Changing interfaces: Photoluminescent ZnO nanoparticle powders in different aqueous environments

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Abstract

We transformed vapor phase grown ZnO nanoparticle powders into aqueous ZnO nanoparticle dispersions and studied the impact of associated microstructure and interface property changes on their spectroscopic properties. With photoluminescence (PL) spectroscopy, we probed oxygen interstitials $\text{O}_2^-$ in the near surface region and tracked their specific PL emission response at $h\nu_{EM} = 2.1$ eV during the controlled conversion of the solid-vacuum into the solid-liquid interface. While oxygen adsorption via the gas phase does affect the intensity of the PL emission bands, the $\text{O}_2$ contact with ZnO nanoparticles across the solid-liquid interface does not. Moreover, we found that the near band edge emission feature at $h\nu_{EM} = 3.2$ eV gains relative intensity with regard to the PL emission features in the visible light region.

Searching for potential PL indicators that are specific to early stages of particle dissolution, we addressed for aqueous ZnO nanoparticle dispersions the effect of formic acid adsorption. In the absence of related spectroscopic features, we were able to consistently track ZnO nanoparticle dissolution and the concomitant formation of sol- vated Zinc formate species by means of PL and FT-IR spectroscopy, dynamic light scattering, and zeta potential measurements. For a more consistent and robust assessment of nanoparticle properties in different continuous phases, we discuss characterization challenges and potential pitfalls that arise upon replacing the solid-gas with the solid-liquid interface.

Keywords

Aerosols; Colloids; Particle agglomeration; Photoluminescence; Oxygen interstitials

1 Introduction

Interfaces of ZnO nanomaterials with a wide spectrum of applications determine their catalytic and electronic properties. This has generated a continuously growing interest in the
synthesis of ZnO nanomaterials as well as in the engineering of related interfaces and defects. The functionality of ZnO varistors, as one example, is based on the non-ohmic current-voltage characteristics of the semiconductor. The respective material is typically derived from ceramic slurries of ZnO particles and specific additives [1]. Drying, calcination, and additional processing steps typically affect nature and composition of the materials bulk and associated interfaces. As another example, ZnO is a widely used inorganic phosphor and the number of publications related to the research topic ZnO nanoparticles and photoluminescence properties have increased exponentially over the last years. Recent research has addressed the relationship of photoluminescence emission properties and different defect types [2–16]. Despite the fact that ZnO nanoparticle surfaces and interfaces can have a key influence on the optoelectronic nanomaterials properties [17], their chemical and physical nature has remained unspecified in most of the reported studies. Considering that minor changes in synthesis, handling, and processing correspond to substantial changes in the interfacial properties, a particularly unsatisfactory situation is created where an increasing number of publications report discrepant results for one and the same material in nanoparticulate form.

Closely related to this, control over defect populations is needed to endow nanomaterials with new and desirable properties for electronics and catalysis. Engineering of defects is extremely demanding. Their generation, the increase or depletion of their concentration is associated with changes of related functional or unwanted properties and requires the address along the entire process chain. This includes the production of particle powders in different reaction media, particle processing, materials integration into devices, and ultimately, device operation which corresponds to materials exposure to electric current, heat, radiation, or mechanical stress. Many of these operation steps involve continuous phase changes and thus modifications of materials interfaces. Moreover, many optically and electronically active defects are expected to be directly linked to ZnO surfaces and interfaces. Systematic studies on the impact of nature and composition of the interface on the PL emission properties are, however, scarce [3,18–20].

In surface science, the PL properties of semiconducting metal oxides have received substantial attention over the past years [13,21]. Ellis and coworkers first related observed PL emission intensity variations on semiconductors to the adsorption of charge-donating and -accepting molecules and concomitant changes in the band bending [22,23]. Very recently, John T. Yates Jr. and coworkers have established on TiO\textsubscript{2} particles firm relationships between UV light induced band structure modification and PL intensity changes and employed respective PL emission properties as a sensitive indicator for surface potential changes [21]. The opposite influence of electron-donor and electron-acceptor molecules on the charge distribution in semiconductors correlates well with charging effects in metal oxide nanoparticles as observed by other spectroscopic techniques such as FT-IR [13,24] and EPR spectroscopy [25].

