Supporting Material for Synthesis of N-Doped Graphene by Chemical Vapor Deposition and Its Electrical Properties

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(9) Czerw, R.; Terrones, M.; Charlier, J. C.; Blase, X.; Foley, B.; Kamalakaran, R.; Grobert, N.;

Terrones, H.; Tekleab, D.; Ajayan, P. M.; Blau, W.; Ruhle, M.; Carroll. D. L. Nano Lett. 2001, 1, 457-460.

(17) Berger, C.; Song, Z.; Li, X.; Wu, X.; Brown, N.; Naud, C.; Mayou, D.; Li, T.; Hass, J.;

Marchenkov, A. N.; Conrad, E. H.; First, P. N.; De Heer, W. A. Science 2006, 312, 1191-1196.

(19b) Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z. Y.; De, S.; Mcgovern, I. T.;

Holland, B.; Byrne, M.; Gun'ko, Y. K.; Boland, J. J.; Niraj, P.; Duesberg, G.; Krishnamurthy, S.; Goodhue,

R.; Hutchison, J.; Scardaci, V.; Ferrari, A. C.; Coleman, J. N. Nat. Nanot. 2008, 3, 563-568.

(22c) Campos-Delgado, J.; Romo-Herrera, J. M.; Jia, X. T.; Cullen, D. A.; Muramatsu, H.; Kim, Y. A.;

Hayashi, T.; Ren, Z. F.; Smith, D. J.; Okuno, Y.; Ohba, T.; Kanoh, H.; Kaneko, K.; Endo, M.; Terrones, H.;

Dresselhaus, M. S.; Terrones, M. Nano Lett. 2008, 8, 2773-2778.

(27a) Das, A.; Pisana, S.; Chakraborty, B.; Piscanec, S.; Saha, S. K.; Waghmare, U. V.; Novoselov, K.

- S.; Krishnamurthy, H. R.; Geim, A. K.; Ferrari, A. C.; Sood, A. K. Nat. Nanotech. 2008, 3, 210-215.
- (33) Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang,

D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Phys. Rev. Lett. 2006, 97, 187401.

2. Experimental Section

Production of the N-doped graphene: A 25 nm thick of Cu film was deposited on a Si substrate as the catalyst, and then the substrate was placed in a quartz tube with a flow of hydrogen (20 sccm) and argon (100 sccm), and was located at the low temperature region of a furnace. When the center of the furnace reached 800 °C, 60 sccm CH₄ and 60 sccm NH₃ were introduced into the flow as the C source and N source respectively, and then the substrate was rapidly moved to the high temperature region. After 10 min of growth, the sample was cooled to room temperature under H₂ ambient.

Production of the pristine graphene: The pristine graphene was produced via a similar CVD process by only using CH₄ as feed stock. A 25 nm thick of Cu film was deposited on a Si wafer as the catalyst, and then the substrate was placed in a quartz tube with a flow of hydrogen (20 sccm) and argon (100 sccm), and was located at the low temperature region of a furnace. When the center of the furnace reached 800 °C, 60 sccm CH₄ were introduced into the flow as the C source, and then the substrate was rapidly moved to the high temperature region. After 10 min of growth, the sample was cooled to room temperature under H₂ ambient.

Fabrication of devices: The N-doped graphene were removed from the substrate by scratching and sonicating in 0.1 M HCl, and then the products were precipitated by centrifugation and washed for several times using deionized water. The N-doped graphene was dispersed in ethanol by mild sonication, and then the solution was spin-coated onto a 500 nm thick thermally oxidized-silicon surface with photolithography-patterned Au/Ti electrodes. N-doped graphene sheets could be found to bridge between some pairs of the Au/Ti electrodes by SEM testing. To obtain better contact between the graphene sheet and the Au/Ti electrodes, thermal annealing was performed in an Ar atmosphere at 350 °C for 15 min using a tube furnace.

Characterization and electrical measurement: After growth, the products on the substrate were characterized by scanning electron microscopy (SEM, Hitachi S-4800, 15 kV), X-ray photoelectron spectroscopy (XPS, ESCA Lab220I-XL), and Raman spectrometer (Lab Ram HR800, with laser excitation

at 633 nm) directly. For the transmission electron microscopy (TEM, Hitachi-2010, 200 kV) and X-ray energy dispersive spectrometer (EDS, equiped on SEM or TEM) measurement, the products were removed from the substrate by scratching and sonicating in 0.1 M HCl, and then the products were precipitated by centrifugation and washed for several times using deionized water. Finally, the products were dispersed in ethanol by sonication and transferred on the lacey carbon TEM grid for TEM and EDS (equiped on TEM) characterization or on Si wafer for the EDS (equiped on SEM) characterization. For high resolution TEM measurement, the products were scratched and sonicated in ethanol, and then transferred on the lacey carbon TEM grid directly. The electrical properties were measured using a probe station (Wentworth Company MP1008) and a semiconductor parameter analyzer (Keithley 4200) at room temperature in air.

