Preparation of Co and Ni doped ZnO nanoparticles served as encouraging nano-catalytic application

M Ali1,6, S Sharif1, S Anjum2, M Imran3,6, M Ikram3, M Naz4 and S Ali5

1 Solar Cell Applications Research Lab, Department of Physics, Government College University, Lahore, 54000, Pakistan
2 Department of Physics, COMSATS Institute of Information Technology, Lahore 54000, Pakistan
3 State key Laboratory of Chemical Resource Engineering, Beijing Advanced Innovation Centre for Soft Matter Science and Engineering, Beijing Engineering Center for Hierarchical Catalysts, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China
4 Biochemistry Lab, Department of Chemistry, Government College University Lahore, 54000, Punjab, Pakistan
5 Department of Physics, Riphah Institute of Computing and Applied Sciences (RICAS), Riphah International University, 14 Ali Road, Lahore, Pakistan
6 M Ali and M Ikram are equal contributors.

E-mail: dr.muhammadikram@gcu.edu.pk

Keywords: doped, catalysis, ZnO, metal ion, dye

Abstract
Nickel (Ni) and cobalt (Co) doped ZnO nanoparticles were prepared using simple and cost-effective sol-gel technique. Effects of various weight ratios (5, 10, 15 and 20) % of Co and Ni-doped into ZnO have been examined. The prepared undoped and doped nanoparticles (NPs) were characterized using XRD, SEM, FTIR, EDX and UV-Vis spectroscopy. By analyzing the catalysis potential of the samples under UV irradiation, the probable mechanism of particles was investigated. XRD results revealed that ZnO and doped ZnO have hexagonal wurtzite phase, the lattice strain and particle size were measured by Williamson and Hall plot. The absorption increased and band gap energy decreased gradually in the range of 2.40–3.62 eV upon doping was identified using UV-Vis spectroscopy. The elemental composition of Zn, Ni and O were confirmed with EDX spectra and FTIR spectra demonstrate the presence of chemical bonding and functional groups at the interface of ZnO. This report highlights the effect of nanocatalyst on the degradation rate of methylene blue through NaBH4, results revealed that doped nanocatalyst has better catalytic action than ZnO and will provide an insight for the synthesis of catalytic agents that could prevent environment pollution issue.

1. Introduction
Nano-scaled semiconductors (SC) are of great interest to scientists owing to their fundamental roles in magnetic, catalytic, electrical and optical applications. However, the size-dependent properties of these SC offer a remarkable opportunity to fabricate new peculiar devices [1].

During the last two decades, zinc oxide (ZnO) inorganic SC is a promising material because of high photochemical stability, catalysis [2], light-emitting diodes [3], thermoelectric devices [4], direct band gap, nontoxic, transparency in the visible range, economic and eco-friendly. Chemical and thermal stability of ZnO is II-VI compound has large excitons binding energy (B.E-60 meV) and band gap energy (Eg around 3.37 eV) [5–7]. Three structures of ZnO are stable wurtzite (Wz), rock salt and zinc blend at room temperature, but in Wz each cation-O−2 of metal oxide (ZnO) is surrounded by four anions Zn+ at the corners of a tetrahedron. Therefore, it has specific applications in photocatalysis, gas sensors, solar energy and an anode material for lithium (Li) ion batteries [8–10]. The interest has been extensively grown to study metal ion-doped ZnO rather than pure zinc oxide. The electronic structure of the material can be modified with doping leads to increase the generation of excitons (e− and h+) pair particularly important for applications in light-induced phenomena.

Doping of inorganic semiconductors can be accomplished by replacing the cation of ZnO with higher valency atoms. The optical, structural and electrical properties of metal oxide NPs might be improved and
controlled using selective elements doping [11, 12]. Moreover, doping improves the number of charge carriers and an increase in conductivity leads to different transporting layers in optoelectronic devices. Furthermore, thin films of doped ZnO NP are a potential candidate for the replacement of tin oxide and indium tin oxide (ITO) coated glass substrate used in the preparation of solar cells as transparent conducting oxide-TCO [13, 14].

