BIOPOLIMER-ASSISTED SELF-ASSEMBLY OF ZnO NANORODS-BASED THREE-DIMENSIONAL ARCHITECTURES AND THEIR PROPERTIES

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INTRODUCTION

Three-dimensional (3-D) ZnO architectures grown along the *c*-axis have been fabricated by new synthetic route based on aqueous-solution method through biopolimer-assisted self-assembly from ZnO nanorods. Field emission scanning electron microscopy, X-ray diffraction (XRD), Micro-Raman spectroscopy, chemical characterization - X-ray photoelectron spectroscopy (XPS) and photoluminescence investigations show that obtained ZnO architectures are of high purity nanocrystal with a wurtzite structure. Radial spherical structures from ZnO nanorods also have been synthesized and characterized. 3-D – ZnO nanoarchitectures could possibly be used as a building units opening opportunities for the self-assembly of multifunctional nanodevices with applications in sensors, bioscience, and photonics.

1. DESINING ZnO - NANOROD - BASED NANOARCHITECTURES

Nanoarchitectures exhibit peculiar and fascinating properties distinct from their bulk counterparts due to the nanometric size structures, high surface area and material properties. In this regards, in the research focus is nanotechnology which has been a significant commercial impact that will continue to manifest in the future. Key to the success of nanometric size structures is the nanostructuring and nanoengineering of building blocks such as nanorods, nanoparticles, nanotubes, etc. Some of the unusual, and often novel properties of nanomaterials, are directly related to the extraordinary nature and properties of the nanoelements.

For the nanotechnology is of importance to synthesize nanostructures with different one-dimensional (1-D), two-dimensional (2-D), and three-dimensional (3-D) architectures in order to synthesize building nanoblocks in self-assembled process. Nanostructured materials can be engineered by the controlled self-assembly of several suitable nano-objects as the building nano-blocks. In this regards for further nanoscience and nanotechnology development is necessary to understand the growth mechanism. Thus, the 1-D, 2-D, and 3-D architectures such as nanowires and nanotubes are under intense research due to of potential applications in novel nanodevices.

Zinc oxide (ZnO) is a semiconductor material that has advantageous properties promising manifold applications [1]. ZnO is a phosphor material with ability to retain a high efficiency, even at low-voltage excitation. At the same time it is a material with various configuration nanoarchitectures much richer that any of known nanomaterials [2-3].

Recently simple process techniques for arranging ZnO phosphor intended to enjoy widespread emission display, with smaller size, higher resolution and better contrast compared to liquid crystal display [1-4]. On the other hand, 3-D ZnO microspheres and radial spherical structures are of particular interest due to of lower densities and higher surface area and find applications in filters, sensors, catalysis, bioscience, photonics, or templates for functional-architectures composite material. Another major effort has been recently dedicated to the goal of establishing the limits and promise of inorganic and bio-inspired functional nanomaterials in a device environment for Microsystems applications.

In the present paper we attempted the 3-D ZnO grow by applying the chemical techniques. This route is used to grow zinc oxide nanorod-based microspheres, and radial spherical structures and also directly grow curved 3-D-ordered assemblies built from 1-D ZnO nanorods through two-step and three-step aqueous solution chemical route at relatively low temperatures.

2. EXPERIMENTAL DETAILS

In the synthesis process, the amorphous glass or crystalline quartz substrates were first cleaned in a diluted HCl (20%) solution for 10 min and then rinsed in de-ionized (DI) water (~ 18.2 MΩ·cm). Subsequently, the substrates were rinsed ultrasonically in an ethanol/acetone (1:1) mixture, then DI water, and dried in air. Solutions of $SnCl_2$/HCl were used for the sensitization of the substrate surface. This cleaning procedure was found to be adequate for generating a uniformly wettable substrate surface. For silicon substrate, the standard procedure was used to clean the substrate.

