

## SUPPLEMENTARY INFORMATION

### Photocatalytic Performance of Undoped and Al-doped ZnO Nanoparticles in the Degradation of Rhodamine B under UV-Visible Light: The Role of Defects and Morphology

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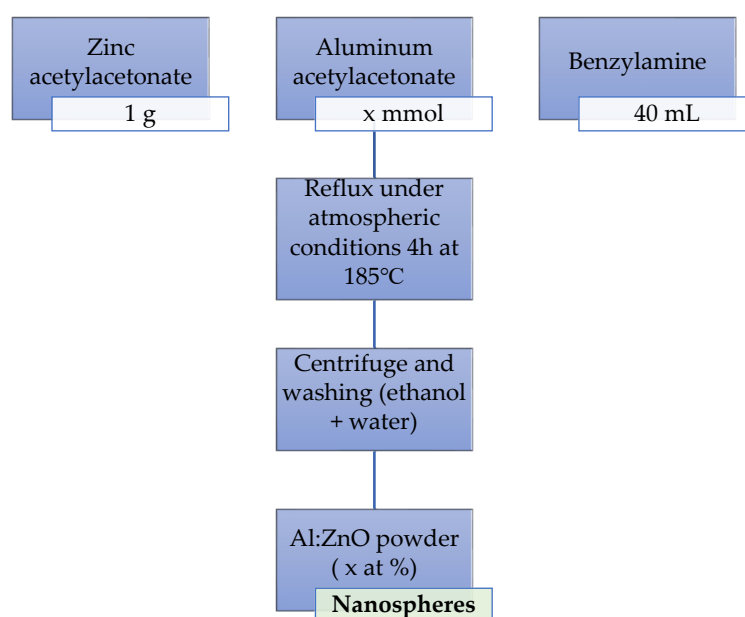
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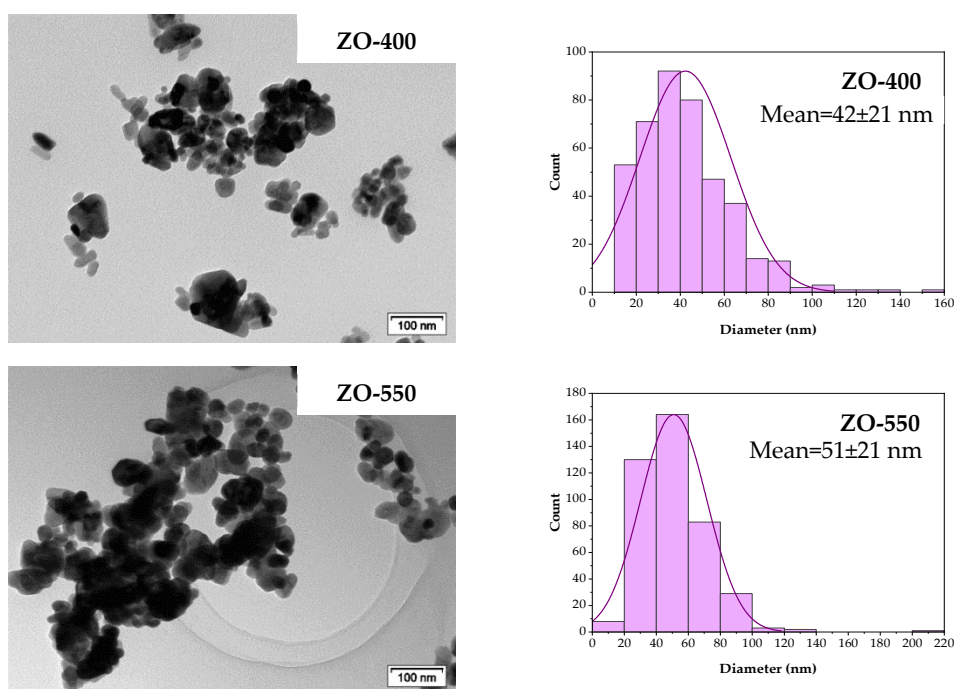
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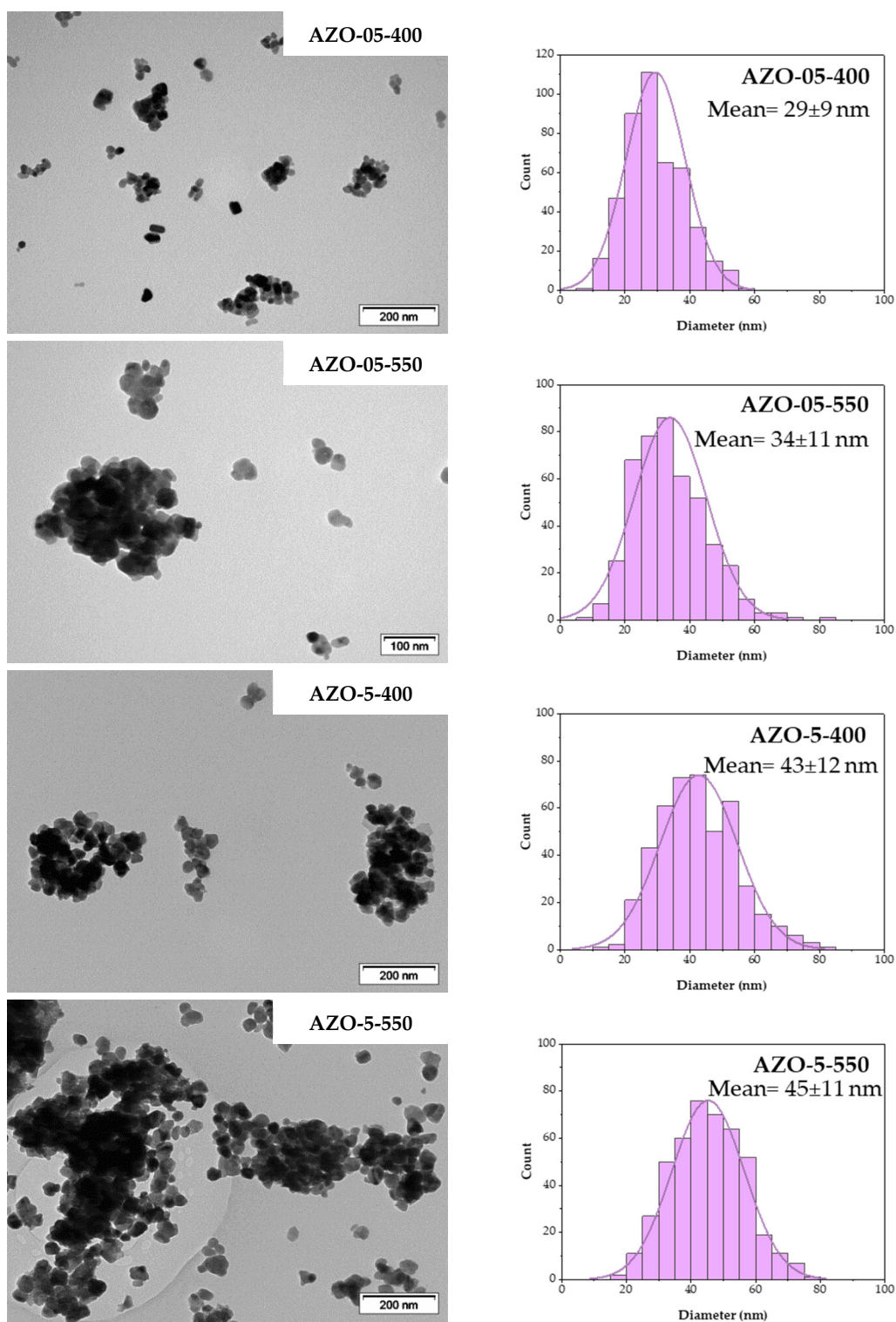
**Figure S1.** Synthesis scheme for AZO quasi-spherical nanoparticles.

