

## Effect of the (OH) Surface Capping on ZnO Quantum Dots

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ZnO quantum dots were prepared by the reaction of  $\text{Zn}^{2+}$  with  $\text{OH}^-$  in alcoholic solution. By annealing (150–500 °C), both the particle size and the surface conditions could be changed intentionally. The structural properties of the dots were characterized by X-ray diffraction and Raman measurements, and the optical properties by photoluminescence. For the as-prepared dots, the excitonic recombination is very weak, while it becomes dominant for the annealed samples. We present evidence that the weak excitonic transition of ZnO quantum dots is strongly correlated with the presence of the surface (OH) groups.

**Introduction** ZnO has been widely investigated and used as a luminescent material for various applications such as field-emission displays and electroluminescence devices. Two competitive emission bands are usually observed: one is a broad green luminescent band in the region between 500–530 nm (2.35–2.50 eV), which is related to oxygen deficiency [1]; the other is a much narrower ultraviolet (UV) emission band at around 380 nm (3.25 eV) due to excitonic recombination. Experiments on ZnO quantum dots so far showed that, compared with good quality ZnO single crystals or ZnO powders, the UV bandgap luminescence in quantum dots is strongly quenched. Though it was observed that the UV band increases slightly with increasing particle size [2], the broad green region is predominant [2–4]. Recent work by Borgohain and Mahamuni [5] found that the surface capping plays a major role for the luminescence properties of ZnO quantum dots, and argued the importance of hydroxyl (OH) groups on the surface. Similarly, the change of surface luminescence by water vapor has also been reported by Liu et al. for bulk ZnO [6]. To understand the crucial factors for the UV emission of ZnO quantum dots, we attempted to change both the dot size and the surface conditions by an annealing process.

**Experimental Procedure** The preparation of the ZnO quantum dots is based on the dehydrating properties of alcohol. Briefly, 5 mmol  $\text{Zn}(\text{NO}_3)_2$  is dissolved in 250 ml absolute methanol, and then 10 mmol sodium hexametaphosphate is added. After vigorous magnetic stirring and an ultrasonic bath, a semi-transparent solution is obtained, leaving most of the undissolved sodium hexametaphosphate at the bottom. The solution

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is separated from the undissolved residue. 10 mmol NaOH powder is added to another 250 ml methanol and placed into an ultrasonic bath to destroy the weakly soluble powder. Slowly mixing the two solutions at first gives a transparent solution. With the addition of  $\text{Zn}^{2+}$ , the solution gradually becomes opalescent. By centrifugation, a white solid is separated from the solution. Washing the solid with a mixture of 70% methanol and 30% distilled water and then air drying leads to a white powder. This preparation procedure is comparable to the one described in [3]. The samples used in this work were obtained by annealing the powder in air at different temperatures from 150–500 °C for 30 min. In comparison, highly purified bulk ZnO powder (Aldrich Co.),  $\text{Zn}(\text{OH})_2$ , and  $\text{Zn}(\text{OH})_2$  (150 °C), i.e., a  $\text{Zn}(\text{OH})_2$  sample annealed in air at 150 °C for 30 min, were studied as reference samples.  $\text{Zn}(\text{OH})_2$  precipitation was obtained by mixing  $\text{Zn}(\text{NO}_3)_2$  and NaOH aqueous solution. It is well established that  $\text{Zn}(\text{OH})_2$  prepared in this way is amorphous.

The samples were characterized by X-ray diffraction (XRD) and Raman measurements. Room temperature photoluminescence (PL) was excited by the 325 nm line of a He-Cd laser.

**Results and Discussion** Figure 1 shows the X-ray diffraction pattern of ZnO quantum dots and the reference samples. In the as-prepared unannealed sample (curve a) the diffraction peaks related to wurtzite ZnO are considerably broad. Upon annealing the diffraction peaks become more intense and narrower (curve b), indicating increasing crystallinity and size. The average size of the particles can be estimated from the half-width of the diffraction peaks applying the Scherrer formula [7], and is approximately 4.3 nm in diameter for the unannealed sample, and 7.0 nm for the sample annealed at 500 °C. Samples annealed at intermediate temperatures have intermediate sizes. The dot sizes are comparable to the exciton Bohr radius  $a_B$  of ZnO ( $a_B = 1.8$  nm).

In addition to the ZnO diffraction pattern, a peak at 59.5° is observed, as indicated by the arrow in Fig. 1. It decreases upon annealing and vanishes above 300 °C. A diffraction peak at the same angle is also present in the XRD spectrum of the freshly prepared  $\text{Zn}(\text{OH})_2$ , and this makes it very likely that it is related to  $\text{Zn}(\text{OH})_2$ . In the  $\text{Zn}(\text{OH})_2$  (150 °C) sample the 59.5° diffraction peak decreases, and sharp ZnO peaks appear. The line width gives evidence that in this case rather large ZnO particles ( $\approx 24$  nm) are formed. The important point here is that upon annealing  $\text{Zn}(\text{OH})_2$  is released while the ZnO quantum dots' size increases.

