

Research Article

Growth, Structural and Optical Characterization of ZnO Nanotubes on Disposable-Flexible Paper Substrates by Low-Temperature Chemical Method

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We report the synthesis of vertically aligned ZnO nanotubes (NTs) on paper substrates by low-temperature hydrothermal method. The growth of ZnO NTs on the paper substrate is discussed; further, the structural and optical properties are investigated by scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and cathodoluminescence (CL), and it was found that the ZnO NTs on paper substrate fulfill the structural and optical properties of ZnO NTs grown on other conventional substrates. This will be more beneficial in future usage of ZnO NTs in different fields and applications. Particularly, this approach opens the ways in research and development for high volume manufacturing of low-cost, flexible optoelectronics devices on disposable paper substrates and can be used in the future miniaturization trends.

1. Introduction

Zinc oxide (ZnO) with a wurtzite structure is an exceptionally important oxide semiconductor material especially to nanotechnology due to the easiness of growing of its nanostructures with diverse varieties. It has some unique and remarkable physical properties with some advantages such as wide and direct fundamental energy band gap ($E_g \approx 3.37$ eV) and relatively large excitation binding energy (~ 60 meV) at room temperature. ZnO is also a green material, that is, it is biosafe, biodegradable, and biocompatible and can be used for biomedical and environmental science applications [1]. Since the last decade, it has attracted the attention of the research community, mainly due to the variety of possible practical applications, for example, in technical and medical fields. ZnO possesses diverse hierarchical nanostructures such as nanorods (NRs), nanowires (NWs), nanobelts (NBs), and nanotubes (NTs), and all these nanostructures can be synthesized under specific growth conditions on different substrates. These one-dimensional (1D) nanostructures provided valuable information regarding the crystal growth mechanisms on the nanometer scale and exhibited high

potential for fabricating novel nanodevices with superior performance [2]. Since the last few years 1D ZnO nanostructures have attracted considerable interest because these nanostructures exhibited extraordinary structural, surface, electrical, optical, magnetic, mechanical, and thermal properties different from those found in bulk ZnO material. The sources of these enhanced properties are high surface-to-volume ratio and possible quantum confinement effects in two dimensions.

Compared with other 1D counterpart nanorods, the tubular or hollow structure possesses some peculiar physical and chemical properties like low dimension, high porosity, low mass density due to the extremely large surface area, high anisotropy, and excellent current-carrying property. High-density and well-aligned tubular morphology with a hollow cylindrical geometry attracted a great technological interest and provide enhanced and smart functionality and serve as functional building blocks for various nanodevice applications like optoelectronic devices [3], piezoelectric nanogenerators [4], photocatalytic activities [5], and field emitter devices [6].

When we talk about the fabrication of basic electronics components, two parameters are vital and must be considered, one important key is its reasonable electrical performance and the other is the production cost. In order to reduce the manufacturing cost, extensive efforts have been devoted to synthesize well-controlled morphology of ZnO nanostructures with appropriate properties. Paper or paper-like substrates have so many advantages over other substrates with special properties like low cost, relative abundance, flexibility, light weight, non-hazardousness, less environmental impact, and full recyclability. Various applications such as electronic displays [7], paper batteries [8], piezoelectric power generation [9], photodiodes [10], and organic thin-film transistor [11] have already been realized on paper substrate.

In this paper, we report the synthesis of vertically aligned ZnO NTs on paper substrate by a simple catalyst-free hydrothermal method at low temperature. Compared to other approaches the hydrothermal technique has become promising for fabricating nanostructures with a variety of morphologies due to its simplicity, low cost, fastness, high yield, and suitability for scale-up in contrast to the other growth methods. 1D ZnO nanorods are synthesized on paper substrates but, to the best of our knowledge, there is no research on the growth of ZnO NTs on the paper substrate. In this regard we synthesized ZnO NTs via a low-temperature hydrothermal method with diameters in the range 150–200 nm and with a wall thickness in the range of 30–40 nm on paper substrates. The grown ZnO NTs were characterized by various techniques such as scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and cathodoluminescence (CL) measurement. The growth of ZnO NTs on paper substrate is discussed and it was found that these ZnO NTs fulfill similar structural and optical properties of other ZnO NTs grown on different substrates.