3. Supporting Figures

Figure S1. D. C. Wei, Y. Q. Liu, et al.

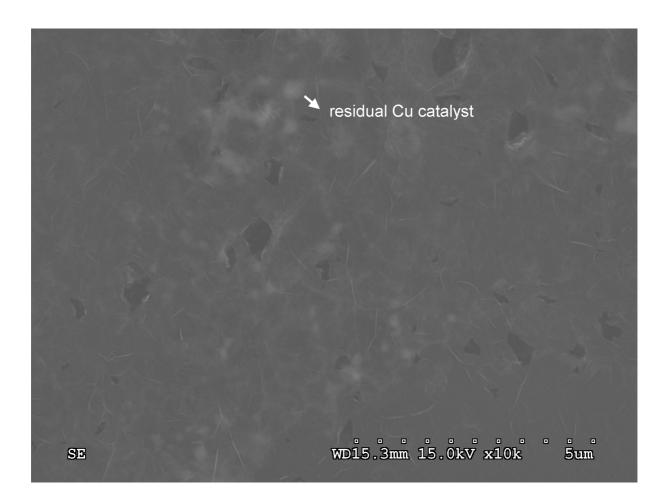


Figure S1. Large scale SEM image of the N-doped graphene film grown on the substrate.

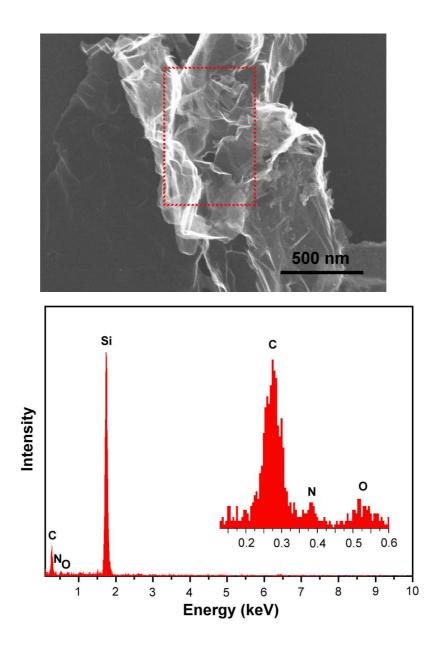


Figure S2. SEM image of the N-doped graphene on the Si wafer and the EDS (equiped on SEM) spectra taken from the area marked by the dashed frame in the SEM image. The Si peak comes from the Si wafer, and the O peak comes from the absorbed oxygen or water.

Figure S3. D. C. Wei, Y. Q. Liu, et al.

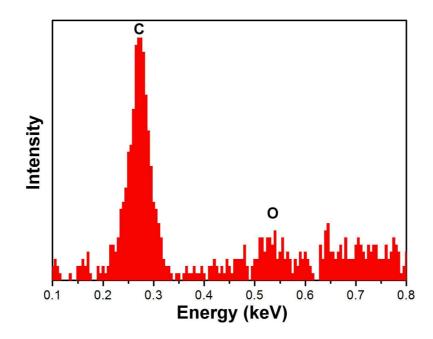


Figure S3. The EDS spectra (equiped on SEM) of the pristine graphene on the Si wafer. The O peak comes from the absorbed oxygen or water.

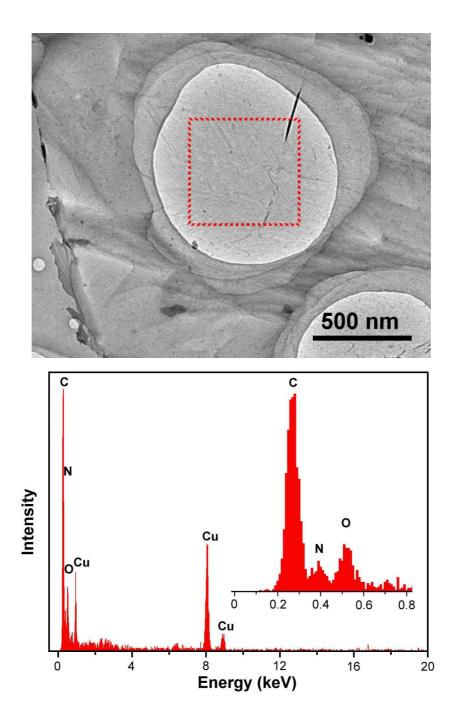


Figure S4. TEM image of the N-doped graphene on the lacey carbon TEM grid and the EDS (equiped on TEM) spectra taken from the area marked by the dashed frame in the TEM image. The Cu peak comes from the TEM grid, and the O peak comes from the absorbed oxygen or water.

