Electronic Supplementary Information

Europium-doped ZnO Nanosponges – Controlling Optical Properties and Photocatalytic Activity

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1. Additional Photocatalytic Data

1.1 Absorbance spectra

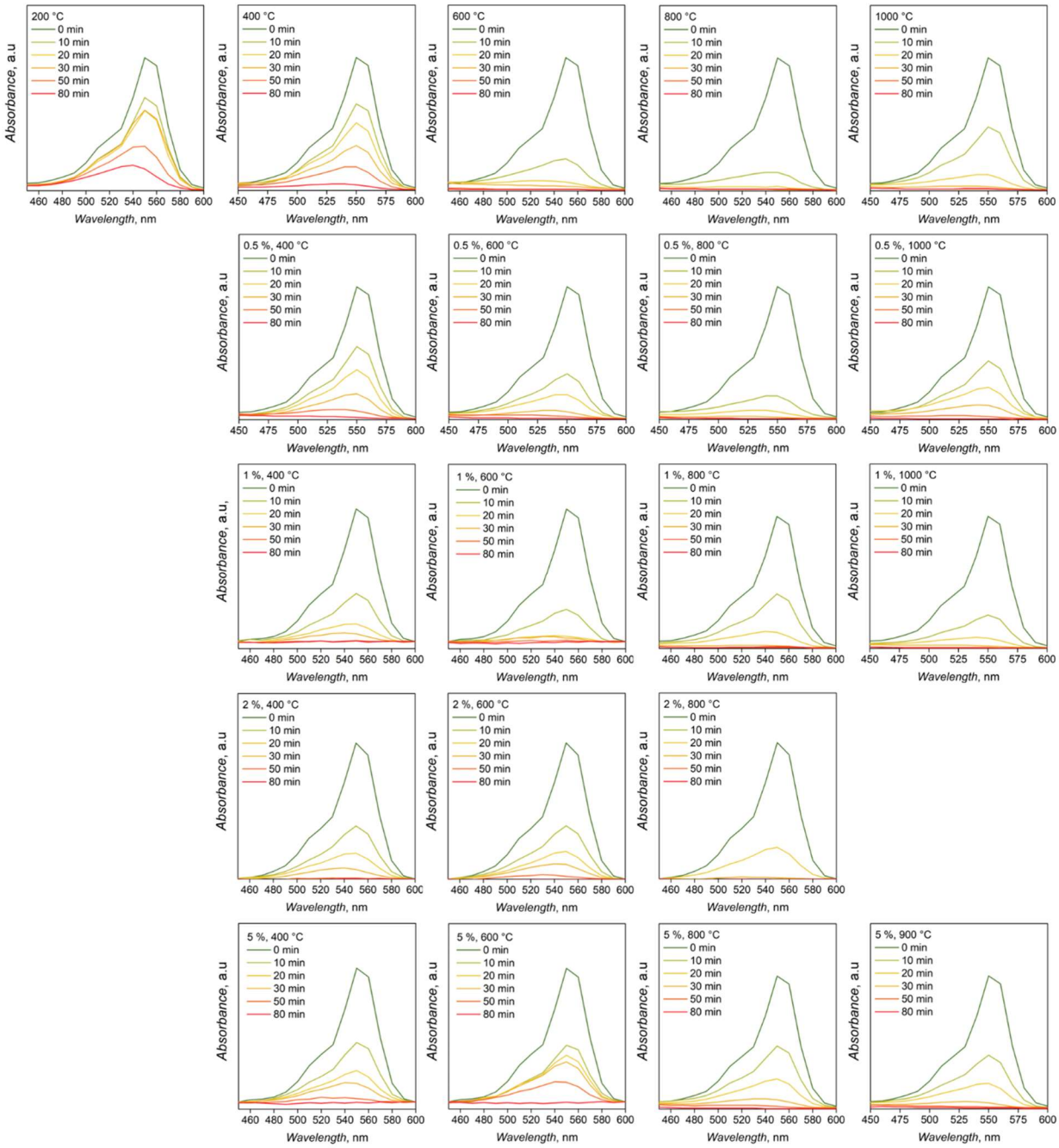

Figure S1. Absorbance spectra reflecting the degradation of RhB upon UV exposure in the presence of undoped and Eu^{3+}-doped ZnO nanosponges annealed at various temperatures.

