

## **Supporting Information**

# **Thermal Conductivity Reduction in Three-Dimensional Graphene-Based Nanofoam**

Pradheep Thiyagarajan<sup>1</sup>, Zhong Yan<sup>2</sup>, Jong-Chul Yoon<sup>1</sup>, Min-Wook Oh<sup>3</sup>, and Ji-Hyun Jang<sup>1,\*</sup>

1. Interdisciplinary School of Green Energy and Low Dimensional Carbon Materials Center, UNIST, Ulsan 689-798, Korea.
2. Nano-Device Laboratory, Department of Electrical Engineering, Bourns College of Engineering, University of California – Riverside, Riverside, California 92521, United States.
3. Creative Electrotechnology Research Center, Korea Electrotechnology Research Institute, Changwon, Korea.

## **Experimental procedure**

### **-Preparation of PVA/NiCl<sub>2</sub>.6H<sub>2</sub>O composite thin film**

Polyvinyl alcohol (PVA,  $M_w = 31,000\text{--}50,000$ ) and nickel chloride hexahydrate (NiCl<sub>2</sub>.6H<sub>2</sub>O) were obtained from Sigma-Aldrich Company and used without any further purification. PVA (10 wt%), a carbon precursor, was dissolved in DI-water at 90°C and then mixed with the 300 phr (phr: parts per hundred parts of resin) by weight of NiCl<sub>2</sub>.6H<sub>2</sub>O, a metal precursor for graphene growth. PVA/NiCl<sub>2</sub>.6H<sub>2</sub>O composite thin films were prepared onto the SiO<sub>2</sub>/Si substrate using spin-coating method. The samples were dried in a vacuum oven for about 12 hrs.

### **Fabrication of 3D-NFG**

The prepared composite films were placed in a 4 inch quartz tube (Scientech Co.) and heated to 1000°C under a flow of hydrogen (H<sub>2</sub>) (100 sccm) and argon (Ar) (~ 3L/min) gas at a pressure of 4 torr. The reaction time was 30 min after which the samples were cooled to room temperature. The detailed scheme of the reaction is given in Figure S1. The 3D-NFG samples containing nickel (3D-NFG/Ni) were spin-coated with PMMA solutions and dried at 120°C for 5 min. PMMA was used to transfer graphene onto other substrates. Then PMMA/3D-NFG/Ni on the 300 nm SiO<sub>2</sub>/Si substrate was floated on solutions consisting of HF (5%) and ammonium persulfate (1 M) for 48 h to remove the SiO<sub>2</sub> layer and nickel simultaneously. Freestanding 3D-NFG was obtained by removing the PMMA layer in acetone for 4 h and then transferred to the desired substrate.

### **Characterization**

The morphology of the structures was visualized using the field emission scanning electron microscope (NOVA NanoSEM 230 FESEM). The pore size and detailed structural characterization were examined using transmission electron microscope (JEM-2100, 200 kV). Surface analysis of 3D-NFG was performed using micro-Raman spectroscopy to determine the quality of graphene. Raman spectra were recorded using a micro-Raman spectrometer (WITec, alpha300R) with an incident wavelength of 532 nm. Optothermal measurements on 3D-NFG were performed by the 532nm visible laser light source using 100x objective lens and the data are shown in Figure 3. By changing the objective lens (10x, 50x) with the same laser source (532 nm), the optothermal measurements yielded the data as shown in Figure S4 & S5. The crystallinity of the 3D-NFG samples was checked using a high power X-ray diffractometer

(Rigaku D/MAZX 2500V/PC HPXRD). The XRD pattern confirms the crystallinity of the samples as shown in Figure S3. In order to confirm the chemical composition of the samples, X-ray Photoelectron spectroscopy system (XPS, Thermo Fischer UK) with an Al K $\alpha$  source was used. Atomic force Microscopy (AFM) imaging was performed to check the roughness of the 3D-NFG films using AFM, Digital Instruments, Nanoscope III equipment.