**Table S1.** Nominal and actual % of aluminum content into the as-synthesized Al-doped ZnO solids.

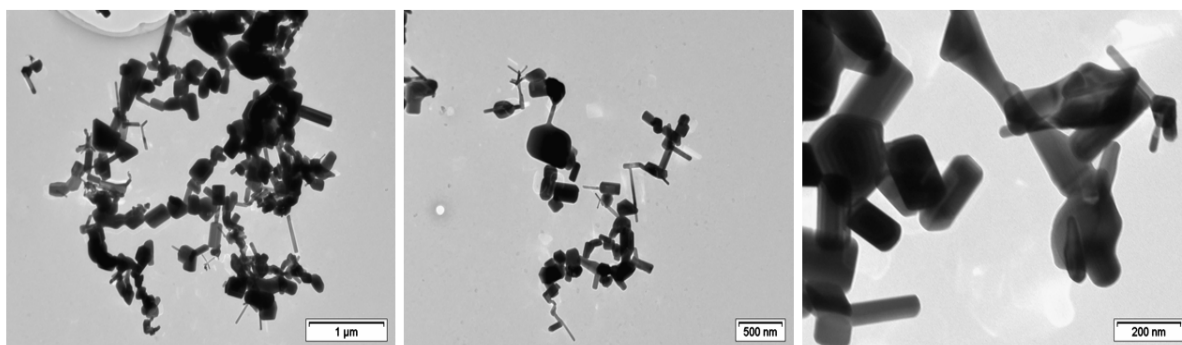
Sample codes	Nominal Al content	Actual Al content
AZO-05	0.05	0.42
AZO-1	1	0.89
AZO-2	2	1.81
AZO-3	3	2.66
AZO-5	5	3.79



