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## Origin of the red emission in zinc oxide nanophosphors

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## ARTICLE INFO

## Article history:

Received 27 February 2013

Accepted 13 March 2013

Available online 21 March 2013

## Keywords:

Defects

Phosphors

XPS

ZnO

## ABSTRACT

UV and orange-red light emitting zinc oxide nano-phosphors (ZnO NPR) were synthesised by a combustion method using zinc nitrate and zinc acetate as precursors and urea as a fuel. Hexagonal wurtzite structures of ZnO were synthesised. X-ray photoelectron spectroscopy (XPS) indicated that the O1s peak consist of three components: O1 (ZnO), O2 (deficient oxygen; OH groups) and O3 (adsorbed species) centred at 530.3, 531.2 and 532.6 eV, respectively. A broad orange-red emission from 500 to 850 nm was obtained from the ZnO NPR prepared with the nitrate precursor which may be attributed to different kinds of defects, and a sharp UV band, due to the possible passivation of defects, at 392 nm from ZnO NPR prepared with acetate precursor.

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## 1. Introduction

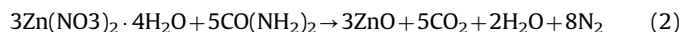
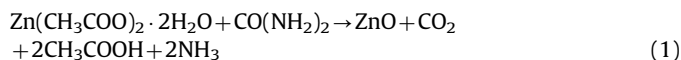
ZnO is a direct band gap (~3.37 eV) semiconductor with a large exciton binding energy (60 meV) [1]. It is a promising candidate for visible and ultra-violet (UV) light emitting diodes (LEDs) and lasing devices [2]. The optical properties of ZnO studied using photoluminescence (PL), photoconductivity and absorption, reflect the intrinsic direct band gap, a strongly bound exciton state and gap states due to the point defects [3,4]. The PL spectra show UV near band edge emission around 380 nm and defect related deep level emission (DLE), which depends upon the preparation methods and growth conditions. The visible emission is a result of DLE bands present in ZnO [5,6]. It is important to understand the origin of these emissions for the development of highly efficient optoelectronic devices. A large number of studies on the luminescence properties of ZnO have been investigated and suggested that, the green and red emissions originated from oxygen vacancies ( $V_o$ ) and zinc interstitials ( $Zn_i$ ) [7–9]. Other authors have attributed the green emission to both  $V_o$  and zinc vacancies ( $V_{Zn}$ ) [10,11]. The violet-blue and blue emissions were attributed to  $Zn_i$  and  $V_{Zn}$ , respectively, in the DLE [12,13]. The origin of the red emission peaks are attributed to deep level defects such as vacancies and oxygen interstitials, usually observed in the oxygen rich system [14].

However, the origin of different DLEs are still not fully understood and the hypotheses to explain the different DLEs have been controversial [8,9,15]. Therefore, considerable interest is still being shown in investigating the DLE in ZnO because of their great

potential for optical applications. In this letter, the synthesis and explanation of red emission ZnO NPR are reported.

## 2. Experimental detail

ZnO NPR were synthesised using the combustion method. Zinc acetate dihydrate and zinc nitrate tetrahydrate were used as precursors. Zinc precursors and urea were mixed and dissolved in distilled water. A homogeneous solution was obtained after stirring for 20 min. The solution was transferred to a pre-heated muffle furnace maintained at a temperature of  $450 \pm 10$  °C. All the liquid evaporated and a large amount of heat released resulted in a flame that decomposed the reagents further and released more gases. The flame lasted for ~60 s and the combustion process was completed within 5 min. These NPR were cooled down to room temperature and were ground gently using a pestle and mortar. The reaction of the two different zinc sources with urea is shown in Eqs. (1) and (2).



ZnO NPR obtained from Eqs. (1) and (2) is identified as ZA and ZN, respectively. The samples were analysed using x-ray diffraction (XRD), XPS and PL spectroscopy. The XPS detailed spectra of the O1s and Zn 2p peaks were obtained from the as prepared samples and after sputtering with  $\text{Ar}^+$  ions for 30 s.

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### 3. Results and discussions

The intensity of the XRD peaks (Fig. 1) shows that the NPr are highly crystalline. The strong diffraction peaks at  $31.7^\circ$ ,  $34.3^\circ$  and  $36.2^\circ$  correspond to the (100), (002) and (101) planes of the hexagonal wurtzite structure of ZnO. The preferred orientation corresponding to the plane (101) is the most prominent peak [16]. The estimated grain sizes were  $22 \pm 2$  and  $30 \pm 2$  nm for ZA and ZN, respectively.

The XPS Zn 2p spectrum (not shown) contained a doublet, whose binding energies were at 1021.3 and 1044.4 eV, indicating that the Zn atoms were in the  $\text{Zn}^{2+}$  oxidation state. Fig. 2 shows the deconvoluted oxygen O1s peaks for both the phosphors. The component on the low binding energy side (O1 peak) on spectrum at  $530.3 \pm 0.3$  eV is attributed to  $\text{O}^{2-}$  ions on the wurtzite structure

