

Supplemental Material

Hybrid 3D Graphene and Aligned Carbon Nanofiber Array Architectures

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Materials and Methods:

CVD: A 4 feet long quartz tube with an inner diameter of 1.8 inches was used with a heated zone of around 10 inches. The CVD processes were also done using copper foils with a thickness of 25- μm (Alfa Aesar, item No. 13382, cut into 1.5cm $\times$ 5cm strips). Before CVD, grids were cleaned by acetone, isopropyl alcohol (IPA), deionized (DI) water, IPA again, and dried in flowing nitrogen. Additional few-second cleaning with diluted (2%) HNO_3 did not produce any changes in appearance of graphene/CNF-forests. A typical growth procedure involves the following steps:

The ceramic boats are loaded with the fresh and clean Cu grids, system is evacuated to reach the lowest pressure possible, (the system background pressure is 1 mTorr). The system is then back filled with hydrogen (99.99% in purity) and a hydrogen pressure of 2.5 Torr is maintained under a flow rate of 20 sccm. The manifold is heated from room temperature to 1035 $^{\circ}\text{C}$ in 35 min.

After reaching 1035 $^{\circ}\text{C}$, the substrates are annealed for 30 min or longer to facilitate the growth of very large Cu grains, to remove residual copper oxide, and to smoothen the surface without changing the hydrogen pressure and flow rate. The growth was then carried out at 1035 $^{\circ}\text{C}$ for a desired period, typically less than 3 min time after adding methane (99.99% in purity) with a flow rate of 60 sccm, keeping both constant pressure and hydrogen flow. Samples were rapidly cooled to room temperature in the same hydrogen atmosphere but without methane flow.

Additional results:

Additional SEM images (Figures S1 and S2) giving a top down view of the CNFs are presented below. Additional HRTEM plots showing a magnified image from Figure 3b in the text (clearly showing lattice fringes) and the electron diffraction patterns of the graphene surface after removal of the CNF by sonication is shown in Figures S3 and S4 respectively. Confirmation of the fact that the graphene grows on the Cu surface prior to any CNF growth is presented in the Raman spectra of the Cu surface obtained at very short deposition times and is shown in Figure S5.

