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Photo-Physical Properties and PL Measurements of ZnO Nanoparticles Synthesized by Sonochemical Method

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Abstract: Nanoparticles of ZnO at different sizes were prepared by a novel sonochemical route from zinc acetate and sodium hydroxide without any requirement of calcinations steps at high temperature and without surfactants. Variations in several parameters and their effects on the structural (crystal size and morphology) properties of nanoparticles were investigated. Characterizations were carried out by X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), Raman spectroscopy, solid state UV and solid state Florescent (PL).

Keywords: Nanochemistry, Sonochemistry, Zinc oxide, UV, PL.

1. Introduction

Nanoparticles are a class of materials with properties distinctively different from their bulk and molecular counterparts and find use in a variety of different areas such as electronic, magnetic and optoelectronic, biomedical, pharmaceutical, cosmetic, energy, environmental, catalytic, and materials applications. Because of the potential of this technology, there have been worldwide increases in investment in nanotechnology research and development. A surfactant-free hydrothermal technique (i.e., high-temperature, high-pressure) has shown to be a suitable way for obtaining materials with small grain size, high specific surface areas, and high crystallinity [1–11]. The sonochemical method has been proven to be a useful technique to obtain novel materials with interesting properties. It is based on acoustic cavitation's resulting from the continuous formation, growth and implosive collapse of bubbles in a liquid [8]. This method has been used for synthesis of many kinds of nanomaterials so far. Also some researchers have used this wet method to prepare different ZnO nanocrystalline. Instead of aqueous system, ethanol, an organic solvent, was chosen for the present study. Zinc oxide is one of the most promising materials for optoelectronic application because of its wide band-gap (3.3eV) semiconductor materials and large excitation binding energy (60meV) which makes the exciton state stable even at room-temperature. ZnO has been extensively study duo to its potential

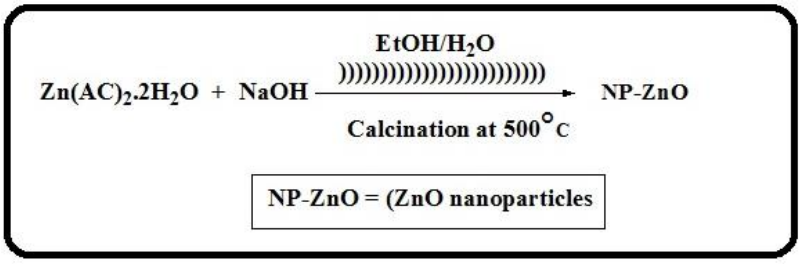
applications in room-temperature, such as ultraviolet (UV) lasers, detector and light emitting device, sensors and photo catalysis duo to its unique electrical and optical properties, such as dielectric constant, high chemical stability, and good photoelectric and piezoelectric behaviors [1-4]. In the present work, we developed a simple sonochemical method to prepare ZnO nanoparticles, using zinc acetate and sodium hydroxide without any additives. The ZnO nanoparticles were characterized by X-ray powder diffraction (XRD), solid state UV spectroscopy and solid state photoluminescence (PL) spectroscopy. Also the morphology and size of the nanoparticles were observed by scanning electron microscopy (SEM). In general, the PL spectroscopy is another powerful tool to obtain information about the electro-optics and photoelectric properties of nanomaterials as it depend on electronic excitations. The PL gives the possibilities to study the key question in nanoparticles and quantum dots (QD) spectroscopy deals with the determination of the discrete energy spectrum. The PL study of the ZnO nanocrystals attributes different mechanisms (band-to-band transition, blue-green emission band related to oxygen vacancy, surface and impurity state and etc.) to the size dependent. We have prepared a series of ZnO nanoparticles with diameter from (150 nm, 100 nm, 50 nm and 20 nm) and investigated the dependence of the PL characteristics on the nanoparticle sizes [9-22].

