A facile approach towards ZnO nanorods conductive textile for room temperature multifunctional sensors

Z.H. Lim a, Z.X. Chia a, M. Kevin a, A.S.W. Wong b, G.W. Ho a,∗

a Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive, Singapore 117576, Singapore
b Institute of Materials Research and Engineering, A*STAR (Agency for Science Technology and Research), 3 Research Link, Singapore 117602, Singapore

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A B S T R A C T
Conductive fabric (smart textile) is an important research area since large part of the surfaces that we interact daily is the clothing that we wear. Here, we have demonstrated facile growth of zinc oxide nanorods fabric via a low cost and temperature as well as scalable solution process. The nanorods are grown uniformly, radially oriented and densely covers on each fibre to form a conductive fabric. The uniformity and high crystallinity of the nanorods allow the fabric to be conductive. Mechanical testing of the nanorods-on-fabric devices shows robustness against stress and washing cycles. The conductive fabric shows excellent multiple sensing (gas and optical) performances at room temperature. These ready-to-wear nanomaterials based clothing addresses the possibilities of multifunctional wearable sensors for healthcare, military and environmental applications.

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1. Introduction

Technological and industrial difficulties in further miniaturization of devices have called for innovative ways to incorporate gadgets into articles of everyday life. Clothing is not only a necessity, it also encompasses a complete industry ranging from the down-to-earth basics to the upmarket and chic. While the development of wearable devices has been actively pursued by several groups [1–3], the incorporation of nano-materials into the designs has not been well explored. In addition, problems such as complex process, mass production, washability, and wearing comforts are not well addressed.

The ease of synthesizing ZnO nanowires (NWs) or nanorods (NRs) on almost any substrates [4–6] welcomes large-scale production for a wide range of applications. Particularly, ZnO NWs/NRs on fabric materials have been synthesized and utilised as anti-bacterial coating [7], flexible field emitters [8], superhydrophobic fabric [9] and for energy scavenging [10]. ZnO nano-structures are believed to be non-toxic and bio-safe [11], allowing their direct usage in daily applications. While the use of nano-materials in daily human activities raised questions on its potential health risks, there is to date no in vivo evidence of toxicity of nano-particulate ZnO [12,13].
in style, have the potential of leading towards a new generation of washable and durable smart garments.

2. Experimental

The substrate used in this work is ordinary cotton fabric cut out from a typical fabric lab-coat. The fabric was cleaned in isopropanol, ethanol and deionised (DI) water by sonicating it in respective order for 5 min each. Following which, a 180 nm thick ZnO seed layer was deposited onto the fabric substrate by radio frequency (rf) magnetron sputtering (base pressure $10^{-3}$ mTorr, Argon plasma, rf power 100 W, working pressure 10 mTorr, deposition rate 12 nm/min). It should be noted here that deposition of the seed layer may also be achieved by solution-based methods [6]. ZnO NRs were fabricated via a hydrothermal route with a growth solution containing an equimolar aqueous mixture of 25 mM zinc nitrate and hexamethylenetetramine and 0.1 g of poly(ethyleneimine) (PEI). The seed layer-coated fabric was then immersed in 50 ml of the growth solution contained in a glass bottle sealed with an autoclavable cap and heated at 90 °C for 6 h. PEI was used to enhance the aspect ratio of the NRs. After growth, the fabric was then washed in ethanol and dried. A simple two-terminal resistor device was made by attaching copper wires to the as grown ZnO NRs-on-cloth sample (≈15 × 5 mm) with silver paint (Rs. 186–3600) as shown in Fig. 1. The morphologies of the nanostructures were characterised using scanning electron microscopy (SEM, Jeol FEG JSM 6700 F, secondary electron imaging). The crystallography and structures of the as-synthesized nanostructures were analysed using transmission electron microscope (TEM, Phillips FEG CM300) and X-ray diffractometer (XRD, Philip X-ray diffractometer equipped with a graphite monochromator Cu Kα radiation $\lambda = 1.541 \text{Å}$). The room temperature photoluminescence (PL) of the nanowires was measured with Accent Rapid Photoluminescence Mapping (RPM 2000) with He–Cd laser at 325 nm.

