Low-temperature seeding and hydrothermal growth of ZnO nanorod on poly(3,4-ethylene dioxothiophene):poly(styrene sulfonic acid)

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Abstract: This work reports a low-temperature seeding process for hydrothermal growth of ZnO nanorods on flexible polymeric materials. The process involved decomposition of zinc (II) amine complex below 100 °C to form ZnO seeds, followed by hydrothermal growth using zinc nitrate hexahydrate and hexamethylenetetramine under 90 °C. The method enabled the growth of ZnO nanorods on the polymeric film (e.g. PET) or the p-type conducting polymer poly(3,4-ethylene dioxothiophene):poly(styrenesulfonic acid) (PEDOT:PSS) film. The UV response of the ZnO/PEDOT:PSS nanostructure was investigated.

Keywords: ZnO nanorods, low temperature seeding, hydrothermal, conducting polymer, UV sensor.

1. Introduction

Zinc oxide (ZnO) is an n-type semiconducting material with wide direct band gap (3.37 eV), high exciton binding energy (60 meV), and piezoelectric and pyroelectric properties. One-dimensional ZnO nanomaterials (such as nanorods, nanowires, nanofibers, nanobelts and nanotubes, *etc.*) have been explored for various applications such as photocatalysis, photovoltaics, electronics, and biosensors [1, 2]. Recent interests in ZnO nanorods for flexible and wearable electronics require synthesis of nanorods on polymeric or elastomeric substrates [3-5], which may be challenging for the existing preparation methods [6, 7]. For example, in the hydrothermal growth of the ZnO nanorods, although the reaction condition is mild (<100 °C), a ZnO seeding process that involves decomposition of the zinc salts at temperature higher

than 200 °C is required prior to the hydrothermal growth [7, 8]. Alternatively, ZnO nanoparticles can be used as the seeds for hydrothermal growth on flexible/polymeric materials [9]. This two-step method may lead to inconsistency in growth of vertically aligned ZnO nanorods from batch to batch because of the aggregation of ZnO nanoparticles in dispersion.

The hybrid material of the n-type ZnO nanorods and p-type conducting polymer Poly(3,4-ethylene dioxithiophene):poly(styrenesulfonic acid) (PEDOT:PSS) may have interesting optoelectronic properties/applications [10, 11]. Typically, the ZnO/PEDOT:PSS hybrid materials are prepared by introducing the ZnO nanorods/nanoparticles into the PEDOT:PSS dispersion followed by spin-coating, or by coating a layer of PEDOT:PSS on the top of the ZnO nanorod arrays [12, 13]. Preparation of ZnO nanorods on the PEDOT:PSS film is difficult because of the stringent condition of ZnO growth.

In this letter, we report a simple and well-controlled process to grow the vertically aligned ZnO nanorods directly on the PEDOT:PSS film. The process involved decomposition of zinc (II) amine complex below 100 °C to form ZnO seeds, followed by hydrothermal growth using zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine (HMTA) under 90 °C. The method allowed to grow ZnO nanorods on polymeric film (e.g. PET) or PEDOT:PSS. The hybrid material of ZnO nanorod/PEDOT:PSS prepared by the low-temperature seeding and hydrothermal growth was further investigated as an ultra-sensitive ultraviolet (UV) photosensor.

2. Materials and Methods

Materials: Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) dispersion, 4-dodecylbenzenesulfonic acid (~90%), ethylene glycol (anhydrous, 99.8%), zinc oxide hydrate ($\text{ZnO} \cdot x\text{H}_2\text{O}$, 97%), ammonium hydroxide solution (28.0-30.0% NH_3 basis), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%), and hexamethylenetetramine (HMTA, 99%) were purchased from Sigma Aldrich and were used as received.

Preparation of ZnO nanorod/PEDOT:PSS hybrid nanostructure: Figure 1 shows the synthesis route schematically. First, the substrate (glass or PET film) was cleaned in detergent, DI water, acetone, and isopropanol under sonication for 15 minutes each. Then, PEDOT:PSS solution was prepared by

mixing 8.0 g PEDOT:PSS dispersion with 2.0 g ethylene glycol and ~0.2 ml of 4-dodecylbenzenesulfonic acid. Then, the PEDOT:PSS film was spin-coated on the substrate and patterned into a long stripe with width of 3 mm and length of 25 mm by wiping off the excess material (Figure S1a). The PEDOT:PSS stripe was then baked in a vacuum oven at 100 °C for 10 hr. Subsequently, a small part of the PEDOT:PSS stripe (3 mm wide and 4 mm long) was seeded by spin-coating of the $[\text{Zn}(\text{OH})_x(\text{NH}_3)_y]^{(2-x)+}$ (0.05 M) aqueous solution (prepared by dissolving the $\text{ZnO} \cdot x\text{H}_2\text{O}$ powder in a concentrated ammonia solution) followed by annealing at 100 °C for 1 hr. The seeding process was repeated 5 times to achieve a good coverage of the ZnO seeds. Finally, the seeded substrate was immersed in the $\text{Zn}(\text{NO}_3)_2$ and HMTA aqueous solution to grow the ZnO nanorods *via* a hydrothermal method. As shown in Figure S1b, the ZnO nanorods were grown selectively on the seeded area of the PEDOT:PSS film. After the hydrothermal reaction, the sample was washed with isopropanol and then dried by N_2 .

