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Probing the dominance of interstitial oxygen defects in ZnO nanoparticles through structural and optical characterizations

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Abstract

ZnO nanoparticles, synthesized adopting a facile chemical precipitation route, are studied here. The structural, optical and electronic properties of prepared ZnO nanoparticles were extensively investigated employing X-ray diffraction (XRD), transmission electron microscope (TEM), energy dispersive analysis by X-rays (EDAX), X-ray photoelectron spectroscopy (XPS), UV–vis absorption and fluorescence (FL) spectroscopy. The XRD analysis revealed hexagonal wurtzite phase 26.1–29.6 nm size ZnO nanocrystallites. This observation gets further support from TEM images where particles of 25–30 nm size are vividly seen. Interestingly, oxygen rich stoichiometry of nanoparticles is detected via zinc and oxygen emission lines of EDAX spectrum. XPS analysis establishes coexistence of lattice oxygen (O_L), interstitial oxygen (O_i) and oxygen vacancy (V_O) in ZnO nanoparticles. In line with EDAX analysis, XPS investigations substantiate interstitial oxygen rich composition of nanoparticles. Blue shift of absorption energy, as observed in the UV–vis spectrum of ZnO nanoparticles, typically manifests quantum confinement effect. Such transitions indicate the occurrence of various discrete energy states of prepared nanoparticles. FL spectroscopic investigations ascertain the existence of these discrete states by probing the radiative transitions arising among such states. Finally, FL study not only demonstrates visible emissions emanating from the oxygen defect states but more remarkably, in concurrence with EDAX and XPS analysis, establishes the excess of interstitial oxygen defects in prepared ZnO nanoparticles.

Keywords: B. Defects; B. Spectroscopy; C. Optical properties; D. ZnO

1. Introduction

Zinc oxide (ZnO) becomes of greater significance as the novel and improved technologically potent properties arise when the material attains the nanosize low-dimensional structures. The unflinching interest of researchers for study of various nanostructures of ZnO is driven not only due to its enormous applications but also due to the fact that this is a suitable wide band gap semiconductor material to investigate the rich science pertaining to the fundamental issues of synthesis, characterization and subsequently study of its novel properties. A huge wealth of literature dealing with the fabrication and characterization of ZnO nanoparticles is available. The subfield of synthesis and characterization of ZnO nanoparticles remains unabated as the scope of exploring new fundamental properties still unexhausted [1–3]. Out of several properties, luminescence of ZnO nanoparticles has been the foremost investigated issue because of its direct band gap semiconductor behavior which enables ZnO nanoparticles to be used for phosphor, opto-electronic and display devices [4–6].

The fluorescence properties of ZnO are significantly influenced as the dimension of material is reduced. The high exciton binding energy (60 meV) in zinc oxide crystal can ensure efficient excitonic emission at room temperature and consequently room temperature ultraviolet (UV) luminescence has been reported in disordered nanoparticles and thin films [7]. A number of theoretical reports are published to elucidate the size-dependent optical properties of semiconductor clusters [8]. The experimental verification of these theoretical predictions can be achieved with the development of novel approaches of synthesis, processing and characterizations of nanoparticles. The size confinement and surface effects of

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nanoparticles not only cause the increase in band gap but also extraordinarily influence the various optical transitions, such as luminescence [6].

The photoluminescence spectrum of ZnO may exhibit three distinct emission regions: a band in the UV (around 380 nm) that is called the near band edge emission, a band of violet–blue emission (400–440 nm approx.) and a band encompassing green, yellow or orange emission (500–750 nm approx.) [9–15]. The near band edge emission in the UV region is the consequence of direct recombination of free or bound excitons triggered by exciton–exciton collision process. This is the reason behind high efficiency UV emission in powders and thin films of ZnO. The origin of the visible luminescence (say green emission) is usually attributed to the presence of various defects such as oxygen vacancies (V_O), zinc interstitials (Zn_i) and oxygen interstitials (O_i) [7]. The visible emission of ZnO nanoparticle could be influenced by various parameters. There are reports mentioning the dissimilar fluorescence of ZnO nanoparticles of the same size prepared by different methods [4,16]. Researches indicate that the surface passivation via surfactant and polymer capping is also an effective scheme to quench the defect-related visible photoluminescence (PL) from nanosized ZnO [17]. The effect of synthesis methodology and surface passivation indicate that green emission is due to surface [16]. In our previous study we reported that although size of nanoparticles remains unaltered, the process of annealing give rise to some changes in the emission spectra of ZnO nanoparticles. It was further revealed by our previous fluorescence studies that the green emission spread and other visible emissions are altered by annealing treatment without affecting the structural parameters of ZnO nanoparticles [6].

