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Synthesis of UV Emitting ZnO Nanosol

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ABSTRACT

Pure UV emitting ZnO nanosol were prepared by sol-gel method using steric cleaner. Their band gap was approximately 6 eV. Hence the increase in band gap compared to bulk ZnO (3.37 eV) is attributed to decrease in particle size to nano-order and quantum confinement effect. Absorbance and photoluminescence property of the ZnO sols were investigated. Novel property of the prepared ZnO nanosol is that they showed no absorption, emission and excitation in the visible region, but only in the UV region. Maximum UV emission was around 340 nm and 320 nm for excitation at 227 nm and 250 nm, respectively. The UV emission is due to excitonic emission and the absence of visible emission is due to absence of intrinsic defects. Such ZnO nanoparticles with pure UV emission and no visible emission is rare, but is on demand, hence it adds advantage to the experimental method. Additionally, the emission spectrum of the ZnO sols showed size dependent stokes shift of around 2.3 eV compared to their absorption spectrum, which is due to decrease in particle size to nano-order and the vibrational relaxation of the excited nanoparticles to the ground state. The ZnO nanosol due to its wide band gap can be used in engineering high voltage and high temperature electronic applications.

1. Introduction

Zinc oxide is well known for its unique advantageous photoelectronic properties with wide direct band gap of 3.37eV and stable high exciton binding energy of 60 meV at room temperature [1-4]. ZnO has wide applications especially in ultraviolet (UV) light-emitting diodes (LEDs), UV lasers and transparent UV-protection films, etc. ZnO nanoparticles are commonly known to have excitonic UV emission and visible emission due to intrinsic defects [4, 5]. Especially, green and yellow emission is commonly observed due to intrinsic surface defects. These defects are thought to increase as the particle size decrease due to corresponding increase in surface-to-volume ratio. Hence it is challenging and demanding to synthesize ZnO nanoparticles without the defects or visible emission. In this paper, we have demonstrated a simple cost effective method for synthesis of ZnO sols with band gap ~6 eV, pure UV emission and no visible emission by sol-gel method using steric cleaner. The wide band gap ZnO nanosol prepared can be used to engineer high voltage and high temperature electronic appliances.

2. Experimental Methods

2.1 Chemicals

For the preparation of ZnO sol, the following materials such as zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), lithium hydroxide ($LiOH.H_2O$) and ethanol (CH_3CH_2OH) were used.

2.2 Synthesis

2.2.1 ZnO Sols Preparation

First, 0.55 g of zinc acetate was dissolved in 50 mL of absolute ethanol and stirred using a steric cleaner at three different temperatures, such as 40 °C, 50 °C and 60 °C, each separately. When each of the solution changed into an emulsion, 0.01 g of lithium hydroxide ($LiOH.H_2O$) was added as a chelating agent. Then each of the preparations was boiled at 60 °C in the steric cleaner until a transparent sol was obtained. In this paper, the obtained ZnO sols has identified as 40 °C sol, 50 °C sol and 60 °C sol, respectively.

2.3 Characterization

The ZnO sols prepared were characterized using UV-Vis absorbance spectrometer and photoluminescent spectrometer.

3. Results and Discussion

From absorption spectra shown in Fig. 1, it can be observed that the ZnO 40 °C, 50 °C and 60 °C sols attains the maximum absorbance of 2.57, 2.49 and 2.55 at wavelength about 203.4 nm, 206.4 nm and 207 nm, respectively.

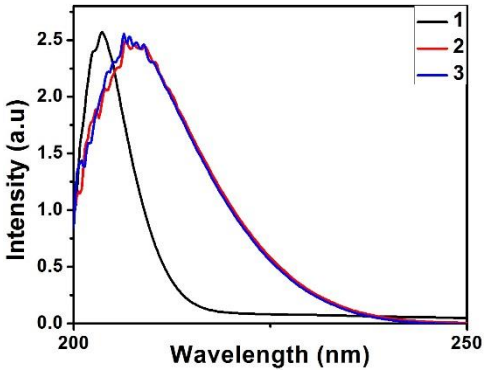

Fig. 1 Absorption spectrum of the ZnO 40 °C sol, 50 °C sol and 60 °C sol, respectively, are indicated by the graphs "1", "2" and "3".

The direct band gap energy of each of the ZnO 40 °C sol, 50 °C sol and 60 °C sol prepared were calculated to be 5.94 eV, 5.64 eV and 5.64 eV, respectively from the Tauc's plot shown in Fig. 2. The bulk ZnO particles attains maximum absorbance at 360 nm, with typical energy band gap of 3.37 eV. Therefore, there is a blue shift in the absorption spectrum of the ZnO sols and consequently an increase in their band gap energy.

