

A convenient route to synthesize hexagonal pillar shaped ZnO nanoneedles via CTAB surfactant

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ABSTRACT

In this work we report the successful formation of hexagonal pillar shaped ZnO nanoneedles with high yield and by using simple cheap method with CTAB as the surfactant. SEM and TEM microscopic observation revealed that the ZnO nanorods were smooth and uniform throughout their length and the functional groups in the molecule were identified by FTIR analysis. PL properties of ZnO nanorods were found to be dependent on the growth condition and the resultant morphology revealed that ZnO nanorods were highly transparent in the visible region. . Copyright © 2013 VBRI press.

Keywords: Characterization; nanostructures; X-ray diffraction; surface structure; hydrothermal crystal growth; oxides; nanoneedles; photoluminescence; inorganic compounds.



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Introduction

Zinc oxide (ZnO) is a well known semiconductor for its wide band gap (3.37 eV) and high excitation binding energy of 60 meV at room temperature. It possesses unique optical, acoustical and electronic properties which initiates wide interest in the scientific arena [1-4]. Recently optical wave confining and lagging action has been demonstrated in ZnS and ZnO nanorods [5-11]. A theoretical predication of the possibility of room temperature ferromagnetism has also stimulated research interest in the field of diluted magnetic semiconductors (DMSc). It is possible to create nanorods and nanoneedles which are ferromagnetic at room temperature and if it becomes possible to increase their magnetization by several orders of magnitude and if it becomes possible to either flip to direction of magnetization by external field, then ZnO nanoneedles may be used as nanosized read/write heads for magnetic data storage. As a result, searching a new methodology to synthesize aligned ZnO nanoneedles structure is of great importance for fundamental study and practical applications. As a consequence it possess unique optical, acoustical and electronic properties which stimulates wide range interest in its potential applications. A particularly striking recent observation is that of room temperature lasing action in ZnO nanorod arrays highlighting the prospects that the functional design of ZnO nanostructure in a highly oriented and an ordered array is of crucial importance for the development of device in practical applications with high performance [12-18] Up to now

various methods [19-27] were utilized to fabricate ZnO nanorods. Among these methods the hydrothermal method is environmental friendly with large area deposition, low synthesis temperature and low production cost. Zinc oxide particles of various morphologies including nanorods, whiskers and nanowires were successfully prepared [28-33]. The ZnO nanoparticles reported were synthesized at higher temperature with sophisticated instruments, expensive chemicals and complex reaction procedures. This article presents the fabrication of hexagonal pillar shaped ZnO nanoneedles via CTAB as a cationic surfactant. The synthesized products are highly crystalline and exhibits good structural and chemical properties providing a cost effective and a convenient route to obtain large quantities of Zinc oxide nanostructures. However, growth technique usually expensive, the choice of substrate restricted, complex process control and high temperature are unfavourable for an industrialized process. Hence we have used CTAB surfactant to overcome these limitations. There are advantages to use this surfactant i.e. the ordered ZnO nanoneedles are synthesized by controlling the density of the nanoparticles distribution which promotes the growth arrangement in a cheaper way to get similar structure of other ZnO compounds. Taking all these factors into consideration the process of study has been focused and the investigation of the relationship between wet chemical conditions size and morphology of the high aspect ratio products. The main objective of the present work is to synthesize wurtzite ZnO nanoneedles, because the lack of centre of symmetry in wurtzite results in strong piezoelectric and pyroelectric properties which is a key property in building electromechanical coupled sensors and transducers. The crystalline structure and surface morphology of ZnO nanoneedles were assessed by X-ray powder diffraction (XRPD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) analyses. The optical performances of the ZnO nanoneedles were characterized by photoluminescence (PL) studies. The functional groups in ZnO nanostructure was ascertained by Fourier transform infrared spectroscopy (FTIR) analysis.

Experimental

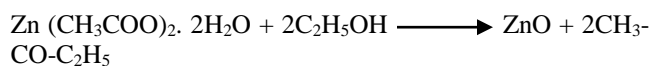
Materials and methods

All chemicals were analytical grade (AR) and used as purchased without further purification. Zinc Acetate $[\text{Zn}(\text{Ac})]_2 \cdot 2\text{H}_2\text{O}$ (Zinc source), cetyltriethylammonium bromide (CTAB) and ethanol were purchased from E-Merck Company (99.99%). The crystalline phase and orientation of products were identified using X-ray powder diffraction (XRPD) technique using a Riga KuD/max - RB diffractometer with $\text{CuK}\alpha$ radiation $\lambda = 1.54056 \text{ \AA}$ under 40 Kv, 40 mA and scan rate of $10^\circ \text{ min}^{-1}$. The functional groups in ZnO nanoneedles were graphed by Fourier transform infrared spectroscopy (FTIR). The spectrum was recorded with a (Bruker IFS - 66V) spectrometer. Photoluminescence (PL) measurements of the as synthesized product were carried out an F-4500 KIMON Fluorescence spectrophotometer at room temperature with a Xe lamp as the excited light source the excitation wavelength was 397 nm. The morphology and microstructure were examined using scanning electron

microscopy (SEM) performed on a (JSM - 6700F) with an acceleration voltage of 16.0 kV and a high resolution transmission electron microscope (TEM), (Philips CM12).