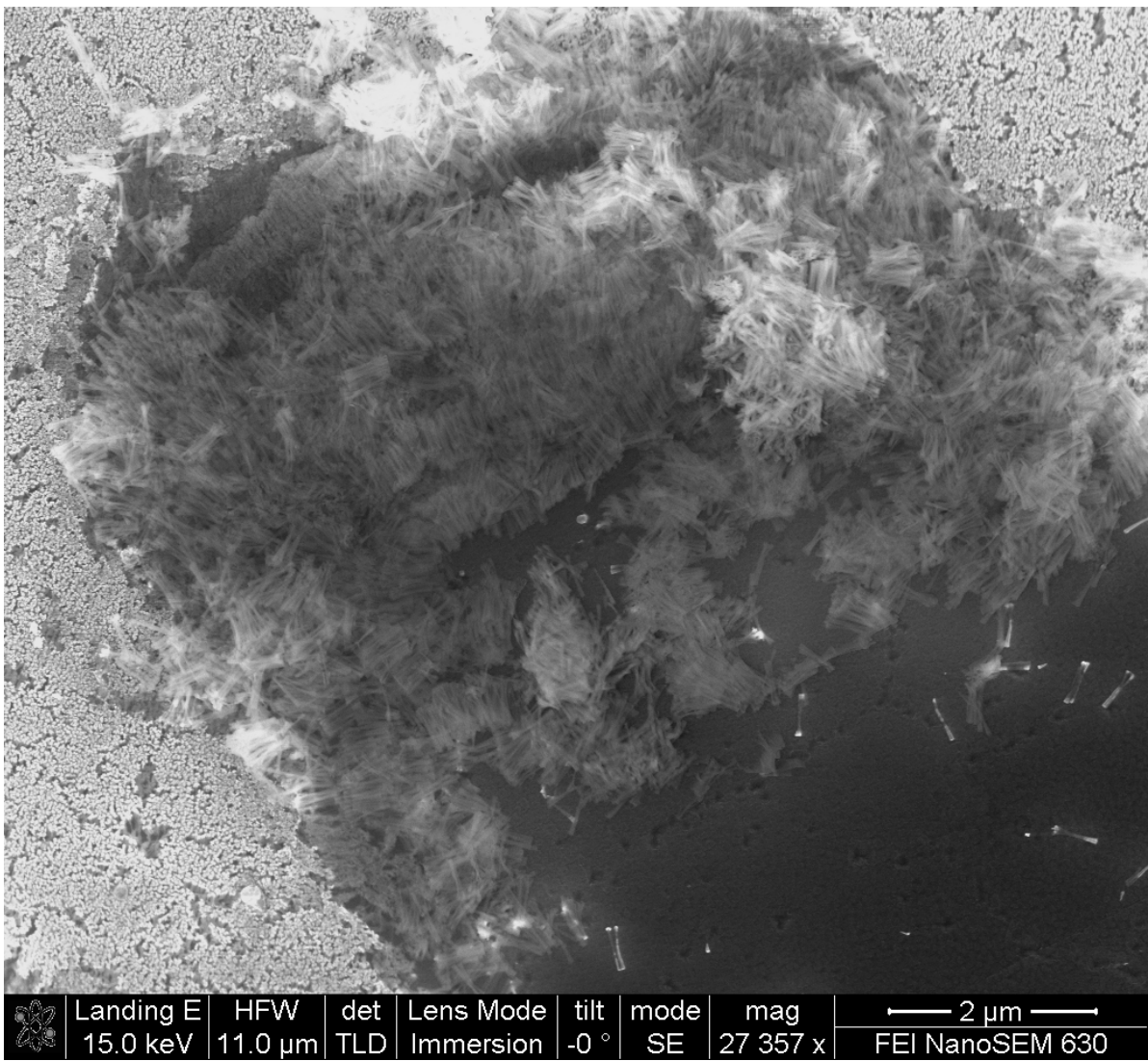
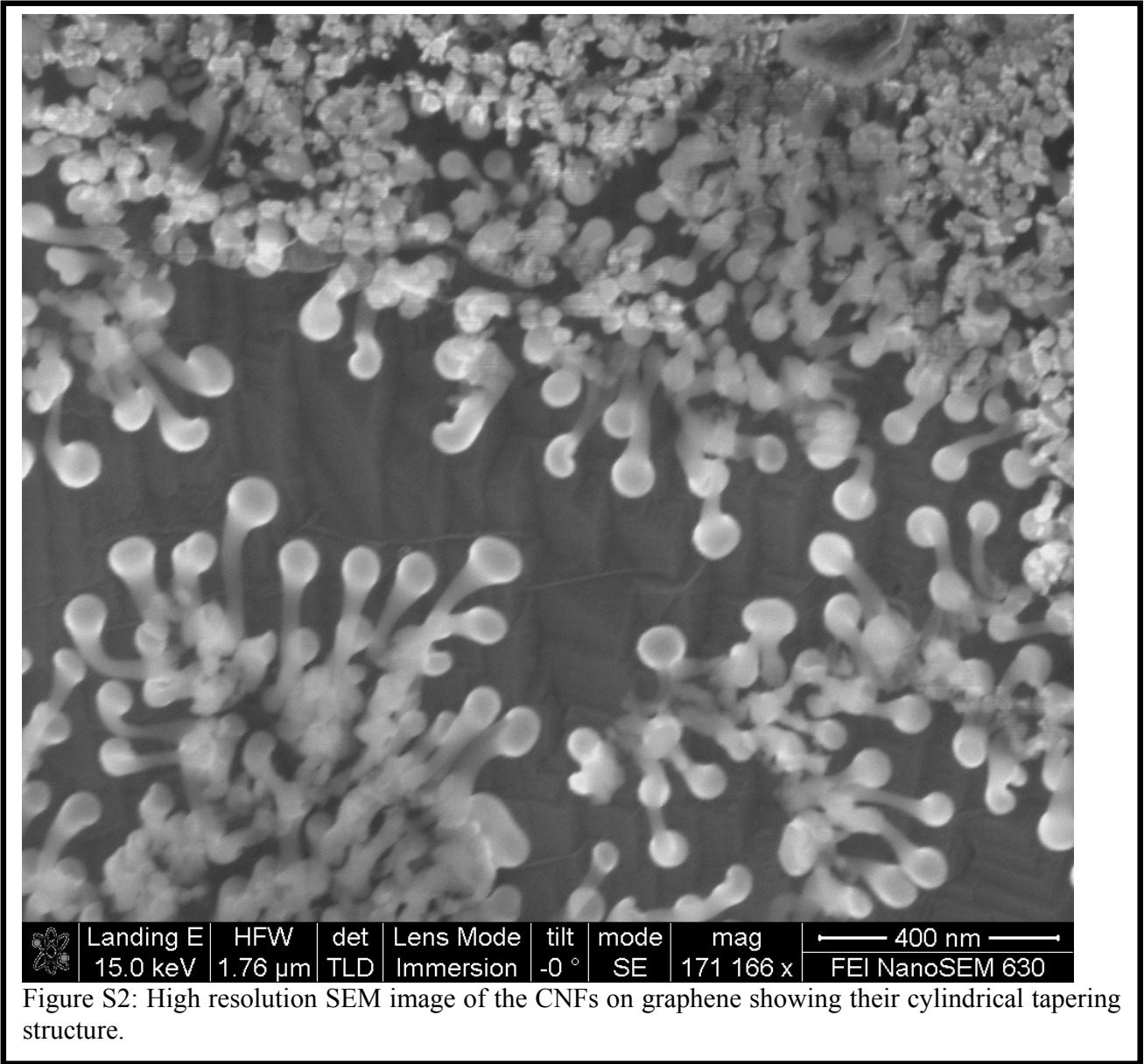
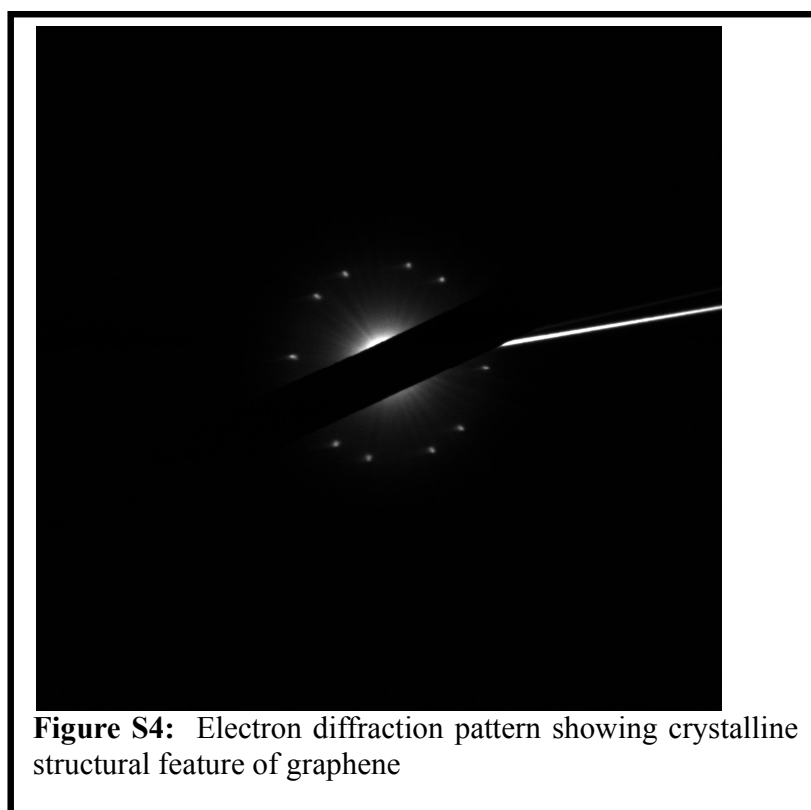
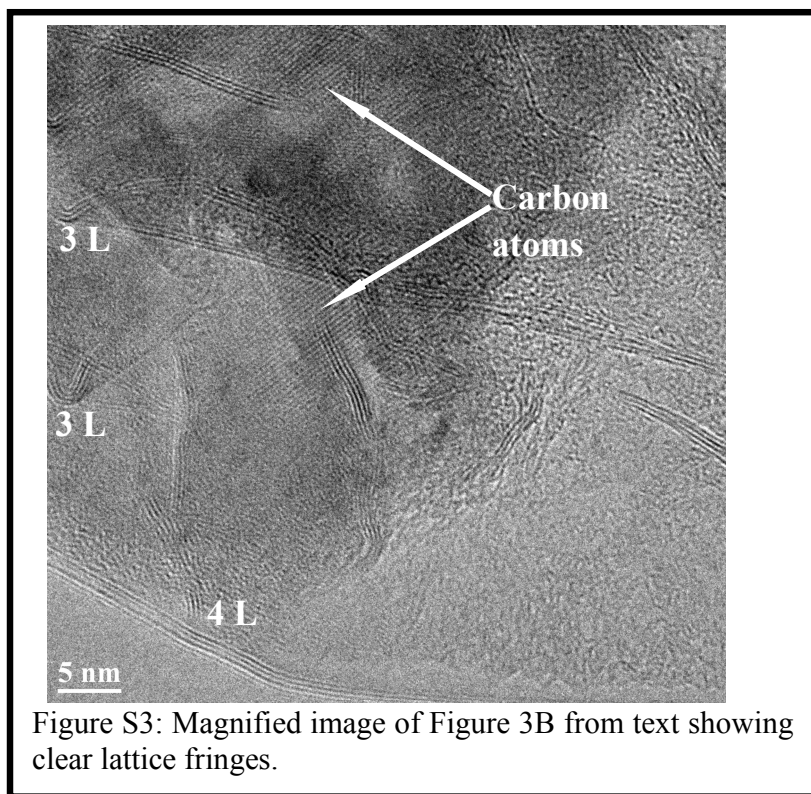


Figure S1. Low resolution top down SEM image of CNF on graphene.





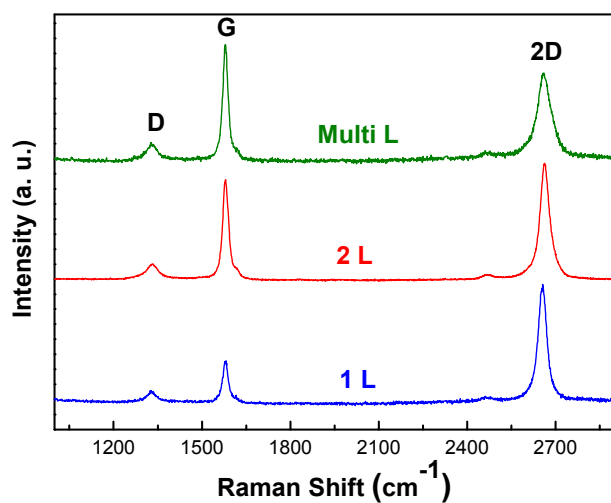


Figure S5: Typical Raman Spectra obtained at very short deposition times (few seconds) showing single-, double-, and multi-layer graphene on the Cu surface before formation of CNF.