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Hot Copper Plate Assisted Synthesis of ZnO Nanoflakes by Cost Effective Modified Spray Pyrolysis Method and its Structural, Morphological & Optical Studies

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Abstract: ***Zinc oxide (ZnO) nanoflakes have been synthesized by a simple and inexpensive Hot Copper Plate assisted and modified Low Cost Simplified Spray Pyrolysis Method using Zinc acetate dihydrate as host precursor source. The structure, optical properties and morphologies of ZnO nanoflakes have been characterized by X-ray diffraction (XRD), UV–Vis spectrophotometry, photoluminescence spectrophotometry (PL), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray analysis (EDAX). The FESEM reveal the formation of ZnO nanoflakes. XRD shows the hexagonal structure of the ZnO nanoflakes. Strong blue shift absorption is observed from the UV–vis spectrophotometry. This blue shift indicates the quantum confinement of the ZnO nanoflakes. The enhanced luminescence property is measured from PL spectrophotometry.***

Keywords: Metal oxide, Spray pyrolysis, Nanoflakes, Nano crystals, Structural and optical properties

1. Introduction

ZnO NPs is an attractive Semiconductor material for nano electronic and nano photonics. Zinc Oxide nanoparticles are commonly applied in Pollutants Removal and disinfectants, because of its high chemical stability, oxidation-reduction capability and poison less characteristics. This type of nanoparticles have interesting and much attention in the past few and current year because of their novel properties that originating from quantum confinement effect [1, 2]. Among all semiconductor materials, the II–VI semiconductor systems have many applications, such as light emitting diodes, anti-bacterial activity, chemical/biological sensors, photocatalysis and solar cells [3–8]. Many approaches have been committed to prepare and control the size and shape of II–VI semiconductor nanoparticles. Zinc oxide (ZnO) is an important II–VI semiconductor material which has wide bulk direct band gap energy and a small exciton Bohr diameter [9]. Due to its wide band gap and exciton binding energy of 60 meV, the synthesis of nanocrystalline ZnO powders with its tunable phase, morphology and size provides alternative variables in tailoring its physical and chemical properties [10,11]. It exhibits great potential applications like UV photonic and transparent electronic applications, photo-luminescent and electroluminescent devices, lasers and thin film solar cells [12]. Recently, a variety of ZnO nanostructured particles with various morphologies including nano crystals , nano rod, quantum dots, belts , needles, sphere, saw and tube, plates , flower like patterns , ribbons and petals [13-20] have been prepared by using various methods. Progressively more research works are contributing to understand the novel properties of semiconductor.

In this paper, we present our investigation to understand the structural, morphological and optical properties of nano crystalline ZnO nanoflakes prepared through a hot copper plate assisted low cost simplified spray pyrolysis method [21-23]. The prepared ZnO nanoflakes have been characterized by X-ray diffraction (XRD), ultraviolet (UV) visible spectrophotometer, photoluminescence (PL), Field emission scanning electron microscopy (FESEM) and Energy dispersive X-ray analysis (EDAX).

2. Experimental Method

All the chemical reagents were of analytical grade and used without further purification. Synthesis was carried out by hot copper plate assisted low cost simplified spray pyrolysis method by using zinc acetate dihydrate [Zn $(CH_3COO)_2$] as Zn^{2+} source, and glycine as fuel.

Zinc acetate dihydrate (Sigma Aldrich, 99% purity) was taken as precursors. Zinc acetate of 0.05 M precursor solution made of 50 ml of deionized water was used to synthesis ZnO nanoparticles. In first step glycine solution of 0.01 M is mixed with precursor solution. Then it is stirred for 2 hours at 50˚c. In Second step the mixed solution is poured in the well cleaned empty perfume spray atomizer without any other impurity. In third step, the copper plate in the dimension of 15cmx12cmx1mm is placed on the hot plate oven at 200˚C. In fourth step the mixed solution is directly sprayed on the hot copper plate with 5 seconds intervals fully and then it is cooled for 30 minutes. Finally,

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ZnO nano powder removed by fine metal strip and collected in glass tube. In overall reaction acetate and fuel escaped as CO_2, H_2O and N_2. Then the sample was calcined in muffle furnace at 150˚C for 3hours.

