Photoluminescence quenching in compressed MgO nanoparticle systems†

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Efficient use of highly dispersed metal oxides for lighting, energy conversion and catalysis requires knowledge about the impact of density and microstructure of the powders on the optical nanoparticle properties. For MgO nanocube powders we present a combined photoluminescence (PL) and electron paramagnetic resonance (EPR) approach which enables for samples of different aggregation states the quantification of the fractional powder volume that becomes illuminated with UV and visible light during the PL measurements. Using O₂ as a PL emission quencher and – after light induced exciton separation and oxygen adsorption – as an EPR active adsorbate we observed clear aggregation dependent trends in PL emission quenching that originate from particle–particle contacts. Upon interaction of low coordinated surface elements with the surfaces of adjacent MgO nanocubes, which occurs even at powder consolidation levels that escape sorption analysis, the radiative decay of excited surface states becomes quenched down to 15% of the original intensity. Our results underline the critical role of microstructure and the aggregation state of a nanoparticle ensemble with respect to spectroscopic properties and related adsorption induced changes.

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Introduction

The fabrication of electronic devices containing nanocrystalline components and catalyst design are two examples where controlled microstructure manipulation on the atomic level plays an outstanding role.¹ Based on particle systems as the primary components for microstructure formation new materials design approaches have emerged. Functional nanocrystalline materials with aggregation levels varying between that of a loose nanoparticle agglomerate and that of a dense polycrystalline ceramic can be engineered through powder compression and subsequent sintering procedures.^{2,3} The properties of such materials depend on the size, chemical composition and structure of constituent grains, as well as the nature of interfacial regions between grains and intergranular pores.^{4–7} However, analyzing and controlling abundance and properties of interfacial regions in nanocrystalline oxides are extremely difficult and pose a major challenge to the design of high performance functional materials. Interfacial regions in MgO may gain

substantial influence with respect to the material properties of the entire particle ensemble. Elastic properties were found to be markedly affected by the nature of grain boundary networks.⁸ Relevant for the field of heterogeneous catalysis it is expected that structurally disturbed zones at the grain boundary areas in consolidated powders of MgO polycrystals exhibit increased surface acidity and basicity in parallel.⁹ This effect has been explained by the electronic perturbation of the coordinatively unsaturated surface ions in the grain boundary region and is reflected by the major enhancement of catalytic activity as measured by Knoevenagel condensation or transesterification reactions.¹⁰

It was found that compression of ensembles of small MgO particles and – concomitantly – the increase of interfacial contacts between them can give rise to new optical features¹¹ as well as to the depletion or enhancement of features, which are linked to free particle surfaces. In order to account for related trends it is necessary to quantitatively assess the optical properties of an entire particle ensemble. This is a challenging task since highly dispersed particle powders exhibit enhanced reflectivity. The penetration depth of photoluminescence (PL) excitation and emission light, for example, strongly depends on the state of aggregation and, thus, on porosity and concentration of particle–particle interfaces in the respective sample volume. As demonstrated by Fig. 1, the porous microstructure of compressed MgO particle powders is responsible for the opaque materials appearance. Particle powder compression shifts the pore size distribution curve to values below the wavelength of visible light.¹²

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Fig. 1 Light scattering effects of uncompressed (left) and compressed powder pellets (right, the same amount of powder). The significant increase in the transmission of visible light (i.e. in the translucence) is demonstrated for a pellet with a relative powder density of 50% (right side) relative to the density of a MgO single crystal ($\rho = 3580 \text{ kg m}^{-3}$).

From a practical perspective, the controlled generation and the precise engineering of nanoparticle interfaces are important for many applications. For most high surface area directed applications which involve adsorption processes and surface reactivity it is important to keep the concentration of solid-solid interfaces and grain boundaries low. For ceramics, on the other hand, it is necessary to transform loose powders into compacted solids and to subsequently subject these compacts to thermal treatment. Sintering is a critical part of ceramics processing and starts with an assembly of contacting particles.² Initial contacts range from point contacts to highly deformed interfaces. Upon sintering the contacts grow in size, and in the initial stage there is extensive loss of surface area. In parallel to these transformations, the structure of the residual pores becomes rounded and the originally discrete particles are less evident. The dramatic impact of such microstructural changes on the nanometer scale on large-scale properties is well illustrated by the development of transparent ceramics. Residual porosity in wide band gap materials like Al_2O_3 , ZrO_2 or MgO leads to substantial loss of visible light transmission *via* light scattering at the oxide-air interface (Fig. 1).^{13–15}

