



Analysis and characterization of ZnO nanowires for sensing applications

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In this work, we synthesize hierarchical ZnO nanowires in a customized atmospheric CVD furnace and investigate their surface modification behavior for prospective nitroaromatic sensing applications. The morphology and crystal structure of pristine nanowires are characterized through FE-SEM, TEM, X-ray diffraction and EDAX studies. Photoluminescence behavior of pristine nanowires is also reported. Surface modification behavior of synthesized nanowires on a ZnO–oleic acid system is studied by utilizing Raman and FT-IR spectroscopy. Based on these findings, 1-pyrenebutyric acid (PBA) has been identified as an appropriate fluorescent receptor for sensing *p*-nitrophenol. Fluorescence quenching experiments on a PBA–*p*-nitrophenol system are reported and a detection limit of up to 28 ppb is envisaged for PBA-grafted ZnO nanowire-based optical sensor.

Keywords: ZnO; Characterization; Sensing.

1. INTRODUCTION

Recently, one-dimensional (1D) mesoscopic systems such as nanowires, nanotubes and nanorods have attracted a great deal of attention due to their numerous potential applications in nanoscale electronics, optoelectronic devices, and sensor development [1–3]. ZnO, a relatively large band-gap (3.37 eV) semiconductor, has been particularly interesting to the research community due to its large exciton binding energy (60 meV), which facilitates room temperature lasing action based on exciton recombination. Due to its excellent optical properties, ZnO has versatile applications in short-wavelength-based optoelectronic devices such as Light Emitting Diodes (LEDs), Laser Diodes (LDs), nanocatalysis, photovoltaics, OLED-based displays and chemical gas sensors [4–11]. The aforementioned applications require ZnO nanostructures in different morphologies such as nanowires, nanorods and nanobelts and must be subjected to specific post-synthesis procedures to achieve desired functionality. Various methods for synthesizing ZnO nanostructures include Pulsed Laser Deposition (PLD), Molecular Beam Epitaxy (MBE), Vapor–Liquid–Solid (VLS) growth,

Chemical Vapor Deposition (CVD) and Metal Organic Chemical Vapor Deposition (MOCVD) [12–17]. Furthermore, template-based synthesis methodologies such as electrodeposition and sol–gel have also been investigated [18, 19]. Fortunately, among all the methods outlined above CVD-based synthesis is relatively cheap and scalable, producing high-quality, defect-free ZnO nanowires.

Most of the unique properties that these nanowires exhibit stem from their single crystalline structure with a significantly increased surface-to-volume ratio over bulk crystals. We therefore expect surface-based effects to be crucial for any electronic and optoelectronic devices based on ZnO nanowires. These surface-related effects, therefore, mandate rigorous investigation in order to control and optimize the nanowire characteristics for their efficient integration in optoelectronic and FET-based devices. The technological relevance of surface-modified ZnO nanowires has already been demonstrated in sensing devices, DSSCs (Dye Sensitized Solar Cells) for efficient light harvesting, and other hybrid photovoltaic devices [20–22]. The polar nature of ZnO and its ability to maintain high-symmetry *c*-axis orientation during growth has also facilitated the growth of densely packed nanowire arrays that are promising candidates for non-linear optical devices. Furthermore, at the surface there is some symmetry loss which can be expected to increase the non-linear optical response of these nanowires over that of bulk crystals. Coating these nanowires with additional organic or inorganic compounds should, therefore, allow the surface to be tailored to its non-linear signal, thereby enabling the design of an efficient nanoscale optical sensor.

Hence, in this paper we (a) demonstrate cost-effective synthesis of high quality ZnO nanowires by Atmospheric Pressure Chemical Vapor Deposition (APCVD), (b) present evidence for organometallic modification of ZnO nanowire surface by oleic acid, and (c) identify the appropriate fluorophore (1-pyrenebutyric acid) and its potential application for fabricating highly sensitive nitroaromatic sensor when grafted onto a ZnO nanowire surface.

2. EXPERIMENTAL DETAILS

2.1 Growth methodology

ZnO nanowires were synthesized utilizing the template-based CVD method reported by Lee and co-workers [23]. Briefly, Si (100) substrates (MTI corp.) were ultrasonically cleaned in acetone for 10 minutes, followed by IPA and DI water for the same amount of time. Subsequently, the substrates were N₂ blow-dried and placed in an E-Beam evaporator. A 4-nm gold coating was deposited onto the cleaned substrates to serve as a template for facilitating VLS growth. Equal amounts of ZnO powder (99.9 %, J.T. Baker) and graphite powder (99 %, 300 mesh, Alfa Aesar) were milled and the mixture was introduced in a customized CVD furnace. The powder mixture serves as a source for precursor vapors that react to form ZnO nanowires at 950 °C by VLS mechanism. Mixed gas (Ar 2 % O₂) was used as a carrier medium to bring the precursor vapors onto the substrate, placed 3 cm away downstream along the furnace. After 30 minutes of growth time a gray coating was observed on the substrate, which was further characterized through the techniques outlined in the next section.