The structure of the dried sample was characterized by X-ray diffraction (XRD) using an (PANalytical – PW 340/60 X'pertPRO) with Cu-Kα radiation (λ = 1.5406 A˚) with 2θ ranging between 20˚ and 75˚ at a scanning rate of 0.051.The surface morphological studies and elemental compositions were investigated using Field Emission Scanning Electron Microscope (FESEM, FEI - QUANTA–FEG 250) and Energy Dispersive X-ray Analysis (EDAX- Quantax 200 with X-Flash – Bruker). Photoluminescence (PL) spectra were studied using spectroflurometer (CARY ECLIPS SPECTRO photometer) in the range 200–700 nm. Also UV study was carried out by using a Shimadzu-1700 series.

3. Results and Discussion

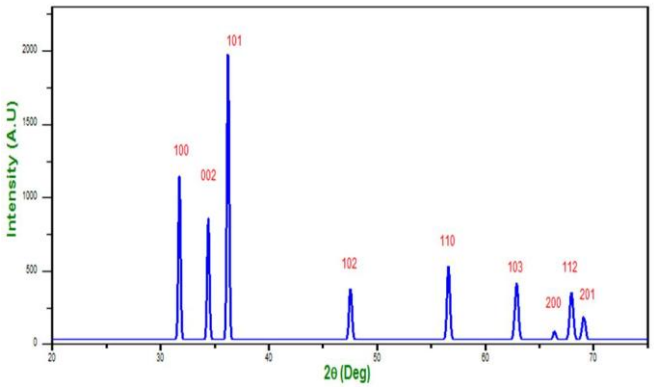

Figure 1: XRD patterns of as prepared ZnO nanoflakes at room temperature

Fig.1 indicates the XRD pattern of ZnO nano- flakes synthesized by hot copper plate assisted low cost simplified spray pyrolysis method at room temperature. The X-ray diffraction (XRD) pattern of ZnO nanoparticles powder is shown in Fig. 1 The peaks at 2θ values of 31.7700, 34.4123, 36.2447, 47.6176, 56.5862, 62.8340, 66.2377, 67.9645,69.1178 can be associated with (100), (002), (101), (102), (110), (103), (200), (112) and (201) respectively. The average crystallite size ranging from 25 to 31 nm was estimated by using Scherrer's formula [24–28]. All the diffraction peaks in the obtained XRD patterns are matched well with the standard hexagonal wurtzite structure of ZnO as found in JCPDS card no.36-1451. The peak corresponding to (101) plane shows the highest intensity. The sharp and intense peaks indicate good crystallinity nature of the sample. Table1 and Table 2 shows that the Crystallite size, d - spacing, Crystallites volume, Lattice parameter, *c*/*a* ratio, cell volume, Number of unit cell, Bond length, dislocation density of ZnO nanoflakes calculated from XRD data.

Table 1. Crystallite size D, d - spacing, Crystallites volume V, Lattice parameters, *c*/*a* ratio, cell volume v of ZnO nanoflakes calculated from XRD data.

2Θ	36.2533
D nm	31.495
d-Spacing (Å)	2.4740
Vx10^3 (nm)^3	67.340
a (Å) **c (Å)**	3.2448 5.2060
c/a	1.6044
v(Å)^3	57.012

Table 2: Number of unit cell, Bond length, dislocation density of ZnO nanoflakes calculated from XRD data

Number of unit cell x10^6	Bond Length (Å)	Dislocation Density x 10^{-4} nm^{-2}
3.5945	1.8730	5.5376

4. Optical Properties

The optical properties of ZnO nanoflakes were investigated by absorption spectrum in the UV–visible wavelength range of 300–700 nm and are shown in Fig.2 The as-prepared ZnO nano flakes depicts a absorption at 343 nm, which is blue shifted compared to the bulk ZnO whose absorption edge is observed at 380 nm [31]. This blue shift indicates the quantum confinement of the particles. The band gap of ZnO nanoflakes is calculated based on the equation $\alpha = A (h\nu - E_g)^{1/2}$ where α, E_g and A are the absorption coefficient, bandgap and constant respectively. Fig.3 shows the variation of $(\alpha h\nu)^{1/n}$ vs. photon energy, hν for ZnO nanoparticles with n values of 1/2. Allowed direct band gap of ZnO nanoparticles is calculated to be 3.39 eV, which is closer to the reported value 3.37 eV [29-30].

