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Photoluminescence properties of zinc oxide nanostructures: A review

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Abstract
Zinc oxide (ZnO) nanoparticles have been extensively studied due to its extraordinary band gap, unique optical, acoustic and electronic properties. It finds applications in numerous fields like solar cells, sensors, photocatalyst, biomedical field, bioimaging, and many others. This review article summarizes various physical and chemical processes used to synthesize of ZnO nanostructures and their applications in various fields. It also discusses the photoluminescence properties of nanostructures and the possible mechanism behind the interesting visible emissions.

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1. Introduction

Semiconducting nanoparticles are of great interest because of their tunable luminescent properties, making them suitable candidates for optoelectronic devices, photocatalytic activities and biological imaging. Metal oxide semiconductor nanoparticles possess unique electronic, chemical and physical properties that are often highly sensitive to the changes in their chemical environment. Due to these properties, metal oxides have been applied for gas sensing properties.

Among the semiconductors, ZnO is one of the most promising materials (II-VI semiconductor) due to its wide band gap (3.37 eV) and high excitonic binding energy (60 MeV), and unique acoustic, optical and electronic properties. Zinc oxide crystallizes in three forms - hexagonal wurtzite, cubic zincblende, and the rarely observed cubic rocksalt. The wurtzite structure is most stable and thus most common at ambient conditions. At ambient pressure and temperature, ZnO crystallizes in the wurtzite (B_4 type) structure. This is a hexagonal lattice, belonging to the space group P63*mc* with lattice parameters a = 0.3296 and c = 0.52065 nm. Primitive unit cell contains four ions, two anions and two cations, with the corresponding basis vectors: (0,0,0), (a/√3, 0, c/2) for the cations and (a/√3, 0, c/8), (0, 0, 5c/8) for the anions. In an ideal hcp lattice, the ratio c/a is equal to √8/3. In practice, depending on the position of the interstitial cations occupying the tetrahedral sites, the c/a ratio may deviate from ideality.

It is composed of a number of alternating planes with tetrahedrally-coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c axis. The tetrahedral coordination in ZnO results in noncentral symmetric structure and consequently piezoelectricity and pyroelectricity grows in the system. Another important characteristic of ZnO is polar surfaces. Along the c-axis, the positively charged Zn-(0001) polar surface and negative charged O-(0001) polar surface are the strongest polarity surfaces. The polar surfaces contribute to the variety of ZnO nanostructures by surface reconstruction to maintain a stable structure. When a stress force is applied, the non-central symmetric structure will lead to the separation of the central point of positive charges and that of negative charges, resulting in a polarization. This is called piezoelectricity, a significant property of ZnO. When Zn and O combine Zn loses two valence electrons to O, thus eventually due to loss of an outer shell the Zn atom shrinks in size from 1.33 A to 0.74 A, while the O atom increases in size due to addition of an outer shell from 0.64 A to 1.4 A. The wide disparity in size between the zinc and oxygen atoms leaves relatively large open spaces thus enabling incorporation of foreign atoms. ZnO occurs as white powder commonly known as zinc white or as the mineral zincite. The mineral usually contains a certain amount of manganese and other elements and is of yellow to red color. Crystalline zinc oxide is thermo-chromic, changing from white to yellow when heated and in air reverting to white on cooling.

This is caused by a minimal loss of oxygen at high temperatures. Zinc oxide is an amphoteric oxide. It is nearly insoluble in water and alcohol, but it is soluble in (degraded by) most acids. Soluble zincates are formed when bases react with ZnO. ZnO decomposes into zinc vapor and oxygen only at around 2248K, reflecting its considerable stability. Heating with carbon converts the oxide into zinc vapor. ZnO is known to have different intrinsic defects which are V_O (oxygen vacancy), Zn_i (zinc interstitial), ZnO (zinc substituted in oxygen antisite), O_i (oxygen interstitial), V_{Zn} (zinc vacancy) and O_{Zn} (oxygen substituted in zinc antisite). Among these, the first three are donor-type defects and the rests are the acceptor-type defects.

