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# Fabrication of ZnO and Mn: ZnO nanostructures and their possible application in design of Biological marker

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***Abstract:*** *ZnO is the most studied wide band gap transparent semiconductor, it has tremendous potential in luminescent device applications due to its properties like: Size dependant emission, broad excitation range, high quantum yield, etc.. Both Undoped and Mn doped ZnO nanostructures, mostly nanorods were fabricated by adopting solid state chemical reaction route. In the study it has been observed that the PL spectra for both bare and Mn doped ZnO samples exhibited different characteristics. The optical study has been extended by recording PL intensities of bare ZnO nanostructures under bacterial environment. A particular bacteria 'Staphylocuccus" has been selected for the study. The significant behaviour of PL spectra in the visible region can be utilized to design efficient biological marker.*

***Keywords****: Biological marker, ZnO nanostructures, luminescent device;*

## I. Introduction

The study of nanostructures with controlled morphology, shapes and size is essential for developing materials with novel properties and tailorable functions. Different types of semiconducting nanomaterials have attracted a large group of scientific community because of their exceptional properties, which are different from bulk materials [1, 2]. Zinc oxide (ZnO), one of the very important and versatile semiconductors with direct band gap of ~3.37 eV and a large exciton binding energy of ~60 meV at room temperature (RT) is a promising candidate for functional components of devices. Selective doping with transition metal ions into ZnO lattice host is capable of tailoring its physical properties. In this paper, the structural as well as optical properties of bare ZnO and Mn doped ZnO is highlighted. We have fabricated Mn doped ZnO and bare ZnO by adopting solid state chemical reaction route. At the end of synthesis, all samples were obtained in the form of powder. Structural and optical investigations of the as fabricated samples were carried out by utilizing XRD, HRTEM, PL spectroscopy. The change of optical properties of bare ZnO and Mn doped ZnO with and without staphylococcus bacteria is the major direction of this investigation. Nanostructured zinc oxide (ZnO) thin films are showing an increasing potential as sensing components in electronic nose instruments [3-5]. These materials have been successfully applied in the detections of volatile organic compounds particularly associated to markers of meat spoilage. With certain markers such as ethanol, the nanostructured ZnO thin films have shown detection levels in the ppb levels, thus outperforming traditional metal oxide semiconductors based on $SnO_2$. In a recent paper Martin Längkvist et al. [6] proposed a fast sensor based on ZnO nanostructured thin film which can be used as fast classification of meat spoilage marker. The application area that they have considering is food safety and in particular they aimed at developing an instrument that can be used in situ for rapid identification of meat spoilage. Mn-doped ZnO is an n-type semiconducting material. When it is exposed to the atmosphere, the oxygen molecules react with its surface and capture electrons from its conduction band. This in turn leads to a decrease in the electron concentration and, hence, increases the surface resistance until equilibrium. The stabilized surface resistance forms the baseline for the sensing studies. When the reducing vapours like ethanol or TMA are presented to the sensing element, the vapour reacts with surface-adsorbed oxygen species and increases the electrons concentration on the surface. As a result, the surface resistance decreases from the stabilized baseline and attains saturation. This change in surface resistance has a strong correlation with the concentration of ethanol/TMA in dry air atmospheric conditions [5]. In the past two decades, the awareness about food safety, particularly with respect to specific pathogenic bacteria, has increased. This is especially true in the case of meat and fish, where microbial spoilage can be dangerous for humans, and where there is a clear requirement for a rapid and accurate detection system. Traditionally, fish and meat quality is assessed by examining the structure of the food (texture, tenderness, flavor, juiciness, color), or by detecting the microorganism and its count, or by detecting the gases generated by these microorganisms. A number of techniques have been used to examine the quality of the meat, namely instrumental mechanical methods, the ultrasound technique, as well as optical spectroscopy [7,8]. In this work the structural and optical properties for both bare and Mn doped ZnO nanostructures were investigated. The PL study of bare ZnO nanostructure was also done with staphylococcus bacteria. The staphylococcus bacteria are mostly responsible for different skin diseases.

## II. Experimental

Nanostructured bare ZnO and Mn doped ZnO were fabricated [9] by adopting law cost solid state chemical reaction route. To fabricate bare ZnO nanostructures, zinc acetate dehydrate (ZAcD), Cetyle trimethyle ammonium bromide (CTAB) and Sodium hydroxide flakes (NaOH) are mixed by keeping their molar ratio as 1:0.5:2. The mixture was ground gently in a mortar at room temperature for few hours (~2 hrs) till a paste like compound is obtained. The mixture was repeatedly washed with double distilled water and then annealed at $60^0$-$80^0$C for about 4-5 hrs. After washing with double distilled (DD) water the as-synthesized product was dried and the final product was obtained in the form of powder. To get Mn doped ZnO system, in the precursor, acetates of Zn and Mn were taken in the appropriate molar ratio to obtain 3at.% Mn. The sample so fabricated was marked as Mn-3. A part of the bare ZnO sample has been cultured with staphylococcus bacteria in the microbial growth medium "Mueler Hintion Agar" at the MBBT department of Tezpur University.

