Magnetic nanoparticles as a seed layer for growing ZnO nanowires for optical applications

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Abstract

In the present work, cerium oxide CeO\textsubscript{2} nanoparticles were synthesised by sol-gel method and used for the growth of ZnO nanorods. The synthesised nanoparticles were studied by x-ray diffraction technique [XRD]. Furthermore, these nanoparticles were used as seed layer for the growth of ZnO nanorods by following the hydrothermal growth method. The structural study of ZnO nanorods was carried out by using field emission scanning electron microscopy [FESEM], and x-ray diffraction [XRD] techniques. This study demonstrated that the grown ZnO nanorods are well align, uniform, good in crystal quality and possess diameter of less than 200 nm. Energy dispersive x-rays [EDX] revealed that the ZnO nanorods are only composed of zinc, cerium as seed atom and oxygen atoms and no any other impurity in the grown nanorods. Moreover, photoluminescence [PL] approach was applied for the optical characterisation and it was observed that the near-band-edge emission [NBE] was same to that of zinc acetate seed layer, however the green emission and orange/red emission peaks were slightly raised due to possible higher level of defects in the cerium oxide seeded ZnO nanorods. This study provides an alternative approach for the synthesis of controlled ZnO nanorods using cerium oxide nanoparticles as seed nucleation layer which in reverse describe the application of these nanoparticles as well as due to controlled morphology of ZnO.
nanorods the performance of nanodevices based on ZnO can be increased using these particles as seed.

**Keywords:** sol-gel method, ZnO nanorods, field emission scanning electron microscopy, photoluminescence, x-ray diffraction

1. **Introduction**

Recently, the researchers are paying more attention towards manganese oxide nanomaterials because of their tremendous applications in the research areas of catalysis, electrochemistry, molecular adsorption, magnetite, and batteries [1-4]. CeO$_2$ is more highlighted oxide member of rare earth oxides and frequently have been used in the glass-polishing materials, as ultraviolet absorbent and automotive exhaust promoter [5-9]. Currently, cerium oxide nanoparticles have been getting more attention due to their extraordinary luminescence, magnetic and electronic properties. Because of these well-known properties, CeO$_2$ nanoparticles significantly behave in different way than the bulk materials [10-13]. Nevertheless, during the practical use the material behaviour is highly dependent on the properties exhibited by the constituent CeO$_2$ nanoparticles. Due to fact of marvellous properties exhibited by the nano sized particles of CeO$_2$, hence several methods have been proposed for the synthesis of cerium oxide nanoparticles including homogeneous precipitation [14], hydrothermal preparation [15-17] and different decomposition methods [18-19]. Among different solution based chemical synthesis methods, the sol gel method has superiority due to following facts such as homogeneity, better stoichiometry, almost free of any impurity phase-powders at low temperature and ease in the formation of dense monoliths, thin films or nanoparticles.

ZnO is becoming more popular among researchers since last two decades due its marked physical properties including wide direct bandgap (3.37 eV), high exciton binding energy (60 meV) which make it highly useful for the optoelectronic applications [20]. ZnO has been doped either intrinsically or extrinsically with different dopants particularly for achieving the desired electrical properties such as metallic, semiconducting and insulating characteristics [21, 22]. ZnO exists in various nanostructures, specially one dimensional nanostructure such as nanorods, nanowires, nanoflowers, nanotubes and nanobelts are widely used due to significantly improved performance for the piezoelectric and sensing devices [23, 24], and
also involved in the fabrication of UV lasers, dye sensitized solar cells and photo catalysis [25].

ZnO nanorods have been grown by several growth methods such as epitaxial Electrodeposition, catalyst-assisted vapor-liquid-solid, thermal evaporation, metal organic chemical vapor deposition, radio frequency magnetron sputtering and solution based methods [26-30]. However, low temperature growth is significantly followed for the growth of ZnO nanorods due to several advantages of this method such as high deposition rate, ease in handling of dopant impurity and the most favourable priority of this method is its low temperature for the growth of ZnO nanorods [25]. The perpendicularly oriented ZnO nanorods to substrate have been remained in attention for the improvement in the performance of light emitting and field emission devices [31-33]. This can be achieved by the gas phase based growth techniques, however these techniques needs highly sophisticated tools, single crystalline substrates of high price for the well aligned growth, high working temperature of 450 -900 °C, and also suffers some other problems such as weak uniformity of grown nanostructures and minimum amount of grown material on the substrate [34].

