Synthesis and characterization of doped ZnO nanoparticles and their potential applications

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Abstract

Pure and doped ZnO nanoparticles are synthesized using direct precipitation method and sol-gel method. After synthesis, the pure nanoparticles of ZnO will be separated out and their various characterizations for the studies of different propertieslike crystallographic structure, optical properties and anti-fungal properties can be studied using XRD, Zeta-Sizer, Photoluminescence Spectroscopy (PL) and UV-VIS Spectroscopy (UV-VIS). These characterizations have also been performed to find out is there any change in the behavior of ZnO nanoparticles was observed by changing or altering the routes/methods of synthesis i.e. byDirect precipitation and Sol-Gel methods. The doping studies have been carried on the ZnO nanoparticles using the various dopants like Aluminum (Al), Copper (Cu), Carbon (C) and Aluminum-Copper (Al-Cu) double doping using the above listed standard procedures and their characterization and behavior was studied using different techniques.

Keywords: ZnO nanoparticles, Direct Precipitation Method (DP), Sol- Gel Method (SG), Zinc acetate dihydrate, XRD, Zeta-Sizer, Photoluminescence Spectroscopy (PL) and UV-VIS Spectroscopy

1. Introduction

Nanotechnology is an emerging field which has the potential to change and shape our future. Since then, varieties nanostructured materials and devices have been synthesized. Because of their extraordinary and unique properties [1–6], they get very famous and are used very extensively [7–10]. ZnO is one such material which finds a wide range of applications because of its versatile nature and properties. This makes it suitable for multidisciplinary applications [11]. It is one of the materials which shows a wide range of different as a result of which properties varies and each morphology possess a new set of properties which can be implemented or applied in various fields. Morphology plays a very important role in deciding the properties of synthesized ZnO nanostructures, which makes it suitable for specific applications. The morphology of synthesized ZnO nanostructures also depends on the route or technique by it get prepared and also depends on the synthesizing conditions e.g. pH of the medium,

substrate/bio template chosen, concentration of the chemicals, calcination temperature, catalyst provided, reaction time, reaction rate, titration rate and many more. ZnO is an important metal oxide that can be easily be synthesized by various method, e.g. vapor-liquid-solid (VLS) growth with the use of a catalyst [12], pulsed laser deposition [13], electrochemicaldeposition in porous membranes [14], metal vapor transport using Zn sources [15] but precipitation andsol-gel are the easy, economical simple methods for their preparation. ZnO is biocompatible, biodegradable by nature and also biosafe for medical and environmental applications [16].

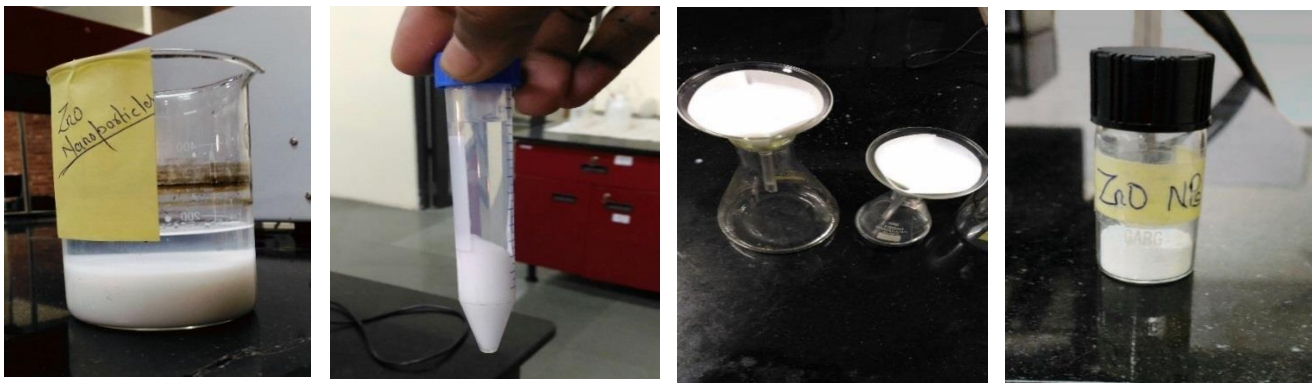
Some of the morphologies of ZnO are nanoparticles, nanospheres, nanorods, nanocores, nanotubes, nanobelts and many more. The list of morphologies of ZnO nanostructures is very long. Because of its various morphologies, it finds a wide range of applications. ZnO remarkable contribution in Photonics,electronics and optics, so they are very much popular for many of the applications such as UV- lasers [17–21], light emitting diodes [22–26], solar cells [27–32], nanogenerators [33–36], gas sensors [37–41], photodetector [42–45], and photocatalysts [46]. ZnO nanowire are also used increasingly as a photocatalyst to inhibit the growth of bacteria and virus and for the degradation of environmental pollutants like dyes, pesticides and volatile organic compounds [47, 48].

Experimental details / Methodology

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_20$) and Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) are taken as the raw or base materials for the preparation of ZnO nanoparticles.

Synthesis of pure ZnO nanoparticles (A). Direct precipitation Method.

Pure ZnO synthesized by using Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_20$) as precursor and Potassiumhydroxide (KOH) as precipitating agent by precipitation method. 0.4M aqueous solution of Zinc nitratehexahydrate and 0.6M aqueous solution of KOH were prepared using deionized water. KOH solutionpoured slowly into Zinc nitrate hexahydrate solution at room temperature and mix the solution for 30 minutes on the magnetic stirrer which leads to the formation of white suspension. The white product formed was centrifuged at 3000 rpm for 10 minutes. The obtained product was washed with water andabsolute alcohol and left for a few hours for filtration. The filtered product was calcinated at 550°C for4 hours and finally grinded using mortar and pestle.



(a) (b) (c) (d)

Figure 1. (a). White suspension formed product, (b). Centrifuged product, (c). Filtered product, (d). ZnO nanoparticles. Final product formed i.e. ZnO nanoparticles undergoes for their characterization for their behavioralstudies.

(B). Sol-Gel Method.

