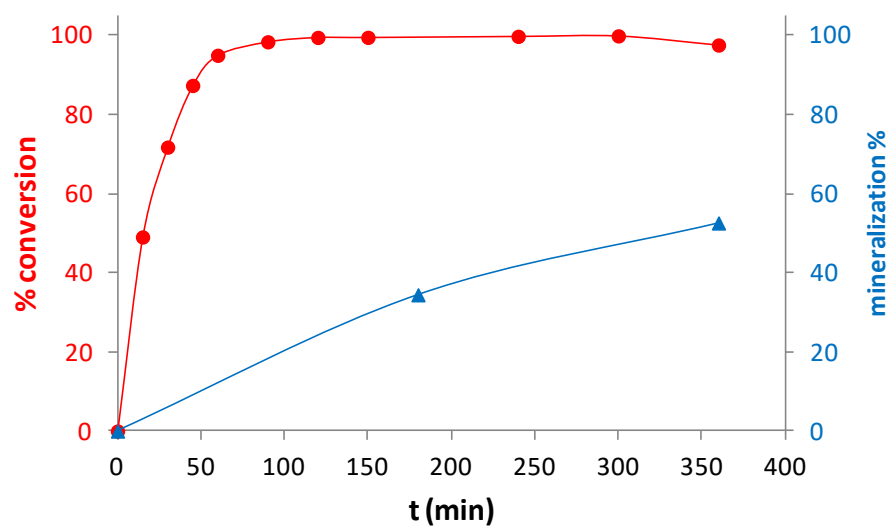


Figure S5 – DCF disappearance and mineralization degree of TiO_2_{ref} during sonophotocatalytic tests in ultrapure water.

S6. Time profile of TPs

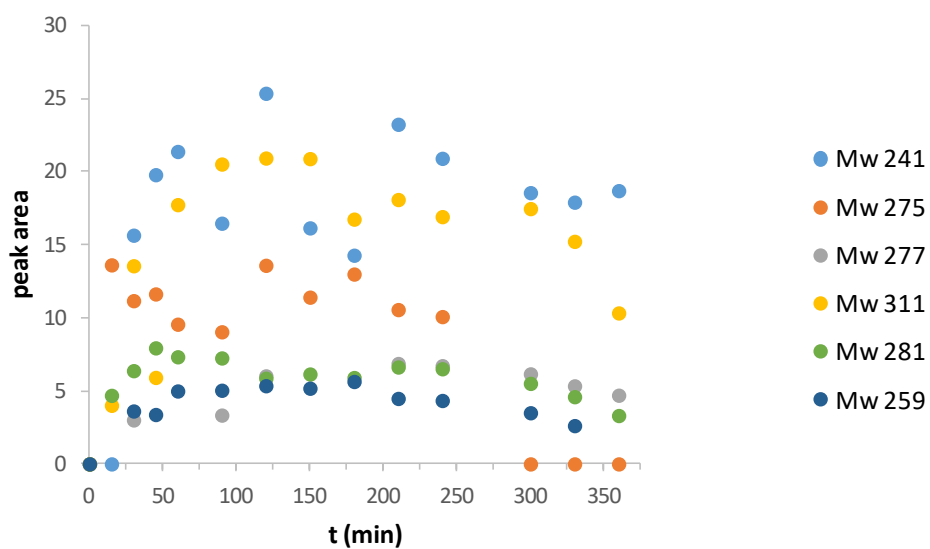


Figure S6: Time profiles of TPs (other Mw 311 reported in Fig. 3) produced in ultrapure water during sonophotocatalytic tests using ZnO_1

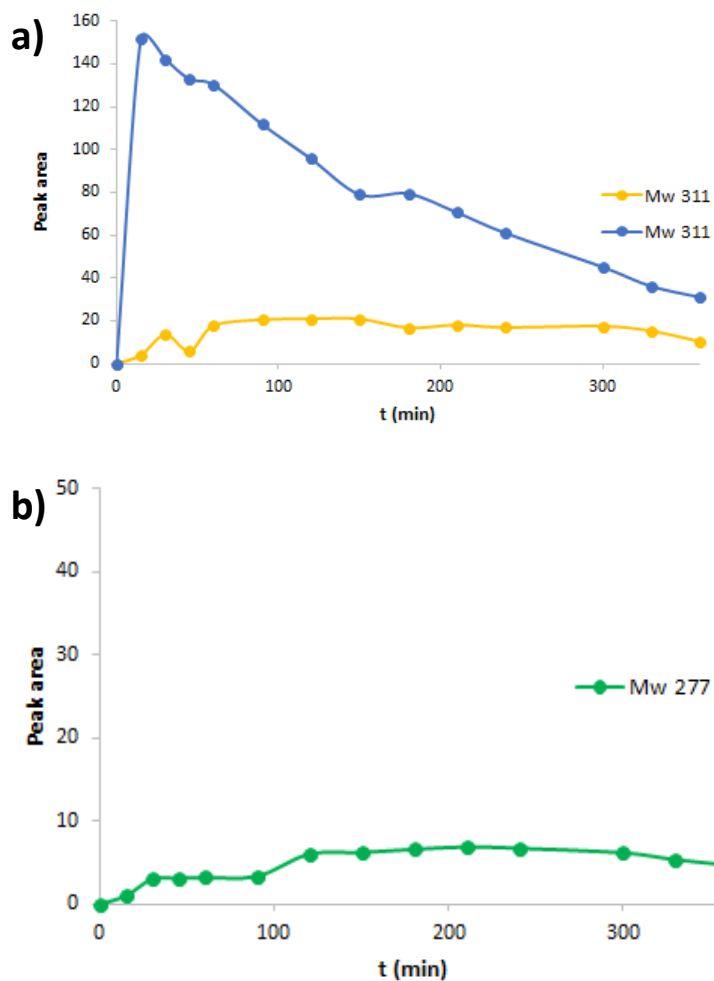


Figure S7: Time profiles of (a) Mw 311 (isomers) and (c) Mw 277 produced in ultrapure water during the sonophotocatalytic tests using ZnO₁

References

- [1] D. Meroni, C. Gasparini, A. Di Michele, S. Ardizzone, and C. L. Bianchi, Ultrasound-assisted synthesis of ZnO photocatalysts for gas phase pollutant remediation: Role of the synthetic parameters and of promotion with WO₃, *Ultrason. Sonochem.*, 66 (2020)