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Supplementary Material

Enhancing NIR Emission in $ZnAl_2O_4$:Nd,Ce Nanofibers by co-doping with Ce and Nd: a Promising Biomarker Material with a Low Cytotoxicity

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Supplementary Information 1.

The morphology of γ -Al_2O_3 is shown in **Figure S1 a and b.** The size distribution of nanofibers is uniform, and the average diameter is about 20-50 nm The as-received γ-Al_2O_3 fibers are of 200 nm to 1.2 μm long.

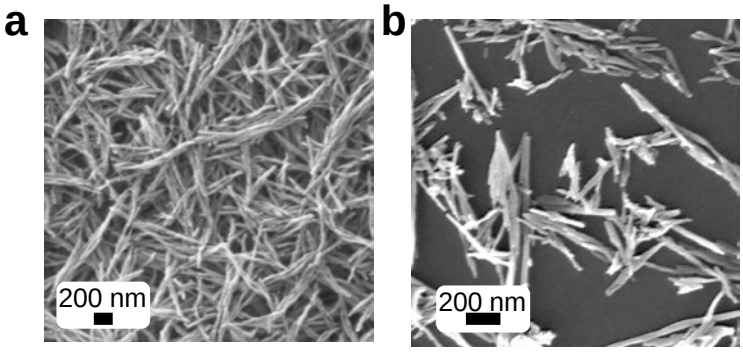

Figure S1. SEM micrographs of as-received γ-Al_2O_3 fibers

Supplementary Information 2.

The Zn K edge XAS spectra of references such as $Zn(NO_2)_3$ 6 H_2O and ZnO together with $ZnAl_2O_4$ undoped and 0.02 Nd, 0.06 (%mol) Ce co-doped nanofibers are shown in **Figure S2a**.

As $Zn(NO_2)_3$ 6 H_2O was employed as a precursor, the XANES study of this compound and ZnO were included. The zinc nitrate shows the main absorption peak at 9667 eV. XANES analysis of ZnO nanoparticles reveal the presence of three main features; the main absorption line is located at 9668 eV, there is a positive absorption line at 9679 eV and a low-energy structure at 9962 eV; these peaks are characteristic features of ZnO particles. [44]

The absorption energy edge of the $ZnAl_2O_4$ undoped and 0.02 Nd, 0.06 (%mol) Ce co-doped nanofibers is located at 9663 eV, confirming the $^{2+}$ oxidation state of Zn cations. There is no pre-edge region due to filled 3d orbitals. For Zn compounds, it has been observed that the near-edge structure exhibit particular characteristics related to ZnO_6 octahedral or ZnO_4 tetrahedral units, showing indeed different features. In the case of the compound with only ZnO_6 octahedral units, a strong initial peak (9670 eV) appears joined with a second well-defined second peak (9682 eV). These features can be observed for example in smithsonite compound ($ZnCO_3$)[45]. On the other hand, for the compounds that have only ZnO_4 tetrahedral units, the XANES has more complexity, showing at least three defined features due to many multiple scattering paths. The first feature is located lower energy (2 eV) in comparison with the octahedral Zn edge (9668), the other two peaks are located at 9671.8 and 9676 eV and a shoulder is situated at 9682.2 eV. Besides, a fourth peak appears at 9690 eV for a spinel structure such as franklinite, $ZnFe_2O_4$.

In comparison with the XANES spectrum of the Zinc nitrate, the spectra of $ZnAl_2O_4$ undoped and 0.02 Nd, 0.06 (%mol) Ce co-doped nanofibers split into three peaks at 9663, 9667 and 9672 eV and a shoulder at 9678 eV. This is consistent with the previous observations done by other authors in Zn compounds that have mainly ZnO_4 tetrahedral units. Specifically, these main three peaks have been observed by other authors in $ZnFe_2O_4$, establishing that the intensity of the second peak increases, and the positions of the peaks shift slightly to lower energies in case of inversion of the spinel. Moreover, the intensity of the shoulder located at 9677 eV decreases moderately. [46] Therefore, a qualitative assignation of tetrahedral and octahedral units can be established. Here, there is no considerable difference between the sample undoped and highly doped, so we can not conclude a

rough indication of tetrahedral or octahedral units. However, the presence of the four features at the energies previously indicated can be assigned mainly to tetrahedral contribution.

