Programmably-Shaped Carbon Nanostructure from Shape-Conserving Carbonization of DNA

*Feng Zhou,[1] Wei Sun,[2] Karen B. Ricardo,[1] Dong Wang,[1] Jie Shen,[2] Peng Yin,[2] Haitao Liu[1,]**

[1] Department of Chemistry, University of Pittsburgh, Pittsburgh, PA, 15260; [2] Wyss Institute for Biologically Inspired Engineering, Harvard University, Boston, Massachusetts 02115, United States, and Department of Systems Biology, Harvard Medical School, Boston, Massachusetts 02115, United States

*Correspondence to: hliu@pitt.edu (H.L.)

Supporting Information

1. Calculation of sp^2 domain size in the 1D DNA crystal:

The sp^2 domain size in carbonized 1D DNA crystal was quantified using the Tuinstra-Koenig relation $I_D/I_G = C(\lambda)/L_a$, where the proportionality constant $C(\lambda)$ depends on the excitation laser wavelength λ.[S1-3]

$C(\lambda) = 2.4\text{x}10^{-10} * \lambda^4$ (for peak-area intensities) = 19.2 nm (for λ = 532 nm)

For 1D DNA crystals, the peak area intensity was 10149 for G peak and 23912 for D peak. The sp^2 domain size L_a = 8.1 nm

2. The stability of DNA-derived graphitic nanostructure

To determine the mechanic stability of the nanostructure, tapping mode AFM was utilized on the same area for 5 times to test whether physical damage during scanning can be introduced. The DNA-derived nanostructure resisted the tip friction in the manner of both surface morphology (Figure S5D) and the average height (from 2.1 ± 0.2 to 2.1 ± 0.3 nm), indicating the good mechanic stability.

Since the laser spot in Raman experiments could heat up the sample up to several hundred degrees, it is important to understand the thermal stability of the graphitic nanostructure in air. Figure S5E shows that there was no change in Raman spectrum after 1 hour of Raman laser illumination. However, the signal disappeared after the sample was illuminated by laser overnight, indicating that oxidation occurred. The typical Raman integration time used in our study was 30-600 seconds and therefore our Raman data is not affected by laser-induced thermal heating effect.

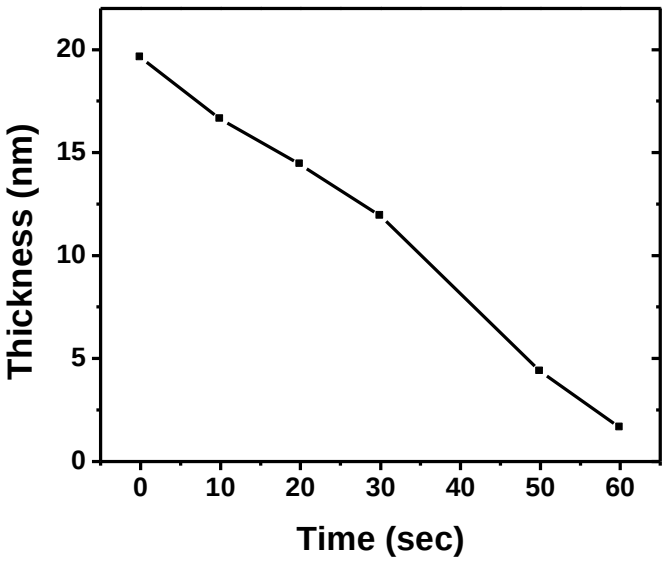

Figure S1. Etching rate of Al_2O_3 in H_3PO_4.

