PREPARATION OF ZINC OXIDE NANORODS COLLOID FROM THIN LAYERS

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Abstract

The interest in ZnO (zinc oxide) nanoparticles is increasing due to low cost of their processing as well as the ability of fabricating ZnO nanostructures with controllable morphology such as size, shape and orientation. Our choice of method of the preparation of the nanostructured thin ZnO layers is the hydrothermal growth of ZnO nanorods on glass substrates coated by the nucleation layer deposited by the reactive magnetron sputtering. We have developed and optimized conditions of the thin layer growth with controllable dimensions of nanorods followed by the ultrasound peeling. The colloid of ZnO nanorods was characterized by measuring the size of particles using the dynamic light scattering (DLS) and the scanning electron microscopy (SEM). We found that the dynamic light scattering (DLS) can't be directly used for size evaluation of ZnO nanorods due to their non-sperical shape. We recommend using scanning electron microscopy (SEM) to determine morfology, length and diameter of ZnO nanorods.

Keywords: ZnO, method hydrothermal growth, thin layer, nanorods

1. INTRODUCTION

Zinc oxide (ZnO) is a versatile functional and the most studied material within metal oxides due to its broad applications. It is a semiconductoring material with wide band gap (3.37 eV [1]) and high exciton binding energy (60 meV [2]) at room temperature. Due to its unique optical properties [3-8], in last decade it was studied in many practical and potential applications e.g. UV lasers and photodetectors [8], optoelectronics (for the construction of new hybrid light emitting diodes) [9, 10], solar cells [11], thin film transistors [12], gas sensing [13] or as catalyst chemical processes [14]. ZnO thanks to such properties as nontoxic environmentally with high chemical stability can be used in medical field [15] as cell labeling [16], biological imaging and labeling [17, 18] and as antibacterial substance or as antifouling agent, eventually. Zinc oxide is used as an additive in the food industry and for cosmetics too.

It is the material with versatility in providing nanostructures such as nanowires, nanorods, nanotubes nanoribbons, nanobelts and nanocables. Several methods for the synthesis of nanostructured zinc oxide have been explored, but some of them are highly energy intensive (in temperature or pressure), or they use sophisticated processes to obtain the materials by means of a vapor-liquid-solid mechanisms.

One of the most promising approarchs for mass-production nanorods of zinc oxide are methods based on chemical synthesis, namely two techniques, the vapor phase thermal decomposition method (TDM) [19, 20] and the solution phase hydrothermal method (HTM) [21, 22].

The growth of ZnO nanorods by hydrothermal process is based on the thermal decomposition of the hexamethylenetetramine (HMTA), acting molecules of water as weak base and produce OH^- ions.This is crucial step the whole process. Zinc nitrate hexahydrate salt provides Zn^{2+} ions for building up ZnO nanorods. We processed the HTM method at mild conditions (temperature 90°C and time of growth 3 h). The time, temperature, concentrations of reactanta and pH are parameters, which we can turn in morphology, size and

shape of the nanorods. The hydrothermal synthesis is environmentally friendly procedure due to the fact that it takes place at lower temperatures and pressures closely to the living conditions on Earth. The next advantage this method is low energy consuming because the treatment steps after process are not necessary. Hydrothermal processes can be combined with electrochemical, mechanical and microwave techniques. Hydrothermal synthesis is a soft solution processing (SSP) [23] which allows in situ fabrication of shaped, sized, oriented ceramic materials without firing, sintering or melting steps. The methodology HTM allows to prepare powders, fibers, single crystals, monolithic bodies, coatings on metals, polymers and ceramics.

Our goal is production of colloid of zinc oxide nanorods from alligned thin layers with a uniform distribution of diameters and lengths by hydrothermal growth method [24]. This method is simple, cost effective and rapid for fabricating ZnO nanorods.

2. EXPERIMENTAL

All reagents were obtained from commercial suppliers and used without further purification. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$) were purchased from Sigma-Aldrich. Isopropyl alcohol and acentone were obtained from PENTA company. Deionized water was purified with a Milli Q plus system (Millipore) to high resistivity >18,2 MΩ.cm (25°C).

2.1. Preparation of substrates with seeding layers by DC magnetron spputering

The growth of ZnO seeding (nucleating) layers was performed on soda-lime glass standard microscopy substrates (26 mm × 76 mm). The glass substrates were cleaned by sonication in acetone for 5 min and subsequently in isopropyl alcohol for 5 min. After being rinsed with deionized water. Finally, the substrates were dried by nitrogen flow. The seeding layer was prepared by magnetron sputtering o fhe Al doped ZnO target (ZnO:Al) by energetic Ar^+ ionts. The deposition chamber was evacuated prior the growth by turbomolecular pump down to the residial pressure 1 mPa. The sputtering was performed by argon (purity 99,999%) at the pressure 1 Pa and the flow rate 2.0 sccm. The ZnO seeding layer was deposited as a thin layer on standard microscopic glass substrates size 1 by 3 inches (25.4 by 76.2 mm) heated by copper stage at 300°C. DC sputtering was performed with the voltage 500V and direct current of 0.14 A for 10 min.

