A Review on the Effect of Quantum Size Effect on Structural Properties of ZnO/ZnS Core/Shell Nanostructure

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Abstract

The growth mechanism of ZnO/ZnS core/shell nanostructures are explained in this review work. The effects at different growth parameters on the structural properties of these core/shell structure are reported. The change in the properties of ZnO/ZnS core/shell nanostructure with respect to the shell thickness and different types of solvents are studied and comparative analyses of their properties are carried out in this work. The type-II nature for the ZnO/ZnS core/shell nanostructures are identified by the previous workers. These new fascinating properties of ZnO/ZnS core/shell nanostructure can be applied for the development of optoelectronic devices.

Key words: Nanostructure, core/shell, Quantum size effect, structural properties.

Introduction

In the recent years semiconductor nanoparticles have attracted the attention of new researchers due to their distinctive physical and optical properties which are unlike from their bulk material. They have a vast area of application such as solar cell, light-emitting diode, optical wavelength, photo conductive devices, sensors and lasers [1,2]. Zinc oxide which is known to be famous II-VI semiconductor nanoparticles with a wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature [3] is a promising material for different application such as piezo electricity, optical transparency [4], optoelectronic devices[5], sensor[6], transparent conducting films[7], catalyst[8] and light-emittimg diode[9]. These nanoparticles can be synthesized by different methods such as hydrothermal method [10], solvothermal method[11], co-precipitation method[12] and sol-gel method[13].

Again ZnS is an important member in II-VI group semiconductor which has two structural forms, the zinc blende structure with a cubic form and the wurtzite structure structure with a hexagonal form. The band energy gap of cubic form of ZnS is 3.60 eV and that of hexagonal form is 3.80 eV[14]. It is found that ZnS is one of the important coating material and has potential application as electroluminescent devices[15], sensors and lasers[16].

The core/shell of ZnO/ZnS nanostructure can be prepared by chemical method and it was reported by the various worker. Most of the workers preferred the synthesis of this core/shell nanoparticles by using solution based wet chemical method at low temperature. Again the radius of the core and shell thickness can be varied by changing the gross parameter . Moreover, the ZnO/ZnS core/shell nanostructure generally formed in uniform manner. Again microwave-assisted solvo thermal (MAS) method can be also employed for the production of ZnO/ZnS core/shell nanoparticles. The structural properties of ZnO/ZnS core/shell nanoparticles confirmed the type-II nature of ZnO/ZnS core/shell system [17-19].

Synthesis of core/shell nanostructure

The ZnO nanoparticles were prepared by Azar Sadollahkhani et al. by using the co-precipitation method. Zinc acetate dehydrate ($ZnAC_2.2H_2O$) and sodium hydroxide (NaOH) were used in deionised water to form the transparent solution of Molarity 0.5 and 1M concentration respectively. They have covered the core ZnO nanoparticles with ZnS nanoparticles by using chemical method. The pH of the solution were maintained at 10 by using ammonium hydroxide (NH_4OH). The structural properties of this core/shell nanostructure were explained by the authors [20].

M. Sookhakian et al. explained a simple method for the synthesis of ZnO/ZnS core/shell nanostructures. They have also prepared the inverted type of ZnS/ZnO core/shell nanostructures. The Zinc acetate dehydrate ($ZnAC_2.2H_2O$) and ammonium hydroxide (NH_4OH) were used for the preparation of core ZnO nanoparticle and sodium sulphide (Na_2S) with zinc acetate dehydrate were used for the formation of shell. The reverse method was adopted for the preparation of inverted type of core/shell nanostructure [21].

The ZnO/ZnS core/shell nanostructures can be also synthesized by using Microwave-assisted Solvothermal (MAS) method. Zinc acetate dehydrate ($ZnAC_2.2H_2O$) and sodium hydroxide (NaOH) solution were used for the preparation of ZnO nanoparticles by Efracio Mamani Flores et al.. They have used polytetrafloroethene (PTFE) autoclave maintaining the temperature at 130°C for 40 minutes in a microwave-assisted oven. Again Zinc acetate dehydrate ($ZnAC_2.2H_2O$) and thiourea were used for decoration of the core ZnO by ZnS shell nanostructure [22].

Zinc sulphate heptahydrate ($ZnSO_4.7H_2O$), Urea (NH_2CONH_2), thiourea (NH_2CSNH_2) and sodium hydroxide (NaOH) were used by Gaurav Hitkari et al. for the growth of ZnO nanoparticles. They have prepared the aqueous solution of Zinc sulphate heptahydrate ($ZnSO_4.7H_2O$) and it was sonicated for 30 minutes in the ultrasonic cleaner. Then an aqueous solution was added to the zinc sluphate solution and the complete solution was stirred by the workers. The pH of the mixture solution was kept at 11 and the reaction mixture was refluxed for 1 hour for 80°C. The ZnS shell was allowed to grow on the core ZnO nanostructure and they have investigated the structural properties of these nanostructures [23].