1.2 Exposure of *RhB* to UV in the absence of any photocatalyst

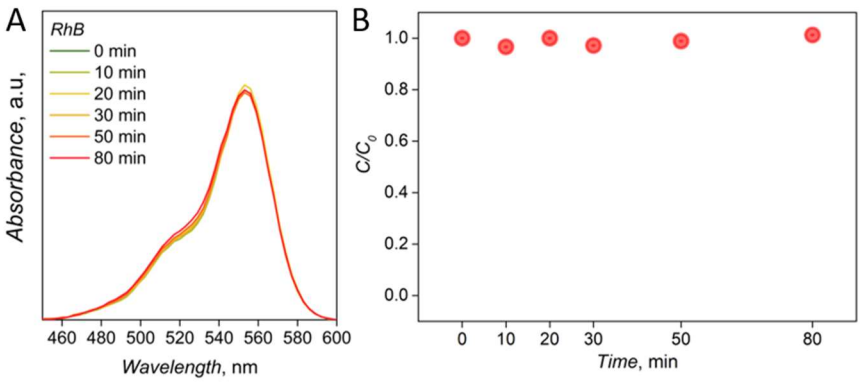

Figure S2. A: Absorbance spectra recorded on solutions of RhB upon UV exposure in the absence of any photocatalyst. B: Time-dependent concentration plots deduced from data shown in (A) indicating that UV illumination alone does not induce any significant degradation of RhB.

1.3 Second, independent photocatalysis experiment on selected samples

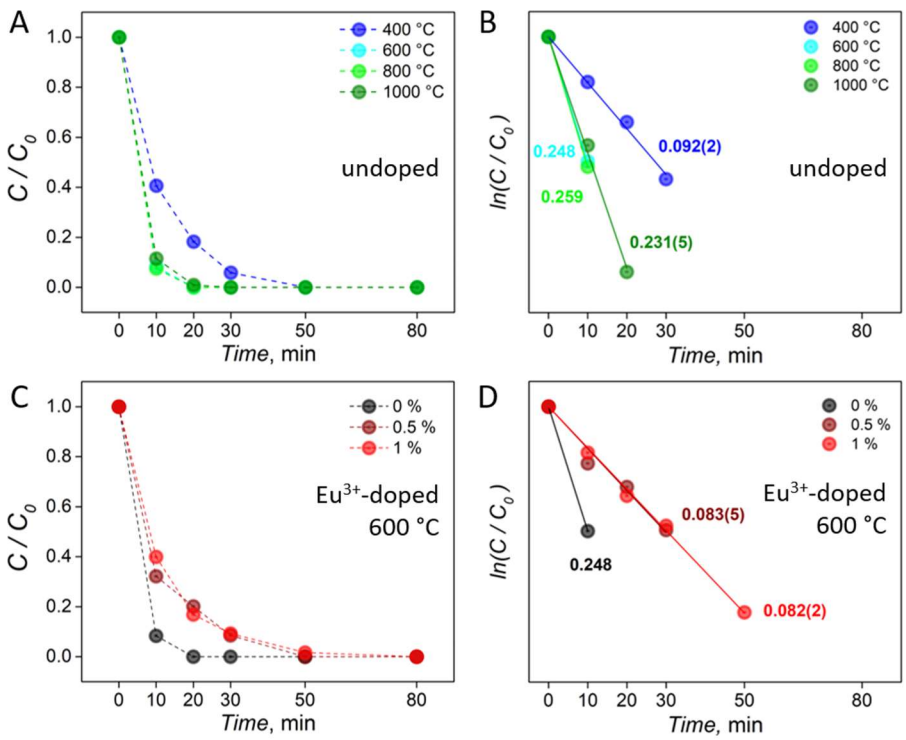

Figure S3. Second, independently conducted photocatalysis experiment performed on selected undoped and Eu^{3+}-doped ZnO nanosponges: Photodegradation curves of RhB using (A) undoped ZnO nanosponges annealed at temperatures between 400 and 1000 °C as well as (C) ZnO doped with 0.5 or 1% Eu^{3+} (annealed at 600 °C) for 80 min of UV irradiation time. (B) and (D) show the respective $\ln(C/C_0)$ *versus* time plots and deduced rate constants; standard errors of the linear fits in (B) and (D) are given in parentheses. These data confirm the trend observed in the first set of experiments: the highest photocatalytic activity was exhibited by undoped ZnO nanosponges annealed at 600 and 800 °C, and loss of photocatalytic performance was observed upon doping with Eu^{3+} ions. Changes in terms of absolute values can be ascribed to slight modification of the experimental set-up (*e.g.* stirring speed, distance between the UV-lamp and the sample).