2. Experimental Details

All the chemicals used in this study were of analytical grade purchased from Sigma-Aldrich and were used without further purification, and all the aqueous solutions were prepared by using deionized water having a resistivity of $18.0 \text{ M}\Omega \text{ cm}$. The process to obtain ZnO NTs is a two-step process. In the first step $50 \times 50 \text{ mm}^2$ clean room paper used as a substrate was first cleaned in DI water and then dried in the air. Then, this substrate was heated at a temperature of 100°C for 20 minutes in order to remove any remaining moisture in the paper. However, due to the high water absorption property the paper substrate suffers from wetting process and bad heat tolerance, so in order to protect the paper substrate from the water and chemicals, a wetting and chemical barrier layer must be used [11]. That layer must provide an effective chemical and moisture barrier with acceptable mechanical and dielectric properties. There are so many methods to deposit such barrier layer on the substrate using sputtering, evaporation, or chemical vapor-phase deposition [11]. Furthermore, these methods require

several complex steps, so in order to avoid those methods we followed a simple and effective method involving a protective layer on the paper substrate for passivation or chemical resistance. For that purpose we used cyclotene 3022-46 advanced electronics resin from Dow Chemical Company USA, which is a polymer suitable for wafer level application where a thin layer is required. This surface modification can also play a vital role in the reduction of surface roughness and damage occurring during synthesis, and it greatly enhances the alignment and uniformity of the ZnO NTs on the paper substrate [12]. After the surface modification of the paper substrate with cyclotene layer by spin coating, we baked it at 100°C for 50 minutes in vacuum. After that time the substrate was then transferred into oven and baked at a temperature of 160°C for about 30 minutes. Then, a seed layer, which provides nucleation sites for the growth of ZnO nanorods, was coated onto the substrate by a spin coater at a rate of 2100 rpm for about 1 minute. This process was repeated five times to obtain a good coverage. The seed layer consisted of ZnO nanoparticles, prepared by mixing zinc acetate dehydrate ($\text{C}_4\text{H}_6\text{O}_4\text{Zn}\cdot 2\text{H}_2\text{O}$) in methanol to obtain a 0.01 M solution concentration. This solution was then heated up to 60°C . Another solution of KOH in methanol (0.03 M) was added to the first solution dropwise under continuous stirring, and the whole solution was kept at 60°C for 2 h. The diameter of ZnO nanoparticles was in the range 5–10 nm [13]. Finally, the substrate was heated at a constant temperature of 180°C for 30 minutes in order to solidify the seed layer. After that the substrate was cooled at room temperature. To grow the ZnO NRs we used a low-temperature method. In this method zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$] (99.998%) and hexamethylenetetramine (HMT) ($\text{C}_6\text{H}_{12}\text{N}_4$) (99.998%) were mixed in equal molar in DI water and kept under continuous magnetic stirring for 30 minutes in order to get a uniform growth solution. The preheated paper substrate was then placed in the solution and was heated at 80°C for 5 h. After that it was washed with DI water to remove any residuals on the surface and allowed to dry in air at room temperature. The second step was to obtain the ZnO NTs; we used the method that involves the transformation of ZnO NRs into NTs with the help of chemical etching [14]. Many research groups successfully employed this technique to fabricate ZnO NTs [15, 16]. For that purpose, the ZnO NRs grown on the paper substrate were immersed in KCL aqueous solution for several hours at a temperature of 80°C , to chemically etch the ZnO NRs to get ZnO NTs. After that the substrate was pulled out and thoroughly washed with DI water to remove any residuals on the surface and it was allowed to dry in air. The surface morphologies and sizes of the resulting ZnO NTs were observed by SEM operating at 12 keV and transmission electron microscope operating at 200 keV. The crystal structure and phase identification of the resulting products were characterized by X-ray diffractometer with Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$ operating at 40 keV, 100 mA. The evidence for the purity and elemental composition of the as grown ZnO NTs was analyzed with an energy-dispersive X-ray spectroscopy (EDS) attached to the SEM operating at 20 keV. The CL measurements were performed using

