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Seed-free electrochemical growth of ZnO nanotube arrays on single-layer graphene

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ABSTRACT

Dense and vertical ZnO nanotubes were directly grown on single-layer graphene by convenient electrochemical deposition method, without ZnO seed layer, O_2 bubbling, electrolyte assistance, or additional etching process. The formation of the ZnO nanotubes was governed by the self-etching process with H^+ generated during the growth process. The hole depth of the nanotubes can be controlled by adjusting deposition time. The nanotubes have weak visible luminescence intensity in photoluminescence spectrum, indicating excellent crystalline properties. The transmittance of the nanotubes on graphene/glass electrode was above 75% over entire visible range.

1. Introduction

One-dimensional (1D) ZnO nanostructures on graphene electrode have attracted much attention because of their potentials for applications in various transparent and/or flexible optoelectronic devices [1–3]. In the hybrid ZnO–graphene structures, graphene, highly conductive monolayer of graphitic carbon, can be used as the transparent and flexible electrode [2–4]. In addition, 1D ZnO nanostructures, as transparent semiconductor with direct band gap of 3.37 eV, can provide flexible and transparent components for the optoelectronic devices [2,5]. To date, significant efforts have been devoted to the synthesis of ZnO nanorods (NRs) on graphene and their applications [1,3,6–10]. Compared to NRs, tubular structure is expected to offer enhanced performance in many applications such as photoluminescence, solar cells, and sensors, due to its larger specific surface area and higher porosity [11,12]. However, ZnO nanotube (NT) vertical arrays on graphene have not been reported yet.

Electrochemical deposition, which has advantages including simplicity, low cost, and rapid growth at low temperature, has become one of the most popular approaches for fabricating ZnO NTs [12–17]. The current methodologies involved both the conversion of nanorods into nanotubes via additionally chemical etching process [12–14] and directly electrochemical growth [15–17]. An additional etching process makes synthesis complicated, and may cause corrosion problems or bring impurities to ZnO. However, previous reports of ZnO NTs synthesized by a direct growth method still utilized AAO template [17] or additives [15,16].

ZnO film was electrodeposited by Izaki and Omi using nitrate ions without any electrolyte assistance or O_2 bubbling [18]. This method is remarkably simple and prevents the chemical contamination of ZnO from additives. Herein, we utilize this simple approach for growing single-crystal ZnO NT arrays directly on graphene electrode for the first time from $Zn(NO_3)_2$ aqueous solution without additional ZnO seed layer, etching additives, or gas bubble. The obtained NT arrays are vertical and exhibit outstanding transparency. The depth of the hole can be controlled by adjusting reaction time. Such ZnO NT/graphene hybrid structure may have potentials for highly transparent optoelectronic nanodevices.

2. Experiments

Single-layer graphene was grown on Cu foils by chemical vapor deposition method [19] and then transferred to glass slide by virtue of PMMA coating in Marble Cu etching reagent. Finally, PMMA layer was removed by acetone. The electrochemical growth of ZnO nanotubes (NTs) on a graphene substrate was carried out in a three-electrode cell at 90 °C using a saturated calomel electrode (SCE), graphite sheet and graphene on glass (G/G) as reference, counter, and working electrode, respectively. During the electrochemical growth, the electrolyte solution (10 mM $Zn(NO_3)_2$) was kept stable without stirring and a current density of -0.5 mA/cm^2 versus the SCE reference electrode was applied on the graphene electrode for 3 h.

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The morphology and microstructure of the NTs were investigated by field emission scanning electron microscope (FESEM, JEOL JSM6700F), transmission electron microscope (TEM, JEOL JEM2100F), and X-ray diffractometer (XRD, Bruker D8 Discover) with Cu Kα radiation. Photoluminescence (PL) spectroscopy was conducted at room temperature using a He–Cd laser. A UV–vis 3600 spectrometer was used to examine the optical transparence. The Raman spectrum was recorded using 514 nm laser source (RM1000-Invia, Renishaw).

3. Results and discussion

Fig. 1(a) and (b) shows optical micrograph and Raman spectrum of the graphene film transferred onto 500 nm SiO_2/Si wafer, respectively. The optical micrograph shows that the graphene has excellent uniformity and continuity over a large area. Fig. 1(b) reveals that the monolayer graphene with ~0.5 intensity ratio of band G (~1587 cm^{-1}) to 2D (~2690 cm^{-1}) was obtained [19]. Using the highly conductive single-layer graphene as a transparent electrode, dense and vertical ZnO NTs were electrochemically grown directly on the single-layer graphene without ZnO seed layer, O_2 bubbling, electrolyte assistance, or additional etching process. The optical image of ZnO NTs grown on a graphene/glass plate (G/G) demonstrates that ZnO can be grown on large-scale graphene surface with high transparency (Fig. 1(c)). A typical top-view FESEM image of the as-grown ZnO NTs shows that aligned NT arrays were successfully deposited onto the G/G with high density (Fig. 1(d)). The high resolution image (inset of Fig. 1(d)) reveals that the obtained ZnO NTs possess hexagonal morphology with a diameter of 200–300 nm and wall thickness of 40–50 nm. The cross-sectional image in Fig. 1(e) demonstrates that the NT arrays are perpendicularly aligned onto the graphene film, with an average length of about 2.0 μm and uniform diameter from bottom to top for arbitrary ZnO NT. A representative TEM image (inset of Fig. 1(f)) further confirms the tubular structure of ZnO with outer and inner diameters of about 300 and 200 nm, respectively, consistent with the SEM observations. From the HRTEM image and selected area electron diffraction (SAED) pattern of single NT shown in Fig. 1(f), it was found that the ZnO NT is single crystalline and grows along [0001] direction with a lattice distance of 0.52 nm, which is indexed to the wurtzite hexagonal structure without dislocations and stacking faults.