Zinc sulfate [$Zn(SO_4)\cdot 7H_2O$] and ammonia (NH_4OH) (Fisher Scientific, reagent grade, without further purification) were used for the synthesis of ZnO nanoarchitectures. $Zn(SO_4)\cdot 7H_2O$ and ammonia solution NH_4OH (29.6%) were mixed with 100 ml DI- water until complete dissolved. The substrates were kept in $SnCl_2$/HCl solution for 3-5 min then rinsed with a jet of DI water. Finally, the glass, quartz, and Si substrates were placed inside aqueous solution in a specially designed reactor. The setup was mounted on a hot plate, and the temperature was increased to 90-95°C and kept constant for 15 min without any stirring. Manipulation and reactions were carried out in air. In our experiment ZnO nanocrystals were formed at a pH value of 10-11.

The ZnO nanorod -based microspheres and radial structures were characterized by X-ray diffraction (XRD) using a Rigaku 'D/B max' X-ray diffractometer (XRD) equipped with a monochromatized CuK_α radiation source (λ=1.54178 Å) and an operating conditions of 30 mA and 40 kV at a scanning rate of 0.02°/s in the 2θ range from 10 to 90°. Data acquisition was made with Data Scan 3.1 and analyzed with Jade 3.1 (from Materials Data Inc.). The composition and morphologies of ZnO films were characterized by energy dispersion X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) were performed using a Hitachi S800. Transmission electron Microscope TEM images were obtained on a FEI Tecnai F30 TEM with an accelerating voltage of 100kV. These investigations confirmed that these nanorods arrays are highly crystalline with regular rods distributed throughout the substrate surface. This morphology is considered to play a vital role in nanodevice applications.

The ex-situ prepared samples were subsequently transferred into an ultrahigh vacuum system (UHV) for electronic/chemical characterization. All in-situ investigations were performed in a modular UHV system (SPECS GmbH) specially designed for the preparation and characterization of nanoscaled materials. The base pressure in this chamber is $1\text{-}2\times10^{-10}$ mbar.

Micro-Raman scattering experiments were performed with a Horiba Jobin Yvon LabRam IR system at a spatial resolution of 2 μm in a backscattering configuration. The 633 nm line of a Helium Neon laser was used for off-resonance excitation with less than 4 mW of power at the sample. The spectral resolution was 2 cm^{-1}, and the instrument was calibrated to the same accuracy using a naphthalene standard.

3. RESULTS AND DISCUTIONS

Figure 1 shows the XRD – results of 3-D-architectures in the range of 30-80° at a scanning step of 0.01°. It can be seen that all of the diffractive peaks are well indexed to hexagonal phase crystalline ZnO (wurtzite structure space group: $P6_3mc$(186); a = 0.3249 nm, c = 0.5206 nm) and the data are in agreement with the JCPDS 036-1451 card for ZnO (JCPDS 036-1451). No characteristic peaks of impurity phases such as Zn or S are observed and no diffraction peaks except ZnO were found. The intensity of ZnO (002) peak is higher than that of bulk ZnO, showing the preferential growth oriented along the *c*-axis in the [002] direction (figure 1) and good crystallinity of the samples.

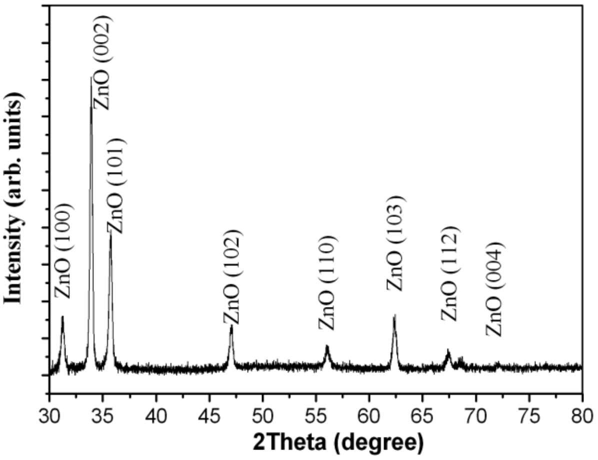

Figure 1. A typical XRD pattern of the ZnO nanorod based microspheres and radial structures.