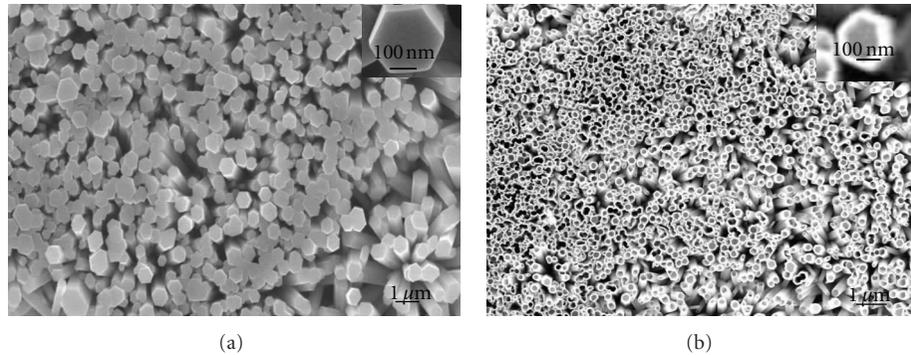


FIGURE 1: (a) Typical SEM image of the ZnO NRs arrays grown on paper substrate. Inset shows high-magnification image of a single ZnO NR. (b) SEM image of the ZnO NTs grown on paper substrate. Inset shows high-magnification image of a single ZnO NT.

nitrogen-cooled charge-coupled device (CCD) camera, and the luminescence was collected by a parabolic mirror and dispersed by a 0.55 meter monochromator equipped with a 600 mm^{-1} grating.

3. Results and Discussion

The morphology and size of the as-grown ZnO NRs and ZnO NTs are shown in Figures 1(a) and 1(b), respectively. The images clearly show that uniform ZnO NTs and ZnO NRs were obtained on the paper substrate. The magnified image shows hollow core structure of the ZnO NTs with single-crystalline, densely packed, faceted hexagonal tabular shape and most of the nanotubes are parallel to each other and predominately in a perpendicular orientation to the substrate. By using statistical analysis, we estimated that the average outer diameter and length of the ZnO NTs were about 200 nm and $\sim 3 \mu\text{m}$, respectively. In order to further investigate the hollow structures and etching depth of the ZnO NTs, TEM characterization was carried out. For that purpose some ZnO NTs were scratched off the substrate, and this was followed by ultrasonication in ethanol to disperse the nanotubes. A drop of the liquid containing ZnO NTs was deposited on a standard holey carbon grid. On the basis of high-resolution TEM the formation of ZnO NTs was further confirmed and the analysis shows that the ZnO NTs grow with a single-crystalline structure and the axial direction is along the [0001] as shown in Figure 2(a). The mean length and wall thickness of the ZnO NTs were about $2.2 \mu\text{m}$ and 40 nm, respectively. The corresponding selected area electron diffraction (SAED) pattern in Figure 2(b) indicates that the ZnO NT has a single-crystal hexagonal wurtzite structure. Figure 2(c) presents a high-resolution TEM image taken from part of the ZnO NTs. It can be clearly seen that the ZnO crystal lattices are well oriented with the lattice spacing of 0.52 nm, which corresponds to the distance between two (0002) lattice planes, indicating that the [0001] is the preferred growth direction for the ZnO NTs. In order to investigate the crystallographic structure and phase purity of the as-synthesized ZnO NTs we performed the XRD measurement. Figure 3 is a typical XRD pattern of the products showing the main reflections characteristics of ZnO