2. Subjects and Methods:

‘’gfvDifferent amounts of NaOH solution with a concentration of 0.1 M were added to the 0.02, 0.01, 0.005 M solutions of $Zn(CH_3COO)_2.2H_2O$ in ethanol. The mixtures were sonicated for 30 min. Different amounts of NaOH solution with a concentration of 0.1 M were added to the 0.02, 0.01, 0.005 M solutions of $Zn(CH_3COO)_2.2H_2O$in ethanol/water. The obtained mixtures were sonicated for 30-60 min with different ultrasound powers. Table. 1. show the conditions of reactions in detail. A multiwave ultrasonic generator (Bandlin Sonopuls Gerate-Typ: UW 3200, Germany) equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 30 kHz with a maximum power output of 780 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. The wave amplitude in each experiment was adjusted as needed. The X-ray powder diffraction (XRD) measurements were performed using Philips diffractometer of X’pert Company with mono chromatized $Cu_{k\alpha}$ radiation. The crystallite sizes of the selected samples were estimated using Sherrer method. The samples were characterized using a scanning electron microscope (SEM) (Philips XL 30) with gold coating. The PL properties were investigated using an F-4500 FL spectrophotometer at room temperature.

3. Results:

The reaction between zinc acetate and sodium hydroxide to form zinc oxide has been shown in scheme 1.



Scheme. 1. Formation of ZnO nanoparticles at different morphology

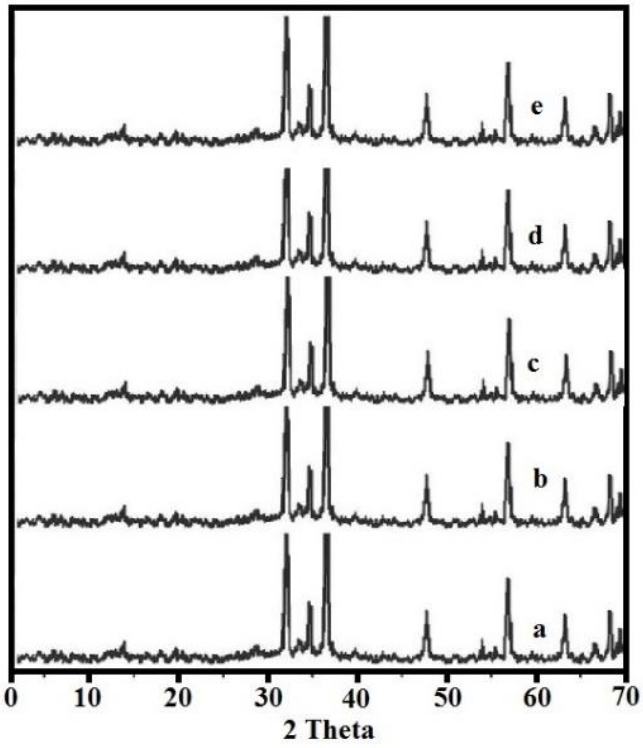


Figure.1. shows the XRD pattern of the ZnO nanoparticles at different sizes that prepared by ultrasonic method. As it has been seen the XRD patterns are quite the same and are in agreement with the typical wurtzite structure ZnO diffraction (hexagonal phase, space group C6v, with lattice constants a = 3.24982(9) Å, c = 1.6021 Å, Z = 2, JCPDS No. 36-1451).

Fig. 1. X- Ray powder diffraction pattern of ZnO nanoparticles at different sizes, a=200 nm, b=150 nm, c=100 nm, d=50 nm and e=20 nm. Sharp diffraction peaks shown in Fig. 1. indicate good crystallinity of ZnO nanoparticles no characteristic peak related to any impurity was observed. The broadening of the peaks indicated that the particles were of nanometer scale estimated from the Sherrer formula, $D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively. The morphology, structure and size of the samples are investigated by scanning electron microscopy (SEM). Fig. 2. indicates that the original morphologies of the ZnO nanoparticles are approximately spherical with the diameter varying between 20 to 200 nm for synthesis by sonochemical method (Fig. 2. a, b, c and d).