Pure ZnO synthesized by using Zinc acetate dihydrate (Zn $(CH_3COO)_2.2H_2O$) and Ammonia (NH_3) bySol-Gel method. 1.2M solution of Zinc acetate dihydrate, is mixed with 40 ml deionized water and the solution was stirred on a magnetic stirrer for 40 minutes at temperature 70°C. Add citric acid ($C_6H_8O_7$)to the solution to adjust pH around 2. Ammonia was added to the gel-forming (15ml-20ml, dependingon gel-formation). The product was formed is centrifuged, filtered and was dried at 80°C for 1.5 hoursin hot air oven. Finally, calcinate the product at 550°C for 4.5 hours and grind it. The product formed i.e. ZnO nanoparticles by sol-gel undergoes for characterization.

Figure 2. ZnO nanoparticles prepared via sol-gel route

Synthesis of Al-doped ZnO nanoparticles

Al doped ZnO nanoparticles can be synthesized by using Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), Aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) and Ammonia (NH_3) by Sol-Gel method[19]. 1.2M solution of Zinc acetate dihydrate along with three Aluminum atomic content of 0.3at%, 0.5at% and 0.9at% is mixed separately with 40ml deionized water and the solution was stirred on a magnetic stirrer for 40 minutes at temperature 70°C. Add citric acid ($C_6H_8O_7$) to the solution to adjust pH around 2. Ammonia was added to the gel-forming (15ml-20ml, depending on gel-formation).The product was formed is centrifuged, filtered and was dried at 80°C for 1.5 hours in hot air oven. Finally, calcinate the product at 550°C for 4.5 hours and grind it. The product formed i.e. Al doped ZnO nanoparticles undergoes for characterization.

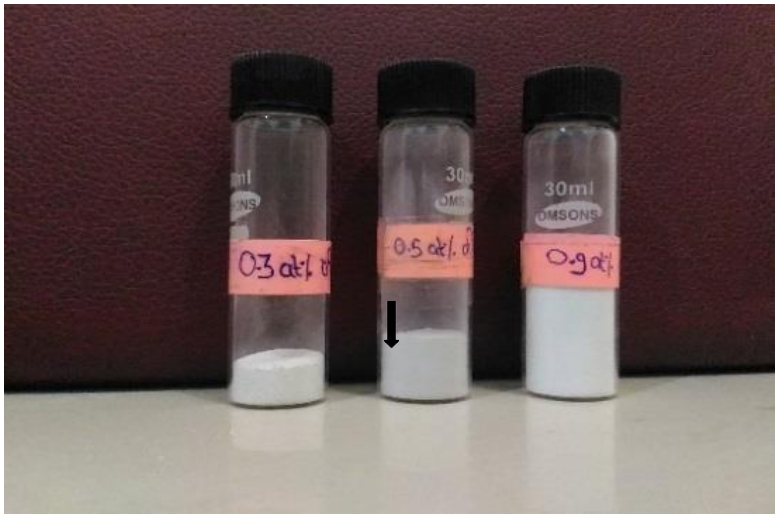


Figure 3. Al doped ZnO nanoparticles of 0.3at%, 0.5at% and 0.9at% respectively.

Synthesis of C-doped ZnO nanoparticles

Carbon doped ZnO nanoparticles can be prepared via using zinc acetate dihydrate (fisher scientific) and Graphite powder (Nike chemical India) as a base material using suitable reagents.

(A). Precipitation method

1.4 M soln. of Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) is prepared and then 1at.% (atomic %) and 2at.% graphite powder was mixed in it. Stir the solution for 40 min. at 60 degree Celsius and allow it to cool. Add citric acid to adjust pH around 3 and add ammonia to gel formation. Centrifuge, filter andwash the product with water and ethanol, dry for 1 hrs at 100 °C and then calcinate it for 5hrs for 500°C and then ground the product.

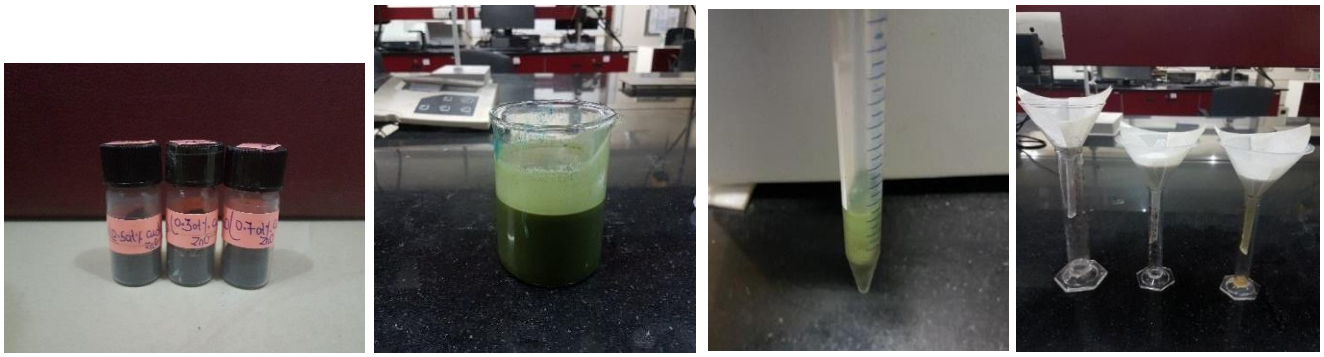
(B). Thermal decomposition method

4gm of ZnO powder is mixed with 1gm of graphite powder (Nike chemical India) , ground for 2hrs and then ethanol was mixed. Mix the solution properly and then dry it in hot air oven for 2 hrs at100 °C and finally calcinate at 600^{o}C for 7 hrs. Ground the final product.

Figure 4. Carbon doped ZnO nanoparticles of 10%,20%, 1at% and 2at% respectively

Synthesis of Cu-doped ZnO nanoparticles

Prepare soln. of 1.4 M Zinc acetate dehydrate (Zn $(CH_3COO)_2.2H_2O$) in ethanol and 0.3at%,0.5at% and0.7at% cupric acetate monohydrate in ethanol separately. Mix both solutions (NaoH soln. in ethanol) was added on magnetic stirrer for 2hrs at room temperature, obtained precipitate was centrifuge, filter and washed with water and ethanol several times and dry at 100 °C for 1 hr and then calcinate at 600 °C for 5 hrs and ground the final product.



(a) (b) (c) (d)

Figure 5. Above figure showing the various intermediate steps involved in the synthesis of Cu-doped ZnO nanoparticles. (a). Final product, (b). gel formation, (c). centrifuge product, (d). filtered product.