Discussion:

There is always a lack of simple, fast and reliable synthesis method for the growth of ZnO/ZnS core/shell nanostructure. Considerable efforts have been made by the different workers for investigation of a good chemical method for the production of high quality ZnO/ZnS core/shell nanostructure. This review work explains a comparative study of various structural and optical properties of ZnO/ZnS core/shell nanostructure for potential application in device physics. These properties are found to be excellent and unique for the fabrication of opto-electronic devices. A. Sadollahkhani et al. observed the effect of change of concentration on the nanostructure with respect to their structural properties in their work. The different XRD planes of ZnO and ZnO/ZnS are shown in Fig.1.

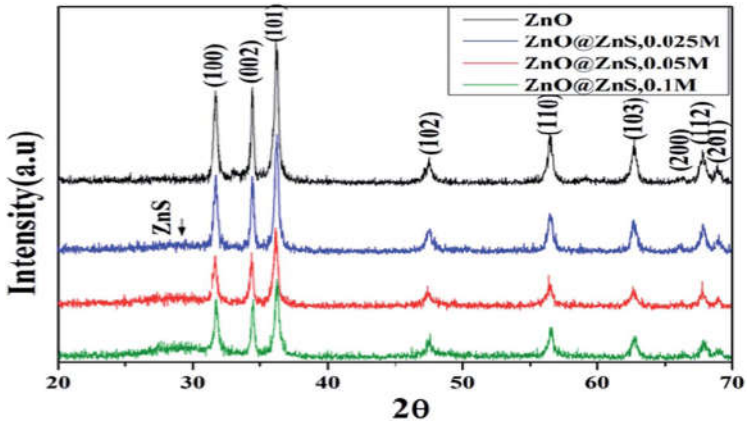

Fig. 1: XRD spectra of ZnO nanoparticle and ZnO/ZnS core/shell nanoparticles(Reproduce from Ref No.20)

The peak indexed for ZnO nanostructures are identified as the hexagonal structure of ZnO with lattice constants of a=b=3.254 Å and c=5.212 Å with an estimated standard deviation of 0.004 Å and 0.005 Å respectively (JCPDF:79-2205). They have calculated the grain size of ZnO nanoparticle by using Scherrer formula.

$$D = (K\lambda)/\beta\cos\theta \quad \text{---------- (1)}$$

Here D is the crystalline size, λ is the x-ray wavelength, θ is the Bragg's diffraction angle of the peak and β is the full- width at half maximum of the diffraction peak. The grain sizes of ZnO nanoparticles were calculated as 19nm by them.

The FESEM images of ZnO nanoparticles and ZnO/ZnS core/shell nanostructure are shown in Fig. 2. They have observed that these nanostructures were not in the spherical shape and agglomerism of ZnS capped ZnO nanoparticles were increased with increasing the concentration of the Sulphur source.

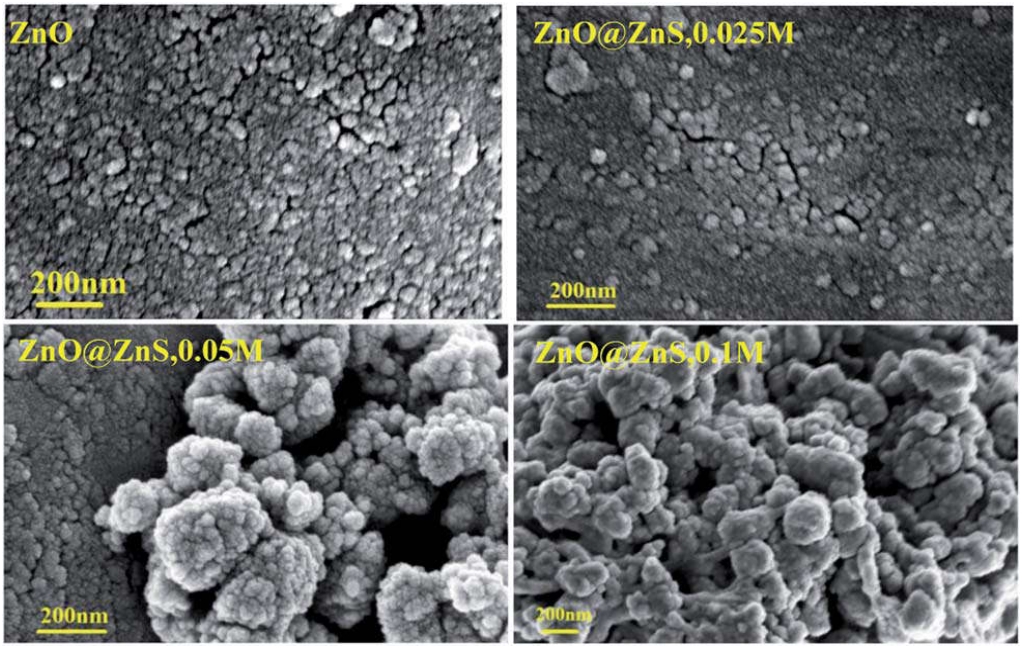

Fig. 2.FESEM images of ZnO NPs and ZnO@ZnS CSNPs (Reproduce from Ref No. 20)