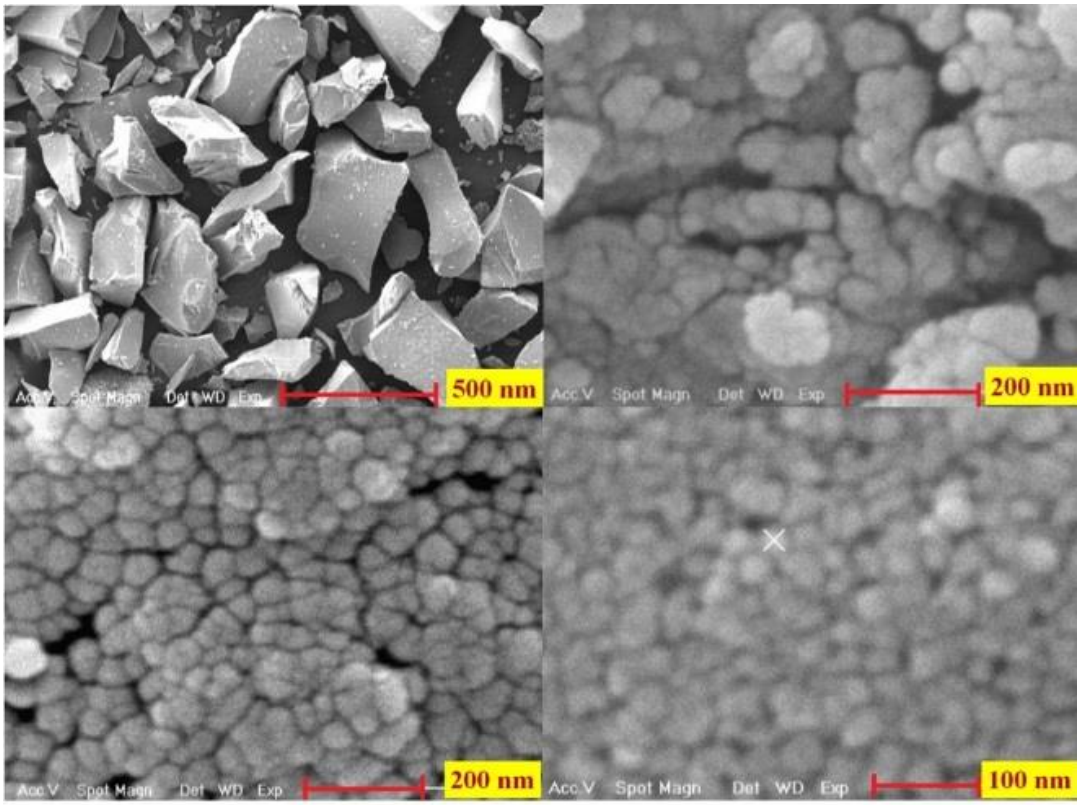


Figure. 2. SEM images of ZnO nanoparticles at different sizes, a=200 nm, b=150 nm, c=100 nm and d=50 nm.

The average size of the particles of samples about 20-200 nm. To investigate the size distribution of the nanoparticles, particle size histograms were prepared for the samples a, b, c, d and e (Fig. 3).