Despite the worldwide intensive research on luminescence of ZnO nanostructures and the effect of various parameters; such as synthesis process, size, shape and distribution of prepared ZnO nanostructure on luminescence; there are still few unexplored issues to understand the fluorescence of nanostructured ZnO [1–17]. To the best of our literature survey, one such unexplored issue is to systematically investigate the effect of fluorescence excitation energy on the fluorescence of ZnO nanoparticles.

In this paper, we report systematic investigation of structural and optical properties of ZnO nanoparticles prepared employing a facile chemical precipitation method. Details of the procedure and underlying mechanism for synthesis of ZnO nanoparticles are provided. Structural and optical properties of prepared ZnO nanoparticles were probed employing XRD, TEM, EDAX, XPS, UV–vis absorption and FL spectroscopies. The structural investigations revealed the hexagonal phase of 25–30 nm size of ZnO nanoparticles. Oxygen rich stoichiometery of prepared nanoparticles is attributed to the dominance of O_i defects in present case. The radiative transitions occurring among the various discrete energy states of prepared nanoparticles were extensively studied through optical characterizations. In contrast to the usually reported size-dependent luminescence of nanoparticles, our FL analysis demonstrates the presence of lattice oxygen along with the coexistence of majority of O_i defects and minority of V_O defects in ZnO nanoparticles, prepared by us.

2. Materials and methods

Zinc Acetate [$Zn(CH_3COO)_2$, Sigma-Aldrich, purity 99.99%], Methyl Alcohol [CH_3OH, Sigma-Aldrich, purity 99.9%] and Sodium Hydroxide [NaOH, Sigma-Aldrich, purity 99.99%] were used as received with further purification. For synthesis of ZnO nanoparticles, we followed previously well established chemical precipitation route [6,18]. In brief, aqueous solutions of 1 M $Zn(CH_3COO)_2$ and 2 M CH_3OH were stirred in a beaker for 30 min as to attain a uniform solution. To this homogeneous mixture, drop by drop addition of freshly prepared 1 M NaOH solution was added via a buret along with continuous magnetic stirring to this product solution for 12 h so as to acquire the white precipitate of ZnO nanoparticles. The precipitate of ZnO nanoparticles was repeatedly washed with distilled water and then dried at 100 °C for 18 h to remove moisture. Furthermore, as reported earlier the ZnO nanoparticles were annealed at 400 °C for 3 h to help us in removing any extraneous impurities (e.g. carbonates etc.) but also assists in formation of pure stable nanophase of ZnO without varying the size of nanocrystals [6,18,19]. The annealed powder of ZnO nanoparticles thus obtained was subjected to various characterizations, as described ahead. The schematic of synthesis procedure is depicted through a flow chart in Fig. 1. The details pertaining to the process, chemical reaction and underlying mechanism for the formation of ZnO nanoparticles can be found elsewhere [6,18]. As elaborated in our previous reports, thermodynamics and kinetics of synthesis method ensures the nanophase formation of ZnO [18,19].

3. Characterization

The X-ray diffraction patterns of prepared powder of ZnO nanoparticles were verified employing *Rigaku MiniFlex II benchtop XRD system* in continuous mode, operating at 30 kV/15 mA to generate the Cu Kα line (1.5419 Å). Transmission electron micrograph (TEM) of ZnO nanoparticles was obtained employing a *Tecnai G^2 Model T30 High-resolution*

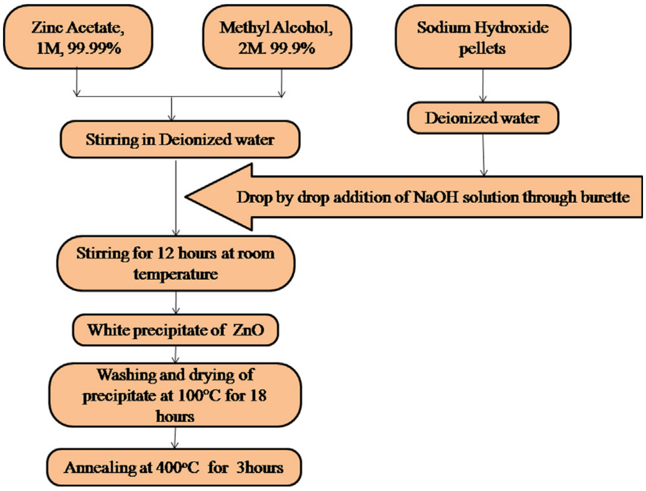

Fig. 1. Flowchart for synthesis of ZnO nanoparticles via chemical precipitation method.