

## Photoluminescence and FTIR study of ZnO nanoparticles: the impurity and defect perspective

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We studied the possible correlations between defects and photoluminescence spectra in ZnO nanoparticles of sizes ranging from 43 nm to 73 nm in diameter. The defects and impurity contents were characterized by Fourier-transform infrared (FTIR) spectroscopy. The results show fewer carboxylate and hydroxyl impurities for particles of larger sizes. No significant variation in oxygen vacancy content was found among samples. Annealing in vacuum at 300 °C significantly reduces the carboxylate and hydroxyl impurities in the samples. The total luminescence intensity (UV + visible) increases as the particle size grows for both the unannealed and annealed samples. This suggests that both types of luminescence are subject to non-radiative quenching by near surface defect centers, possibly carboxylate and hydroxyl impurities. There may be quenching due to intrinsic lattice defects too. It is found that annealing in vacuum enhances the visible luminescence both absolutely and relative to the UV exciton luminescence. In addition to the 2.5 eV green luminescence peak, a peak centered at 2.8 eV can also be resolved, especially for the 43 nm sample.

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**1 Introduction** ZnO has attractive properties for possible development of blue light emitting devices (LED) [1], dye-sensitized solar cell [2], and photocatalysis [3]. Understanding the roles of defects and especially surface defects are important for these applications utilizing nano-structured ZnO. During or after nanostructure synthesis, the surfaces can often be easily contaminated by impurities and other defects. These surface defects usually reduce the performance for such applications. For example, surface defects such as hydroxyl are known to quench the exciton luminescence in ZnO [4]. It can also prevent efficient charge transfer between ZnO and adsorbed molecules at the interfaces. The most obvious trend versus particle size is that the surface-to-volume ratio increases for smaller particles, and the transport distance from any interior point to surface traps and recombination sites decreases in the same trend. Examining nanoparticle ZnO photoluminescence (PL) spectra provides us a way to understand the roles of defects in the above photon-excited processes. In this paper, we report our study of ZnO nanoparticles ranging from 43 to 73 nm. The defect and impurity content in these materials were characterized by Fourier transfer infrared spectroscopy (FTIR). We correlate the particle size and defects/impurities to the measured PL spectra. It is found that annealing treatment significantly reduces the surface impurities.

**2 Experimental** Three commercial nanoparticle ZnO samples provided by Nanophase Technologies Corporation [5] were used in this study. The ZnO samples were produced via a plasma synthesis technique. The sizes of as-grown samples were measured by specific surface area analysis (by the manufac-

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turer) and confirmed by our X-ray diffraction (XRD) peak profile analysis using Scherrer's equation. Transmission electron microscopy study was also performed. Although a small size distribution can be found for each sample, the particle sizes estimated from XRD and SSA analysis can be regarded as good statistical average. Accordingly, the samples are labelled by their average crystallite sizes, namely **43 nm**, **58 nm**, and **73 nm**, respectively. The XRD experiment was performed with a Philips General Purpose X-ray Diffractometer (Model 3040) using Cu-K $\alpha_1$  line. FTIR spectra were acquired on a Perkin-Elmer Spectrum GX FT-IR spectrometer. For FTIR studies, 1 mg of each of the ZnO samples was mixed with 99 mg of dry KBr homogeneously to make pellets of 7 mm diameter and 0.5 mm thick. Energy dispersive X-ray (EDX) analysis and morphological evaluation of the samples were performed with a JEOL JSM 5300 scanning electron microscope attached with a Thermo Noran Super dry II analyzer.

For the PL measurement, the ZnO nanoparticles were mechanically sandwiched between two Si quartz slides. A sufficient amount of nanoparticles was used to ensure that the prepared samples were optically dense. The PL were excited by the third harmonic of a Ti:sapphire oscillator (273 nm, 76 MHz). The corresponding laser irradiance is 6.4 W/cm<sup>2</sup> (peak intensity 650 kW/cm<sup>2</sup>, pulse energy 8 $\times$ 10<sup>14</sup> J). After these measurements the samples were annealed in vacuum (1 $\times$ 10<sup>-5</sup> Torr) at 300 °C for 2 hours. Thereafter FTIR and PL spectra were measured for the annealed samples. The results after annealing treatment were compared with the unannealed samples.