Using energy dispersion X-ray spectroscopy, we found that the Zn:O ratios in our nanostructures to be 1:1 atomic ratio in all samples. SEM has been used to examine the surface morphology and to estimate of the obtained structure sizes. Typical SEM micrographs of the ZnO architectures obtained by biopolymer-assisted self-assembly method is shown in figure 2. Under the right circumstances, described in section 2, it is possible to grow ZnO nanorod-based radial structures and microspheres using biopolymer concentration in the range 0.005–0.02 M and reaction duration from 10 to 30 min at 100 °C. The overall morphology of the same size ZnO spheres presented in high quantity on a substrate is shown in figure 2 (a), which indicates the 3-D architectures consisted of 1-D nanorods with an average diameter of 100 nm (upper inset in figure 2a). From the insets in figure 2 (a) we can see that the ZnO nanorods are arranged in a perfect spherical structure. The radius of ZnO nanorods-based spheres are around 5 μm for duration of reaction of 30 min at 100 °C and occupied entire volume in the sphere.

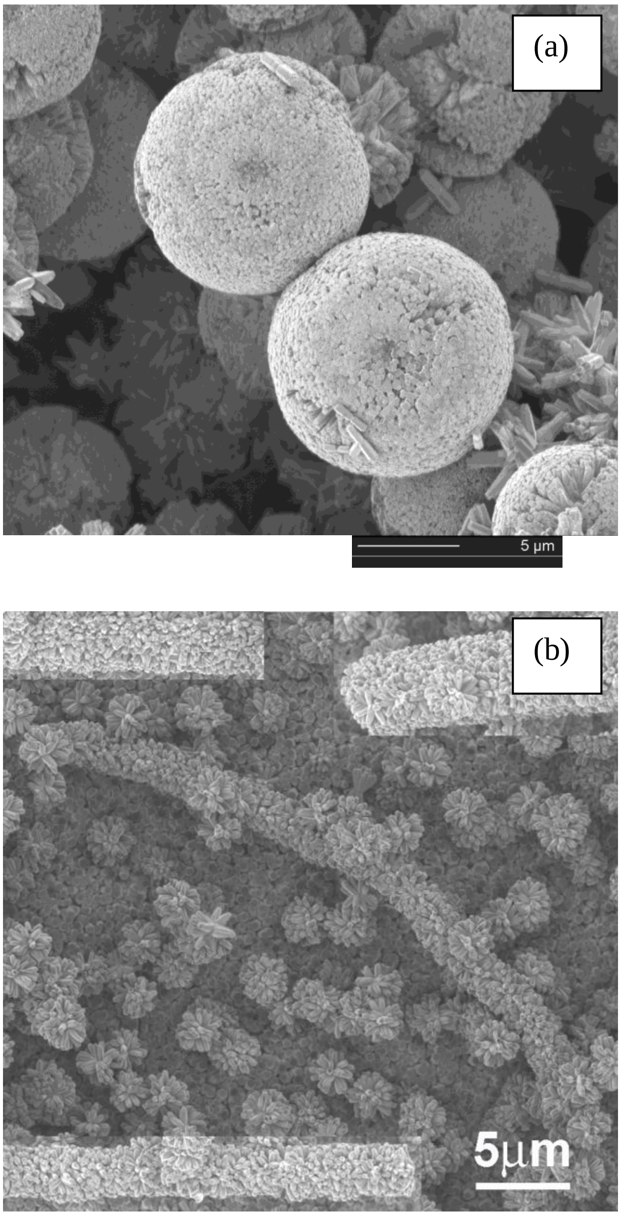

Figure 2. Scanning electron SEM images of the ZnO architectures chemically grown by biopolymer-assisted self-assembly method: (a) overall morphology of ZnO nanorod-based microspheres; (b) ZnO radial architectures and insets are their magnified images in different regions of the substrate.

New 3-D ZnO radial structures are presented in figure 2 (b) obtained by self-assembly method in 10 min at 100 °C using half of the concentration of biopolymer comparing to results shown in figure 2 (a).

We investigate the possibility to control self-assembly process of 1-D nanorods in 3-D superstructures by different concentrations of organic biopolymer along with growth parameters. The inset SEM images shown in figure 2 clearly display 1-D hexagonal nanorods radial self-assembled in different 3-D architectures under biopolymer support.