Experimental details

In a typical synthesis, 150 ml of 1M Zinc acetate aqueous solution was mixed with 25 ml of 1M ethanol and the resulting mixture was stirred thoroughly using a magnetic stirrer. The precursor of white precipitate was obtained. The as-obtained white precipitate was collected and washed with deionised water twice. Nearly 2.5 g of precursor was added to 50 ml of 0.5 M concentration of CTAB solution, to get a precipitated liquid. Then the above solution was transferred to Teflon lined autoclave at 240° C in an oven for 24 hrs. After 24 hrs white crystalline product was collected and thoroughly washed with ethanol twice. Supported by the above analyses the whole reaction process may be represented by the following equation. Thus the Zinc acetate ion was transferred to zinc oxide when CTAB was introduced into the solution, Thus CTAB acts as the dissolution of the formed Zinc oxide. Based on the above equation under present wet chemical condition, then this reaction would gradually condense into solid phase ZnO and seeds (nanoneedles) which appeared in the heating solution through a homogeneous nucleation. The nanoneedles grew longer and shaped into separate nanoneedles. Hence CTAB may be more suitable for the formation of long and uniform ZnO nanoneedles due to its chain like structure. We also came to know that the length of CTAB had little influence only on the shape of the products. The reaction process is



Results and discussion

X-ray powder diffraction analysis

Fig. 1 shows the XRPD pattern of the ZnO nano samples. The diffraction peaks are in good agreement with a typical wurtzite type ZnO crystal (hexagonal, $\text{P6}_3\text{mc}$, JCPDS No. 36-1451) and no impurity phase was detected. The sharpness of the peaks reveals a high degree of crystallinity of the as-synthesized ZnO samples. No peaks from either ZnO in other phases or impurities were observed. It is well noted that the (101) diffraction peak dominates the spectra of all the ZnO nanoneedles synthesized in this study and other diffraction peaks are normal, ascertaining that the well aligned (101) oriented ZnO nanoneedles were harvested which is in good consistent with the SEM micrograph, and also the highest peak assigned to (1011) plane indicating wurtzite structure [34].

FTIR spectroscopy

Fig. 2 shows the FTIR spectra of the as synthesized ZnO nanoneedles in the wavelength range of $4000 - 400 \text{ cm}^{-1}$. A peak at 3419 cm^{-1} is attributed to O-H group. The peak at 1725 cm^{-1} is assigned to asymmetric COO- stretching vibration modes of acetate group. The band appearing at 1371 cm^{-1} is attributed to the symmetric COO- stretching vibration mode of acetate group. The peak at 817 cm^{-1} is

binding of R-CH₂OH. The characteristic peak of Zn-O bond is observed at 488 cm⁻¹ [35]. Thus IR studies indicate that ZnO peaks were formed due to the direct decomposition of Zinc acetate.

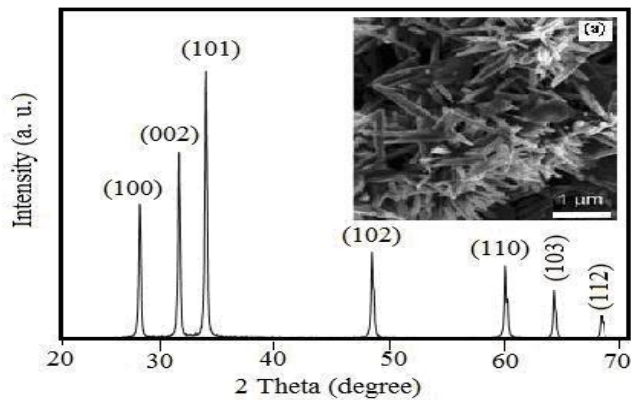


Fig. 1. XRPD pattern of ZnO nanoneedles.

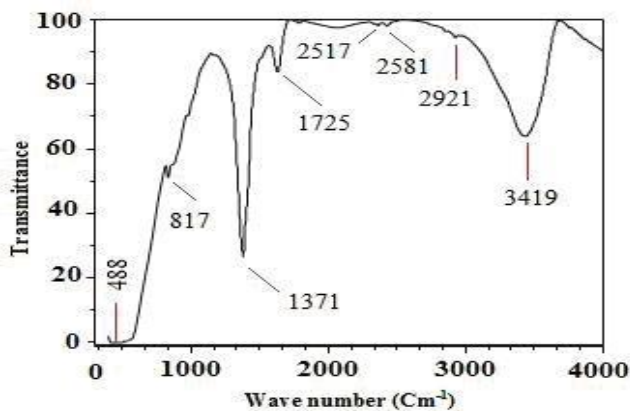


Fig. 2. FTIR spectrum of ZnO nanoneedles.

