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Electronic Supplementary Information

On the agent role of Mn^{2+} in redirecting the synthesis of $Zn(OH)_2$ towards nano-ZnO with variable morphology

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XRD parameters

Table S1. Results of the Rietveld refinement of the XRD patterns of the undoped and Mn^{2+} doped samples.

Mn^{2+} nominal concentration	**Observed crystalline phase**	**Lattice parameters (Å)**	**Crystallite mean size - XRD (nm)**
0 (undoped)	ε –$Zn(OH)_2$	a = 8.4864(5) b = 5.1495(4) c = 4.9109(4)	> 100
1 ppm – 1000 ppm	ZnO	a = 3.253(3) c = 5.209(5)	38 ± 2
5000 ppm	ZnO	a = 3.253(3) c = 5.211(5)	32 ± 2

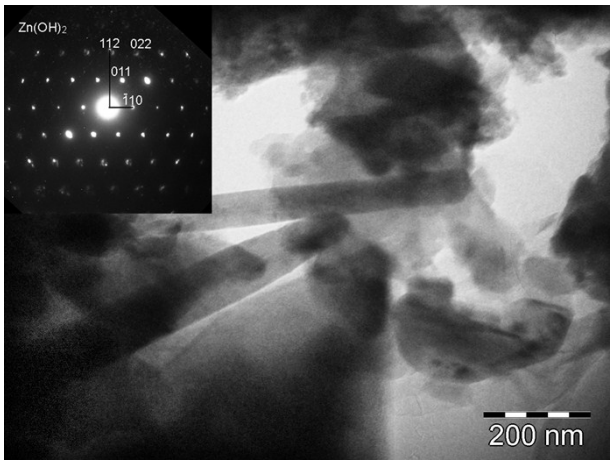

Fig. S1. TEM image of the undoped $Zn(OH)_2$ sample revealing its rod-like, plate-like morphology. The inset shows an indexed diffraction pattern of a large (1.2 μm) plate-like $Zn(OH)_2$ crystallite.

Analysis of the EPR spectra of the Mn^{2+} centers

The EPR spectra of the Mn^{2+} paramagnetic centers were analyzed using the following spin Hamiltonian (SH):[1]

$$H = \mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + D\left[S_z^2 - \frac{1}{3} S(S+1) \right] - \mu_N g_N \mathbf{B} \cdot \mathbf{I}$$

The first two terms represent the main Zeeman and hyperfine interactions of the $S = 5/2$ electron spin with the external magnetic field B and the $I = 5/2$ nuclear spin of the ^{55}Mn (100% abundance) isotope, respectively. The next second-order zero-field-splitting (*ZFS*) term describes the interaction of the electron spin with the local axial crystal field, while the last term describes the nuclear Zeeman interaction. The SH parameters of the Mn^{2+} centers, determined by simulation and lineshape fitting of the X- and Q-band spectra of the undoped and doped samples, are given in Table S2 together with reference parameters for the Mn^{2+} ions in other (nano)crystalline materials of interest.

Table S2. SH parameters *g, A* and *D*, as well as the individual linewidth (ΔB) and the standard deviation $\sigma(D)$ describing the line broadening, for the Mn^{2+} centers in the undoped and Mn^{2+} doped samples discussed in this work, along with reference data.

center / host	***g***	***A*** **[10^{-4} cm^{-1}]**	**$\lvert D\rvert$ [10^{-4} cm^{-1}]** **$\sigma(D)$ [%D]**	**ΔB [mT]**	**ref**
Mn^{2+}(a) / $Zn(OH)_2$	2.0010 ± 0.0003	-87 ± 0.3	> 210 $\sigma(D)$ = 43	ΔB(Q) = 0.8	2 this work
Mn^{2+}(c) / ZnO:Mn (100ppm)	2.0012 ± 0.0001	-74 ± 0.1	238 ± 2 $\sigma(D)$ = 11 ± 1 (100-1000 ppm) $\sigma(D)$ = 13 ± 1 (5000 ppm)	ΔB(Q) = 0.12	This work
Mn^{2+}(d) / ZnO:Mn (100ppm)	2.0011 ± 0.0001	-74.3 ± 0.1	238 ± 2 $\sigma(D)$ = 43	ΔB(Q) = 0.12	This work
Mn^{2+}(x) / ZnO:Mn (100ppm)	2.0012 ± 0.0001	-84.7 ± 0.2	150 - 240 $\sigma(D)$ = 43	ΔB(Q) = 0.5	This work
Mn^{2+}-d / disordered ZnO (200ppm)	2.0012 ± 0.0001	-73.5 ± 0.1	242[a] $\sigma(D)$ = 43	ΔB(X/Q) = 0.2	3
Mn^{2+}-c/ ZnO nanocrystals (200ppm)	2.0012 ± 0.0002	-74 ± 0.2	242±4,$\lvert a\text{-}F\rvert$= 5.5[a], $\sigma(D)$ = 7	ΔB(X/Q) = 0.1	3
Mn^{2+} / ZnO single crystal (35000ppm)	2.0012	-73.4	225, $\lvert a\text{-}F\rvert$= 5.5 $\sigma(D)$ = 3		4
Mn^{2+} / ZnO thin film (17000ppm)	2.0012	-75.05	238.5, $\lvert a\text{-}F\rvert$= 5.5 $\sigma(D)$ = 3		4

[a] Included in the fitting as a fixed parameter.

FTIR absorption bands assignments

Table S3. FTIR absorption bands assignments (in cm^{-1}) for the investigated ZnO:Mn samples.

ZnO:Mn (1 ppm)	**ZnO:Mn (50 ppm)**	**ZnO:Mn (1000 ppm)**	**ZnO:Mn (5000 ppm)**	**Absorption band assignment**
3450 w	3420 m	3420 m	3450 m	ν(-O-H)
1640 vw	1640 vw	1640 vw	1640 vw	ρ(-O-H)
1460 m	1500 w	-	-	ν_{as}(-O-NO_2)
1390 m	1380 w	1390 w	1380 w	ν_{s}(-O-NO_2)
1025 vw	1025 vw	1025 vw	1025 vw	ν(-N-O)
840 vw	840 vw	-	-	δ_{as}(-O-NO_2)
760 vw	-	-	-	δ_{s}(-O-NO_2)
565 m; 440 s; 390 s	565 m; 440 s; 390 s	565 m; 440 s; 390 s	565 – 425 s	ν(Zn-O)

ν – stretching; ρ – rocking; δ - bending vibration modes
vw – very weak; w – weak; m – medium; s – strong: (band intensity).

References

1 A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, U.K., 1970.

2 S. V. Nistor, D. Ghica, M. Stefan, I. Vlaicu, J. N. Barascu and C. Bartha, Magnetic defects in crystalline $Zn(OH)_2$ and nanocrystalline ZnO resulting from its thermal decomposition, *J. Alloys Compd.,* 2013, **548**, 222-227.

3 S. V. Nistor, L. C. Nistor, M. Stefan, D. Ghica, Gh. Aldica and J. N. Barascu, Crystallization of disordered nanosized ZnO formed by thermal decomposition of nanocrystalline hydrozincite, *Cryst. Growth Des.*, 2011, **11**, 5030-5038.

4 M. Diaconu, H. Schmidt, A. Poeppl, R. Bottcher, J. Hoentsch, A. Klunker, D. Spemann, H. Hochmuth, M. Lorenz and M. Grundmann, Electron paramagnetic resonance of $Zn_{1-x}Mn_xO$ thin films and single crystals, *Phys. Rev. B: Condens. Matter Mater. Phys*., 2005, **72**, 085214(6).