1.4 Scavenger experiments

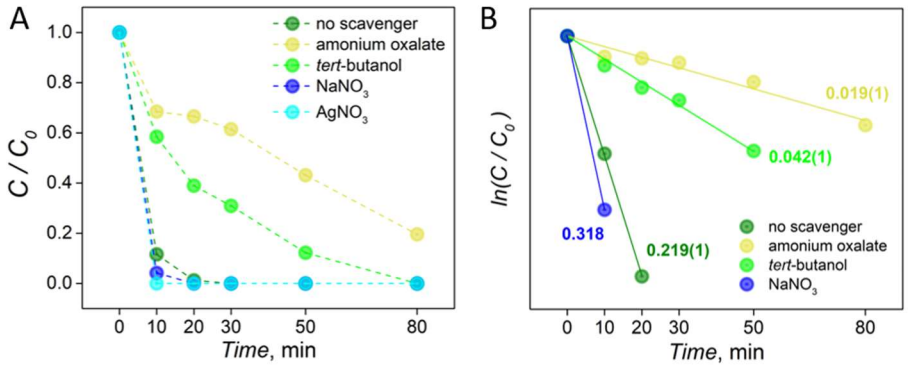

Figure S4. Photocatalytic activity of ZnO nanosponges (annealed at 1000 °C) in the absence and presence of various scavengers under UV illumination. $NaNO_3$ and $AgNaO_3$ were chosen as electron scavengers (e^-), ammonium oxalate (AO) as hole scavenger (h^+), and *tert*-butanol (*t*-BuOH) as scavenger for hydroxyl radicals ($^\bullet$OH). Degradation curves as well as ln(*C/C₀*) plots and rate constants are reported in (A) and (B), respectively. Standard errors of the linear fits in (B) are given in parentheses. Note that no ln(C/C_0) plot is provided in case of $AgNO_3$ as the decoloration was already complete after 10 min. The slower degradation kinetics in the presence of AO and *t*-BuOH identify hydroxyl radicals ($^\bullet$OH) and holes (h^+) as major species involved in the RhB degradation. This is corroborated by the faster *RhB* degradation in the presence of electron scavengers ($NaNO_3$ and $AgNO_3$), preventing the e^--h^+ recombination and promoting decoloration *via* direct transfer of photogenerated holes.

1.5 Photodegradation curves of *RhB* using europium-doped ZnO

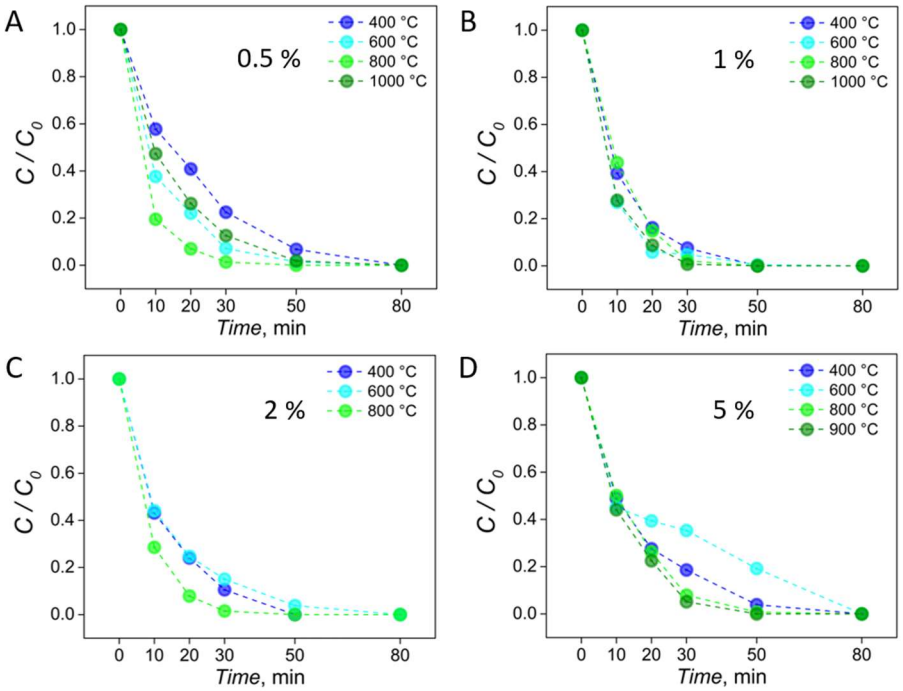

Figure S5. Photodegradation curves of RhB using ZnO nanosponges annealed at temperatures between 400 and 1000 °C doped with (A) 0.5%, (B) 1%, (C) 2%, and (D) 5% Eu^{3+} (efficiencies were determined in 10, 20, and 30 min intervals; dashed lines are guidance for the eye).

