

ZnO nanoparticles by citric acid assisted microwave solution combustion method

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ZnO nanoparticles were prepared by citric acid assisted microwave solution combustion method and its microstructure and optoelectronic properties had been investigated. The XRD, TEM, SEM and FT-IR analyses confirm that the ZnO crystallites with the hexagonal wurzite structure were directly formed. The crystalline grain size of ZnO was 9 nm and its specific surface area reached 19 m²/g. The room temperature photoluminescence proved that it had a blue emission, which increased remarkably with treated temperatures.

Key words: ZnO, Citric acid, Nanocrystalline, Combustion, Microwave synthesis.

Introduction

ZnO nanoparticles, as an n-type semiconductor with a direct wide band gap ($E_g = 3.37$ eV), have been attracting much attention due to wide range of applications in gas sensors [1], optoelectronic devices [2], dye-based solar cells [3], and catalysts [4]. ZnO has been used as the predominant sensing materials in the field of solid state gas sensors for environmental monitoring such as H₂, CO, NO₂, H₂S, C₃H₈, C₂H₅OH, CH₃COCH₃ and NO_x etc [5, 6]. Furthermore, nanosized-ZnO could enhance the gas sensor performance because of their characteristic microstructural and electronic properties. It is generally accepted that increasing the surface/bulk ratio and decreasing grain size for rutile ZnO nanoparticles is crucial to achieving high-sensitivity gas sensors.

One of the most common methods to modify the properties of ZnO is introducing dopants. Many results have showed that several additives could lead to an increase of the surface area of ZnO-based powders. The added active elements could stabilize the ZnO surface, and decrease its grain size. However, a problem arising from the use of such dopants is that their migration and segregation can possibly occur during the heat treatment or the operation, leading to irreproducibility and aging of the sensors. Moreover, for practical applications in sensor devices, ZnO particles need to be printed on substrates and annealed at 300-600 °C. The operation temperature of the sensors should also be high enough (typically 400 °C) to obtain good response to gases. So, it is still of prime importance to develop a novel and simple synthetic

route for pure ZnO nanoparticles that are stable against heat.

Therefore, the technological importance of ZnO has motivated several studies on the synthesis of this material using various methods, such as pulse laser deposition [9], vapor phase transparent process [7], thermal evaporation [8], aqueous solution deposition [9], template-based growth [10], combustion synthesis [11], sol-gel [12], chemical vapor deposition [13] and vapor transparent deposition have been developed for the preparation of nano size ZnO [14]. Generally, these preparation methods are carried out at require specific apparatus, vacuum conditions, chemicals costs and high-temperature synthetic process, respectively. In the process, the surface areas decrease and particle sizes increase due to the particle growth and sintering.

The microwave synthesis processing is an alternative method for the crystallization of ZnO under mild temperatures. It has been found a number of applications in chemistry. But it was still difficult to control the size of nanoparticles. Therefore, a citric acid assisted microwave solution combustion method was used to prepare ZnO nanoparticles with a fairly narrow particle size distribution, high specific surface areas owing to short reaction time. The resultant particles were characteristic at a room temperature photoluminescence showed remarkably increased blue emission peak with treated temperatures.

Experimental Procedure

In this work, commercially available zinc nitrate (possesses hygroscopicity) and citric acid in analytical grade was purchased from MERCK. All solutions were prepared with tri-distilled water. The reactant mixture is easy to absorb moisture from the air and to become a transparent slurry matter. Therefore, the citric acid fuel were directly mixed at a desired molar ratio with a

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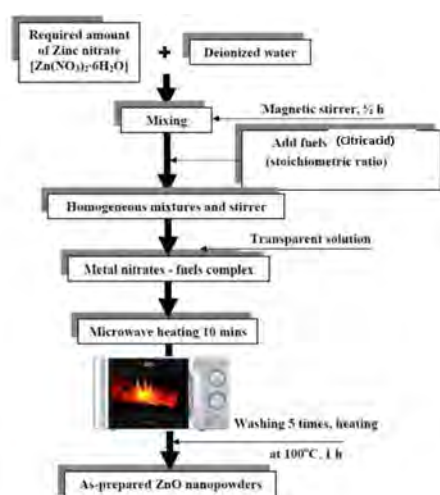