The TEM images indicate that the 1-D nanorod is single-crystalline ZnO with a wurtzite structure grown along the [0001] direction, which is consistent with the XRD results. The parallelisms of the HRTEM lattice fringes and SAED patterns shown in figure 3 reveal that, the crystallographyc axes of the nanorods are parallel and possess a single crystal hexagonal structure without dislocations and stacking faults. With TEM characterizations we found that 1-D nanorods are not bent with a smooth in surface and therefore provide direct evidence for the oriented-attachment growth mechanism.

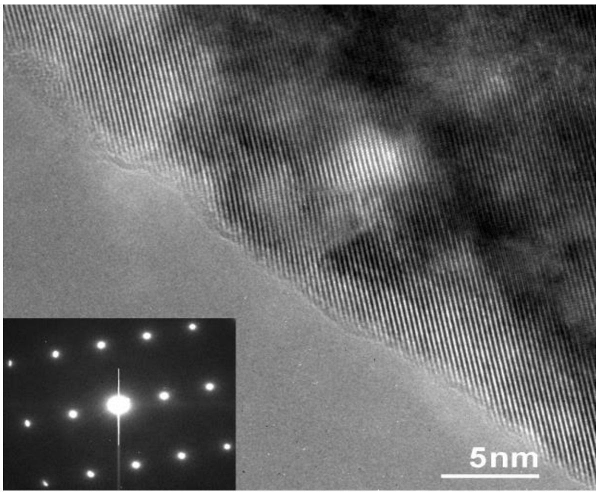

Figure 3. The high-resolution TEM images and the inset with the select area diffraction patterns-SAED of the single-crystalline ZnO nanorods grown by self-assembly method.

Effective approach to investigate the phase and purity of the low-dimensional nanostructures is micro-Raman scattering. Room temperature micro-Raman spectroscopy was performed to examine the properties of the self-assembly ZnO 3D structures. When considering the ZnO which belongs to the wurtzite space group C_{6v}^{4}, phonon modes E_2 (low and high frequency), A_1 [(TO)-transverse optical and (LO)-longitudinal optical] and E_1 (TO and LO) are expected all being Raman and infrared active. The eight optical phonons at the Γ point of the Brillouin zone belong to the representation [5]:

$$\Gamma_{opt} = 1A_1 + 2B_1 + 1E_1 + 2E_2 \quad (1)$$

Representative micro-Raman spectra of the self-assembly ZnO nanorod-based spheres and radial spherical structures are shown in figure 4. Dominant peaks at 100 cm^{-1} and 438 cm^{-1}, which are commonly detected in the wurtzite structure ZnO [6], are attributed to the low- and high-E_2 mode of non-polar optical phonons, respectively.

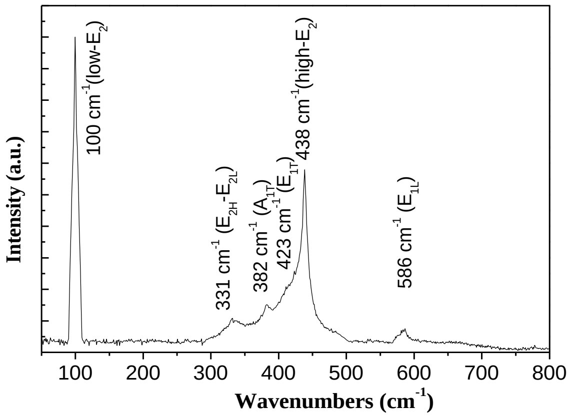

Figure 4. Micro-Raman scattering spectra of the self-assembly ZnO nanorod-based microspheres and radial structures.

The weaker peak at 331 cm^{-1} has been attributed to a second order nonpolar E_2 mode which is Raman active only. The Raman peak at 382 cm^{-1} came from the polar A_1 mode of ZnO. The B_1 modes are infrared and Raman inactive (silent modes) [5]. The strong Raman peak at 438 cm^{-1} was one of the characteristic peaks of wurtzite ZnO attributed to the high frequency E_2 mode [7] assigned to multiple-phonon processes. According to the recorded Raman spectra the E_2(high) is clearly visible at 438 cm^{-1} with a width of 10 cm^{-1} (figure 4), indicating the good crystal quality [7-8] of self-assembly radial structures. The E_1(LO) mode near to 586 cm^{-1} are allowed in the $x(zz)x'$ scattering configuration can be from the tilted nanorods.