### - Calibration procedure

The calibration procedure employed<sup>1</sup> to extract the thermal conductivity of 3D-NFG is outlined. The power dissipated in 3D-NFG was determined through the calibration procedure based on comparison of the integrated Raman intensity of 3D-NFG's G peak ( $I_{G\ 3D-NFG}$ ) and that of reference bulk graphite ( $I_{G\ BULK}$ , data not shown). Figure 3c (in the main text) shows measured data for 3D-NFG. Each addition of an atomic plane leads to an  $I_{G\ 3D-NFG}$  increase and convergence with the graphite whereas the ratio ( $I_{G\ 3D-NFG}/I_{G\ BULK}$ ) stays roughly independent on excitation power, indicating proper calibration.

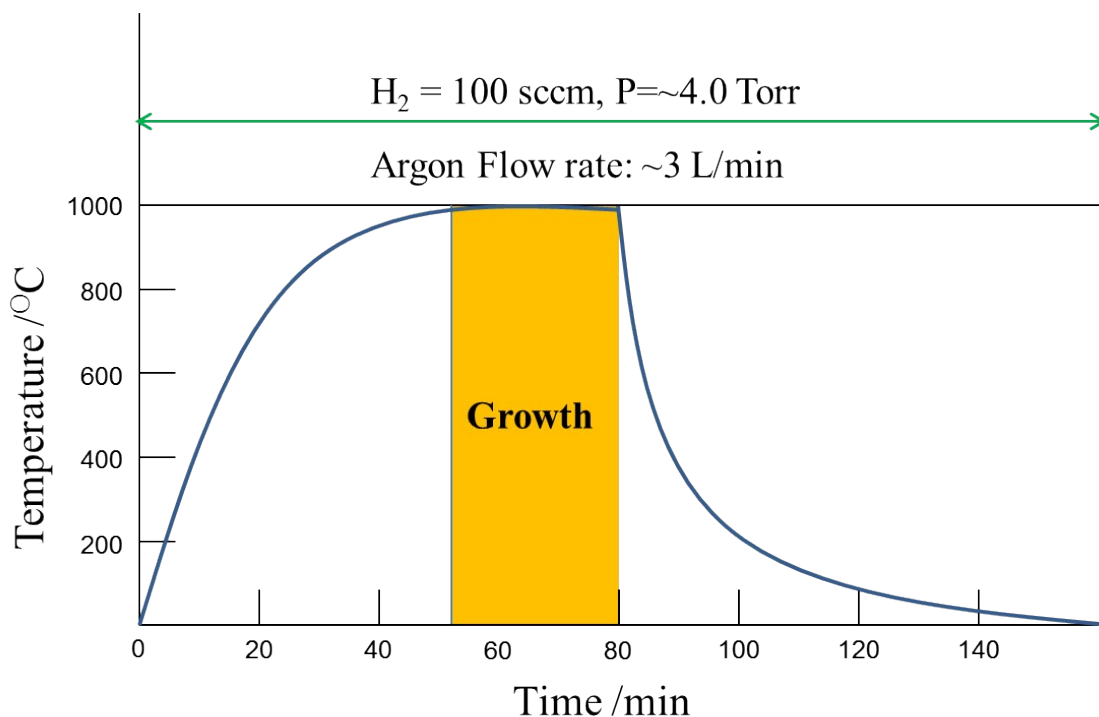


Figure S1: Schematic diagram showing the experimental (CVD) conditions for making 3D-NFG