Synthesis of Al-Cu double doped ZnO nanoparticles

1.4 M solution of zinc acetate dihydrate and 0.3at. % and 0.5at. % cupric acetate monohydrate and 0.2at. %and 0.4at. % in 75ml Ethanol were prepared prepared separately and mixed on the magnetic stirrer for half an hour separately and then all the soln. added together and then mixed for 1 hr on the magnetic stirrer. Then NaOH soln. in ethanol were added by constant magnetic stirring for two hrs. till the gel formation. The obtained gel was collected and centrifuge and filtered overnight and then it is washed with water and ethanol several times and then dried at 100°C for 1 hrs in the hot air oven and then calcinate at 400°C for 4 hrs and then grounded finally to obtain final product. The other sample is prepared by same method by varying the concentration only.

Figure 6. Al and Cu double doped ZnO nanoparticles. First one is 0.3at. % Cu and 0.2at. % Al doped ZnO and other one is 0.5at.% Cu and 0.4.at% Al doped ZnO.

The product formed i.e. Al-Cu double doped ZnO nanoparticles undergoes for characterization to study about their behavior and property.

Results and analysis

Characterization techniques used for the analysis of the different samples

Size distribution

Size distribution is an important structural aspect to rationalize between structure and property of material.

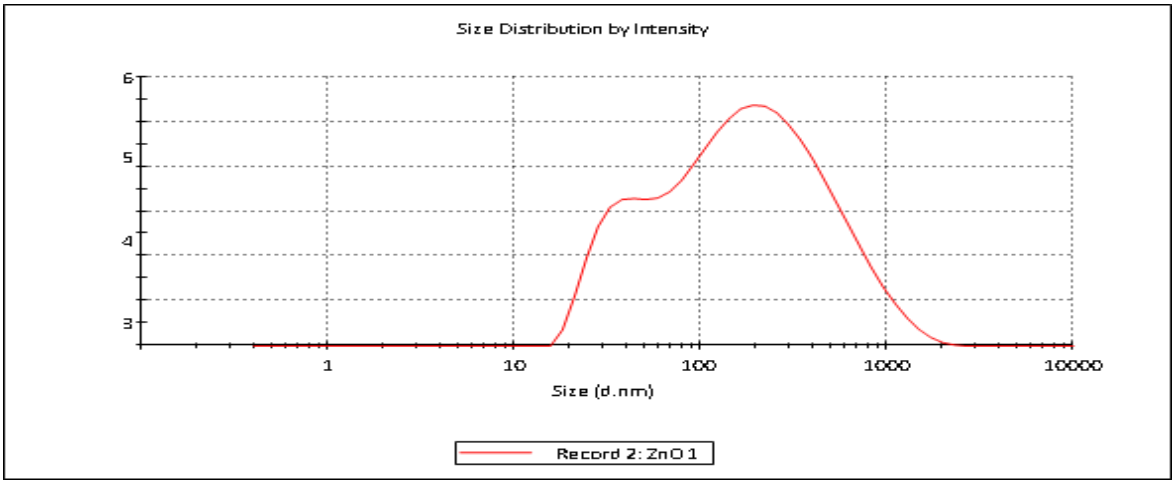


Figure 7. Size distribution vs intensity

The graph shows the size variation of ZnO nanoparticles (DP) by intensity in the solvent or dispersantmedium. Water was chosen as the dispersant medium. Particle size analyzer shows that the synthesizedZnO sample resides in nanosized range. The average particle size of synthesized ZnO is about 103.4nm.

XRD Analysis

The aim of doing XRD is for the crystallographic analysis i.e. for the study of ZnO nanoparticle's structure, shape and size.

Pure ZnO nanoparticles (Direct precipitation (DP) and Sol-Gel (SG))

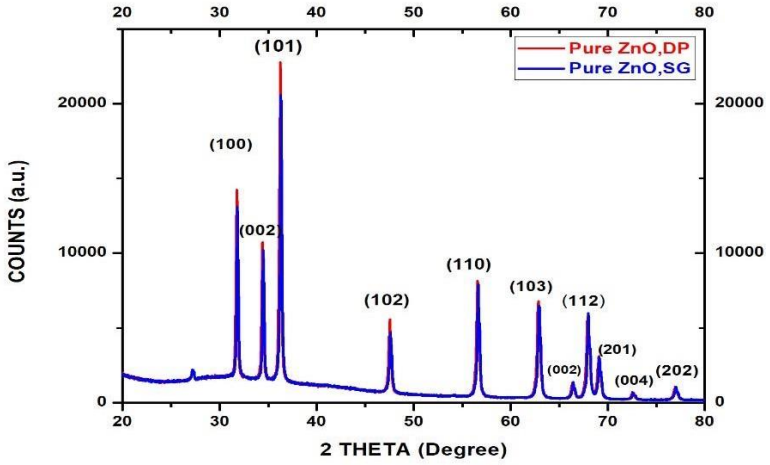
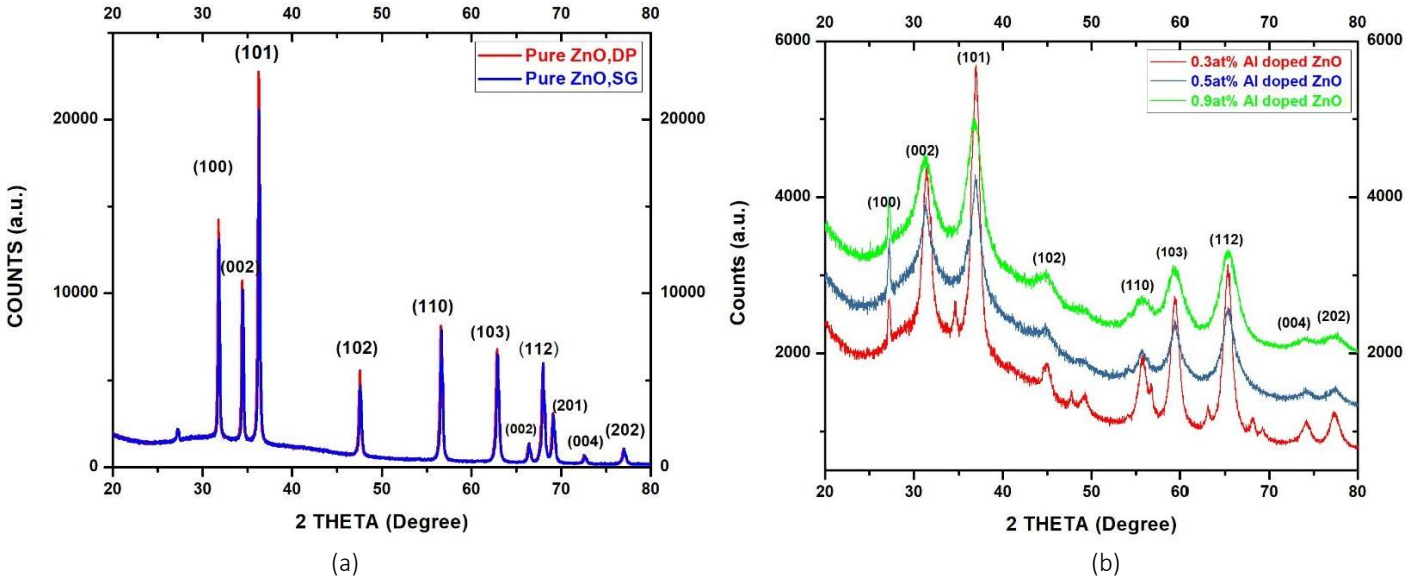
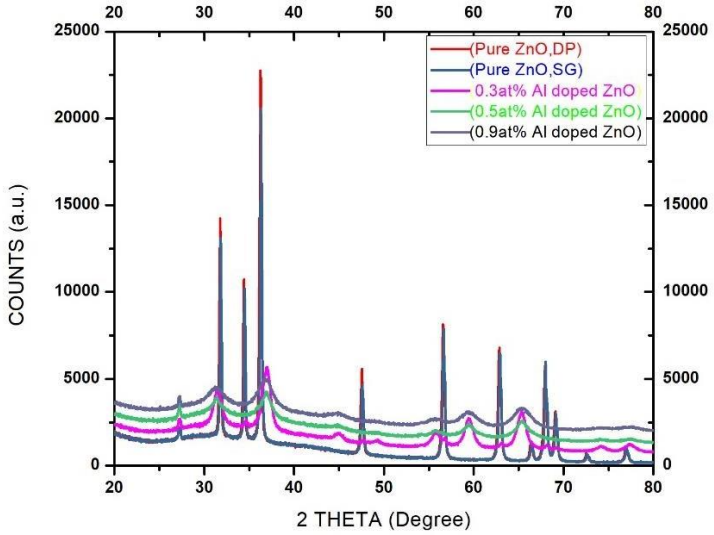


