Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPLEMENTARY INFORMATION

When sonochemistry meets heterogeneous photocatalysis: designing a Sonophotoreactor towards sustainable selective oxidation

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EXPERIMENTAL

1. Materials and Chemicals

The studied commercial metal oxides nanoparticles were: TiO_2 (P25 Evonik Degussa), Fe(III) oxide nanopowder (<50 nm particle size, Sigma Aldrich), Co(II,III) oxide (<50 nm particle size, Sigma Aldrich), and ZnO (<100 nm particle size, Sigma Aldrich). The rest of chemicals used as received: HPLC grade of Acetonitrile (AcN), benzyl alcohol (BnOH), benzyl aldehyde (PhCHO), luminol (3-aminophthalhydrazide, Acros, 98%), NaOH (Stanlab). MiliQ water was used in all cases.

2. Adsorption experiments

For the interaction/adsorption in the dark experiments (3 hours of interaction under 600 rpm stirring) were used either 20 mg or 100 mg of each material at 20 mL of 1M BnOH. The results are expressed as % of removed BnOH, neither adsorbed nor oxidized/degraded. The adsorbed amount is also expressed as mg of BnOH retained per gram of material. The obtained results are collected in Table s1. The removal of BnOH and as a result the decrement of its concentration can be due to adsorption phenomena and/or conversion to other products. The HPLC analysis revealed that the BnOH removal was 3.2, 1.4, 4.0, and 0.1 % for TiO_2, Fe_2O_3, Co_xO_y, and ZnO, respectively. The solitary detected byproduct was PhCHO and only in the case of Co_xO_y, and in this case the 92 % of the removed BnOH was due to oxidation to aldehyde. This fact showed that CoO possess a limited capability to oxidize BnOH even in dark condition, while all the samples have a minimal BnOH adsorption ability. It should be pointed out that analogues tests were performed with ultrasound irradiation instead of magnetically stirring, and the results were found the same.

Table s1. Results from the interaction/adsorption of the material under dark conditions.

material	BnOH concentration decrease (%)	PhCHO selectivity (%)	BnOH adsorption capacity (mg/g)
TiO_2	3.2	0	3.2
Fe_2O_3	1.4	0	1.4
Co_3O_4	4.0	92	0.3
ZnO	0.0	0	0.0

3. Ultrasound source and characterizations

A Qsonica sonicators, cup horn model (20 KHz) was utilized for the experimental setup. A schematic illustration of the system can be seen in the main manuscript, while a photo of the entire setup in Figure s1.