Various 3d transition metals Fe, V, Cu, Co, Ni, Ti are used as doping agents in ZnO NPs [15–17]. However, the efficiency of dopant elements depends on the electronegativity and radius difference between the Zn ion and dopant ion. The transition dopant agents, Fe and Co are more chemically stable have ionic radius 0.58 Å and 0.64 Å respectively close to ionic radius of zinc (0.74 Å) and can easily incorporate into zinc lattice sites either substitutionally or interstitially without change in the crystal structure of ZnO produce more charge carriers that improve its conductivity [18, 19]. Several physio-chemical techniques are reported to fabricate ZnO include thermal hydrolysis technique [20], hydrothermal processing [21] and sol-gel method [22]. Sol-gel process is being extensively used on account of low processing temperature, precise control over the stoichiometry, low equipment cost, great homogeneity, increased crystallinity and purity [23–25] considered as most appropriate to fabricate nanopowders.

Wastewater treatment, energy shortage and pollution degradation are major issues that need to be addressed. In general, pollutants from textile industries contain organic dyes and aromatic compounds that must be treated before discard [26]. Dyes are the main pollutants of surface water, most are not readily biodegradable, present a potential hazard at very low concentration as 1 ppm [27, 28]. Therefore, proper treatment of dyes is required to improve the quality of all life such as adsorption and catalytic degradation are the proposed method for the removal of dyes. Adsorption is economical but the issue of recoverable is still which will contribute to toxic materials. Catalytic degradation is comparatively easy; however, a bit more expensive than adsorbents and can be reused.

In this study, Ni and Co-doped ZnO nanostructures with various weight ratios (5, 10, 15 and 20) % were fabricated via a sol-gel technique to increase the catalytic activity. The efficiency of various dopant concentrations on the structural, optical, morphological and catalytic properties of ZnO is investigated.

2. Experimental details

2.1. Materials
Zinc acetate dihydrate- Zn(CH₃COO)₂·2H₂O, nickel acetate tetrahydrate- Ni(CH₃COO)₂·4H₂O, cobalt acetate tetrahydrate- Co(CH₃COO)₂·4H₂O, methylene blue (MB) and sodium borohydride (NaBH₄) were procured from Sigma-Aldrich and methanol (CH₃OH) was obtained from Unichem.

2.2. Synthesis of doped free and doped ZnO
The simple and low-cost sol-gel technique was adopted to synthesized undoped and Co and Ni-doped ZnO NPs. Firstly, 0.5M of Zn(CH₃COO)₂·2H₂O was dissolved in methanol-CH₃OH (50 ml) and stirred for 2 h at 80 °C. During stirring, white precipitates were obtained, washed several times with deionized water (DIW), dried at 120 °C and subsequently annealed at 300 °C for 2 h. For the synthesis of doped Zn₁₋ₓCoₓO and Zn₁₋ₓNiₓO NPs, where (x = 0.05, 0.10, 0.15 and 0.20 mol %), a calculated amount of Co, Ni (CH₃COO)₂·4H₂O and Zn(CH₃COO)₂·2H₂O were dissolved individually in 50 ml of CH₃OH. The above method was adapted to synthesis the Co, Ni-doped ZnO at 300 °C for 2 h. The annealed nanopowders of pure and doped ZnO were used for further studies.

2.3. Catalysis
Freshly prepared (100 mM) sodium borohydride (NaBH₄) solution was added with 1mM methylene blue (MB). Later, 400 μl undoped and doped (Co and Ni) ZnO nanoparticles (1 mg ml⁻¹) were incorporated into the solution and stirred for few minutes. The decolorisation of the mixture indicates a reduction of MB to leucomethylene blue (LMB) in the presence of NaBH₄ (figure 1). The reaction in the absence of nano-catalyst is conducted as a reference. The absorption spectrum was monitored at 200–800 nm at 25 °C.

