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# Study of Zinc Oxide nano/micro rods grown on ITO and glass substrates

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ABSTRACT

Highly oriented multilinked ZnO nano and micro rods were deposited using aqueous solution growth technique on ITO and glass substrates. Their study provides a basic understanding of effect of the base material on the growth of nanorods. An equimolar aqueous solution of Zinc nitrate and hexamine (HMT) was used for the preparation of ZnO nanorods arrays. ZnO was deposited on ITO and glass substrates after establishing the optimal pH and concentration, which yield the best substrate coverage for precursor solution. To achieve uniform growth and high density of ZnO nanorods, the prepared solution was heated at certain constant temperature. The experimental results have been obtained by using Scanning Electron Microscope (SEM), X-ray diffractometer (XRD) and Fluorescence Spectroscope which shows highly oriented nanorods perpendicular to the surface of substrates and a comparative study of ITO and glass grown nanorod arrays shows that the structural chemistry of the substrate clearly affects the growth nanostructures. The high variation in optical properties can be attributed by the heating temperatures and limited presence of reactants available for the controlled growth on substrates. It is also observed confined and decreased particle size with enhanced nucleation on ITO substrate as compared to glass. Due to the physical limitations in the growth, this kinetically controlled nucleation would be responsible for producing the highly uniform, dense and perpendicularly oriented nanorods.



## 1. Introduction

ZnO is one of the widely used and studied material for its number of exciting properties. It is a wide band gap semiconductor material with Eg ~ 3.3 eV and a large exciton binding energy of 60 meV at room temperature. Semiconducting oxides, with many novel properties, from electrical, chemical, and optical to magnetic, are fundamental to the development of smart and functional materials, devices and systems [1]. These properties make ZnO feasible for application in many field, such as energy conversion [2–4], optoelectronics [5,6] and sensing devices [7–9], in particular when it is synthesized in one-dimensional (1D) geometry [10–12]. Hexagonal structure among all the geometries the most feasible for such type of applications are nanowires [1,13,14], nanobelts [15,16], nanotube and nanorods, and arrays of them [17,18]. Most of the properties of ZnO strongly depend on its structures, including the morphology, size and aspect ratio [19]. These structural characteristics have an important role in optoelectronic applications [20]. There fore, as an attractive functional material, the synthesis of nanostructures of the functional oxides, with a controlled structure and morphology, is critical for scientific and technological application. The strong exciton binding energy which is much larger than the thermal energy at room temperature (ca. 25 meV) can ensure an efficient exciton emission at room temperature. Therefore, ZnO is recognized as a promising material with excellent optoelectronic properties [21–23]. One-dimensional ZnO nanostructures were synthesized by various processes, such as chemical vapor deposition (CVD) [22,24] and chemical solution deposition [25]. Direct deposition techniques in aqueous solution, based on heterogeneous nucleation and subsequent crystal growth on a specific substrate, have attracted much attention to prepare ZnO nanorods films [26]. The aqueous solution usually contains zinc source (i.e., $Zn(NO_3)_2$ $Zn(CH_3COO)_2$,) and some additives, such as complex or chelating agents (i.e., urea, hexamethylentetraamine, ethane-1,2-diamine). By means of controlling process parameters, well aligned single-crystalline hexagonal rods of ZnO were grown along the *c*-axis direction in a perpendicular fashion onto the substrates. The control of the nanorods orientation and the ability to align them into three dimensional arrays onto various types of substrates is a challenging task to develop smart and functional materials [27,28]. However, some fundamental information about ZnO nanorod arrays and its growth evolution in an aqueous solution, which concerns the shape, orientation and alignment of nanocrystallites, has not been evaluated yet [1].

This present work reports the microstructural evolution of multi-linked ZnO nano and micro rods using direct deposition method in an aqueous solution growth technique and comparative studies for nucleation and growth on ITO and glass substrates were characterized by scanning electron microscopy and Fluorescence spectroscopy. Crystalline zinc oxide microstructures have

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been prepared by mixing aqueous solutions of zinc nitrate and hexamethylenetetramine (HMT) at 95 °C for different durations. ZnO particles of comparatively large size have been obtained with ammonium hydroxide as a hydrolysis agent without HMT. In summary, HMT is an ammonium-hydroxide source in the reaction, a surfactant for retaining the size and hexagonal structure, and not necessarily a template for the nucleation of ZnO particles, and in our work we provide systematic studies for the same.

## 2. Synthesis details

### 2.1. Aqueous solution growth technique

This novel technique has emerged recently as a simple and powerful tool to fabricate material at low cost with mild temperatures, which provide large area to metal oxide micro to nano particulate thin films. The synthesis involves the controlled heteronucleation of metal oxides in aqueous solutions.

The aqueous chemical growth method consists of heating an aqueous solution of metal salts or metal complex compounds in the presence of a substrate at moderate temperatures (below 100 °C) in a closed vessel [29]. Therefore, such technique does not require high-pressure containers and is also entirely recyclable, safe and eco friendly because only water is used as a solvent. Such a process avoids the safety hazards or organic solvents and their eventual evaporation and potential toxicity. In addition no organic solvents or surfactants are present, the purity of the materials is substantially improved. The residual salts are easily washed out by water due to their high solubility. In most of the cases no additional heat or chemical treatment is necessary.