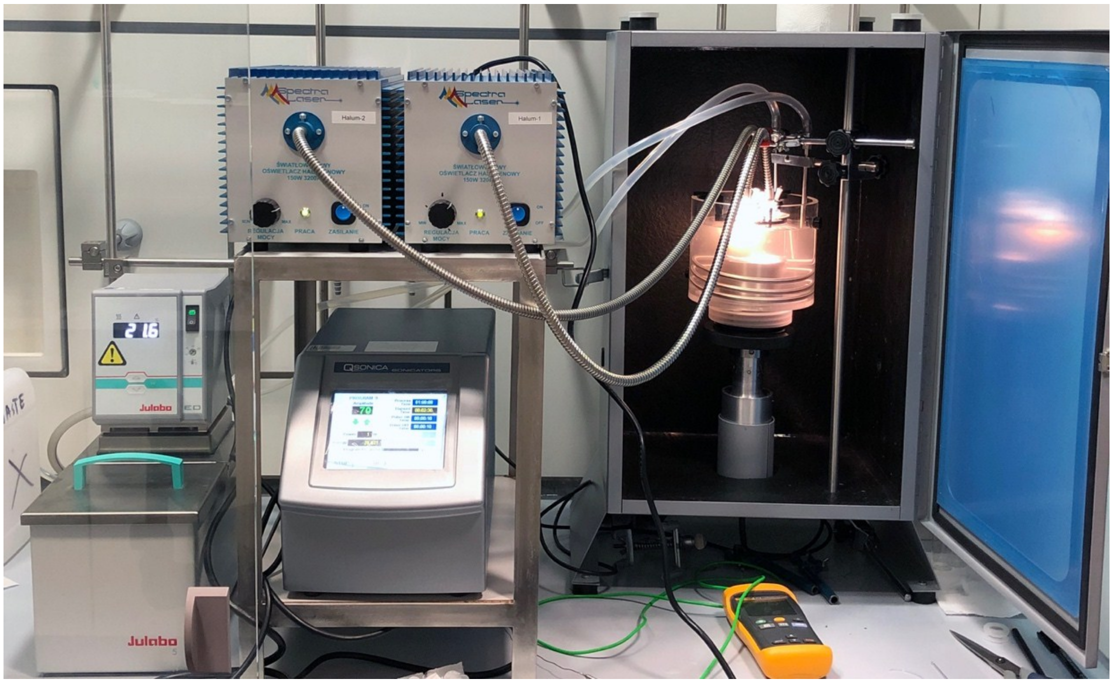

Figure s1. The experimental setup of the SonoPhotoReactor.

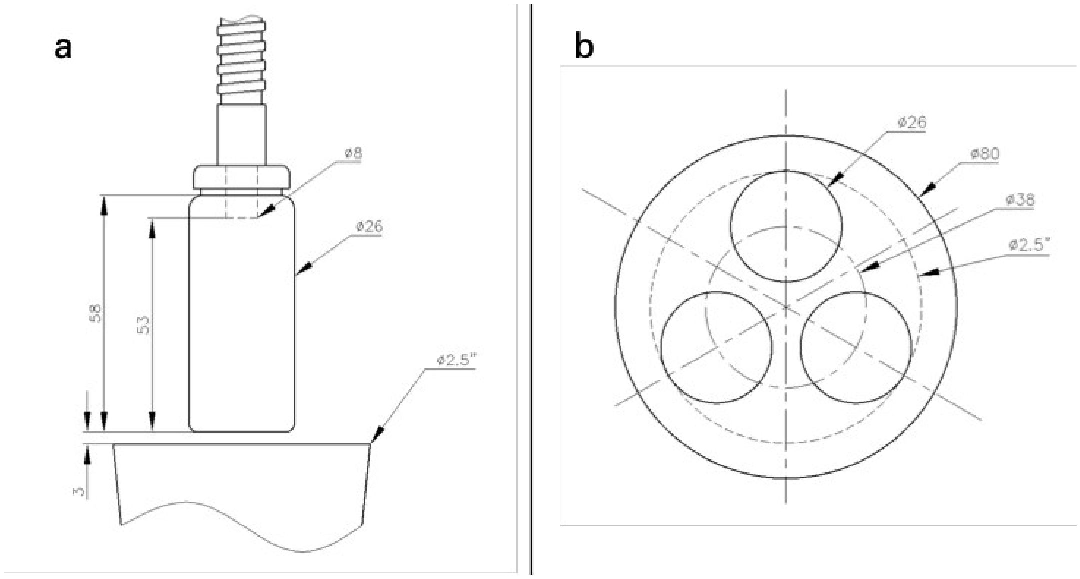

Figure s2. Technical drawings of the sonophoto-reaction vessel (a) and for the home-made holder for the vessels (b).

3.1. Ultrasound irradiation protocol. Pulse mode: 10 sec ON, 10 sec OFF for up to 90 min of US irradiation (3 h in total). Four different amplitudes were studied: 15, 30, 50, and 70 %. For the continuous irradiation, the irradiation of ultrasound was occurred for 3 h at an amplitude of 30 %.

3.2. Power of US. The calculated energies per surface and per volume of the solvent are collected in Table s2.

Table s2. Details regarding the ultrasound power inside the cup horn water bath.

