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Investigation on the synthesis, structural and optical properties of ZnO nanorods prepared under CTAB assisted hydrothermal conditions

N.S. Nirmala Jothi, R. Gunaseelan and P. Sagayaraj*

Department of Physics, Loyola College, Chennai- 600 034, India

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ABSTRACT

A simple approach has been adopted to prepare ZnO nanorods with N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB) assisted hydrothermal route at 200 ˚C. The presence of CTAB favours the orientation growth of ZnO nanorods. The effect of reaction conditions on the morphology, crystallization and optical properties of the ZnO nanoparticles are investigated by using X-ray diffraction (XRD), UV-Vis absorption spectroscopy, photoluminescence (PL), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDAX) and transmission electron microscopy (TEM) techniques. Powder X-ray diffraction reveals the formation of phase pure ZnO particles with wurtzite structure. The optical absorption spectral study identified the blue shift of the sample in comparison to bulk ZnO. The room temperature PL spectrum confirms the strong UV emission around 330 nm and a weak visible emission at 485 nm. The TEM micrograph shows the presence of ZnO nanorods with diameter around 50 nm for the short ones and 80 nm for the long rods.

Keywords: Metal oxides; 1D nanostructure; Optical microscopy; Optical characterization; CTAB

INTRODUCTION

As a versatile semiconducting material, the nano structured zinc oxide (ZnO) has attracted intensive research for its applications in antireflection coatings, transparent electrodes in solar cells, chemical sensor, antibacterial agent, photocatalysis and photonic material [1-2]. It is identified as one of the most promising materials for short-wavelength light emitting devices and for a wide range of technological applications due to its wide band gap energy of 3.37 eV, high exciton binding energy (60 meV) and optical transparency [3]. Another added advantage of ZnO lies in its environment benignity, which is desirable especially for bio-medical applications [4].

The properties of zinc oxide are strongly dependent on its structure, including the morphology, aspect ratio, size, orientation and density of crystal and these structural characteristics play an important role in many applications. Therefore, development of a shape controlled zinc oxide synthesis method is indispensable for exploring the potential of this material as a smart and functional material [5]. In recent years, one dimensional (1D) nanostructures in the form of nanorods, nanowires or nano tubes, appear as an exciting research area for their great potential of addressing space-confined transport phenomena as well as applications in nanodevices [6]. Though many methods have been proposed to synthesize 1D ZnO structures, the high processing temperatures are unfavourable to make ZnO nanorods because of the problems with scale-up and high energy consumption and also the employment of catalysts or template introducing impurities into the desired products, thus, the preparation of ZnO nanorods with high purity and at low cost calls for a convenient, low temperature and tractable method [6]. In this regard, few research groups have successfully demonstrated the low cost synthesis of ZnO materials with 1D structure, using hydrothermal method [1,7,8]. However, the controlled organization of rod-like building blocks and the growth of nanorods in ordered aggregative structures are still challenging research topics [9]. Hence, inquiry into reaction conditions that affect the growth of 1D material will throw light on the growth mechanism of the 1D material [9].

In general, it is rather difficult to synthesize small sized zinc oxide with 1D morphology in aqueous or ethanol solution via a wet chemical method, because the growth speed is too fast for the precursor to control the crystal size. Some kinds of organic substances used as structure directing reagents, such as specific surfactants, organic molecules, catalysts, etc., are introduced into the reaction process in order to decrease the crystal size [10]. Among different capping agents employed to prepare ZnO nano particles, CTAB ($C_{19}H_{42}BrN$) has been identified as an excellent capping agent. The chain length of non-polar moiety in the CTAB surfactant is sufficient to form proper capping, resulting in the formation of nano sized ZnO [3]. The hydrothermal synthesis of ZnO nanoparticles carried out by Maiti et al confirmed that with optimised CTAB concentration, it will be possible to develop high optical quality one dimensional ZnO nano structure for UV nano laser application and for field emitter in emission display industry [11]. Jiaqiang et al [7] prepared ZnO nanorods by a hydrothermal process with CTAB and zinc powder. The gas sensing characteristics of ZnO nanorods were investigated and the results indicate that the ZnO nanorods show much better sensitivity and stability than the conventional materials [7].