Fig. 1. A schematic representation of the synthesis process.

starting solution in beaker can be mixed well by magnetic stirring for 30 minutes, which makes them almost homogeneous mixtures. This solution was taken in a quartz container and was irradiated with microwaves in a domestic microwave oven (BPL India Limited, Bangalore, India, Model No. IFB, 17 PG1S, microwave 700 W, input range 210-230 V-ac 50 Hz, microwave frequency 2.45 GHz) to produce ZnO nanomaterial. A schematic representation of the synthesis process used in this study is shown in Fig. 1. Within a few seconds of irradiation, reaction mixture was converted into a clear solution and started boiling and a large volume of gases with white fumes occurs coming out from the exhaust opening provided on the top of the micro oven. Finally, the mixture solution boils, ignites, burst into flames and resulted into a foamy white powder. During this process, the solution became more and more viscous and changed from a clear solution. Then, the clear solution was swelling into foam and undergoing a strong self-propagating combustion reaction with the evolution of large volume of gases and changed from colorless to ashes. The color of the ashes changed from gray to white with the treated temperatures. The entire microwave-assisted combustion reaction was completed within few minutes and resulted in voluminous powder. The resulting as-prepared white products were washed five times with distilled water and then dried at 100 °C for 1 hr to get the fine dried powder. Then ZnO nanoparticles were obtained. To compare the effect of temperature on the nanoparticle properties, the sample was calcined at 400 to 600 °C in air for 1 hr.

The crystalline phase ZnO nanoparticles were determined by X-ray diffraction (XRD) method using a 'X' Pert PRO PANalytical diffractometer using nickel-filtered Cu-K α radiation as source and operated at 40 K and 30 mA. The sample was scanned in the 2 θ ranging from 10 to 80° for 2 sec in the step scan mode. The observed peak positions were compared with the standard ICDD data and Miller indices were assigned

to the Bragg peaks. The morphological features of the as-prepared and annealed samples were examined by SEM (Jeol 6360) and TEM (Hitachi H-7100). The prepared powders specific surface area was measured using multi point BET (Gemini 2360) using nitrogen as adsorption method. The chemical structure information of the particles was collected by FT-IR spectra (Nicolet Avatar 360 FTIR spectrometer) using KBr pellets. UV-Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The photoluminescence (PL) spectrum was recorded by Varian Cary Eclipse spectrophotometer with 265 nm as the excitation wavelength of a 15 W Xenon pulse lamp. All emission spectra were recorded for the detector response and excitation spectra for the lamp profile.

Results and Discussion

The XRD patterns of ZnO nanoparticle powders are displayed in Fig. 2. The experimental peak positions

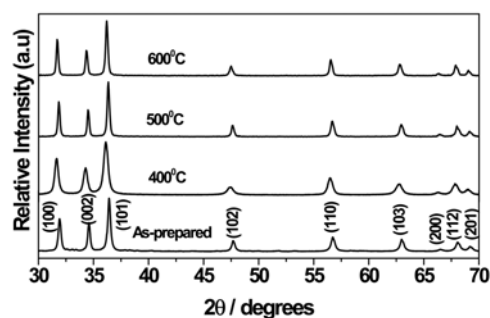


Fig. 2. XRD patterns of ZnO nanoparticles treated at different temperatures.

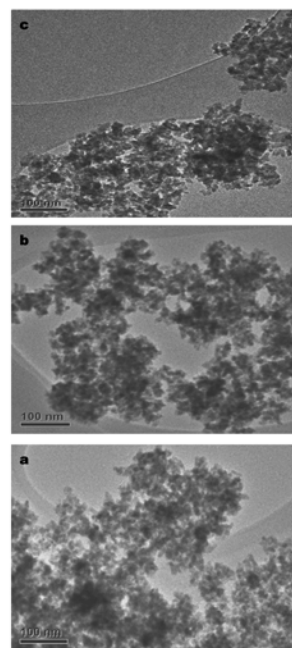


Fig. 3. TEM of ZnO nanoparticles (a) as-prepared, (b) 400 and (c) 600 °C for 1 hr.