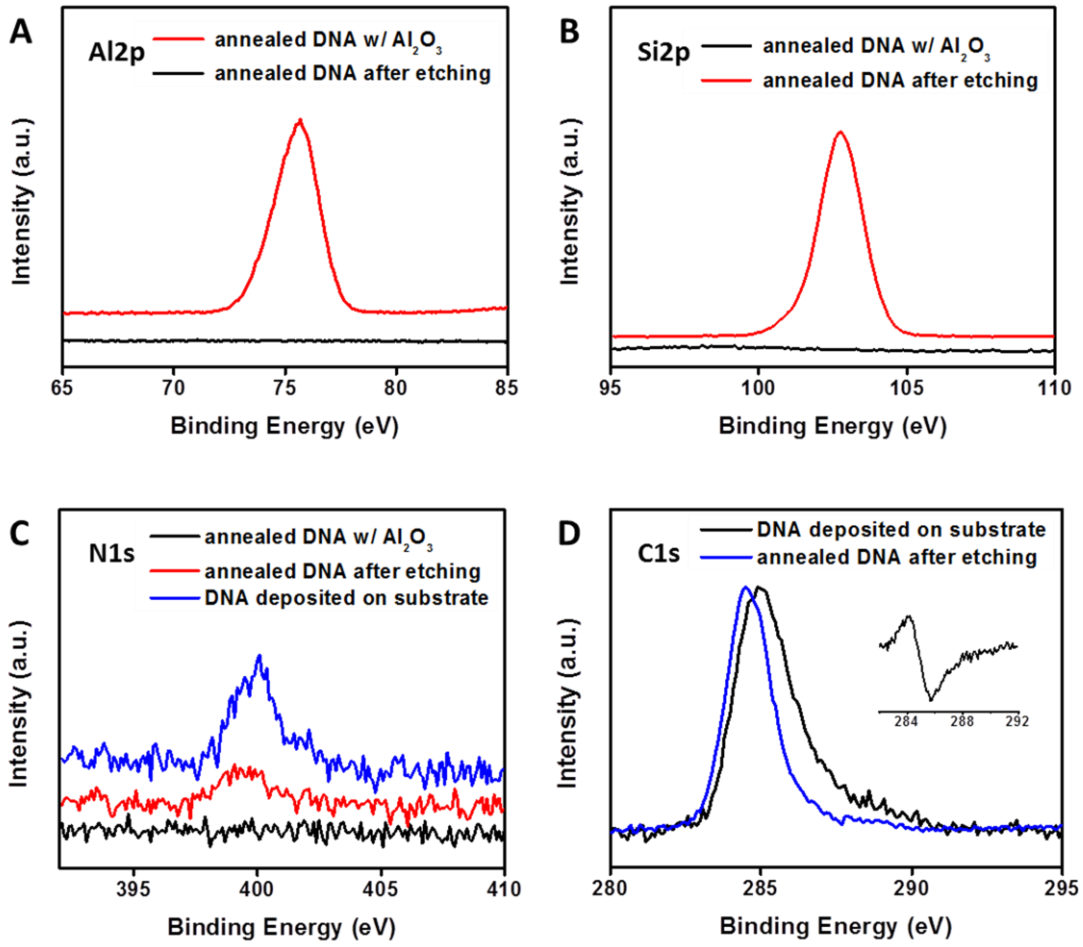

Figure S2. XPS analysis of DNA triangles after deposited on substrate, after annealing with Al_2O_3 in the presence and after removal of Al_2O_3 film. Inset in Figure D: difference between DNA before and after annealing. Also see Table S1.

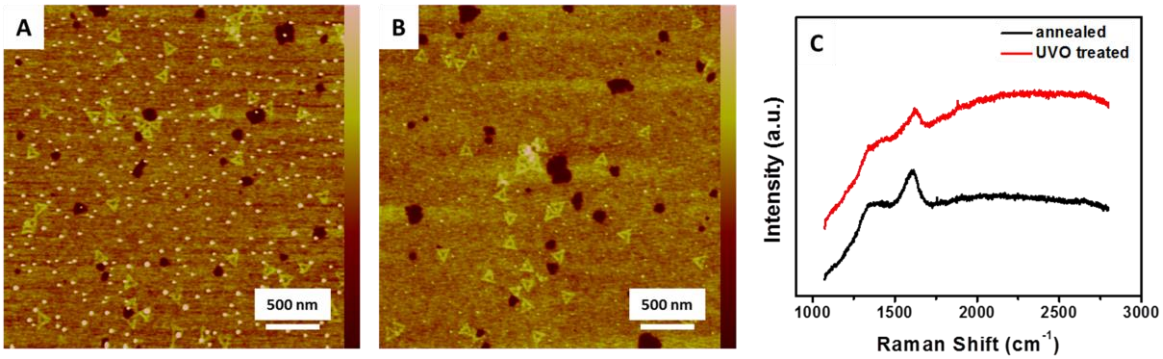

Figure S3. AFM images of (A) the annealed Si/DNA and (B) the same wafer after 2 hour UV/Ozone treatment; (C) Raman spectra of both samples. The height bar for A and B is 5 nm. Note that the Al_2O_3 coating was not removed in this case.