In normal spinel. $ZnAl_2O_4$ the zinc atoms are tetra-coordinated by oxygen at 1.996 Å and 12 Al atoms are at 3.500 Å as second neighbors.

X-ray absorption spectra were also collected at the Zn K edge at 9659 eV to examine the EXAFS(**Figure S2b**). The resulting data are plotted in **Fig. S2b.** Data are not phase corrected, to be consistent with previous literature reports. In the Fourier transform (FT) at the Zn K-edge, two main peaks are observable at 1.5 Å attributed to the first coordination shell related to Zn-O interaction that represents the [ZnO_4] tetrahedra. The second peak is located at 3 Å ascribed the second and third coordination shell related to the Zn- Al interaction and the Zn-Zn interaction ([ZnO_4]). A shoulder is also observable at 2.5 Å.

The Zn K edge EXAFS spectra for $ZnAl_2O_4$ undoped and 0.02 Nd, 0.06 (%mol) Ce co-doped nanofibers were fit up to the second shell using the ARTHEMIS software. The scattering paths were obtained from FEFF6.

For the Zn K-edge EXAFS spectrum of $ZnAl_2O_4$, the only large second peak was found at 3 Å, indicating the occupancy of all Zn^{2+} ions in the tetrahedral (A) sites. [47] (**Figure S2b**). The appearance of an additional peak at 2.5 Å indicates Zn octahedrally coordinated, it means Zn atoms occupy B sites, appearing a new shell of Al atoms from central Zn. The contribution around 2.5 Å in the FT should increase if the inversion rate is higher and the opposite trend should occur for the peak located at 3Å [48]. From experimental results obtained, a low degree of inversion seem to be present since at the Zn K-edge the most intense peak is centered at about 3Å (mostly tetrahedral environment). These results corroborate the results obtained in XRD refinement.

Table 1. Fitting results around Zn^{2+} of at Zn K-edge spectra EXAFS

Sample	**ZnO**		**$ZnAl_2O_4$ undoped**		**$ZnAl_2O_4$ 0.02 Nd, 0.06 (mol%)**	
Shell	Interionic distance (Å)	σ (10^{-3} Å^2)	Interionic distance (Å)	σ (10^{-3} Å^2)	Interionic distance (Å)	σ (10^{-3} Å^2)
Zn-O	1.969 ± 0.003	6.3 ± 0.9	1.937 ± 0.012	6 ± 1	1.936 ±0.012	6 ± 1
Zn-Al 2nd Shell	-		3.313 ± 0.022	5 ± 2	3.313± 0.022	5 ± 2
Zn-O 2nd Shell	-		3.249± 0.033	9 ± 5	3.249 ±0.033	9 ± 6
Zn-Zn 2nd Shell	3.239 ± 0.001	9.5 ± 0.5	3.535± 0.017	5 ± 1	3.5343± 0.017	5 ± 1