They have confirmed the formation of ZnO/ZnS core/shell nanostructure by using HRTEM analysis. The BF-TEM images were taken and it was observed that the ZnO core is rather rough than the shell ZnS as shown in the Fig. 3(a) and 3(b) . They have also studied the SAED pattern of the above nanostructure and the images are shown in Fig. 4 [20].

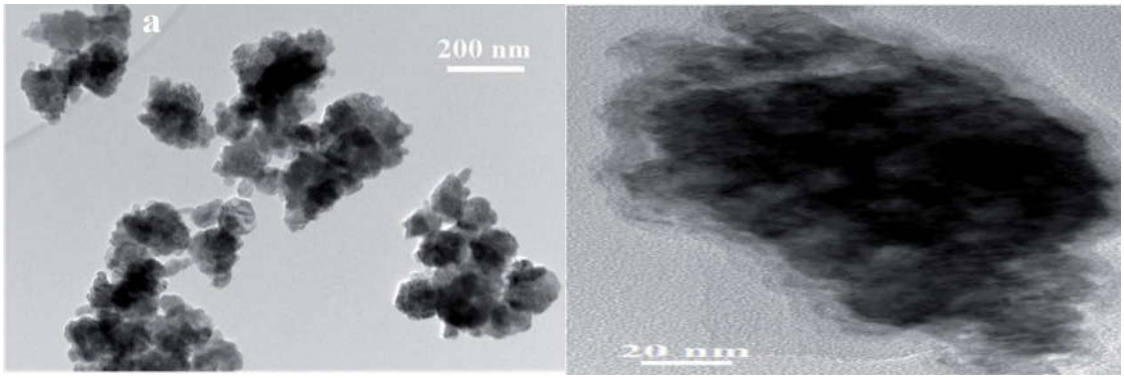

Fig. 3. (a) Bright field TEM image of pure ZnO nanoparticles . (b). Bright field TEM image of a ZnO/ZnS core/shell (Reproduce from Ref No. 20)

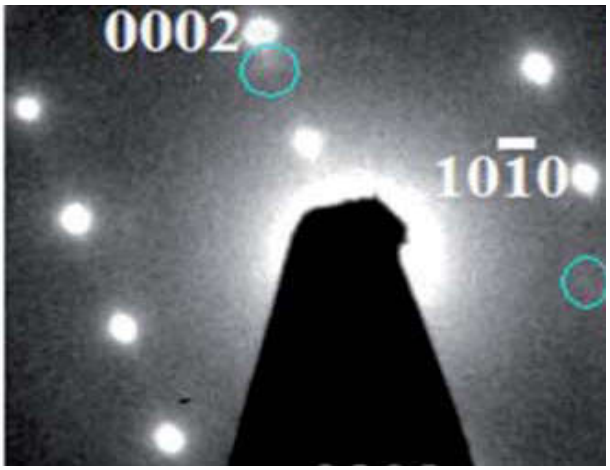

Fig. 4 SAED pattern (Reproduce from Ref No. 20)

M. Sookhakian et al. presented the XRD pattern of pure ZnS quantum dots and different types of ZnS/ZnO nanocomposite prepared at different mole fraction of sodium hydroxide (NaOH). Again they have also reported the XRD pattern of pure ZnO and ZnO/ZnS core/shell nanostructures with different concentration of Na_2S (0.01M,0.1M and 0.2M). Their XRD pattern are reproduced in the Fig.5 (a) and Fig.5 (b). They have observed that the crystallite size of ZnS quantum dots were decreased in presence of NaOH but the crystal structure remains the same. The reason for this effect was explained as the reaction of zinc acetate with sodium hydroxide in aqueous solution yield zinc hydroxide and it is a well known surfactant. Again the increase in the mole fraction of NaOH facilitate the growth of ZnO nanoparticle. If the pH of the solution is kept above 6 then both cubic ZnS and hexagonal ZnS were found to exist as ZnS/ZnO nanocomposite mixture. There were two sets of diffraction peaks in the XRD pattern ZnO/ZnS core/shell nanostructure as shown in the Fig.5(b). They have observed the hexagonal wurtzite ZnO nanostructure as well as the plane of cubic Zinc blende ZnS quantum dots. They have suggested that the intensity of diffraction peaks of ZnS(111) crystal plane was gradually increased with increasing the concentration of Na_2S. It is sign of steady growth of ZnS nanoparticle. The formation of ZnO/ZnS core/shell nanostructure were attributed to the overlap of the peaks of (102) and (110) planes of ZnO with a peak of (220),(311) planes of ZnS nanostructure. It was also observed that the inter planar spacing for the strongest peak intensity of pure wurtzite ZnO(d_{101}) and zinc blende ZnS(d_{111}) were considerably changed. They have also reported that the diffraction planes of ZnS nanostructure becomes more dominant with the increase in the concentration of Na_2S. The crystallite grain sizes of core ZnO and shell ZnS nanostructures were calculated by using Debye-Scherrer equation and the estimated sizes were estimated as 22.65nm and 6.95nm respectively .