## III. Result and discussion

The transmission electron micrographs (TEM) of the bare ZnO and Mn-3 samples give clear visual evidence on the formation of nanorods as presented inset of Figure: 3. Nanorods of different lengths and diameters with a random orientation can be seen from the micrographs. The HRTEM study was performed on the isolated ZnO nanorod as presented in the inset (a) of figure: 1, the resolution was increased to get the pattern shown in the inset (b) of figure: 1. On further increasing the resolution, lattice planes with few defect states were observed (figure: 1). The lattice spacing was estimated to be ~2.1Å at a position where lattice fringes are clear enough, this lattice spacing 'd' corresponds to the plane (102) as calculated from the XRD pattern (not shown) of the ZnO. Compared to bare ZnO sample a slight decrease in aspect ratio was observed for Mn doped sample. Mn-3 sample yields nanorods with average length as 91 nm.

High resolution transmission electron microscopy (HRTEM) image for the Mn-3 sample as presented in figure: 2(A) yields formation of high crystalline nature of the nanocrystals as prepared. The lattice spacing as measured from the image is 2.5 Å corresponding to the plane (101), it indicates the growth direction of the nanocrystal is along (101). Clear fringe pattern also reveals nonexistence of lattice distortion of the as fabricated Mn-3 sample. The selective area electron diffraction (SAED) pattern for the sample Mn-3 is presented in Figure: 2(B). It reveals diffused rings which correspond to the hexagonal wurtzite structure of ZnO without any impurity phase. As observed from the pattern, we ascribe two inner rings as (100) and (002) planes for which the *d*- spacing is calculated to be 2.86 nm and 2.47 nm. The values correspond to the *d*- spacing parameters as calculated from XRD data.

In this study we have observed that the PL spectra for both bare and Mn doped samples exhibited different characteristics. Intense luminescent intensities have been exhibited by both bare ZnO (figure: 3A) and TM doped ZnO (figure: 3B). Compared to doped samples, bare ZnO displayed maximum luminescence in the UV region (figure: 3C). In case of TM doped samples the UV intensity gets lowered along with additional peaks in the visible region. This effect is attributed due to radiative recombination of 'd' electron transfer of transition metals. This property can be utilized for colour tunable effect for sensing purpose. We have little bit extended our study to observe PL intensity of undoped ZnO nanostructures in bacterial environment. We have selected a particular bacteria "staphylococcus" which is responsible mostly for different kinds of skin diseases. Our study revealed that in bacterial environment, PL intensity of ZnO nanostructures exhibited wide spectrum in the visible region.

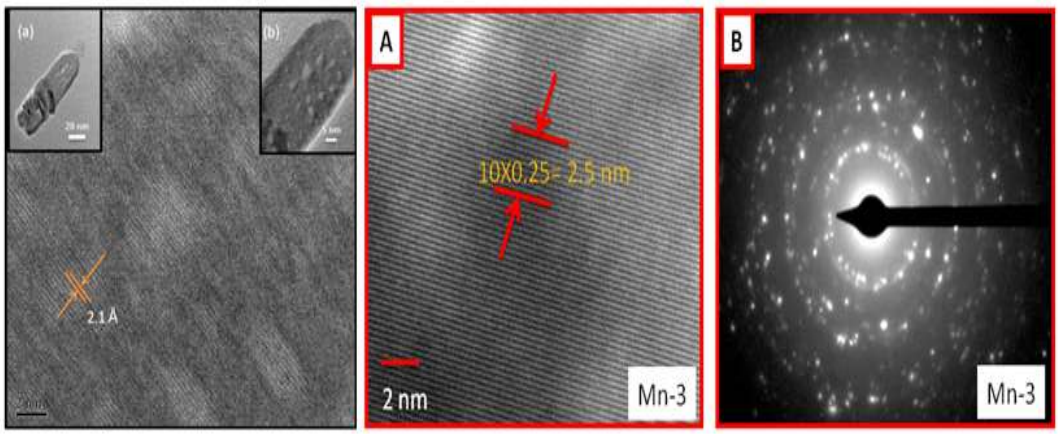


**Figure 1: HRTEM** image of ZnO nanorod, inset isolated nanorod on which the beam is focused, Inset: **(**a) at 20 nm scale, (b) at 5 nm scale.