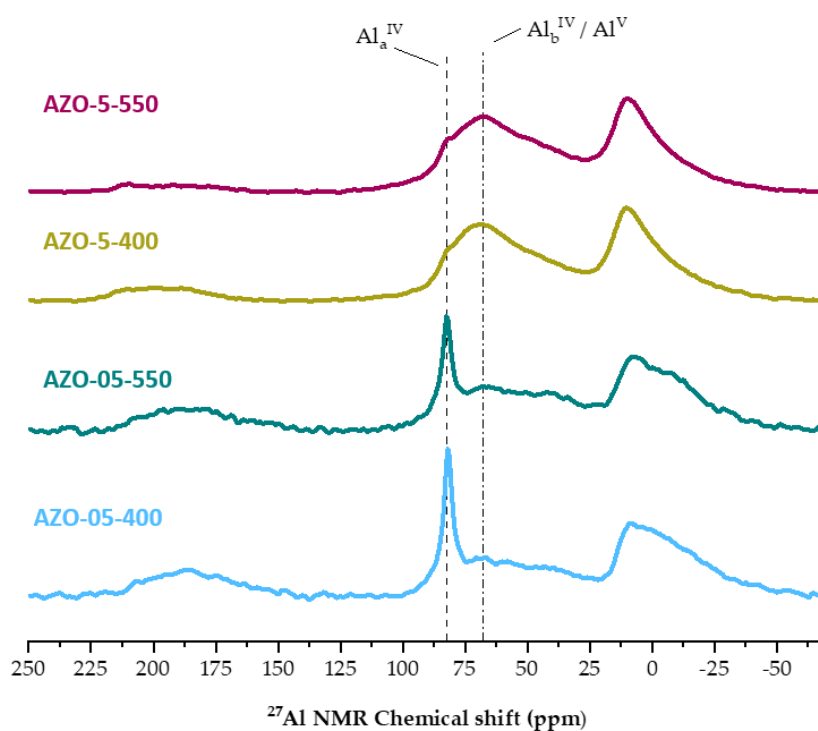
**Figure S2.** TEM micrographs of ZnO annealed at 400 and 550 °C in N<sub>2</sub> atmosphere supported with the corresponding particle size histograms.



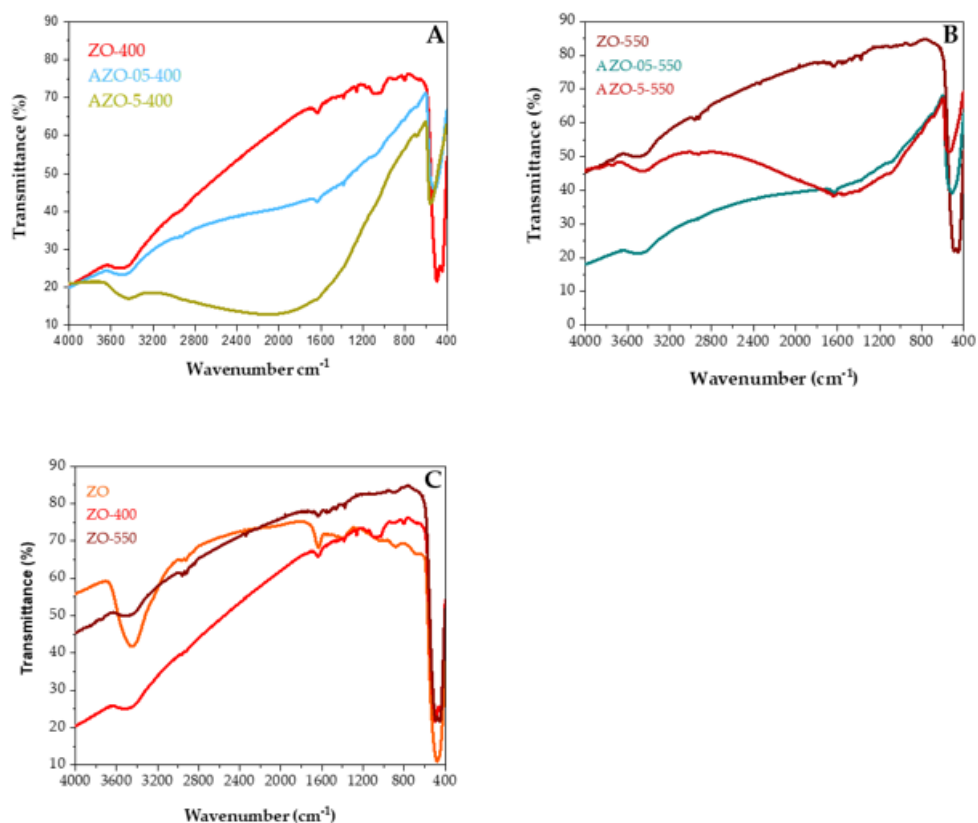
**Figure S3.** TEM micrographs of the AZOs annealed at 400 and 550 °C in N<sub>2</sub> atmosphere supported with the corresponding particle size histograms.