2.2 Surface modification

For surface modification, pristine ZnO nanowire grown substrates were dipped in oleic acid (1 % v/v) solution prepared in hexane for 10 minutes. Subsequently, the specimens were copiously rinsed in pure solvent for 5 minutes to remove any non-covalently bonded residual oleic acid.

The morphological and compositional characterization of the synthesized ZnO nanowires was performed using Field Emission-Scanning Electron Microscopy (FE-SEM, JEOL 7000) and EDAX analysis (Oxford Instruments). For analyzing the crystal structure, Transmission Electron Microscopy (TEM, FEI-Tecnai) equipped with LaB₆ source operated at 200 kV and X-ray Diffraction (XRD) (Bruker AXS) were used. Surface modification of the pristine nanowires was probed using vibrational spectroscopic techniques such as Raman (Jobin Yvon HR800 UV) and Fourier Transform-Infra Red (FT-IR, Bruker Vertex-70) spectroscopy. Raman analysis was conducted with a 633-nm He–Ne laser, while for FT-IR measurements an IR transparent crystal was employed. Fluorescence measurements were obtained on FluoroMax-3, Jobin Yvon, with a standard 1-cm quartz cuvette.

3. RESULTS AND DISCUSSION

The FE-SEM images of the ZnO nanowires in Fig. 1(a) and (b) confirm that the synthesized nanowire ensembles have random orientations and lack vertical alignment with the Si substrate. This can be attributed to the relatively large lattice mismatch (ca. 40 %) between Si (100) and ZnO. Furthermore, Fig. 1(b) clearly indicates that the synthesized nanowires have a smooth and clean surface with a high aspect ratio, although a small amount of lateral hierarchical growth towards the base of the nanowires is evident. Zhang and co-workers empirically determined that such effects are present due to a high supersaturation of Zn vapor in the furnace or due to the depletion of catalyst from growth fronts [24]. The latter effect is expected to be dominant in our case, as confirmed by the absence of gold catalyst nanoparticles from the nanowire tip. EDAX analysis of the pristine nanowires, as presented in Fig. 1(c), shows that no contaminant phase is present in the synthesized wires. The atomic percentages of Zn and O were found to be in agreement with the stoichiometric ratio of the molecule indicating ZnO as the only constituent of the nanowires.

The orientational preference of the ZnO nanowire during growth was probed with XRD. Figure 2 shows the X-ray diffractogram of the synthesized nanowires. It was observed that the nanowires were preferentially oriented along the [101] direction with a significant proportion grown along the [002] direction. Furthermore, the crystal structure was determined using TEM to characterize a single nanowire. Figure 3(a) shows a typical low-magnification image of a ZnO nanowire that is fully consistent with FE-SEM investigations. The selected area electron diffraction pattern (SAED) of the corresponding nanowire in the inset of Fig. 2(a) confirms very high crystallinity (single-crystal nature) of the

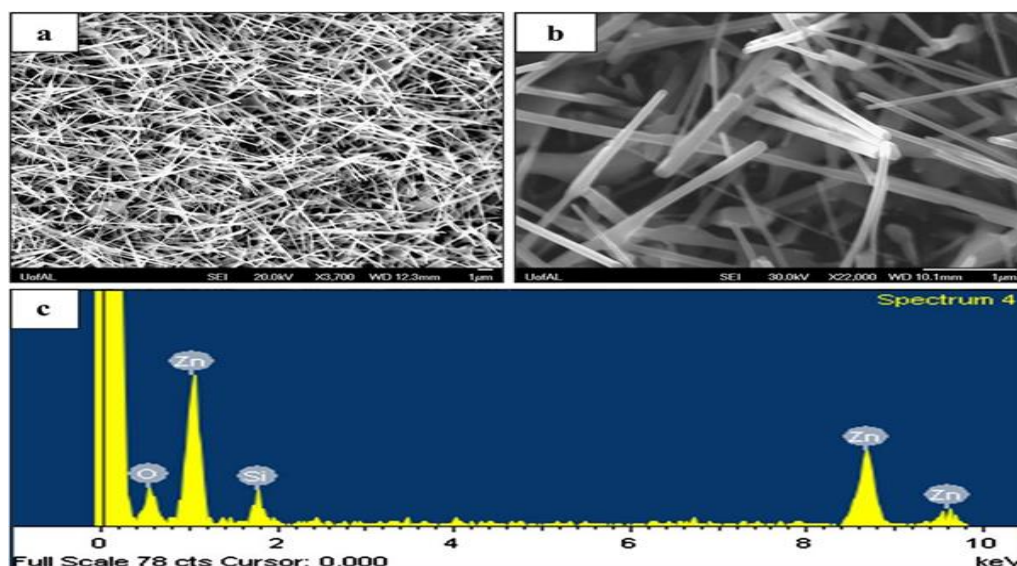


Figure 1 (a), (b) FE-SEM micrographs of as-synthesized ZnO nanowires, (c) EDAX spectrum of as-synthesized ZnO nanowires.

synthesized nanowires. In addition, Fig. 2(b) presents the HR-TEM (High-Resolution TEM) image of the as-grown nanowire, which conforms to the empirical observations of a preferential *c*-axis growth direction of ZnO nanowires via VLS process and typical inter-planar spacing of 0.52 nm.