MgO nanocube ensembles have been the subject of numerous previous investigations and are perhaps some of the best understood ceramic nanomaterials.^{16–19} In previous work, a variety of spectroscopic techniques^{20–25} as well as first-principles theoretical calculations^{26–29} have been used to investigate the electronic properties of MgO nanocubes formed by the controlled combustion of magnesium vapor. UV diffuse reflectance spectroscopy reveals two absorption bands far below the bulk absorption threshold of MgO (7.8 eV) which have been attributed to corner (4.6 eV) and edge sites (5.2 eV).¹¹ Photoluminescence spectroscopy detects two closely spaced photoemission bands at 3.2 eV and 3.4 eV that result from photoexcitation of corners and edges, respectively.^{30,31} While it was usually assumed that photons with sub-band-gap energy exclusively excite low coordinated surface sites more recent studies recognized the importance of the interactions between nanocrystals and contributed to a more complete description of metal oxide nanoparticle powders. We identified a PL emission process at 2.5 eV that is linked to nanocube interfaces.¹² First principles calculations provide plausible candidates for both light absorbing and emitting sites which involve different interface features.^{27,28}

It was found that interfaces between nanocube edges and terraces induce a significant electrostatic perturbation of the interfacial electronic states leading to exciton generation and luminescence at lower energies than those related to corners and edges of MgO nanocubes.¹²

The aim of the present study is to describe in a systematic and quantitative way how interfacial contacts between MgO nanocubes inside a given nanoparticle ensemble affect surface excited states. Obtained insights should methodologically advance the investigation of optical property changes associated with solid-solid interfaces in strongly scattering particle systems. Respective characterization work is motivated by the fact that solid-solid interfaces do interact with other point defects, impact radiation damage evolution,^{32–34} mass transport and sintering,^{2,35} adsorption on nanocrystalline materials,⁴ and catalysis in general.^{9,10,36}

Experimental

MgO nanocube powder synthesis, compression and thermal activation

For the purpose of the present study we made use of four MgO nanocube ensemble types at different states of pressure induced aggregation and, thus, concentrations of solid-solid interfaces. Structural, microstructural and the general spectroscopic properties were described elsewhere¹¹ and are briefly summarized in Table 1 and described in more detail in the ESI.†

For the production of MgO nanocubes we use a chemical vapor synthesis (CVS) procedure corresponding to the controlled evaporation and subsequent oxidation of alkaline earth metals under reduced pressure.¹¹ After production, the MgO nanocrystal powder is transferred into quartz glass cells, which allow one to perform thermal activation of the nanocrystal powders in defined gas atmospheres. To obtain well-defined cubic MgO nanocrystals, the as-prepared MgO powder is cleaned of organic contaminants by heating to 1123 K at a rate of 5 K min^{-1} and exposing to molecular oxygen at this temperature (10 mbar). Then, the sample temperature is raised to 1173 K at pressures $p < 5 \times 10^{-6}$ mbar and kept at this temperature for 5 h until full dehydroxylation of the sample surface is achieved. This procedure forms low-density

Table 1 Nanocrystalline MgO pellets produced by applying different uniaxial pressures. The table contains the samples' relative densities, surface and interface areas

Sample MgO	Pressure/Pa	Relative density ^a $\rho_{\text{MgO}}/\%$	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	Interface area ^b / $\text{m}^2 \text{ g}^{-1}$
RD 0.01	0	<1	303 ± 30	0
RD 0.15	5×10^7	15	292 ± 29	0
RD 0.30	1×10^8	30	163 ± 16	0
RD 0.50	1.7×10^8	50	108 ± 10	99

^a The relative density of the pellet is given as a fraction of the density of a MgO single crystal (3580 kg m^{-3}). ^b The interface area between nanocubes increases with relative density at the expense of surface area. For its determination we used the difference between the calculated value which was derived from the Scherrer equation (crystallite domain size) and the measured surface area S_{BET} obtained *via* application of the BET-model. Further details and assumptions related to this approach are provided in the ESI and in ref. 12.

