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Enhanced band-edge photoluminescence from MgO passivated ZnO nanocrystals

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Abstract

Intense band-edge photoluminescence is observed from ZnO nanocrystals with an average diameter of about 3 nm. It is found that the growth from high temperature (70 °C) precursor solution and succeeding surface passivation by MgO layer together lead to a five times enhancement of band-edge luminescence, in comparison to those grown by conventional low-temperature method without surface passivation. It is also found that above-band-gap illumination on the nanocrystals further enhances the luminescence intensity by five times. The strong photo-enhancement is considered to be aided by the reduction of surface non-radiative recombination path.

Key words: ZnO, nanocrystal, luminescence, surface passivation

1 Introduction

The wide-band-gap semiconductor ZnO has been extensively studied in recent years due to its potential applications in optoelectronic devices such as light-

emitting diodes, operating in the blue/ultraviolet spectral region. Recently, much interest has been focused on ZnO nanocrystals because they exhibit strongly size-dependent optical properties and these characteristics are expected to be employed in UV-emitting devices, sensors, biolabels and so on. A particularly successful synthetic method for preparing stable ZnO colloids was developed, which involved the reaction of a Zn^{2+} salt in a basic alcoholic solution.[1–3]

The main deficit caused by preparing semiconductor in nanocrystal size, is that their optical properties are greatly affected by the surface properties. Most of the semiconductor nanocrystals with strong confinement effect tend to exhibit strong trap-related broad luminescence and only very weak band-edge luminescence is observed. Great efforts have been devoted to put proper surface passivation on these nanocrystals. The methods of passivation are classified in two ways. One is to prepare a nanocrystal in a core-shell structure and the other is the passivation of the surface by configuring organic molecules. In CdSe related nanocrystals the two method have been properly applied and the strongly band-edge emitting nanocrystals have been prepared so far.[4,5] In ZnO nanocrystals, however, the surface passivation is not equally successful. The luminescence from ZnO nanocrystal is usually dominated by visible emission that is believed to be related with oxygen vacancy. Despite the efforts of several surface passivation, the quantum yield of the band-edge luminescence remains as low as 2×10^{-4}.[6] For the use in realistic application, further surface passivation is demanded.

In this paper, we report an improvement of the quantum efficiency of band-edge emission achieved by high temperature preparation of nanocrystals and succeeding MgO passivation of the nanocrystal surface. In addition we also

2

report about the 5 time enhancement of the band-edge luminescence by the UV laser irradiation.

2   Experimental Procedure

Zinc oxide nanocrystals are prepared as follows. First 1.10 g of zinc acetate dehydrate ($ZnAc_2 \cdot 2H_2O$) is dissolved in 50 mL of absolute ethanol by boiling, and 0.29 g of lithium hydroxide monohydrate ($LiOH \cdot H_2O$) is dissolved in 50 mL of absolute ethanol ultrasonically. Typically, 10 mL of the Zn solution is heated to 70 °C before the same amount of LiOH solution of room temperature is poured under vigorous stirring. The resulted solution with generated ZnO nanocrystals is stored at -5 °C in a refrigerator. We call this solution sample A. A 5 mL aliquot of the solution is then taken into a vial and 50 mg of magnesium acetate tetrahydrate ($MgAc_2 \cdot 4H_2O$) is added and dissolved ultrasonically. The Mg-added solution is stored at room temperature at least for 3 days. We call this solution sample B. After the addition of Mg, the suspension becomes very stable even at room temperature and no turbidity is observed after one year. Another sample solution is also prepared following the method introduced by Meulenkamp[3], that is, the two precursor solutions are cooled at 0 °C and the LiOH solution is added drop-wise into the Zn solution. This sample is kept at room temperature until desirable particle size is obtained before it is moved to refrigerator. We call this sample C.

The crystal structure of generated ZnO nanocrystals is confirmed by a X-ray diffraction measurement. For this measurement the twice volume of heptane is added to the sample solution and the nanoparticles are separated by centrifugation. The sample is dried in vacuum before the measurement. Absorption

3

measurements of the solution sample are done with a self-made apparatus constructed with a monochromated light source and a photomultiplier. Photoluminescence (PL) spectra are excited by 296 nm line of a 150W mercury-xenon lamp and detected by a 25 cm monochromator equipped with an photomultiplier. The measurements are done under a reflection configuration to avoid the absorption by the sample. Typical excitation power is 1.4 mW/cm². The quantum yield of the luminescence is evaluated by comparing the integrated PL intensity with that of a coumarine 120 solution obtained under the same measurement configuration. All measurements are done at room temperature.

