

# Supporting Information for Mechanochemically designed bismuth-based halide perovskites for efficient photocatalytic oxidation of vanillyl alcohol

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## Section 1. Materials Synthesis

### 1.1. Starting Materials

Reagents were received and used without further purification: CsBr (cesium bromide, Alfa Aesar, 99.9 %), AgBr (silver bromide, Alfa Aesar, 99.5 %), BiBr<sub>3</sub> (bismuth tribromide, Alfa Aesar, 99 %).

### 1.2. Mechanochemical synthesis

Mechanochemical milling process was carried out into a Retsch Emax high-energy ball mill. Precursor powders were placed into two reaction chambers of 125mL of capacity along with nine stainless steel spheres. Perovskite powders were obtained by grinding the starting materials for 30 min at 900 rpm, with intervals of 10 min and pauses of 2 min in between.

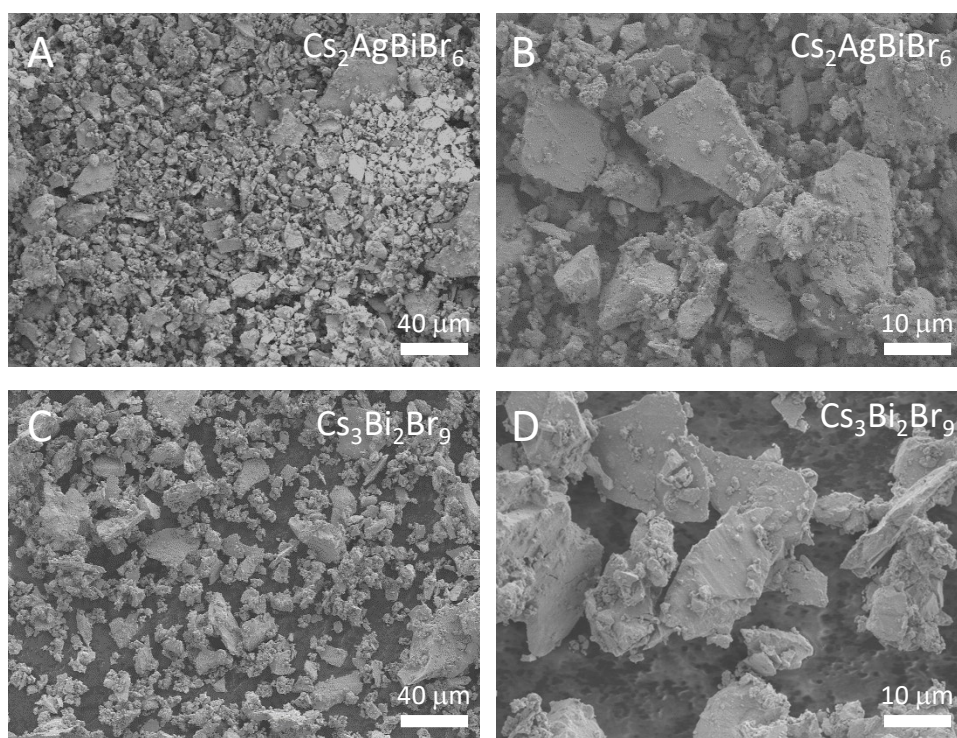


**Figure S1.** As-synthesized powders via ball milling of Cs<sub>2</sub>AgBiBr<sub>6</sub> (left) and Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> (right) perovskites.