powders (less than 1% of the bulk MgO density, $\rho_{\text{MgO}} = 3580 \text{ kg m}^{-3}$), and transmission electron microscopy (TEM) demonstrates that they consist of agglomerated cubic nanocrystals. A defined mass of the powder is transferred into a 0.05 cm^3 cavity and a hydraulic press is used to compact the powder. By varying the pressure applied, compressed powders of densities up to 50% can be obtained in a controlled and reproducible way (Table 1). After pressing, the MgO pellets were subjected to oxidation in 10 mbar oxygen at 1123 K for 10 min and an additional vacuum annealing procedure at 1173 K for 5 h at pressures below 5×10^{-6} mbar to achieve perfect sample dehydroxylation.

Photoluminescence measurements

Room temperature photoluminescence (PL) measurements were carried out using Suprasil quartz glass tubes which guarantee vacuum conditions better than 5×10^{-6} mbar. (The same cells were employed for electron paramagnetic resonance (EPR) measurements.) PL spectra were measured using a Perkin-Elmer LS 50B system and a pulsed Xe discharge lamp served as an excitation source as well as an irradiation source for UV-induced surface chemistry (generation of oxygen radicals, see below). The light power was specified by Perkin Elmer to be equivalent to 20 kW for 8 μs pulse duration. Further details about the optical properties of MgO nanocube powders including the spectral data of the used instruments are provided in ref. 11.

Electron paramagnetic resonance measurements

For EPR measurements, the powder sample was contained within the above mentioned Suprasil quartz glass tube connected to an appropriate high vacuum pumping system with a base pressure $p < 10^{-6}$ mbar. This allows for thermal sample activation and UV irradiation *in situ*. A 300 W Xe lamp (Oriel) was used as an UV source. The light beam was passed through a water filter to exclude IR contributions from the excitation spectrum and a bandpass filter (265 FS 10-50 (P228-01)) to set an irradiation wavelength of $\lambda = 270 \text{ nm}$. Light power was measured using a bolometer (International Light). It was held constant at $P_{\text{irr}} = 0.2 \text{ mW cm}^{-2}$ at $\lambda = 270 \text{ nm}$ throughout all experiments. During UV exposure, the samples were held at a temperature of $T = 293 \text{ K}$. For EPR measurements the samples were cooled to $T = 140 \text{ K}$. X-band EPR measurements were performed on a Bruker EMX Micro spectrometer using a Bruker ER 4119 HS resonator. For measurements at $T = 140 \text{ K}$ an ER 4131 VT variable-temperature accessory was used. EPR computer simulations were done using the SIM 14S program. The g values were determined on the basis of a DPPH standard.

Results and discussion

Photoluminescence quenching by O_2

Surface excitons are well suited quantitative probes for the characterization of optical powder properties. The photoluminescence emission related to the photoexcitation of MgO nanocube corners ($h\nu = 4.6 \text{ eV}$, quantum yield $\Phi = 0.05$) and

Fig. 2 Relative PL emission band intensity development on MgO nanocube samples with increasing O_2 pressure. The spectra shown in (a) correspond to the emission process which is linked to the photoexcitation of MgO nanocube edges ($h\nu_{\text{exc}} = 5.4 \text{ eV}$). (b) Plots related to PL intensity decrease in the oxygen partial pressure range $0.05 \text{ mbar} \leq p \leq 10 \text{ mbar}$. The values related to relative intensity = 100% correspond to the PL emissions acquired on a MgO powder sample at $p < 5 \times 10^{-6}$ mbar.

nanocube edges ($h\nu = 5.4 \text{ eV}$, quantum yield $\Phi = 0.20$) are characterized by two closely spaced emission bands at 3.2 eV and 3.4 eV, respectively.¹¹ PL emission from MgO nanoparticle surfaces competes with nonradiative pathways of surface exciton deactivation. In Fig. 2a the impact of molecular oxygen as a photoluminescence quencher³⁷ is demonstrated for the emission process that originates from the photoexcitation of MgO nanocube edges with $h\nu = 5.4 \text{ eV}$ light. Fig. 2b shows that the O_2 pressure dependent relative emission intensity decreases corresponding to the two processes of radiative surface exciton deactivation.³¹