were in good agreement with the standard diffraction patterns (ASTM, 04-008-8198) of hexagonal wurtzite structure of ZnO ($a = 3.265 \text{ \AA}$, $c = 5.219 \text{ \AA}$, space group: P6₃mc (186). The crystallite grain size could be estimated as 6 nm according to Scherrer formula $D = 0.9\lambda/\beta\cos\theta$, where D is the average crystalline size, λ is the wavelength of CuK α , β is the full width at half maximum (FWHM) of the diffraction peaks, and θ is the Bragg's angle. It is well known that annealing would result in the growth of ZnO crystallite. XRD results of ZnO that was calcined at 400, 500 and 600 °C, the diffraction peak intensity of ZnO became gradually increases and sharp with narrow full width at half maxima (FWHM) due to the better crystallizing and bigger particles. The crystalline grain size ZnO was 9, 19 and 13 nm when it was calcined at 400, 500 and 600 °C, respectively. It could be seen that the growth of crystallite size was slow before 400 °C. But at 500 and 600 °C, there is significant grain growth with sintering.

The TEM micrographs of ZnO nanoparticles are shown in Fig. 3. It illustrated that the diameter with a fairly narrow particle size distribution and were well dispersed. This result was similar to that obtained from XRD analysis. By the BET surface area analyses, the specific surface area of ZnO nanoparticles were $19 \text{ m}^2 \text{ g}^{-1}$. It was $31 \text{ m}^2 \text{ g}^{-1}$ after calcined at 400 °C for 1 hr. The calcinations process took place slight effect on the specific surface area. The reason should be that the samples prepared by citric acid assisted hydrothermal route were well dispersed and with less uniform size. So, it was an effective method to synthesize the ZnO nanoparticles with large surface areas by the citric acid assisted hydrothermal route. Because the prepared ZnO nanoparticles owned much larger specific surface areas than that of bulk ZnO, a high fraction of the atoms should present at the surface of ZnO nanoparticles. The large surface areas should be in favor of gas sensors. The ZnO nanoparticles prepared by citric acid assisted hydrothermal process could be as high-sensitivity gas sensors material for environmental monitoring.

The FT-IR transmission spectra of ZnO nanoparticle are drawn in Fig. 4. The Zn-O-Zn vibration appeared in the range of $400\text{--}700 \text{ cm}^{-1}$ as the result of condensation reaction. The bands at 1059 cm^{-1} were assigned to the vibration of different types of surface hydroxyl groups. A doublet bands were observed in the range 1330 and 1550 cm^{-1} , assigned to the stretching vibration absorption bands of carboxyl (C=O) groups like fuel [15, 16]. Additionally, those bands at 2610 and 2725 cm^{-1} were assigned to C-H vibrations. The C-H was attributed to the organic traces residuals. The absorption of atmospheric carbon dioxide with water on the metallic cations at $\sim 2350 \text{ cm}^{-1}$ is also present and bonding between Zn-O ($\sim 400\text{--}650 \text{ cm}^{-1}$) are clearly represented [17]. The absorption peaks of 3350 cm^{-1} were broad, suggesting that there were more O-H bonds on the ZnO nanoparticle. Then the O-H bonds were reduced due to

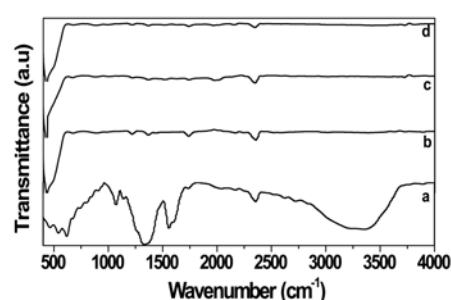


Fig. 4. FTIR spectra of citric acid used ZnO synthesized by a microwave-assisted combustion process (a) as-prepared, (b) 400, (c) 500 and (d) 600 °C for 1 hr.