Figure 5 of ZnO microspheres reveals an intensive UV emission at around 389 nm, which should correspond to the near band edge emission of the wide band gap of ZnO due to the annihilation of excitons.

Photoluminescence (PL) spectrum of the ZnO nanorods-based radial spherical structures exhibits an intensive UV emission at 389 nm at room temperature, which suggests a new candidate for fabricating optoelectronic devices. The method is simple, and may be extended to synthesize other inorganic materials with complex structures.

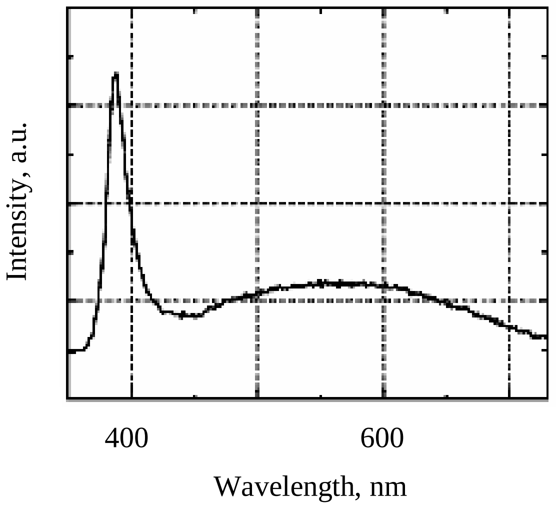

Figure 5. Photoluminescence spectrum of the 1-D ZnO nanorods-based three-dimensional radial spherical structures.

Chemical characterization - X-ray photoelectron spectroscopy (XPS) was used to monitor changes in the chemical composition of the nanorods-based structure. Figure 6 shows XPS spectra from the Zn-2p (a) and O-1s (b) core level regions. Charging effects due to the low conductivity of the glass slides used as substrates have been minimized by calibrating the binding energy (BE) scale using the O-1s XPS peaks of ZnO (531.2 eV) and C-1s (285 eV) as references. In figure 6 sample show XPS peaks at ~1022.5 eV and ~1045.5 eV, corresponding to the $2p_{3/2}$ and $2p_{1/2}$ core levels of Zn in ZnO. No significant changes in the Zn-2p core levels were found for the pure ZnO samples upon annealing at 150°C and 650°C. In figure 6, all samples show a clear photoelectron peak at ~ 531.2 eV, corresponding to the O 1s core level in ZnO.

According to our experimental results, a possible chemical mechanism for the reaction process and model for self-assembly of ZnO-nanorods into radial superstructures by biopolymer-assistance can be proposed as follows. Due to the fact that the heterogeneous nucleation takes place at a low level of supersaturation of the complex solution, we can grow different ZnO nanoarchitectures (figure 2) by controlling the reactant concentration, pH value, process temperature, and duration.

Lowering the concentration of ammonia hydroxide permit the growth of smaller 1-D ZnO nanorods with radius less than 50 nm.

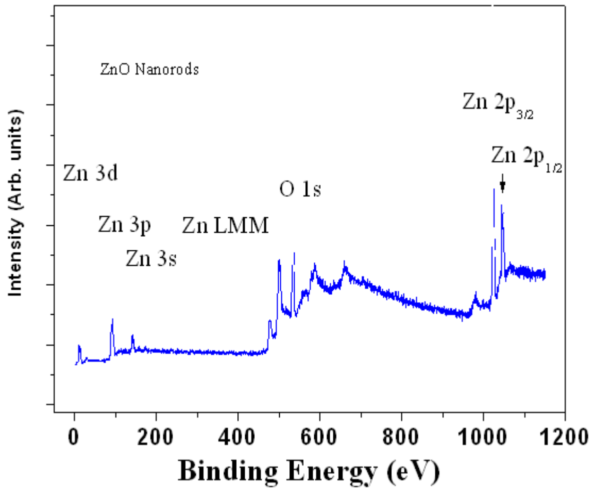

Figure 6. X-ray photoelectron spectroscopy XPS spectra (Al Kα = 1486.6 eV) corresponding to the Zn-2p and O-1s core levels of ZnO nanorods.