Electron paramagnetic resonance: UV induced oxygen radical formation

In addition to collisional PL quenching of surface excited states by O_2 molecules impinging from the gas phase (Fig. 2), there exists also exciton splitting.^{32,38} This process corresponds to the decomposition of a surface excited state into a hole and an ejected electron.^{39,40} Being subject to the temperature of the powder this either leads on MgO surfaces to O_3^- (Fig. 3a and b) or O^- (Fig. 3c) with characteristic EPR signatures of hole acceptors.^{39,41}

Fig. 3a shows a characteristic EPR spectrum which was acquired after the powder had been exposed to monochromatic UV light ($h\nu = 4.6 \text{ eV}$) in an O_2 atmosphere and which was then cooled from $T = 298 \text{ K}$ to $T = 140 \text{ K}$. The three component signal is associated with a specific surface ozonide anion type at oxygen terminated corners (first and second rows of Fig. 3).^{39,41,42} Upon pumping the sample volume down to $p < 10^{-6}$ mbar the spectral features become more distinct (Fig. 3b). This effect is attributed to the removal of physisorbed paramagnetic O_2 molecules which can interact with paramagnetic surface species *via* spin-exchange interaction and lead to O_2 pressure dependent signal broadening (Fig. 3a). In addition to the O_3^- specific g factors (Fig. 3b and Table 2) an additional feature at $g = 2.008$ related to the g_{yy} component of superoxide anions O_2^- emerges.^{41–43} Its presence provides evidence for an efficient transfer of surface trapped electrons to molecular oxygen. Consistent with earlier studies,^{39,41} sample warming to temperatures above $T = 200 \text{ K}$ decomposes the ozonide signal upon release of O_2 molecules into the gas

Fig. 3 EPR spectra related to uncompressed MgO nanocrystal samples after UV exposure to 4.6 eV light in an O_2 atmosphere. (a) Spectrum acquired in the presence of O_2 (1 mbar), (b) after subsequent pumping at the spectrum acquisition temperature $T = 140$ K and (c) after intermediate warming to room temperature.

Table 2 EPR parameters of oxygen radicals detected with EPR spectroscopy at $T = 140$ K (Fig. 3)

O_2^-	$g_{\perp} = 2.0358$	$g_{\parallel} = 2.0023$	
O_2^-	$g_{yy} = 2.0080$	$g_{xx} = 2.0023$	
O_3^-	$g_{zz} = 2.0103$	$g_{yy} = 2.0157$	$g_{xx} = 2.0023$

phase and the emergence of a two component EPR signal with $g_{\perp} = 2.036$ and $g_{\parallel} = 2.002$ (Table 2) as a EPR spectroscopic fingerprint of trapped hole centers located at an oxygen terminated corner.

Determination of the fractional illuminated powder volume V_i by combined PL and EPR measurements

We prepared MgO nanocube powder samples with different levels of particle aggregation (Table 1). Since light scattering and, consequently, the penetration depth of light are subject to the aggregation state inside the illuminated particle volume (Fig. 1),¹¹ the integral intensity values of PL emission need to be corrected for the fractional powder volume that is effectively illuminated. For this purpose we developed a combined PL and EPR spectroscopic approach that addresses the effect of O_2 adsorption on nonradiative exciton annihilation (PL quenching, Fig. 2) and determined at the same time the evolution of oxygen radicals emerging from exciton separation and interfacial charge transfer (EPR, Fig. 3b).

The combined EPR and PL measurements were organized in the following way: for each type of powder sample – compressed or uncompressed – we determined with EPR spectroscopy the maximum number of spins related to O_3^- ions inside the entire powder sample after exposure to UV excitation in an oxygen atmosphere (Fig. 3b). For this purpose the sample cell, which was connected to a flexible high vacuum tubing, was shaken and rotated for a couple of times in order to achieve a sufficient intermixture between the different powder regions. For determining the concentration of O_3^-

ions per sample mass we used a previously established quantification approach which is outlined in detail in ref 44 and 45. By accounting for the average particle size¹¹ these values were then translated into EPR intensities/particle.

