Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Synthesis of Chemically Bonded CNT–graphene Heterostructure Arrays

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1. **Synthesis of the graphene arrays on aligned CNTs:** We adopt a simple microwave plasma chemical vapor deposition (MPCVD) technique to induce growth of graphene layers on aligned CNT arrays.[1] Methane gas mixed with H_2 was used as the source of carbon, where H_2 assisted in creating hydrogen plasma inside the chamber and breaks the methane molecules to achieve carbon. The process can be approximated to three different stages of growth. A schematic of the process is presented in Figure S1.

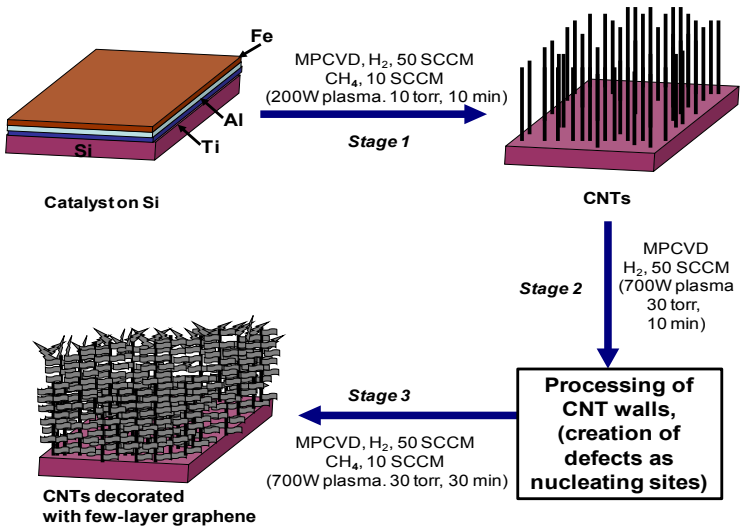

Figure S1: Schematic of the growth of the graphene arrays on aligned CNTs

(i) Growth of CNT arrays: Aligned CNTs bundles were grown on ~1cm×1cm Si substrates covered with a trilayer (30 nm Ti/ 10 nm Al/ 3 nm Fe) catalyst in a SEKI AX5200S microwave plasma CVD system. Herein, 50 cubic centimeter per minute (SCCM) of H_2 and 10 SCCM CH_4 were passed over the catalyst loaded substrate at a growth pressure and temperature of 10 Torr and 900 °C, respectively. A 200 W plasma was formed in the growth chamber. The length of the CNTs increases with the duration of growth. In the present case, the synthesis was carried out for 10 min. An SEM image of the cross section of the CNT layer is shown in Figure S2a. As seen from the images, the entire Si substrate was covered with CNTs. Figure S2b is a top view SEM image of the CNTs. The magnified images of the CNT layers revealed that the CNTs are roughly parallel to each other. While an overall growth direction perpendicular to the substrate is maintained, the CNTs

[1] (a) Cola, B.A.; Xu, X.; Fisher, T.S. *Appl. Phys. Lett.* **2007**, 90, 093513; (b) Cola, B.A.; Xu, J.; Cheng, C.R.; Xu, X.F.; Fisher T.S.; Hu, H.P. *J. Appl. Phys.* **2007**, 101, 054313.

are not straight locally and the growth orientation may deviate up to 60^0 from the overall direction. (Figure S2c and d). As seen from the top view image, the CNTs do not appear to be aligned. This might be important, since in the later stage of growth, graphene layers may grow along these CNTs, forming an interconnected network. Figure S3 shows TEM images of the CNTs. The CNTs are multiwall in nature. The diameter of the CNTs varies from 40 to 80 nm. The CNTs are closed at one end.