Keeping in mind the importance attached to ZnO nanostructured materials, in this article, a systematic investigation has been carried out to synthesize ZnO nanorods by a simple and cost effective hydrothermal route. The nanorods were prepared under hydrothermal condition with the vision to obtain 1D ZnO nano rods of good crystalline quality with moderate aspect ratio. Surface modification of the nanoparticle has been carried out using ionic surfactant of CTAB. By careful optimization of experimental conditions, we have obtained ZnO nano rods of reduced diameter 50-80 nm and length up to 300-600 nm, which show improvement over the previously reported works. The structural, morphological and optical properties are investigated by powder XRD, TEM, SEM, EDAX, UV-visible absorption and photoluminescence spectroscopy.

MATERIALS AND METHODS

2.1. Materials

Zinc acetate (Zn $(CH_3COO)_2.4H_2O$) Merck) and potassium hydroxide (KOH, Merck) were used as the starting materials. All the chemicals were of high purity and no further purification was done. N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB) was used as the surfactant.

2.2. Synthesis of ZnO

In a typical synthesis, initially 4.938 g of $Zn(CH_3COO)_2.2H_2O$ was dissolved in 75 ml of Millipore water and stirred magnetically for about 1 h at room temperature. To this, 2 g of CTAB dissolved in 30 ml of Millipore water was added. The KOH solution was separately prepared by dissolving 15.149 g of KOH in 75 ml of Millipore water and then it was added to the above solution. The pH of the solution was maintained as 12. The stoichiometric ratio of $Zn(CH_3COO)_2.2H_2O$ and KOH was taken as 1:10. The prepared solution was transferred into a Teflon-line coated 200 ml capacity autoclave and then heated in an electrical oven at a constant temperature of 200 ºC for 8 h. The final product was taken and then dried at 80 ºC for 5 h after centrifugation.

2.3. Characterization Techniques

The powder XRD pattern for the as prepared ZnO nanopowder was recorded by a RICH SEIFER, X-ray diffractometer using monochromatic nickel filtered CuK_α (λ=1.5416 Å) radiation. Scanning electron microscope (SEM) was employed for morphological study using a JEOL JSM 6310 operated at 10 kV with Energy Dispersive X-ray analyser (EDAX). The optical absorption spectrum of the sample was taken in the range between 200-800 nm using double beam CARY 5E UV-Vis-NIR spectrophotometer. The photoluminescence study was done using a JOBIN YVON FLUROLOG-3-11 spectroflurometer with an excitation wavelength (λ_{ex}) of 300 nm. TEM images were recorded on a JEOL JEM 3010 with an accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

3.1. X-ray powder diffraction

Fig. 1 shows the X-ray diffraction pattern of the hydrothermally synthesized ZnO nanoparticles prepared with CTAB as capping reagent. The Bragg's peaks at (100), (002), (101), (102), (110) and (103) are conveniently indexed to the hexagonal ZnO phase (Wurtzite structure) by comparing the obtained values with the standard JCPDS (Card No. 80-0075) data. Further, the strong and narrow diffraction peaks reveal the high purity and good crystallinity of the obtained nanopowder. Under the hydrothermal conditions, the growth velocity of polar planes is faster than other planes to minimize surface energy. This fast anisotropic growth along (0 0 1) direction of the wurtzite structure leads to the formation of ZnO nanorods, which is confirmed by the XRD results. For the CTAB capped ZnO, it is to be noticed that the (1 0 1) diffraction peak is stronger and narrower than the other peaks, which indicates a preferential orientation along the *c*-axis [10]. Further, the result indicates that the product consists of pure phase ZnO and there are no traces of impurity reflection peaks.