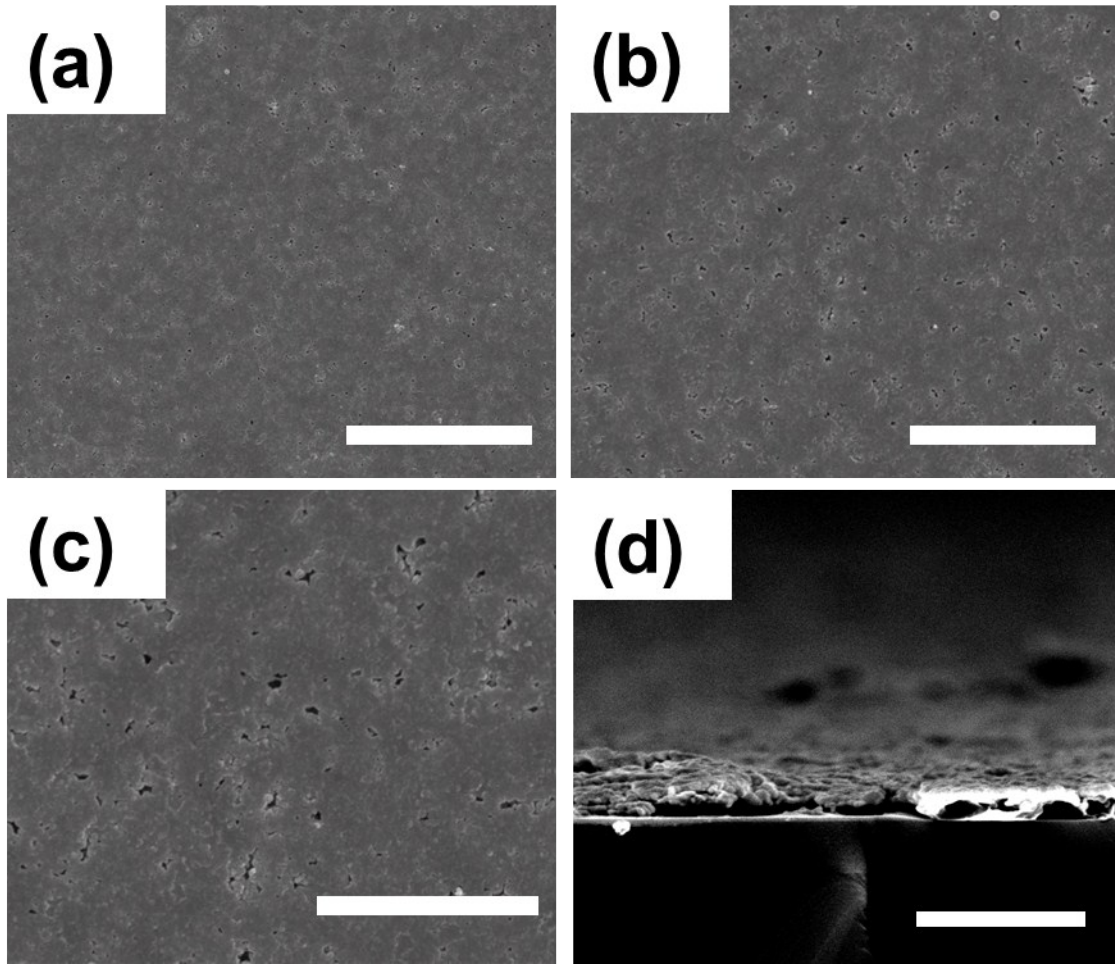


Figure S2: Large area SEM image of 3D-NFG obtained after Ni etching (a) scale bar: 10 $\mu$ m, (b) scale bar: 5  $\mu$ m(c) scale bar: 3 $\mu$ m and (d) Cross sectional SEM image of 3D-NFG films after nickel etching (scale bar: 1  $\mu$ m).

Figure S2 shows the porous structure of the 3D-NFG films over a large area. The pore size varies from 40-180 nm. The density of the pores can be varied by changing the polymer/metal precursor ratio. The high density of pores in graphene degrades the quality of graphene films; however it helps in blocking the phonon transport. At an optimized ratio of polymer/metal precursors (as given in experimental details), we obtained ~150 nm thick 3D-NFG as shown in Figure S2d which shows promising properties.