5(a) 5(b)

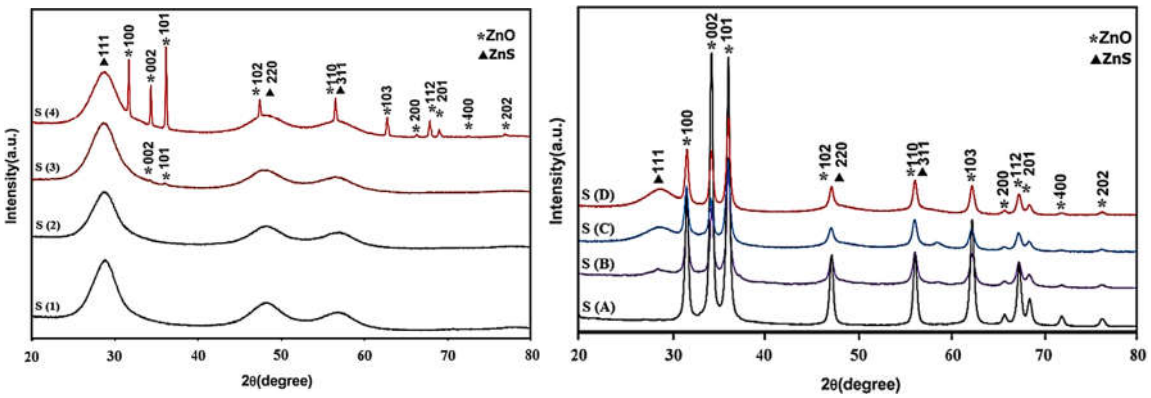

Fig. 5 (a)- XRD pattern of pure ZnS in the absence of NaOH and in the presence of different amounts of 0.5 M NaOH(20ml,30ml and 50ml) and (b)- XRD pattern of the pure ZnO and ZnO/ZnS core/shell nanostructures with different concentration of Na_2S(0.01M,0.1M and 0.2 M) (Reproduced from Ref No. 21)

The FESEM images of pure ZnS quantum dots without NaOH and pure ZnO nanostructure are shown in the Fig.6 (a) and 6(b). They have observed that both samples were agglomerated due to absence of capping agent.

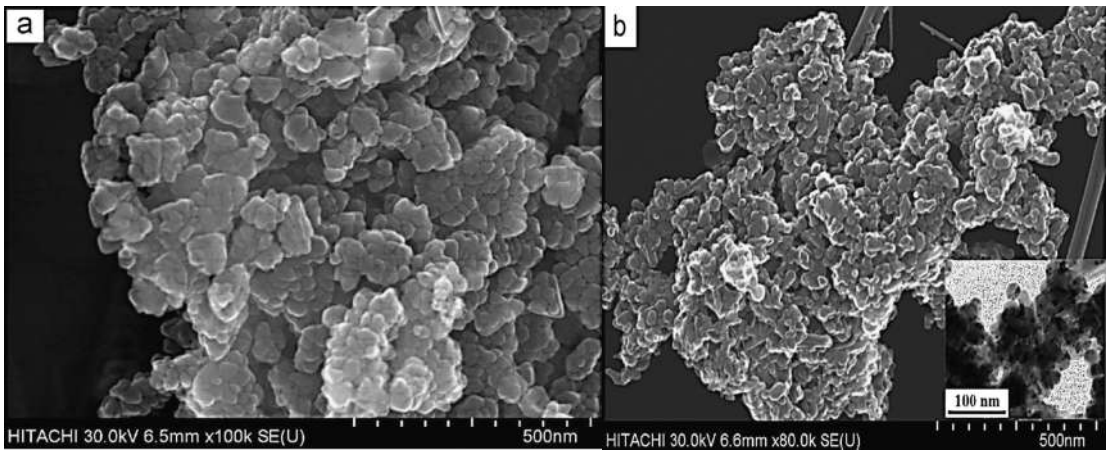

Fig. 6. FESEM images of (a) ZnS QDs and (b) ZnO nanoparticles (Reproduce from Ref No. 21)