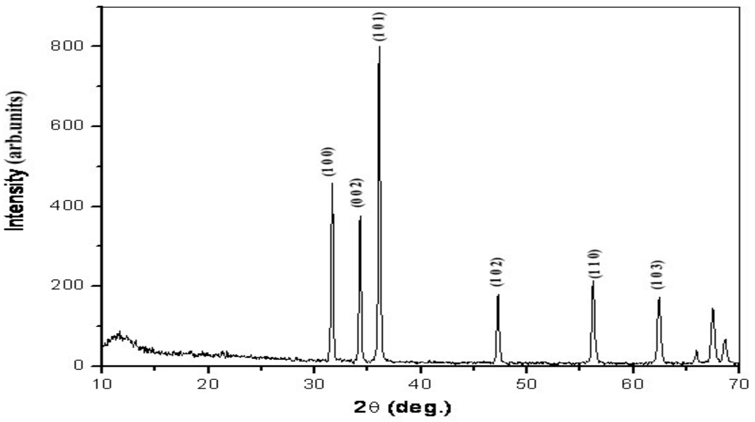

Fig. 1. X-ray diffraction pattern of CTAB capped ZnO nanoparticles

3.2. EDAX analysis

Fig. 2 shows a representative EDAX, the pattern indicates that the ZnO structures are composed of only Zn and O, since the quantitative analysis shows that the mean atomic ratio of Zn/O of ZnO structure is 45 % and 55 % respectively. No evidence of other impurities was found and ZnO structure is nearly stoichiometric. The data nearly confirms the high purity of the as prepared ZnO nanoparticles.