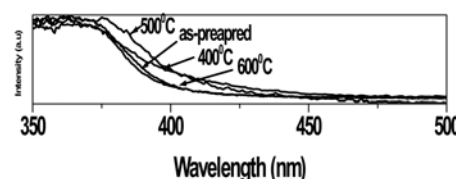


Fig. 5. The absorption spectra of samples treated at different temperature.

the increase in treated temperatures at 400, 500 and 600 °C for 1 hr.

The absorption spectra of samples treated at different temperatures are depicted in Fig. 5. Below 500 °C, the spectra for ZnO nanoparticles displayed a blue shift in the band gap transition of the treated temperature. It could be attributed to the well-known quantum size effect of semiconductors [18]. The results of XRD had proved that the crystalline grain of ZnO increased with treated temperature. According to size quantization, a decrease in the band gap happened with the increase in nanoparticle dimensions [19]. But for the ZnO nanoparticles treated at 600 °C, a remarkably blue shift in the band gap transition was found. The blue shift should due to the so-called Moss-Burstein effect caused by electrons generated by oxygen vacancies [20]. It meant that the lifting of the Fermi level into the conduction band of the degenerate semiconductor due to the increase in the carrier density led to the energy band broadening effect. In the case, the Moss-Burstein effect should cause by electrons generated by the bridging and in-plane oxygen vacancies of ZnO nanoparticles. The surface of ZnO nanoparticles was covered with chemisorbed OH. When the ZnO nanoparticle was heated at 600 °C, their associated Zn-OH groups were decreased remarkably, and in the process, the bridging and in-plane oxygen vacancies formed. The absorption peak shoulder onset peaks is located at 385 nm corresponding to the band gap of 3.22 eV. Compared with the other methods, nanocrystalline ZnO obtained by this microwave-assisted combustion method have larger band gap energy. In general, the hexagonal wurtzite ZnO structure has a direct band gap (E_g) energy for the ZnO powders can be determined by extrapolation to the zero absorption coefficient (α) which is calculated from

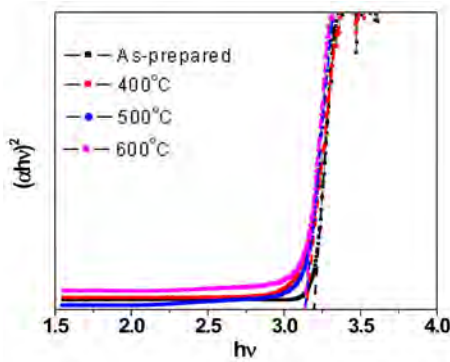


Fig. 6. Plots of $(\alpha hv)^2$ as a function of $h\nu$ for citric acid used ZnO powders at various treated temperatures in air for 1 hr.

Table 1. A band gap values of ZnO powders prepared by microwave-assisted combustion method.

Fuel	Temperature	Average crystalline size (D) based on PXRD (nm)	E_g^a (eV)	E_g^b (eV)
Citric-acid	As-perpared	6	3.38	3.19
	400 °C	9	3.37	3.15
	500 °C	19	3.37	3.14
	600 °C	13	3.37	3.13

^acalculated from effective-mass model.

^bcalculated from Tauc's equation.

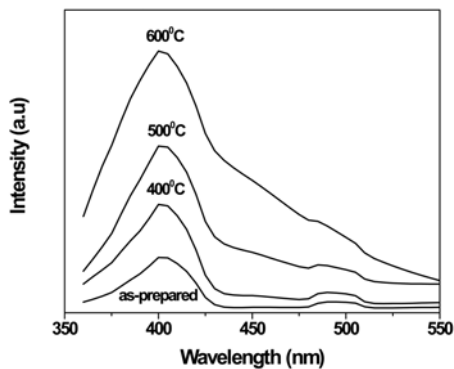


Fig. 7. The room temperature photoluminescence (PL) of citric acid used ZnO nanoparticles using an excitation wavelength of 320 nm.

the following equation:

$$\alpha = \frac{2.303A\rho}{IC} \quad (1)$$

where A is the absorbance of a sample, ρ is the density of ZnO powder, C is the concentration of the particles, and I is the optical path length.