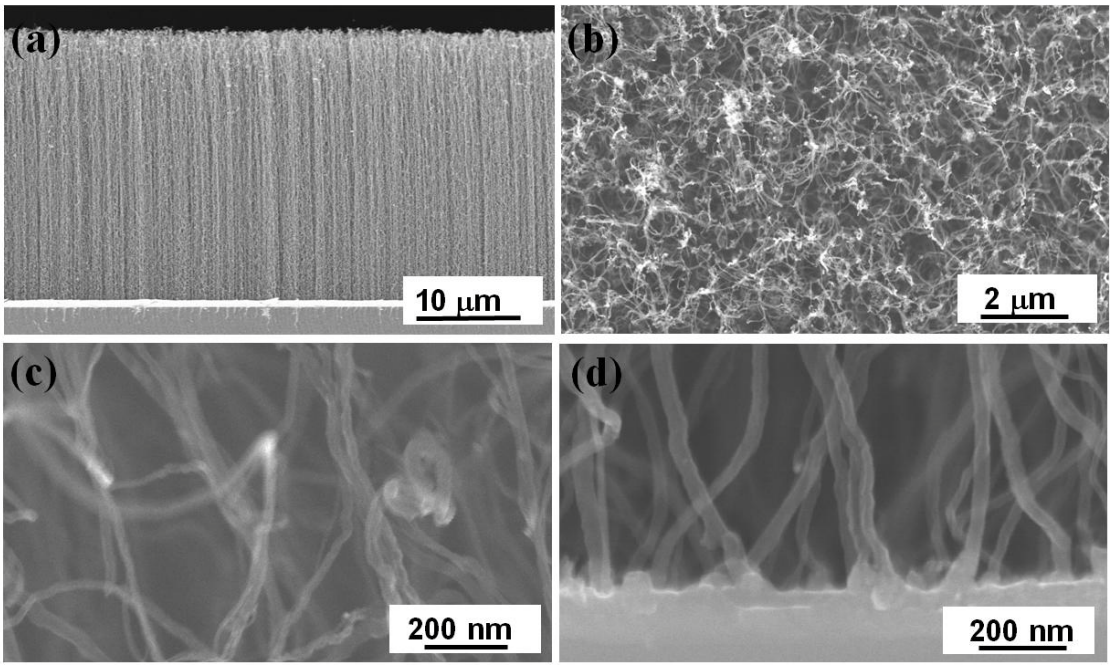

Figure S2: (a) A cross-section SEM image of the CNT layers grown on a Si substrate. (b) A top view SEM image of the CNT arrays. (c-d) A high magnification SEM image displaying the CNTs near the Si substrate.

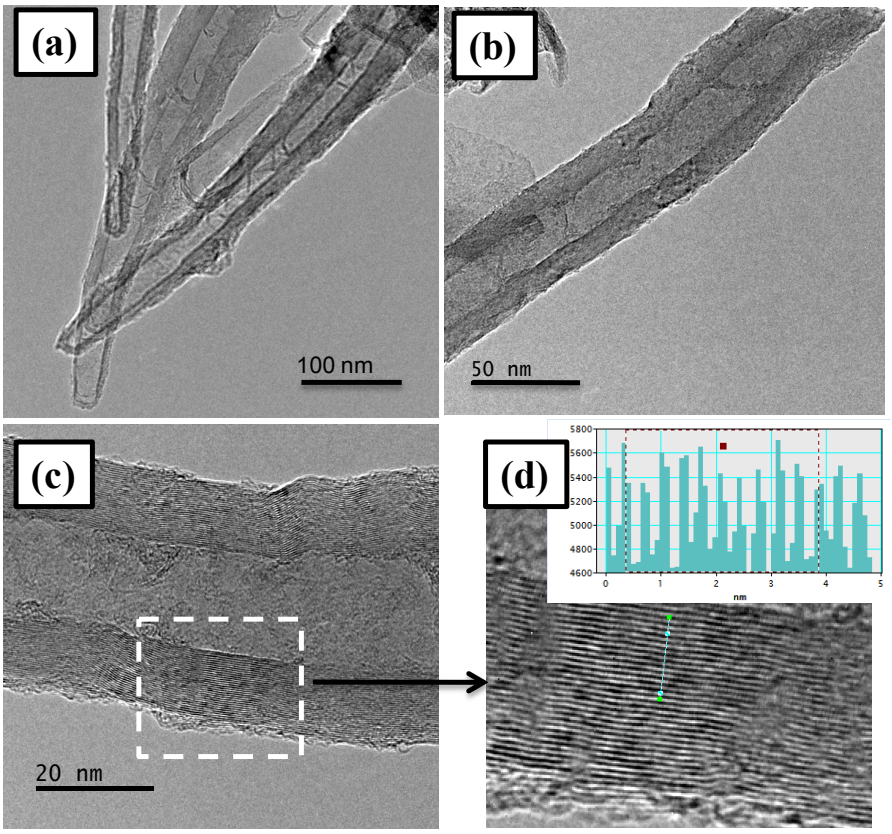

Figure S3: (a, b) Low magnification TEM images of CNTs obtained by a MPCVD method (c, d) High magnification TEM image of a CNT. Inset in D displays the spacing of ~3.45 Å between the CNT walls.