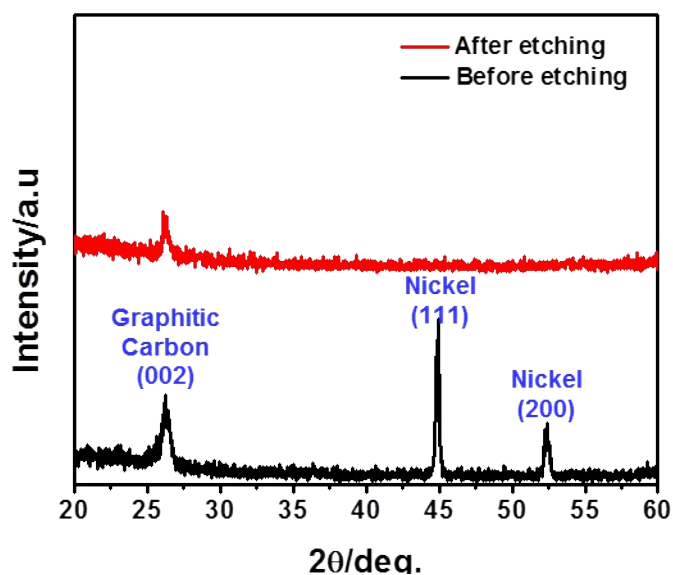


Figure S3: XRD results of the 3D-NFG before and after nickel etching

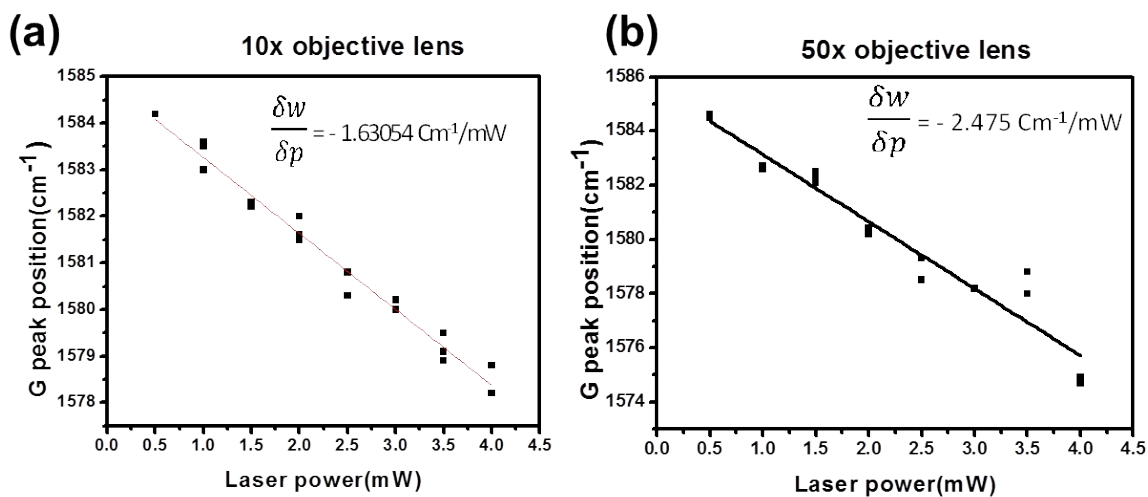


Figure S4: (a) Shift in the G peak position due to a change in the excited laser power in suspended 3D-NFG samples measured using a 10x objective lens and (b) Shift in the G peak position due to a change in the excited laser power in suspended 3D-NFG samples measured using a 50x objective lens.