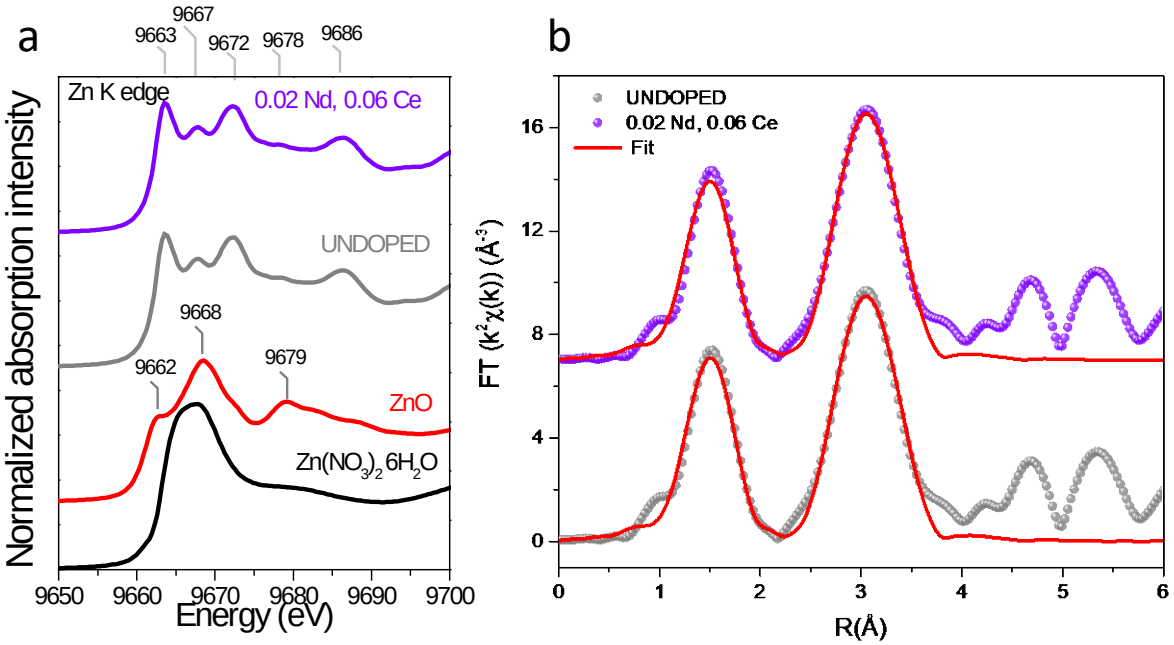

Figure S2. XANES and EXAFS study of Zn K edge of $ZnAl_2O_4$ undoped and 0.02 Nd, 0.06 (%mol) Ce co-doped nanofibers **a** XANES Zn K edge spectra. **b.** FT k2-weighted magnitude of the Zn K EXAFS across $ZnAl_2O_4$ undoped and 0.02 Nd, 0.06 (%mol) Ce co-doped nanofibers. The first coordination shell Zn-O is aroun 1.5 Å and the second coordination shell for Zn-Zn, Zn-O and Zn-Al scattering paths is around 3.0 Å. Data are not phase corrected, to be consistent with previous literature reports.

Supplementary Information 3.

To carry out the cytotoxicity study, assays wre performed on tumor epithelial cell line HeLa. The HeLa cells were incubated with a 1, 10 and 100 µg/mL concentration of $ZnAl_2O_4$ nanofibers for 24h. After that, cell viability was determined by the (3-(4,5-dimethylthiazol-18 2-yl)-2,5-diphenyltetrazolium bromide, called as MTT assay.

The cell survival was determined from the 540 nm absorption band is measured in each assay. The results were expressed as a percentage in comparison with control cells.

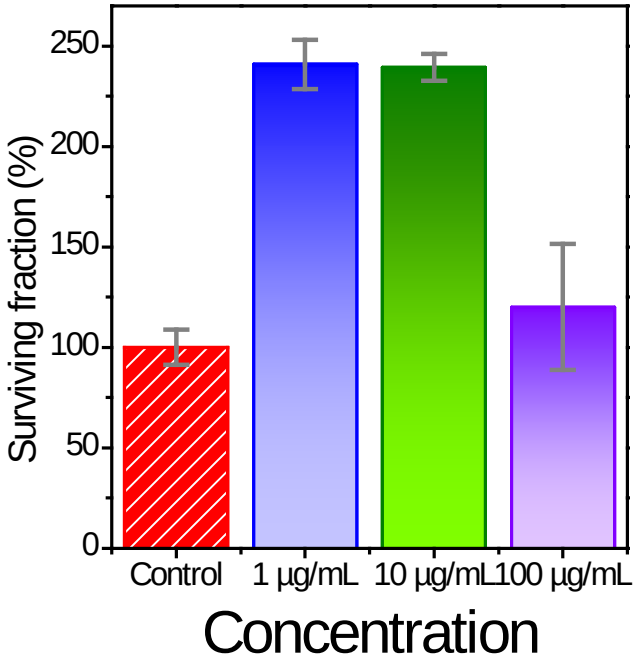

Figure S3. Cytotoxicity of nanofibers. Each data represents the mean values at least five independent experiments. The results were expressed as a percentage in comparison with control cells.