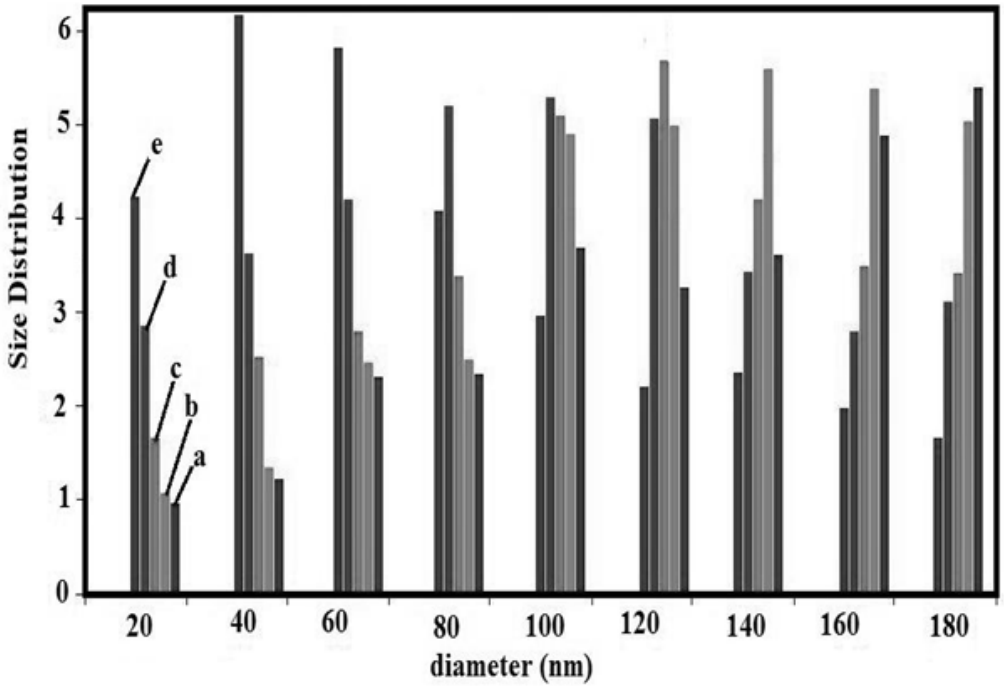


Figure. 3. Particle size histograms of ZnO nanoparticles at different sizes, a=200 nm, b=150 nm, c=100 nm, d=50 nm and e=20 nm.

Most of the particles possess sizes in the range from 20 to 200 nm for this sonochemistry method. For further demonstration, the EDAX was performed for the sample b. The EDAX spectrum in Fig. 4. (Chancy sample 100 nm) show the presence of Zn and O are the only elementary component.

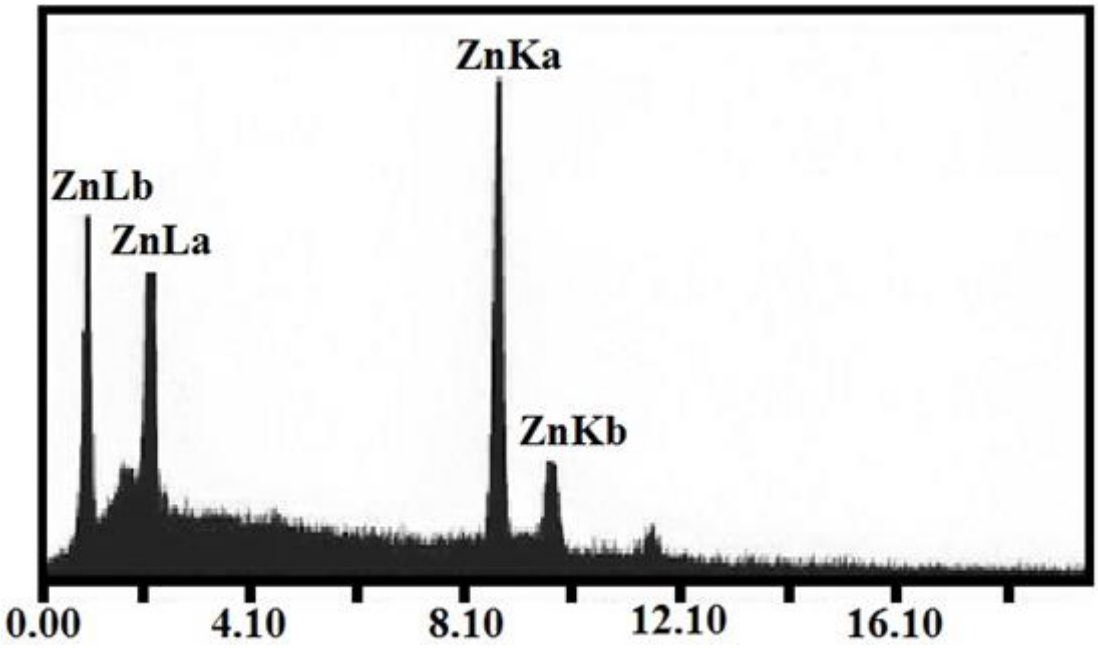


Figure. 4. The EDAX analysis of ZnO nanoparticles (chancy 100 nm).