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 ($h\nu = 4.6$ eV and with light power of 0.03 mW cm^{-2}).¹¹ 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 the 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 spectrometer system and cooled to 140 K for subsequent EPR spectrum acquisition (Fig. 3a). Spin concentrations related to photo-generated 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 (Fig. 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 (Fig. 2), for the different compressed particle samples (Table 3).

Significant differences in the V_i values can be concluded from Table 3. Their non-monotonous development with an increasing level of pressure induced consolidation is explained by the fact that various microstructure related factors, such as grain size growth, pore size distribution and the amount of solid–solid interfaces, contribute to the overall scattering characteristics of each sample in different ways.⁴⁶

Typical UV exposure times of less than 3 hours were sufficient to achieve for a given sample cell orientation the maximum radical concentration inside a fractional powder volume. Fig. 4 demonstrates for a compressed MgO nanoparticle powder (MgO RD 0.50) with a relative powder density of 50% that only a part of the entire sample volume, *i.e.* the coloured region in the image of Fig. 4a, is accessible to UV light. Clearly visible to the eye, the brownish powder part corresponds to an optical absorption feature with a maximum at 2.9 eV plotted in the UV diffuse reflectance spectrum (Fig. 4b).

Table 3 Nanocrystalline MgO pellets and the correction factors for the fractional illuminated volume V_i

Sample	Relative density $\rho_{MgO}^a/\%$	Fractional illumination volume ^b $V_i/\%$
MgO (RD 0.01)	< 1	28 ± 3
MgO (RD 0.15)	15	20 ± 2
MgO (RD 0.30)	30	46 ± 5
MgO (RD 0.50)	50	28 ± 3

^a The relative density of the pellet is given as a fraction of the density of a MgO single crystal (3580 kg m^{-3}). ^b The fractional illumination volume corresponds to the ratio of number of illuminated particles/total number of particles (or volume of illuminated particles/total sample volume).

Fig. 4 Powder coloration of compressed MgO nanoparticle samples after UV exposure in an O_2 atmosphere (1 mbar). The brown coloured powder region at the front side of the quartz glass cell in image (a) corresponds to the broad absorption in the visible light region (brown line) of the diffuse reflectance spectrum in (b). As a reference, the black line corresponds to the UV-Vis diffuse reflectance spectrum of the sample backside which was not reached by UV light.

In terms of oxygen partial pressure and temperature dependent stability this effect displays similar characteristics to the EPR fingerprints of O^- radicals which start to degrade upon pumping at temperatures above $T = 373$ K. Consequently, we attribute this absorption feature to surface trapped hole centers rather than to O_3^- ions as their oxygen adducts.^{47,48}

Particle aggregation dependent PL emission yield trends

The ionic character of chemical bonding in MgO implies a strong dependence of the electronic structure on the local coordination of surface ions. The question arises to what extent interactions between nanocube corners and edges on adjacent particles do influence their electronic structure and in particular the fate of associated surface excitons. Comparison of Fig. 5a (uncorrected data) with those corrected for light scattering loss (Fig. 5b) points to the importance to account for the number of nanocubes reached by UV light as well as for pressure induced microstructural changes inside the powders. After correction, we observe a dramatic decrease in PL emission even for a slightly compressed sample such as MgO RD 0.15 (Table 1 and Fig. 5b).

Fig. 6 underlines an important point concerning the sensitivity of radiative exciton deactivation towards the mutual distance between particles. Comparison of the PL emission intensities observed for a loose MgO nanoparticle powder sample (MgO RD 0.01, Fig. 6a) with that of a compressed MgO powder of low relative density (MgO RD 0.15, Fig. 6b) reveals a significant PL emission intensity decrease. The high specific surface areas of the two samples, however, are comparable (Table 1). In other words, sorption analysis excludes a significant loss of surface area which is accessible to N_2 molecules. This indicates that the electronic structure of (i) oxygen terminated corners and/or of (ii) MgO nanocube edges which guide excitons from the excitation sites to the emission sites⁴⁰ become significantly perturbed as PL emission sites upon low levels of aggregation.