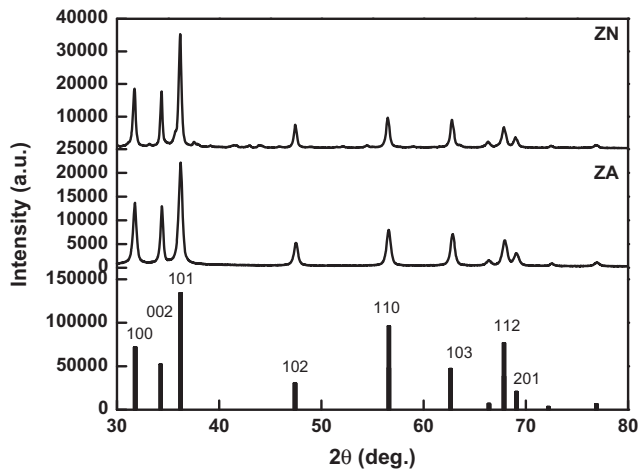


Fig. 1. XRD spectra of different ZnO NPr as well as the standard (ICSD-52362).

of a hexagonal  $\text{Zn}^{2+}$  ion array, surrounded by Zn atoms with their full complement of nearest neighbour  $\text{O}^{2-}$  ions [17]. In other words, the intensity of this component is a measure of the number of oxygen atoms in a fully oxidised stoichiometric surrounding. The medium binding energy (O2 peak) component centred at  $531.2 \pm 0.3$  eV is associated with  $\text{O}^{2-}$  ions that are in oxygen deficient regions within the matrix of ZnO [18] and/or Zn–OH groups [19]. Therefore, changes in the intensity of this component may be partly connected to the variation in the concentration of oxygen defects ( $V_o$  or/and oxygen interstitial ( $\text{O}_i$ )). The higher binding energy (O3 peak) at  $532.6 \pm 0.3$  eV is usually attributed to chemisorbed species (such as  $\text{CO}_3$ , adsorbed  $\text{H}_2\text{O}$  or  $\text{O}_2$ ) on the surface of the ZnO [20]. The intensity of the O3 peak has decreased after sputtered cleaning due to the removal of surface contaminants. After sputtering, Table 1, the relative intensity of the O2 peak is much higher for the ZN with respect to the ZA sample, meaning that the concentration of oxygen defect is higher in the case of the ZN. Hydrogen can passivate the defects (reducing the visible emission) and consequently enhances the UV emission as in the case of the ZA sample [8].

Emission behaviour of ZnO NPr is shown in Fig. 3(a), spectra obtained with 325 nm He–Cd laser. The main features of PL

Table 1  
Peak positions of different O1s peaks.

Sample	Peak name	Before sputtering		After sputtering	
		Peak position	Area (%)	Peak position	Area (%)
ZA	O1	530.3	42.7	530.0	73.2
	O2	531.2	40.9	531.4	14.0
	O3	532.6	16.2	532.1	12.7
ZN	O1	529.9	45.4	529.9	52.0
	O2	530.9	33.8	531.5	38.6
	O3	532.2	20.7	532.9	9.3

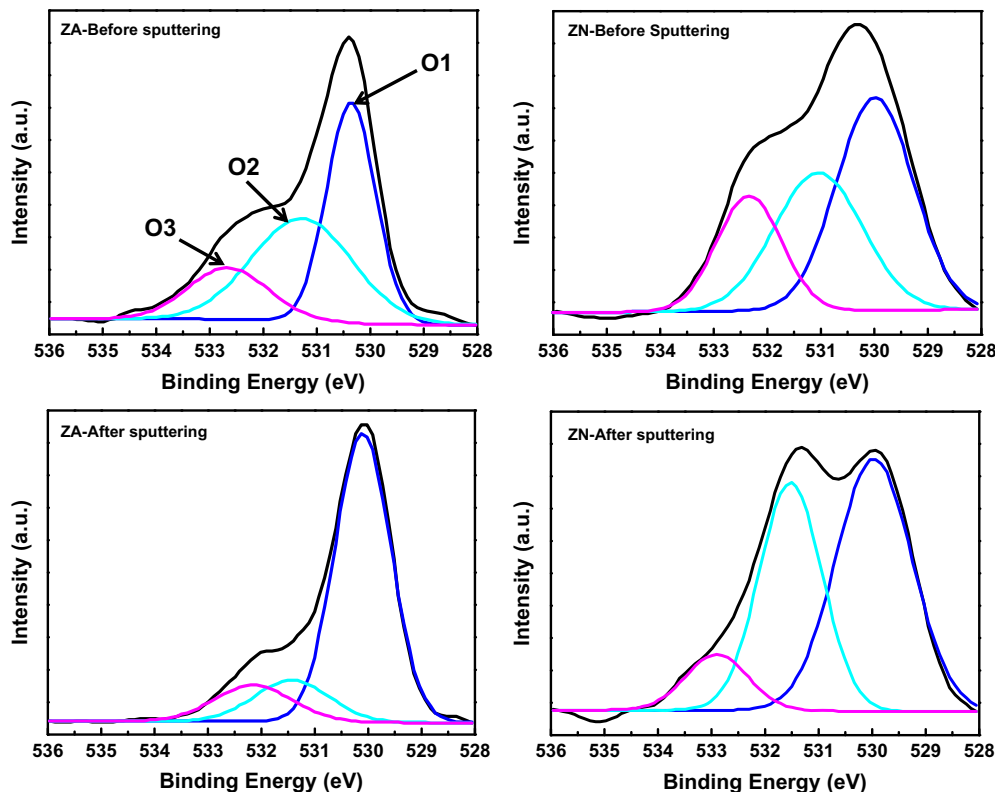


Fig. 2. O1s XPS peak of ZnO NPr before and after sputtering.

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