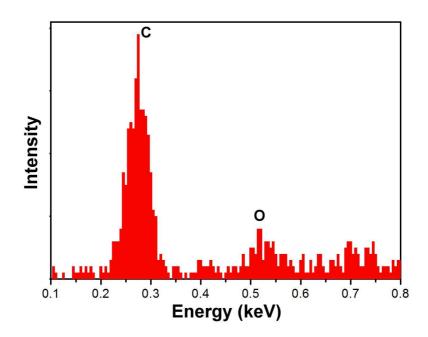


Figure S5. The EDS spectra (equiped on TEM) of the pristine graphene on the lacey carbon TEM grid. The O peak comes from the absorbed oxygen or water.

Figure S6. D. C. Wei, Y. Q. Liu, et al.

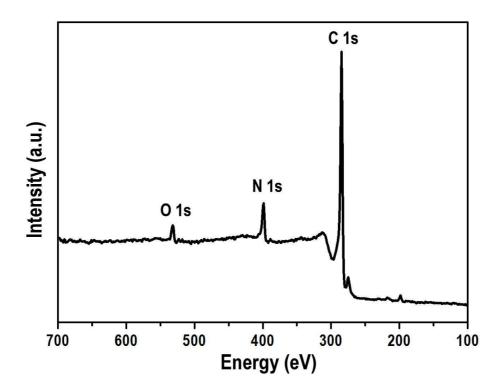
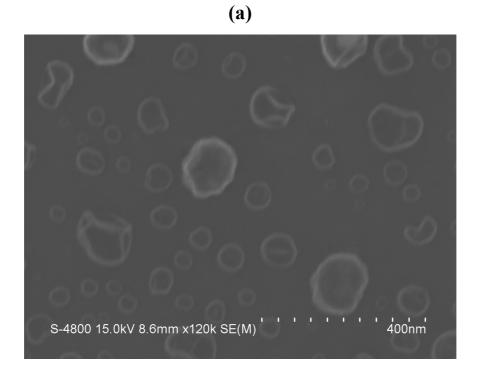


Figure S6. The XPS spectrum of the N-doped graphene after heating at 200 °C in vacuum for 2 days. We can clearly observe the decrease of the O 1s peak.

Figure S7. D. C. Wei, Y. Q. Liu, et al.



(b)

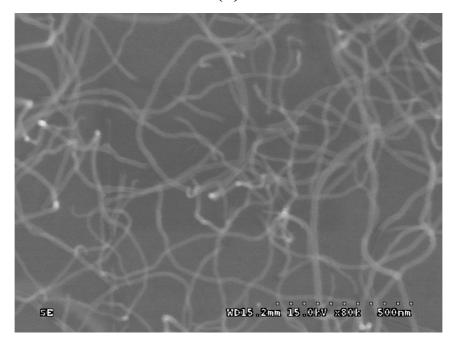


Figure S7. SEM images of the samples produced by slow heating of the catalyst film. We can find the products are carbon nanocages (a) or carbon nanotubes (b).

Figure S8. D. C. Wei, Y. Q. Liu, et al.

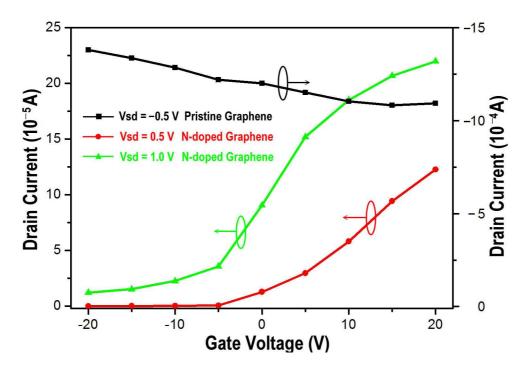


Figure S8. The transfer characteristics of the pristine graphene (V_{ds} at -0.5 V) and the N-doped graphene (V_{ds} at 0.5 V and 1.0 V).