The spectroscopic properties of dry nanoparticle powders can be very different from those of identical materials in liquid dispersions. In the absence of efficient stabilization metal oxide nanoparticles in liquid dispersions undergo agglomeration upon changes of local particle concentrations. With regard to spectroscopic measurements interrogating a given sample
volume such effects generate severe experimental artifacts. This study focuses on the interplay between interface condition and photoluminescence properties of vapor phase grown ZnO nanoparticles. It explores their response to oxygen, gaseous and liquid water, and ultimately, to formic acid in aqueous dispersions.

2 Materials and methods

2.1 Nanoparticle synthesis

For the production of ZnO nanoparticle powders, we employed metal-organic chemical vapor synthesis (MOCVS) with zinc acetate dihydrate (≥99.0%, Sigma-Aldrich) as precursor. Details about the particle synthesis and - relevant for the activated samples - the thermal activation procedure applied to remove synthesis related impurities are provided in Reference [26] and in the Supplementary Information (Fig. S1).

2.2 Materials characterization

Powder X-ray diffraction (XRD) measurements were performed on a Bruker AXS D8 Advance diffractometer (Cu Kα radiation, λ =154 pm) to reassure the ZnO-specific wurtzite phase and to determine the average crystallite domain size. For this purpose, we employed the Scherrer algorithm and used the integral width related to the reflexes at 2θ = 48°, 57°, and 63°. The size distribution of individual particles was derived from the analysis of transmission electron microscopy (TEM) data. For related measurements with a TECHNAI F20 microscope which was equipped with a field emission gun and S-twin objective lens the nanoparticle powder samples were cast on a holey carbon grid.

Dynamic light scattering (DLS) measurements on aqueous ZnO nanoparticle dispersions were performed with a Malvern Zetasizer Nano ZSP ZEN5600 to determine the size distribution of agglomerates. The zeta potential was calculated from the electrophoretic mobility using the Smoluchowski approximation. The applied voltage on the disposable folded capillary zeta cell was 40 V. To ensure an appropriate dispersity of the suspensions for the DLS measurements, an ultrasonic finger UP200St (Hielscher Ultrasonics GmbH) was used for typical irradiation times of 10 min while the sample dispersion was cooled in an ice bath for temperature control.

2.3 Spectroscopy

Photoluminescence (PL) emission spectra were recorded on a FLS980 PL spectrometer from Edinburgh Instruments. Two different measuring assemblies, i.e. the standard right angle geometry for liquid dispersions as well as a front-facing sample holder suitable for powder samples, were used.

FT-IR spectra of ZnO nanoparticle powders were measured in transmission mode using a high-vacuum cell developed by J.T. Yates Jr. and coworkers [27]. The sample powders were pressed into a tungsten grid that subsequently was mounted in the high-vacuum cell. The cell was aligned in the optical path of the IR beam of a Bruker Tensor 27 spectrometer system. The resolution was 3 cm⁻¹ and 20 interferograms were averaged for a reasonable signal-to-noise ratio.
For IR measurements of aqueous solutions, we used a glass cell in contact with the ZnSe prism that was placed in an ATR reflection unit (PIKE Technologies, Veemax II). This unit was attached to a Bruker Vertex 70 FT-IR spectrometer equipped with a MCT detector. Measurements were performed at an incident angle of 55° using unpolarized light. Spectra were obtained by averaging 100 scans at a resolution of 4 cm\(^{-1}\) and are represented as \(-\log(R/R_0)\), where \(R_0\) and \(R\) correspond to the reflectance values of the reference and the sample, respectively.