The TEM images were obtained for these nanocomposite and they have found the hexagonal shape of the nanoparticles. To overcome the agglomeration effect they have used NaOH to obtain smaller and narrower particles size distribution and also to control the morphology of ZnS quantum dots in the final product. Therefore, they have presented the pure nanoparticles with and

without NaOH in their HRTEM images. They have suggested that NaOH as capping agent is able to separate the nanoparticles and it will prevent the agglomerism effect also. The HRTEM images of the nanostructure are shown in the Fig.7 (a), (b) and (c)[21].

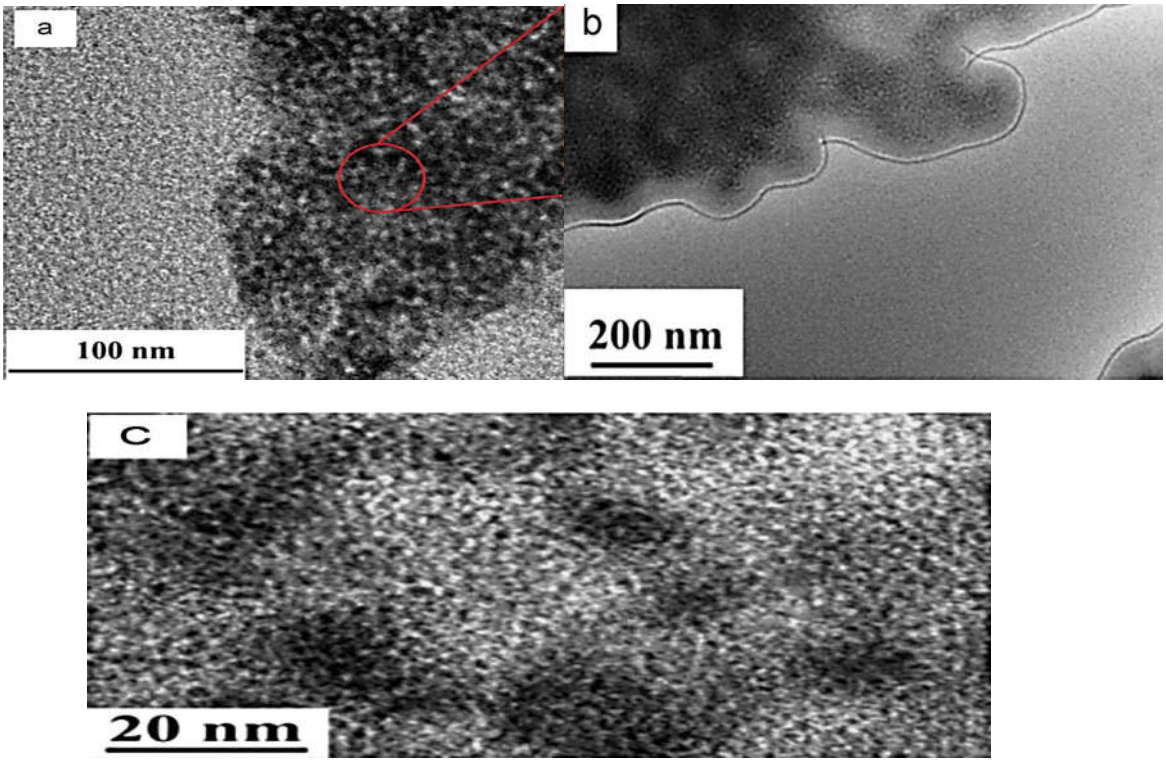

Fig. 7. TEM images of ZnS QDS (a) with the absence of NaOH, (b) and (c) with the presence of NaOH in different magnification (Reproduce from Ref No. 21)

The XRD spectra of the nanostructure ZnO and ZnO/ZnS core/shell are reproduced as reported by E. M. Flores et al. and shown in Fig.8. They have found that the diffraction peaks of ZnO(EG) has a lower intensity as compared to ZnO(H_20), indicating the degradation of crystalline structure of ZnO synthesized in EG. The Fig. 8(a) and Fig.8 (b) depicts the effect of solvent EG and H_2O on the structural properties of ZnO nanostructure.