According to quantum confinement theory, as a particle size decreases comparable to the wavelength of the electron, the electron out of its interaction with that particle, gets confined to discrete quantum energy levels, which will give rise to an enlargement in the energy band gap [2, 3, 6]. Therefore, the increased band gap energy of our ZnO sols should be due to decrease in their particle size to nano-order and the above

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described quantum size effect according to the quantum confinement theory. It also confirms that the increase in band gap to the order of 6 eV is due to the quantum size effect. That is, because of the decrease in size of the ZnO particle to nano-order, comparable to the wavelength of electrons, the electrons interact with the ZnO and get confined into quantum energy levels. This leads to increase in the band gap of the ZnO nanoparticles and hence the blue shift in the absorbance spectrum. Consistent with the result, similar kind of blue shift in the band gap of ZnO nanoparticles were reported [4, 7]. This further confirms that we have obtained a ZnO nanosol.

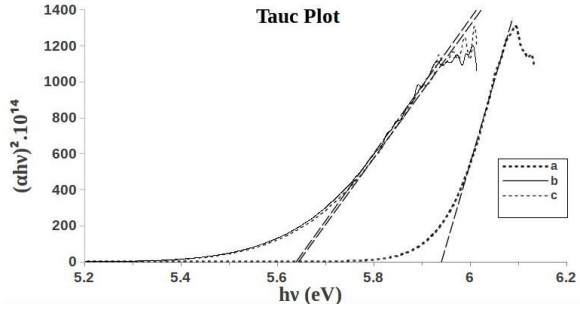

Fig. 2 Tauc plot of the 40 °C sol, 50 °C sol and 60 °C sol, respectively, are indicated by the graphs "a", "b" and "c". The straight line in the plot are Tauc's extrapolation straight line.

There is no any absorbance in the visible region of the absorption spectrum of all the ZnO sols prepared, indicating that the sols do not have common native defects like Zn interstitials and O vacancies. In recent years, many efforts are put to reduce these native defects or prepare ZnO nanoparticles with no emission in the visible region [1, 4, 8]. So absence of the defects in the prepared ZnO sols, makes our experimental method an exceptional one. Additionally, the absence of the absorption in the visible region indicates that the prepared ZnO sols are transparent to the visible light.

The spectra at right in Figs. 3 and 4 show the emission spectra of ZnO sols, when excited by UV light of wavelength 227 nm and 250 nm respectively. Their spectral characteristics are summarized in the Table 1. When excited at 227 nm, the emission spectra of all the sols show two bands around 330 nm and 340 nm, which together cover the UV region. When excited at 250 nm, all the sols show a single band with emission peak at 320 nm.

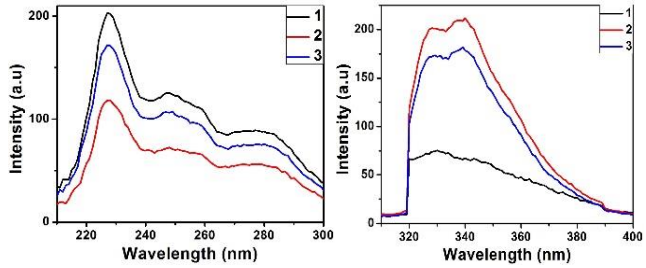

Fig. 3 a) The graphs 1,2,3 are excitation spectrum of the ZnO 40 °C sol, 50 °C sol and 60 °C sol, respectively, obtained by monitoring emission at 330 nm. b) The graphs 1,2,3 are emission spectrum of the ZnO 40 °C sol, 50 °C sol and 60 °C sol, respectively, obtained while the sols were excited at 227 nm

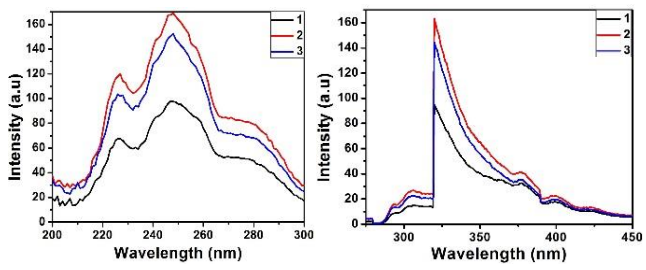

Fig. 4 a) The graphs 1,2,3 are excitation spectrum of the ZnO 40 °C sol, 50 °C sol and 60 °C sol, respectively, obtained by monitoring emission at 320 nm. b) The graphs 1,2,3 are emission spectrum of the ZnO 40 °C sol, 50 °C sol and 60 °C sol, respectively, obtained while the sols were excited at 250 nm

Typical ZnO emission spectra consist of a band in the UV region and a second band in the visible region which are due to excitonic emission and intrinsic defects, respectively [2, 4, 5]. The emission spectrum corresponds to the typical excitonic emission in the UV region, which is characteristic of ZnO nanoparticles. Absence of emission in the visible region, as in the absorption spectra indicates that the sols obtained are free from intrinsic defects. Similar optical property with pure UV emission in ZnO nanoparticles were reported by very few [8, 10, 11]. Wang et al have also attributed that such a pure UV emission is due to good quality ZnO nanoparticles [11].