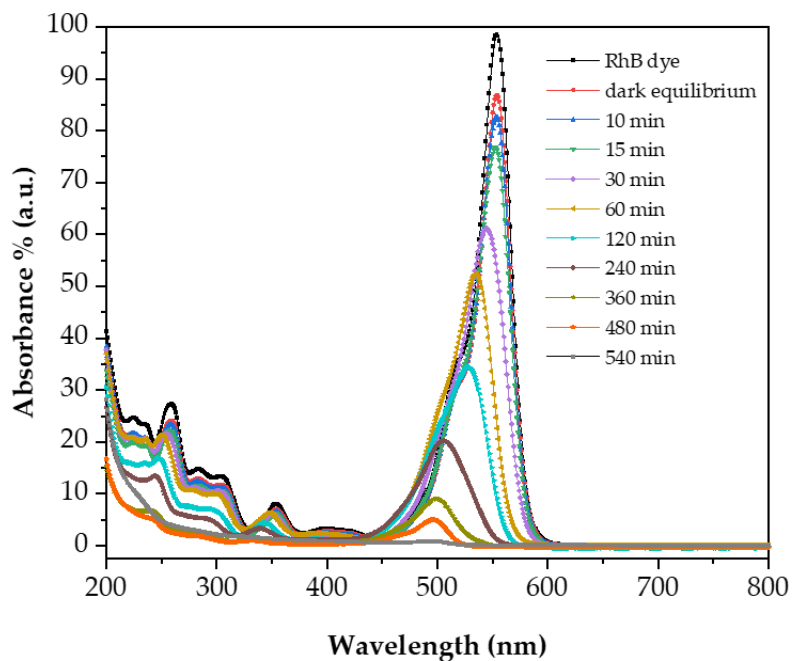
**Figure S4.** TEM micrographs of the commercial ZnO, CZO.



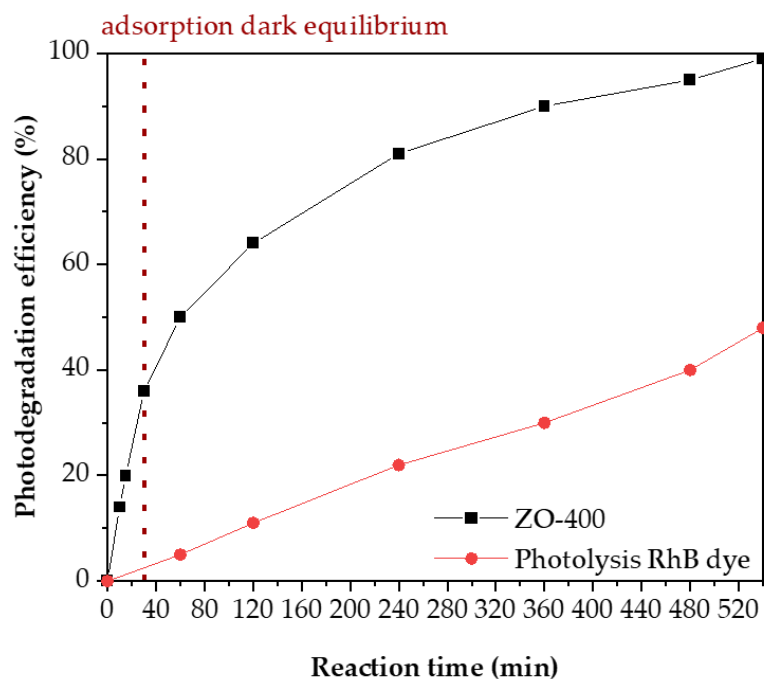
**Figure S5.**  $^{27}\text{Al}$  MAS NMR comparison between AZO-05 and AZO-5 quasi-spherical nanoparticles annealed in  $\text{N}_2$  at 400 and 550  $^{\circ}\text{C}$ . The two lines highlight  $\text{Al}_a^{\text{IV}}$ , assigned to four-fold coordinated aluminum and  $\text{Al}_b^{\text{IV}} / \text{Al}^{\text{V}}$ , assigned to distorted four-fold coordinated and five-fold coordinated aluminum sites, respectively.



