EFFECT OF ALKALINITY ON STRUCTURAL AND OPTICAL PROPERTY OF ZnO NANOSTRUCTURE

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ABSTRACT

Here we present the effect of alkalinity on the structural and optical properties of ZnO nanostructures. These nanostructres are synthesized by a wet chemical co-precipitation route using bases having different alkalinities. The structural and optical properties of the ZnO nanomaterials were chracterized through X-ray diffraction (XRD) technique and UV-Vis Spectroscopy. Nanostructures with good crystallinity and high purity were obtained through this green and cost effective synthetic route. UV-visible optical absorption spectrum of the as obtained ZnO nanostructures showed a blue shift as compared the bulk spectrum. Variations in the precursor constitution caused a remarkable change in the size and shape of these nanostutures.

Keywords : Green synthesis,Nanostructure,UV-vis Spectrosopy, X-ray differaction, ZnO.

I. INTRODUCTION

In all semiconductor nanostructures, ZnO nanostructures have got much attention due to their unique optical, magnetic, chemical, mechanical and electrical properties [1]. ZnO nano structures are more capable to form different morphologies like nanodots, nanorods, nanowires, nanobelts, nanowells etc. It has wide band gap of 3.37eV at room temperature (RT) [2] with large exciton binding energy of 60meV [3] which makes them immensely suited for a wide range of electronic applications. There are various synthetic routes reported for well controlled growth of ZnO nanostructures [4-6]. The quality of ZnO nanostrures depend largely on the synthesis methodology.

In this work, we present the UV – vis optical absorption study of ZnO nanostructures which are prepared by a wet chemical co-precipitation route. It was observed that the morphology and size of ZnO nanostructures strongly depend on the precursor material. The wet chemical co-precipitation route is a low cost and energy efficient method over chemical vapour deposition and lithography method etc. We used PVA as a template in this process to synthesize the size and shape controlled nanostructures, as there are many reports for the synthesis of various nanostructure using polymer as surface modifiers [7-9]. The advantage of PVA is that there is no need to add toxic chemicals as surface modifiers and secondly PVA is easily removed during annealing and so the as synthesized samples need no further purification. It makes the method green for the environment. The performance of PVA templates varies according to the alkalinity of the precursors. Present study specifically analyzes the effect of various bases on the controlled growth of ZnO nanostructures. The crystal structure and optical properties of the as prepared samples were characterized by XRD and UV-Visible absorption spectrometry.

II. MATERIAL PREPARATION

All chemicals were analytical grade (Merck), and were used without further purification. ZnO nanostructures were synthesized through the hydrolysis of Zinc acetate dihydrate ($Zn(C_2H_3O_2)_2.2H_2O$) in presence of PVA with different bases e.g. Sodium hydroxide (NaOH), Lithium Oxide (LiOH) and NH_4OH. Briefly, 2.19 gm of Zn $(C_2H_3O_2)_2{\cdot}2H_2O$ (0.1 M) was dissolved in 100 ml of double distilled (DD) water. 50mg of PVA was separately dissolved in 10 ml DD water with a vigorous stirring at 60˚C using magnetic stirrer and was added drop vice to zinc acetate solution. 0.2 M solution of various base solutions was added in a similar way. A white precipitation was obtained, which was collected by filtration, rinsed with ethanol and DD water several times and finally dried in air at 80˚C. The annealing was done in a muffle furnace for evaporation of PVA matrix; at various temperatures between 300˚C - 800 ˚C for 1h under air ambient atmosphere. For studying the effect of variation in the base solution three samples were prepared; B_1 using NH_4OH , B_2 and B_3 using NaOH and LiOH respectively. The XRD patterns were obtained by using Bruker “D2 PHASER” diffractometer with Cu Kα radiation (λ= 1.5406Å), Optical absorption spectra were recorded by using Shimadzu Pharmespec-1700 Spectrophotometer over the wavelength range 200-500nm.

III. RESULT AND DISCUSSION

3.1 X-Ray diffraction

Fig.1 shows the XRD patterns of the as prepared ZnO nanostructures. Characteristic peaks of ZnO are observed as per the COD file no.9011662 in the XRD pattern . The sharpness of peaks shows good crystallinity of samples. The crystal plane (1 0 1), (0 0 1) and (0 0 2) indicate hexagonal crystal structure. The preferred orientation for the sample B_1 (Fig 1a) was (0 0 2) plane in the XRD pattern. However intensity of this peak was lower for the other samples B_2 and B_3. The particle size was the highest for B_1, which gradually decreased for B_2 and B_3. In the XRD study ,the highest intensity and lowest particle sizes were obtained for B_3, so it can be concluded that LiOH is the strongest base , which can be used to produce nanostructures with the smallest sizes. This can be attributed to the lower ionic radii and higher electro-negativity of Li^+ ions. The particle size of these nanostrucutres are calculated through the following Equation given by Scherrer:

$D = 0.89\lambda/(\beta \cos\theta)$.................................(1)

where, λ is the wavelength of Cu Kα and β is the full width at half maximum and θ is differaction angle. The particle size show an increase from 45nm to 40 nm in accordance with the decreasing FWHM of XRD peaks.