The UV emissions correspond to a range of energy from 3.6 to 3.9 eV. Neumark et al have reported ZnO nanorods of size 1.1 nm to have UV emission in the energy range of 2.6 to 3.5eV [12]. Comparatively, our ZnO nanoparticles, being smaller (~0.8 nm) should have a blue shift in the emission spectrum due to quantum size effect and hence the UV emission in the range of 3.6 to 3.9 eV.

Table 1 Spectral characteristics of ZnO emission spectrum of the ZnO sols

Excitation wavelength in nm (energy eV)	Emission band maximum of the samples					
	40 °C sol		50 °C sol		60 °C sol	
	Wave length (nm)	Energy (eV)	Wavelength (nm)	Energy (eV)	Wavelength (nm)	Energy (eV)
227 (5.46 eV)	330	3.76	328	3.78	329.07	3.77
	340	3.65	340	3.65	339.07	3.66
250 (4.96 eV)	320	3.88	320	3.88	320.00	3.88

Unanimously, it can be observed that while excited at 227 nm, the emission band maximum of all the ZnO sols prepared are red shifted by approximately around 133 nm compared to their absorption band giving rise to stokes shift. Stokes shift can be calculated using the formula,

$$\text{Stokes shift } \Delta E = E_g - E_L, \quad (1)$$

where E_g is absorbance energy or band gap energy and E_L is PL emission energy. Stokes shift of the emission spectrum for ZnO 40 °C sol, 50 °C sol and 60 °C sol - while excited at 227 nm, as tabulated in Table 2, are 2.45, 2.36 and 2.33 eV, respectively, and the same while excited at 250 nm was calculated to be 2.22, 2.13 and 2.11 eV, respectively. Stokes shift increases as particle size decreases and this stokes shift enhancement is a characteristic property of ZnO nanoparticles [2]. Additionally, stokes shift occurs as the excited ZnO nanoparticles vibrationally relax to ground state [3]. Collectively, it further confirms that we have obtained ZnO nanosol.

Comparing the two emission spectra, it can also be observed that higher the excitation energy, higher the emission energy and emission intensity of the ZnO particles prepared.

Table 2 Stokes shift of emission spectra of the ZnO sols while excited at 227nm

Sample	PL emission spectra maximum		Absorbance spectra maximum		Strokes Shift = E_g - E_L (eV)
	Wavelength (nm)	Energy E_L (eV)	Wavelength (nm)	Energy E_g (eV)	
40 °C sol	340.00	3.65	203.4	6.10	2.45
50 °C sol	340.00	3.65	206.4	6.01	2.36
60 °C sol	339.07	3.66	207.0	5.99	2.33

The spectra at left in Fig. 3a and 3b show the excitation spectra of the ZnO sols obtained by monitoring the emission at 320 nm and 330 nm respectively. All the ZnO sols prepared exhibit two prominent excitation peaks around 227 nm and 248 nm, when emission wavelength was set to 320 nm and 330 nm, though there is change in shape of the spectra due to relative increase in the intensity of the peaks. That is, for emission at 320 nm, excitation peak around 248 nm have maximum intensity, while for emission at 330 nm, the excitation peak around 227 nm have maximum intensity. On the other hand, the emission spectra show consistent results. In emission spectra, excitation at 250nm show strong emission at 320 nm, while excitation at 227 nm though shows emission around 330 nm, maximum emission is around 340 nm. Hence it can be speculated that the prepared ZnO sols are getting excited to 2 different excited states corresponding to 227 nm and 248 nm, which upon excitation may probably undergo non-radiative transition by vibrational relaxation or internal conversion to lower energy state and radiatively transit to ground state giving rise to strong emission at 340 nm and 320 nm, respectively. Preparing ZnO showing excitation in the range of 200–250 nm and emission in the range of 320–340 nm has been challenging and is less reported, hence electronic transitions explaining these spectra of ZnO in these range of wavelength are not yet reported.

4. Conclusion

Pure UV emitting ZnO nanosols were obtained by sol-gel method using steric cleaner at three different temperatures, at low cost effectively. The ZnO nanoparticles were found to have band gap ~ 6 eV. Additionally, they also exhibited emission in the UV region which is attributed to excitonic emission. Due to decrease in the particle size of the ZnO nanoparticles compared to bulk ZnO, there was (i) blue shift in the absorption spectrum of ZnO nanoparticles compared to that of bulk ZnO, and (ii) stokes shift of around 2.3 eV in its emission spectrum compared to its absorption spectrum. Unanimously, the absorbance spectrum, photoluminescence emission and excitation spectrum confirm that the prepared ZnO is UV emitting nanosol. Additionally, the prepared ZnO have a significantly large band gap compared to the conventional semiconductors, it can be used to engineer electronic devices operating at high voltage and high temperature, cost effectively.

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