2.2. Hydrothermal growth of ZnO nanorods

The ZnO nanorods were grown on patterned ZnO:Al substrates. ZnO nanorods were prepared in bath containing equimolar (2.5 mmol) solutions of zinc nitrate hexahydrate and hexamethylenetetramine both were dissolved in 100 mL deionized water. The solutions were blended at room temperature and stirring was continued for 30 min ar 350 rpm. Reaction mixture was poured in reaction - growth chamber. Then the substrates with ZnO seed layers were immersed in the growth solution. The reaction mixture was heated at 90°C for 3 h. At the end of growth period, the substrates were removed from the solution and rinsed with deionized water to remove the residuals from the surface nanorods. Finally, the substrates were dried by nitrogen flow at room temperature.

2.3. Ultrasound peeling ZnO nanorods from substrates

The substrate with grown nanorods ZnO was dipped in 2 mL deionized water. The vessel with nanorods on substrate in water was placed in a sonication bath. The preparation of colloid of ZnO nanorods in deionized water were carried out at four different amplitude (intensity) setting power of sonication (from 30% to 100%) at working frequency 37 kHz.

2.4. Characterization of the size and morphology of nanorods

Dynamic light scattering (DLS) was applied as a standart method for the evaluation of the particle size distribution of colloids. DLS measurements were performed with a Zetasizer Nano ZS (Malvern Instruments Ltd., GB) with detector in position 173° on Backscatter detection. Each sample of suspension ZnO nanoparticles was sonicated for 5 minutes before measurements. Size measurements were performed at 25°C and using clear disposable folded capillary cell (DTS1070).

Scanning Electron Microscopy (SEM) (MAIA3, TESCAN) was used for morphology characterization and size analysis of ZnO nanorods spread on conductive substrates. The images were taken at 5 to 10 keV using InLens detector. The top view images give an information about the density and distribution of ZnO nanorods, since the cross section view shows the height of ZnO nanorods. The colloids after sonication peeling were deposited for SEM on gold mirrors by spin coating method (at 2 000 rpm for 1 min). Prior the deposition the gold mirrors were treated by oxygen plasma (100 W/1 min) to increase the hydrophilicity of gold surface.

3. RESULTS AND DISCUSSION

The ZnO nanorods were prepared by hydrothermal growth on seeding layer. The nucleating layer was set up by magnetron sputtering of the ZnO target doped with aluminium. The quality of the seeding layer was controled by measuring the electrical resistivity. The thickness of nucleaction layer was calculated from interference fringes measurement by reflectance interferometry. Values thicknesses of individual nucleation layers were determinated to be about 150 nm. These values were confirmed by SEM, see **Figure 1a**.

The hydrothermal growth was based on thermal decomposition hexamethylenetetramine (HMTA) in presence of zinc nitrate in water [24]. We used optimized synthetic process (reaction time, temperature and composite of growth solution) for preparation nanorods with specified morphology and demanded length and diameter. Our approach was economic also because we have used several substrates simultaneously for growth nanorods. After reaction the surface morfology of nanorods grown on substrates were investigated by SEM. **Figure 1b** shows a typical hexagonal structure of nanorods with the diameter about 100 nm. The SEM image cross section view in **Figure 1a** shows that the leght of ZnO nanorods is about 600 nm in contrast to longer ZnO nanorods grown randomly on glass substrates in flower-like structures as shown in **Figure 1c**.

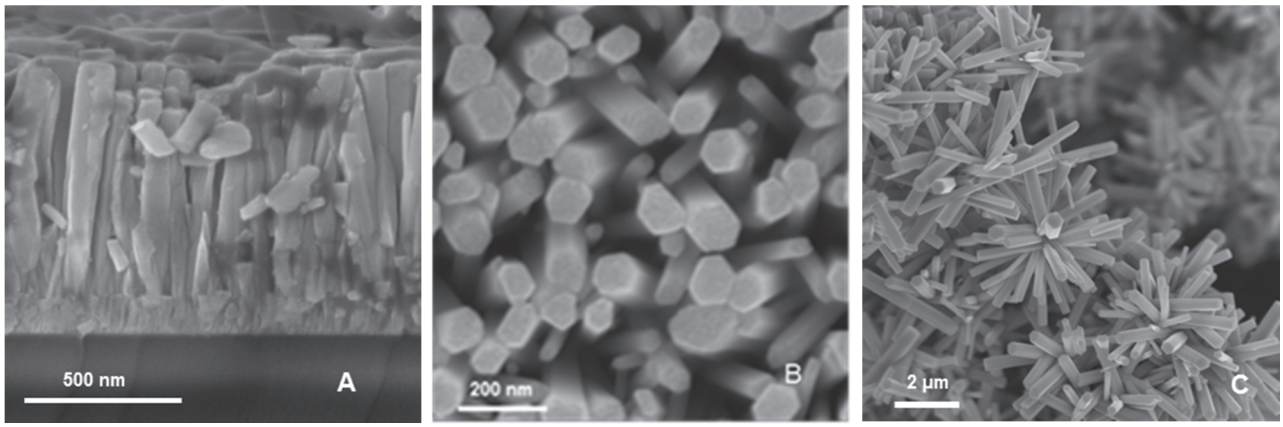

Figure 1 SEM image of ZnO nanorods cross section view (A) shows the height of ZnO nanorods, top view image the distribution of ZnO nanorods (B) shown in A and the SEM image flower-like ZnO nanostructures (C)