3.2 Reaction Mechanism

The Chemical reaction responsible to form ZnO when LiOH is used as precursor is as follows :

Zn $(C_2H_3O_2)_2$ + 2LiOH ----> ZnO + 2 $LiCH_3COO$ + H_2O.............(2)

The Chemical reaction responsible to form ZnO when NH_4OH is used as precursor is as follows :

Zn $(C_2H_3O_2)_2$ + 2 NH_4 OH ---> ZnO + $2CH_3COO$ + NH_4 +H_2O ....(3)

Further equation (3) show the chemical reaction which is responsible to form ZnO, when NaOH is used is as follows:

Zn $(C_2H_3O_2)_2$ + 2NaOH ----> ZnO + 2 $NaCH_3COO$ + H_2O.............(4)

Sodium acetate is water soluable and could be remove from the end product.

3.3 UV-visible absorption optical spectral studies

The UV-Visible absorption spectrum of various ZnO nanostructures is shown in Fig.2. The excitonic absorption for various samples appeared at 218nm, 205 nm and 200 nm for NH_4OH, NaOH and LiOH respectively. The ZnO nanostructures have a wide band gap leading to the UV absorption. This makes them suitable for many important technological applications. The absorption and emission in the visible region occurs in case of intrinsic or extrinsic defect levels present in the lattice. So, in present case, optical absorption observed purely in the UV region shows that the samples prepared are pure. Furthermore, the extended slope of the absorption spectra also shows impurity energy levels present in the band gap region. It can be observed that the steepness of the absorption spectra was highest for the sample B_3. The most intense direct band to band transition was observed for sample B_3, which can be attributed to the smallest particle sizes i.e. widest band gap obtained with the highest purity in this case. Results showed a blue shift in the spectrum as compared to the reported bulk values, which shows that the as obtained nanostructures were well within the quantum confinement regime.The details of UV- Visible absorption spectra were tabulated in Table 2. UV-Visible spectra shows peaks 218 nm, 205 nm, 200 nm.

IV. FIGURES AND TABLE

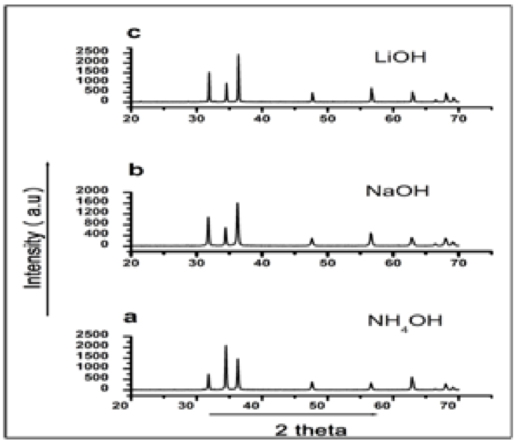

Fig.1 XRD pattern of ZnO nanostructures formed using various base (a) B_1 , (b) B_2 , (c) B_3.

Table 1: Effect of alkalinity of various bases on Structure

Sample	Base used	Particle size	Prefered plane	Intesity of XRD Peak (a.u)	Crystallinity(in %)
B1	NH_4OH	45.15 nm	0 0 2	2000	86
B2	NaOH	42.69nm	1 0 1	1600	77
B3	LiOH	40.55 nm	1 0 1	2400	83

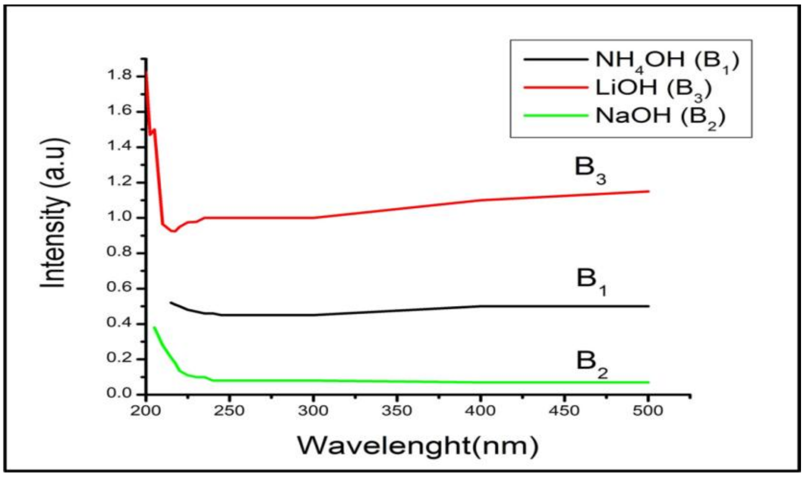

Fig. 2 UV-Visible absorption spectra of ZnO nanostructres prepared with (a) NH_4OH (b) Li(c) NaOH.

Table 2 : Effect of alkalinity on UV-VISIBLE spectra

Sample	Base used	Absorption peak (λ)
B1	NH_4OH	218nm (5.6eV)
B2	NaOH	205 nm (6.0eV)
B3	LiOH	200 nm (6.2 eV)

V. CONCLUSIONS

This study shows that the chemical composition and surrounding environment during preparation can be used to tune the structural and the optical properties of ZnO nanostructures. A controlled growth of ZnO nanostructures can be observed in the wet chemical route by simply varying the alkalinity of the precursors. Particles with better crystallinity and smaller sizes within the quantum confinement regime, and having good optical properties were obtained through this green and cost effective method. A blue shift in the UV-Visible spectra was observed, which indicated quantum confinement effect due to a smaller size of nanostructures obtained through this simple method.

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