As mentioned before, the binding of oleic acid was carried out as a proof-of-concept experiment for the functionalization of ZnO nanowires with a bifunctional fluorescence receptor, which can be covalently linked onto a ZnO nanowire surface while concomitantly maintaining its fluorescence characteristics. Since a carboxylic acid ($-\text{COOH}$) moiety is known to form covalent linkages onto metal oxides [25], it is pertinent to investigate the effect of a long chain carboxylic acid ($-\text{COOH}$) compound on our as-synthesized ZnO nanowires. Oleic acid was appropriate choice for this investigation due to its excellent surfactant properties as well as the potential for it to be reversibly replaced by pyrenebutyric acid (PBA) in a metal oxide nanoparticle solution [26]. The justification of utilizing PBA as an appropriate receptor on ZnO nanowire for nitroaromatic sensing is presented later in the paper. Consequently, Raman and FT-IR studies were conducted on modified- and unmodified ZnO nanowires to determine the surface structure information and nature of binding of oleic acid.

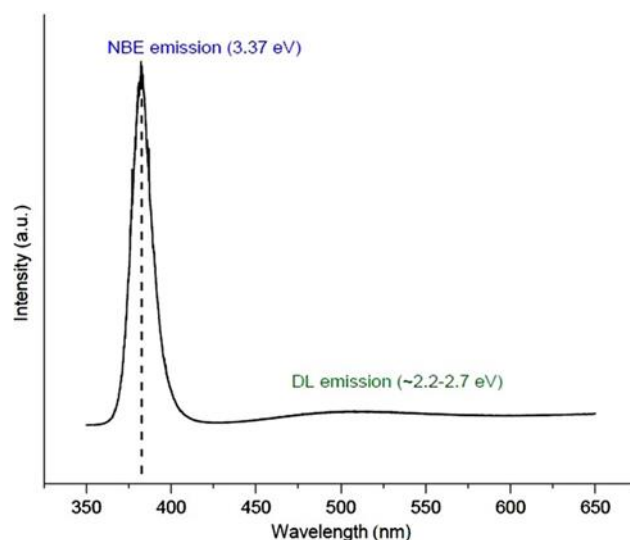


Figure 2 PL spectrum of as-synthesized ZnO nanowires showing band-edge emission.

In Fig. 3, curve A is the FT-IR spectrum of pure oleic acid, which serves as a control to identify peak changes post- modification. The broad peaks at 937 and 1464 cm^{-1} are attributed to out-of-plane and in-plane OH deformations, respectively. The peak at 1284 cm^{-1} is assigned to the C–O stretch, while the intense peak at 1710 cm^{-1} is typical of a bound carbonyl (C O) moiety. The peaks at 2570 and 2673 cm^{-1} are indicative of oleic acid dimeric forms. The group of peaks at 2825 – 2950 cm^{-1} illustrates CH_2 and CH_3 asymmetric and symmetric stretches. The spectrum resulting from the oleic acid modification of pristine ZnO nanowires is depicted in Fig. 3, curve B. Changes in the spectrum occur mostly in features associated with carboxylic acid moiety ($-\text{COOH}$), which is indicative of bound surface carboxylate. The peaks at 2570 and 2673 cm^{-1} are weaker, which rules out presence of an oleic acid dimer. The C O band at 1710 cm^{-1} , the C–O stretch at 1284 cm^{-1} and the O–H out-of-plane deformation no longer appear in the spectrum. Consequently, new features indicative of bonding via carboxylate moiety appear. Peaks at 1407 and 1589 cm^{-1} are attributed to $-\text{COO}$ symmetric and asymmetric stretching, respectively. The remaining peaks not previously mentioned are characteristic of a long hydrocarbon chain of oleic acid. The region from 1180 to 1350 cm^{-1} contains multiple weak bands that are evidence of fatty acids. The peaks at 1454 and 1465 cm^{-1} are due to CH_3 and CH_2 deformation modes, respectively.