3   Results and Discussions

[Fig. 1 about here.]

Figure 1 shows a X-ray diffraction pattern obtained for the sample A shown together with that for the commercially available bulk ZnO powder. The diffraction pattern for sample A clearly shows the generation of ZnO crystals. The intensity for reaction byproducts (such as zinc hydroxide[7,8]) are negligibly small. The averaged particle diameter can be deduced from the peak width of the diffraction pattern by applying Scherrer's formula for the spherical particles[9]

$$D = \frac{1.107\lambda}{W \cos\frac{\theta}{2}}$$

where W is a full width of the half maximum (FWHM) of the peak. From the formula we obtained 3.28 nm as a averaged diameter.

[Fig. 2 about here.]

Figure 2 shows absorption and PL spectra of the nanocrystal dispersions. The absorption spectrum is presented only for the sample A because those for three samples are almost identical except for the slight difference in their intensities. The energy of the absorption edge is about 3.61 eV. This is by 0.29 eV greater than the bulk absorption edge.[10] The blue shift of the absorption edge is a result of the quantum confinement of the electron hole pair caused by the crystal size smaller than the twice of the exciton Bohr radius of 1.8 nm.[11,12] The dependence of the absorption edge on the crystal size in ZnO nanocrystals has been investigated by Meulenkamp and an empirical formula for ZnO nanocrystals has been obtained.[3] Applying the formula we obtained 3.29 nm for the average diameter and this value is in good agreement with the X-ray diffraction result.

In the PL spectra we see two peaks. One is at ultraviolet (UV) spectral region and the other is at visible spectral region with broader spectral width. The peak in UV region is considered to be a radiative recombination of an electron-hole pair near conduction and valence bands. It shows a slight red-shift from the absorption peak, but it still exhibits a large confinement energy from the bulk zero-phonon energy of the excitons (3.31 eV[13,14]), showing its excited state extends in the nanoparticle. The broader visible luminescence peaked at 2.3 eV is commonly observed in bulk and nano-structured ZnO and called "green photoluminescence". The origin of this luminescence is considered to be the electronic transition including a state at oxygen vacancy.[15]

In the figure, sample A (grown from 70 °C Zn precursor) shows stronger band-edge PL (BEPL) and weaker green PL (GPL) compared with sample C (grown at 0 C). The decrease of the GPL intensity implies the reduced number of oxygen vacancies in sample A. The suppression of the vacancy is also expected

to reduce the energy flow to GPL and increase the BEPL intensity. So we think that starting the reaction at high temperature and succeeding sudden cooling suppress the generation of defects, as in the case of CdSe nanocrystals grown in TOPO bath.[16] After the addition of $Mg(Ac)_2$ (sample B) we observed an about 100 % increase of BEPL intensity together with the 30 % increase of GPL intensity. The addition of the Mg ions will result in the formation of a MgO layer on the ZnO nanocrystal surface[17] which is expected to passivate the surface-related non-radiative centers and increase the overall quantum efficiency of the nanocrystal. MgO is known to have a band-gap energy of 7.6 eV which is far greater than 3.37 eV of ZnO, and act as a potential wall both for electrons and holes.[17] By these methods, we achieve an overall 5 times increase of BEPL in about 3nm sized ZnO nanocrystals, improved from conventional low temperature precipitation method without surface passivation.

These luminescence properties of MgO passivated sample is found to be very stable. We observed about the same intensity of the PL after one year storage at room temperature. The sample shows no turbidity after the long term storage and we think that the stable dispersion should be responsible for the stability of the PL properties.

[Fig. 3 about here.]