Photoluminescence spectrum of ZnO nanoflakes is shown in Fig.4. Here the excitation wavelength was at 320 nm and the emission peaks were found at different wavelengths such as 359 nm, 492 nm and 518 nm. These emission peaks observed in visible region are attributed to various defects like zinc interstitials (Zni), zinc vacancies (Zn_V), oxygen interstitials (Oi) and oxygen vacancies (O_V) along with their excited states. These broadened peaks are due to the trap state emission of ZnO nanoflakes. The rate of this hole trapping must be much faster than the radiative recombination rate of the exciton emission. Because of the large surface-to-volume ratio of our ZnO particles, efficient and fast trapping of photo generated holes at surface sites can be expected. Probable candidates for the trapping of holes are O_2^- ions at the surface. Trapping of a photo-generated hole at the surface is also in agreement with the size-dependence of the emission intensities [32]. The rate for a surface trapping process increases as the particle size decreases since the surface-to-volume ratio increases.

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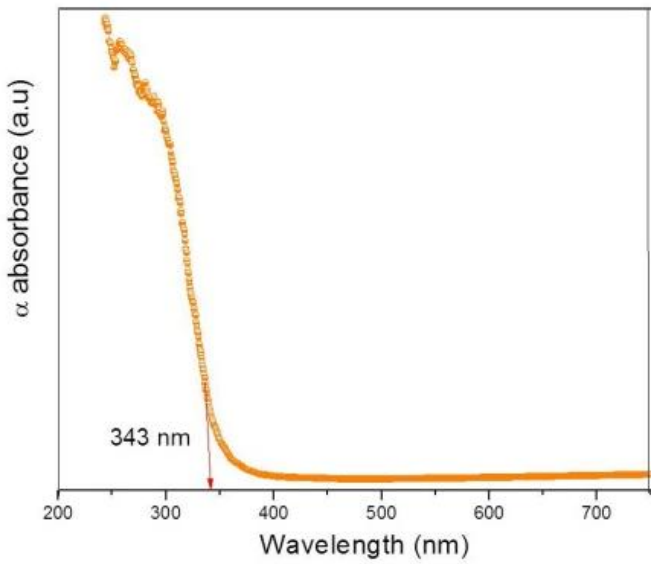

Figure 2: UV-Vis absorption spectra of as prepared ZnO nanoflakes

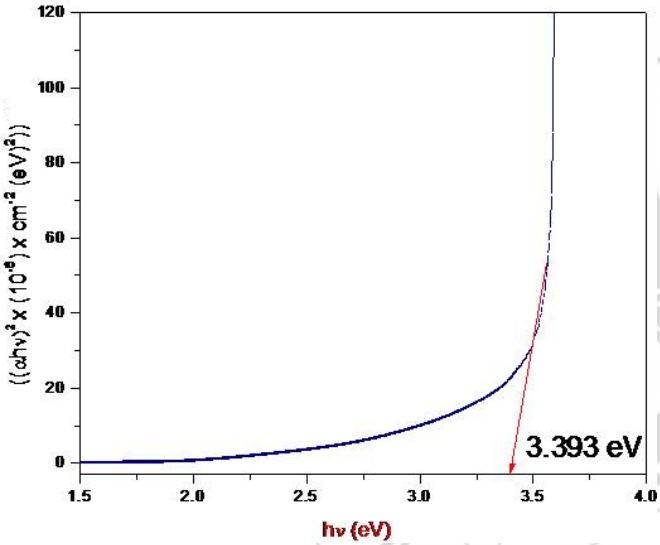

Figure 3: Optical band gap of as prepared ZnO nanoflkes, Plots of Variation of $(\alpha h\nu)^2$ with hν for as a function of wavelength at n value of 1/2.