A home-made gas sensing setup was made with vacuum parts connected to gas cylinders of clean dry air (CDA) and hydrogen gas (0.5%, He balanced) coupled with corresponding mass flow controllers to provide controlled environments of variable hydrogen concentrations. Electrical leads from the sample were connected via an electrical feed-through to an external source-meter (Keithley 4200 SCS). Fig. 1 shows the schematic and photograph of the gas sensing setup with a ZnO NRs-on-cloth device sewn onto the shirt of a toy soldier placed in the sensing chamber. In a typical hydrogen sensing experiment, the chamber with the device enclosed was flushed with CDA to create a dry environment for sensing. Current ($I$) were measured in continual time acquisition under a bias source voltage while the environment in the sensing chamber cycled between pure CDA and a programmed hydrogen concentration. Preliminary measurements were made to check the stability of the measured current (reflective of the stable environmental condition in the chamber) before the introduction of the hydrogen gas. Resistance ($R$) across the ohmic device was calculated with $R = V/I$. Response of the device to $H_2$ gas was calculated by

$$\text{Response} = \frac{R_H - R_{CDA}}{R_{CDA}} \times 100\%,$$

where $R_H$ and $R_{CDA}$ are the resistances of the device in the presence of hydrogen and in the dry environment, respectively.

Fig. 1. Schematic and photograph of gas sensing setup. A photograph of a working device sewn on the shirt of a toy is also shown.

Fig. 2. SEM images of (a) cotton fabric substrate in low magnification, (b) bare cotton fibres, (c) ZnO NR-coated cotton fibres and (d) high magnification images of ZnO NRs on a cotton fibre. Scale bar in the inset represents 100 nm. (e) Photograph bare and ZnO NRs coated fabric. (f) Ready-to-wear ZnO NRs-on-fabric multifunctional sensing device sewn on a toy dress.
Fig. 3. (a) XRD spectra of ZnO nanoparticles and NRs. Inset: PL spectra of ZnO NRs. (b) High resolution TEM image showing the high crystallinity of a ZnO NRs. Inset: low resolution TEM image of the ZnO NRs.

where \( R_H \) and \( R_{CDA} \) are resistance of the device in H\(_2\) gas and CDA, respectively.

Electro-mechanical behaviour of the fabric device was analysed using a mechanical testing system (Testometric M250-2.5 CT) coupled with a source-meter (Yokogawa GS 610). The device was first clamped onto the system in the relaxed state and subjected to multiple stress and relaxation cycles by stretching the fabric device with a controlled speed and force. The device was also subjected to manual stretching and twisting cycles (see video in Supplementary Information) and pseudo washing in ultrasonic bath.

3. Results and discussion

SEM images of the fabric and NRs displayed in Fig. 2a–d show radially oriented NRs (diameter \( \sim 80 \) nm) with hexagonal cross-section grown along the cylindrical fibres (diameter \( \sim 15 \) \( \mu \)m). Length of the NRs is \( \sim 1 \) \( \mu \)m. The NRs form a uniform and dense coverage around entire lengths of the fibres to form a cross-linked semi-conductive fabric. Fig. 2e shows a photograph of bare and ZnO NRs coated fabrics. Apart from being slightly less reflective, the ZnO NRs coating effects in minimal change in the macroscopic physical appearance of the fabric. Fabric devices can thus be made and sewn onto clothing as demonstrated in Fig. 2f where the ready-to-wear ZnO NRs device was fashioned as a belt on a toy dress. The successful synthesis of such ordered nanostructures on fabric thus allows easy incorporation of nanomaterials device in our daily life without comprising comfort and style. Furthermore, as we will show later, the NRs shows little or no observable signs of wear and tear after repeated stretching, twisting and washing of the fabric.