Fig. 5 PL emission intensities of loose MgO nanocube powders in comparison to consolidated samples (MgO RD 0.01 versus MgO RD 0.15 to RD 0.50). While panel (a) shows the obtained intensity values panel (b) plots the values which were corrected for changes in the fractional illumination volume (Table 3).

For grain boundaries in ionic metal oxides theory predicts that the boundary structure has an important impact on point defect-boundary interactions.⁴⁹ Furthermore, as a particularity of nanocrystalline ceramics, the small average crystallite size leads to a situation where the volume fraction of interfacial regions between the randomly oriented crystallites can become as high as that of the bulk. Consequently, a significant fraction of the material consists of interfaces and these may induce particular functions to the integral solid. A recent study in the field of heterogeneous catalysis revealed that densification of MgO aerogel derived nanostructures increases their acid-base properties by a factor of 1.8 to 3.⁹ These experimental findings were rationalized by the hypothesis that coordinatively unsaturated surface ions near the grain boundaries, *i.e.* at the distance of the first four atomic layers from the geometrical contact plane, become displaced upon consolidation. Resulting occupied states in the band gap alter the materials' catalytic activity. Apart from the difference in particle synthesis – gas phase synthesis as a solvent free technique *versus* the sol-gel

Fig. 6 Corrected intensity values related to the PL emission originating from the photoexcitation of MgO nanocube edges ($h\nu_{\text{exc}} = 5.4$ eV). The associated specific surface areas were determined using the BET model for the analysis of N_2 sorption isotherms (S_{BET}). The points labeled (a)–(d) are associated with the MgO samples RD 0.01, 0.15, 0.30 and 0.50, respectively.

based fabrication of aerogels – the here employed particle system with a relative density of 15% (MgO RD 0.15, Table 1 and Fig. 6b) exhibits a significantly lower level of consolidation than those discussed in ref. 9. PL spectroscopy is a particularly sensitive technique and well-suited for the characterization of oxide surfaces relative to adsorption, catalysis, and photocatalysis. As an example adsorption processes which involve submonolayer surface coverages of hydrogen can be tracked on nanocrystalline MgO systems.²⁵ Here we show that only minor changes in the aggregation level have a strong effect on the electronic properties of MgO corners and edges. The non-radiative annihilation of surface excitons clearly indicates surface electronic structure changes upon particle powder compression. When nanocrystalline metal oxides are employed as catalysts or as bare catalyst supports particle consolidation is usually performed to achieve sufficient mechanical strength of the material against gas stream induced loss of particles. So far neglected structural features such as particle contacts which may lead to distinct spectroscopic features¹¹ may also deplete those associated with specific surface elements of free particle surfaces and potentially affect the chemical reactivity of the entire particle ensemble.

Sample preparation for materials characterization is connected to another important aspect related to particle–particle interfaces. In order to perform spectroscopic measurements in the transmission mode, nanoparticle powders are usually pressed into pellets, inevitably generating nanocrystal interfaces. A deeper understanding of how interfaces affect optical properties may open the way to use optical spectroscopy as a probe of the electronic properties of interfaces between nanocrystals, which are thought to be important for effects such as magnetism in nanopowders⁵⁰ and for understanding the dynamics of electrons and holes under irradiation. More research in experiment and theory is needed to address the complex problem of interface activity of consolidated high surface area materials.

Summary

Electron paramagnetic resonance was used to measure the concentration of oxygen radicals which emerge from UV excitation of MgO nanocube powders in an O_2 atmosphere. At the same time we tracked the O_2 dependent PL quenching effects and employed the combination of both spectroscopic techniques to determine the fractional powder volume accessible for UV light of metal oxide nanoparticles at different states of aggregation. On this basis we realized for compressed MgO nanocube ensembles a disproportionate reduction of PL intensity with an increasing level of consolidation. Even at concentrations of particle contacts that are below a level that can be tracked by N_2 sorption analysis they critically affect the optical material properties. From a methodological point of view the here reported approach provides a base for a correct determination of the number of illuminated particles and to reliably compare PL emission trends that originate from the photoexcitation of corners and edges in compressed nanocube powders.¹¹ A related impact of particle–particle contacts on surface excitonic transitions in insulating polycrystalline metal oxides is relevant to radiation damage evolution, mass transport and sintering and adsorption on nanocrystalline materials.

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