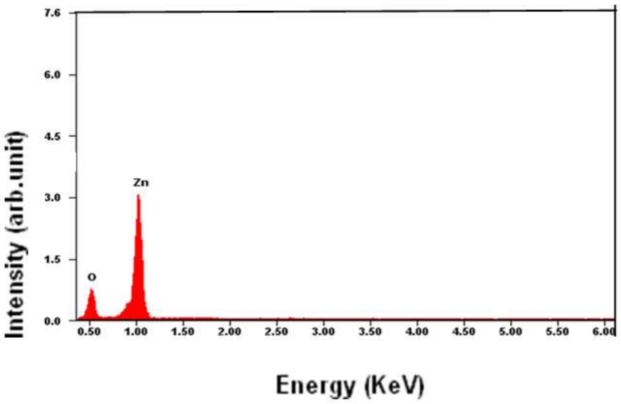

Fig. 2. EDAX pattern of ZnO nanoparticles

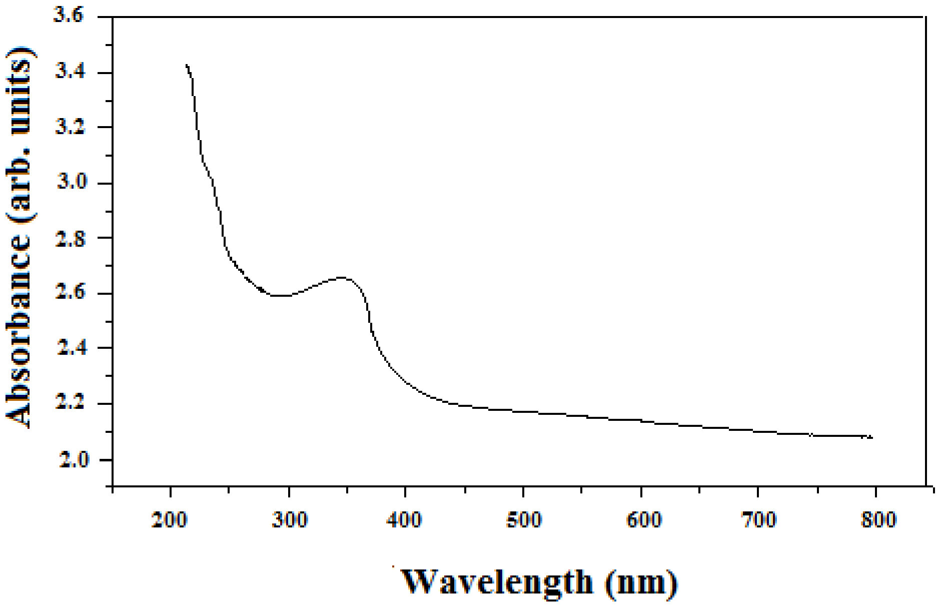

Fig. 3. UV-Vis spectrum of ZnO nanorods

3.3. UV-visible absorption spectrum

The optical studies are performed to evaluate the potentially useful optical qualities of the nanoparticles. The UV-Vis absorption spectrum of the ZnO nanocrystals prepared under hydrothermal conditions is shown in Fig. 3. A sharp absorption edge of 360 nm (3.44 eV) is observed in the sample. Thus, there is a significant blue shift in the excitonic absorption for the ZnO nanoparticles capped with CTAB surfactant when compared to the bulk exciton absorption of 373 nm (3.324 eV). The blue shift in the exciton absorption indicates the quantum confinement property of nanoparticles. Usually, for small size ZnO nanoparticles, the blue shift will be very large. However in the present case, the observed shift is only 13 nm. The reason could be attributed to the smaller Bohr radius of 2.23 nm for ZnO, which is not comparable to 1D ZnO nanostructure with much larger size. The size distribution may be another reason. For 1D nanostructures, the quantum confinement effect has to depend on the change of the width or diameter and is very different from the ZnO nanoparticles [10]. The sloppy absorption onset observed in the ZnO nanopowder further supports the typical characteristic of one dimensional semiconductor materials [12].

3.4. Photoluminescence (PL) study

The study of photoluminescence spectrum is an effective way for investigating the defect structures of ZnO nanoparticles. Fig. 4 shows the PL spectrum of the sample with two emission bands; one centred around 330 nm and the other one at 485 nm. The UV emission peak observed at 330 nm is strong as well as sharp, this strong UV luminescence is an indicator of the good quality of the ZnO nanoparticles. The UV emission of the sample can be attributed to the near band-edge emission, coming from radioactive recombination of electrons in the conduction band and holes in the valance band [13]. The broad photoluminescence band of the ZnO nanorods observed at 485 nm presents an interesting case. Several research groups have identified this weak broad emission in and around 530 nm [12]. The mechanism of this visible emission has been explained in terms of defect levels associated with oxygen vacancies or zinc interstices [12,14]. The role of surfactants in modifying the visible emission has been discussed by Guo et al and Singla et al with specific reference to PVP capped ZnO nanoparticles. The surfactant on the surface of ZnO plays a dual role; firstly, it helps to form defect free nanocrystal during nucleation and secondly it attaches to the surface of nanoparicle so as to keep the particle size minimum. Thus, in the present case, the capping of ZnO by CTAB has resulted in the reduction of surface trap state and therefore, the obtained ZnO nanorods, have weaker green emission and correspondingly stronger UV emission. However, Maiti et al have mentioned about the absence of the green band emission in the ZnO nanoparticles prepared with CTAB assisted hydrothermal synthesis procedure and attributed it to the presence of strong oxidization agent (ammonium peroxodisulfate) used by them [11]. But in our case, only KOH was added and no oxidizing agent was employed. Further, the observed 2.2:1 ratio of the UV emission to visible emission in PL spectra indicates the moderate size range of the ZnO nanorods formed with CTAB capping [10].