### 2.4 Particle ensemble transfer from vacuum to aqueous dispersions: Generation of solid-liquid interfaces

Aqueous ZnO colloidal dispersions were prepared via vacuum transfer techniques to avoid the uncontrolled influence of oxygen and other contaminants from the air. From high-purity water (specific resistance: 18.2 MΩ cm at 298 K), we removed dissolved gases using the freeze-pump-thaw method. The was added to the native and activated ZnO nanoparticle powders by condensing water from the vapor phase on the particle powders. The thermal activation procedure applied up to 673 K is outlined in Fig. S1 of the Supplementary Information [26].

### 2.5 Particles, primary particle agglomerates, and particle size distribution plots

Vapor phase grown nanoparticles adopt complex structures at the mesoscale level. While the primary aerosol particles can be identified by transmission electron microscopy (TEM) as smallest discrete objects, secondary particles are described as agglomerates or aggregates depending on the interaction forces which hold the secondary particles together [28,29]. The particle size distribution (PSD) plots in Fig. 1 compares ZnO nanoparticle data which were obtained via TEM analysis with size distribution curves (blue and red curve) that were acquired by dynamic light-scattering (DLS) measurements of ZnO nanoparticle dispersions in water.

The as-obtained ZnO\(_{\text{nat}}\) and ZnO\(_{\text{act}}\) nanoparticle powders with crystallite domain sizes of \(d_{\text{XRD}} = 4 \pm 0.5\) and \(9 \pm 0.5\) nm, respectively, display similar size distribution curves. While the primary particle size distribution shifts from \(d_{\text{TEM}} = 6\) to 14 nm as a result of thermal activation, neither size nor stability of associated agglomerates in aqueous dispersion (red and blue curve) seem to be affected by such treatment. For aqueous ZnO nanoparticle dispersions, the particle size distribution (PSD) functions with maxima at 70 nm (ZnO\(_{\text{nat}}\)) and 60 nm (ZnO\(_{\text{act}}\)) have been obtained after sonicating the particle dispersion for a period of \(t \geq 10\) min (Fig. 1).

### 3 Results and discussion

#### 3.1 Annealing induced spectroscopic property changes of ZnO nanoparticles

The IR spectrum of a powder of ZnO\(_{\text{nat}}\) nanoparticles shows broad absorptions in the region between 1700 and 1200 cm\(^{-1}\) and in the region between 3700 and 2500 cm\(^{-1}\) where sharper bands at 3665, 3618, and 3442 cm\(^{-1}\) do also appear (Fig. 2a). These contributions correspond to stretching vibrations of hydrogen bonded OH groups and are attributed to adsorbed water and remnants of the metal-organic precursor [30,31]. Characteristic OH bands have been
observed at 3572 and 3670 cm\(^{-1}\) on H—(1 x 1) O—ZnO(000-1) \cite{32} and mixed terminated ZnO(10-10) \cite{33} single crystal surfaces and at \~3495 cm\(^{-1}\) on powder samples \cite{34,35}. The region between 1700 and 1200 cm\(^{-1}\) contains contributions from antisymmetric \(v_{as}(\text{COO})\) and symmetric \(v_{s}(\text{COO})\) stretching vibrations as well as the \(\delta(\text{CH}_3)\) and the \(\delta(\text{HOH})\) vibrations related to remnants of the metal-organic precursor \cite{26,30,31,36}. Sample activation to 673 K produces significant changes in the IR spectrum (ZnO\(_{\text{act}}\)) such as the intensity decrease of the broad absorption between 3700 and 2500 cm\(^{-1}\) and the simultaneous emergence of sharper bands at 3665, 3617, and 3442 cm\(^{-1}\). Bands at 1519, 1386, 1331, and 1032 cm\(^{-1}\) point to the presence of carbonate and carboxylate species \cite{30,31}. We conclude from our FT-IR observations that thermal sample activation leads to a substantial depletion of surface bound water. The concentration of precursor related carbonaceous species, however, remains essentially constant. This is consistent with a previous Auger Electron Spectroscopic (AES) surface analysis which revealed comparable carbon concentrations at the level of 5% for both types of powders, ZnO\(_{\text{nat}}\) and ZnO\(_{\text{act}}\) \cite{26}. In terms of morphology, the thermal activation procedure has not affected the particles’ aspect ratios or shape, while we observed a shift of the primary particle size distribution maximum from 6 to 14 nm (Fig. 2b and c).