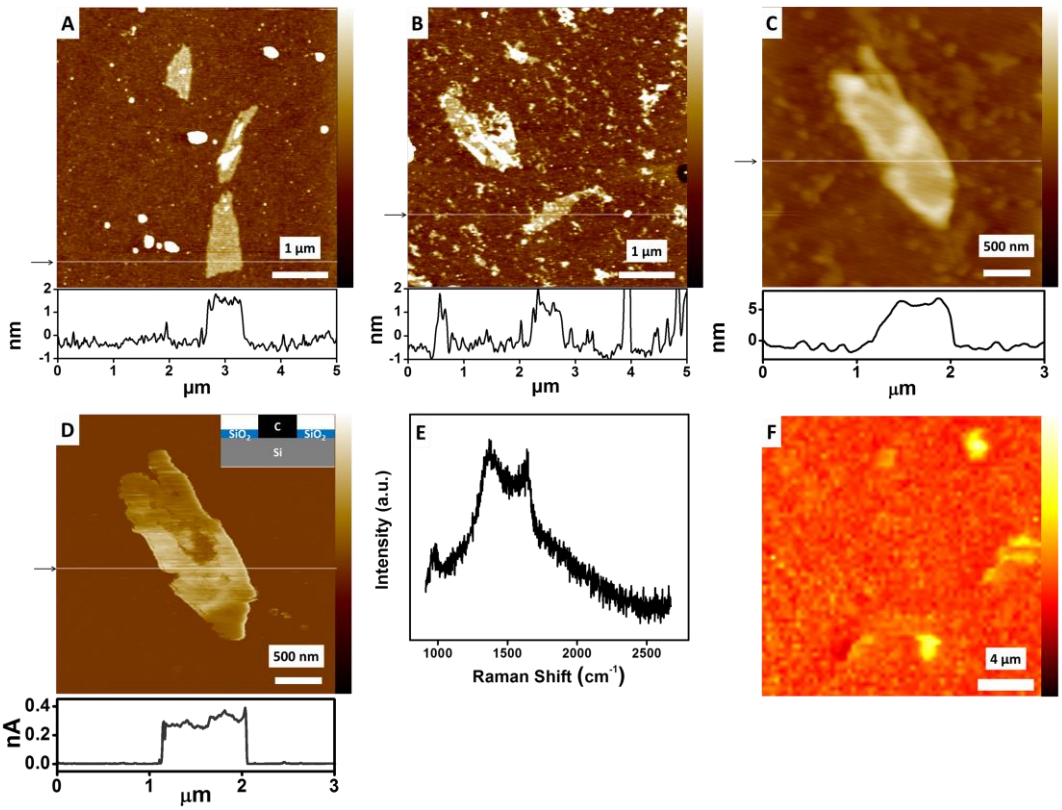

Figure S4. Tapping mode AFM topographic and cross-sectional images of (A) a 2D DNA crystal sample (1.82±0.15 nm in height before ALD) after ALD deposition of Al_2O_3 film and (B) after annealing at 800 ºC. (C) Contact mode AFM topographic and cross-sectional image and (D) conductive AFM and cross-sectional image of another 2D DNA crystal sample (11.3±0.4 nm in height before ALD) after annealing and removal of Al_2O_3 coating. The height of sample (C) is 7.3±0.7 nm. The inset in (D) shows a proposed structure of the sample. (E) Raman spectra of sample (B) after background subtraction. The background data was collected on a DNA-free Al_2O_3/Si sample that was soaked in buffer and rinsed with ethanol water mixture before ALD; the Si overtone peak was used for intensity calibration. (F) Confocal Raman mapping of sample (B) at using intensity at 1611 cm^{-1}. Height bars represent 5 nm in (A) and (B), 20 nm in (C), 1 nA in (D), and 372 a.u. (arbitrary unit) in (F).