2.4. Characterizations
To check the crystallite size, phase information and strain of samples, x-ray diffractometer using PAN Analytical Xpert PRO- XRD with Cu-Kα radiation (1.54 Å) and position 2θ values are between (20°–80°) was employed. The absorption of the undoped and doped ZnO was recorded by UV-visible spectrophotometer (Genesys 10S). The field emission electron microscopy- FESEM (JEOL JSM-6460LV) was used to obtain nanopowders morphology and microstructures. The FTIR spectra (600–4000 cm⁻¹) of the prepared nanopowders have been measured using Perkin Elmer spectrometer.
3. Results and discussion

XRD patterns of ZnO, Co and Ni-doped ZnO with various concentrations are displayed in figures 2(a)–(b) respectively. The peaks of Co:ZnO (figure 2(a)) were matched well (JCPDS card number 01-080-0074) have a single wurtzite phase with the hexagonal crystal structure. The intensity and variation in position peak were increased with the increasing amount of doping relative to the control sample. This shift in peaks position indicated that cobalt is substituted in the ZnO lattice without any impurity phase (CoO and Co3O4) represents doping is substitutional [29].

Figure 2(b) depicts the XRD pattern of various ratios of Ni to ZnO has small shifting in the peaks towards lower angle. The addition of Ni in a crystal lattice of ZnO produces defects depend upon the size of the doped particle. The ionic radii of Ni (0.55 Å) and Co (0.58) are smaller than Zn (0.60Å) results reduces the crystallite size [30]. This decrease in radii of doped materials in ZnO lattice reduces the crystallite size with doping amount (5, 20)% and (5,10)% and this trend inverse with concentrations (10, 15)% and (15, 20)% of Ni and Co with ZnO respectively results significant increase in particle size. The higher dopant amount is caused to enhance the nucleation growth which supports crystalline growth. The observed d-spacing of undoped ZnO nanoparticles for corresponding diffraction planes of (100), (002), (101), (102), (110), (103), (112), (004) and (202) are comparable to JCPDS card data (01-080-0075) with space group (P63mc). The high intensity peak confirms better crystallinity of the prepared samples.

Figure 1. Schematic diagram of catalysis steps involved in dye degradation.

Figure 2. XRD spectra of prepared (a) Co:ZnO and (b) Ni:ZnO.
XRD pattern is also useful in evaluating lattice stress and strain which is mainly due to vacancies and defects by using Williamson-Hall relation as under

\[ \Delta hkl \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta \]  

(1)

Here \( \lambda \) is wavelength of x-ray, \( k \): shape factor (0.89), \( \Delta hkl \): line broadening at half-height, \( \varepsilon \): microstrain and \( \theta \) is Bragg angle of the particles. Incorporate as the W-H plot of \( \Delta hkl \cos \theta \) Vs \( 4 \sin \theta \) of various concentrations of Co and Ni doped ZnO is shown in figure 3 (a-b) respectively.

Hook defines a direct relation stress and strain having Young’s modulus (modulus of elasticity) as the constant of proportionality. (\( \Delta hkl \)) the above equation (1) can also be written as

\[ \Delta hkl \cos \theta = \frac{k\lambda}{D} + \frac{4\sin \theta \sigma}{E_{hkl}} \]  

(2)

Where \( \sigma \) represents uniform stress. The equation (2) shows a straight line between \( 4\sin \theta \sigma/E_{hkl}(x\text{-axis}) \) and \( \Delta hkl \cos \theta (y\text{-axis}) \). Uniform stress (\( \sigma \)) is obtained from the slope of straight line while crystallite size (\( D \)) by intercept of the line [31].