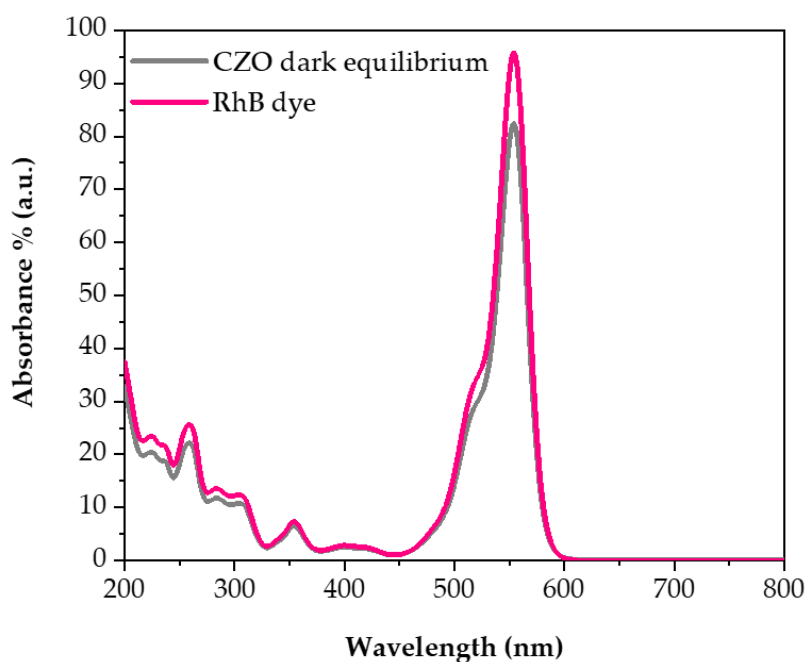
**Figure S6.** FT-IR spectra of the KBr pellets of quasi-spherical nanoparticles: A, comparison of ZO, AZO-05 and AZO-5 annealed at 400°C; B, comparison of ZO, AZO-05 and AZO-5 annealed at 550 °C; C, comparison of ZO as-synthesized and annealed at 400 and 550 °C.



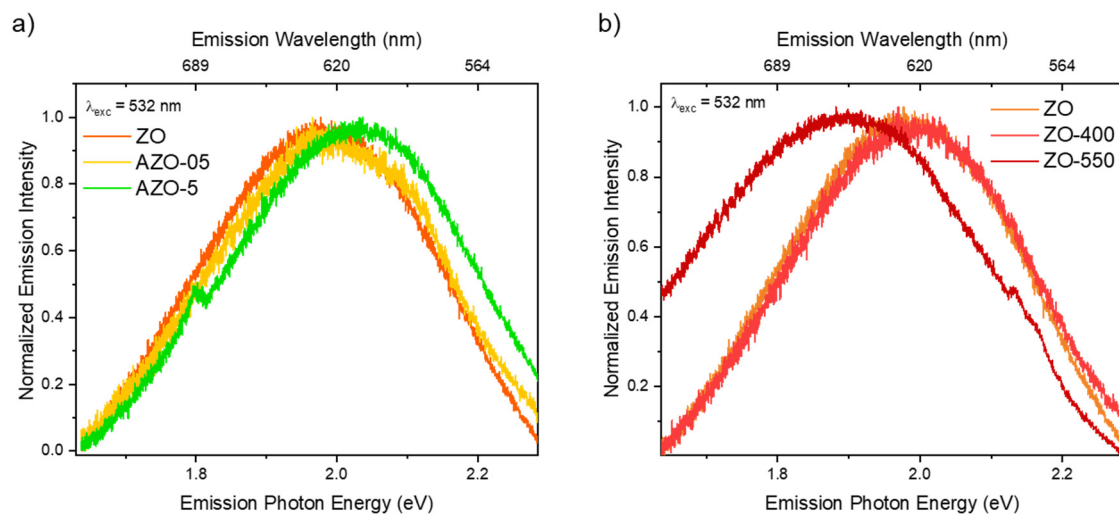
**Figure S7.** UV-Vis absorbance spectra of photodegraded Rhodamine B dye aqueous solutions with ZO-400 catalyst under green light irradiation at different time intervals. Rhodamine B dye adsorption during dark equilibrium is also reported.