Figure 3 shows an illumination effect on sample B. After 10 minute illumination by He-Cd laser (3.81 eV) of 40 mW/cm^2, the intensity of GPL is remarkably reduced and the intensity of BEPL is enhanced by about 5 times. The quantum yield for BEPL reach to 0.54 %, which is comparable to that of bulk ZnO crystals at room temperature[18]. In addition to the enhance-

ment, the spectrum of BEPL after the illumination shows a red-shift by about 0.07 eV from the original spectrum. On the contrary, the sample C (shown in the inset) shows less prominent enhancement after the illumination. We observe only 40 % enhancement in this sample while the red-shift and the suppression of GPL are observed. The photo-enhancement of BEPL has been observed so far in CdSe[19,20] and ZnO[1,21,22] nanocrystals. In these reports, the origin of the enhancement of BEPL in CdSe nanocrystals was attributed to be photo-induced rearrangement of ligand molecules[20] while that in ZnO nanocrystals was interpreted as the charging of the nanocrystals.[22] Due to strong photo-catalytic activity of ZnO, photo-generated holes are scavenged by adsorbed solvent molecules while electrons are left in the crystal. As a result, the nanoparticles are negatively charged. The excess electrons are believed to alter the charge state of the oxygen vacancy and lead to the quenching of GPL and accordingly the enhancement of BEPL. After the illumination is switched off, the PL intensities and the peak energy gradually return to their original values in about 20 minutes. This temporal recovering is consistent with the observation in the reference[22] and the decharging of the nanocrystals should be responsible for the recovery.

In the reference[22], they also observed 5 times BEPL enhancement after the illumination on nanocrystal dispersion even though their sample was grown at 0 °C. In contrast, we observed only 40 % enhancement in sample C. The charging of sample C can be confirmed by the red-shift of BEPL and the suppression of GPL. We think that the different enhancement of BEPL should be attributed to the different particle size. Their nanocrystals have larger diameter of about 6 nm and ours about 3 nm. The smaller enhancement in smaller particles is understandable if we consider that the smaller particles have larger

7

surface/volume ratio and therefore larger non-radiative paths. With large non-radiative relaxation path, the passivation of the GPL does not necessarily lead to the enhancement of the BEPL because the excess energy saved by the passivation is consumed by the non-radiative path. We think that the photo-enhancement of BEPL, observed in our sample despite the small nanocrystal size, is achieved by the reduced defect concentration and surface passivation achieved by our preparation method.

4 Conclusions

We found that the growth from high temperature Zn precursor and succeeding cooling process suppress the generation of oxygen vacancy or the defects in ZnO nanocrystals prepared by chemical reaction in ethanol bath and lead to the enhancement of the band-edge luminescence intensity. Succeeding MgO coating of the surface leads to the further enhancement of the luminescence. These nanoparticles exhibit strong photo-enhancement effect caused by the illumination of above-band-gap light, despite their large surface/volume ratio.

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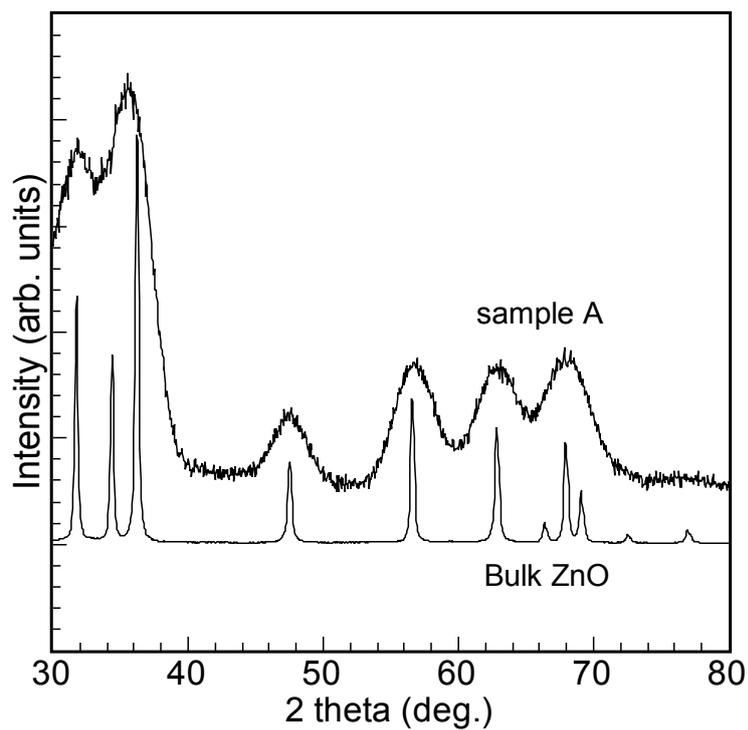
List of Figures