3.2 From dry powders to colloidal dispersions

In a previous study, we studied vapor phase grown ZnO nanoparticles in order to establish a relationship between photoluminescence emission properties and the composition of the solid-gas interface \cite{26}. The main results for ZnO\(_{\text{nat}}\) and ZnO\(_{\text{act}}\) nanoparticle powders are summarized in Fig. 3.

UV excitation light of \(h\nu_{\text{Exc}} = 4.6\) eV (\(\lambda_{\text{Exc}} = 270\) nm) produces a strong and broad PL emission band at \(h\nu_{\text{Em}} = 2.1\) eV (\(\lambda_{\text{Em}} = 590\) nm) on ZnO\(_{\text{nat}}\) nanoparticle powders (Fig. 3a). Underlying deep trap states are attributed to oxygen interstitials in the surface or near surface region \cite{3,37}. Consistent with this assignment, we identified an oxygen excess with Auger electron spectroscopy (AES) \cite{26}. Oxygen adsorption and resulting changes in the band bending of the ionic semiconductor \cite{13,26} were found to increase the intensity of the overall emission feature in a reversible way. The shift of its maximum points to the contribution of different spectral emission components the origin of which is not understood at the present.

Thermal sample annealing leads to changes in the PL emission spectra (Fig. 3b). While the maximum of the emission feature is shifted by 0.2 eV to lower energies, the band widths of a less intense orange PL emission at \(h\nu_{\text{Em}} = 1.9\) eV (\(\lambda_{\text{Em}} = 650\) nm), which is observed for the ZnO\(_{\text{act}}\) nanoparticle powder, is comparable to that of yellow emission band at \(h\nu_{\text{Em}} = 2.1\) eV related to the ZnO\(_{\text{nat}}\) powder. Both types of emissions have been related to excess oxygen in ZnO nanostructures \cite{6}. Similar annealing-induced changes in the emission energies have been observed for ZnO nanostructures which have been synthesized by very different chemical approaches like hydrothermal growth in solution \cite{23,38,39}. The activation-induced changes in the PL emission properties can be due to a variety of reasons that include changes in the level of non-stoichiometry of the oxide, the concentration of luminescent-related defects, particle size and shape and, ultimately, the composition of the
particle surfaces. In the present case, IR spectroscopy reveals that sample activation partially dehydrates the nanoparticle surfaces (Fig. 2), whereas the concentration of organic remnants seem to remain unaffected.

Since particle synthesis and subsequent sample activation have been performed under oxygen-rich conditions (p\([\text{O}_2]\) = 650 mbar), we can rule out changes in the stoichiometry of the oxide. The significant increase of the particle size from 6 nm for the native nanoparticle powder (ZnO\(_{\text{nat}}\)) to 14 nm for the activated nanoparticle powder (ZnO\(_{\text{act}}\)) (Fig. 1) points to significant mass transfer through the solid and ion mobility at the activation temperature of 673 K. Considering this we attribute the activation induced shift of the emission band maximum from 2.1 to 1.9 eV to the migration of oxygen interstitials toward the surface, in other words, to their conversion into surface defects.

On ZnO\(_{\text{act}}\) the PL emission at 1.9 eV is partially quenched by molecular oxygen (Fig. 3b) and exhibits a markedly different dependence on the oxygen pressure as compared to the band at 2.1 eV (ZnO\(_{\text{nat}}\), Fig. 3a). Powder density and related scattering properties of the samples [40] have a strong impact on the measured PL emission intensities. In addition to adsorption-induced effects, which are addressed in this study, we also found that the time of sample exposure to UV excitation light plays an important role. This is related to excitation light-induced charge separation processes which are similar to those observed on TiO\(_2\) particles [21,25] where associated modifications in electronic structure can occur on the time scale of minutes. A detailed investigation of these effects is underway. Important for this work is that all spectra shown were acquired under identical experimental conditions and spectrometer settings which also include comparable time of sample exposure to the excitation light of the spectrometer system (\(h\nu_{\text{Exc}} = 4.6\) eV, \(P = 0.4\) mW-cm\(^{-2}\), \(t < 10\) min).