Figure 8. XRD graph of pure ZnO nanoparticles (DP & SG).

Fig.8 shows the phases presence in ZnO nanoparticles. Above graphs are the resulting patterns of ZnO nanoparticles in various profiles of peaks and diffraction angle 2Ɵ (=20° to 80°) which shows thediffraction of ZnO nanoparticles. Sharp peaks are shown by the graphs which show crystallinity in nature. The synthesized ZnO sample showed a single phase with a clear diffraction peak. The reporteddata (JCPDS Card No. 36-1451) which corresponds the indexed value of the peaks. Comparing the XRDs graph of ZnO synthesized by direct precipitation and sol-gel showed that they are almost identical. The peaks are obtained in the same phase having the same crystallinity and it also suggests that they have almost identical lattice parameters.

1.1.1. Al-doped ZnO nanoparticles





(c)

Figure 9. XRD pattern of ZnO nanoparticles (a). pure ZnO, (b). Al-doped ZnO, (c). pure and Al-doped ZnO.

Fig.9 shows the phases presence in ZnO and Al doped ZnO nanoparticles. Above graphs are the resulting patterns of pure and Al doped ZnO nanoparticle in various profiles of peaks and diffraction angle 2Θ (=20° to 80°) which shows the diffraction of ZnO nanoparticles. Sharp peaks are shown by the graphs, which show crystallinity in nature. The synthesized ZnO sample showed a single phase witha clear diffraction peak. The reported data (JCPDS Card no. 36-1451) which corresponds the indexed value of the peaks for pure ZnO nanoparticles. Comparing the XRDs spectra of pure ZnO and Al dopedZnO, it can be observed that the nature of the spectra is almost identical in both cases; the difference isin the intensity parameter. As the concentration of Aluminum as dopant is increasing from 0.3at% to 0.9at%, there is an increase and shift of the intensity values to above the Y-axis. The peaks are obtainedin the same phase having the same crystallinity.

Fig.10 shows the phases presence in ZnO and C doped ZnO nanoparticles. Above graphs are the resulting patterns of pure and Al doped ZnO nanoparticle in various profiles of peaks and diffraction angle 2Θ (=20° to 80°) which shows the diffraction of ZnO nanoparticles. Sharp peaks are shown by the graphs which show crystallinity in nature. The synthesized ZnO sample showed a single phase with a clear diffraction peaks. The reported data (JCPDS Card no. 36-1451) which corresponds the indexed value of the peaks for pure ZnO nanoparticles. Comparing the XRDs spectra of pure ZnO and C- dopedZnO, it can be observed that the nature of the spectra is almost identical in both cases, the difference is in the intensity parameter. As the concentration of Carbon as dopant is increasing, there is no change in the phases and the structure remains independent of the concentration of the carbon. The peaks are obtained in the same phase having the same crystallinity.

