

Electronic Supplementary Information for

Electrochemical growth of vertically aligned ZnO nanorod arrays on oxidized bi-layer graphene electrode

By C. Xu,^a J.-H. Lee,^a J.-C. Lee,^a B.-S. Kim,^a S. W. Hwang^b and D. Whang^{a,b}

^a School of Advanced Materials Science & Engineering and Sungkyunkwan Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon 440-746, Republic of Korea

^b Research Center for Time-Domain Nano-functional Devices and School of Electrical Engineering, Korea University, Seoul 136-701, Republic of Korea

Experimental Details

Graphene growth and Transfer: Graphene was synthesized from Cu foil (Alfa Aesar, item No.13382) at 1000 °C in the LPCVD system.^{S1} A typical process for Cu catalyzed graphene was: (1) introduce the Cu foil into the furnace and evacuate it; (2) heat the furnace at 1000°C and maintain with H₂ (50 sccm) for 30 min; (3) flow the gas mixture of CH₄ (15 sccm) and H₂ (5 sccm) at 10 Torr for 30 min; (4) rapid cooling of the resulting sample to room temperature under vacuum. To transfer the as-grown graphene to the desirable substrate, poly-methyl methacrylate (PMMA) was used to prevent cracks during the transfer process. Since graphene grows on both sides of the Cu foil, we coated the top surface with PMMA and bottom surface was etched by oxygen plasma treatment. After that Cu is dissolved the Marble reagent. The PMMA/graphene film was washed with deionized water more than 3 times. And then PMMA/graphene film was transferred to other desired substrates such as glass and PET film. PMMA layer was then removed by acetone. The surface defects of graphene were generated by oxygen plasma for 15 s with oxygen flow rate of 20 sccm and power of 5 W.^{S2}

Growth of ZnO nanorods on graphene: The ZnO nanorod arrays on graphene were prepared by electrochemical deposition from a pure zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, Aldrich, 98% purity) aqueous solution in a three-electrode cell. A saturated calomel electrode (SCE), graphite sheet and graphene/glass (G/G) or graphene/PET (G/P) were used as reference, counter, and working electrode, respectively. Before electrodeposition, the graphene was

consecutively cleaned with acetone, ethanol, and de-ionized water, then dry with nitrogen gas, and finally followed by UV treatment at 245 nm for 10 min. The electrodeposition process was carried out at 90 °C with a constant current density from -0.05 to -1 mA/cm² versus the SCE reference electrode and the reaction time ranged from 15 min to 1h. The concentration of the zinc nitrate was varied from 50 to 0.5 mmol/L and the system was kept stable without stirring or gas bubble. After deposition, the obtained ZnO nanorods film was rinsed with ethanol and distilled water, then dried at 40 °C. Meanwhile, ZnO nanorods on ITO bare substrate were also prepared using the same procedures for a comparison. ITO substrate was ultrasonically cleaned with acetone, ethanol and de-ionize water for 5 min, respectively. Finally it was treated in oxygen plasma for 5 min with the oxygen flow rate of 100 sccm and the RF-bias power of 100 W to remove any adsorbed organic compound.

Characterization: The size and morphology of the ZnO NR products were characterized by field emission scanning electron microscope (FESEM, JEOL JSM 6700F). The microstructure of ZnO NR was investigated by high-resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED) using a JEOL JEM 2100F instrument with accelerating voltage of 200 kV. The photoluminescence (PL) spectroscopy was obtained at room temperature using a He-Cd laser. A UV-VIS 3600 spectrometer was used to examine the optical transparence. The Raman spectrum for graphene was measured using a 514 nm laser source with power below 4 mW (RM1000-Invia, Renishaw). The surface chemical state of oxidized bi-layer graphene was measured via X-ray photoelectron spectroscopy (XPS, ESCA2000 spectrometer) using an Al K α as X-ray source.