Fig. 2(a) shows the XRD pattern of the NTs on G/G substrate. All the diffraction peaks can be indexed as the hexagonal wurtzite ZnO structure (JCPDS card no. 36-1451). It is clearly observed that the intensity of (002) diffraction peak is much stronger than other peaks in the XRD pattern, which implies that the as-grown ZnO NTs are highly oriented with their *c*-axis being perpendicular to graphene electrode [14]. The optical properties of the NTs were examined by UV–vis and PL spectroscopy at room temperature. The NTs on G/G show one strong and sharp peak centered at ~382 nm (Fig. 2(b)), which is attributed to ZnO near-band-edge (NBE) emission. The very weak peak associated with crystalline defects in visible region indicates that the as-grown ZnO NTs have high crystallinity and chemical purity. The optical transparency spectra of G/G and the ZnO on G/G are shown in Fig. 2(c), where both samples show high transparency in the wavelength range of 400–1200 nm, with a transmittance of above 95% for graphene and 75% for the ZnO on graphene. The highly transparent ZnO NTs/graphene hybrid structure may be effectively integrated in various transparent optoelectronic nanodevices.

In order to investigate the formation mechanism of ZnO NTs, the controlled experiments were conducted by varying electrodeposition time. Fig. 3 shows SEM images of the samples obtained from different reaction intervals. ZnO NRs were formed on graphene electrode when electrochemical deposition lasted 2 h (Fig. 3(a)). Interestingly, the core of the NR end was found to be partially dissolved as the deposition proceeded for 130 min (Fig. 3(b)). The depth of the hole increased to hundreds of nanometers with deposition time further increasing (Fig. 3(c)). Complete tubular structure was finally obtained after 3 h, as shown in Fig. 1(d) to (f). The reaction nearly stopped at this stage probably due to the increase of resistance after growth of the ZnO semiconductor [15].

It is well known that ZnO can be dissolved by H^+, and it is easier to etch the metastable polar crystal plane (001) of wurtzite ZnO with H^+ than other non-polar facets, which can result in the formation of tubular structure [20]. Based on the experimental results, the growth of ZnO NTs could be ascribed to selective self-etching of NRs, as shown in Fig. 4(a). According to the chemical reactions in our current electrochemical deposition system (Fig. 4(b)), there are two competitive reactions including ZnO growth on cathode and ZnO etching by H^+ generated from anodic oxidation of water [20,21]. The growth of ZnO NRs is predominant within the initial 2 h, whereas, with reaction proceeding, concentration of H^+ increased and etching became the main process.

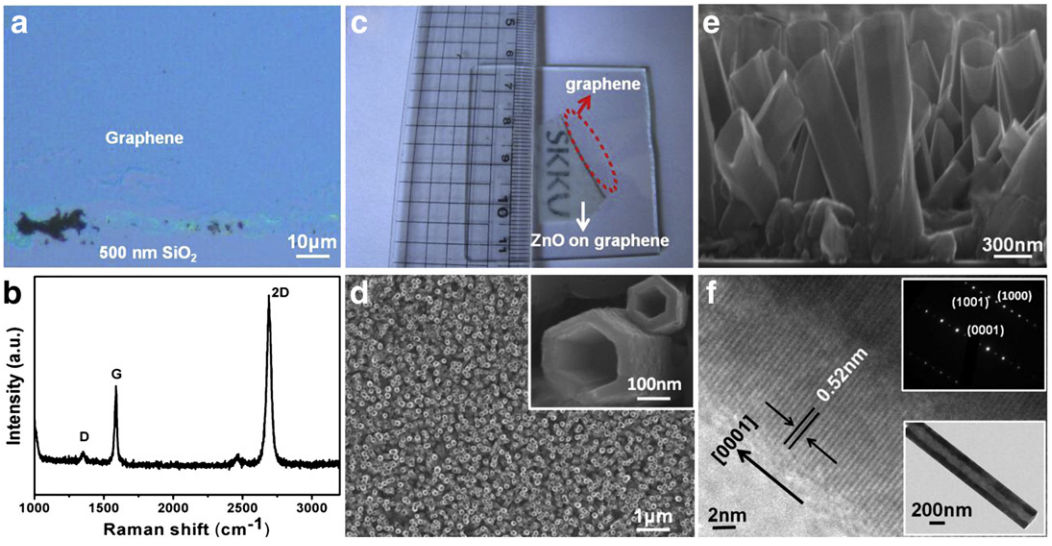

Fig. 1. (a) Optical microscope image and (b) micro-Raman spectrum of graphene on 500 nm SiO_2/Si wafer. (c) Photograph, (d) top-view FESEM image (the inset is a high resolution view), (e) cross-sectional SEM image, and (f) HRTEM image (the insets show the SAED pattern and low resolution TEM image) of the ZnO NTs electrodeposited on graphene/glass.