Amplitude (%)	Power (W)	Power density per surface (W/cm^2)	Power density per volume above the surface (W/cm^3)
15	49 ± 3	1.6 ± 0.1	0.09 ± 0.1
30	86 ± 6	2.7 ± 0.2	0.16 ± 0.1
50	185 ± 10	5.7 ± 0.3	0.33 ± 0.2
70	280 ± 12	8.8 ± 0.4	0.52 ± 0.2

3.3. Mixing extent. The mass transfer capability upon ultrasound irradiation for different amount of catalyst can be seen in Figure s2.

Figure s3. Captures of the reaction vessel after ultrasound irradiation with 30 % amplitude and different amount of catalyst.

3.4. Cooling system details. A homemade stainless-steel spiral cooling system consisting of three windings was used inside the cup horn water bath. The internal diameter of the winding is 107 mm and the height 32 mm. The diameter of the tube is 6.4 mm. The used water circulator was an open-bath obtained by Julabo company. The total volume of water was around 4.5 L and the fixed flow rate 15 L/min.

3.5. Temperature evolution monitoring. The temperature evolution of the system upon ultrasound and/or light irradiation was studied by temperature monitoring at five different spots of the experimental setup. Four of them can be seen in Figure s4. The first two locations were inside the cup horn bath; the one above and in the middle of the horn's surface (Top) and the second under the upper surface of the horn, between the side horn's surface and the cooling spiral (Bot). The other two locations were at the open-bath cooling system; the first inside the bath (CB), while the second was the indication of the internal thermometer (CBi). At the end of each reaction and after sampling, the temperature inside the reaction vessel was also recorded.

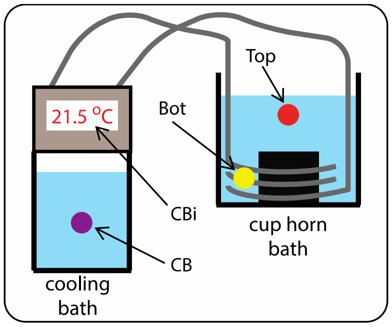

Figure s4. The different spots for monitoring the temperature evolution.

In all cases, the temperature at the cooling bath at both spots was remained stable. Regarding the two spots inside the cup-horn bath, the temperature above the surface of horn was around 0.5 °C higher than the BOT, due to low mixing extend/low mass transfer inside the water bath. Since the most important area of monitoring the temperature was above the horn where the reactions vessels were placed, the monitoring of the temperature at this area and inside the vials provides enough evidence. The temperature evolution inside the bath (Top) under different ultrasound amplitudes (15, 30, 50, and 70 %) and reaction-cooling temperature (21.5 and 26.5 °C) are collected in Figure s5.

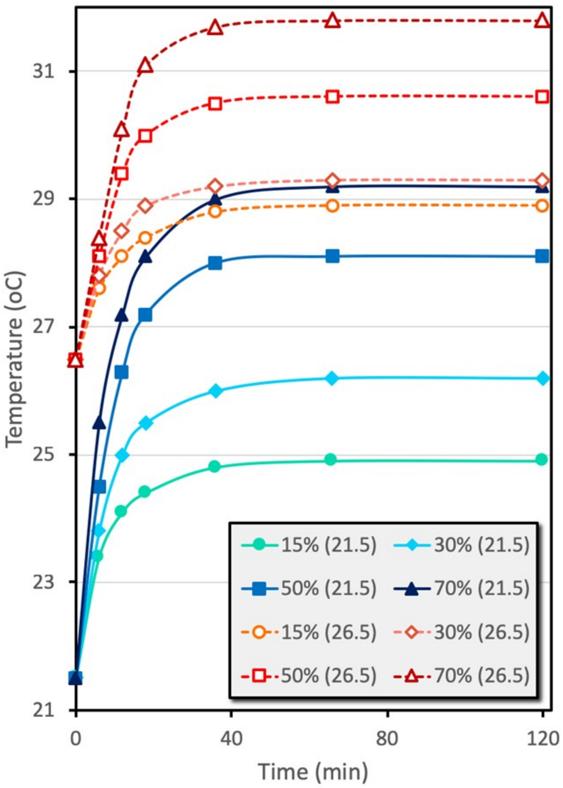

Figure s5. The temperature evolution inside the bath (Top) under different ultrasound amplitudes (15, 30, 50, and 70 %) and reaction-cooling temperature (21.5 and 26.5 ^{o}C).