Characterization: The morphologies and structures were characterized by Field Emission Scanning Electron Microscopy (FE-SEM, Zeiss Supra 40 VP) and High-resolution Transmission Electron Microscopy (HR-TEM, Hitachi H-7000 FA with a Kevex energy-dispersive X-ray spectrometer). The current-voltage characterization of the device was performed using Keithley 2612 Source Meters. A 365 nm ultraviolet lamp was used as the light source, and the light intensity was modulated with a neutral density filter (Ocean Optics) and was measured with a photometer.

3. Results and Discussions

The zinc(II) amine complex was chosen as a seeding precursor because of its low decomposition temperature. The complex could be decomposed to form ZnO nanoparticle seeds at temperature as low as 90 °C [14]. The low decomposition temperature was ideal for seeding of the ZnO nanoparticles on the polymeric materials. The *in situ* annealing of the spin-coated precursor on the PEDOT:PSS (or PET) film results in homogeneous coverage of the ZnO seeds *via* physical adsorption. Figure 2a and 2b shows the SEM images of a spin-coated pristine PEDOT:PSS film and PEDOT:PSS film coated with the ZnO seeds, respectively. No pronounced morphological difference between the seeded and neat PEDOT:PSS films was observed. Energy dispersion spectrum (EDS) and the elemental quantitative

data of the PEDOT:PSS film and the ZnO seeds/ PEDOT:PSS on a silicon substrate in Figure S2 confirms the formation of ZnO on the PEDOT:PSS film after the low-temperature seeding process. A TEM image in Figure 2c shows that the ZnO seed layer composed of many well-connected ZnO grains with the sizes of ~10 nm. The high-resolution TEM (HRTEM) image (Figure 2d) shows that the lattice spacing of the crystalline grains was about 0.26 nm, consistent with that of the (101) plane of the wurtzite crystal structure of ZnO [2, 14]; and the selected area electron diffraction (SAED) image (inset of Figure 2d) indicates that the ZnO seed layer was polycrystalline.

The concentration of $\text{Zn}(\text{NO}_3)_2$ and HMTA, hydrothermal reaction temperature, and reaction time were optimized for the ZnO nanorod growth (see text and Figures S3, S4, S5 in Supplementary material). Upon the optimization, the concentrations of 0.050 M for both $\text{Zn}(\text{NO}_3)_2$ and HMTA, hydrothermal reaction temperature of 90 °C, and reaction time of 5 hr were selected for growth of the ZnO nanorods on PEDOT:PSS film. Figure 3a shows a photo of the as-synthesized ZnO nanorods/PEDOT:PSS on a transparent and flexible PET film. The top and cross-sectional SEM images (Figures 3b and 3c) show that the hexagonal wurtzite ZnO nanorods with the average length of ~2 μm and diameter of ~200 nm were uniformly synthesized on the PEDOT:PSS film. TEM (Figure S6) and HRTEM (Figure 3d) images reveal that the ZnO nanorods were grown along [0001] direction and the fringe spacing of (001) planes was about 0.52 nm. The value is consistent with the c lattice constant of the ZnO wurtzite crystal structure [2]. HRTEM image and electron diffraction pattern (inset of Figure 3d) confirms that the synthesized ZnO nanorods were single crystals.

The UV photoresponse of the ZnO/PEDOT:PSS nanostructure was tested using a device configuration shown in Figure 4a. Silver paste was used to form the two electrode contacts that were 4 mm apart. It is worth noting that the silver paste electrodes were not in contact with the ZnO nanorods of the device. The width of the PEDOT:PSS strip was 3 mm, and the thickness of the film was ~50 nm. The current through the PEDOT:PSS film was measured when the device was exposed to the UV light. Figure 4b presents the current-voltage (I-V) curves of the pristine spin-coated PEDOT:PSS film, the PEDOT:PSS film after hydrothermal treatment, and the ZnO nanorod/PEDOT:PSS film (in dark). The