Peak broadening may not only originate from the size effect but can also be due to strain in the particles. W-H expression (3) is very helpful in extracting the stress due to particle size from that due to strain as given below

\[ 2d \sin \theta = n\lambda \]  

(3)
Where $\eta$ is the strain in the particles while the average strain ($\varepsilon$) can be written as below

$$\varepsilon = \frac{\beta}{4 \tan \theta}$$  \hspace{1cm} (4)

From figures 4(a)–(b) indicate an increase in the lattice strain with increasing amount of Co and Ni incorporated in ZnO. This increase is attributed to the stronger tensile and more O$_2$ vacancies are introduced in ZnO matrix with incorporation of Co and Ni [32]. These trends reverse suddenly on further increase in dopant concentration [33]. It is revealed from W-H plot (figure 4(b)) that variation in crystallite size, as we added Co and Ni to ZnO. Upon mixing, the crystallite size decreases subsequently increases upon increasing the doping concentration upto 15% and finally decreases with further increase in doping (20%) in both samples.

The absorption spectra of control samples and doped (Co:ZnO and Ni:ZnO) are represented in figures 5(a)–(b) respectively. The control ZnO has absorption peaks around 295 nm with a shoulder at 370 nm. Upon the addition of Co and Ni in ZnO, the absorption increased accompanied blue shift with wide wavelength range and red shift respectively attributed to an increase in the crystalline phase of ZnO. This shift and absorbance in the UV region are well reflected in the sharp change in sample color with the incorporation of Co and Ni as reported [34].

The band gap energies of Co and Ni-doped ZnO were calculated from absorption spectra using Tauc’s equation as shown in figures 6(a)–(b). A decrease in the band gap (E$_g$) upon doping of various ratios of metal ions doped ZnO was observed. A drastic decrease in the optical gap was found with an optimum amount of Co and Ni doping. This decrease in E$_g$ is ascribed to shift in the band edge upon doping. The observed shift in the
wavelength upon Ni and Co doping can be attributed to increasing sp–d interactions between band electrons and localized d-electrons of dopant ions substituting Zn$^{2+}$ ions [35]. The decrease in band gap energy and observed electronic transition of doped materials (Ni and Co) confirmed the doping Ni and Co into ZnO lattice.

The FTIR spectra of pure, Co and Ni-doped ZnO were recorded at ambient temperature are shown in figures 7(a)–(b). The recorded graphs show identical peaks position (figures 7(a), (b)) and the peaks observed at 3472, 1421 1570 and 1027 cm$^{-1}$ are corresponding to O–H stretching vibrations, symmetric and stretching of C=O and C–H stretching mode respectively. The peak observed around 850 cm$^{-1}$ is attributed to vibration of Zn–O–Ni bonds (figure 7(b)) [36]. The peak centered at 500–670 cm$^{-1}$ is manifested to Zn–O stretching mode in tetrahedral coordination [37].
FESEM micrographs of various ratios of Co and Ni substituted ZnO nanopowders are shown in the figures 8(a)–(i) respectively. Figure 8(a) reveals the image of a doped free ZnO has irregular nano-grains distribution with sizes between 20–50 nm on the surface consists of densely packed likely sphere and ellipsoidal. Upon Co doping, the quasi-spherical and rod shape surface morphologies by increasing the amount of Co to ZnO is shown in figures 8(b)–(e). It is noteworthy that the microstructures of the nanopowders and nanorods are strongly affected by doping, alteration in particle size and nanorods sizes increased. With higher doping, nanoparticles and nanorods sizes increased which representing a difference in crystal growth velocity (from nanoparticles to nanorods with Co) in different direction. The incorporation of Co to precursor solution could be creating thermodynamic barrier which delays the nucleation and growth rate of ZnO. Due to this delay, effective ions have much time to connect with nanoparticles for the formation of nanorods. With higher amount of Co doping (20%), nanorods size between 50–150 nm increased compared to low concentrations of doping [38]. Conversely, the surface morphologies of various ratios of Ni (5, 10, 15 and 20) % to ZnO are shown in
The images show non-homogenous and non-uniformly grains agglomeration with increasing concentration of Ni in ZnO. It is noted that the Ni-doped samples morphologies are combination of agglomerated nanoparticles and nanorods. The alteration in particle size upon doping can be attributed to the surface to volume ratio enhances the attraction between grains and leads to agglomeration. These nanostructures size increased with the increasing amount of Ni than pure ZnO (figure 8(a)) [5, 39].