For both ZnO\(_{\text{nat}}\) and ZnO\(_{\text{act}}\) nanoparticles, band bending is subject to hydroxylation and hydration. It depends on the surface abundance of mixed H\(_2\)O ad-layers, 1-coordinated hydroxyls and protons [41]. Allen and coworkers [42] have studied surface band bending on nonpolar (10-10) and (11-20) ZnO faces which are expected to correspond to the predominant surface terminations of ZnO micro- and nanocrystals. On these surfaces, the band bending was found to sensitively depend on nature of surface layer, i.e. the concentration of H\(_2\)O, OH\(^-\), or protons. At high OH coverage, downward band bending (and thus surface electron accumulation) is observed. The decrease of OH coverage as induced by UHV annealing reduces this effect and gives ultimately rise to upward bending at low coverage. The observations were rationalized by the surface modulating activity of water as an electron donor. Downward band bending (and thus surface electron accumulation) at high OH coverages can thus be converted into an upward bending at low coverage [42]. Consistently, the higher coverage with surface bound water on ZnO\(_{\text{nat}}\) as compared to ZnO\(_{\text{act}}\) nanoparticles (Fig. 2) must correspond to a decreased upward band bending at \(p < 10^6\) mbar (Fig. 4a). Addition of O\(_2\) as an electron acceptor, on the other hand, increases on ZnO\(_{\text{nat}}\) nanoparticles the surface depletion region (Fig. 4b).

Thermal activation decreases the level of surface hydration and hydroxylation (Fig. 2). Consequently, for ZnO\(_{\text{act}}\) nanoparticle powders, we expect an increased upward band bending at \(p < 10^6\) mbar and a minor effect of O\(_2\) on band bending (Fig. 4d and e).
During transformation of dry ZnO$_{\text{nat}}$ and ZnO$_{\text{act}}$ nanoparticle powders, we tracked the effect of H$_2$O addition via the gas phase with PL spectroscopy (Fig. 5) taking the properties of ZnO$_{\text{nac}}$ and ZnO$_{\text{act}}$ nano-particle powders (Fig. 3) as a reference. Addition of water vapor to ZnO$_{\text{nac}}$ and ZnO$_{\text{act}}$ significantly weakens the intensities of the emission band at 2.1 eV (Fig. 5a) and 1.9 eV (Fig. 5c), respectively. The relative changes of the PL emission in the visible light region of the two types of particle powders are attributed to adsorbed water as an electron donor [22,42], which leads to the flattening of the bands in the surface region (Fig. 4c,f).

PL spectra of ZnO$_{\text{nac}}$ and ZnO$_{\text{act}}$ particle dispersions are shown in Fig. 5b and d. Dry ZnO nanoparticle powders and aqueous ZnO nanoparticle dispersions exhibit entirely different scattering properties with strong implications on the respective PL emission yields. Consequently, different experimental setups for PL emission measurements are required. This renders a quantitative comparison of the PL emission of powders (Fig. 5a and c) with that of colloidal dispersions (Fig. 5b and d) impossible. However, there are interesting trends in the relative band intensities. A characteristic ZnO PL emission feature at $h\nu_{\text{Em}} = 3.2$ eV ($\lambda_{\text{Em}} = 390$ nm) originates from a near band edge (NBE) emission. It is only observable in the aqueous dispersion and gains intensity with respect to the PL emissions in the range of visible light ($h\nu_{\text{Em}} = 2.1$ eV — ZnO$_{\text{nac}}$ and 1.9 eV — ZnO$_{\text{act}}$). This effect is again subject to band bending and adsorption-induced changes thereof. Different to the PL emission of O$_2$ as deep traps, band flattening increases the relative intensity of the NBE emission (Fig. 4c and f) [44,45].