1.6 Rate constants for the photodegradation of *RhB* using europium-doped ZnO

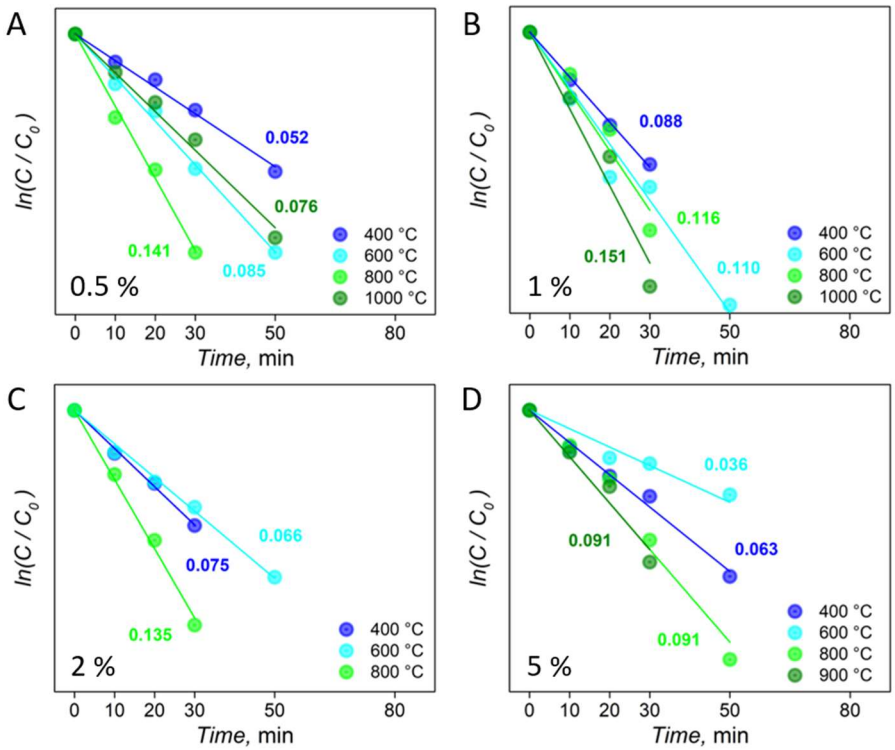

Figure S6. ln(C/C_0) plots and rate constants (in min^{-1}) for the photodegradation curves of RhB using ZnO nanosponges annealed at temperatures between 400 and 1000 °C doped with (A) 0.5%, (B) 1%, (C) 2%, and (D) 5% Eu^{3+} (solid lines are linear fits of the experimental data).

2. Photograph of ZnO Annealed at Various Temperatures

Figure S7. Photograph of ZnO powders annealed at various temperatures. Upon increase of the annealing temperature, the sample colour changed from light brown to pure white indicating increased chemical purity.

3. Band Gap Estimation

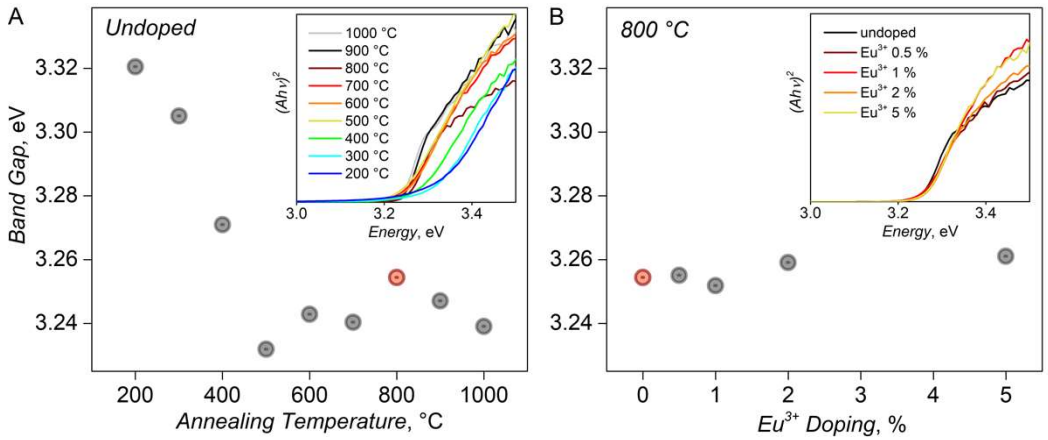

Figure S8. Estimated band gap as a function of (A) the annealing temperature (undoped ZnO) and (B) the Eu^{3+} concentration (the sample annealed at 800 °C has been selected due to its superior photocatalytic activity). The insets show the corresponding Tauc-plots.