wurtzite structure. It reveals that all the diffraction peaks are indexed to the hexagonal wurtzite structured ZnO phase. The relatively enhanced intensity and sharp dominant peak at 34.4° corresponding to ZnO (0002) diffraction indicate that a single crystal grows preferentially along the c -axis normal to the substrate surface plane. ZnO possesses two oppositely charged polar surfaces perpendicular to the [0001] direction. These surfaces are terminated exclusively by Zn^{2+} or by O^{2-} on the (0001) and (000 $\bar{1}$) ZnO surfaces, respectively, and induce a net electrostatic dipole moment parallel to the c -axis [14]. But, due to the etching, the quality of ZnO NTs lowers the intensities of the ZnO NTs diffraction peaks compared with ZnO NRs. Also with the help of the relative texture coefficient we can find the degree of the orientation that the ZnO NTs have a preferential growth along the c -axis [17]. The intensity of the ZnO (0002) peak in the XRD pattern depends on the number of grains with the c -axis orientation in the ZnO. The ZnO NTs exhibit other peaks such as (101), (103), and (101), which may correspond to a granular structure of the nanotubes, while the full width half maximum (FWHM) of these peaks is 0.11° . Such a narrow line width implies that the ZnO NTs are well aligned along the growth direction. A homogeneous strain in the ZnO NTs gives rise to a sharp peak in the intensity of the X-ray beam at the Bragg angle. However, if the mismatch strain distribution in the ZnO NTs were spatially inhomogeneous, local gradients in strain within the region sensed by the incident X-ray beam would cause X-ray peak broadening, resulting in a more diffused intensity plot [18]. The hexagonal shapes of the ZnO NTs revealed by the SEM images are consistent with the XRD data. The diffraction peaks can be indexed to hexagonal ZnO corresponding to the structure of bulk ZnO with cell constants of $a_0 = 3.248 \text{ \AA}$ and $c_0 = 5.205 \text{ \AA}$, which is consistent with the standard value for bulk hexagonal ZnO ($P6_3mc$, JCPDS card no. 36-1451), no diffraction peaks of Zn and other remnant impurities have been detected in our samples.

Energy-dispersive spectroscopy was performed by EDS attached to the SEM. The typical energy-dispersive X-rays pattern of the ZnO NTs is shown in Figure 4; this confirmed that the ZnO NTs were composed of zinc and oxygen. Quantitative analysis indicates that in the final product the

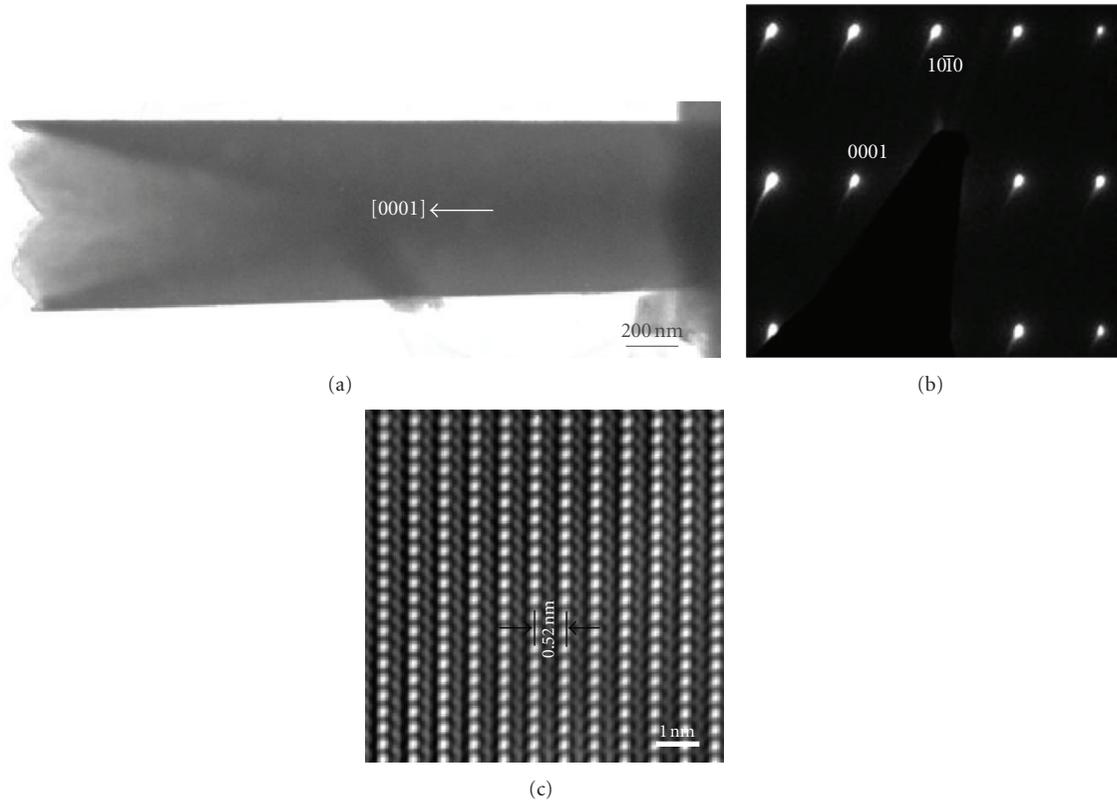


FIGURE 2: (a) High-resolution TEM image of a single ZnO nanotube showing the hollow structure with etching depth. (b) SAED pattern of single nanotube. (c) HRTEM image of the ZnO nanotubes.