In order to investigate the role of sonication on the composition, size and morphology of the products, we carried out the reaction without sonication with the same conditions of the optimized samples. The XRD patterns of the obtained product corresponds to ZnO (Fig. 5), but the SEM images show that the nanoparticles of the samples without using sonication have larger sizes as compared with the samples obtained via the sonochemical route.

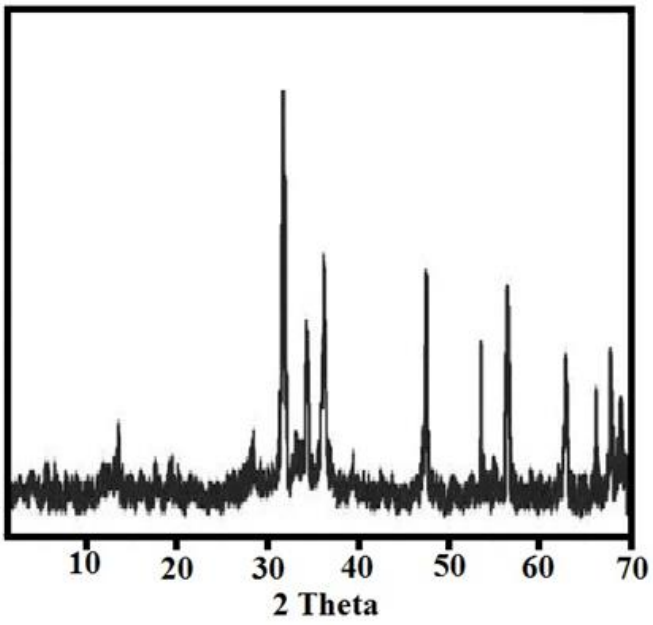


Figure. 5. XRD pattern of ZnO powder at bulk size.

It was indicated that the ZnO nanoparticles could decompose the organic pollutants by formation of exceed super oxides and/or hydroxyl radicals at the ZnO interface in sonochemical. Fig. 6. shows the solid state UV-vis spectra of the compounds (all ZnO nanoparticles) display one absorption wide band with the maximum intensity of 376 nm. Zinc oxide (ZnO) a representative II-VI compound semiconductor has attractive properties, such as the direct wide band-gap (3.4 eV).

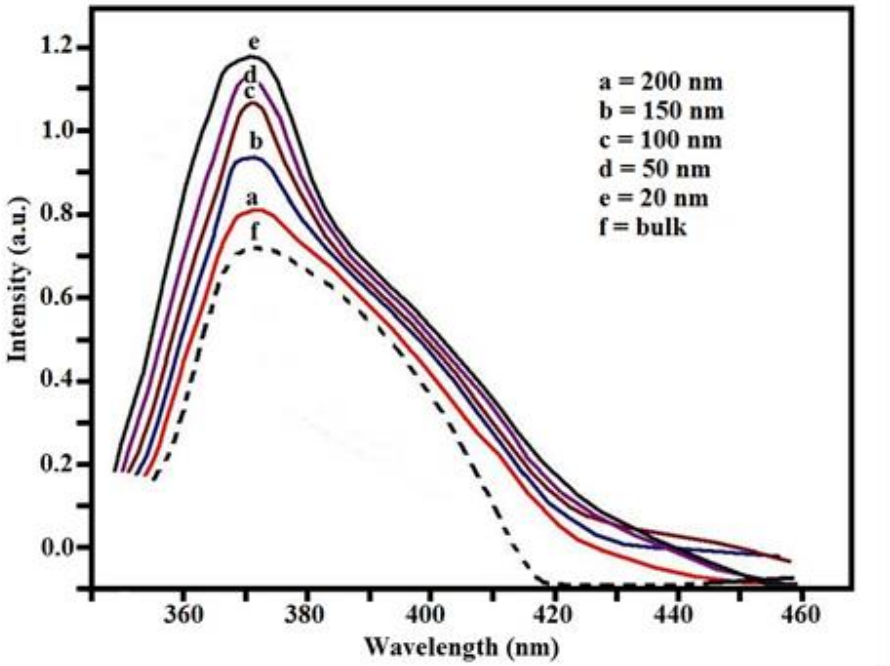


Figure. 6. The UV-vis absorption of ZnO nanoparticles at different sizes, a=200 nm, b=150 nm, c=100 nm, d=50 nm, e=20 nm and f=bulk size of ZnO at room temperature.