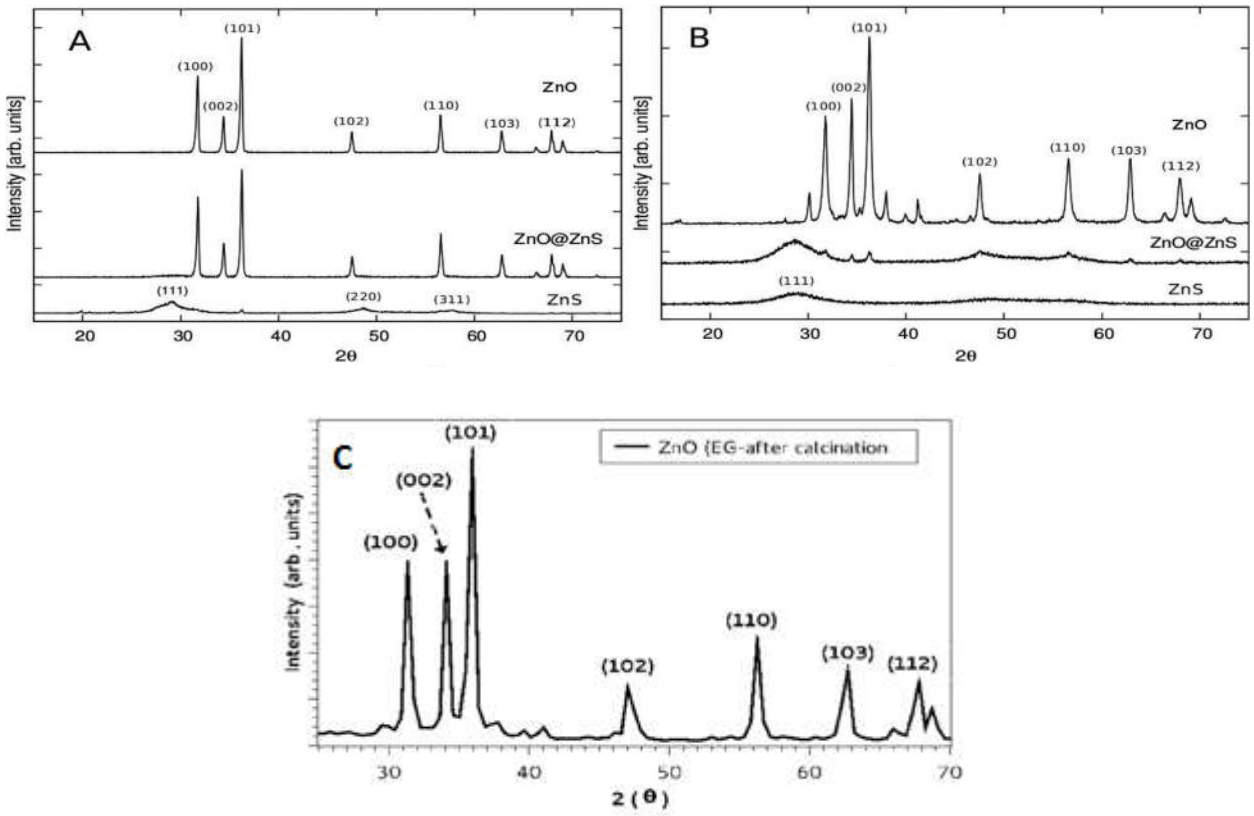

Fig. 8: XRD powder pattern of the ZnO and ZnO/ZnS core/shell synthesized in (a)shows the XRD of samples with solvent H_2O,(b) shows the XRD of samples with solvent EG,(c)XRD of ZnO (EG after calcination) (Reproduced from Ref No. 22)

The hexagonal crystalline structure of ZnO are observed for the nanostructure prepared in H_2O then in EG solvent. Therefore from the XRD spectra, they have suggested that the ZnO synthesized with solvent H_2O has better crystalline quality than the nanostructure prepared by using EG as a solvent. After calcination of EG from ZnO nanostructure, the XRD spectra obtained is presented in the Fig. 8(c). This all results demonstrate that the samples are strongly influenced by the solvent and the selection of the proper solvent is important in case of solvo thermal route.

They have investigated the morphology and the structure of prepared nanostructure by using FESEM and images are reproduced in Fig. 9 . The flower like structure were obtained for ZnO nanoparticles. They have also observed that ZnO multi wires present a smooth surface whereas ZnO (EG) were look like worm type mesoporous surface. Furthermore, the efficient images of ZnO/ZnS core/shell prepared in water and prepared in EG were clearly different and they have reported the effect of capping agent on the structural properties of this nanostructures [22].