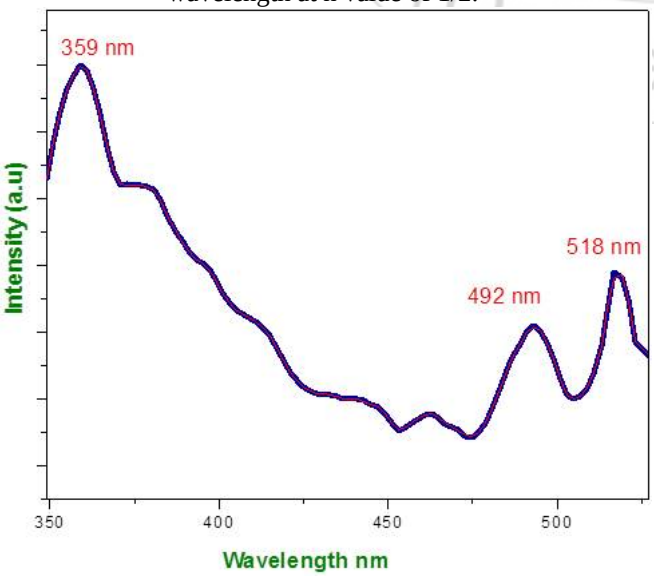

Figure 4: Photoluminescence spectrum of as prepared ZnO nanoflakes

5. Morphological Study

Fig.4 shows the SEM images of ZnO nanoflakes. These images confirmed the size of the nanoflakes and showed the particle distribution ranging from 25 nm to 31 nm. The process calcination and spraying on hot copper plates plays an important role in the morphology of ZnO nanoflakes with little agglomeration and is clearly observed from the figure where the nanoparticles began to align themselves to form magazine, were laid out as it is. Fig.6 shows the EDAX spectrum which is confirmed the composition ZnO nano particles. This spectrum successfully confirms that hot copper plate assisted low cost simplified spray pyrolysis method is a successful method for the preparation of ZnO nanoflakes.

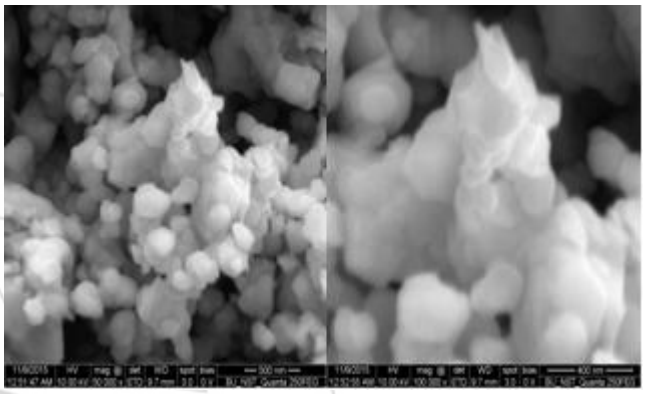

Figure 5: FE-SEM image of as prepared ZnO nanoflakes

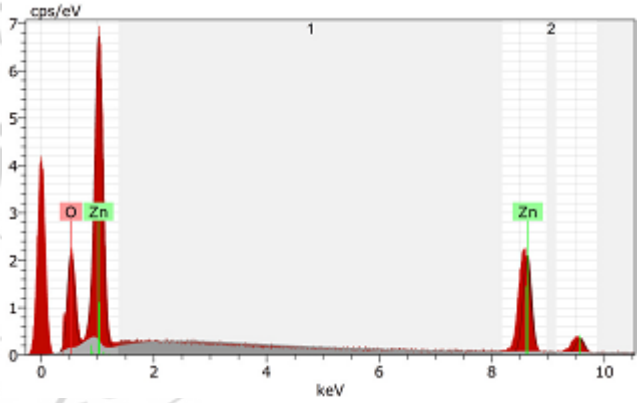

Figure 6: EDAX spectrum of as prepared ZnO Nano flakes

6. Conclusion

The ZnO nanoflakes have been successfully synthesized through by hot copper plate assisted low cost simplified spray pyrolysis method at room temperature. The surface morphological studies using FESEM confirm the formation of ZnO nanoflakes. XRD reveals that the synthesized ZnO nanoflakes were well formed and had hexagonal structure with a crystallite size distribution of 31 nm. The optical properties of the synthesized nanoflakes indicate the quantum confinement effect with a strong blue shift. This approach brilliantly makes the surface of the ZnO nanoflakes. This inexpensive approach will be very useful for the synthesis of semiconductor nanostructures in various recent trends in nano material applications.

