Electronic Supplementary Information

Photoluminescence quenching

in compressed MgO nanoparticle systems

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Materials characterization data of different compressed particle systems.

Table S1. Average nanocrystal sizes determined using the Debye Scherrer equation (d_{XRD}), specific surface area calculated from average nanocrystal sizes (S_{XRD}), specific surface area determined from N₂ adsorption (S_{BET}), and the resulting interface area.

	ρ_{MgO} < 1%	$\rho_{MgO} = 15\%$	$\rho_{MgO}{=}30\%$	$\rho_{MgO} = 50\%$
d _{XRD} / nm	7.6 ± 1.0	8.4 ± 1.0	12.0 ± 1.0	11.1 ± 1.0
$S_{XRD} / m^2 g^{-1}$	221 ± 29	200 ± 24	140 ± 12	151 ± 14
normalized S_{XRD} / $m^2 g^{-1}$	303 ± 40	274 ± 33	191 ± 16	207 ± 19
$S_{BET} / m^2 g^{-1}$	303 ± 30	292 ± 29	163 ± 16	108 ± 10
Interface area (S _{XRD} - S _{BET}) / $m^2 g^{-1}$			28	99



Figure S1. Distribution in pore sizes as determined from analysis of N₂-adsorption isotherms of MgO powders with relative densities of $\rho_{MgO} < 1\%$ up to $\rho_{MgO} = 50\%$.

Nitrogen sorption isotherms were obtained at 77 K using an adsorption porosimeter (Micromeritics ASAP 2020) (Figure S1). Samples were outgassed for 6 h in the degas unit of the adsorption apparatus at 473 K under vacuum prior to analysis. The BET surface area SBET was evaluated using adsorption data in a relative pressure range p/p0 from 0.05-0.2.



Figure S2: Representative TEM images of compressed MgO nanocube samples of MgO powders with relative densities of $\rho_{MgO} < 1\%$.



Figure S3: Representative TEM images of compressed MgO nanocube samples of MgO powders with relative densities of $\rho_{MgO} = 50\%$.

Organization of the combined PL and EPR measurements

The combined EPR and PL measurements were organized in the following way: for each type of powder sample - compressed or uncompressed - we determined the maximum number of spins related to O_3^- ions which were generated by UV excitation in oxygen atmosphere with EPR spectroscopy. Comparable masses of particle powders in the range 10 and 100 mg were used and the filling height inside the quartz glass cell was adjusted to similar values. For determining the concentration of O_3^- ions per sample mass we used a previously established quantification approach which is outlined in detail in reference [1]. By accounting for the average particle size² these values were then translated into EPR intensities/ particle. In a typical room temperature experiment we exposed the nanoparticle ensemble to UV light with a photon energies of hv = 4.6 eV and a light power of 0.2 mW•cm⁻². Total illumination times were typically in the range between two and four hours. The geometric alignment of the quartz glass cell with respect to the light source was changed for approximately 2-3 times per experiment to achieve a maximum number of radicals corresponding to $\gamma = 1$ (Figure S4).



Figure S4: Schematic showing the organization of the experiment to determine the the fractional illumination volume.

In a second step we exposed the powder samples inside the PL/ EPR quartz glass tubes simultaneously to oxygen ($p(O_2) = 1$ mbar) and UV light using the excitation source of the PL spectrometer system (hv = 4.6 eV and with light power of 0.03 mW·cm⁻²).³ In the course of this type of experiment which corresponds to the typical PL measurement we kept the same position and orientation of the sample cell with respect to the light source. After that and without breaking the vacuum or – in case of oxygen gas containing sample volumes – without changing the gas phase composition the sample cells were connected to the high vacuum rack of the EPR spectrometers system and cooled to 140 K for subsequent EPR spectrum acquisition (Figure 3a). Spin concentrations related to photogenerated O_3^- ions were determined via the peak to peak amplitudes of the distinct EPR signals in conjunction with double integration of the signal after evacuation (Figure 3b). As a result we obtained the fractional illumination volume V_i , i.e. the percentage of particles that can be reached by UV excitation and emit light during the PL measurements (Figures S4 and 2), for the different γ .

References

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