TUNING ZINC OXIDE NANORODS ON SiO_2 SUBSTRATES BY INCORPORATING GRAPHENE

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In this study, graphene was added into the ZnO seed layer and spread on the substrate to tune the aspect ratio of ZnO nanorods (NRs) on SiO_2 substrates, respectively. Compared with ZnO NRs with sol gel/hydrothermal growth in a normal condition, the aspect ratio of ZnO NRs could be enhanced by incorporating graphene into the seed layer. Furthermore, the c-axis crystallinity and hydrophobic properties could be strengthened, too. On the other hand, ZnO NRs grown on graphene/SiO_2 substrate exhibited lower aspect ratio but stronger antibacterial capability. These graphene-incorporated ZnO NRs growth shows promise for future ZnO nanostructure-based applications.

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1. Introduction

Owing to high electrical and thermal conductivity[1], graphene has been receiving growing attention for versatile applications such as solar cells[2], super capacitors[3], and high-speed transistors[4]. In addition, ZnO nanostructures [5, 6] incorporating graphene to form ZnO/graphene nanocomposites have been intensively studied for their antiseptic, optoelectronic, and electronic properties [7, 8]. Recently, diversified ways were investigated to include graphene into the ZnO-based nanocomposite fabrication process. Chen et al. spread a graphene layer on top of the ZnO nanorods (NRs) [9] and inserted a graphene layer between the ZnO NRs and a Si substrate [10]. In 2015 and 2016, Pruna et al. incorporated graphene oxide into ZnO seed layers to grow ZnO NRs hydrothermally [11,12].However, the aspect ratio tuning effects by incorporating graphene into the seed layer for ZnO NRs have not been clearly reported yet. In this research, we incorporated graphene containing solution into the ZnO seed layer solution and inserted a graphene layer between ZnO NRs and the SiO2 substrates to form different types of ZnO NRs. Compared with ZnO NRs grown on SiO_2in a normal condition, ZnO NRs with the seed layer containing graphene exhibited much higher aspect ratio, better hydrophobic properties, and stronger c-axis (002) indexed crystallinity. Recently, some studies have been reported to control the aspect ratio ZnO nanostructures by adding various ingredients into the ZnO NR growth solutions. Wang et al. incorporated polyethyleneimine (PEI) in the hydrothermal process to enhance (002) c-axis growth to deposit ZnO NRs with high-aspect ratio [13]. Similarly, Pihon et al. added surfactant to suppress (002) c-axis growth to form ZnO NRs with low-aspect ratio [14]. Therefore, adding graphene into the seed layer solutions may have similar effects like PEI to expedite the reaction between Zn^{2+} and OH^- ions on polar Zn-terminated c-plane. Furthermore, a graphene layer inserted between ZnO NRs and SiO_2 substrate could enhance antibacterial properties of the ZnO nanocomposites. Since ZnO

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NRs/SiO2 structures have been used as gas sensors [15], biochemical sensors [16], and electrical nanodevices [17], tuning the ZnO NR geometrical size and physical properties may be able to optimize the ZnO nanostructure-based device behaviors [18].

2. Experimental details

To fabricate ZnO NRs with seed layer incorporating graphene and with a graphene layer inserted between ZnO NRs and SiO_2, graphene solutions first prepared by the Graphage company (Model S-ON10) with N-methyl pyrrolidone (NMP) as the solvent for graphene[19]. To include graphene into the seed layer solution, DV-100 (Ted Pella Inc.) pipettes were used to add graphene solution with 0.7 ml into the seed layer solution. After the seed layer was coated on the substrate with sol-gel methods, the ZnO NRs were grown on ZnO seeded SiO_2 substrates by using hydrothermal methods. The ZnO seeded SiO_2/Si substrates were immersed in the glass bottle filled with aqueous solution of 0.05M zinc nitrate ($Zn(NO_3)_2$. $6H_2O$) and 0.07Mhexamethylenetetramine (HMT) and put in the water bath at 85˚c for 1 hour. The chemical reactions to form ZnO NRs are as follows.

$$(CH_2)_6N_4 + 6H_2O \leftrightarrow 4NH_3 + 6HCHO$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