The EDX spectra of pure ZnO and various ratios of each Co and Ni (5, 10, 15 and 20) % into ZnO are shown in figures 9(a)–(i) respectively. The compositional analysis of various ratios of elements involved in the final product such as Zn, Ni, Co and O (wt%) was confirmed with EDX analysis and fixed in the respective figures respectively. Doped materials (Co and Ni) concentrations are gradually increasing in the primary nuclei (ZnO) as illustrated in inset of each EDX image.

The catalytic activity of undoped and doped ZnO NPs towards the reduction of MB in the presence of NaBH₄ was monitored spectrophotometrically. Figure 10(a) show reducing the capacity of NaBH₄ with dye after 40 min, the addition of ZnO with NaBH₄ has not affected reduction significantly (b). The catalytic efficiency of Co–doped ZnO NPs with NaBH₄ representing a quick successive decrease in concentration of MB (c), (f). MB
degraded to leucomethylene blue in the presence of NaBH₄ with 5% Co-doped ZnO and decolorization was recorded within 35 min in figure 10 (c). 10% Co-doped ZnO reduces MB within 30 min in figure 8 (d) while 15 and 20% Co-doped ZnO NPs efficiently degraded MB within 15 and 10 min respectively.

The catalytic reduction of MB was also investigated using NaBH₄ as the reducing agent and different concentrations of Ni-doped ZnO as the nano-catalyst. Reducing capacity of NaBH₄ and Ni-doped ZnO is increased by increasing the concentration of doped Ni figures 11 (a), (d). Figure 11 (a) depicts that relative absorption intensity was recorded for 40 min, however appreciable reduction of dye was not recorded. 10% Ni-doped ZnO reduces the MB within 35 min at room temperature while from (figure 10 (b)) it is noteworthy that 15 and 20% Ni-doped ZnO significantly reduces MB with in 25 and 23 min respectively. It was observed that the rate of reaction increases with increasing reaction time. On the contrary, in the absence of the doping, the reaction rate of reducing MB was very slow; suggesting the catalytic function of synthesized NPs. Current work presents that reduction reaction of doped ZnO NPs displays significant performance as a nano-catalyst.

4. Conclusion

Sol–gel technique has been successfully used to synthesis ZnO nanoparticles with various weight ratios of doped materials (Ni and Co). The XRD pattern revealed sharp and intense peaks with Co and Ni-doping represent the increase in crystallinity while small shifting in peaks was observed with higher amount of Ni. W-H plot indicates that variation in crystallite size and lattice strain upon doping to ZnO. The bandgap energies decreased from 3.62 to 2.40 eV upon doping which can be attributed to increasing sp–d exchange interactions among localized d–electrons and band electrons of dopant (Co and Ni) ions substituting Zn²⁺ ions. The presence of functional group and dopant materials were confirmed by FTIR and EDX analysis respectively. The morphology of the product showed quasi-spherical, rod shape and non-uniform grain agglomerations surface morphology with the increasing amount of dopant materials to ZnO. The higher quantities (15 and 20) % of Co-doped ZnO efficiently reduced MB as compared to Ni-doped ZnO NPs. Co doped ZnO NPs have potential catalytic activities against MB that offer an efficient and economical route to environmental protection and open up new ways for advance catalytic applications.
Acknowledgments

The authors are very thankful to Higher Education Commission (HEC) Pakistan for financial support through Start Research Grant Project No. 21-1669/SGRP/R&D/HEC/2017.