XRD spectra of Fig. 3a were obtained from the seed layer (nanoparticles) and one-dimensional NRs. Both spectra exhibit typical diffraction peaks of a well-crystalline wurtzite ZnO structure. In comparison, the diffraction peaks for the nanoparticles are observed to be broader than that of the NRs which corresponds to the well-known Scherrer formula of crystallites particle size decrease with an increase in diffraction peak width. In addition, the nanorod spectra shows a higher (0 0 2) diffraction peak which is consistent with the one-dimensional nanorod formation along the c-axis. The photoluminescence from ZnO consists of two emission bands at room temperature, a near-band-edge (UV) light emission, and a broad, deep-level (visible) emission (Fig. 3a inset). The visible emission is usually associated to various intrinsic defects produced during the growth process while the UV emission is the band-edge emission resulting from the recombination of excitonic centers [22–25]. The yellow-orange deep-level luminescence is characteristic of solution-grown ZnO NRs [22]. Fig. 3b and inset show the low and high resolution TEM image of NRs with well-oriented lattice fringes of interplanar distance \( \sim 0.26 \) nm indicate wurtzite ZnO structure. It is noted that there is an absence of amorphous coating on the surfaces and the NRs grown on the fabric are well-crystalline.

Our fabric sensor displays excellent electrical responses to H\(_2\) gas and UV irradiation as shown in Fig. 4a and b respectively. As-grown ZnO NRs are typically n-type semiconductors due to its intrinsic defect states such as oxygen vacancies and zinc interstitials. When left in air atmospheric ambient, oxygen molecules
adsorbs onto the surface of the NRs:

$$O_2(g) \leftrightarrow O_2(ad). \quad (2)$$

The physisorbed oxygen draws electrons from the conduction band of the surface molecules to form chemisorbed oxygen species of $O_2^-$, $O^-$, and $O^{2-}$. At room temperature, $O_2^-$ is favourably chemisorbed [14,26]:

$$O_2(ad) + e^- \rightarrow O_2^-(ad). \quad (3)$$

The electrons donated from the conduction band to the oxygen adsorbate result in an electron-depleted space charge region at the surface of the NRs. This increases (i) the resistance of the individual NR due to the decreased effective area of the conduction channel and (ii) the resistance of the bulk (of interlinked network of NRs) due to the surface potential barrier formed in the space charge region, inhibiting electron flow across the grain boundaries. In the presence of hydrogen gas, chemisorbed oxygen ions are reduced to release electrons to the conduction band of the ZnO surface.

$$2H_2 + O_2^-(ad) \rightarrow 2H_2O + e^- , \quad (4)$$

resulting in an increase in conductivity. In addition, the reduction reaction decreases the surface density of the oxygen adsorbate, leading to a reduction in the width of the depletion region and the height of the surface potential barrier, thus resulting in the decrease in the resistance of the sensor. Detailed mechanism of hydrogen sensing has been widely reported [14,15,26–28].

The mechanism for UV sensing is similar to that of hydrogen sensing, with holes from the photo-generated electron–hole pairs playing the role of removing the adsorbed oxygen molecules instead. When illuminated with UV light, the photo-generated holes migrate towards the oxygen adsorbates to release the latter off the surface of the NRs reducing the depletion region [14]:

$$h^+ + O_2^-(ad) \rightarrow O_2. \quad (5)$$

This leaves behind unpaired electrons available for conduction leading to an effective decrease in resistance of the sensor. The change in conductivity upon UV-illumination is comparable to that of bare ZnO nanobelts devices fabricated by Lao et al. [29].

While as grown ZnO NRs shows good sensing capabilities to H$_2$ gas, it has been found that coating a thin layer of Pt or Pd metal greatly enhances the response due to the effective catalytic dissociation of H$_2$ to atomic hydrogen on the surface of the metal-coated ZnO NR [16]. For this purpose, we sputtered a thin layer of Pt (nominal thickness of ~5 nm) on the ZnO NRs-on-cloth and observed indeed a significant increased response in H$_2$ gas sensing. As shown in Fig. 5a, response after 10 min exposure of 1000 ppm H$_2$ gas was ~83% compared to 27% without Pt catalyst. Just as the use of a metal (Pt) catalyst can increase the response of ZnO NRs to hydrogen gas sensing, it was found that the ZnO nano-structures functionalized with polymers such as polystyrene sulphate (PSS) and poly N-isopropylacrylaamide has enhanced photo-electronic response compared to pristine ZnO [24]. The role of these polymers is to provide a “hopping states” between the valence and conduction band of ZnO, thereby increase the probability of electron transfer to the conduction band after the photoinduced electron–hole pair generation.