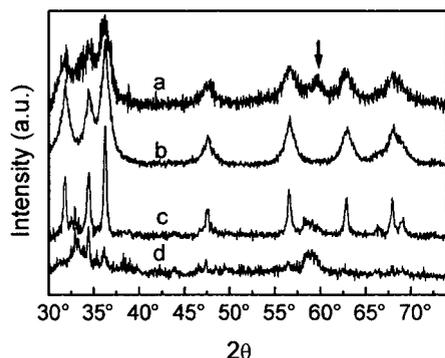


Fig. 1. X-ray diffraction pattern of ZnO quantum dots (a, b) and reference samples (c, d): unannealed (a) and annealed at 500 °C (b),  $\text{Zn}(\text{OH})_2$  (150 °C) (c) and  $\text{Zn}(\text{OH})_2$  (d)

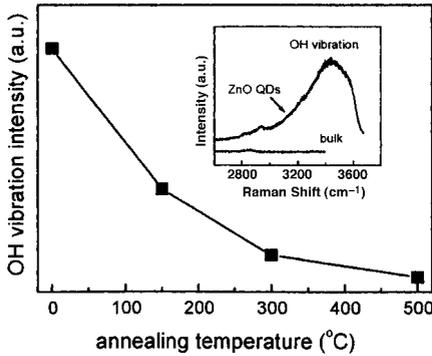


Fig. 2. Dependence of the OH vibration upon annealing temperature. The inset shows Raman spectra of ZnO quantum dots and bulk ZnO in the range from 2800 to 3600  $\text{cm}^{-1}$

Further evidence of the existence of  $\text{Zn}(\text{OH})_2$ , or at least of OH groups, is obtained from Raman spectroscopy (inset in Fig. 2). In the range from 3200 to 3600  $\text{cm}^{-1}$ , where the OH stretching mode should appear, we observe a strong broad and unstructured band in the as-prepared ZnO quantum dots, while no signal is seen in the reference bulk ZnO. Upon annealing the intensity of this band rapidly decreases, as shown in Fig. 2.

Figure 3 shows the room temperature PL spectra of the ZnO quantum dots and the reference samples. The spectra are normalized to the maximum intensity. The green and UV emission bands are observed in most samples. For the unannealed ZnO quantum dots (curve a), the green luminescence band with a maximum at 2.34 eV is very strong, while the UV peak around 3.32 eV is much weaker. The intensity ratio is around 0.09. Upon annealing, this ratio increases, and the UV band eventually evolves into an overwhelming sharp peak at 3.25 eV for the sample annealed at 500 °C (curve b). No obvious PL was detected for  $\text{Zn}(\text{OH})_2$ . For the  $\text{Zn}(\text{OH})_2$  annealed at 150 °C sample, the weak UV band and the strong visible band at 2.16 eV (curve c) should come from ZnO with much larger particle sizes. Only UV emission at 3.21 eV is observed for the reference bulk ZnO which is free of OH groups (curve d). It thus seems that, for ZnO quantum dots, the appearance of strong UV emission is closely related to the annealing process.

We now discuss the appearance of the strong UV emission in ZnO quantum dots. As the dot size grows with annealing, it might be concluded that the strong UV emission is related to bigger particle size. If this would be the case, even stronger UV emission should have been observed for the reference  $\text{Zn}(\text{OH})_2$  (150 °C) sample, i.e., ZnO dots with much bigger size (24 nm in diameter). This is, however, in contradiction with the observation. It is therefore not sufficient to correlate the strong UV emission in this work only with the growth of the particles.

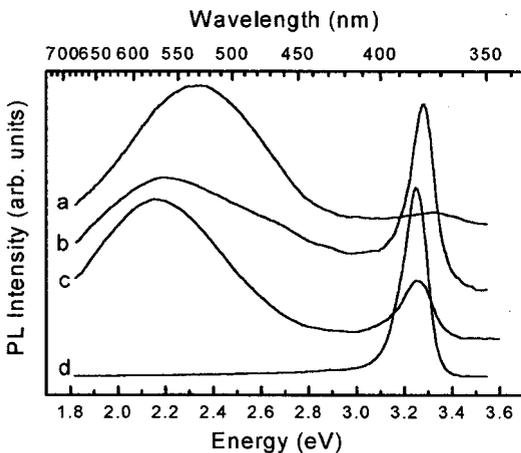


Fig. 3. PL spectra of ZnO quantum dots (a, b) and reference samples (c, d) at room temperature: unannealed (a) and annealed at 500 °C (b),  $\text{Zn}(\text{OH})_2$  (150 °C) (c) and bulk ZnO (d)

Considering the presence of  $\text{Zn(OH)}_2$  in ZnO quantum dots, it is reasonable to suggest that  $\text{Zn(OH)}_2$  forms a thin layer on the surface of ZnO quantum dots. When the surface  $\text{Zn(OH)}_2$  is present, the excitonic emission from ZnO is suppressed. Upon annealing, the surface  $\text{Zn(OH)}_2$  begins to decompose (when the temperature is higher than  $125^\circ\text{C}$ ) and nucleates to ZnO. The inner ZnO quantum dots grow and become better crystallized. Accordingly for the two competitive recombinations, the process that the photo-generated carriers form excitons will become dominant. The capping of ZnO quantum dots by  $\text{Zn(OH)}_2$  perhaps explains the reason why strong UV emission was not observed before in as-prepared unannealed ZnO quantum dots by other groups (for example, Refs. [2–4]). The weak UV emission in the  $\text{Zn(OH)}_2$  ( $150^\circ\text{C}$ ) sample is then also due to the presence of large amounts of  $\text{Zn(OH)}_2$  on the surface of the big ZnO particles.

**Conclusions** In summary, the structure of ZnO quantum dots prepared via the wet chemical method was investigated. Our investigations provide strong evidence that for ZnO quantum dots prepared in such a way, a thin layer of  $\text{Zn(OH)}_2$  covers the surface. When  $\text{Zn(OH)}_2$  is present, the excitonic transition is quenched. This is probably the main reason behind the commonly reported weak excitonic emission of ZnO quantum dots. Strong UV emission is obtained for dots annealed at high temperatures, when the surface  $\text{Zn(OH)}_2$  is released.

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