$$Zn^{2+} + 4NH_3 \leftrightarrow [Zn(NH_3)_4]^{2+}$$

$$Zn^{2+} + \leftrightarrow 2OH^- Zn(OH)_2$$

$$Zn(OH)_2 ZnO \leftrightarrow + H_2O$$

3. Results and discussion

The same ZnO NR fabrication processes were performed on the SiO_2 substrate with and without coating a graphene layer except the seed layer solutions without graphene. To illustrate the schemes of three types of nanostructures, the ZnO NRs/SiO_2 structure is shown in Fig. 1 (a), the ZnO NRs/graphene/SiO_2 is shown in Fig. 1(b), and the ZnO NRs with the seed layer containing graphene on SiO_2 substrate is shown in Fig. 1(c). To characterize those tuned ZnO NRs with addition of graphene, multiple material analyses have been used. Field-emission scanning electron microscopy (FESEM) was used to view the surface morphology and the diameter size of the NR. Surface contact angle measurements were conducted to investigate the hydrophobic properties. Photoluminescence (PL) was used to examine the defect related to oxygen vacancies within the ZnONRs. Moreover, X-ray diffraction (XRD) was used to investigate the crystalline structure influenced by the amount of graphene and surface contact angle measurement was used to reveal the changes of the surface properties with various amount of graphene. Finally, OD 600 tests were used to study the antibacterial effects of each sample. These analyses provide a comprehensive view on how graphene could transform the material behaviors of the ZnONRs and project future applications of ZnONRs/SiO_2 structures in various fields.

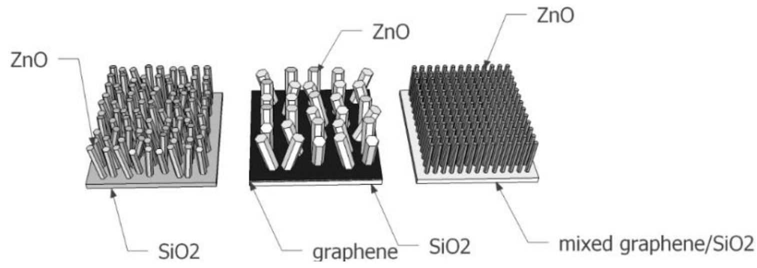


Fig. 1. Illustration of the ZnO NRs (a) on a SiO2 substrate(b) on a graphene/SiO2 substrate(c) with the seed layer containing graphene on a SiO2 substrate.

To observe the surface morphologies of different types of ZnO NRs, FESEM was used to monitor the ZnO NRs affected by adding graphene. Results indicate that the diameter of the NRs became much smaller (the aspect ratio became larger) with graphene added to the seed layer solution compared with the other types of NRs as illustrated by Fig.1 (a), (b), and (c) and FESEM images of three types of ZnONRs are shown in Fig. 2 (a), (b), and (c). Moreover, the ZnO growth became denser as graphene was added into the seed layer solution. Based on previous reports [20, 21] substrate structure may influence the ZnO growth. For example, closely compact ZnO NRs can be grown on GaN substrates because GaN has hexagonal structures as ZnO does [20]. SiO_2 does not have a hexagonal structure but graphene does as shown in Fig.2 (d). Therefore, higher aspect ratio of graphene could be grown on graphene incorporating structures. Furthermore, as we examine the FESEM images of the seed layer without and with graphene as shown in Fig.2 (e) and (f). We can see the grains density of the zinc acetate thin film seed layer formed by spin-coating which is much finer than the seed layer with graphene, so the nanorods with the graphene seed layer might be more compact. Moreover, as the ZnO NRs grows denser, the contact angle will increase and the surface become more hydrophobic as shown on the top-left subfigures of Fig. 2(a), (b), and (c). .

On the contrary, the aspect ratio for the ZnO NRs on graphene/SiO_2 became smaller (the rod diameter became larger) compared with ZnO NRs grown on SiO_2 without coating a layer of graphene. Furthermore, consistent with surface morphology observations, the hydrophobic properties were enhanced for the high aspect ratio and dense ZnO NRs with the seed layer containing graphene as shown on the top left subfigures of Fig. 2 (a), (b), and (c). In line with FESEM images, XRD patterns as shown in Fig. 3 (a) reveal that the (002) peak for the ZnO NRs with the seed layer containing graphene was much stronger than the other two types of ZnO NRs. A single ZnO NR have eight planes, the top and bottom planes are polar planes with Zn^{2+} and O^{2-} terminated while the side six planes are nonpolar planes without charged ions as shown in Fig. 3(b). Adding ingredients into the ZnO NR growth solutions might enhance the perpendicular growth or the lateral growth. Incorporating graphene into the seed layer solution may boost the reaction the Zn^{2+}-terminated top plane and OH^- to form $Zn(OH)_2$ as the precursor of ZnO NRs in the longitude direction. Therefore, the growth along the c-plane could be expedited and caused the NRs with higher aspect ratio (longer and thinner). The charged surface could be grown along the (002) direction with graphene added in the seed layer solution just as PEI did.