To investigate potential O$_2$ adsorption effects at the ZnO liquid water interface, we flushed the aqueous ZnO nanoparticle dispersions with molecular oxygen and observed for ZnO$_{\text{nac}}$ as well as ZnO$_{\text{act}}$ nanoparticles an apparent increase in PL intensity. This enhancement effect may in principle originate from adsorption induced changes in band bending. A control experiment with Argon, that exhibits neither electron- accepting nor electron-donating properties has, however, revealed the same intensity development as in the case of flushing with O$_2$ gas (Fig. 6). Information from DLS measurements on identical nanoparticle dispersions point to significant agglomerate size increases (Fig. 6). The maxima of both distribution curves shift to 260 nm after 2 h of flushing with O$_2$ or Ar.

As determined by the experimental set-up of the PL emission measurements and the geometric details of the spectrometer system, only a fraction of the total sample volume is addressed by the excitation beam and via its emission light can be interrogated by the detector system. The here investigated ZnO nanoparticles are exempt from any surface active agents that stabilize them against agglomeration. Consequently, agglomeration-induced local particle concentration increase in the specified zone of the optical cell are proposed to generate the here observed intensity enhancement (Fig. 6). Thus, this effect represents an artifact rather than presenting the result of adsorption-induced changes in the electronic structure of the photoluminescent nanoparticles.

### 3.3 From formic acid adsorption to ZnO nanoparticle dissolution

In colloidal chemistry, ligand adsorption provides means to stabilize particle dispersion via control over their agglomeration [31,46]. In addition, the optical properties of ZnO
nanoparticle dispersions can also be modified by capping agent adsorption [47–49]. These often contain carboxylic groups as chemical linkers [48–50]. In acid aqueous environments, ZnO exhibits only limited chemical stability and interaction with organic acids may give rise to reactive attack of the nanoparticles and ultimately to their dissolution [30,31]. Against this background, we addressed the question whether formic acid adsorption [50] and early stages of particle dissolution can be accessed by PL spectroscopy. Starting from standard experiments addressing the influence of formic acid on particle stability in the aqueous dispersion (Fig. 7), we continued with PL emission measurements on this well-characterized particle dispersions and solutions (Fig. 8).

Upon addition of an equimolar amount of formic acid ($C_{\text{HCOOH}} = 9 \text{ mmol-L}^{-1}$), the zeta potential of ZnO nanoparticles ($c_{\text{ZnO}} = 9 \text{ mmol-L}^{-1}$) increases slightly from 26 to 32 mV (Fig. 7a). At the same time, the hydrodynamic diameter of particle agglomerates increases from 60 to 110 nm (Fig. 7b). Further increase in the formic acid concentration ($C_{\text{HCOOH}} > 15 \text{ mmol-L}^{-1}$) converts the previously turbid particle dispersion into a transparent solution. Consistently, DLS reveal the completion of ZnO dissolution which is supported by complementary conductivity and pH measurements (Fig. S2, Supplementary Information).

In aqueous environments, ZnO particles will hydrolyze to form hydroxide layers (Zn(OH)$_2$) at the surface. Adsorbing ligands on the oxide surface polarize and weaken the metal-oxygen bonds to favor dissolution [30]. At neutral pH the relevant transformation steps are [51]

\begin{align}
\equiv \text{Zn} - \text{OH}(s) + \text{H}^+ & \leftrightarrow \equiv \text{Zn} - \text{OH}_2^+ (S) \quad (1) \\
\text{Zn(OH)}_2(s) + \text{H}^+ & \leftrightarrow \text{Zn(OH)}^+ (aq) + \text{H}_2\text{O} \quad (2) \\
\text{Zn(OH)}^+ (aq) + \text{H}^+ & \leftrightarrow \text{Zn}^2+ (aq) + \text{H}_2\text{O} \quad (3) \\
= \text{Zn} - \text{OH}(S) + \text{HCOOH} & \leftrightarrow = \text{Zn}^2+ (\text{HCOO}^-)(ads) + \text{H}_2\text{O} \quad (4) \\
\equiv \text{Zn}^2+ (\text{HCOO}^-)(ads) & \leftrightarrow \equiv \text{Zn}^2+ (\text{HCOO}^-)(aq) \quad (5)
\end{align}

