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Growth and Characterization of ZnO Nanotetrapod for the Biosensor Application

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Abstract:
High chemical stability, low threshold intensity, wide band gap (3.37eV) and large excitation binding energy (60meV) make ZnO an excellent candidate for fabrication of electronic and optoelectronics devices which seek potential use in biomedical applications. While the applications of nanowires and straight nanorods are straightforward, more complex shapes are also of interest both for fundamental studies and practical applications [2]. ZnO nanotetrapods were obtained by carbo-thermal reduction of ZnO. The structure and phase present were verified by X-ray diffraction and X-ray photoelectron spectroscopy. The morphology and microstructure of the product were studied by scanning electron microscopy and study was extended for gas sensing.

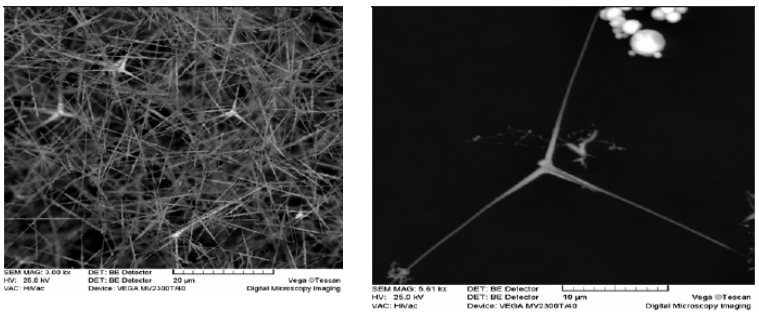
Keywords: Nanotetrapods, biosensor, nanobelts, scanning electron microscope (SEM).

INTRODUCTION

Zinc oxide (ZnO) has received considerable attention because of its unique optical, semiconducting, piezoelectric, and magnetic properties. ZnO nanostructures exhibit interesting properties including high catalytic efficiency and strong adsorption ability. Recently, the interest has been focused toward the application of ZnO in biosensing because of its high isoelectric point, biocompatibility, and fast electron transfer kinetics. Such features advocate the use of this exciting material as a biomimic membrane to immobilize and modify biomolecules. This review highlights the synthesis and potential use of ZnO nanotetrapod in modified electrodes and biosensing. The growth of ZnO nanowire arrays on a variety of substrates using a chemical wet process is presented. ZnO seeds can act as a nucleation layer for wire growth and ZnO nanowire, tetrapods etc. Arrays can have direct contact with a variety of substrates [1].

MATERIALS AND METHODS

Growth of ZnO tetrapods has been reported in literature [2] by oxidation of Zn powder, thermal evaporation of Zn powder, heating a mixture of ZnO and carbon materials or a mixture of zinc carbonate and graphite. A conventional horizontal tube furnace with gas supply system was used for the synthesis of ZnO tetrapods. Mixture of ZnO and graphite in 3:1 ratio (by weight) was used as a source material. It was loaded into a quartz boat and placed in the centre of 1 m long quartz tube. High purity gas was introduced through one side of the furnace and other side of the quartz tube was connected to a water bubbler. The flow was controlled with a rotameter. The material was heated to 1050°C under a constant flow of argon gas. On stabilizing the temperature, the gas atmosphere was switched to 95% argon and 5% oxygen at same flow rate. The furnace was maintained under these conditions for 5 hrs and then cooled to room temperature at a rate of 6ºC/min. White spongy, fluffy material was deposited all along the tube in gas flow direction. Surface morphology of the samples was studied using a scanning electron microscope (SEM, VEGA MV2300T/40, TS 5130 MM, TESCAN). Chemical composition of the nanotetrapods was confirmed by recording energy dispersive x-ray analysis spectrum (Oxford Instruments Inca Energy 250 System). The phases present and structure of nanotetrapods were identified by x-ray diffraction (XRD) carried out using Cu-Kα radiation. x-ray photoelectron spectra (XPS) were recorded using MgKα (1253.6 eV) source in XPS system (RIBER-CX700) comprising of a twin anode x-ray source and a MAC-2 electron analyzer. Powder of synthesized ZnO tetrapod is very loose and looks like white cotton. Tetrapod consists of four needle shaped tetrahedrally arranged legs connected in the center (Fig 1) [3]. Room temperature photoluminescence measurements were carried out with a spectrometer using a xenon arc lamp for excitation.