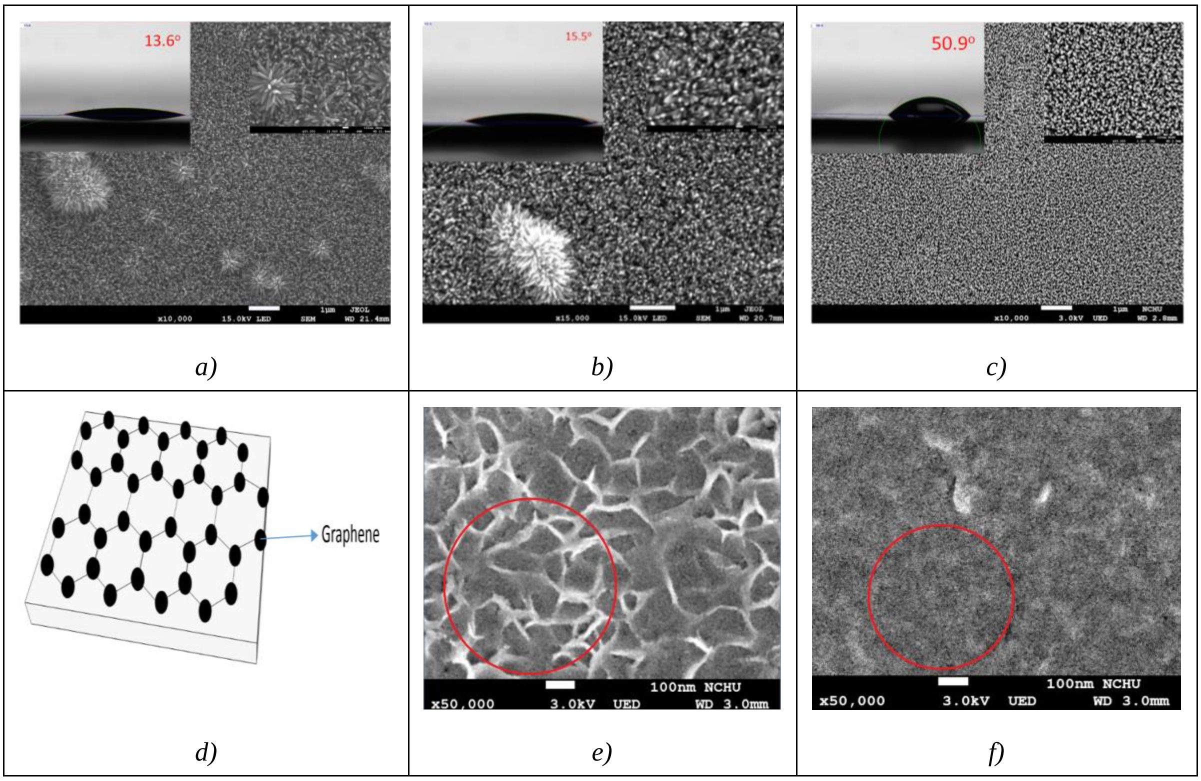
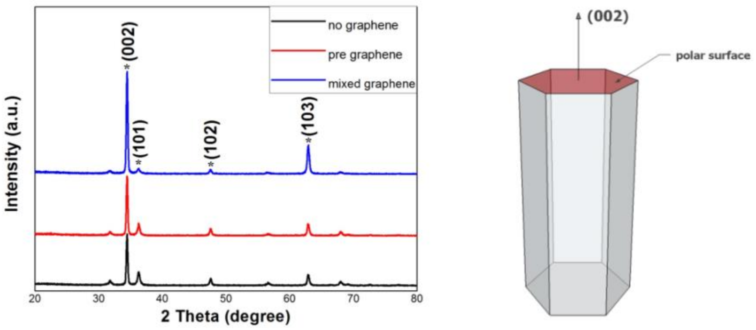


Fig. 2 FESEM images of the ZnO(a) on a SiO_2 substrate (b) on a graphene/SiO_2 substrate (c) with the seed layer containing graphene on a SiO_2 substrate. (FESEM images with a larger magnification rate on the top-right subfigures and surface contact angle measurements on the top-left subfigures.)(d) Illustrations of graphene (e) Seed layer without carbon (f) Graphene seed layer



(a) *(b)*

Fig. 3 (a) XRD patterns of ZnO NRs on a SiO_2 substrate, ZnO NRs on a graphene/SiO_2 substrate and ZnO NRs with the seed layer containing grapheneon a SiO_2 substrate. (b) a scheme of a single ZnO NR.

In addition, the optical properties of these three types of ZnO NRs were studied by the PL measurements as shown in Fig. 4. It is observed that the PL peak around 375 nm in the spectrum signifying the band-to-band recombination emission, and the PL peak around 560 nm in the spectrum signified the defect luminescence, attributed to oxygen vacancies in the ZnO NRs. It can be observed that the normal ZnO NRs/SiO_2 structure had much stronger band-to-band emission and the defect luminescence than the NRs with addition of graphene in the seed layer or with coating graphene between ZnO NRs and SiO_2 substrate. The graphene contained ZnO NRs may have less concentration of ZnO and oxygen defects because carbon atoms were included in the ZnO NRs. Therefore, the two luminescence peaks became weaker, especially for the ZnO NRs with graphene added into the seed layer because more carbon concentration may be included into the ZnO NRs.