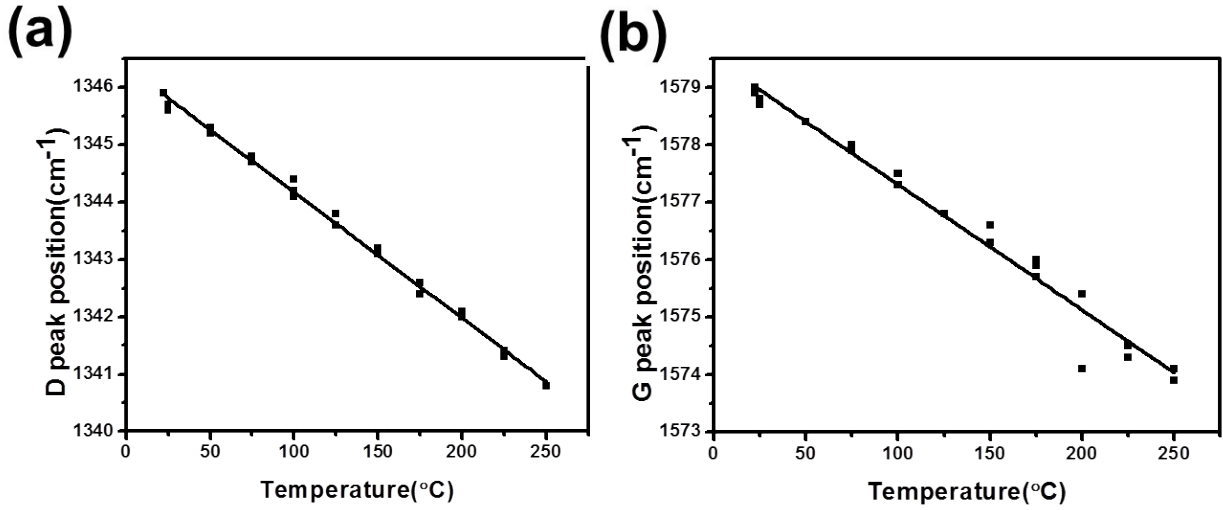


Figure S5: (a) Temperature coefficient data of D peak and (b) Temperature coefficient data of G peak of suspended 3D-NFG measured using 50x objective lens.

The temperature dependence of the Raman spectra of the suspended 3D-NFG was studied in the temperature range from 22 °C to 250 °C. The sample was put in a cold-hot cell where the temperature could be controlled externally with 0.1° C accuracy. The Raman peak positions of the D and G peak at different temperatures are shown in Figure S5a & S5b. The D and G peak positions move to lower wavenumber range (red shift) when temperature increases, and within the measured temperature range the temperature dependence of the G peak can be approximately described by a linear function  $\omega = \omega_0 + \chi T$ , where  $\omega_0$  is the frequency of the Raman peak when temperature T is extrapolated to 0 K, and  $\chi$  is the first-order temperature coefficient. The extracted temperature coefficient of the D peak is -0.02194 cm<sup>-1</sup>/°C. Similarly, the temperature coefficients of the G peak are -0.02185 cm<sup>-1</sup>/°C as shown in Figures S4b. The data presented in Figure S4b can be utilized as calibration curves for determining the local temperature rise in 3D-NFG films. The temperature can be extracted from the shift of Raman peak positions. During the Raman temperature coefficient measurements, the Raman excitation laser power was kept at low value to avoid any local heating effect. The heating power from the laser ( $\Delta P$ ) is focused on the 3D-NFG layer and the corresponding temperature rise was measured using Raman spectrometer. The low power of about 2 mW was utilized on the 3D-NFG to limit local heating during measurements. The amount of heat dissipated from the 3D-NFG was calculated from the intensity of the G peak. Correspondingly, the local temperature rise induced by the Raman laser can be calculated to be 457 °C. The ambiguity of temperature rise measured by Raman spectroscopy was under 10% range, which was limited by the spectrum resolution of Raman instrument. By changing the objective lens, the working

distance and spot size are drastically changed. The corresponding Raman peak shift using different (10x, 50x) objective lens is given in supporting Fig S4.

