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Density- and adhesion-controlled ZnO nanorod arrays on the ITO flexible substrates and their electrochromic performance

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ABSTRACT

We report large-scale density- and adhesion-controlled ZnO nanorod arrays (NRs) directly grown on flexible ITO/PET substrates and have studied their absorption capability to viologen molecules and electrochromic performance. The density can be readily controlled by adjusting the thickness of pre-preparated ZnO seed layers. And the adhesion property of the ZnO NRs to substrates can be controlled by different methods of pre-preparation ZnO seed layer. The effect indicates that the ZnO NRs using sputtering-prepared seed layers show superior adhesion property to substrate and resistance capacity to ultrasonicating and bending when compared with the spin-coated method. Moreover, it has been found that the ZnO NRs, with optimum density and occupied space ratio (OSR) (density, $\sim 3.34 \times 10^9$ rods cm^{-2}; diameter, ~140 nm; and OSR, ~52%), demonstrate optimal absorption capability to viologen molecules and excellent electrochromic performance.

1. Introduction

ZnO nanorod arrays (NRs), as an excellent member in the family of one-dimensional (1D) nanostructures, have been received increased attention because of their excellent electrical and optical properties. Moreover, it has been found that spectacular applications in fabricating electronic, optoelectronic, electrochemical, and electromechanical devices such as ultraviolet (UV) lasers [1], light-emitting diodes [2], field-emission devices [3–6], field effect transistors, transparent conductors [7], solar cells [8] and piezo-nanogenerators [9,10], especially in the field of electrochromic devices (ECs) [11] including flexible and transparent ECs, have also showed considerable merit owing to reversibly changing their optical properties upon charge injection and extraction induced by the external voltage. Due to the ECs' quick response time and great repeatability, low operation voltage and energy consumption, high coloration efficiency and rich color availability, flexible substrate and large scale but lightness of weight, and long open circuit memory effects, enabled them to possess many potential applications including electrochromic (EC) displays, smart windows, electropapers and electrobillboards [11–14].

It is well known that one-dimensional ZnO nanostructure materials (e.g., ZnO NRs) are excellent working electrodes of the ECs made of one working electrode, one counter electrode, and one ion conductive layer in between because of their large surface area [11], high crystallization performance and good electron transport properties. Furthermore, ZnO, as a nontoxic n-type semiconductor (Eg = 3.37 eV), is even more attractive for high-efficiency short wavelength optoelectronic nanodevices on account of its large exciton binding energy of 60 meV and high mechanical and thermal stabilities. On the other hand, ZnO is a wide band gap II–VI semiconductor and a cheap and nontoxic material. Utilization of ZnO in ECs may further reduce the cost. However, there are few reports on the fabrication of density- and adhesion-controlled ZnO NRs on flexible ITO/PET (indium tin oxide/polyethylene terephthalate) transparent substrate (IPS), though lots of papers have focused on fabrication of ZnO nanostructures [6,15–18].

In this communication, we embarked on for the first time a study that the large-scale ZnO NRs were grown directly on flexible IPS, especially more attention was paid to investigate the density, occupied space ratio (OSR) and adhesion property to the substrate of ZnO NRs. Meanwhile, relevant kinetics conditions of NRs growth were discussed as well, including concentrations and ratios of the starting reactants, such as zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) to hexamethylenetetramine ($C_6H_{12}N_4$), and including the growth temperature and time. And then, EC performance study was divided into two steps, modifying methyl viologen and exploring EC performance using three electrodes sys-

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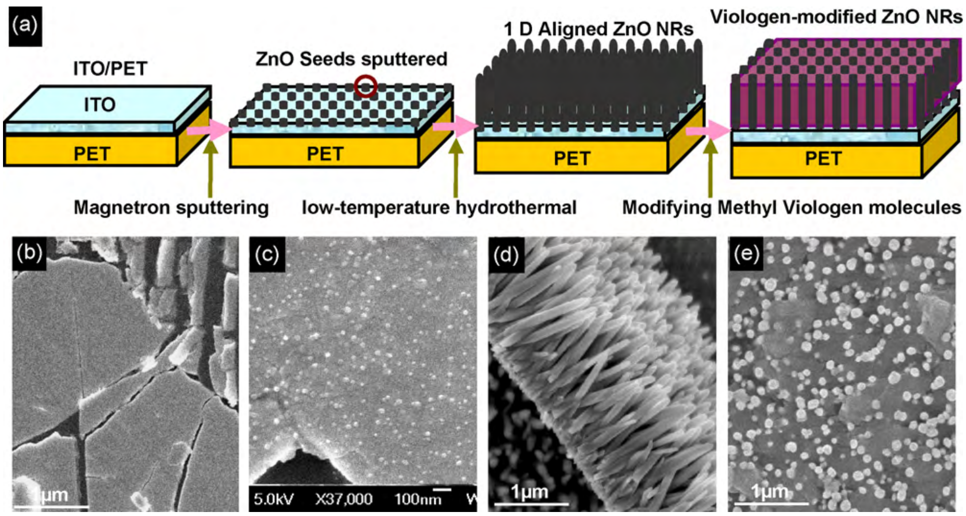

Fig. 1. (a) The schematic approach of growing ZnO NRs on IPS and modifying with viologen molecules, (b) before and (c) after sputtering ZnO seed layers on the original IPS, (d) the image after growth 1D vertically aligned ZnO NRs on (c), and (e) the image after (d) modified methyl viologen molecules.

tem. SEM, TEM and XRD were also employed to characterize the ZnO NRs.