Fig. 5b shows the $I$–$V$ characteristics of ZnO seed layer, ZnO NRs and Pt-coated ZnO NRs-on-cloth devices, in the order of increasing conductivity. Measurements were conducted in room ambient conditions. The increased conductivity of the Pt-coated device compared to that of the as grown is expected. However that mere factor of 2 increase suggest that the Pt do not form a continuous film of Pt across the topology of NRs but rather forms discontinuous islands of nano-particulate deposits on the NRs. We thus believe that the role of the Pt is to catalytically activate the dissociation of hydrogen molecules into hydrogen atoms, which adsorbed onto the ZnO NRs surface to facilitate the reduction of the adsorbed oxygen molecule, thereby increasing the rate of the reaction in Eq. (3).

A notable feature of the ZnO NRs-coated fabric device is its fine morphological and electrical stability under multiple stress and washing cycles. A critical challenge of semi-conductive yarns and fabric is its durability and constancy of electrical performance. To address this issue, we first subject our ZnO NRs-on-cloth to repeated stretching, twisting and pseudo washing (in ultrasonic bath) cycles. SEM analyses (Fig. 6a–d) of the NRs-on-cloth before and after stretching, twisting and washing cycles which shows no cracks or delamination of the NRs from the fibres respectively. Fig. 6e shows a schematic of the electro-mechanical testing. Electrical characterisations made before and after each stretching and twisting cycle (Fig. 6f) show good electrical stability. Video of stretching and twisting of ZnO NRs-on-cloth sample can be found in Supplementary Information. We further perform electrical conductivity measurements while stretching and relaxing the fabric device in a controlled manner. To the best of our knowledge, this is the first electromechanical study of ZnO NRs-coated fabric. Interestingly the semiconducting fabric exhibits a higher conductivity when stretched. This is explained by the tighter packing of the ZnO NRs-coated fibres in the stretched fabric sample, resulting in more contacts between the NRs network. When the stress is released, conductivity falls and stabilises to the original state. Again the
Fig. 6. SEM images of (a) low resolution ZnO-NRs-coated fabric with selected area (circled in red) for subsequent studies (b) the selected ZnO Nrs-coated yarns before stretching, twisting and sonication, (c) the same yarns after repeated stretching and twisting and (d) 5 min of water sonification. (e) Schematic diagram of the electromechanical testing and (f) electrical properties before and after each stretching and twisting cycle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 7. Electrical measurement of ZnO NRs-on-cloth device while subjected to controlled stress cycles with a mechanical testing system.

4. Conclusion

In summary, we have successfully fabricated ZnO NRs on fabric and have utilised them as ready-to-wear fabric multifunctional sensors. The response and selectivity of the device may be enhanced and tuned with the additives such as Pt-catalyst for hydrogen sensing. The morphology and electrical characteristic of the NRs-on-fabric device are found to be robust against mechanical handling. The low cost and scalable fabrication process, room...
temperature sensing capabilities and non-toxicity of the ZnO NRs-on-cloth device bode well a delightful marriage between fashion and nanotechnology.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.snb.2010.09.037.

References


Biographies

Z.H. Lim is currently Research fellow in National University of Singapore. He received his M.Sc from Physics Department, National University of Singapore. His current research work is on the nanostructured materials for sensors and transistors applications.

Z.X. Chia is currently a bachelor degree (honours) student from Electrical and Computer Engineering, National University of Singapore. His current research work is on the oxide nanomaterials for various sensors applications.

M. Keven is currently M. Eng. student in National University of Singapore. He received his Bachelor (honours) degree in 2008 in Electrical and Computer Engineering, National University of Singapore. His current research work is on the thin films and nanomaterials for nanoelectronics applications.

A.S.W. Wong received his Ph.D. degree from the Department of Materials Science and Engineering at the University of Cambridge in 2006. His current research interests are thin film solar cell, sensors and electron microscopy.

G.W. Ho is an assistant professor of Electrical and Computer Engineering in National University of Singapore. She received her Ph.D. degree in Engineering from Nanoscience Centre, University of Cambridge in 2006. M.Sc. and B.Sc. from National University of Singapore in 2001. Her current research is focused on the study of the phenomena and manipulation of material at the nanoscale which revolves around the realization of solar cell, chemical sensor and energy harvesting systems.