4. Additional TEM Images and Elemental Mapping (Electron Energy Loss Spectroscopy, EELS)

4.1 ZnO doped with 2 % europium and annealed at 800 °C

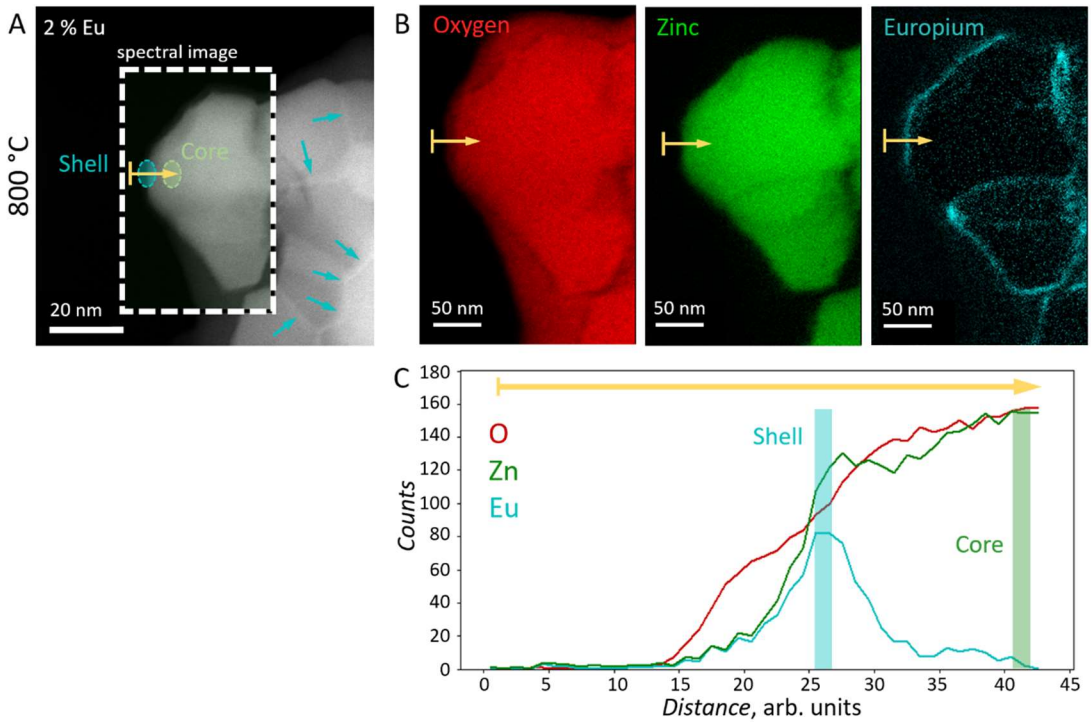

Figure S9. HAADF-STEM image (A) and EELS elemental mapping (B) of ZnO doped with 2% Eu^{3+} and annealed at 800 °C. Arrows in cyan in A indicate grain boundaries. B: Elemental distribution revealing europium segregation at the ZnO grain boundaries. C: Eu/Zn/O line profiles over the shell region of ZnO marked by the yellow arrow in A and C confirming surface and grain boundary segregation of europium (as EuO_x).