(ii) To decorate CNT arrays with graphene, a secondary growth procedure by MPCVD was followed.[2] The CNT arrays were first exposed to an MPCVD condition under 50 sccm H_2 primary feed gas flow at 30 Torr total pressure and 700 W plasma power at 900°C substrate temperature for a period of 10 min. The outer walls and the caps of the CNTs yield to these conditions and defect sites are created on them, which acts as nucleating sites for the growth of graphene layers. Figure S4 shows a TEM image of such a CNT with its tip open as a result of high energy plasma treatment.

[2] Rout, C.S.; Kumar, A.; Xiong, X.; Irudayaraj, J.; Fisher, T.S.; *Appl. Phys. Lett.*, **2010**, 97, 133108.

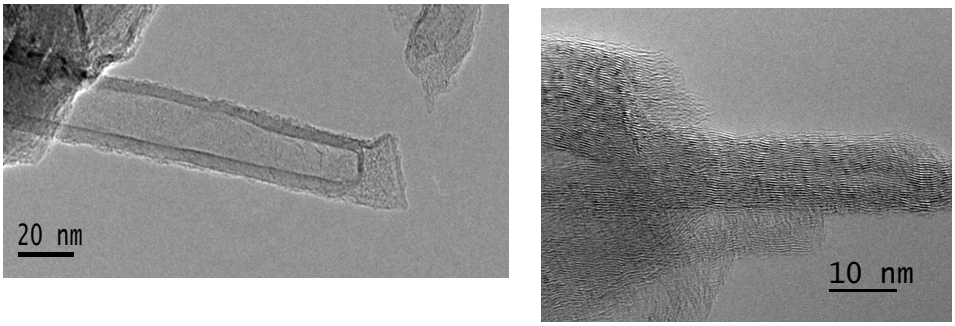

Figure S4: TEM images of two CNTs treated under H_2 gas flow under high plasma conditions. A typical opening at the tip of the CNT and numerous defects across the length of the CNT helps the growth of graphene layers in the next stage of synthesis.

(iii) In the last stage, immediately after the H_2 treatment, CH_4 was introduced into the chamber, while maintaining all other conditions and H_2 gas flow constant. The growth was carried out for 30 min under the same plasma power and pressure.

2. **Growth mechanism of the CNT on Si substrate**: Nanotube growth on catalyst layer on substrate takes place due to the gas-solid interaction process which includes diffusion of precursors, adsorption of species onto the surface, surface reaction and desorption of product species.[3] In our experimental process, methane molecule adsorbed onto the catalytic particle surface release carbon upon decomposition which dissolves and diffuses into the particle. When a supersaturated state is achieved, carbon precipitates in a crystalline tubular form and electrostatic force creates a uniform tensile stress across the entire particle/CNT interface which helps to achieve highly aligned MWCNTs.[4]

Growth mechanism of the graphene layers on CNT arrays: Growth of graphene layers are likely to have occurred preferentially at the defect sites on the exposed CNT surface which may be accentuated by the hydrogen plasma pretreatment. Previous studies show that disorder and defect density in CNTs increases plasma treatment.[5,6] As stated by Petherbridge et al. and Garg et al., the ratio of atomic hydrogen to precursor hydrocarbon in the plasma mixture is critical in determining the preference for diamond sp^3 or graphene sp^2 like growth upon deposition. [7,8] Also, from other studies on vertically aligned carbon nanosheets, it is

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[3] Meyyappan, M.; Delzeit, L.; Cassell, A.; Hash, D.; *Plasma Sources Sci. Technol.* **2003**, 12, 205,

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[5] Zhi, C.Y.; Bai, X.D.; Wang, E.G. *Appl. Phys. Lett.*, **2002**, 81, 1690.