Related to the completed dissolution of ZnO nanoparticles, we measured the resulting solution with ATR-IR spectroscopy and indeed identified formate species in solution (Fig. S3, Supplementary Information).

With regard to the PL emission properties, formic acid adsorption on the surface of dispersed ZnO nanoparticles does neither produce a change of the respective band energies nor in their intensities. However, the ongoing dissolution of the oxide nanoparticles in the aqueous dispersion is also reflected in the development of the PL emission spectra (Fig. 8). The intensity of the band at $h\nu_{\text{EM}} = 2.1 \text{ eV}$ decreases and a new emission band, the maximum of which slightly shifts from $h\nu_{\text{EM}} = 2.6$ to 2.5 eV, is formed. The latter band has also been observed in a clear solution (Supplementary Information) which - according to

Surf Sci. Author manuscript; available in PMC 2020 September 03.
DLS measurements (Fig. 7) - does not contain dispersed nanoparticles anymore. A control experiment with an aqueous Zn formate solution (Fig. S4) proves that the respective PL emission originates from solvated Zn formate species.

4 Conclusions

Processing related materials modifications of semiconducting metal oxide nanoparticles include the annealing-induced annihilation of point defects as well as changes in nature, size, and composition of interfaces. In addition to the optoelectronic properties inherent to the electronic structure of the material also the microstructure of the nanoparticle ensemble becomes affected by continuous phase changes. These can give rise to local concentration changes inside the volumes that are sampled by the respective spectroscopic technique. This paper describes the experimental challenges one faces when nanoparticle powders, which have been synthesized and processed in dry and solvent free reaction media, are compared to their colloidal materials counterparts that are dispersed in an aqueous continuous phase. With PL spectroscopy, we tracked a characteristic emission process at $h\nu_{EM} = 2.1$ eV that is associated with oxygen interstitials as deep trap states and explored its response to annealing and/or O$_2$ and H$_2$O adsorption.

Oxygen adsorption-induced PL emission enhancement was exclusively observed for as-synthesized NP powders prior to exposure to gaseous or liquid water. The corresponding particle surfaces still host layers of synthesis related remnants such as acetate groups and water. Annealing in oxygen-rich atmosphere leads to partial dehydration which in turn changes surface composition and electronic structure in such a way that both O$_2$ and H$_2$O adsorption leads to PL quenching. As a result of thermal activation to 673 K oxygen interstitials in the near surface region are driven into the surface where their photoluminescence emission properties become quenched upon adsorption of molecular oxygen or water.

Using vapor phase transfer techniques, we transformed ZnO nanoparticle powders into aqueous colloidal systems. In the absence of surface active stabilizers, typically employed in colloidal chemistry, these nanoparticles were found to undergo agglomeration. For the systematic spectroscopic comparison of materials properties, this requires to discriminate between artifacts which arise from agglomeration and sedimentation induced local concentration changes and real adsorption-induced changes in the electronic structure of the semiconductor within liquid water. Thus, for robust statements about spectroscopic and optoelectronic properties of semiconducting oxide nanoparticles and their interfaces an integrated characterization approach is required. Related activities must involve surface analysis at the solid-vacuum interface [17,26] as well as colloidal measurement techniques (surface potential, dynamic light scattering) that provide key information about agglomeration and microstructure of the oxide nanoparticles inside the liquid.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.
Acknowledgments

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft project DI 1613/2-1 and from the COST Action CM1104 “Reducible oxide chemistry, structure and functions”. T.B. gratefully acknowledges support from the Austrian Science Fund (FWF): [P 28211-N36]. We thank Augusto Marquez for performance of the ATR-IR measurements.