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References

[1] Ruoxue Yan, Daniel Gargas, Peidong Yang. Nature Photonics, 2009; 3:569–576
[2] Pankaj Kumar, Yogesh Kumar Walia. Asian J. of Adv. Basic Sci, 2014; 2: 39-49
[3] M. Haase, H. Weller, A. Henglein, J. Phys. Chem, 1998; 92: 482
[4] D. Gedamu, I.Paulowicz, S.Kaps, O.Lupan, S.Wille, G.Haidarschin, Y. K. Mishra. Adv.Mater 2014; 26: 1541–1550.
[5] C. Xu, J. Tamaki, N. Miura, N. Yamazoe. Sens. Actuators B 1991; 3:147–155.
[6] T.Y. Wei, P.H. Yeh, S.Y. Lu, Z.L. Wang. J. Am. Chem. Soc 2009; 131:17690–17695.
[7] S. Choopun, N. Hongsith, P. Mangkomtong, N. Mangkomtong. Physica E 2007; 39:53–56.
[8] X.G. Han, Q. Kuang, X. Zhou, X.H. Zhang, T. Xu, Z.X. Xie, L.S. Zheng. J. Phys. Chem. C 2009; 113:584–589.
[9] Z. L. Wang, Nanostructures of zinc oxide. J. Material Today 2004; 26:26-33.
[10] S. J. Pearton, D. P. Norton, K. Ip, Y.W. Heo, T. Steiner. J. Superlattices Microstructure 2003; 34–32.
[11] Z. L.Wang, Materials Today, 2004; 7:25
[12] S. K. Kim, S. Y. Seong C. R. Cho, Appl. Phys. Lett, 2003; 82:562
[13] C.G. Van de Walle, Phys. Rev. Lett, 2000; 85:1012
[14] J. E. Jaffe, J. A. Snyder, Z. Lin A. C. Hess, Phys. Rev. B, 2000; 62:1660.
[15] U. Rossler, Phys. Rev, 1969; 184:733
[16] D. Vogel, P. Krüger J. Pollmann, Phys. Rev. B, 1995; 52:14316
[17] B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straburg, M. Dworzak, U. Haboeck A. V. Rodina, Phys. Stat. Sol. (b), 2004; 241, 231.
[18] S. Suwanboon, S. Chukamnerd U. Anglong, Songklanakarin, J. Sci. Technol., 2007; 29:1563.
[19] Fan Xi-Mei, Zhou Zuo-Wan, Wang Jie, Tian Ke, Trans. Nanoferrous Met. Soc. China, 2011; 21:2056.
[20] Mansidhingra, Lalit Kumar, Sadhna Shrivastava, P. Senthil Kumar, S. Annapoorni, Bull. Mater. Sci., 2013; 36,647.
[21] S Sumetha, C Suchada A Utsanee Songklanakarin, J.Sci. Technol, 2007; 29:1563.
[22] Shuyan Gao, Hongjie Zhang, Xiaomei Wang, Ruiping Deng, Dehui Sun, Guoli Zheng J. Phys. Chem. B 2006; 110: 15847-15852.
[23] K. Ravichran, P. Philominathan, Materials Letters, 2008; 62:2980-2983.
[24] K. Ravichran, P. Philominathan, Solar Energy, 2008;82,1062–1066.
[25] P. Ponsurya, B. H. Abbas Shahul Hameed, D. Saravanakkumar, M. Kashif, S. Sivaranjani, R. Perumalsamy, A. Ayeshamariam, Int.J. ChemTech Res, 2014; 7:917-920
[26] S. Sakohara, M. Ishida, M. A. erson, J. Phys. Chem. B,1998;102:10169
[27] M. Haase, H. Weller, A. Henglein, J. Phys. Chem.1988;92:482
[28] L. E. Brus, J. Phys. Chem. 1986;90:2555.
[29] D. H. Zhang, Z. Y. Xue, Q. P. Wang, J. Phys. D Appl. Phys. 2837; 35:2837.
[30] H. Hayashi, A. Ishizaka, M. Haemori, H. Koinuma, Appl. Phys. Lett.2003;82:1365.
[31] Y.C. Kong, D.P. Yu, B. Zhang, W. Fang, S.Q. Feng, Appl. Phys. Lett, 2001;78: 407.
[32] J. Zhou, Y.Wang, F. Zhao, Y.Wang, Y. Zhang, L. Yang, J. Lumin, 2006; 119:248.
[33] H. Rensmo, K. Keis, H. Lindström, S. Södergren, A. Solbr, A. Hagfeldt, S.-E. Lindquist, L.N.Wang, M. Muhammed, J. Phys. Chem. B1997; 101: 2598.
[34] Y. Sun, G.M. Fuge, M.N.R. Ashfold, Chem. Phys. Lett, 2004; 396:21.
[35] W. Chiou,W.Wu, J. Ting, Diamond Relat. Mater, 2003; 12:1841.

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