conductivities of the pristine PEDOT:PSS, the PEDOT:PSS after the hydrothermal reaction, and the ZnO/PEDOT:PSS (in dark) were 10.06 S/m, 7.04 S/m, and 0.27 S/m, respectively. The hydrothermal growth conditions decreased the conductivity of the PEDOT:PSS film by about 30%, likely due to the neutral and slightly basic reaction solutions. Growth of the ZnO nanorods on the PEDOT:PSS film led to more than an order of magnitude decrease of the conductivity of the ZnO nanorod/PEDOT:PSS film. The I-V curves of the ZnO nanorod/PEDOT:PSS device under various UV ($\lambda=365$ nm) light intensities are shown in Figure 4c. The linear I-V curves indicated that the device had Ohmic contacts. The current increased with increase of the UV intensities; the current of the device in dark was about 0.10 μ A at the bias voltage of 10 V, whereas it increased to about 0.75 μ A when irradiated under 450 μ W/cm² UV intensity. Figure 4d shows the dynamics of the current response of the device at a bias of 10 V to the various UV light intensities. An increase of the current was observed under UV intensity as low as 2 μ W/cm² (Figure S7); the photocurrent increased linearly until ~ 100 μ W/cm², and then gradually saturated for the UV light intensity above 150 μ W/cm². The rising time of the photocurrent under UV irradiation was less than 30 seconds; the decay time of the photocurrent after turning off the UV irradiation was about two orders of magnitude longer than the rising time. For example, under the UV intensity of 450 μ W/cm², the rising time was 18 seconds while the decay time was 2600 seconds (Figure S8).

Typically, the conductivity of ZnO is modulated by the photo-generated carriers under UV exposure in a ZnO-based UV sensor [5, 15]. The device of ZnO nanorod/PEDOT:PSS shown in Figure 4a may have a different mechanism for the UV photoresponse. In the ZnO/PEDOT:PSS UV sensor, the charge transport of the PEDOT:PSS film is modulated by UV light, and the ZnO nanorods serve as an antenna to generate charge carriers. Since ZnO is a n-type semiconductor and PEDOT:PSS is a p-type conducting polymer, a depletion layer is formed at the interface of the ZnO nanorod and the PEDOT:PSS, leading to significant decrease of the conductivity of the material in dark, as observed in Figure 4b. The dark current is dominated by the conduction through the PEDOT:PSS film. Under the UV irradiation, the photo-generated holes are known to react with the negatively charged O₂⁻ on the ZnO surface to release the trapped electrons, leading to increase of the free electrons and the resultant conductivity of ZnO [15].

The increased number of electrons in the ZnO nanorods under UV irradiation might have two effects: the photo-generated electrons would further deplete the ZnO/PEDOT:PSS interface, leading to decrease of the conductivity of PEDOT:PSS; on the other hand, the increased photoconductivity of the ZnO nanorods might dominate the conduction of the device, resulting in increase of the device photocurrent. The thickness and the conductivity of the PEDOT:PSS film, as well as the UV light intensity, may be the major factors to affect the photoresponse of the device. Work to understand the fundamental device physics of the ZnO/PEDOT:PSS sensor is ongoing.

4. Conclusions

In summary, ZnO nanorods were vertically grown on the conducting polymer PEDOT:PSS film *via* low temperature seeding followed by hydrothermal growth. ZnO nanoparticle seeds were prepared on the PEDOT:PSS film by decomposition of a zinc(II) amine complex at 100 °C, and the following ZnO nanorods were grown in zinc nitrate and hexamethylenetetramine solution at 90 °C. The conductivity of the ZnO/PEDOT:PSS film was reversibly modulated under UV intensity as low as 2 $\mu\text{W}/\text{cm}^2$. The preparation method can be readily used to grow the ZnO nanorod on various flexible substrates (e.g., plastic films, polymer fibers), leading to potential applications of the ZnO/PEDOT:PSS materials for flexible and wearable electronics and sensors.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at
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Figure 1. Schematic of hydrothermal growth of the ZnO nanorods on the PEDOT:PSS film.

Figure 2. SEM images of a) pristine PEDOT:PSS film and b) the seeded PEDOT:PSS film; c) TEM image of the ZnO seeds; d) High-resolution TEM image of the ZnO seeds, inset shows the SAED image.

Figure 3. a) ZnO nanorod/ PEDOT:PSS on a flexible PET substrate; b) Top view SEM image of ZnO nanorods grown on PEDOT:PSS (Inset: image of a single hexagonal ZnO nanorod); c) Cross-sectional view SEM image of the ZnO nanorod array grown on PEDOT:PSS; d) High-resolution TEM (HRTEM) image and electron diffraction pattern (inset) of a ZnO nanorod.

Figure 4. a) Schematic of the ZnO nanorods/ PEDOT:PSS device for UV sensing; b) The current–voltage (I - V) curves of the spin-coated pristine PEDOT:PSS, the PEDOT:PSS after hydrothermal treatment, and the ZnO nanorod/ PEDOT:PSS (in dark); c) The I - V curves of the ZnO nanorods/ PEDOT:PSS under UV irradiation with different intensities (from bottom to top: dark, 2 μW/cm², 10 μW/cm², 36 μW/cm², 57 μW/cm², 150 μW/cm², and 450 μW/cm²); d) Time dependence of the current measured at the bias voltage of 10 V under varied UV light intensities.

Graphical abstract

Low-temperature seeding allows hydrothermal growth of the ZnO nanorods on the conducting polymer PEDOT:PSS film, which leads to an UV sensor based on the change of the conductivity of the ZnO nanorods/PEDOT:PSS film.