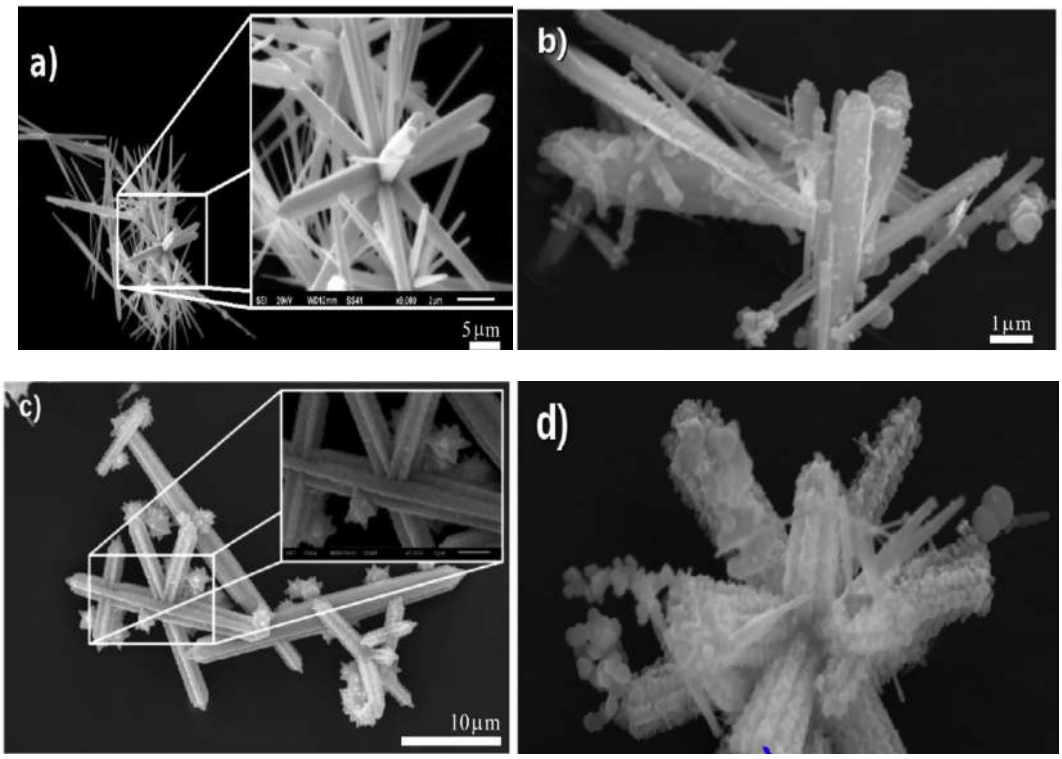

Fig. 9. FE-SEM images of crystals synthesized by MAS method a) ZnO H_2O b) ZnO/ZnS H_2O, c) ZnO-EG, d) ZnO/ZnS-EG (Reproduce from Ref No. 22)

The structural properties of ZnO and ZnO/ZnS core/shell nanostructure were reported by G. Hitkari et al. by using XRD diffraction pattern as shown in Fig. 10.

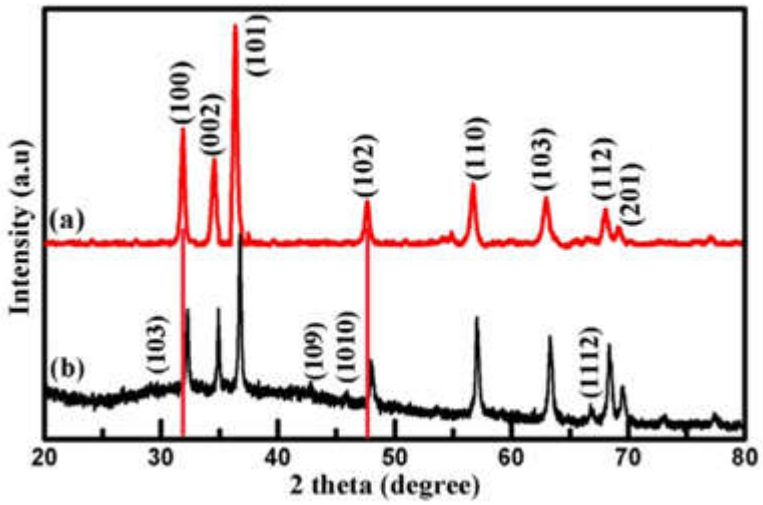

Fig. 10: XRD pattern of (a) ZnO nanoparticle, (b) ZnO/ZnS nanocomposite (Reproduce from Ref No. 23)

The sharp and intense peaks of the XRD pattern indicated the good crystalline nature of the prepared sample. They have identified the hexagonal wurtzite phase of ZnO corresponding to planes (100), (002), (101), (102), (110), (103), (112) and (201) respectively (JCPDS card no. 8000075, a = 3.253 and c = 5.209). They have also observe additional peaks apart from ZnO peaks at 2θ values 29.1°,42.59°,45.78° and 66.4° which are respectively (103), (109), (1010) and (1112) planes of ZnS hexagonal phase (JCPDS card no. 72-0163, a = 3.820, c =24.96). They have measured the lattice parameters of ZnO as a = b = 3.2454 Å and c = 5.6212 Å. They have calculated the average particle size by using Scherrer equation. The calculated average crystallite sizes of ZnO nanoparticles and ZnO/ZnS core/shell nanocomposite were 26nm and 25nm respectively.