Since the most important area of monitoring the temperature was above the horn where the reactions vessels were placed, the monitoring of the temperature was focused at this point. The experiments were performed after one hour of ultrasound irradiation of the bath in order to stabilize the temperature of the cup horn water bath. The temperature inside the reaction vessels during the experiments were higher by 0.1-0.2 ^{o}C, so we considered that the temperature above the cup horn is equal to the one inside the reaction vessel.

4. Calorimetry test

We performed calorimetry tests in order to determine the actual ultrasonic power entered inside the cup-horn water bath, as well as inside the reaction vessel (15 mL water or acetonitrile). The temperature against time was recorded by a data acquisition system (KEITHLEY, DAQ6510) using a J-type thermocouple. The entered US power was calculated by the equation [9]:

$$\text{power} = (dT/dt) * C_p * M$$

where M is the mass of the bath (1184 g) or of the reaction vessel (14.4 g water or 11.5 g acetonitrile), C_p the heat capacity at 25 ^{o}C (water = 4.2 J g^{-1} K^{-1}, acetonitrile = 2.2 J g^{-1} K^{-1}). The calorimetric tests were carried out at two different amplitudes (30 and 70 %). The temperature evolution during the ultrasonication for two amplitudes (30 and 70 %) can be seen in the plots in Figure s6.

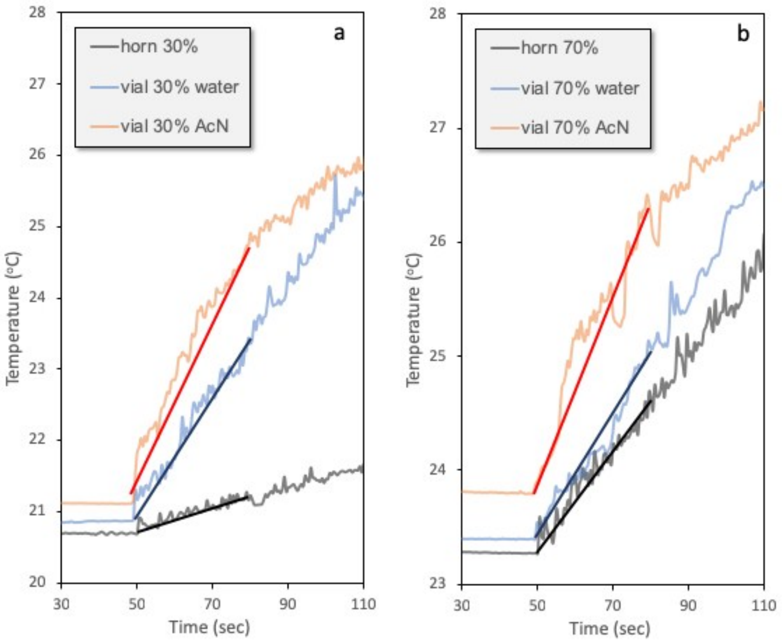

Figure s6. The temperature evolution during the ultrasonication for two amplitudes (30 and 70 %) above the cup horn and inside the reaction vials, filled with ~15 mL of water or acetonitrile.

5. Determination of sonochemically active zones by luminesce tests

A basic luminol (3-aminophthalhydrazide) aqueous solution (10^{-3} M or 0.1 g/L luminol and 10^{-2} M or 1 g/L NaOH) was used for the sonochemiluminescence (SCL) in the dark experiments and at a temperature of around 28 ^{o}C, for the visualization of the sonoreactor's ultrasonic active zones. The SCL images were captured by an exposure-controlled digital camera and the pictures were constructed by thresholding to highlight the most intense regions. The exposure time was 40 seconds.