In this research large exciton binding energy (60 meV) at room temperature studied. This suggests a host of possible practical applications, notably in the area of ultraviolet/blue-green emission devices. Fig. 7. displays the PL spectra of the bulk and nanocrystalline sizes (a, b, c, d and e) ZnO nanoparticles at room temperature. The PL peaks blue-shift is indicated by a decreased diameter nanoparticle size, exhibiting the quantum confinement effect. Based on the simple effective-mass theory, the emission photon energy is given by equation 1.

$$E_g(d) \approx E_{ex} + \frac{\pi^2 \hbar^2}{2d^2}\left(\frac{1}{m_e^*} - \frac{1}{m_h^*}\right) \quad \text{(Eq. 1)}$$

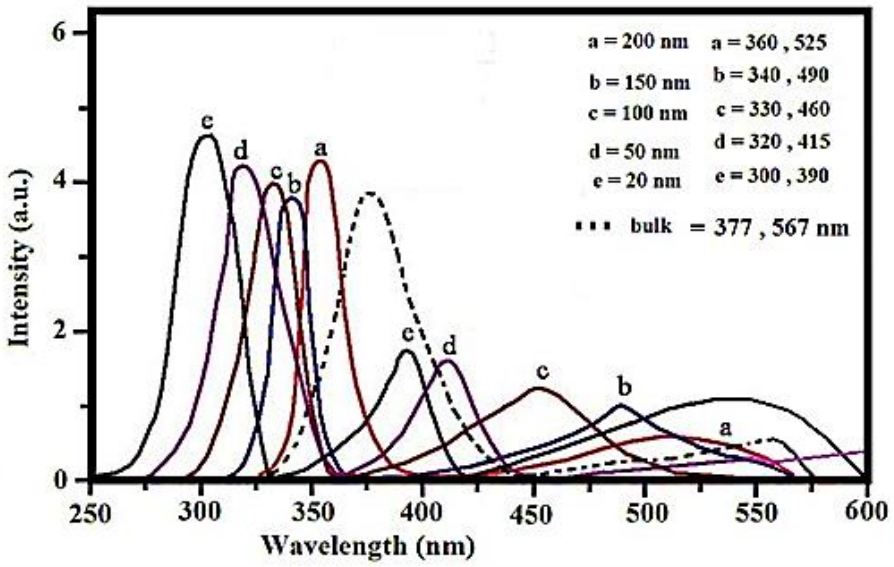


Figure. 7. The PL spectra of ZnO nanoparticles at different sizes, a=200 nm, b=150 nm, c=100 nm, d=50 nm, e=20 nm and f=bulk size of ZnO at room temperature.

Where Eg(d) is the photon energy, Eex is the free- exciton energy of bulk ZnO, me and mh are the effective mass of electron and hole, and d is diameter of ZnO nanoparticle, respectively. PL spectrum was observed for all sizes of ZnO nanoparticles, covering from the short wavelength at high UV-blue emission (300-380 nm) to long wavelength at weak blue-green emission (390-550 nm). The strong room temperature UV emission intensity should be attributed to high purity with perfect crystallinity of the synthesized samples. Also the strong UV emission corresponds to the excitation recombination related near-band edge emission of ZnO nanopractices. The broad peak at weak blue-green emission was observed which is caused by defect levels occurring mainly due to oxygen vacancies in the bulk and nanoparticles of the surface which might be in the form of OH ions [6]. In fig. 7. the blue-shift of band-edge and defect levels seems to be related to the size-dependent stokes shift, which is observed on other semiconductor nanoparticles such as InP and CdSe [7]. The size-dependent electron-phonon processes and spin-orbit exchange interactions are suggested to be responsible for the strong size dependent stoke shift [7 and 8]. It may also be noted that PL spectra of ZnO is strongly dependent on the nanoparticles size. The values of size (20-200 nm), band-edge energy (4.13 eV to 303 eV), band defect (3017 eV to 2.24 eV) and wavelengths (300 to 360 nm), (390 to 525 nm) for a ZnO semiconductors are listed in Table. 1.