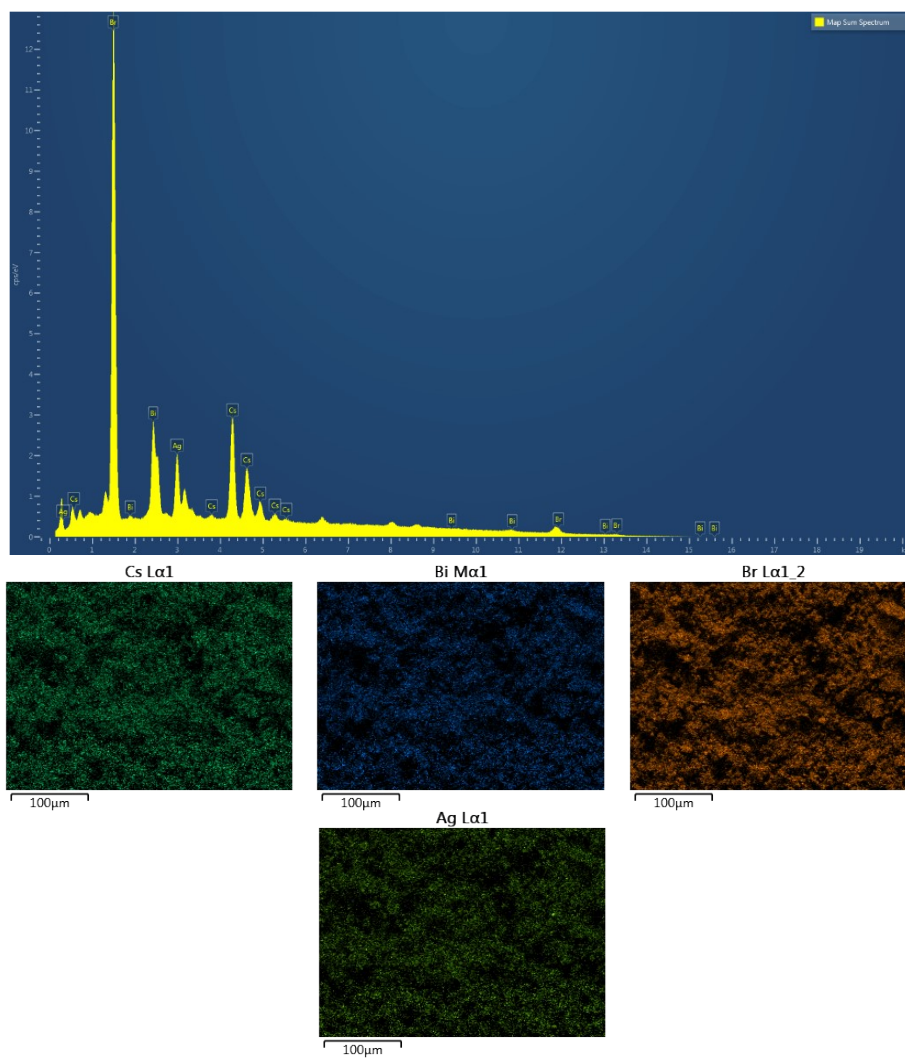
## Section 2. Materials Characterization

### 2.1. SEM-EDX measurements

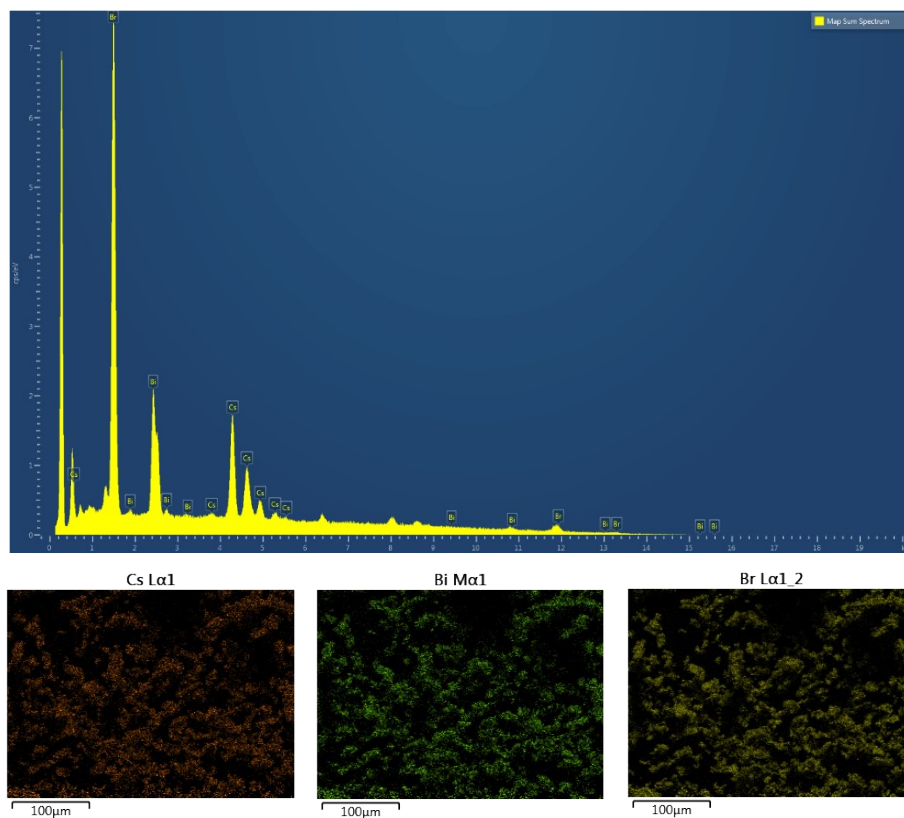
SEM and EDX images were acquired in a JEOL-SEM JSM-7800 microscope working at 2 and 15 kV, respectively, with a work distance (WD) of 10 mm.