4.2 ZnO doped with 5 % europium and annealed at 800 °C

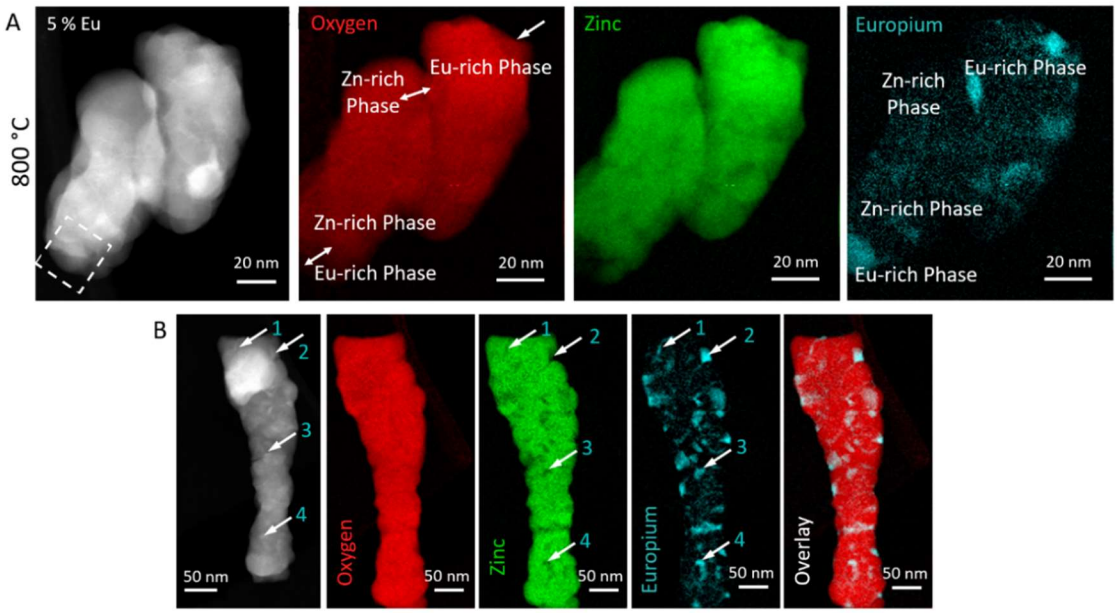

Figure S10. HAADF-STEM images and EELS elemental mapping of ZnO doped with 5% Eu^{3+} and annealed at 800 °C, revealing europium- and zinc-rich phases as a result of phase segregation (A and B showing two different samples of the same batch). A zoom-in representation of the region of interest marked in A is given in Figure S11.

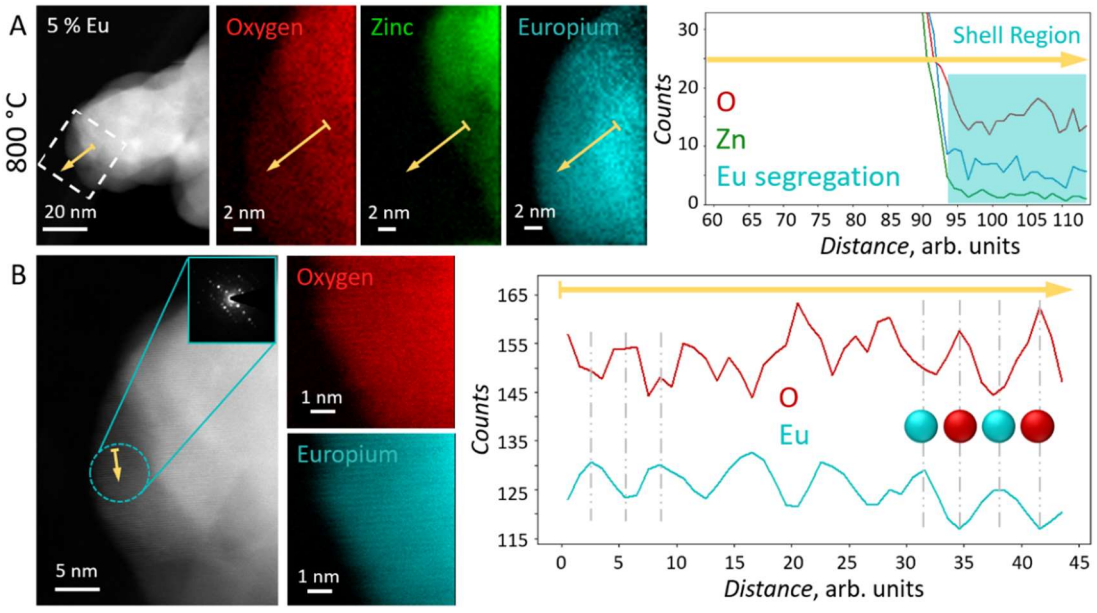

Figure S11. A: Zoomed region over an area captured by the HAADF-STEM image, EELS elemental mapping and Eu/Zn/O line profiles of the region of interest marked in Figure S10A. Upon doping with 5% Eu^{3+} and annealing at 800 °C, the shell region of the doped ZnO sponge-like structure displayed strong europium aggregation. B: HAADF-STEM, chemical images and Eu/O line profiles of the region of interest marked in A. Chemical imaging with atomic resolution confirmed europium segregation at the ZnO surface. Inset: Diffraction pattern confirming the crystallinity of EuO_x phase (as opposed to amorphous surface-contaminations). No evidence for zinc was found in this area.