In the hydrothermal method, ZnO crystals layers have been considered important for the growth of ZnO nanorods along with calcination at higher than 300 °C for the crystallization of ZnO crystal seed layers using oxidized zinc foil in the absence of seed layer [35]. Wu et al. has shown the well oriented ZnO nanorods on zinc oil substrate at high temperature, and Naoyuki Ueno et al. has grown ZnO nanorods on silicon substrate coated with seed layer of organic–inorganic composite using low temperature aqueous chemical growth technique [36]. Wu et al. approach can only be applied on zinc foil plate and it is also accompanied by calcination and Naoyuki Ueno et al. used silicon substrate which is expensive substrate relative that of glass and gold coated substrates [35-36].

In this study, we have grown well aligned, highly dense and uniform ZnO nanorods on the glass and gold coated substrates using and CeO$_2$ magnetic nanoparticles as seed layer without zinc acetate seed solution by following the hydrothermal growth technique.

2. Materials and experimental section

2.1 Materials

Zinc nitrate hexahydrate, zinc acetate dihydrate, hexamethylenetetramine [HMT], Cerium (III) nitrate [(Ce(NO$_3$)$_3$•6H$_2$O)], ammonium hydroxide [NH$_4$OH], hydrochloric acid
HCl] were purchased from sigma Aldrich Sweden. All other chemicals used were of analytical grade.

2.2. Synthesis of cerium oxide and manganese oxide nanoparticles

For the synthesis of CeO$_2$ nanoparticles (NH$_4$)$_2$Ce(NO$_3$)$_6$ and NH$_4$OH were used as starting precursor without any further purification. 1.0 g Ammonium cerium nitrate [(NH$_4$)$_2$Ce(NO$_3$)$_6$] or Cerium (III) nitrate [(Ce(NO$_3$)$_3$•6H$_2$O)] was dissolved in 20 ml distilled water after that 5 ml ammonium solution (1M) was added into the solution mixture with the constant stirring at 70 °C for 30-45 minutes. A grey colour precipitate was occurred by the addition of ammonia solution. Ammonia solution was added in excess by drop-wise until a pH of 9.0 was achieved. The resulting mixture was left to stir continuously at 70 °C for 3 h to complete the reaction. After complete stirring, the pale yellow precipitates of Ce(OH)$_4$ were appeared, then centrifuged and washed several times with deionized water to remove the excess ammonium ion and nitrate from the mixture. The prepared yellow precipitates were dried in air at 100 °C temperature and afterwards annealed at 300 °C for 2 h.

2.3. Preparation of seed solution of prepared magnetic nanoparticles for the growth of ZnO nanorods

The preparation of homogeneous and completely dissolved solution of magnetic metal oxide nanoparticles as a seed layer is critical issue and in this work we prepared seed solution of manganese oxide and cerium oxide into 0.1 M solution of hydro chloric acid. The concentration of each metal oxide nanoparticle was 85 mg /5 ml as seed layer for the growth of ZnO nanorods after the optimization.

2.4. The fabrication of ZnO nanorods on the glass and gold coated substrates

Following steps have been used for the growth of ZnO nanorods on the glass substrate and gold coated glass substrate. Firstly, the glass substrates were washed with isopropanol in ultra-sonic bath for 10 minutes and cleaned by deionized water at room temperature. In order to have coated layer of gold on the glass substrates the evaporator Satis (725) was used for the deposition of 10 nm thickness titanium as adhesive layer, then followed by 100 nm thickness of gold. Then the cleaned substrates were spin coated three times with seed layer of magnetic nanoparticles at 2500 r.p.m and annealed at 120 °C for 20 minutes. Afterwards, the seeded substrates were fixed in Teflon sample holder and dipped in equimolar solution of
zinc nitrate hexahydrate and HMT, and then samples were left in oven at constant temperature of 93 °C for 5 to 7 hours. After the completion of growth duration samples were taken out from oven, washed with deionized water and dried with nitrogen gas. The grown ZnO nanostructures were further characterised by field emission electron microscopy, x-ray diffraction technique, and transmission electron microscopy.

3. Results and discussion

3.1. The XRD characterisation of synthesised magnetic nanoparticles and grown ZnO nanorods with seed layer of these magnetic nanoparticles

Fig. 1 (a) shows the X-ray powder diffraction pattern of the sol-gel prepared CeO₂ nanoparticles. The results of XRD pattern indicate that the CeO₂ nanoparticles are well-crystallized and patterns are in good agreement with a cubic structure. The principle reflection peaks of CeO₂ in diffraction pattern are measured, which correspond to the (111), (200), (220) and (311) planes. These reflection peaks can be indexed to the pure cubic fluorite structure of CeO₂. The intensities and positions of the diffraction plane which are perfectly similar to the JCPDS card and no differences between them and reported data. The broadened peaks in the diffractogram confirm the nanocrystalline nature of the prepared CeO₂ nanoparticles. According to the Scherrer equation, the strongest peak (111) at $2\theta = 28.4^\circ$ and the peak (220) at $2\theta = 47.17^\circ$ were used to calculate the average crystallite size of CeO₂ nanoparticles, determined to be around 3-4 nm.