### 2.2. Materials used

The starting materials employed were zinc nitrate tetrahydrate ($(Zn(NO_3)_2 \bullet 4H_2O$, purity: 98.5%, Scientific Ltd) and hexamethyltetramine ($C_6H_{12}N_4$, HMT, purity: 99.5%, Scientific Ltd). Both reagents were used as received without further purification. Regular laboratory beakers were filled with an equimolar (0.1 M) aqueous solution of $(Zn(NO_3)_2 \bullet 4H_2O$ and HMT.

### 2.3. Aqueous solution growth technique of multilinked ZnO nano and micro-rods

For the synthesis of linked ZnO micro-rods, and comparative study of ITO Vs glass substrate, an equimolar (0.1 M) aqueous solution of $(Zn\,(NO_3)_2 \cdot 6H_2O)$ and HMT was prepared at room temperature. ITO and Glass slides cleaned with ethanol and acetone were used as substrates. The cleaned substrates were dipped in the prepared solution; the solution was kept in a temperature controlled oven at 95 °C for different durations of time. The influence of different time-period of heating process was then investigated [30], and it was found that the annealing treatment of temperature on ZnO thin films has strong influences on the diameter and orientation of the ZnO nanorod arrays when prepared by non-aqueous sol–gel synthesis technique. And another one, multilinked microrods using hydrothermal deposition technique [20].

Sample 1: The cleaned Indium tin Oxide (ITO) coated glass slide and normal glass were used as the substrate. The cleaned substrate were placed in the prepared solution and heated at a constant temperature of 95 °C for 1 h, after the solution gets cooled in a laboratory oven. The substrates were taken out from the solution after over night. Finally the thin film was deposited on the substrate and then thoroughly washed with distilled water to eliminate residual salt, and dried in air at room temperature.

Sample 2: The cleaned Indium tin Oxide (ITO) coated glass slide and normal glass were used as the substrate. The cleaned substrates were placed in the prepared solution and heated at a constant temperature of 95 °C for 5 h, after the solution get cooled in a laboratory oven. The substrates were taken out from the solution after over night. Finally the thin film was deposited on the substrate and then thoroughly washed with distilled water to eliminate residual salt, and dried in air at room temperature.

### 2.4. Material characterization

Structural studies and surface morphology of the prepared samples were characterized by using scanning electron microscope (JEOL-JSM-6390) and X-ray diffractometer (Rigaku, Miniflex II). And optical Properties were studied through photoluminescence (PL) spectra at room temperature and the data were recorded using fluorescence spectrometer (F-7000 Hitachi) exiting with its xenon lamp at 325 nm.

## 3. Results and discussion

### 3.1. Scanning electron microscopy

The morphology and microstructures of our samples were determined by the images taken from scanning electron microscope.

#### 3.1.1. Growth morphologies of ZnO micro-rods on ITO and glass after 1 h heating

Generally the interfacial energy between crystals and substrates is smaller than the energy between crystals and solutions. Therefore, nucleation in homogeneous solutions is expected to occur at a high degree of super-saturation, whereas in the case of film growing on a substrate, heterogeneous nucleation takes place spontaneously at relatively low degree of super-saturation [20]. The morphology-controlled synthesis of ZnO nanorods is of great interest for future ZnO nanodevice applications. By adjusting the precursor concentration of HMT and reaction temperature, different sizes of 1-D hexagonal ZnO nanorod structures have been prepared via an aqueous solution route.

As compare Fig. 1(a) and (b) shows some crystals on the ITO and glass substrate surfaces after 1 h with deposition time 95 °C. These images convey that the multilinked microrods with and hexagonal shape formation on ITO and glass substrates. Due to 1 h heating and over night ageing nucleation site were developed more dense and precise particle size also decrease on ITO substrate as compared to glass substrate. The reason attributed for this difference is that, the crystal structure of glass and ITO is different and the nano and micro rods formation depends upon the crystal structure of the base as the nucleation sites created and the ease of rod formation in vertical side, both depends upon the specific base material on which the rods are grown. Some particles appeared to be aggregated in the former image and in the later one small particles of ZnO seeds at micro-level are seen for sample 1.

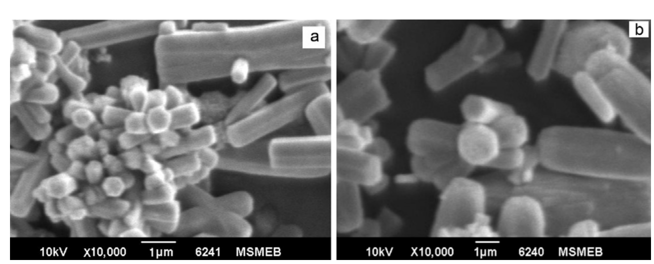


**Fig. 1.** SEM image of prepared ZnO micro-rods with multi-linked morphology, regular hexagonal shape and nucleation site developed, sample 1 (a) On ITO substrate (b) On glass substrate.