- S1. X. Li, W.Cai, J.An, S.Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E.Tutuc, S. K. Banerjee, L. Colombo, R.S. Ruoff, *Science*, 2009, **324**,1312-1314.
- S2. Y.J. Shin, Y. Wang, H. Huang, G. Kalon, A.T.S. Wee, Z. Shen, C. S. Bhatia and H. Yang, *Langmuir*, 2010, **26**, 3798-3802.

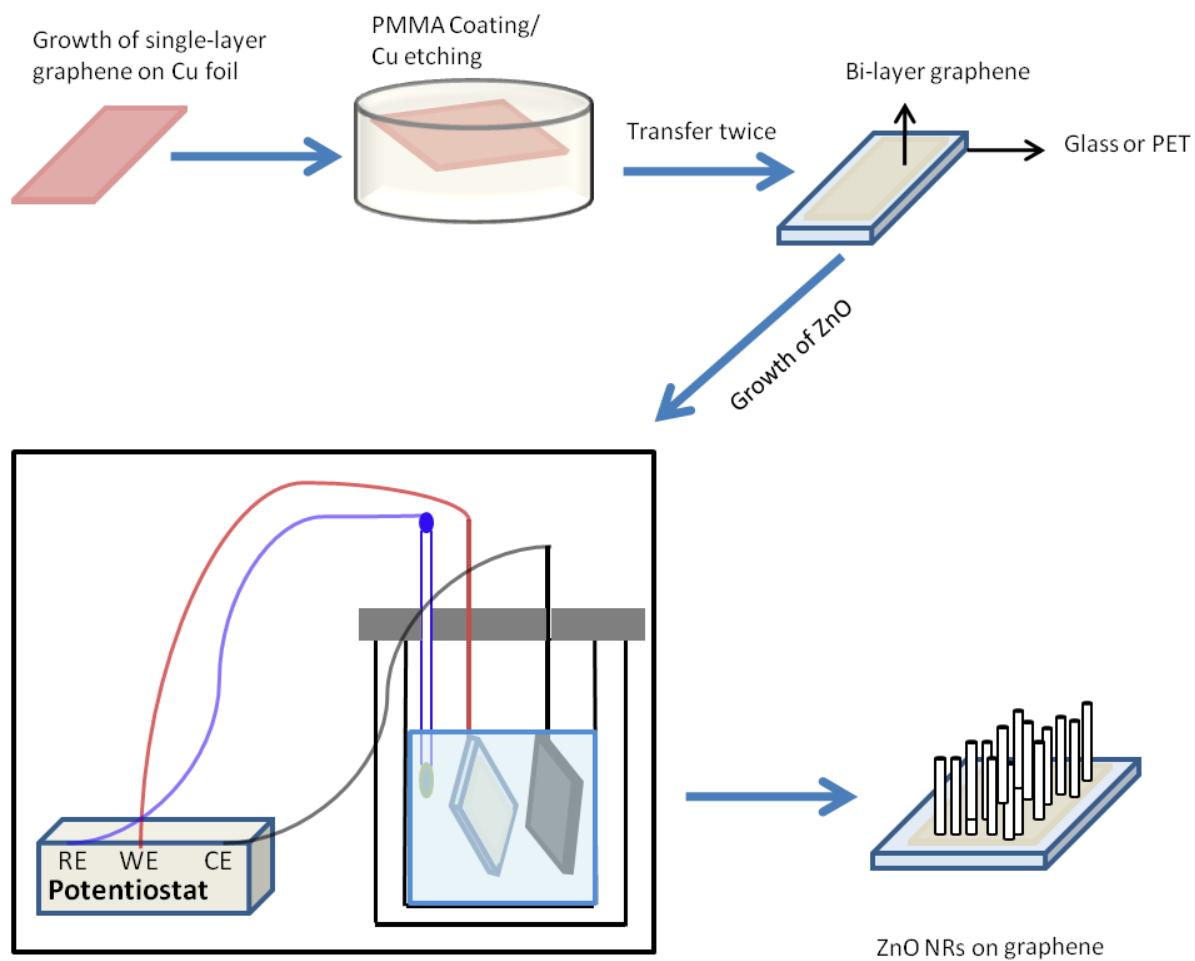


Fig. S1 Scheme of experimental process

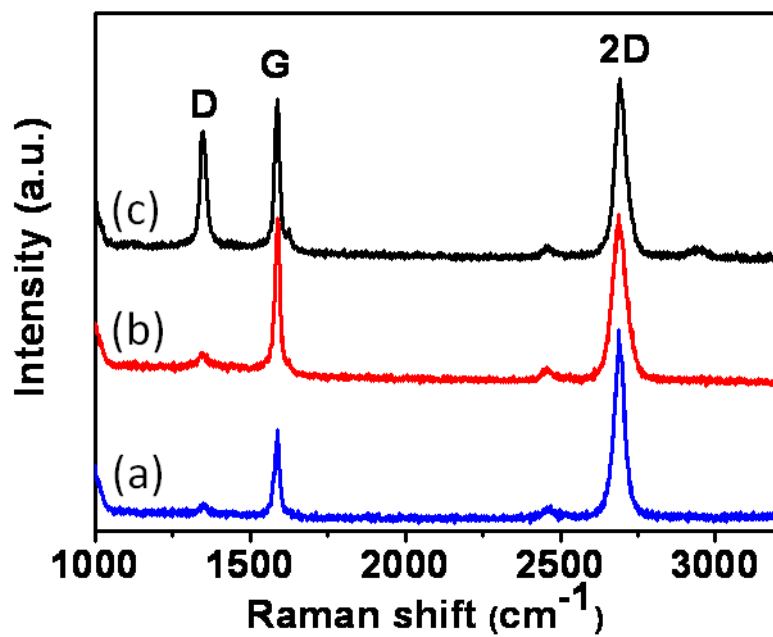


Fig. S2. Raman spectra of (a) as-grown single-layer graphene, (b) unoxidized bi-layer graphene, and (c) partially oxidized bi-layer graphene.