**Figure S8.** Photodegradation of Rhodamine B dye plotted as a function of the green light exposure time for the as-synthesized ZnO-400 material along with photolysis of Rhodamine B dye at indicated time intervals. The first 30 minutes correspond to RhB adsorption during dark equilibrium.



**Figure S9.** UV-Vis absorbance spectra of Rhodamine B dye without catalyst and Rhodamine B dye with CZO catalyst during one-hour dark equilibrium experiment.

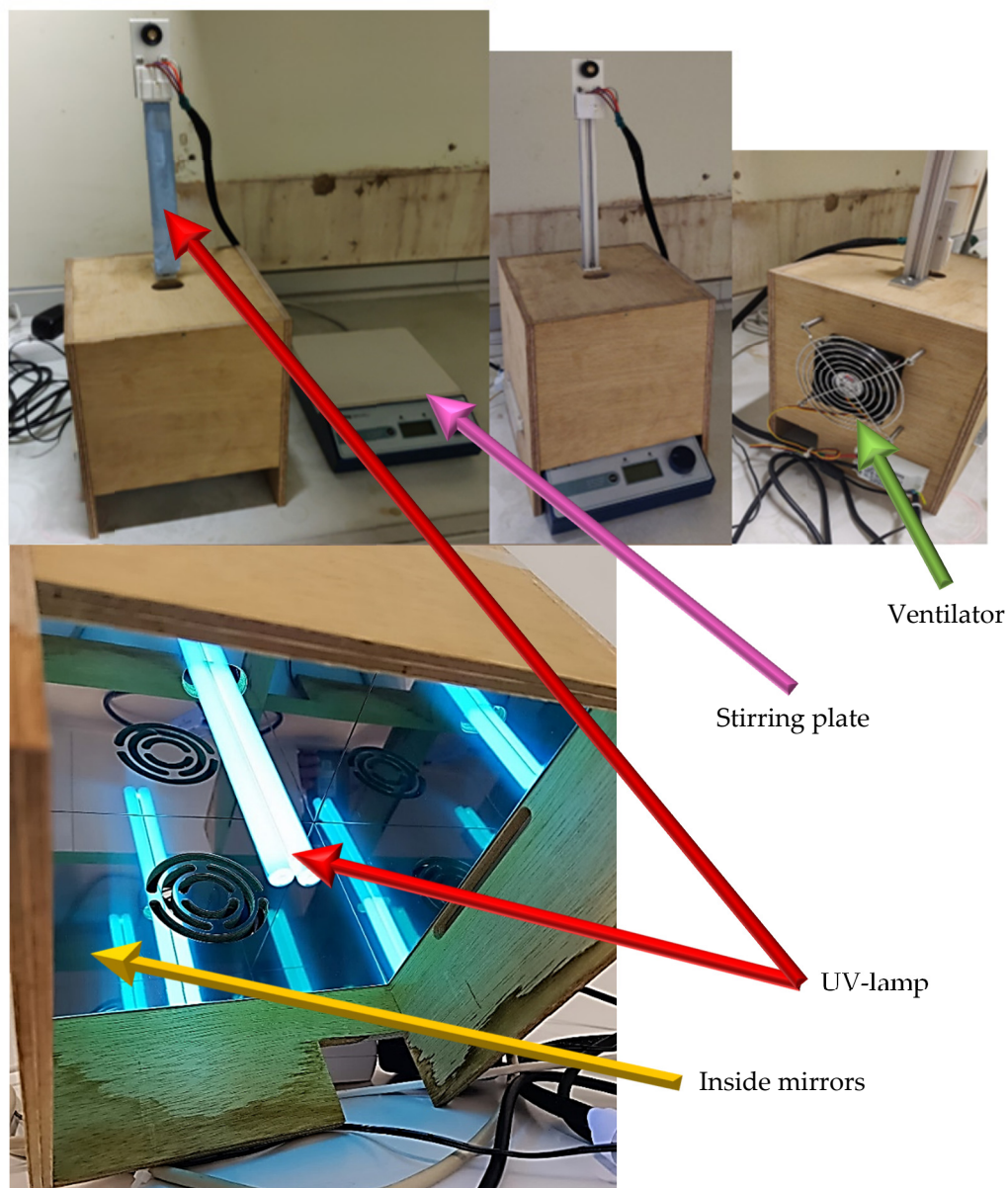


**Figure S10.** Normalized PL spectra of all samples excited at 532 nm. Comparison among different Al-doping percentages (b), and annealing temperatures (c) are displayed.