The sonication peeling was used to transform aligned nanorods from the substrate to the colloid. We tried sonication power from 30% to 100% at frequency 37 kHz for 10 min. The peeling process was monitoring by

measuring the size of nanorods in the colloid by dynamic light scattering (DLS). Zetasizer using DLS method gave diffusion coefficient as for spherical objects. This fact affected the value of size nanorods (z-average). The colloid obtained at the highest power of sonication was used to prepare sample for SEM imaging that correctly reflects the non-spherical shape of nanorods. Therefore, the value of the size distribution of the nanorods obtained by SEM is therfore much more accurate.

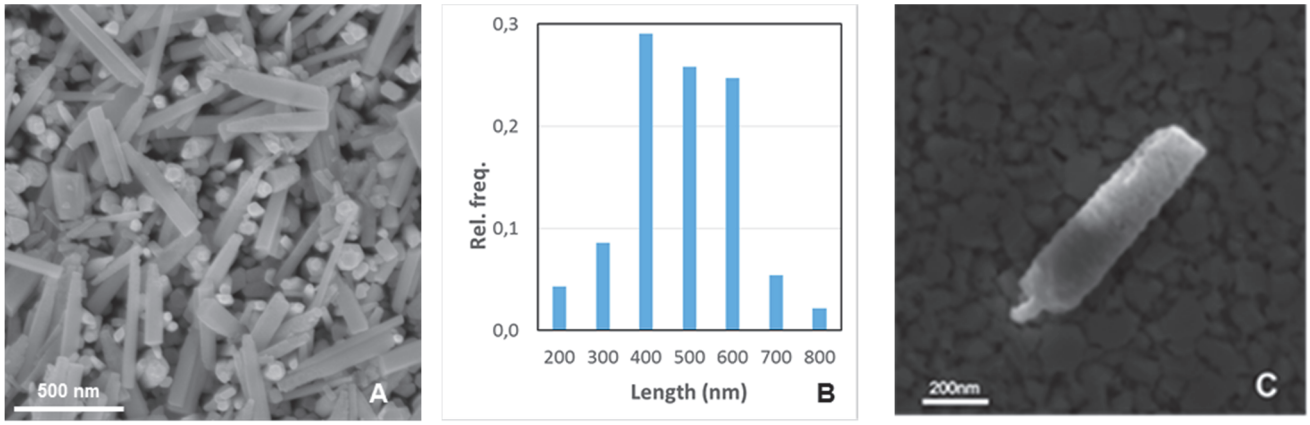

Figure 2 A top view SEM image nanorods on substrate after 10 min sonication (A) the histogram of the distribution ZnO nanorods shown (B) and the SEM image of separated ZnO nanorods (C)

Figure 2a shows SEM image of alligned ZnO nanorods after 10 min sonication at 37 kHz and 100 % power. The majority fraction of separated nanorods have similar morphology, length and shape. The histogram in **Figure 2b** shows the length distribution centered around 400–600 nm. The colloid obtained at the same conditions was used for separating single nanorods by spin coating technique on gold mirror, see **Figure 2c**. As it is shown here, the length of the single nanorod fully coresponds to the length of the nanorods shown in cross section veiw SEM (**Figure 1a**).

4. CONCLUSION

We have optimized the simple, cost effective and rapid method for fabricating ZnO nanorods suitable for economical mass production of zinc oxide nanorods. Our approach is based on hydrothermal growth of nanorods on seeding layer prepared on standard microscopic glass substrates by DC magnetron sputtering of the Al doped ZnO target. The method uses thermal degradation hexamethylenetetramine (HMTA) as source OH^- ions which reacted with Zn^{2+} ions from zinc nitrate hexahydrate. Amongst the different methods of synthesis of ZnO nanostructures, the hydrothermal method is attractive for its simplicity and environment friendly conditions. The seeding layer controls morfology (shape, diameter and lenght) the growth ZnO nanorods. We compared this method at equivalent conditions without using seeding layer. The seeding layer leads to the nanorods alignment, whereas the lack of the seeding layer leads to the random growth of the flower-like ZnO nanostructures. We transfered the ZnO nanorods from the seeding layer to colloid in deionized water by sonication. The colloid prepared at the most effective sonication (frequency 37 kHz with 100 % amplitude of power) was applied for size measurement of ZnO nanorods. We found that the dynamic light scattering (DLS) can't be directly used for size evaluation of ZnO nanorods due to their non-sperical shape. We recommend using scanning electron microscopy (SEM) to determine morfology, length and diameter of ZnO nanorods.

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