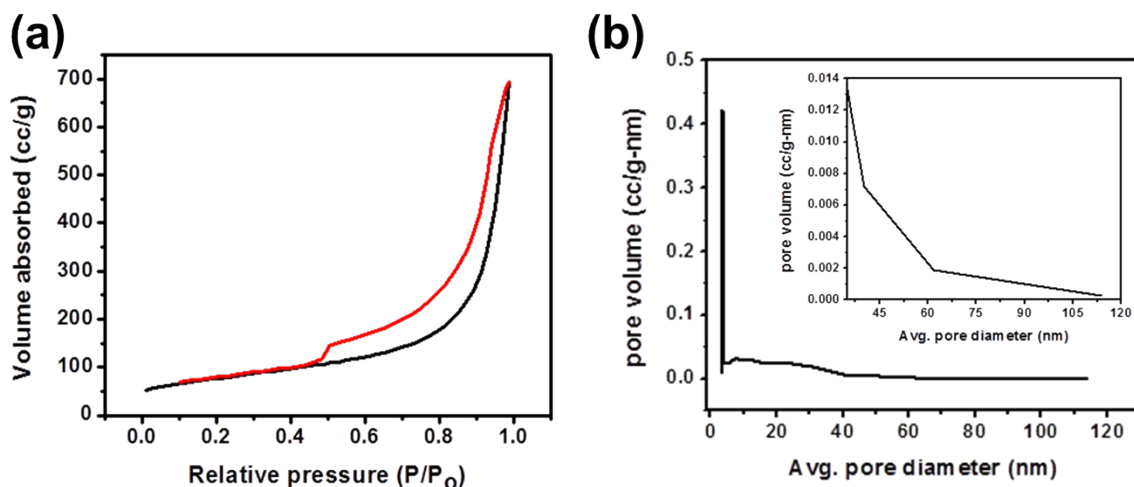


Figure S6: (a) Nitrogen adsorption–desorption isotherm of 3D-NFG powders and (b) Pore size distribution of 3D NFG power (inset shows enlarged view of avg. pore diameter from 20-120 nm) .

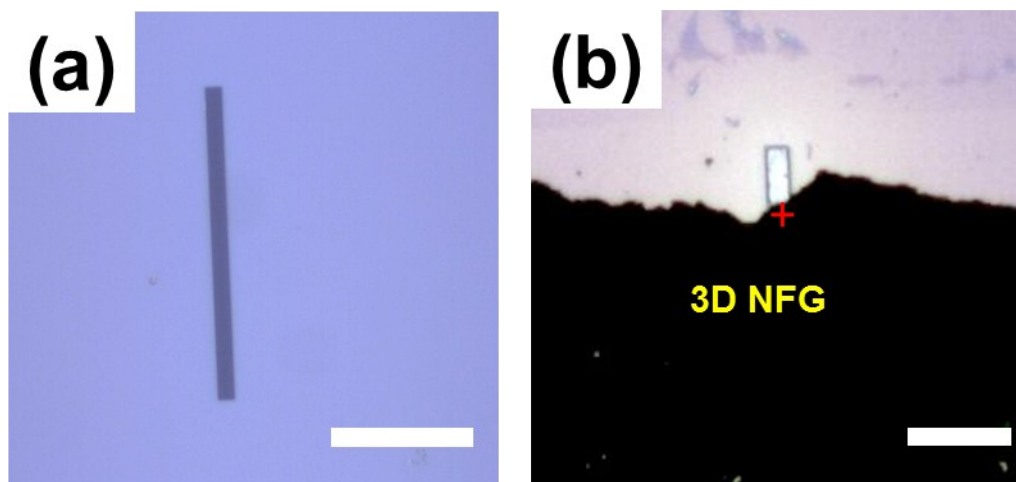


Figure S7: Optical microscopy images of (a) SiO<sub>2</sub>/Si substrate with trench dimension of 6  $\mu\text{m}$  (width), 100  $\mu\text{m}$  (length), 300 nm (depth) and (b). Suspended 3D- NFG films transferred onto the trench (denoted by the red color crossbar). Scale bar size is 50 $\mu\text{m}$  for both images.

## References

1. Ghosh, S.; Bao, W. Z.; Nika, D. L.; Subrina, S.; Pokatilov, E. P.; Lau, C. N.; Balandin, A. A., Dimensional crossover of thermal transport in few-layer graphene. *Nat Mater* **2010**, *9* (7), 555-558.