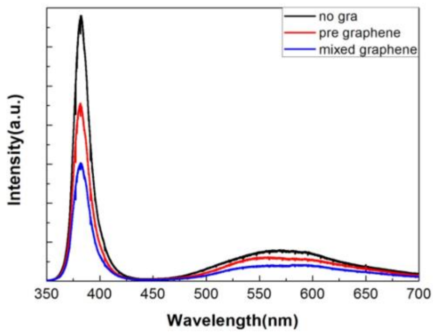
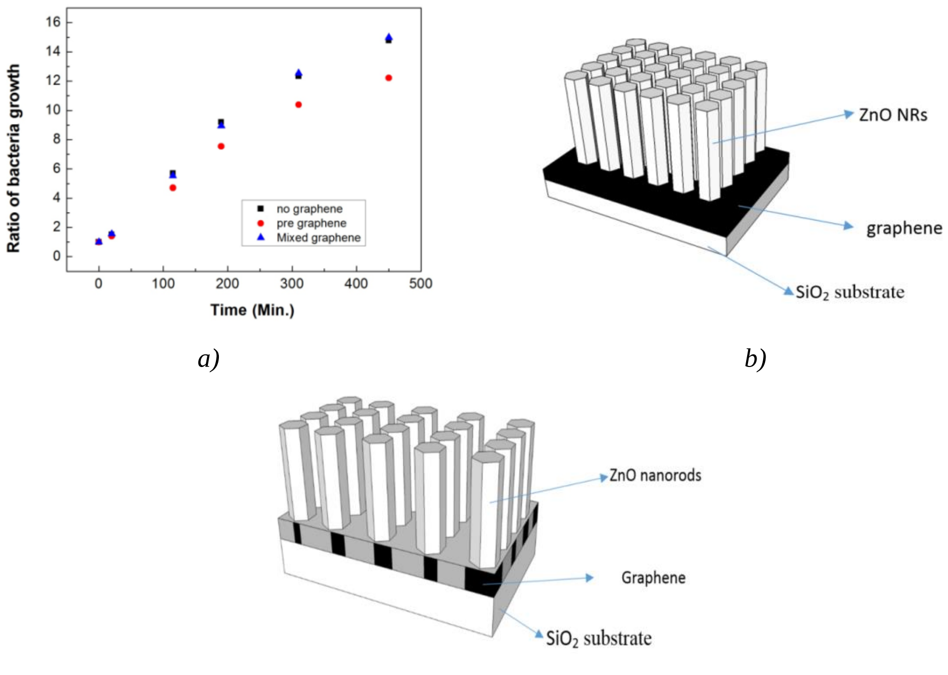


Fig. 4 PL measurements of ZnO NRs on a SiO_2 substrate, ZnO NRs on a graphene/SiO_2 substrate and ZnO NRs with the seed layer containing graphene on a SiO_2 substrate.

Finally, OD 600 antibacterial tests were performed on these three types of ZnO NRs as shown in Fig. 5(a). Results indicate that ZnO NRs grown on the graphene coated SiO_2 substrate had much stronger antibacterial capability than the other two types of ZnO NRs. Since graphene had the bacterial killing capability, the ZnO NRs grown on graphene coated SiO_2 substrate had the largest graphene contacting areas because graphene was spread on the surface on SiO_2 as shown in Fig.5 (b). On the other hand, as for the ZnO NRs with graphene added in the seed layer had similar antiseptic effects with normal ZnO NRs because most graphene may be contained inside the NR and hence could not enhance the antibacterial properties as shown in Fig. 5(c).



a) *b)*

c)

Fig. 5 (a) OD 600 antibacterial tests for ZnO NRs on the SiO_2 substrate, ZnO NRs on the graphene/SiO_2 substrate and ZnO NRs with the seed layer containing graphene on the SiO_2 substrate. (b)ZnO NRs grown on the graphene/SiO_2 substrate (c) ZnO NRs growth in the seed layer mixed graphene on the SiO_2 substrate

4. Conclusions

In this study, ZnO NRs were grown sol gel-hydrothermally on SiO_2 substrates with the seed layer containing graphene and ZnO NRs were grown on graphene/SiO_2 substrates. Results indicate that incorporating graphene into the seed layer solution could enhance the longitude growth of ZnO NRs and enlarge the aspect ratio. On the other hand, ZnO NRs grown on graphene/SiO_2 substrate could exhibit lower aspect ratio and strong antibacterial capability. Tuning ZnO NR growth have potential to enhance future ZnO NRs/SiO2nanostructure-based device applications.

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