Fig. 1 (b) shows the X-ray powder diffraction pattern of grown ZnO nanorods on the gold coated glass substrate using cerium oxide CeO₂ nanoparticles as a seed layer. It can be seen from the diffractogram that peak at 002 planes is quite dominant over other appeared peaks which clearly demonstrates the well orientation of ZnO nanorods in c-axis and the growth patterned of ZnO nanorods could be perpendicular to the gold coated substrate. Fig. 1(c) shows the energy dispersive x-ray study of the cerium oxide seeded ZnO nanorods and it can be seen from the figure that the ZnO nanorods are composed of Zn and O atoms and the cerium atoms are also present on the surface which acted as catalyst for the proper oriented growth of ZnO nanorods.
3.2. The field emission scanning electron microscopy (FESEM study of magnetic particles seeded ZnO nanorods

Fig. 2 shows the FESEM image of ZnO nanorods grown on the gold coated glass substrate using CeO$_2$ nanoparticles as seed layer and this study has shown that ZnO nanorods were very well aligned, highly dense and uniform on the substrate. The diameter of the present nanorods is about 100 nm to 20 nm with length of 1µm. The diameter of ZnO nanorods depends on the concentration of precursors and duration of the growth process. The length is function of time and it increases with time. The FESEM and XRD results are consistent with one another. The diameter of ZnO nanorods is about 100 nm to 200 nm and length of 1µm. The length and diameter depend on the conditions of reaction bath. The FESEM characterisation repeated the same results as XRD has shown for the magnetic nanoparticles seeded ZnO nanorods and both analyses are fully agreed to one another.

2.3. Optical characterisation of cerium oxide CeO$_2$ seeded ZnO nanorods

The aim of this investigation was to determine the imperfection of crystal structure of nanomaterial, so for this analysis photoluminescence (PL) technique is potential analytical tool. It is well known that ZnO materials with high defect densities such polycrystalline thin films or powders, usually exhibit strong PL bands of defect origin within the visible spectral region. On other hand, these emissions are suppressed in single crystalline epitaxial films or bulk ZnO, where near-band-edge (NBE) emission due to free exciton recombination with in the near-ultra-violet spectral region dominates. In case of ZnO nanostructures, such as ZnO nanorods due to their high surface to volume ratios which increases the importance of recombination via surface states. Moreover, it is found that presence of boundaries and pilling of nanorods might lead to the enrichment of the defect states. The presence of these defects in nanostructure in higher intensity of defect – related visible emissions as compare to that of the band edge emission.

In our case, we observed the increased in the green emission peak around 530 nm and a red or orange emission around 673 nm for CeO2 seeded ZnO nanorods as compare to zinc acetated seeded ZnO nanorods as shown in figure 5 (a-b). The increased green and red or orange peaks could be assigned to the oxygen vacancies, interstitial zinc ions and impurities [37-39]. However, the near–band-edge emission (NBE) was found to be same in the both cases.
3. Conclusion

In this study, cerium oxide magnetic nanoparticles were synthesised and applied as a seed layer for the growth of ZnO nanorods using low temperature growth technique. The cerium oxide nanoparticles were characterised by [XRD]. In addition to this, the structural characterisation of grown ZnO nanorods was carried out using field emission scanning electron microscopy, [EDX] and [XRD] techniques. These techniques revealed that the grown ZnO nanorods are well aligned and perpendicular to the substrate and the obtained results for each technique are consistent to one another. Moreover, optical characterisation was performed for the understanding of photocatlytic effect shown by the cerium oxide nanoparticles for ZnO nanorods. It was observed that the green emission peak and orange/red emission peaks were slightly increased as compare to the zinc acetated seeded ZnO nanorods. The present study has shown that the cerium oxide nanoparticles can be used as seed layer for controlling the alignment of ZnO nanorods which in result enhances the working performance of nanodevices based on the ZnO nanostructures.

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Figure 1(a-c) : 

a. The XRD pattern for a. CeO$_2$ nanoparticle b. ZnO growth with CeO$_2$ seed, c. The EDX pattern for ZnO nanorods grown with CeO$_2$. 
Figure 2: The FESEM image for ZnO nanorods grown with CeO2 seed.
Figure 3: The PL study of ZnO nanorods a. growth with Zinc acetate seed, and b. growth CeO2 seed.