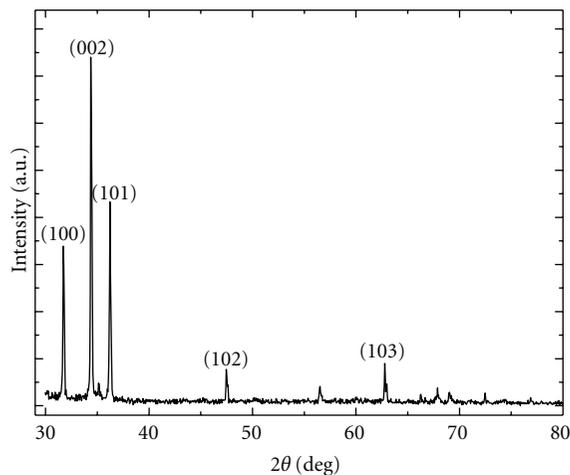


FIGURE 3: Typical XRD pattern of ZnO NTs.

approximate molar ratio of zinc and oxygen is close to the expected value ($\approx 1:1$), with the measured value of oxygen being about 53.84% and 46.16% zinc, no other element like carbon was found, which could be attributed to the oxidation reaction with oxygen.

In order to compare the deep defect chemistry in ZnO NRs and NTs, we measured the CL spectra at RT. Figure 5 shows CL spectra at accelerating voltage of 10 kV

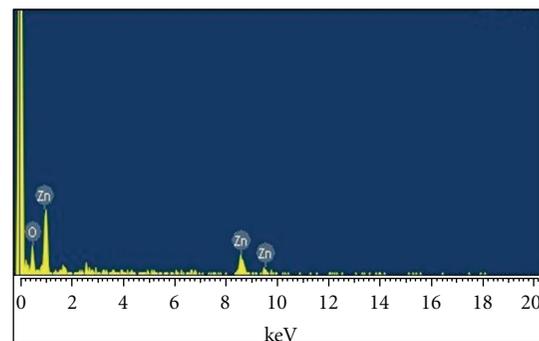


FIGURE 4: EDS spectrum of the ZnO NTs.

shows a UV emission at 382 nm, which is related to the direct recombination of photon-generated charge carriers (excitonic emission), two deep level emissions (DLEs) with violet emission at 417 nm, and broad DLE band centered at 625 nm (red). The CL spectra of ZnO NTs in Figure 5 indicate that ZnO NTs have more deep level emissions than the ZnO NRs.

In order to distinguish the emission bands we used a Gaussian function to simulate the CL spectra of ZnO NTs and ZnO NRs as shown in Figures 6(a) and 6(b). The simulated CL spectrum shows five emissions at 381 nm, 420 nm, 557 nm, 626 nm, and 695 nm, which are associated

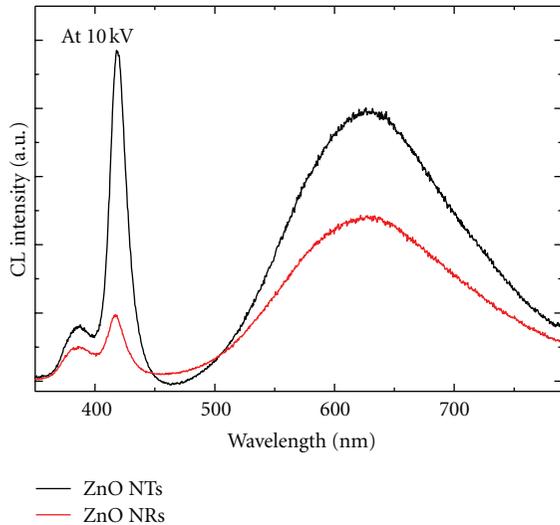


FIGURE 5: The comparison of the CL spectra of ZnO NTs and ZnO NRs.