The flake like structure of ZnO nanostructure and the sheet like structure of ZnO/ZnS core/shell nano composite were observed in FESEM analysis by the authors. The images are reproduced in Fig. 11

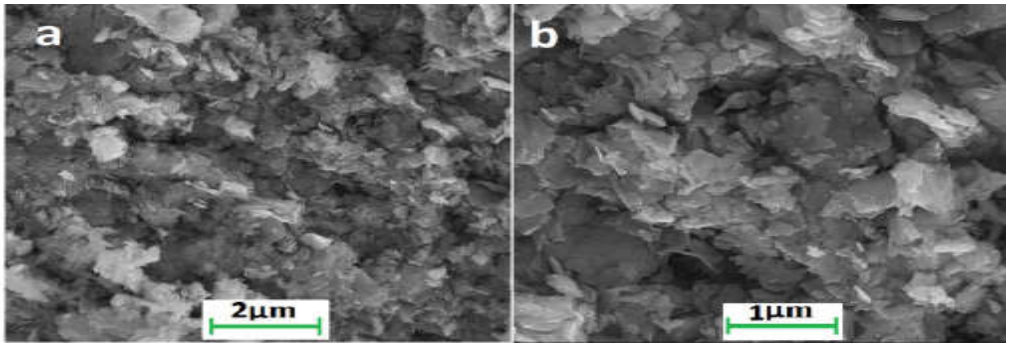

Fig. 11(a) and (b) FESEM images of ZnO(Reproduce from Ref No. 23)

Again they have employed HRTEM analysis for the morphological investigation of ZnO and ZnO/ZnS core/shell heterostructure . In the HRTEM analysis they have observed the flake like structure of the nanoparticles and ZnO nanostructure were observed as spherical in shape with a diameter of 9-16 nm. From the HRTEM images they have suggested that the small spherical ZnO particles were associated to form ZnO nanoflakes Fig.12(a), (b), (c). [23].

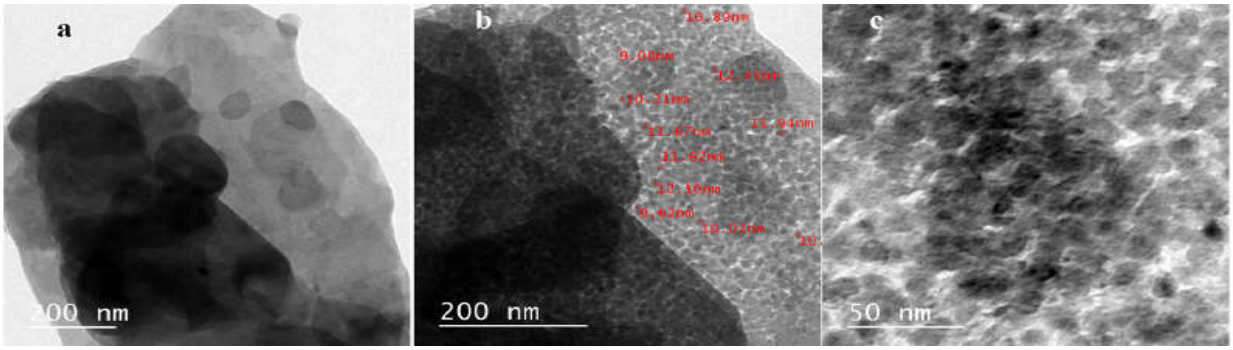

Fig. 12 (a),(b) and (c) HRTEM images (Reproduce from Ref No.23)

Conclusion

This review work clearly explains the effect of different capping agent and the growth parameter on the structural properties of the ZnO nanostructure as well as ZnO/ZnS core/shell nanostructure. Different types of synthesis method have been discussed for the preparation of ZnO/ZnS core/shell nanostructure . It was observed that in low temp chemical synthesis , the uniform growth of ZnO/ZnS core/shell nanostructure were observed . The Micro Assisted Solvo thermal (MAS) method was also reported as one of the cost effective and reliable method for the synthesis of ZnO/ZnS core/shell heterostructure. The structural properties like shape and size of the particles were also varied with respect to the capping agent. In most of the cases the formation of core/shell was confirmed by HRTEM images. Therefore, the growth mechanism has the ability to control the structural properties of the core/ shell nanaostructure . The optimum growth parameter should be identified for the growth of good quality ZnO/ZnS core/shell nanostructure.

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