C-doped ZnO nanoparticles

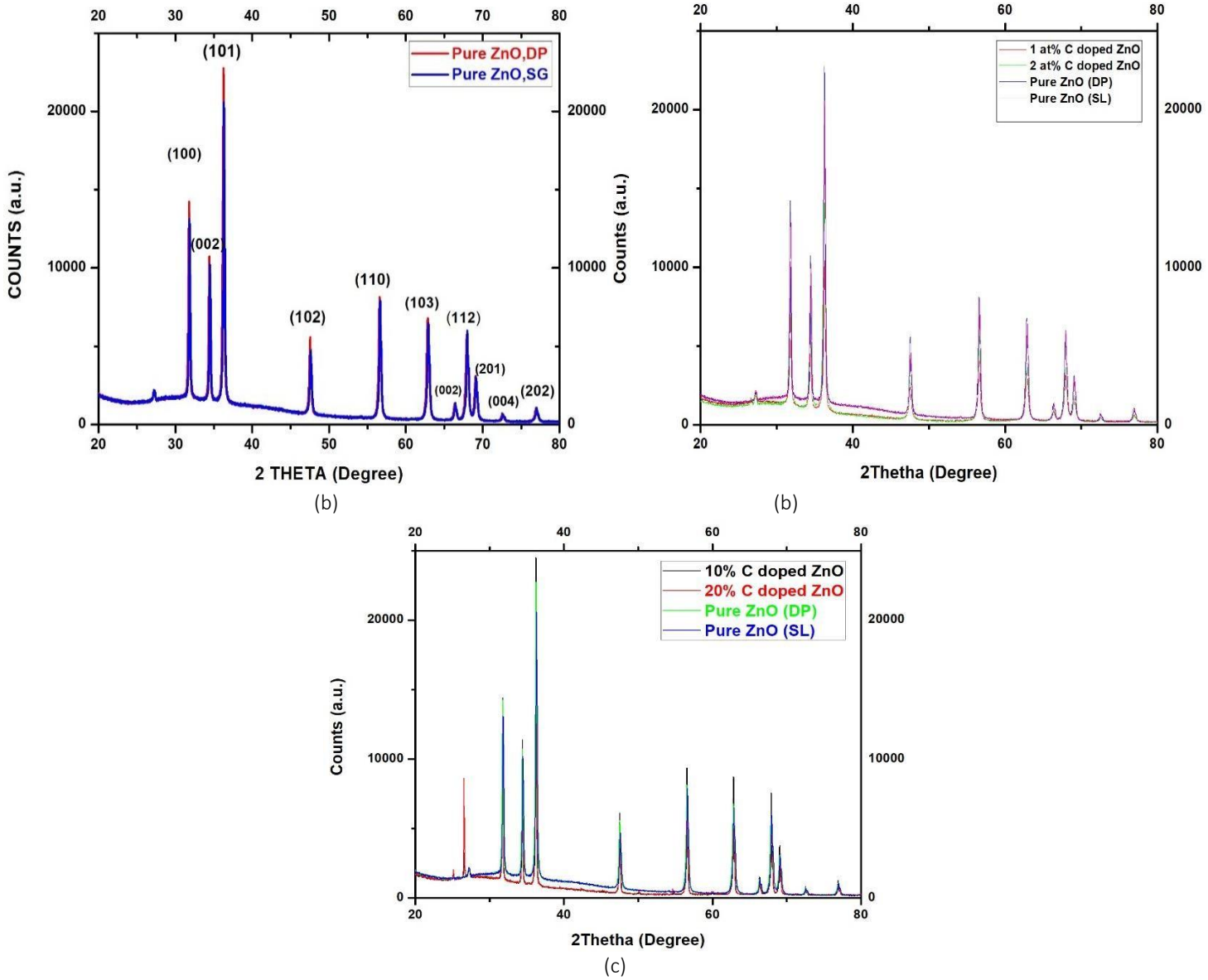


Figure 10. XRD pattern of ZnO nanoparticles (a). pure ZnO, (b). pure & C-doped ZnO (1at.% and 2at.%), (c). pure and C-doped ZnO (10% and 20% C).

Cu-doped ZnO nanoparticles

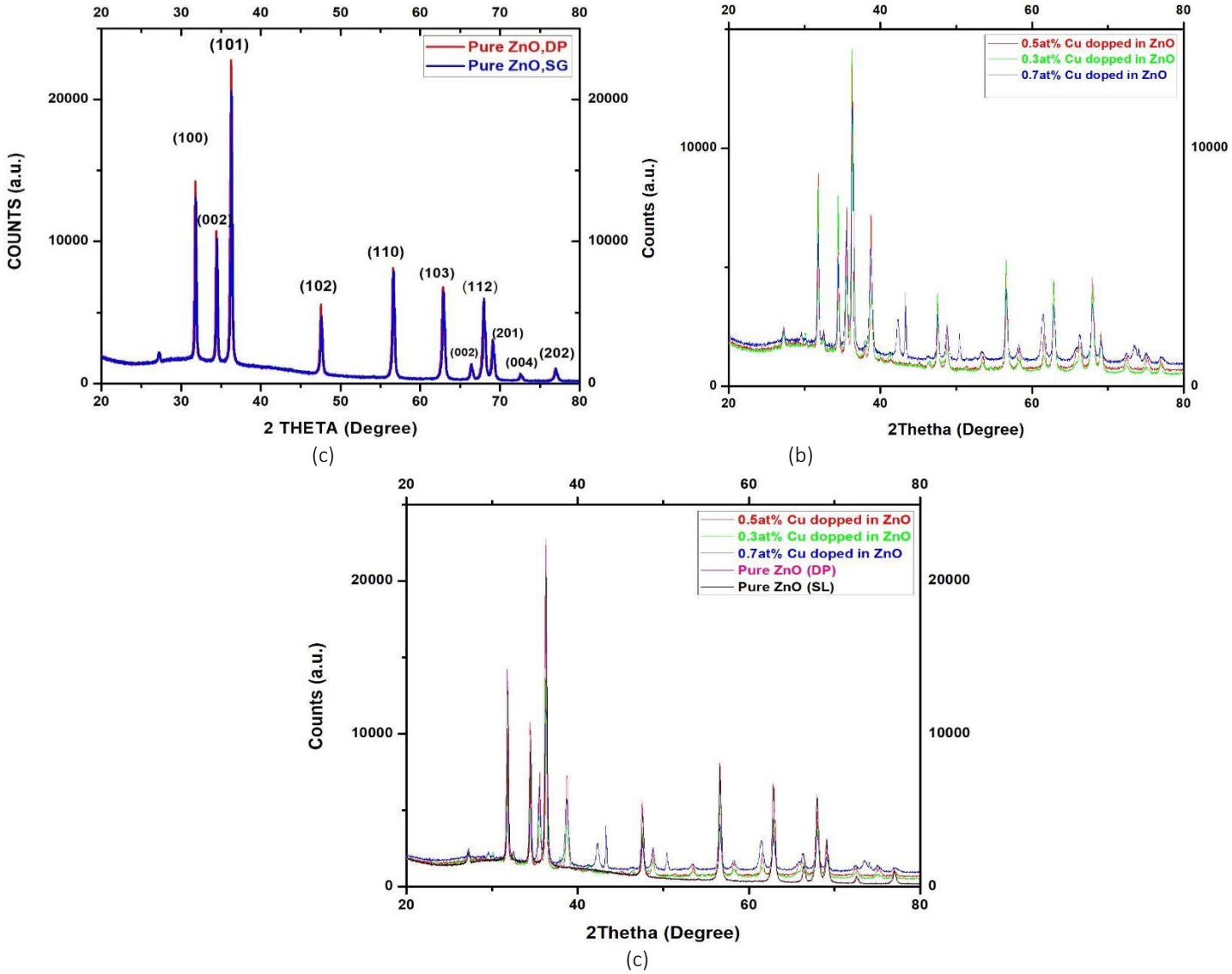


Figure 11. XRD pattern of ZnO nanoparticles (a). pure ZnO, (b). Cu-doped ZnO (0.3at.%, 0.5at.% and 0.7at.%), (c). pure andCu-doped ZnO (0.3 at.%, 0.5at.% and 0.7at.%).