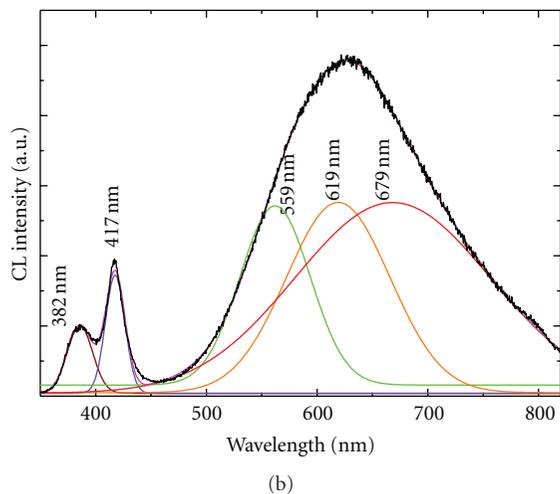
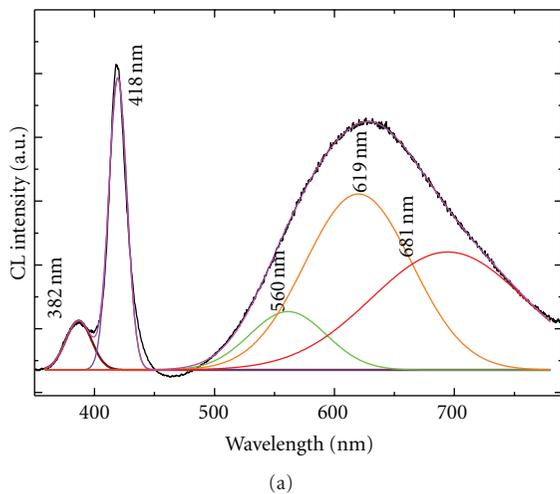


FIGURE 6: (a) CL spectra of ZnO NTs after the Gaussian fitting. (b) CL spectra of ZnO NRs after the Gaussian fitting.

with UV, violet, green, orange, and red emissions, respectively. The violet emission at 420 nm is attributed to the transition from Zn_i to valance band [19]. Figure 5 shows that the intensity of the violet emission in CL spectra of ZnO NRs is greater than the intensity of violet emission from ZnO NTs. Most recently the emission in the violet region is increased by introducing zinc interstitial defects in the ZnO nanostructures. The emissions from ZnO could be realized by controlling the growth process and conditions of the ZnO nanostructures for the selection of the precise defects [16]. Therefore, we used etching procedure to trim the ZnO nanorods to nanotubes to introduce more defects and as a result we had more violet emission in ZnO NTs than ZnO NRs. The green luminescence band at 557 nm is the most investigated and most debated band in the ZnO. Most recently, the green emission has been explained to be originating from more than one deep level defect, and V_O and V_{Zn} with different optical characteristics were found to contribute to the broad green luminescence band [20]. Moreover, the orange emission at 626 nm was recently attributed to oxygen interstitial, while the red emission at 695 nm was proposed to be due to transition associated with zinc interstitials (Zn_i) [21]. However, no consensus has been reached regarding the origin of the different observed colors, partly due to the different defect configurations in different samples grown by different methods.

4. Conclusion

In summary, we have demonstrated the growth of vertically aligned ZnO NTs on paper substrates by a low-temperature hydrothermal method. Structural and optical properties are discussed by using different techniques such as SEM, XRD, EDS, and CL. These investigations reveal that the NTs on paper substrates fulfill the structural and optical properties of ZnO NTs grown on other substrates. This work can provide significant platform for future soft, disposable, and high-performance electronic device based on paper substrate. The combination of low temperature ZnO NTs growth and low cost, disposable and flexible paper substrates make it attractive for the development of large-area electronic devices and flexible electronics that can be folded up. The mechanical flexibility of paper substrate allows it to change its shape to meet the space requirement of modern optical devices.

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