**Table S2.** Gaussian band deconvolution data of samples excited at 405 nm.

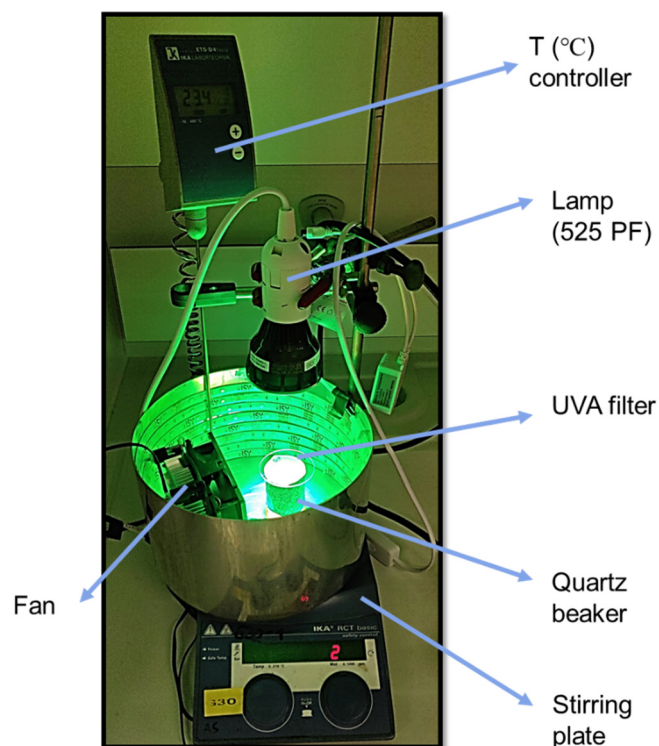
	Peak 1 (eV-nm)	Relative (%)	Area	Peak 2 (eV-nm)	Relative (%)	Area	Peak 3 (eV-nm)	Relative (%)	Area
CZO	1.87 - 663	22		2.76 - 449	43		2.88 - 430	35	
ZO	1.93 - 642	75		2.38 - 521	22		2.85 - 435	3	
AZO-05	1.94 - 639	71		2.39 - 519	26		2.86 - 433	3	
AZO-5	2.06 - 602	47		2.44 - 508	53		-	-	
ZO-400	1.94 - 639	77		2.38 - 521	18		2.87 - 432	5	
ZO-550	1.84 - 674	88		2.36 - 525	12		-	-	



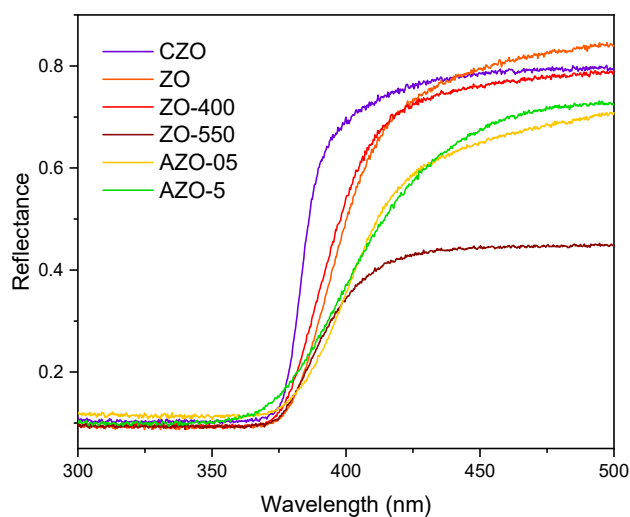


**Figure S11.** Home-made photoreactor. It consists of a wooden-box internally covered by mirrors, a pulley to carry the lamp, a lamp, a ballast, a socket, a magnetic stirrer plate with one single motor and four identical positions for beakers and a fan to keep the temperature constant while running reactions.





**Figure S12.** Home-made photoreactor working under visible light irradiation (green light, 525 nm). It consists of a metal-box, lamp support, a lamp, a ballast, a socket, a magnetic stirrer plate with one single motor with one position for a quartz beaker, temperature controller and a fan to keep the temperature constant while running reactions.