6. Light source wavelengths and power

As the source of the solar light (SL) driven experiments was served a 150W 3200K Fiber Optic Illuminator from Spectra Laser. The undesired produced from the halogen heat was eliminated by a dichroic filter (Hot Mirror). The spectrum of the light ranged from 400 nm to 1300 nm, but the predominant energy was in the visible range. A flexible fiber bundle (1 cm in diameter and 95 cm in length) was used for the light irradiation of the reactors, as can be seen in the schematic Illustration (Figure 1) and on the photo (Figure s1). Based on the manufacture, the light power behind the optical fiber is about 1.2W, while the maximum intensity is ~430,000 lux. The intensity of light was regulated by a potentiometer. A UV filter was also used in order to cut the ultraviolent and infrared region of the solar light simulator, and this light source is referred to as SL>400. Three other light LED-based sources were used in order to irradiate the reaction vessel with a light beam of a specific wavelength (Omikron laserage, LEDMODx.450.V2, Rodgau, Germany). The three chosen wavelengths were 365, 455, and 510 nm. The emission spectra of all the utilized sources of light are collected in Figure 4, while photos of the reaction vessel under different light source irradiation are shown in Figure s7.

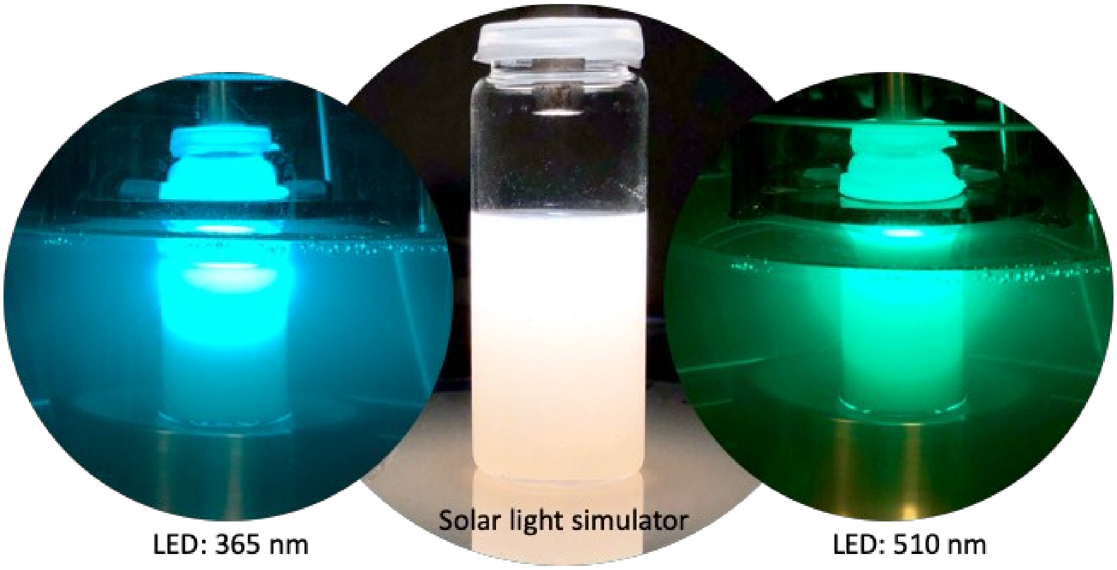

Figure s7. Photos of the reaction vessel under different light irradiation (taken by iPhone X).

The power of the irradiated light was determined by a Photo-Radiometer (Delta OHM Model HD2302.0 LightMeter) using two different probes at a distance of 2 cm from the light source, one for the UV range (Delta OHM, LP 471 UVA Probe, spectral range: 315-400 nm) and one for Vis range (Delta OHM, LP 471 RAD Probe, spectral range: 400-1050 nm). The measured powers expressed in W/m^2 are collected in Table s3. The solar light simulator irradiates a minimal amount of light in ultraviolent range (~ 0.12 % of the total beam power), while the use of UV-IR filter cuts totally the ultraviolent and infrared regions of irradiation.