Fig.11 shows the phases presence in ZnO and Cu doped ZnO nanoparticles. Above graphs are the resulting patterns of pure and Al doped ZnO nanoparticle in various profiles of peaks and diffraction angle 2Ɵ (=20° to 80°) which shows the diffraction of ZnO nanoparticles. Sharp peaks are shown by the graphs which show crystallinity in nature. The synthesized ZnO sample showed a single phase witha clear diffraction peak. The reported data (JCPDS Card no. 36-1451) which corresponds the indexed value of the peaks for pure ZnO nanoparticles. Comparing the XRDs spectra of pure ZnO and Cu- doped ZnO, it can be observed that the nature of the spectra is almost identical in both cases, the difference is in the intensity parameter. As the concentration

of Copper as dopant is increasing from 0.3at.% to 0.7.at%, there is no change in the phases and the structure remains independent of the concentration of the carbon. The peaks are obtained in the same phase having the same crystallinity.

Al-Cu double doped ZnO nanoparticles

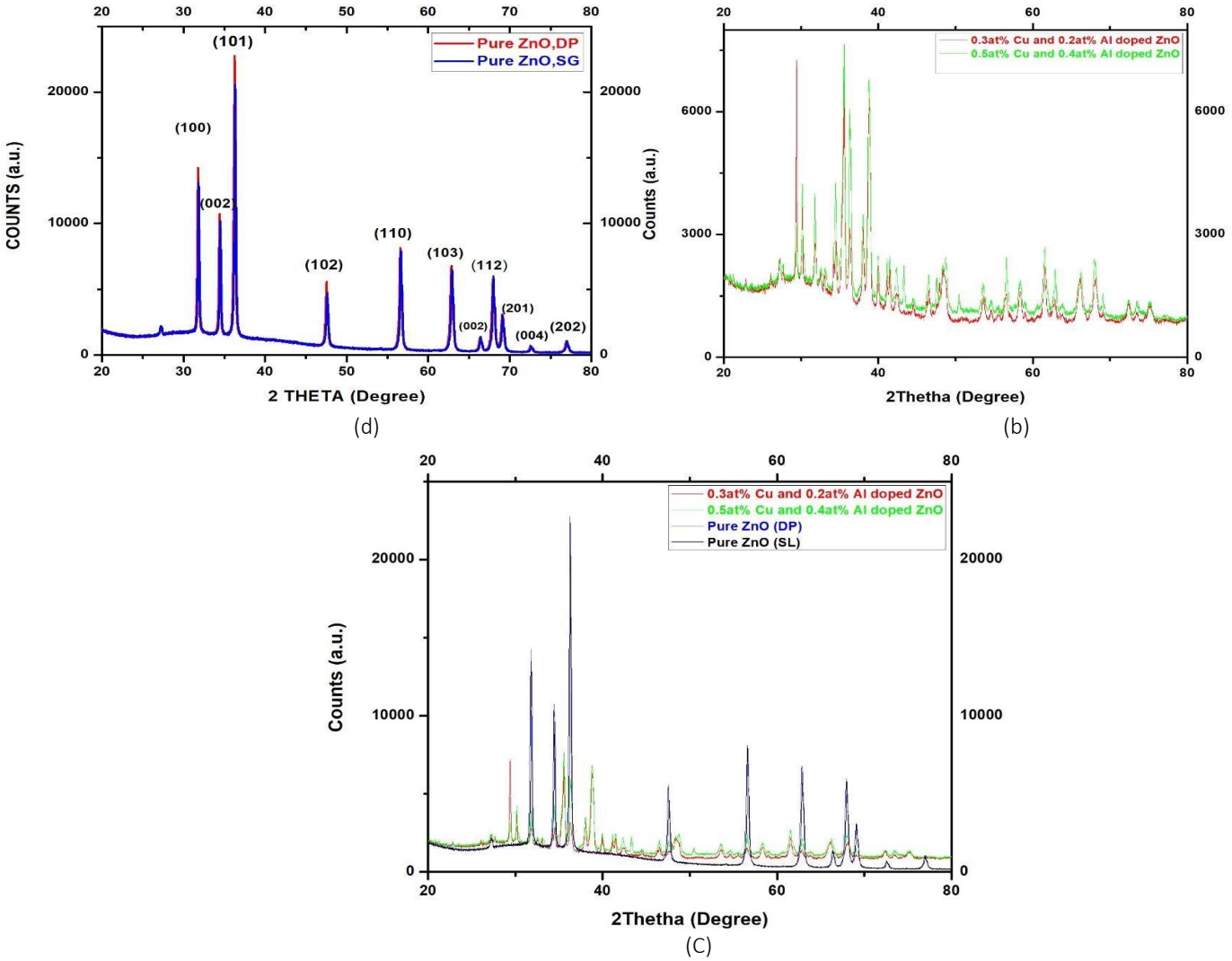


Figure 12 XRD pattern of ZnO nanoparticles (a). pure ZnO, (b). Al-Cu double doped ZnO (0.3at.% Cu-0.2at.% Al and 0.5at.% Cu-0.4at.% Al), (c). pure and Cu-doped ZnO (0.3at.% Cu-0.2at.% Al and 0.5at.% Cu-0.4at.% Al).