### 3 Results and discussions

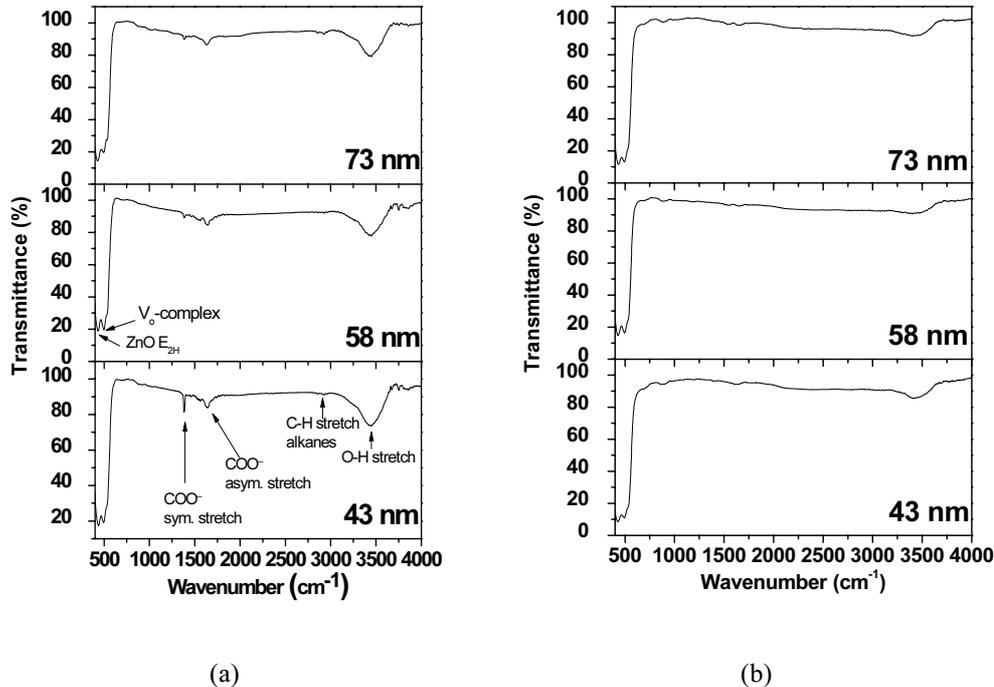
**3.1 FTIR spectra** Figure 1 shows the IR spectra of the ZnO samples before and after vacuum annealing. For the IR spectra of unannealed samples (Fig. 1a), a series of absorption peaks from 1000 to 4000 cm<sup>-1</sup> can be found, corresponding to the carboxylate and hydroxyl impurities in materials. To be more specific, a broad band at 3500 cm<sup>-1</sup> is assigned to the O-H stretching mode of hydroxyl group. Peaks between 2830 and 3000 cm<sup>-1</sup> are due to C-H stretching vibration of alkane groups. The peaks observed at 1630 and 1384 cm<sup>-1</sup> are due to the asymmetrical and symmetrical stretching of the zinc carboxylate, respectively. As the size of the nanoparticles increases, the content of the carboxylate (COO<sup>-</sup>) and hydroxyl (-OH) groups in the samples decreased. The carboxylate probably comes from reactive carbon-containing plasma species during synthesis and the hydroxyl results from the hygroscopic nature of ZnO [6]. Together this suggests that these FTIR-identified impurities mainly exist near ZnO surfaces.

Annealing in vacuum at 300 °C significantly reduces the carboxylate and hydroxyl impurities in all samples, as shown in Fig. 1(b). The spectral signatures of carboxylate impurities essentially disappear, indicating the possible dissociation of zinc carboxylate and conversion to ZnO during annealing. The intensity of the hydroxyl peak follows a similar trend as seen in the unannealed samples vs. particle size. However, the intensities are much weaker compared to the unannealed samples. The residual hydroxyl peak may come from the surface adsorption of ambient water.

For all samples in the study, two strong absorption bands were observed at 437 and 505 cm<sup>-1</sup>. While the band at 437 cm<sup>-1</sup> corresponds to the E<sub>2</sub> mode of hexagonal ZnO (Raman active), the band at 505 cm<sup>-1</sup> may be associated with oxygen deficiency and/or oxygen vacancy (VO) defect complex in ZnO [7]. The intensity of the oxygen-deficiency related defect-complex band does not appear to change much vs. the particle size, indicating they are probably bulk defects. After vacuum annealing, the VO intensity increases somewhat although a quantitative analysis is not feasible (Fig. 1(b)). This result is confirmed by EDX stoichiometry analysis. Our EDX results revealed a reduction of O/Zn atomic ratio in the samples after vacuum annealing. The reduction of O/Zn ratio is highest for the sample with smallest particle size. It must be noted that we performed FTIR measurements on the KBr pellets containing same amounts of ZnO samples to monitor the variation of defect contents in them qualitatively.

**3.2 PL spectra** The room-temperature PL spectra are plotted in Fig. 2. Each spectrum consists of some broad bands in the visible region. The peak centered at approximately 2.5 eV is known as the green defect luminescence of ZnO, generally attributed to oxygen vacancies [8], although other assignments were also proposed in the literature [9]. Another peak centered at 2.8 eV can also be found, especially for the annealed spectrum of the 43 nm sample (Fig. 2(b)). Only a few papers have reported the 2.8 eV PL in

nominally undoped ZnO. The mechanism of the 2.8-eV luminescence is not understood, although there are suggestions that it is associated with oxygen vacancies or Zn interstitials [10, 11]. The peak in the UV region at approximately 3.26 eV is the envelope of phonon replicas of free exciton luminescence (FE+LO) [12].