Table s3. The measured power of light irradiation at the ultraviolent and visible range.

Light source	Power in UV region (W/m^2)	Power in visible region (W/m^2)
SL	4.4	3623
SL>400	0.2	3574
365 nm	95.0	0
455 nm	0.0	361
510 nm	0.0	328

7. Photocatalytic experiments

The photoreactors were filled with 15 mL of BnOH solution (1 mM) and 15 mg of the catalyst (1 g/L) and left under continuous stirring (600 rpm) for 3 hours, for a direct comparison with the sonophotocatalytic results. The reactors and the appliance of the light source was the same as in the case of sono- and sonophoto-catalytic experiments. Filtrated solution samples were analyzed after specific time intervals. Tests with hermetically sealed vials and sampling only after 6 hours and 40 min were performed. The headspace of these tests was analyzed by GC. All the experiments were performed more than three times and the standard deviation/error bars were adapted to the results and the Figures.

8. Sono- and Sonophoto-catalytic experiments

A homemade Sonophotoreactor was designed, constructed, and used for these series of experiments as can be seen in the main manuscript. The temperature control of the cup horn bath was achieved by an open-bath water circulator obtained by Julabo company was used for the water circulation at a specific temperature, as described above. All the experiments were performed more than three times and the standard deviation/error bars were adapted to the results and the Figures.

9. Chromatographic analytical methods

Products analysis

An HPLC (Acquity Arc Waters) equipped with a 2998 *Photodiode Array detector* using a mixture of Acetonitrile and Mili-Q water as mobile phase was used for the analysis of the filtrated solutions. BnOH and PhCHO were well separated by a C18 Thermo scientific column (250 x 4.6 mm). The compounds were detected by a UV detector at 270 nm. The mobile phase was composed of acetonitrile and Mili-Q water with 55:45 v/v ratio. The flow rate was set at 1.0 mL/min and the temperature of column oven was kept at 25 ^{O}C. The concentrations of BnOH and PhCHO were determined based on the HPLC chromatograms (two well separated peaks for BnOH and PhCHO at retention time of 2.69 and 3.65 min, respectively) and the calibration curves.

In order to double-check if the sonophotocatalysis tests led to the formation of products non-detectable by HPLC, gas chromatography was also performed by a GC-2010 Plus (Shimadzu). In no case additional compounds were detected using GC method.

10. Calculation of BnOH conversion - products yield and selectivity - carbon balance

The initial concentration of BnOH ($C_{\mathrm{BnOH},in}$), the final concentration of BnOH ($C_{\mathrm{BnOH},f}$), the concentration of PhCHO (C_{PhCHO}) and the concentration of benzoic acid PhCOOH (C_{PhCOOH}) were determined by the HPLC analyses. BnOH conversion (%), PhCHO Yield (%), PhCOOH Yield (%), PhCHO selectivity (%), and aromatic carbon balance (%) were estimated by using the following equations:

$$\text{BnOH conversion (\%)} = 100 * (C_{BnOH,in} - C_{BnOH,f}) / C_{BnOH,in}$$

$$\text{PhCHO Selectivity (\%)} = 100 * C_{PhCHO} / (C_{BnOH,in} - C_{BnOH,f})$$

$$\text{PhCHO Yield (\%)} = 100 * C_{PhCHO} / C_{BnOH,in}$$

$$\text{PhCOOH Yield (\%)} = 100 * C_{PhCOOH} / C_{BnOH,in}$$

$$\text{Aromatic Carbon Balance (\%)} = 100 * (C_{BnOH,f} + C_{PhCHO} + C_{PhCOOH}) / C_{BnOH,in}$$

11. Air-purging Sonophoto-catalytic experiments

The reaction vessel was purged with air, starting 10 min prior the start of irradiation by UV light and ultrasound. The air purging (flow rate of ~0.2 mL/min) was continuous during the 3 hours of performing the sonophotocatalytic experiments. The presented results are the averages of the three series of experiments (error derivation less than 3%).