In this review article, we have extensively discussed on the various fabrication techniques of ZnO nanoparticles and nanostructures with interesting morphology. In the next part, the photoluminescence properties of ZnO nanostructures have been explained.

2. Synthesis

Several fabrication techniques are used to produce ZnO nanoparticles (NPs) such as co-precipitation technique, thermal hydrolysis techniques, hydrothermal processing, sol-gel method, vapor condensation method, spray pyrolysis and thermochemical techniques, biosynthesis schemes using biological materials as reducing and stabilizing agents. Puneetha *et al.* (2020) [17] synthesized ZnO NPs using simple co-precipitation process. The synthesized NPs possessed enhanced photocatalytic activity. The nanostructures, in the presence of H_2O_2, exhibited highest photodegradation rate of Crystal Violet solution under alkaline pH. Guo *et al.* (2000) [9] synthesized highly monodispersed polyvinylpyrrolidone (PVP) capped ZnO nanoparticles, by reaction of Zn acetate with NaOH in presence of PVP. The average particle size of uncapped and capped ZnO nanoparticles was 4.0±0.6 nm and 3.7±0.3 nm, respectively. The position of absorption peak of capped ZnO NPs were blue shifted to 303 nm compared to uncapped ZnO (~ 312 nm), which can be attributed to smaller particle size. Single crystal wurtzite structured ZnO have been synthesized using trouble free and scalable hydrothermal process (Bharti and Bharati 2016) [2]. Using different co-surfactant in the process resulted in different morphology of ZnO which had different applications as a catalyst in various organic reactions and could also be used as a photocatalyst and fuel cell, solar cell. Chung *et al.* (2015) [5] employed sol-gel method to synthesized minimal size ZnO NPs, with average size of 13 nm. Minimal size could be achieved by optimising synthesis parameters such as ratio of starting materials, molar concentration and calcination temperature. There are various reports of low cost green synthesis of ZnO NPs. ZnO was synthesized using *Azadirachta indica* (Neem) leaf extract (Bhuyan *et al.* 2015) [3], Ixora coccinea leaf extract (Yedurkar *et al.* 2016) [22], *Mangifera indica* leaves (Rajeshkumar *et al.* 2018) [18]. The ZnO nanoparticles synthesized using Neem leaf extract, were pure, spherical in shape with size ranging from 9.6 to 25.5 nm. In contrast, use of Ixora coccinea leaf extract resulted in formation of larger particles with average size 145 nm. Use of Magnifera indica helped in formation of ZnO NPs withaverage size 45-60 nm and showed anti-cancer activity against lung cancer. Synthesis using biological materials is an eco-friendly approach to nanoparticle production. This process is devoid of using toxic chemicals, high temperatures, and costly equipment needed for traditional physical and chemical synthesis methods. Extensive research has been performed on synthesis of ZnO nanoparticles with various morphologies. Kong *et al.* (2001) [11] synthesized Zno nanowire monocrystallites using physical vapor deposition approach. The unidirectional growth of the ZnO nanowires was controlled by the conventional vapor-liquid-solid mechanism. Ring shaped ZnO nanostructures was synthesized by water based wet chemical route without using any template (Mondal and Pal 2011) [16]. Use of surfactant cetyl trimethyl ammonium bromide (CTAB) enhanced the formation of annular ring shaped ZnO. Shinde *et al.* (2012) [21] reported the synthesis of hexagonal pillar shaped ZnO nanorods with different sizes by spray pyrolysis technique. The ZnO nanorods thin films showed much better sensitivity and stability than the conventional materials to H_2S gas. The hexagonal pillar shaped ZnO nanorods can improve the sensitivity and selectivity of the sensors. Defect free, crystalline wurtzite structured ZnO nanorods have been synthesized hydrothermally by Kumar *et al.* (2021) [13]. The synthesized nanorods were used as photoanodic material for dye-sensitized solar cells. Hydrothermal synthesis technique was also applied to synthesize monodispersely sized ZnO nanowires from randomly sized seeds (Zhao *et al.* 2020) [24]. Multibranched flower like ZnO nanostructures with enhanced antifungal activities, have been synthesized using eco-friendly hydrothermal process (Chang *et al.* 2020) [4]. Fabrication of hexagonal ZnO nanopyramids was successful using electrochemical method (Samanta & Basak 2012) [19]. The pyramidal structure formed due to anisotropic growth of various crystal facets of ZnO. ZnO nanosheets with thickness ranging from 20 to 50 nm have been synthesized using microwave-assisted hydrothermal based method (Aljaafari 2020) [1]. The synthesized nanosheets showed higher efficiency in photodegradation of organic dyes. Thinner sheets showed higher efficiency owing to increased surface area. There is report on synthesis of ZnO nanoshells, by thermal evaporation of Zn at 500 °C in a tube furnace, under the flow of argon:oxygen (10:1) gas mixture (Leung *et al.* 2005) [14]. Owing to the stability and non-toxicity of ZnO, researchers have explored all the possible morphologies of ZnO. Brush-like hierarchical ZnO nanostructures assembled from initial 1D ZnO nanostructures were prepared from sequential nucleation and growth following a hydrothermal process (Zhang *et al.* 2009) [23]. These nanostructures were reported to have excellent ethanol-sensing properties. The main advantages are excellent selectivity, fast response (less than 10 s) and low detection limit.