**Figure S73.** Reflectance spectra of the ZnO samples.

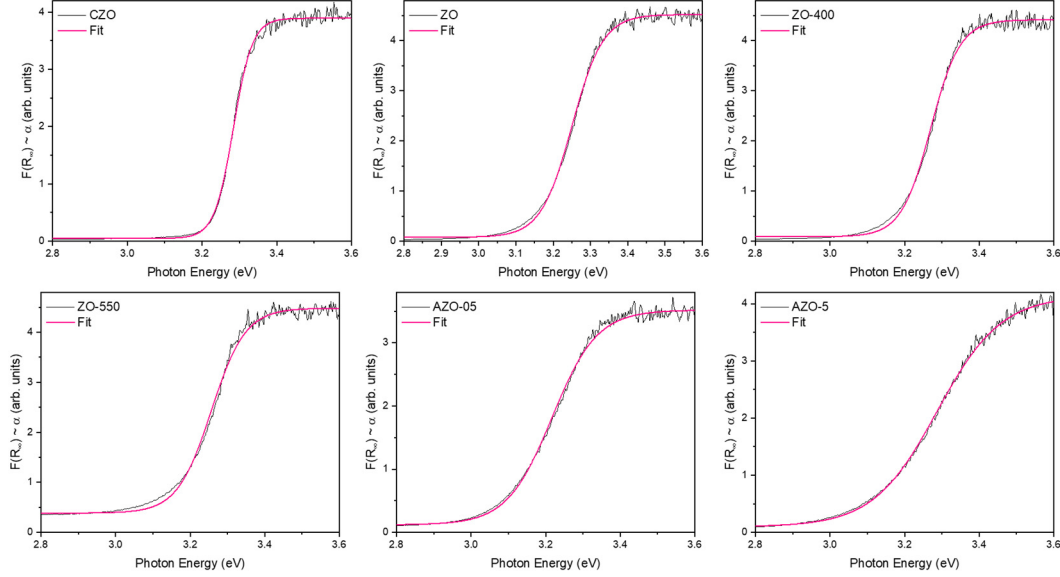
#### *Calculation of the bandgap.*

In order to calculate the bandgap of our powder samples, the reflectance values obtained were converted in a function  $F(R)$  of the apparent absorption  $K$  and diffuse reflection  $S$  coefficients via the Schuster-Kubelka-Munk formula[64-67]:

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{K}{S}$$

Where  $R_{\infty}$  is the diffuse reflectance of the sample.

This pseudo-absorption function can be plotted as a function of energy and fitted with a sigmoid-Boltzmann function with good results according to a methodology recently studied by Zanatta in his excellent paper[68].



**Figure S14.** Plot of  $F(R)$  functions of our ZnO samples fitted with a sigmoidal-Boltzmann function.

Indeed, the fitting formula is:

$$\alpha(E) = \alpha_{max} + \frac{\alpha_{min} - \alpha_{max}}{1 + \exp\left(\frac{E - E_0^{Boltz}}{\delta E}\right)}$$

Where  $\alpha_{min}$  is the minimum absorption value,  $\alpha_{max}$  is the maximum absorption value,  $E_0^{Boltz}$  is the energy value at which the absorption has an intermediate value between  $\alpha_{min}$  and  $\alpha_{max}$  and  $\delta E$  is the energy range linked to the slope of the curve.

Once fitted, the value of the bandgap  $E_{gap}^{Boltz}$  can be obtained according to this empirical relationship:

$$E_{gap}^{Boltz} = E_0^{Boltz} - n_{dir-ind}^{Boltz} \times \delta E$$

where  $n_{dir-ind}^{Boltz}$  is a parameter experimentally determined that is equal to 0.3 for direct type bandgap (more details in Zanatta's work). In the following table, the calculated bandgaps.

**Table S3.** Calculated bandgaps.

	$\alpha_{min}$	$\alpha_{max}$	$E_0^{Boltz}$ (eV)	$\delta E$ (eV)	$E_{gap}^{Boltz}$ (eV)	$E_{gap}^{Boltz}$ (nm)
<b>CZO</b>	0.05	3.89	3.28	0.03	3.28	378
<b>ZO</b>	0.08	4.52	3.25	0.04	3.24	383
<b>ZO-400</b>	0.09	4.42	3.27	0.04	3.26	381
<b>ZO-550</b>	0.38	4.48	3.26	0.05	3.24	382
<b>AZO-05</b>	0.12	3.52	3.22	0.06	3.20	388
<b>AZO-5</b>	0.10	4.14	3.29	0.09	3.26	380