ORCID iDs

M Ikram https://orcid.org/0000-0001-7741-789X

References

[1] Karthik K, Pandian S K and Jaya N V 2010 Effect of nickel doping on structural, optical and electrical properties of TiO2 nanoparticles by sol–gel method Appl. Surf. Sci. 256 6829–33
[2] Curri M, Comparelli R, Cozzioli P, Mascolo G and Agostiano A 2003 Colloidal oxide nanoparticles for the photocatalytic degradation of organic dye Mater. Sci. Eng. C 23 285–9
[3] Kim H, Horwitz I, Kim W, Makenin A, Kafali Z and Chrisey D 2002 Doped ZnO thin films as anode materials for organic light-emitting diodes Thin Solid Films 420 539–43
[4] Ohtaki M, Tsubota T, Eguchi K and Arai H 1996 High-temperature thermoelectric properties of (Zn1-xAlx)O J. Appl. Phys. 79 1816–8
[5] Pearton S J, Norton D P, Ip K, Heo Y W and Steine T 2005 Recent progress in processing and properties of ZnO Prog. Mater. Sci. 50 293–340
[6] Shinde V, Gujar T, Lohande C, Mane R and Han S H 2006 Mn doped and undoped ZnO films: a comparative structural, optical and electrical properties study Mater. Chem. Phys. 96 326–30
[7] Decreppe F, Pellicer-Porres J, Saitta A M, Chervin J-C and Polian A 2002 High-pressure Raman spectroscopy study of wurtzite ZnO Phys. Rev. B 65 092101
[8] Zayim E 2005 Effect of calcination and pH value on the structural and optical properties of titanium oxide thin films J. Mater. Sci. 40 1345–52
[9] Tang H, Prasad K, Sanjines R and Levy F 1995 TiO2 anatase thin films as gas sensors Sens. Actuator B-Chem. Biochemical Sensors 26 71–5
[10] Ramakrishna G and Ghosh H N 2003 Optical and photochemical properties of sodium dodecylbenzenesulfonate (DBS)-capped TiO2 nanoparticles dispersed in nonaqueous solvents Langmuir 19 505–8
[11] Aimouch D E, Meskine S, Boukortt A and Zaoui A 2018 Effect of (Mn, Cr) co-doping on structural, electronic and magnetic properties of zinc oxide by first-principles studies J. Magn. Magn. Mater. 451 70–8
[12] Rana S B, Bhardwaj V K, Singh S and Kaur A N 2013 Synthesis and optical characterization of ZnO nanoparticles capped with 2-aminothiols Journal of material: Material in Electronics Springer 24 20–6
[13] Kim S, Yoon H, Kim D Y, Kim S-O and Leem J-Y 2013 Optical properties and electrical resistivity of boron-doped ZnO thin films grown by sol–gel dip-coating method Opt. Mater. 35 2418–24
[14] Aragones A C, Palacios-Padros A, Caballero-Briones F and Fausto S 2013 Study and improvement of aluminium doped ZnO thin films: limits and advantages Electrochim. Acta 109 117–24
[15] Panigrhy B, Aslam M and Bahadur D 2010 Aqueous synthesis of Mn- and Co-Doped ZnO Nanorods J. Phys. Chem. 114 11758–63
[16] Rana S B and Singh R P P 2016 Investigation of structural, optical, magnetic properties and antibacterial activity of Ni-doped zinc oxide Journal of material science: material in Electronics Springer 27 9346–55
[17] Rana S, Singh R and Arya S 2017 Structural, optical, magnetic properties and antibacterial activity of Cobalt doped zinc oxide nanoparticles Journal of material science: material in Electronics Springer 28 2660–72
[18] Thambidurai M, Kim Y, Song I, Ko Y, Muthukumarasamy N, Velauthapillai D and Lee C 2014 Nanocrystalline Ga-doped ZnO thin films for inverted polymer solar cells Sol. Energy 106 95–101
[19] Chen K, Hung F-Y, Chang S-J and Hu Z 2009 Microstructures, optical and electrical properties of In–doped ZnO thin films prepared by sol–gel method Appl. Surf. Sci. 255 6308–12
[20] Park H K, Kim D K and Kim C H 1997 Effect of solvent on titania particle formation and morphology in thermal hydrolysis of TiCl4 J. Am. Ceram. Soc. 80 743–9
[21] Hirano S-I 1987 Hydrothermal processing of ceramics J. Am. Ceram. Soc. Bull. 66 1342–4
[22] Dhilouaih H and Larbi A B C 2017 Scratch Resistance and Wear Energy Analysis Stainless of Steel TiO2 Coatings on 316L J. Mater. Sci. 52 2322–30
[23] Khanna P, Singh N and Charan S 2007 Synthesis of nano-particles of anatase–TiO2 and preparation of its optically transparent film in PVA Mater. Lett. 61 4725–30
[24] Wang C-Y, Böttcher C, Bahmann D W and Dohrmann J K 2003 A comparative study of nanometer sized Fe(III)-doped TiO2 photocatalysts: synthesis, characterization and activity J. Mater. Sci. 13 2322–9
[25] Farley N R, Staddon C R, Zhao L, Edmonds K W, Gallagher B L and Gregory D H 2004 Sol–gel formation of ordered nanostructured doped ZnO films J. Mater. Chem. 14 1087–92
[26] Yang Y, Zhang H, Lee S, Kim D, Hwang W and Wang Z L 2013 Hybrid energy cell for degradation of methyl orange by self–powered electrocatalytic oxidation Nano Lett. 13 863–8
[27] Mehra M and Sharma T 2012 Photo catalytic degradation of two commercial dyes in aqueous phase using photo catalyst TiO2 Adv. Appl. Sci. Res. 3 149–53
[28] Fosso-Kankeu E, Mittal H, Mishra S R and Mishra A K 2015 Gum ghatti and acrylic acid based biodegradable hydrogels for the effective adsorption of cationic dyes JIEC. 22 171–8
[29] Ram M, Arya G, Parmar K, Kotnala R and Negi N 2015 Structural, Microstructural and Raman study of co-doped ZnO nanocrystals synthesized by solution combustion method, International Journal of Advances in Engineering & Technology 8 329
[30] Shannon R D 1976 Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography 32 751–67
[31] Janotti A and Van de Walle C G 2005 Oxygen vacancies in ZnO Appl. Phys. Lett. 87 121102
[32] Mukhtar M, Munisa L and Saleh R 2012 Co-precipitation synthesis and characterization of nanocrystalline zinc oxide particles doped with Cu$^{2+}$ ions MSA. 3 543