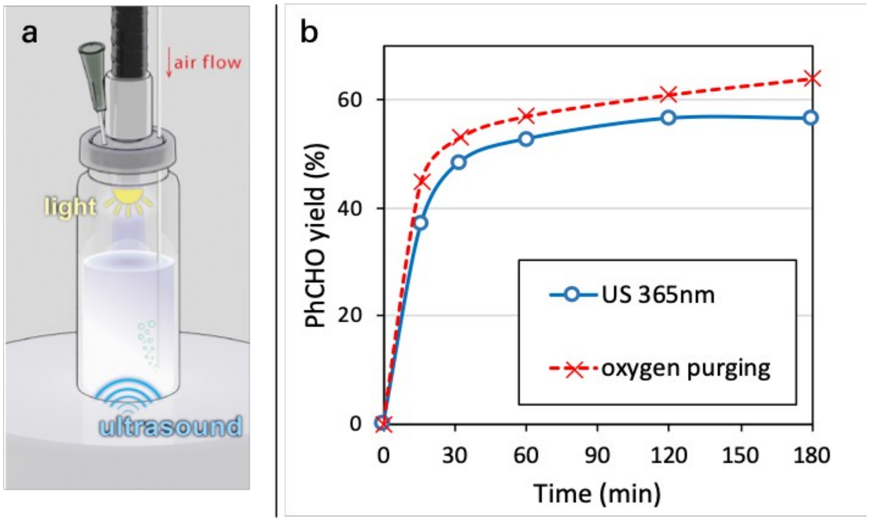

Figure s8. Schematic illustrator of the way the suspension was purged with air (a) and the yield of benzyl aldehyde formation under ultrasound irradiation (pulse mode, 1 g/L catalyst, 1 mM BnOH, in acetonitrile at 21.6 ^{o}C) under UV light exposure with (~0.2 mL/min) and without air purging (b).

12. Leaching determination - Catalyst stability

After the completion of the reaction, the obtain solution after the filtration of the suspension was analyzed using an energy dispersive X-ray fluorescence (EDXRF) spectrometer (Mini- Pal 4, PANalytical &Co.) with Rh tube and silicon drift detector. The spectra were gathered in air atmosphere (without a filter), at a tube voltage of 30 kV. The acquisition time was 30 s and the current of the tube up to 50 μA.

The stability of the catalysts (TiO_2) as a result of leaching after 3 hours of exposure to the highest used amplitude of 70 % and light was evaluated by analysis of the filtrate of the suspension by XRF. The absence of titanium traces at the XRF spectrum (Figure s8) reveals that the catalyst is stable even after the exposure to the harshest experimental protocol of US irradiation.

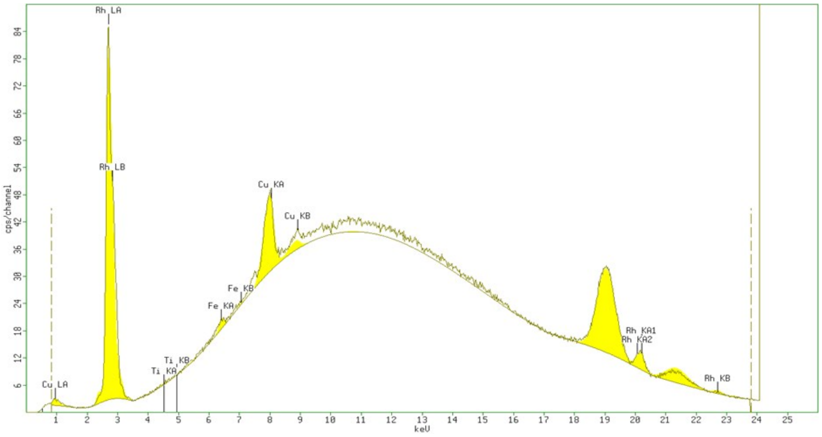

Figure s9. The XRF spectrum of the filtrate after 3 hours irradiation by ultrasounds (70 %) and light.