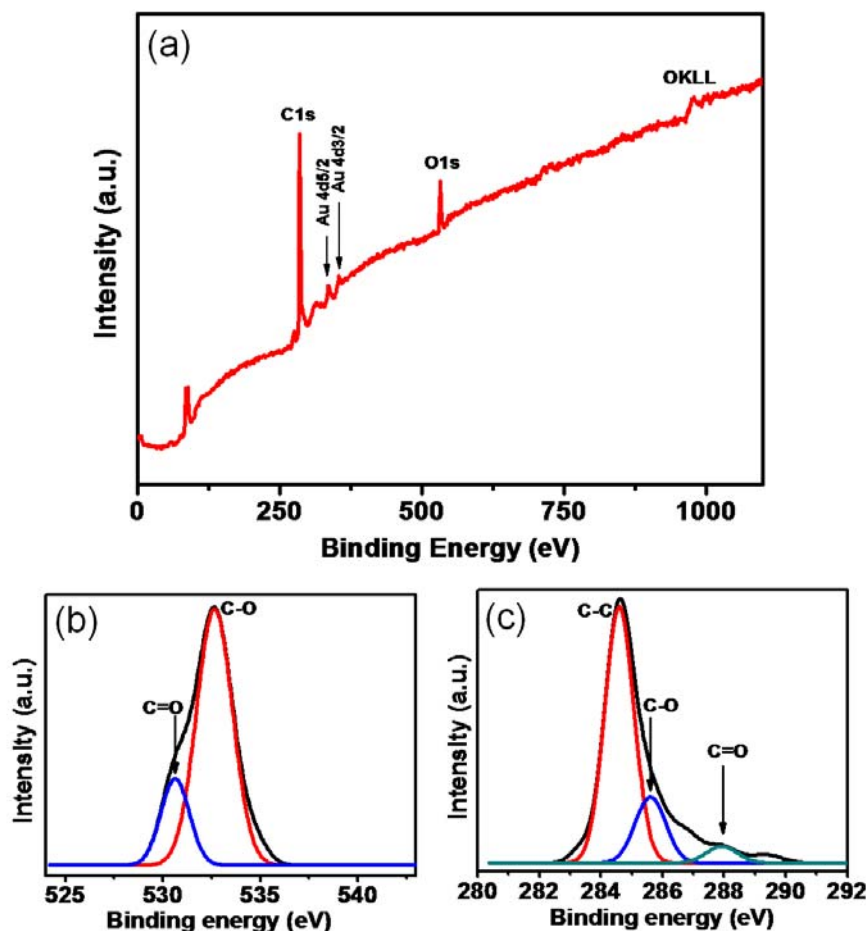


Fig. S3. (a) XPS spectra of oxidized bi-layer graphene. (b) O1s core-level XPS spectra of oxidized bi-layer graphene. (c) C1s core-level XPS spectra of oxidized bi-layer graphene. For XPS analysis, graphene was transferred to Si wafer coated with 50 nm Au film which is for eliminating oxygen signal from the native silicon oxide. The oxygenated carbon groups of C-O or C=O can be observed from the O1s and C1s core-level spectra, consistent with the previous reports.^{S3,S4} The weight percentage of oxygenated carbon atoms by analysis of C1s spectra from oxidized graphene is ~ 16%..

S3. D. Yang, A. Velamakanni, G. Bozoklu, S. Park, M. Stoller, R. D. Piner, S. Stankovich, I. Jung, D. A. Field and C. A. Ventrice Jr, *Carbon*, 2009, **47**, 145-152.

S4. G. Jo, M. Choe, C. Y. Cho, J. H. Kim, W. Park, S. Lee, W. K. Hong, T. W. Kim, S. J. Park and B. H. Hong, *Nanotechnology*, 2010, **21**, 175201.