[33] Chauhan V P, Stylianopoulos T, Martin J D, Popović Z, Chen O, Kamoun W S, Bawendi M G, Fukumura D and Jain R K 2012 Normalization of tumour blood vessels improves the delivery of nanomedicines in a size-dependent manner Nat. Nanotechnol. 7 383–8

[34] Talam S, Karumuri S R and Gunnam N 2012 Synthesis, characterization, and spectroscopic properties of ZnO nanoparticles ISRN Nanomater. 2012 372505

[35] Kim K J and Park Y R 2002 Spectroscopic ellipsometry study of optical transitions in Zn$_{1-x}$Co$_x$O alloys Appl. Phys. Lett. 81 1420

[36] Vijayaprasath G, Murugan R, Palanisamy S, Prabhu N, Mahalingam T, Hayakawa Y and Ravi G 2016 Role of nickel doping on structural, optical, magnetic properties and antibacterial activity of ZnO nanoparticles Mater. Res. Bull. 76 48–61

[37] Saravanan R, Santhi K, Sivakumar N, Narayanan V and Stephen A 2012 Synthesis and characterization of ZnO and Ni doped ZnO nanorods by thermal decomposition method for spintronics application Mater. Charact. 67 10–6

[38] Kartawidjaja F C, Lim Z Y, Ng S L G, Zhang Y and Wang J 2010 Morphology, optical, and magnetic properties of Zn$_{1-x}$Co$_x$O nanorods grown via a wet chemical route J. Am. Ceram. Soc. 93 3798–802

[39] Arshad M, Azam A, Ahmed A S, Mollah S and Naqvi A H 2011 Effect of Co substitution on the structural and optical properties of ZnO nanoparticles synthesized by sol–gel route J. Alloys Compd. 509 8578–81