Scanning electron microscope

Fig. 3 (a-c) depicts SEM images of as synthesized ZnO nanoneedles with different magnification respectively. From the images it is clear that the smooth solid hexagonal rods were observed. Hence it can be said that the product from solvothermal synthesis in ethanol was ZnO nanoneedles and it is invariably longer due to the presence of ethanol [36].

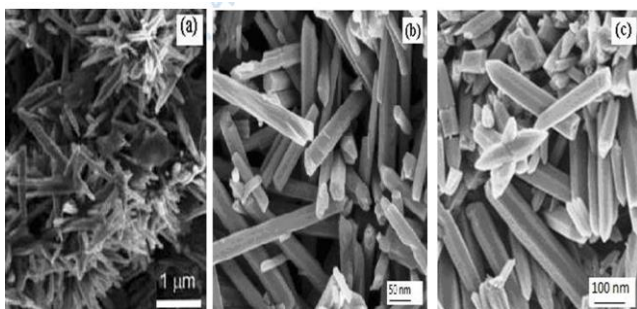


Fig. 3. SEM photographs of ZnO nanoneedles.

Transmission electron microscope

Fig. 4 shows the TEM image of as synthesized ZnO nanoneedles. As seen from the figure, it is clear that only

the polygranules are visible and these granules congregate. A special granule indicated by a circle shows the general uniform is hexagonal. The particles are nearly spherical and remains assembled together with the long grain and the adjacent particle coalesces together forming spherical particles [37]. Thus the result is consistent with the SEM micrographs and XRPD studies.

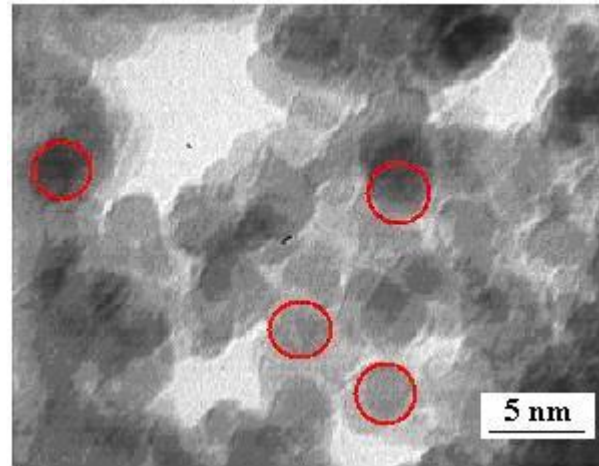


Fig. 4. TEM photograph of ZnO nanoneedles.

Photoluminescence spectroscopy

Fig. 5 shows the PL spectrum of the as synthesized ZnO nanoneedles. The spectrum has wide broader peak ranging from 390 to 400 nm and a sharp one centered on at 397 nm which is in tune with Wang, Peng and Wu et al [38-40]. The blue luminescence may be considered to be result of radioactive recombination of photo generated holes within singularly ionized oxygen vacancies. In our case, no green light emission peak was found implying ZnO nanoneedles has very low concentration of oxygen vacancies. In our study, based on calculation, the energy (3.07 eV) of the UV emission peaked at 397 nm is well consistent with the energy interval from the bottom of the conduction band to V_{zn} level (3.06 eV) [41]. Hence it may be well said that the UV emission of needle like ZnO nanostructure in our work is due to zinc vacancy.

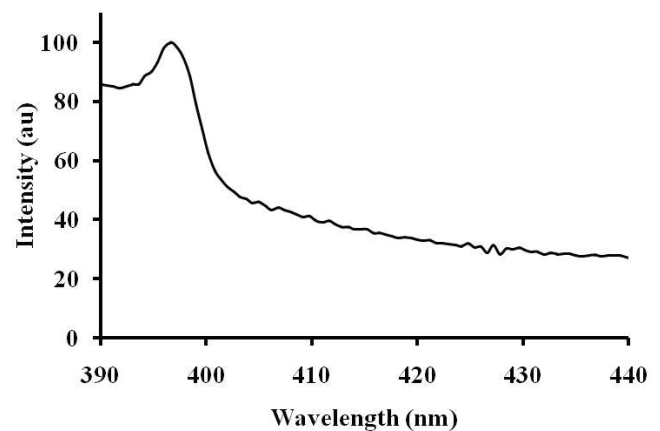


Fig. 5. PL spectrum of ZnO Nanoneedles

Conclusion

In summary, we have developed, a simple and a cost effective method to synthesize hexagonal pillar shaped

nanorods under the assistance of CTAB surfactant. As identified by XRPD analysis, the ZnO nanoneedles are single crystalline free from defects possessing wurtzite hexagonal phase. Additionally FTIR spectrum also shows good chemical properties of zinc oxide. The proposed work is supportive based an SEM and TEM observation. The PL studies reveal a sharp UV emission peak central at 397 nm at room temperature. We firmly believe that hexagonal ZnO nanorods will pave a way for the development of nanoscale electronics, flexible solar cells, gas sensing applications and optics.

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