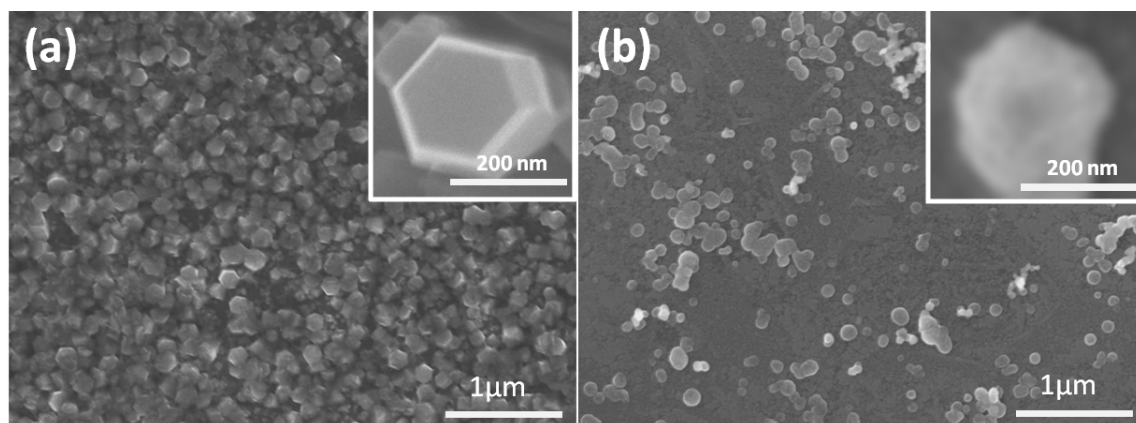


Fig. S4. SEM images of ZnO seeds electrodeposited from 5 mM $\text{Zn}(\text{NO}_3)_2$ solution with current density of -0.15 mA and deposition time of 3 min on (a) oxidized bi-layer graphene and (b) unoxidized bi-layer graphene. The images clearly show that high density ZnO particles with uniform size and hexagonal planar ends are grown on the more active oxidized graphene electrode to form orderly seed layer at the very beginning deposition stage. Instead, a small amount of irregular ZnO particles are randomly attached on strong hydrophobic unoxidized graphene. It is evident that these ZnO particles with random disperse are not epitaxially grown on the unoxidized graphene directly. Therefore, ZnO NRs with low density and arbitrary orientations are developed in the following growth process.