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Spectra were measured using the front-facing sample holder geometry suitable for powder samples (a, c) or the standard right angle geometry (b, d).
Fig. 1.
Particle size distribution (PSD) plots related to dry ZnO nanoparticle powders in vacuum as derived from TEM analysis (black bar histograms) and the same material dispersed in liquid water. The red colored DLS curves that peak at 70 nm and 60 nm for (a)\textit{ZnO}_{nat} and (b) \textit{ZnO}_{act} nanoparticles, respectively, correspond to the smallest achievable values that can be obtained already after 10 min of sonication treatment. Upon discontinuation of sonication the nanoparticle ensembles become subject to enhanced agglomeration. After 2 h of
dispersion flushing with Ar or O
2 gas the maxima of the DLS curves reproducibly shift to
250 and 160 nm for ZnO
\text{nat}
(a) and ZnO
\text{act}
(b) nanoparticle dispersions, respectively.
Fig. 2.
FT-IR spectra (a) and TEM images (b, c) of ZnO\textsubscript{nat} and ZnO\textsubscript{act} nanoparticle powders. The scheme in the inset illustrates modification of the ZnO surface which was induced by sample activation. The surface of the ZnO\textsubscript{nat} nanoparticles is covered with synthesis-related organic remnants such as acetates and multilayers of adsorbed water. Sample annealing to 673 K induces dehydration but - as revealed by AES and FT-IR analysis - does not affect the concentration of organic remnants.
Fig. 3.
Photoluminescence emission spectra (a) ZnO\textsubscript{nat} and (b) ZnO\textsubscript{act} nanoparticle powders in dynamic vacuum (black) and in O\textsubscript{2} gas atmosphere at a pressure of 10 mbar (gray). The spectra were acquired at room temperature using $h\nu_{\text{Exc}} = 4.6$ eV ($\lambda_{\text{Exc}} = 270$ nm) light for excitation.
Fig. 4.
Photophysical and photochemical processes on ZnO\textsubscript{nat} and ZnO\textsubscript{act} nanoparticle powders. Luminescent interstitial oxygen ions (O\textsubscript{i}), electron traps (ET) in the bulk, surface defects (SD), and hole traps (HT) in the surface.
Fig. 5.
PL emission spectra of ZnO$_{\text{nat}}$ and ZnO$_{\text{act}}$ samples in different chemical environments: (a,c) powders at $p < 10^{-5}$ mbar or exposed to water vapor ($p[H_2O] = 25$ mbar), (b,d) aqueous particle dispersions (directly after sonication and after $O_2$ flushing). The spectra were acquired at room temperature using $h\nu_{\text{Exc}} = 4.6$ eV ($\lambda_{\text{Exc}} = 270$ nm) light for excitation [43].
Fig. 6.
Digital images of sample cells, DLS curves and PL emission spectra of ZnO nanoparticles in aqueous dispersions. Particle agglomeration and sedimentation lead to the enrichment of PL active material in the sampling volume of the cell. This effect is proposed to generate the PL emission intensity increase which was observed for nanoparticle dispersions after flushing with Ar (green curve) or O₂ (orange curve) for 2 h.
Fig. 7. Evolution of ZnO\textsubscript{nat} nanoparticle (C\textsubscript{ZnO} = 9 mmol-L\textsuperscript{-1}) properties such as a) zeta potential and b) hydrodynamic diameter of particle agglomerates, upon stepwise addition of formic acid.

*Surf Sci.* Author manuscript; available in PMC 2020 September 03.
Fig. 8.
Photoluminescence emission spectra acquired on ZnO_{nat} nanoparticle dispersions (12.3 mmol.L\(^{-1}\)) with different concentrations of formic acid. The measurements were performed using the front face geometry where the excitation light is focused to the front part of the sample cell and then luminescence is collected from the same region at an angle that minimizes scattering and specular reflection.