Table. 1: The size (nm) effect on band-edge energy and wavelength for ZnO semiconductors.

Particle size (nm)	Wavelength (nm)		Emission energy (eV)	
	Band-gap	Band-defect	Band-gap	Band-defect
Bulk (250)	377	567	3.3	2.19
200	360	525	3.44	2.36
150	340	490	3.64	2.53
100	330	460	3.75	2.69
50	320	415	3.87	2.98
20	300	390	4.13	3.17

The variations of nanoparticle size of ZnO are also shown as a function of wavelength in Fig. 8. As seen this figure the nanoparticle size decreases with linear increasing band-edge energy and band defects. Therefore by using the Fig. 8. we can directly estimate the nanoparticle size from the measured PL spectra. It is seen, there is a threshold size (250 nm) for ZnO nanoparticles so that the band energy of PL spectra are blue-shifted as the nanoparticle size decreases.

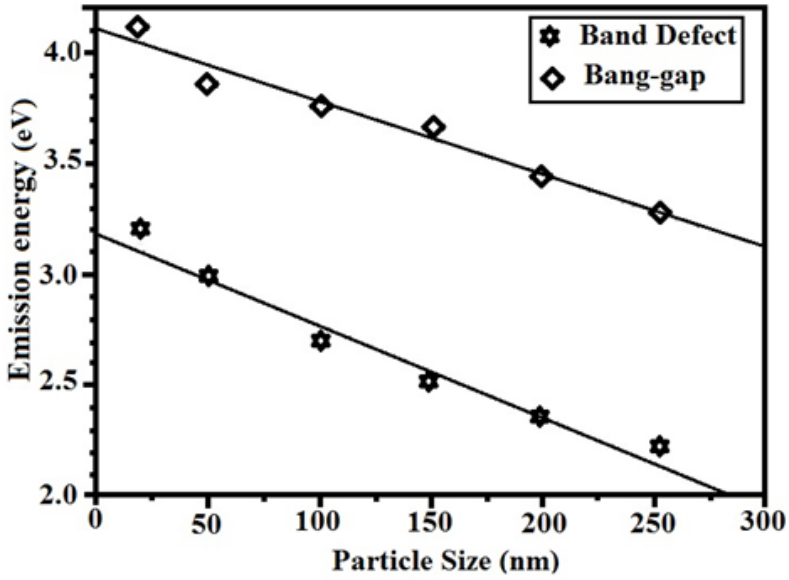


Figure. 8. The variation of ZnO nanoparticle as a function of emission energy (eV).

4. Conclusions:

A simple sonochemical method has been presented by the direct transformation of Zn(OAc)2.2H2O precursor to create the ZnO nanoparticles. The properties of nanoparticles were studied by SEM, XRD, Raman, Solid state UV-vis and Solid state florescent (PL). SEM analysis shows that ZnO nanoparticles have an average diameter of 20 to 200 nm which varied by different factors. Comparing with the gas-phase approaches such as thermal evaporation and chemical vapor deposition which require high temperature and expensive equipment, wet chemical methods have been proven to be simple and versatile approaches for preparing ZnO nanostructures due to their relatively low growth temperature and good potential for mass production, so preparation of ZnO via solution chemical routes provides a promising option for large-scale production of this material. In the present work we have expected to obtain

zinc hydroxide as the intermediate product in sonochemical method. It shows that the type of the metal ion, the type of the sonicator device, the power of ultrasound in sonochemical method have probably affected on the type of the product.
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