Fig. 1. X-ray diffraction patter of dried ZnO nanocrystals grown from 70 C precursor solution, shown together with that of bulk ZnO powder. The result clearly shows the growth of the ZnO structure. The average diameter estimated from the Sherrer's formula is 3.2 nm.
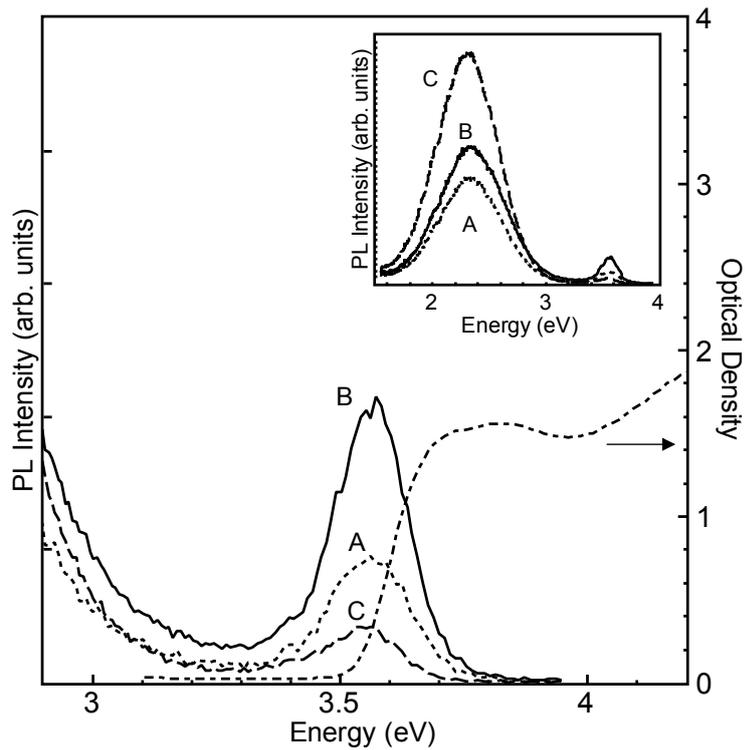
12

Fig. 2. Photoluminescence and absorption spectra obtained for three different samples. Sample A is grown from 70 °C precursor. Sample B is MgO coated on sample A. Sample C is grown at 0 °C. Sample B shows strongest band-edge photoluminescence. The inset show the whole luminescence spectra.
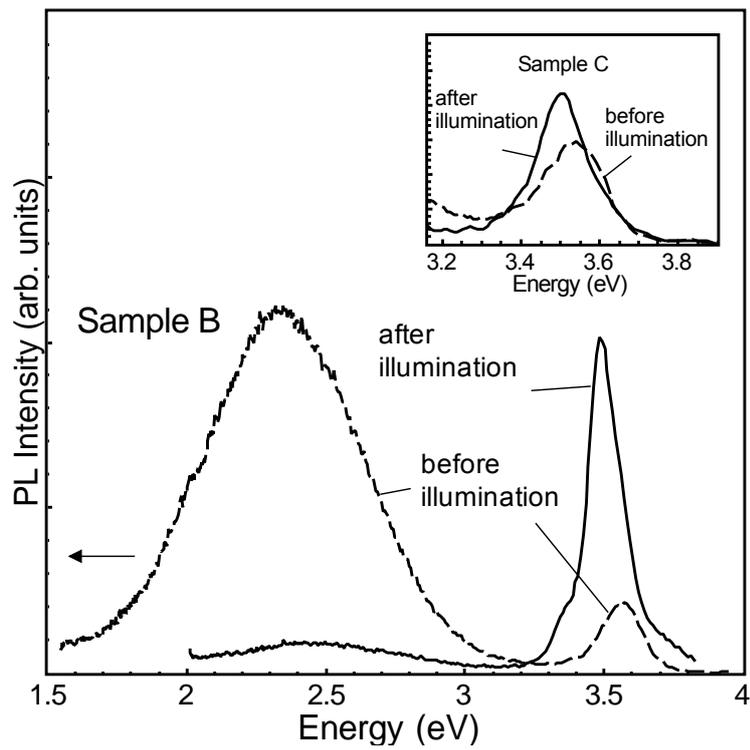
Fig. 3. UV light Illumination effect on sample B. After 10 minutes illumination, the trap luminescence is greatly suppressed and band-edge PL is enhanced 5 times. Only small enhancement is observed in sample C after the same illumination.