Fig.12 shows the phases presence in ZnO and Al-Cu double doped ZnO nanoparticles. Above graphs are the resulting patterns of pure and Al-Cu doped ZnO nanoparticle in various profiles of peaks and diffraction angle 2Θ (=20° to 80°) which shows the diffraction of ZnO nanoparticles. Sharp peaks areshown by the graphs which show crystallinity in nature. The synthesized ZnO sample showed a singlephase with a clear diffraction peak. The reported data (JCPDS Card no. 36-1451) which corresponds the indexed value of the peaks for pure ZnO nanoparticles. Comparing the XRDs spectra of pure ZnOand Al-Cu- doped ZnO, it can be observed that the

base material or the host material ZnO showing itspeaks with multiple phases present in it. These phases are appeared as the ZnO is double doped by aluminum and copper and the extra peaks and phases confirming the presence of aluminum and copper present in the ZnO nanoparticles.

Potential applications of ZnO nanoparticles

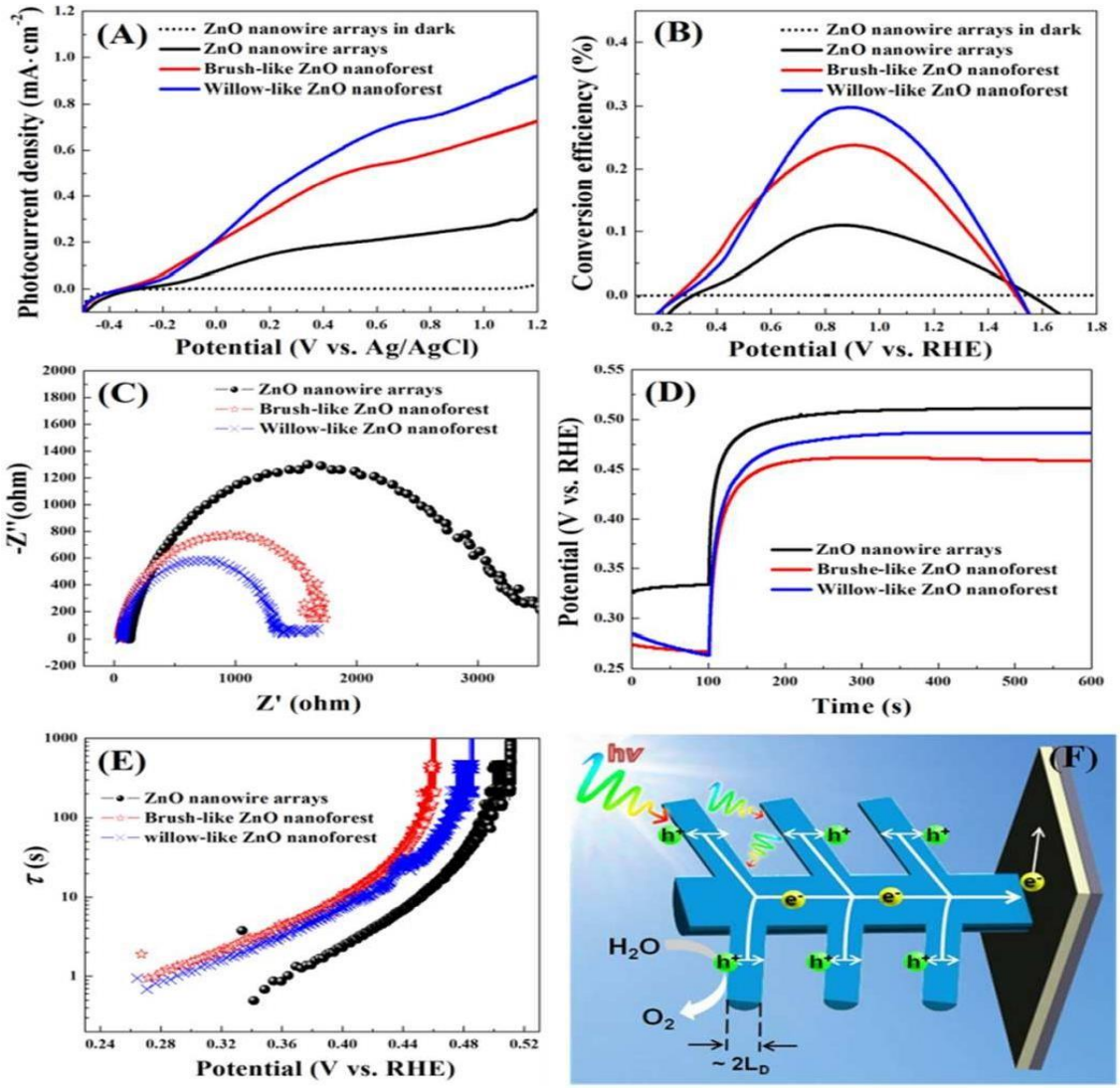


Figure 13. Photocurrent density-potential curves; (B) photoconversion efficiency; (C) impedance spectra; (D) response of Voc; and (E) photoelectron lifetime from three nanostructured ZnO architectures: nanowire arrays, short- branched nanoforest, and willow-like nanoforest; (F) Schematic model displaying the illuminated photoanode to explain the enhanced charge transport and light trapping in willow-like ZnO nanoforest [61].

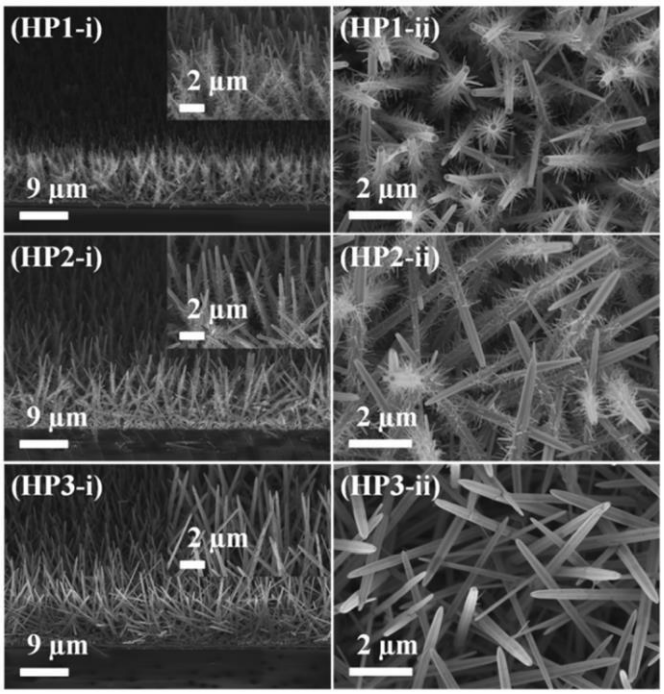


Figure 14. SEM images of the obtained ZnO nanoforests after growing ZnO Nano branches onto the preformed ZnO nanowire arrays in precursor solutions with no ammonia but different concentrations of PEI (polyethyleneimine). HP1: *c*(PEI) = 0.0035 M; HP2: *c*(PEI) = 0.005 M; and HP3: *c*(PEI) = 0.007 M [61].