**Figure S2.** Top-surface scanning electron microscopy (SEM) images of the Cs<sub>2</sub>AgBiBr<sub>6</sub> (A and B) and Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> (C and D) photocatalysts. Scale bar, 40 (A and C) and 10 (B and D) μm.



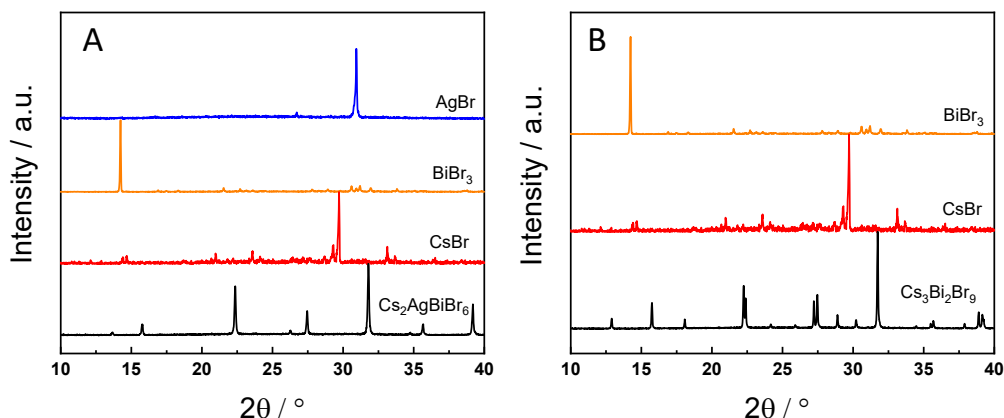
**Figure S3.** Energy dispersive X-ray (EDX) profile analysis (upper panel) and elemental mapping (lower panel) of the  $\text{Cs}_2\text{AgBiBr}_6$  photocatalyst.



**Figure S4.** Energy dispersive X-ray (EDX) profile analysis (upper panel) and elemental mapping (lower panel) of the  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  photocatalyst.

## 2.2. X-Ray Diffraction Spectroscopy (XRD)

X-ray diffraction patterns of both materials were collected on a Bruker D8 Discover diffractometer operating at 40 kV and 40 mA and using Cu-K $\alpha$  radiation (1.54059 Å). The measurements were recorded at room temperature and done from 10 to 40° Bragg angles.



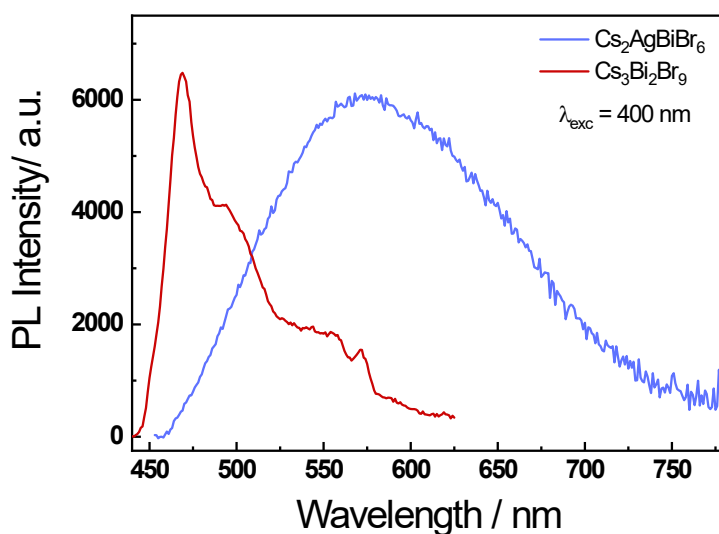
**Figure S5.** Powder X-ray diffraction (XRD) measurements of the powders obtained after ball milling when synthesizing the Cs<sub>2</sub>AgBiBr<sub>6</sub> (A) and Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> (B) Bi-based perovskites. The experimental XRD diffractograms of all precursors are also shown for comparison.