(a) (b)

Figure 1. SEM image of ZnO tetrapods in the combined form (a) one isolated ZnO Tetrapod (b)

RESULTS AND DISCUSSION

The sample is composed of hexagonal ZnO crystals with lattice parameters $a = b = 0.324$ nm and $c = 0.520$ nm. Recently Zhi-Gang Chen et al reported synthesis of tetrapod structures with less than 25% wt unoxidized metal Zn present in their samples [4]. In our samples no peaks of Zn or other impurities were detected in the spectrum indicating that the grown samples are pure ZnO.

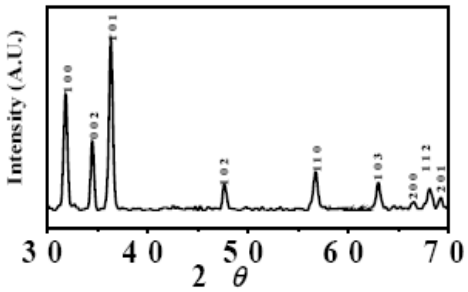


Figure 2. X-ray diffraction pattern of ZnO nanotetrapods.

UV-Visible absorption spectrum of ZnO nanotetrapods dispersed in ethanol solution was recorded (Fig. 2). It exhibits a strong absorption feature at ~ 371 nm ($E = 3.3$eV). Frequency dependence of absorption coefficient of semiconductors is given by:

$$\alpha(\nu)\, h\nu = A\,(h\nu - Eg)m/2$$

where, α is the absorption coefficient, ν is the frequency of photons, A is a proportionality constant and $m = 1$ for direct transitions.

Photoluminescence spectra of ZnO tetrapods were measured at room temperature using Xenon lamp as excitation source (Fig 3). We observed that the near band edge ultraviolet peak at 382 nm is considerably weak while the green emission at 475 nm is very strong. It is generally accepted that the green emission is due to the single ionized oxygen vacancies in ZnO and the emission results from the radiative recombination of a photo-generated hole with an electron occupying the oxygen vacancy.

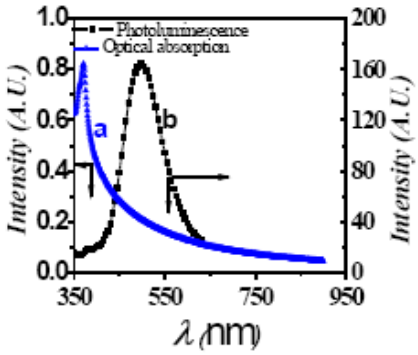


Figure: 3. Absorption and Photoluminescence spectra of ZnO nanotetrapods.

Thermal evaporation of a mixture of ZnO and graphite has been used to grow ZnO nano-tetrapods in large quantity. These have been characterized thoroughly and Photoluminescence spectra of tetrapods exhibits wide visible green emission band at 475 nm generally accepted due to presence of single ionized oxygen vacancies in ZnO. Photoluminescence spectra revealed that green emission originating from oxygen vacancies overwhelmed that of the near-band-edge ultraviolet peak. A band gap of 3.27 eV was calculated from optical absorption spectra which agreed well with that estimated from PL spectra [5].

CONSLUSION

ZnO has three key advantages: First, it is semiconductor, with a direct wide band gap of 3.37 eV and a large excitation binding energy (60 meV). It is an important functional oxide, exhibiting near-ultraviolet emission and transparent conductivity. Secondly, because of its noncentral symmetry, ZnO is piezoelectric, which is a key property in building electromechanical coupled sensors and transducers. Finally, ZnO is bio-safe and biocompatible, and can be used for biomedical applications without coating. With these three unique characteristics, ZnO could be one of the most important nanomaterials in future research and applications. The diversity of nanostructures presented here for ZnO should open up many fields of research in nanotechnology [6,7].

This simple method of fabricating ZnO based biosensor can be extended to immobilize other enzymes and other bioactive molecules on various 1D metal oxide nanostructures, and form versatile electrodes for biosensor studies.

We have been working on ZnO and its nanostructures, and we are constantly looking for new applications of these nanostructures. We can expect a cheap and high sensitivity biosensor as a result of our work.

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