The novel ZnO NRs grown on IPS have at least three advantages. First, it provides a way to fabricate vertically aligned ZnO arrays on flexible IPS. Second, the flexible substrates could be easily designed into various sizes and shapes, and thus providing tremendous flexibility for ZnO NRs' applications. Third, these unique advantages make ZnO nanorods a promising matrix electrode for EC dye molecule loading.

2. Experimental

All chemicals (from Shanghai Chemicals Co. Ltd.) used in this work were of analytical reagent grade and used as received without further treatments.

2.1. Preparation process

The viologen-modified ZnO NRs (VMZs) EC working electrodes were achieved by three main steps. The first step was that a thin layer of ZnO film, about 4–5 nm thickness, was deposited on the IPS as seed using spin-coating or sputter-coating method [11] before the growth of ZnO NRs. The coating solution was obtained by mixing 0.03 M NaOH solution of ethanol and 0.01 M zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) solution of ethanol, the volume ratio is 1–3, and then the coating solution was spin-coated onto IPS at 500 rpm for several times according to the expected thickness of ZnO seed layer [19], and between every two layers, the seeded IPS was subsequently baked for about 15 min in oven at 50 °C. With regard to magnetron sputtering method, the ZnO seed layer was readily obtained by FJL560 magnetron sputtering equipment, and which was deposited at a distance of 57 mm between target and IPS, a base vacuum of 5×10^{-4} Pa, a sputtering power of ~55 W, an argon pressure of 0.5 Pa and ~80 s sputtering time. Different density ZnO NRs were obtained mainly by adjusting the sputtering time. The second step was the growth of, as we know, the ZnO nanostructure array was hydrothermally prepared using the procedures reported elsewhere [6,20–22]. In our work, the seeded IPSs obtained from the first step were suspended in 300 mL of aqueous solutions containing 0.05 M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.06 M $C_6H_{12}N_4$ in a sealed beaker [23] following by heating at a temperature of 75 °C for 24 h. Changing the molar ratio of reactants, the growth temperature and time resulted in the formation of 1D ZnO NRs with different densities and OSRs. Slight stirring was maintained throughout the entire process. After the reaction, these substrates covered tightly with ZnO nanostructures were rinsed with ethanol and dried in air for further characterization. Finally, the as-grown ZnO NRs of different densities and OSRs were first treated by oxygen plasma for 5 min and baked in an oven at 60 °C for 1 h. Then these arrays were immersed in a 0.02 M aqueous solutions of methyl viologen at 40 °C for 72 h, followed by a wash with 2-propanol to remove the unattached viologen. Subsequently, the VMZs electrodes were dried in air and stored in a vacuumed dark chamber for 24 h prior to use.

2.2. EC performance

The VMZs of different OSRs were assembled as working electrodes of the three electrodes system and immersed in an electrolyte containing 0.2 M $LiClO_4$ γ-butyrolactone solution. Then the EC photographs and EC current potential (CV) curves of the various electrodes were obtained for further research. It is worth pointing out that all the chemical materials and the electrolytes were bubbled with dry N_2 prior to the experiment since the performance of the EC is sensitive to oxygen.

2.3. Characterization

The morphology, size and property of the products were characterized by field-emission scanning electron microscopy (FESEM, JEOL, JSM-6700F), and the identity and the phase were analyzed using an X-ray diffractometer (XRD, Cu Kα radiation; $\lambda = 1.5418$ Å) at a scan rate of $0.06\,s^{-1}$. The selected area electron diffraction (SAED) pattern, transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) observations of the products were all carried out on a JEOL JEM-2010 instrument. The cyclic voltammograms (CVs) of the ZnO nanowire electrode were recorded by a CHI660C electrochemical instrument, and the test was carried out in a standard three electrodes system (vs Ag/AgCl sat. KCl reference electrode).

3. Results and discussion

3.1. Schematic approach and images of EC working electrode

Herein, the formation mechanism of the VMZs is schematically illustrated in Part a of Fig. 1 and its corresponding FESEM images in Parts b–e of Fig. 1 (some big cracks in Fig. 1b and c made for the comparison with their substrates). Part b of Fig. 1 shows the bare IPS. Through the pre-sputtering process on Part b, a thin layer ZnO seed made of little crystalline nanoparticles with a diameter of 10–20 nm was coated on the IPS, as shown in Part c of Fig. 1. And then, Part d of Fig. 1 shows the ZnO NRs grown using a low-temperature hydrothermal decomposition method. Finally, the VMZs used as EC working electrode is shown in Part e of Fig. 1.

3.2. Morphology and microstructure

The top-view and cross-sectional scanning electron microscopy (SEM) images of the as-prepared ZnO NRs on IPS can be clearly shown in Fig. 2 (Fig. 2a, the low-magnification; Fig. 2b, the relatively high-magnification with two inserts: the regular cross-section and magnificent enhanced images). ZnO NRs is characterized by large-area hexagonal ZnO nanorod arrays with uniform growth density, and it was obtained by using the mixing solution of 0.05 M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.06 M $C_6H_{12}N_4$ at 75 °C for 24 h.

XRD patterns of the above-mentioned ZnO NRs are summarized in Fig. 2c. The strongest peaks are (0 0 2), indicating that individual ZnO nanostructures and crystallized along the *c*-axis direction