Synthesis and characterization of ZnO nanorods with narrow size distribution

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Materials

All chemicals were of reagent grade and used as received without further purification: hexamethylenetetramine also known as hexamine (C₆H₁₂N₄, Fisher Scientific, \geq 99%), zinc nitrate hexahydrate (Zn(NO₃)₂· 6H₂O, Acros Organics, 98%), sodium hydroxide (NaOH, Sigma-Aldrich, reagent grade, \geq 98%). The water used in all experiments was deionized (DI) and had a resistivity of 18 M Ω cm.

FE-SEM imaging of ZnO-NR porous papers

The porous structure of ZnO-NR papers produced with 0.1 g and 0.3 g of precursor is observed through FE-SEM investigations, as show in Figs. S1 A and B. We can notice the different morphology of NRs on the top and bottom faces of both papers.



Figure S1. Cross-section image of the ZnO-NR porous paper grown using 0.1 g (A) and 0.3 g (B) of precursor, for 12 h.

Synthesis of ZnO Microrods

ZnO microrods were synthesized through the simple and cost-effective hydrothermal process established by G.Amin et al.¹ but without the use of any seed layer. Briefly, an aqueous growth solution was prepared by dissolving a 0.02 M equimolar ratio of zinc nitrate hexahydrate and hexamethylenetetramine together in 200 ml DI water. The solution was magnetically stirred at 500 rpm for 30 min at room temperature yielding a clear solution. The growth solution was transferred into a laboratory Pyrex glass beaker, which was then placed inside a pre-heated laboratory oven maintained at 90°C for 4.5 h. During the reaction the solution temperature reached 60°C. The growth reaction resulted in the deposition of white sediment at the bottom of the beaker. Following the growth, a short bath sonication of five minutes was carried out by introducing fresh 200 ml DI water into the beaker. This bath sonication was helpful to detach the sediment from the beaker which was dispersed into the DI water. The white powder in large quantity was collected onto an anopore membrane disk (Whatman Anodisc, 0.02 μ m pore size, 47 mm diameter) under vacuum filtration, and was subsequently dried in oven at 120°C for 15 min. The yield obtained was 94 mg. In addition to this, the influence of reaction solution concentration was evaluated at two other equimolar concentrations of 0.2 M and 0.002 M while maintaining the growth time of 4.5 h and the influence of short growth time of 2 h was evaluated for the reaction concentration of 0.02 M.

Figures S2A-C present typical FE-SEM images of the obtained product prepared with reaction concentrations 0.002 M, 0.02 M and 0.2 M, for a growth time of 4.5 h. It can be seen from the images the occurrence of rods-like morphology for the products prepared at concentrations of 0.002 M (Fig. S2A) and 0.02 M (Fig. S2B), whereas dumbbells-like morphology can be seen for the product prepared with concentration of 0.2 M (Fig. S2C). In order to validate the morphological evolution of ZnO, a reaction time dependent experiment is carried out for the growth period of 2 h fixing the solution concentration at 0.02 M. From Fig. S2D, as obtained product shows that the formed hexagonal rod-like structures have narrow size distribution though the rod formation is often incomplete. This suggests that an extended growth time, beyond 2 h, is necessary to obtain the complete formation of the rod structure.



Figure S2. FE-SEM images of ZnO-MRs grown by hydrothermal process in different conditions: 0.002 M of precursor, 4.5 h at 90°C (A); 0.02 M of precursor, 4.5 h at 90°C (B); 0.2 M of precursor, 4.5 h at 90°C (C); 0.02 M of precursor, 2 h at 90°C (D).

Synthesis of ZnO Nanoparticles

ZnO nanoparticles were synthesized through the hydrothermal chemical precipitation route reported earlier by M. A. Moghri Moazzen et al.². In brief, 0.5 M zinc acetate di-hydrate was dissolved in 25ml of DI water using magnetic bar stirring at 250 rpm at room temperature for 15 min. Another homogeneous solution was prepared by dissolving 0.5 M of sodium hydroxide in 25ml of DI water using magnetic stirring at room temperature at 250 rpm for 15 min. As prepared zinc acetate di-hydrate solution was added drop wise to the sodium hydroxide solution under continuous stirring within 10 min. The solution was left under continuous stirring at room temperature for two hours, yields Zn(OH)₂ in the form of a white precipitate. The precipitate was repeated twice with DI water and ethanol. Finally, as obtained gel like product was calcinated in a muffle furnace (Lenton UAF 15/10) at 300°C for 12 h during which Zn(OH)₂ decomposes into ZnO nanoparticles. The yield obtained was 2 g which means about 73% of the zinc acetate precursor used was converted into ZnO.



Figure S3. FE-SEM image of ZnO-NPs grown by hydrothermal process.

TEM Analysis of ZnO-NR obtained through SS and LS

Transmission Electron Microscopy (TEM) characterization has been carried out on FEI Tecnai F20 ST TEM, equipped with Schottky emitter, a Fischione® High Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM) detector, and EDAX® Energy Dispersive X-Ray (EDX) spectrometer, and operated at a beam energy of 200 keV. It is worth noting that, in the HAADF_STEM Z-contrast mode, the image intensity is proportional to $Z^{1.7}t$, where Z is the atomic number and t is the thickness.

Figures S4 and S5 shows the obtained results for ZnO-NR samples produced through short sonication (SS) and long sonication (LS), respectively.



Figure S4. TEM analysis of ZnO-NR produced from paper P2 by SS. (A) Z-contrast HAADF-STEM image, showing the thickness and the uniform composition. (B) Elemental analysis (EDS spectrum acquired at the center of the red line), showing only the presence of Zn, and O, while C and Cu come from the TEM grid. (C) EDS profile taken on the red line crossing the NR showing the uniform and stoichiometric composition.



Figure S5. TEM analysis of ZnO-NR produced from paper P2 by LS. (A) Z-contrast HAADF-STEM image, showing the thickness and the uniform composition, as well as the damaged surface of the NR. (B) Elemental analysis (EDS spectrum acquired at the center of the red line), showing only the presence of Zn, and O, while C and Cu come from the TEM grid. (C) EDS profile taken on the red line crossing the NR showing the uniform and stoichiometric composition.

PL Spectra Analysis

The optical properties and crystal defects of the ZnO nanostructures were obtained through room temperature photoluminescence using as excitation source the 266 nm line of a Nd:YAG pulsed laser (Thomson DIVA), with 10 ns pulse length and 20 Hz repetition rate, as described in the manuscript³. The dependence of PL signals on incident laser power was investigated by

repeating the spectra on each sample at three different mean power levels (700, 900 and $1300 \pm 100 \text{ W/m}^2$).

The obtained results at the maximum power of 1300 W/m^2 are reported in the manuscript³. Figs. S4A and S4B show the measured spectra for power level of the incident laser of 700 W/m^2 and 900 W/m^2 , which are in good agreement with the ones measured at higher laser power.



Figure S6. Photoluminescence spectra of of ZnO-NRs produced from paper P2 by either SS or LS, and of ZnO-MRs and ZnO-NPs synthetized as described in the SI: (A) incident laser power = $900\pm100 \text{ W/m}^2$; (B) incident laser power = $700\pm100 \text{ W/m}^2$.

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