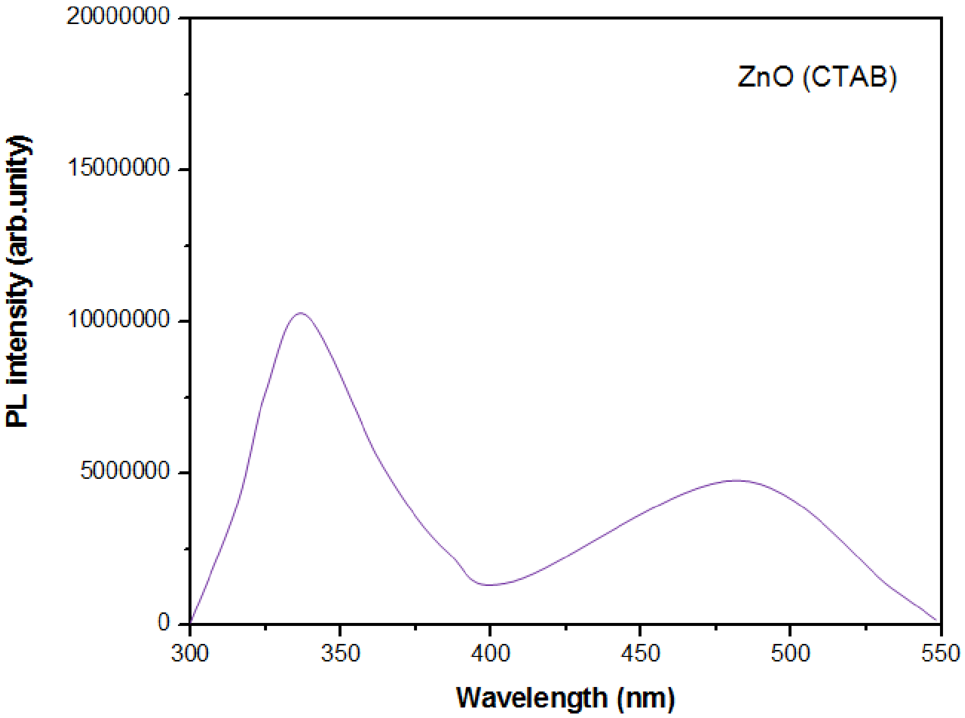

Fig. 4. Photoluminescence spectrum of ZnO nanorods

3.5. Scanning electron microscopy (SEM) analysis

As the surface to volume ratio is the dominant factor in nanostructured materials, probing the material's surface features is the prerequisite for many important applications. The surface morphology of the as prepared sample was examined by SEM. Fig. 5 shows the SEM micrograph of ZnO nanoparticles prepared with CTAB, under hydrothermal condition. The image indicates the presence of predominantly rod-like structure having diameter 1-2 μm with the length in the range of 8-10 μm. It is evident that these rods are united by the clusters. There is also a visible number of secondary structures grown on the surface of ZnO products and these would also be a potential contributor for all the blue shift emission in the UV spectrum, a result confirmed already in our UV absorption spectrum. There are literature evidences to prove that in ZnO nanostructure, the capping agents like PVP, PEG and CTAB have marked influence in modifying the morphology of the nanocrystals; especially its influence is strongly felt in the 1D nanostructure formation [5,11,15,16].