The optical absorption coefficient (α) of a semiconductor is close to the band edge which is estimated from the Tauc's [21] relationship as follows:

$$(\alpha hv)^2 = A(hv - E_g) \quad (2)$$

where α is the absorption coefficient, h is the Planck's constant, ν is the frequency of the incident photon, E_g is the optical energy (direct band gap) and A is a

constant. The exact value of the band gap is calculated by extrapolating the straight line portion of the $(\alpha hv)^2$ versus $h\nu$ axis. Plotting $(\alpha hv)^2$ as a function of photon energy and extrapolating the linear portion of the curve to the photon energy axis (absorption equal to zero) as shown in the Fig. 6.

The dependence of particle size of the ZnO powders can be determined experimentally from the band gap energy inferred from the optical absorption spectra which is expressed from an effective-mass model [22]. The quantum size effect in the ZnO powder can be described from the following equation:

$$E_g^{(nano)} = E_g^{(bulk)} + \frac{h^2}{2D^2} \left[\frac{1}{m_e^* + m_h^*} \right] - 0.248 E_{RY}^* \quad (3)$$

where $E_g^{(nano)}$ is the band gap energy for the synthesized ZnO particle, $E_g^{(bulk)}$ is the energy bandgap of the bulk material as 3.37 eV, h is Planck's constant, D is the average crystalline size calculated from PXRD results of ZnO powders, the electron and hole effective masses are taken as $m_e^* = 0.242 m_0$ and $m_h^* = 2.31 m_0$, the bulk exciton binding energy E_{RY} is 60 meV, i.e. $0.248 E_{RY}^*$ representing the correlation energy, which can be expressed in terms of the excitonic binding energy E_{RY}^* reported by Ellilarassi and Chandrasekaran [23]. After simplification of the equation, the band gap (E_g) value is $E_g^{(nano)} = E_g^{(bulk)} + 7.0989D^{-2}$ (nm). The optical band gap (E_g) calculated from Tauc's relation and the effective-mass are as shown in Table 1, which shows they are in close agreement with each other. Hence the optical band gap value appears slightly lower than the calculated band gap value (effective-mass model) due to a tight-binding model used in experimental data (optical absorption spectra).

The room temperature photoluminescence of ZnO nanoparticles at an excitation wavelength of 320 nm was shown in Fig. 7. A narrow near-UV emission peak at 385 nm was observed. It should be the interference from the source in the equipment used. A visible blue wideband peak was observed. The blue emission was related to the singly ionized oxygen vacancy, and this emission resulted from the recombination of a photo generated hole with a singly ionized charge state of the specific defect [24]. When the treated temperature is increases, the blue emission intensity was dramatically increased. It suggested that there was a high concentration of defects (oxygen vacancies) in the ZnO nanoparticles likely due to the evaporation of O. This behavior should be due to the competition between the O atoms getting into the lattice and those evaporating out of the ZnO lattice in O_2 atmosphere. The kinetic energy of the surface atoms was large, resulting in a larger escaping rate of O atoms than the adsorption rate to make more O vacancies in the ZnO lattice. It should be noted that the position of the blue emission peak seems to a small

shift due to the particle size. The similar results are found in ZnO nanoparticles. A possible explanation was due to the changes in the local environments of the defect centers.

Conclusion

ZnO nanoparticles were prepared by citric acid assisted microwave solution combustion method. The wurzite ZnO crystallites with hexagonal structure could form directly during citric acid assisted microwave solution combustion method. It led to well-dispersed, spherical ZnO nanoparticles with narrow size distribution and large specific surface area. The specific surface area of ZnO nanoparticles was high as 19 m²/g and it had well thermal stability against particle growth. The room temperature photoluminescence showed a near-UV emission and a blue emission. And the blue emission increased remarkably with treated temperatures. Narrow size distribution nanoparticles, excellent dispersibility and large surface areas of ZnO nanoparticle prepared by citric acid assisted microwave solution combustion method make it particularly appealing in applications of gas sensors and optoelectronic devices.

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