At the same time by varying the concentration of long-chain biopolymer - SA in solution different radial superstructures was obtained (figures 2a and 2b). A possible growing mechanism of 3D architectures during self-assembly under bio-polymer assistance have been investigated and discussed on the base of "lowest-energy" theory. At the beginning the decomposition of $Zn(OH)_4^{2-}$ complex conduct to the supersaturated with ZnO solubility. Instantaneously formed nanostructures in solution may attach to the surrounding bio-polymer and spontaneously cluster together into colloidal spherical aggregates to minimize their surface area [9]. At relatively high temperature, oxygen atoms could coordinate with the neighbor complexes and cause self-assemble of 3-D ZnO architecture to condense. The nanorods, which tends to grow toward the exterior and non-oriented growth, is physically limited due to of ZnO polar crystal growth. By the "lowest-energy" theory [9] that dictates the preferred growing direction, the 1-D nanorods growth mechanism can be explained. The representation of electrostatic attraction between the Zn^{2+} and carboxylic groups within negatively charged biopolymer skeletal and SEM images of self-assembly radial spherical structures are shown in figure 7. The kinetic conditions in the formation mechanism of self-assembling process, shown in figure 4, may be regents' concentrations, reaction temperature, pH value of aqueous solution and different organic biopolymers added.

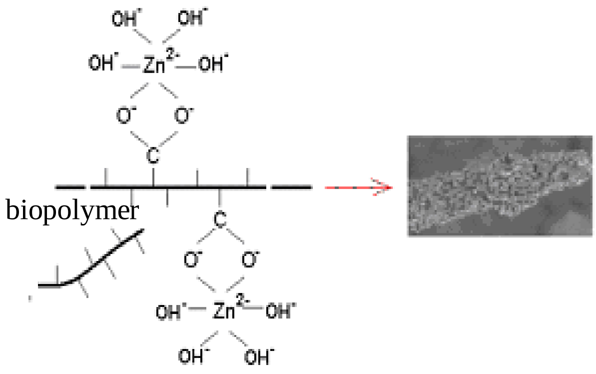

Figure 7. Representation of the proposed growing model and chemical mechanism for ZnO radial-spherical structures build from nanorods under biopolymer-assisted self-assembly.

Repeated experiments demonstrate that without biopolymer in the solution only ZnO nanorods can be obtained [7]. The water-soluble long-chain biopolymer is the nucleation site for the self-assembly of radial structures and offer possibility to control growth process. Thus designing nanoarchitectures by self-assembly can be controlled using chemistry, which involves van der Waals forces, electrostatic forces, or hydrophobic interactions [10]. At the same time monostructure are influenced by external forces which provide flexibility for designers – electrostatic, hydrodynamic forces permit to guide process.

4. CONCLUSION

In summary, ZnO 3-D spheres and radial structures were synthesized through a novel, low temperature, biopolymer-assisted self-assembly route without template. The architectures are constructed of high-quality ZnO 1-D nanorods of 100 nm in diameter and 2-5 µm in length.

X-ray diffraction, energy dispersion X-ray spectroscopy, scanning electron microscopy, transmission electron microscopy, micro-Raman spectroscopy measurements have been used to characterize the samples. These characterizations reveal that the ZnO 3-D architectures assembled from hexagonal faced 1-D nanorods are found to have good crystal quality with *c*-axis orientation.

The benefits of this method are that it is possible to control the thickness in nano order and to construct heterostructures using different salts.

This self-assembly technique seems to be promising for the preparation of the low-dimensional materials such as quantum-wires and dots. Applications of nanoarchitectured materials may overrun different industries including energy, electronics, medicine, display, and others. From the standpoint of such a versatile design, further investigations are currently underway.

Further work on the optimization of pure and doped ZnO 1-D nanorod –based 3-D architectures may lead to an extension of the proposed cost-effective and efficient self-assembly technique for fabrication of nano-scale devices and nano-system applications are in progress. It is anticipated 3-D self-assembly will be used to explore new phenomena and materials behaviors in order to synthesize nanometer sized electronic and optoelectronic device [11-14] in near future to revolutionize up-to-date life.

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