3. Photoluminescence Properties

ZnO is a II-VI group semiconductor with wide band gap of 3.37 eV. Interestingly, it produces very bright luminescence in the ultraviolet region. The UV emission is usually attributed to the interband transition or the exciton combination in ZnO. Reports show that manipulating crystal structure and morphology, introducing dopants, and change in excitation wavelength can produce luminescence in the complete spectrum of visible range. The origin of the visible emission has been investigated for a long time and various mechanisms are proposed. Violet- blue emission at around 410 and 430 nm have been observed in ring shaped ZnO nanostructures (Mondal & Pal 2011) [16], Gd^{3+} doped ZnO (Sambasivam *et al.*, 2015) [20]. The strong violet emission originates from recombination of an electron in the defect state of Zn_i with a hole in the valence band. The blue emission

is ascribed to transition from a surface defect state (Ss) to the valence band. Very strong green luminescence peaked at around 2.3 eV, was exhibited by hydrothermally grown ZnO single crystal (Čížek *et al.* 2015) [6], ZnO nanocages (Snure & Tiwari 2007) [15], ZnO nanorods (Hasabeldeim *et al.* 2019) [10]. It was found that green luminescence originates from recombination of electrons of the conduction band by zinc vacancy acceptors. Another origin of green luminescence is transition between the photoexcited holes and singly ionized oxygen vacancy. García-Velasco *et al.* (2022) [8] observed strong yellow-orange luminescence ZnO nanostructures such as nanoislands, nanosheets, microflowers and nanoparticles, synthesized by hydrothermal route. Strong red emission have been observed in Eu^{3+} doped ZnO, makeing it important for applications in red emitting diode (Vinod Kumar *et al.* 2014) [13]. Hence, various luminescence centres can be induced by defect states. Role of defect states in the origin of visible emissions is significant and makes ZnO an efficient candidate for light emitting diode, bioimaging, photocatalytic activities. Djurišić *et al.* (2006) [7] studied the excitation wavelength dependent emission properties of ZnO with various morphologies. Photoluminescence spectra from shells, rods, and needles of ZnO were measured for excitation wavelengths 325, 380, 390, and 400 nm. The emission from the needles was observed to be orange for excitation at 325 and 380 nm, and green for 390 and 400 nm. With increase in excitation wavelength, the emission peaks mainly orange emission blue shifted to yellow. The shift was more prominent in needles than the rods and shells. The green yellow and orange emissions originated from defect related states and depend on excitation wavelengths.

4. Conclusion

ZnO NPs have significant optical potential. The use of various methods of synthesis, use of capping agent, synthesis temperature affects the physical and morphological characteristics of nanoparticles which in turn leads to change in photoluminescent properties. These NPs finds applications in optoelectronic, photocatalysis and biomedical fields.

6. References

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