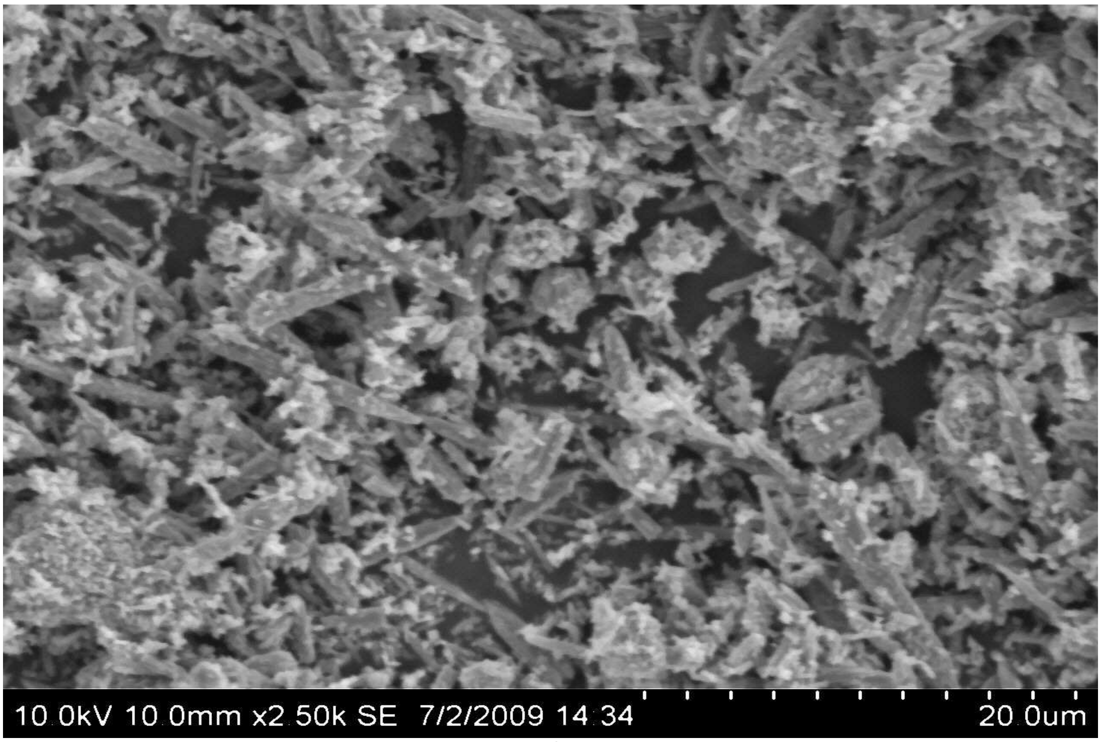

Fig. 5. SEM image of ZnO nanoparticles

3.6. Transmission electron microscopy (TEM)

The transmission electron microscopic (TEM) analysis allows one to visualize particles at nanosize regime with high degree of accuracy and to analyze the actual size of the particles, shape and growth pattern. The study of the shape evolution process of hexagonal ZnO phase (Wurtzite structure) nanocrystals is an interesting case. Fig. 6 a,b shows that the as prepared nanopowder predominantly exhibits rod-like structure with equal proportion of long nanorods as well as short nanorods for the ZnO nanocrystals grown by CTAB assisted hydrothermal method at 200 °C. There are short nanorods with diameter close to 50 nm and length ~ 300 nm (Fig. 6b) with aspect ratio of 6 and the long rods have their average diameter around 80 nm and length exceeding 600 nm with an aspect ratio of 8. A comparison of the size of the ZnO nanorods synthesized via CTAB assisted hydrothermal method by different workers indicates that the nanorods synthesized in the present investigation have reduced diameter and moderate aspect ratio and thus confirming the improvement in both size and quality of the nanocrystals than the previously reported work. Maiti et al have reported the formation of ZnO nanorods of diameter 100 nm under appropriate experimental conditions and similarly, Sun et al have obtained nanorods of diameter close to 70 nm with CTAB assisted hydrothermal method [1,11] . These one dimensional rods are hexagonal in cross section which is due to the typical crystal habit and growth form of hexagonal wurtzite phase of ZnO. When the cationic surfactant CTAB is used in the growth solution it ionizes completely in the solution as CTAB becomes $CTA^+ + B^-$. The resulted cation is a positively tetrahedral with a lone hydrophobic tail which electrostatically attach with $Zn(OH)_4^{2-}$. Furthermore, surfactant CTAB may also cap the ZnO nanorods to inhibit the lateral growth [1]. One of the major challenges in the preparation of ZnO nanostructure is the development of nanorods of reduced diameter as they have very low defect and can be directly used for UV nano laser application, field emitter in emission display industry and in gas sensing [3,7].

The TEM micrographs indicate that the ZnO nanorods do not show any branching and the crystal boundaries of the rods are well defined. It further reveals that the ZnO nanorods appear with either tapered or conical ends. The nanorods mostly appear as distinct rods without bending and agglomeration is minimised to a larger extent, which implies that the ZnO nanorods were grown from spontaneous nucleation with high crystal perfection [17]. For the growth process of the rod-like structure, the role of the precursor and the surfactants must be taken into account. Thus our result demonstrate that the ionic surfactant CTAB and KOH play important role in controlling the ZnO rod-like morphology. CTAB is capable of increasing the reaction rate between zinc and water to about 8 fold higher, favouring higher crystallinity of the products [1]. We believe that the appropriate concentration of CTAB, the ratio of the source materials and reaction temperature chosen in the present synthesis procedure encouraged the formation of ZnO nanorods of reduced diameter.

The insert of Fig. 6b shows the SAED pattern of the ZnO nanorods. The SAED pattern confirms that the ZnO nanorods are single crystalline and the preferential growth direction is along the *c*-axis of the crystal lattice. The pattern can be indexed as the hexagonal ZnO phase, and we do not witness any splitting of the diffraction spots.