**Figure 1:** (A) HRTEM image collected for the sample Mn-3(MN:ZnO), (B) SAED pattern for the sample Mn-3.

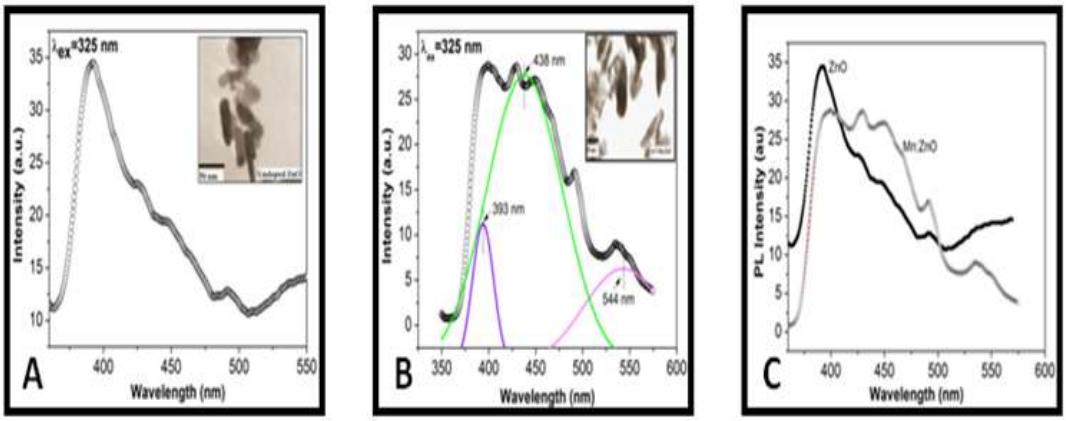


**Figure 2:** Change of PL intensity of ZnO nanorods due to Mn doping, (A): PL spectra of bare ZnO nanorods, (B) PL spectra for Mn:ZnO nanorods and (C) Comparative spectra for both bare and Mn doped ZnO nanorods.

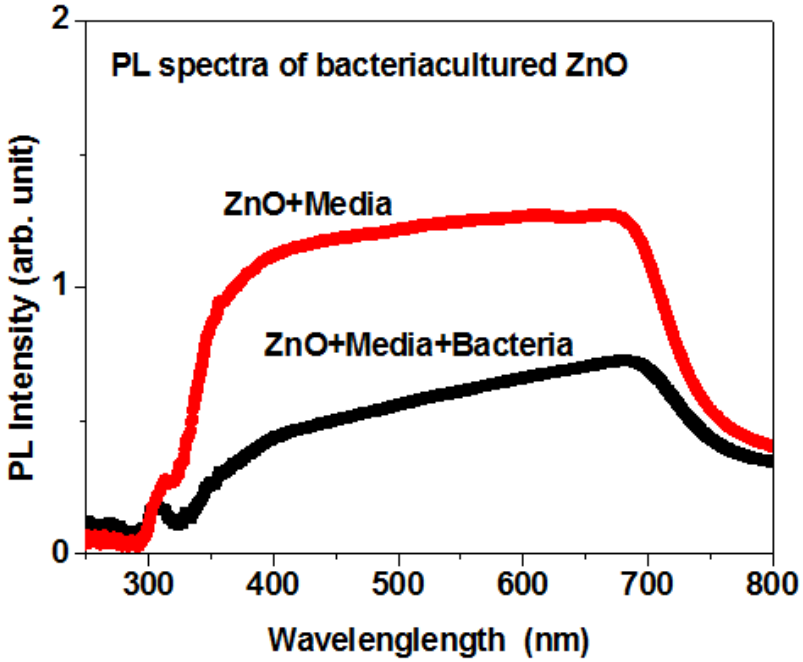


**Figure 3:** PL spectra of bare ZnO NSs with media and staphylococcus bacteria environment.

PL intensities observed in the wide visible region is considered to be remarkable property exhibited by the as synthesized ZnO sample, which in turn can efficiently be applied to design biological marker to detect these particular bacteria. Initially, we have studied the PL spectra of bare ZnO nanostructures in a medium "Mueler Hintion Agar". It is a microbiological growth medium that is commonly used for antibiotic susceptibility testing. The PL spectra of bare ZnO nanostructures with "Mueler Hintion Agar" medium alone and with the staphylococcus bacteria cultured environment is presented in figure: 4. From the PL spectra, it has been observed that for both cases a wide visible spectra appears, when bacteria is added with ZnO and media, the PL intensity gets lowered by about 50%. The sharp UV peak of ZnO changes to wide spectrum within 350 nm to 750 nm. This suggests that more different PL characteristics would be possible when TM doped ZnO NSs are utilized for the above study.

## IV. Conclusion

It was predicted that nanorods with smaller length is useful for Oxygen gas sensor, while nanorods with larger dimension is more useful in UV optical sensor. Thus, by controlling the synthesis protocol the aspect ratio of the nanorods can be controlled which in turn will give the opportunity to apply them in desired Luminescent device applications. In this study, the significant behaviour of PL spectra in the visible region can be utilized to

design efficient biological marker. Apparently, it opens a wide possibility for practical applications, but extensive measure will have to be undertaken for complete practical design of a biological marker.

## V. Acknowledgements

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