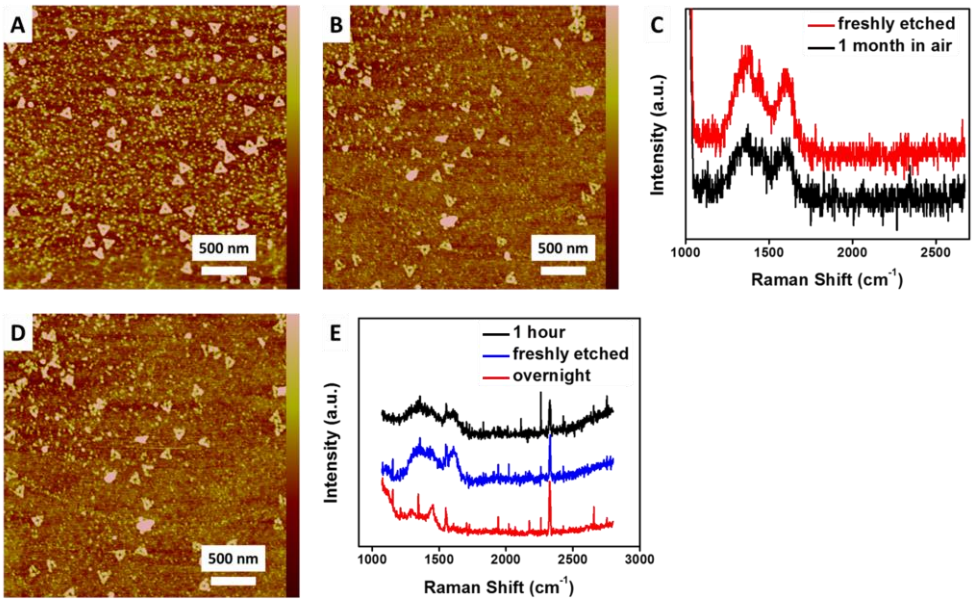

Figure S5. AFM images of carbonized DNA (A) right after etching to remove Al_2O_3, (B) after stored in lab for 1 month and (D) after 5 times same location tapping mode AFM scanning. (C) Raman spectra of freshly etched carbonized DNA and that after 1 month storage in lab. (E) Raman spectra of freshly etched carbonized DNA and that under Raman laser illumination for 1 hour and overnight in Raman experiments. The height scale bars represent 5 nm in all AFM images.