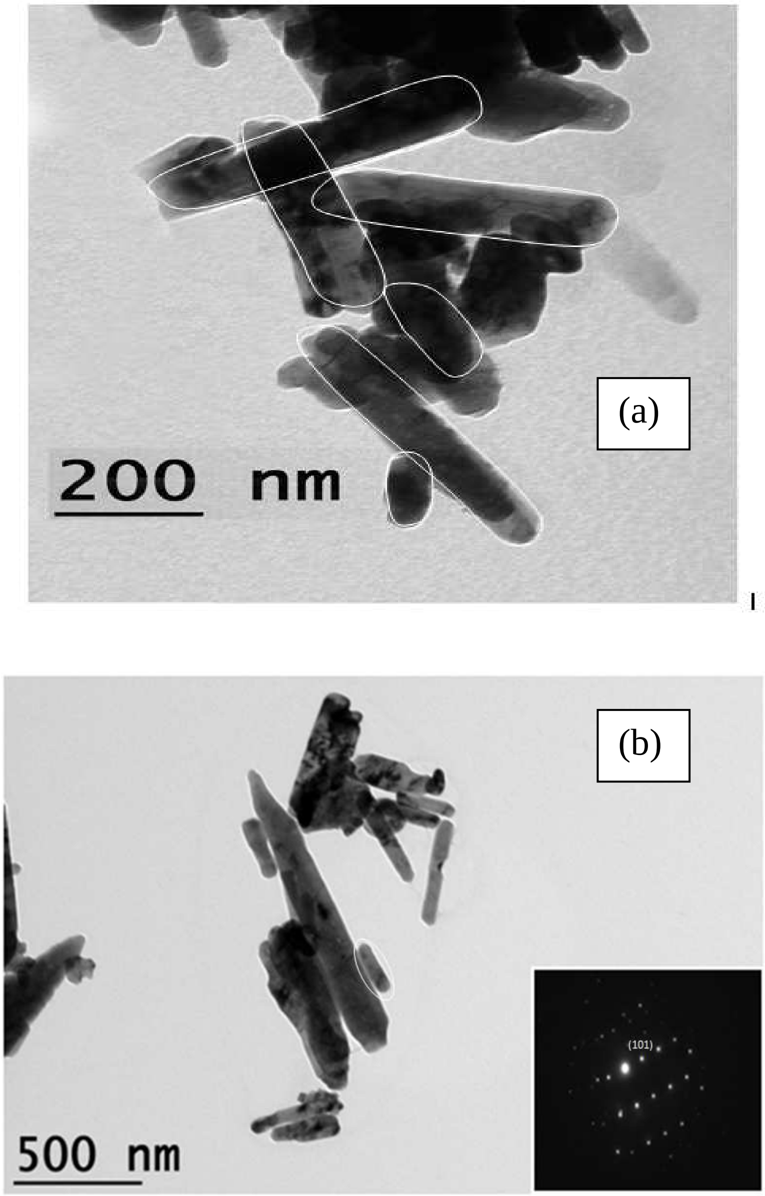

Fig.6. TEM image of CTAB capped ZnO nanorods (a) formation of short and long nanorods of ZnO with diameter ranging from 50 to 80 nm. (b) ZnO nanorods seen with tapered and conical ends with low level of agglomeration (insert of Fig. shows the hexagonal structure of SAED pattern)

CONCLUSION

In summary, ZnO nanorods are synthesised by a cost effective hydrothermal route. The powder XRD pattern and EDAX analysis confirmed the structure, purity and composition of the obtained product. For the CTAB capped ZnO, the (1 0 1) diffraction peak is found stronger and narrower than the other peaks, which indicated a preferential orientation along the *c*-axis. The optical absorption spectrum shows a sharp absorption edge at 360 nm and a significant blue shift in the excitonic absorption for the ZnO nanoparticles. The PL study reveals that the capping of ZnO by CTAB has resulted in the reduction of surface trap state and therefore, the ZnO nanopowder has weaker green emission and correspondingly stronger UV emission. The morphology of the aggregates is identified from SEM analysis. The SEM image indicates the presence of predominantly rod-like structure having diameter 1-2 μm with the length in the range of 8-10 μm. TEM observation revealed the formation of ZnO nanorods of reduced diameter and reasonable aspect ratio with CTAB assisted hydrothermal procedure. This method authenticates the idea of using CTAB to direct the favourable growth of 1D nanomaterials. The hydrothermal route employed in our case is cost effective and free of pollution and therefore, the technique can be extended to prepare many other important semiconducting metal oxide nanorods.

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