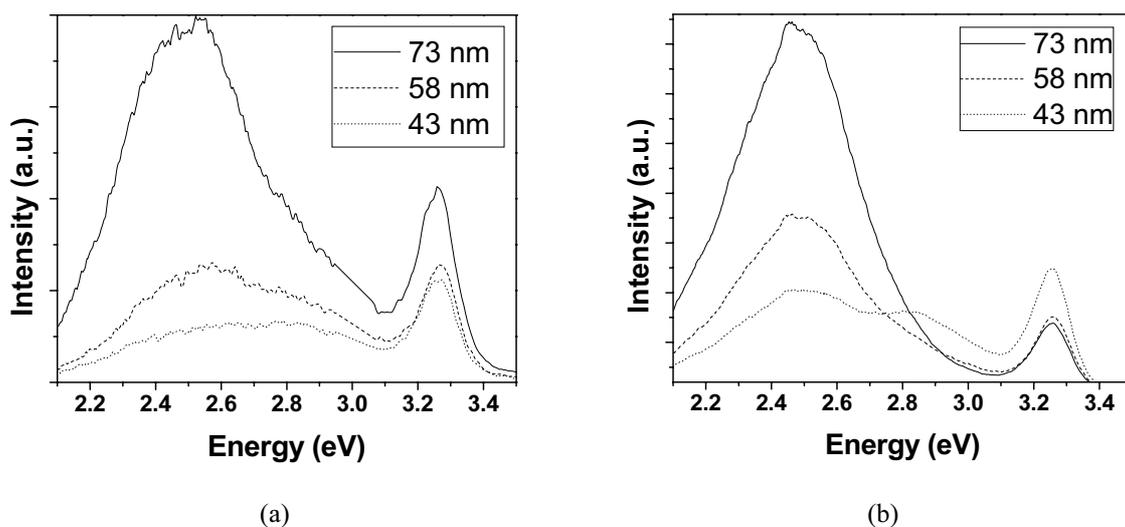
**Fig. 1** The FTIR spectra of ZnO samples; (a) before annealing, (b) after annealing.

We begin our analysis with the unannealed samples. The integrated intensities of both the exciton and the defect luminescence band monotonically increase with the increase of particle size. It appears that although the luminescent mechanisms for these two bands are very different, the quantum yields are both partially limited by non-radiative processes. This is consistent with the surface impurities probed by FTIR spectroscopy, which revealed less carboxylate and hydroxyl impurities in samples of larger particle size. These impurities and defects likely serve as non-radiative recombination or trapping centers to compete with the radiative recombination. While the exact role of carboxylate impurities is not clear, the hydroxide defects are good hole scavengers, as reported in studies of ZnO [4] and other metal-oxides [13].

Annealing partially removes the surface impurities. Due to the presence of some remaining surface impurities, the overall luminescence (visible+UV) intensity still grows as the particle size grows. Although we have not conducted an exact analysis on the luminescence quantum yields for the samples before and after annealing, the PL intensities after annealing appear to be brighter under similar experimental conditions. In particular, an improved signal/noise ratio for the annealed spectra can be observed (Fig. 2).

Comparing the unannealed PL spectra to the annealed spectra, it is found that annealing in vacuum enhances the defect luminescence in the visible region. We summarize the intensity ratios between visible and UV luminescence in Table 1. It can be seen for each sample after annealing that the visible/UV ratio increases. This may be explained assuming that the defect luminescence at the visible wavelengths originates from oxygen deficiency in materials such as oxygen vacancies [8]. It is generally true that

annealing in vacuum causes the samples to lose oxygen and help create oxygen deficient type defects, as partially confirmed by our FTIR and EDX analysis. Due to the increased concentration of oxygen-deficient type defects after annealing, the corresponding defect luminescence appears stronger. On the other hand the excitonic luminescence may become suppressed due to increased defect concentration through trapping or non-radiative recombination at these defect centers. As a result the visible/UV luminescence intensity ratio would become larger after annealing.



**Fig. 2** The photoluminescence spectra of ZnO nanoparticle samples; (a) before annealing, (b) after annealing.

**Table 1** The visible/UV luminescence ratio for the ZnO nanoparticles before and after thermal annealing. After thermal annealing, the ratio increased for all the samples.

	43 nm	58 nm	73 nm
Before annealing	2.4	3.6	5.9
After annealing	3.4	7.4	15.5

**4 Summary** We have studied ZnO nanoparticles of diameters ranging from 43 to 73 nm. FTIR spectroscopy showed an increased carboxylate and hydroxyl concentration in samples of smaller size, indicating that they are probably near-surface impurities. It is believed that these surface carboxylate and hydroxyl impurities serve as primary non-radiative recombination centers during the relaxation processes of photo-excited valence electrons in our samples. As the result, the intensity of radiative recombination decreases for samples of smaller size. Annealing in vacuum significantly reduces the carboxylate and hydroxyl impurities in material. On the other hand, FTIR and EDX evidences showed an increased oxygen-deficient type defect concentration upon vacuum annealing. Possibly due to the increased oxygen defect concentration, the ratio between the visible luminescence and the UV luminescence increases.

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