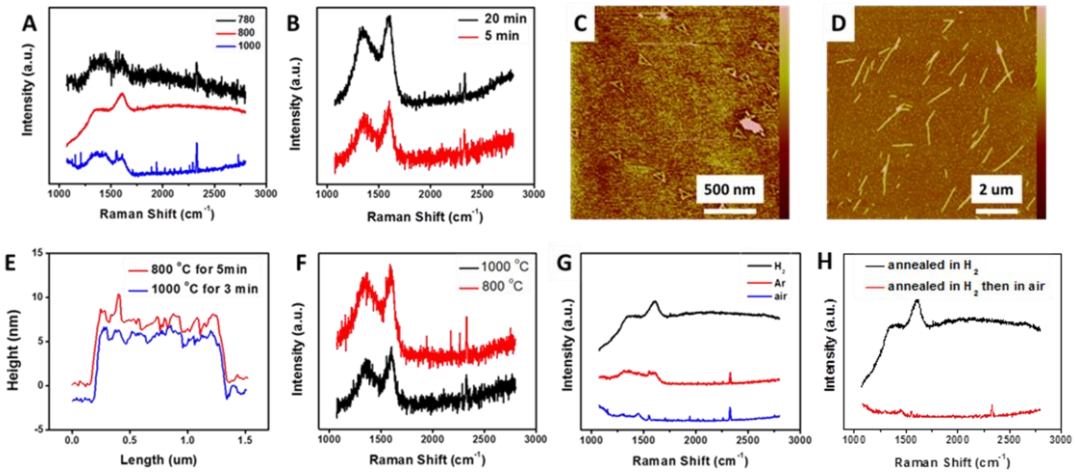

Figure S6. Raman spectra of annealing experiments (A) at various temperature, (B) in different duration and (G) environment. (C) AFM image of DNA triangles annealed for 20 min. (D) AFM image of 1D DNA crystal annealed at 1000 ^{o}C for another 3 min. (E) Height profile and (F) Raman spectra of 1D DNA crystal after annealing at 800 ^{o}C for 5 min and at 1000 ^{o}C for another 3 min. (H) Raman spectra of DNA triangles after annealing in H_2 for 5 min and in air for another 5 min. The height scale represents 2 nm in C and 20 nm in D, respectively.

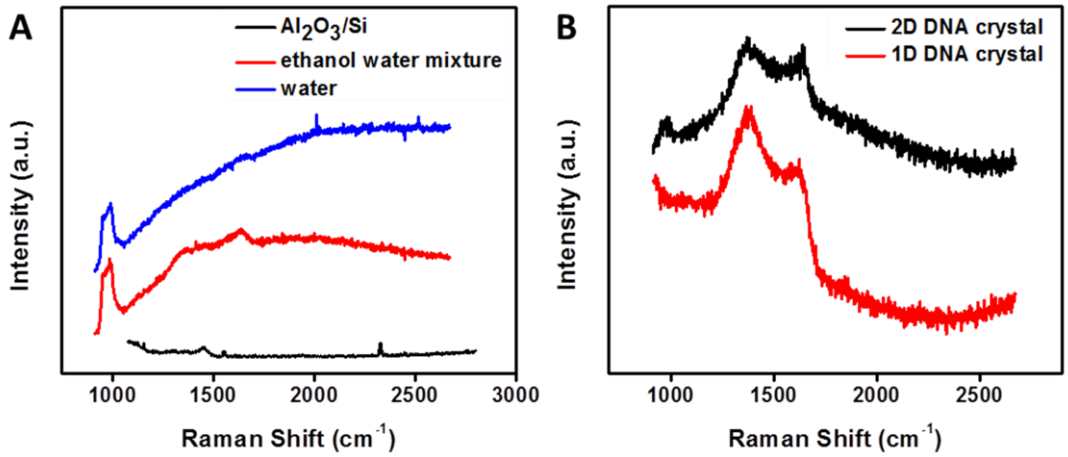

Figure S7. (A) Raman spectra of annealed Al_2O_3/Si, Al_2O_3/Si (Si soaked in buffer and rinsed with **ethanol water mixture** before ALD) and Al_2O_3/Si (Si soaked in buffer and rinsed with **water** before ALD). (B) Raman spectra of 1D DNA crystal and 2D DNA crystal after subtraction against the Raman spectra of annealed Al_2O_3/Si (soaked in buffer and rinsed with **ethanol water mixture** before ALD). The Si overtone peak was used for intensity calibration.

	C=C	C-C	C-H	C-O-C	O=C-O
BE (eV)	284.4	284.8	285.2	286.4	288.9
DNA	22.2	1.7	48.3	24.7	3.1
Annealed DNA	69.8	2.0	25.0	3.0	0

Table S1. Relative area (%) of the deconvoluted components in the C1s XPS peak of DNA and annealed DNA samples (Figure S2D).

3. References

S1. Tuinstra, F.; Koenig, J. L. Raman Spectrum of Graphite. *J. Chem. Phys.* **1970,** *53*, 1126-1130.

S2. Cançado, L. G.; Takai, K.; Enoki, T.; Endo, M.; Kim, Y. A.; Mizusaki, H.; Jorio, A.; Coelho, L. N.; Magalhães-Paniago, R.; Pimenta, M. A. General Equation for the Determination of the Crystallite Size La of Nanographite by Raman Spectroscopy. *Appl. Phys. Lett.* **2006,** *88*, 163106.

S3. Lucchese, M. M.; Stavale, F.; Ferreira, E. H. M.; Vilani, C.; Moutinho, M. V. O.; Capaz, R. B.; Achete, C. A.; Jorio, A. Quantifying Ion-Induced Defects and Raman Relaxation Length in Graphene. *Carbon* **2010,** *48*, 1592-1597.