The longer branches can facilitate charge migration, electrochemical impedance spectroscopy (EIS) was measured for these three typical ZnO nanoarchitectures over the frequency range of 10^{-2}-10^{6} Hz. The Nyquist plots consist of one dominant semicircle, whose diameter is associated to charge transfer resistance at ZnO/electrolyte interface. With longer branches, the ZnO nanoforests exhibited smaller diameters comparing with the nanowire array counterpart, implying that the branchingof nanowire arrays motivated better charge transfer.

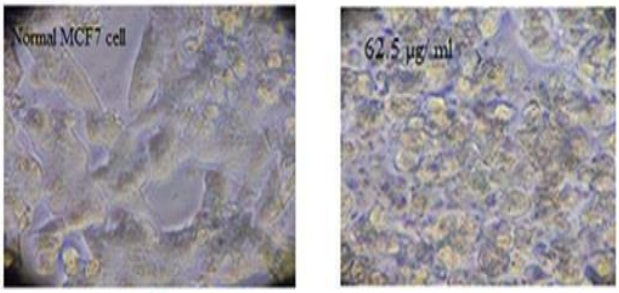
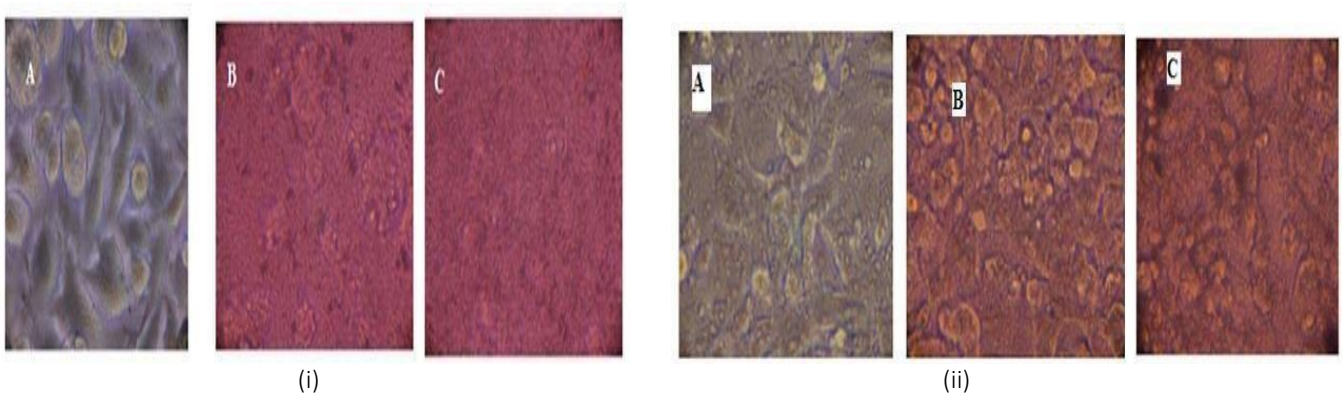


Figure 15. (A)MCF7- Human Breast Cancer Cell (B) MCF7after exposed to 62.5µg/ml synthesized ZnO nanoparticles.



(i) (ii)

Figure 16. (i). (A) A549-Human Lung cancer cell (B) A549 after exposed to 62.5µg/ml synthesized ZnO nanoparticles(C)A549after exposed to 62.5µg/ml Commercial ZnO.

(ii). (A) VERO - Normal kidney cell (monkey) (B) VERO after exposed to 62.5µg/ml synthesized ZnO nanoparticles (C) VEROafter exposed to 62.5µg/ml Commercial ZnO.

Result showed that the exposure of MCF7 and A549 cells to ZnO nanoparticles at the various concentrations for 72h significantly reduced the cell viability in a concentration dependent manner. However, the cell viability at the higher concentration of 1000 µg/ml was not significant. As the concentration increases the cell viability% significantly decreases. For ZnO nanoparticles from7.8µg/ml to 31.2 µg/ml concentration the cell viability% significantly decreased from 78.7 to 54.2(A549) and 82.8 to 50.8(MCF7) and for commercial ZnO the cell viability decreased from 91.4 to 75.5(A549). Analysis showe d that the exposure of VERO cells to ZnO nanoparticles at the various concentrations for 72h reduced the cell viability in a concentration dependent manner. However, the cell viability at the higher concentration of 1000 µg/ml was not significant. As the concentration increases the cell viability decreases significantly in the case of commercial ZnO than with ZnO NPs.For ZnO nanoparticles at concentrationfrom62.5µg /ml the cell viability decreased to 68.6% whereas for commercial ZnO the cell viability significantly decreased to 55.6%.

The study explores the potential anticancer activity of DMC synthesized ZnO nanoparticles on A549,MCF-7 cancer cell lines. The synthesis method reported here is easily scalable for large scaleproduction, economically feasible, biocompatible and cost effective. The results suggest that with the aid of oxide-based nanoparticles conditional chemotherapeutic agents may have even broader range ofapplications in the treatment of cancer cells. The dosage particles' size dependent activity against cancer cells and the variation in toxicity need to be further investigated to establish optimum standards.

Conclusion

The pure ZnO nanoparticles has successfully been synthesized by the Sol-gel and precipitation method. The various characterization of ZnO nanoparticles shows that the behavior of ZnO nanoparticles are independent of routes of synthesis and the optical property and crystal structure structure remains same in both the routes. There after Al-doped ZnO with various withconcentration of Al (0.3at. %, 0.5at. % & 0.7at. %) have been prepared. The Al-doped ZnO nanoparticlesshows a good optical property and a promising material material for optical devices. The PL spectra of C-doped ZnO nanoparticles shows it's a good photocatalytic material. Al-Cu double doped ZnO material XRD analysis confirms the presence of Al and Cu in the ZnO nanoparticles.

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