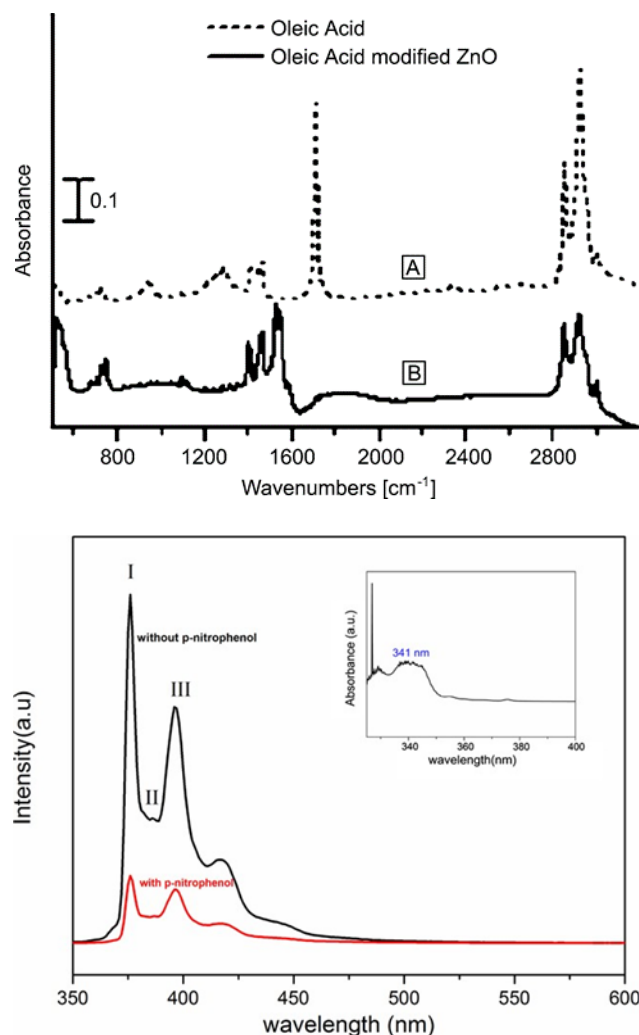


Figure 3 (A) FT-IR spectrum of pure oleic acid, (B) FT-IR spectrum of oleic-acid-modified ZnO nanowires.

All peaks beyond 2800 cm^{-1} , associated with CH_3 , CH_2 and $\text{C}-\text{C}$ stretching modes, remain in the same positions pre- and post-modification. Based on these observations we investigated an appropriate receptor molecule that can then be grafted onto the ZnO nanowire surface through carboxylate bonding while retaining its optical properties to effectively sense nitroaromatic compounds with high sensitivity. Pyrene-based compounds have been used previously for luminescent oxygen sensing, metal-nanoparticle-based chemo-sensors, bio-electrocatalysis, etc. [27–29]. Furthermore, pyrene derivatives exhibit high quantum yield and strong affinity with analyte, which, coupled with an effective photosensitization process, could potentially be exploited to fabricate highly sensitive optical chemo-sensors. Therefore, we believe that ZnO nanowires are promising candidates that, when functionalized with pyrenebutyric acid (a pyrene derivative), have the ability to effectively sense nitroaromatics with detection limit up to ppb ranges. We It was observed that when nitrophenol, the fluorescence of PBA was quenched considerably. Therefore, we firmly believe that a pyrene moiety, post-grafted on the ZnO nanowire surface, will retain its fluorescence characteristics and exhibit similar sensitivity towards nitroaromatics as in the solution phase. The detailed functionalization behavior of PBA on the nanowire surface as well as its mechanism will be the subject of an upcoming manuscript. Based on these preliminary findings, we suggest that ZnO nanowires are a rational choice for fabricating nitroaromatic sensors, if appropriately functionalized with PBA.

Furthermore, forced packing of PBA into films restricts analyte permeability, leading to slow the sensors' response rate.

We envisage that highly sensitive nitroaromatic sensors could be fabricated using PBA functionalized ZnO nanowires, and that fluorescence quenching characteristics such as those of the PBA-*p*-nitrophenol system, can be effectively tuned to sense a wide spectrum of similar analytes.

4. CONCLUSIONS

In this work, ZnO nanowires were synthesized in a customized atmospheric CVD furnace and characterized by FE- SEM, TEM and EDAX. The optical properties of the pristine nanowires were determined by photoluminescence analysis and it was determined that the synthesized nanowires were almost defect-free. Thereafter, surface functionalization studies were conducted with oleic acid, and mode-of- bonding and surface modification characteristics were deduced from Raman and FT-IR analysis. Based on these findings, pyrenebutyric acid (PBA) was identified as a receptor that could be grafted onto the ZnO nanowire surface and subsequently utilized to sense *p*-nitrophenol and other similar nitroaromatic compounds. A detection limit of 28 ppb was shown to be achievable on the ZnO-PBA-*p*- nitrophenol system through photosensitization and fluorescence quenching studies.

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