## 2.3. Diffuse Reflectance UV/Vis Spectroscopy

Diffuse-reflectance measurements were performed on the UV-Vis Lambda 365 spectrophotometer, working in a range from 400 to 650 nm. Spectra were expressed using the Kubelka Munk's equation.

## 2.4. Steady-State and Time-Resolved Photoluminescence

All experiments were carried out with an FLS980 (Edinburgh Instruments) photoluminescence spectrometer. Steady-state fluorescence measurements were performed by using the R298P photomultiplier detector and the 450 W Xe1 xenon arc lamp. To acquire time-resolved photoluminescence data a R2658P photomultiplier was used as detector. Samples in all experiments were excited at 406.4 nm with an 86.8 ps pulse width diode laser and applying the time-correlated single photon counting (TCSPC) technique.



**Figure S6.** Photoluminescence spectra of Cs<sub>2</sub>AgBiBr<sub>6</sub> (blue line) and Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> (red line) photocatalysts.  $\lambda_{\text{exc}} = 400 \text{ nm}$ .

### Section 3. Reaction mechanism

#### 3.1. Electron Spin Resonance (ESR)

ESR experiments to detect superoxide radicals were accomplished on the Bruker EMX-Micro spectrometer. The EPR settings were: center field, 3506.75 G; sweep width, 100 G; sweep time, 60 s; g-Factor, 2; modulation amplitude, 1 G; and receiver gain, 30 dB.

5,5-Dimethyl-1-pyrroline (DMPO) 100 mM was employed as the spin-trapping agent. Measurements were carried out after 20 min of irradiation with white LEDs of 35W.

### Section 4. Photocatalysis

#### 4.1. Reagents

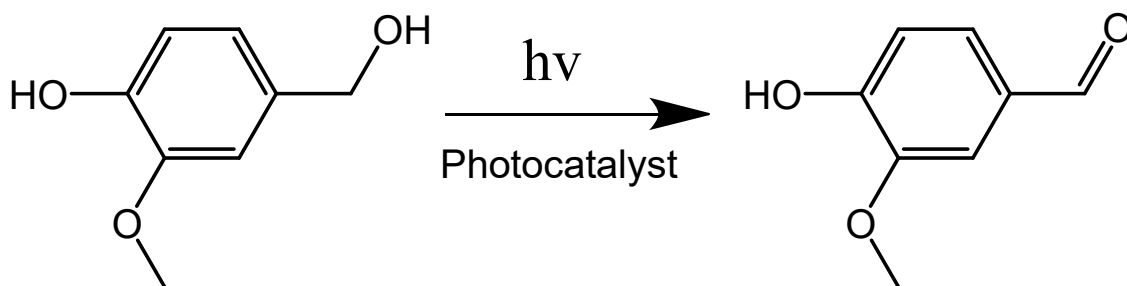
Reactants used in photocatalytic reactions were the following: homemade perovskites Cs<sub>2</sub>AgBiBr<sub>6</sub> and Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> as catalyst in a concentration of 1 mg/mL, vanillyl alcohol (Sigma Aldrich, 98%) in a concentration of 0.5 mM, and acetonitrile (Sigma Aldrich, 99.9%) as solvent.



Photocatalytic reactions were carried out into a photoreactor batch-type. As source of UV light, a 12 V efficient emission LED lamp with 395 nm of wavelength was used. And as source of visible light, a white light LED lamp of 35 W was employed.

#### 4.2. Procedure

An acetonitrile solution (25 mL) of vanillyl alcohol 0.5 mM and 25 mg of catalyst (1 mg/mL) were placed into photoreactor. The mixture remained stirring during all reaction time. An oxygen flow was applied for 20 min over the solution, following by closure completely the photoreactor, obtaining an oxygen saturated solution. First 20 min after oxygen saturation were without light, to take an aliquot as blank. After this time, light is turned on and reaction starts. Samples were taken at different times and filtered before analysis.

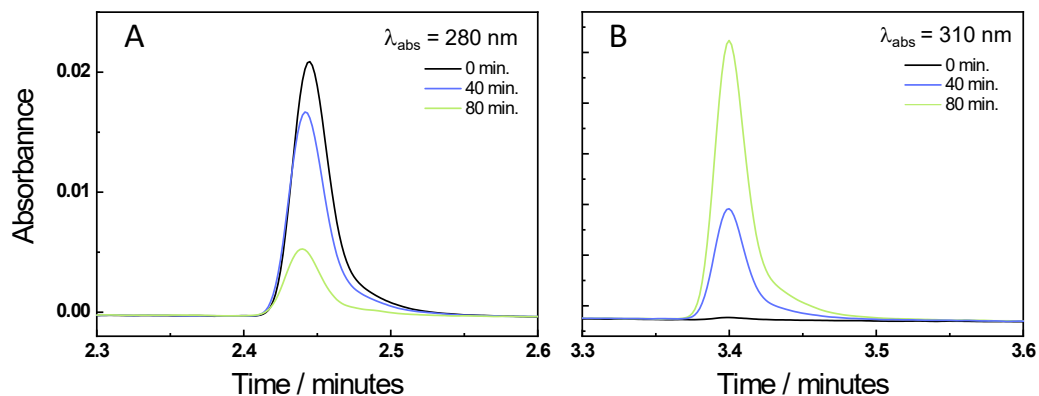


**Scheme S1.** Reaction scheme of the photocatalytic conversion of vanillyl alcohol in vanillin under light irradiation.

#### 4.3. Chromatographic analysis

Chromatographic analyses were carried out on a Waters-Acquity™ Ultra Performance LC system (Waters Corp., Madrid, Spain) using an Acquity UPLC® BEH C18 column (2.1 mm × 100 mm; 1.7 μm particle size) kept at 35°C during analysis. The mobile phase composition was (A) water+0.1% formic acid and (B) acetonitrile. Gradient elution profile at a flow rate of 0.4 mL/min was as follows: the initial composition was fixed at 95% A for 1 min, the percentage is decreased to 40% in 6 min. After this, B composition is increased to 90% and kept for 3 minutes and returning to initial conditions for column re-equilibration before the next injection. The injection volume was 2 μL using partial loop mode. The

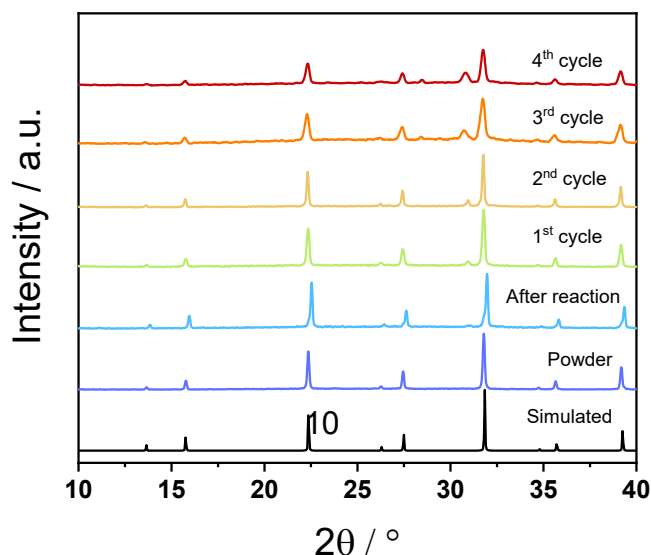
separated analytes were determined by a photo diode array eλ® Detector (Waters Corp.) using 278 nm and 310 nm detection wavelengths for vanillyl alcohol and vanillin respectively. Target analytes identification was achieved by direct comparison of retention time with analytical standards (Sigma-Aldrich, Madrid, Spain). System control and chromatograms analysis was run through Empower® software.



**Figure S7.** Chromatographic analysis of the reaction mixtures. Absorption signal at 280 nm (A) and 310 nm (B) corresponding to the vanillyl alcohol and vanillin at three different reaction times, respectively.

#### 4.4. Catalyst Recycling

To study the behavior of the catalyst after several uses, catalysts were separated by decantation of the reaction mixture and washed several times with acetonitrile and acetone. After dry with  $\text{N}_2$  gas flow, a portion of material was analyzed by XRD to obtain its diffraction patterns. This process was repeated for four cycles in addition to the main reaction.



**Figure S8.** Powder X-ray diffraction (XRD) measurements of the  $\text{Cs}_2\text{AgBiBr}_6$  photocatalyst after different reaction cycles. Simulated and as-prepared powder XRD diffractograms are also shown for comparison.