[6] Choi, W.S.; Choi, S.-H.; Hong, B.; Lim, D.-G.; Yang, K.-J.; Lee, J.H. *Mater. Sci. Eng.: C*, **2006**, 26, 1211.

[7]. J.R. Petherbridge, P.W. May, M.N.R. Ashfold, . *J. Appl. Phys.,* **2001**, 89, 5219.

known that carbon atoms from the carbon source or sputtered carbon serve as activated carbon to diffuse on the surface of carbon nanosheets and the diffusion process makes the carbon atoms more likely to be captured by defects present on the CNTs surface, resulting the formation of graphene layers on CNT walls.[9-11] While further elucidation of the growth mechanism will require detailed plasma diagnostics experiments, clearly the current deposition conditions favour sp^2-type graphene-layers growth.

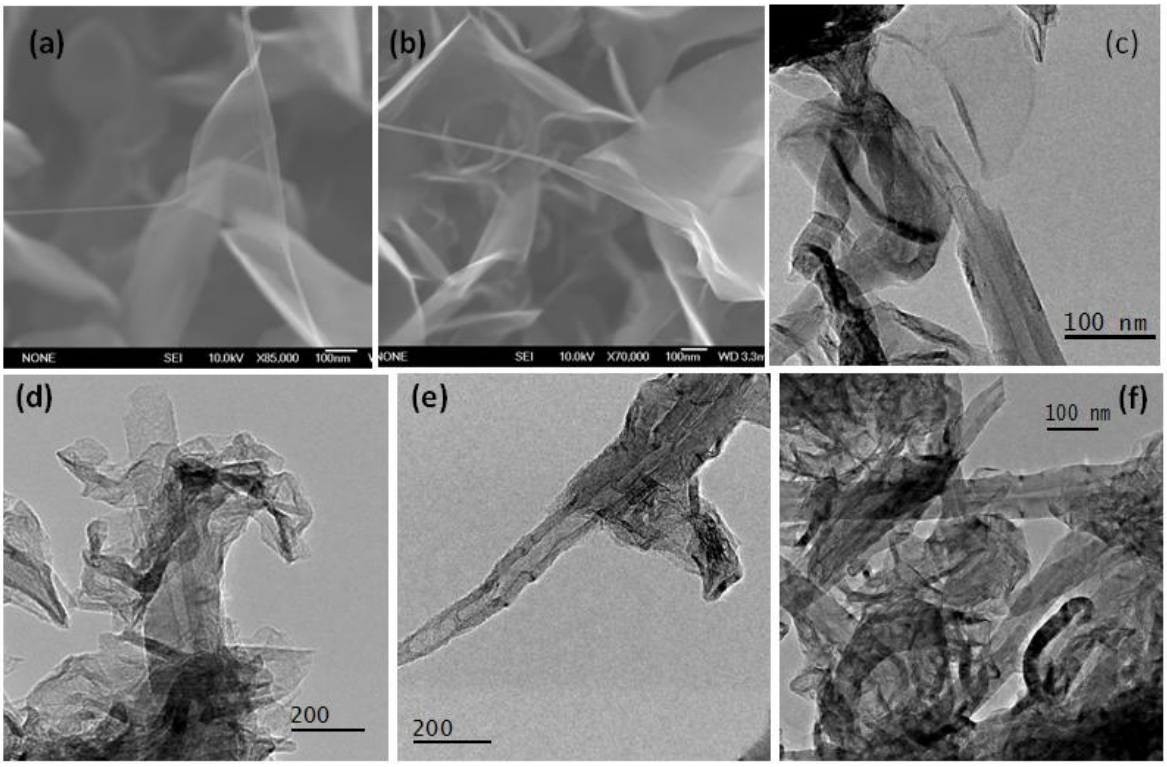

Figure S5: Images showing various junctions between CNT and graphene sheets. (a, b) SEM images showing a graphene sheet are connected to various CNTs. While some of the graphene sheets are crystalline in nature, a large portion of the graphene sheets appear highly defective. In particular, while preparing TEM grids by scrapping the sample off the Si substrate and by prolonged sonication to unwind and disperse them in toluene, the structures seem to crumble somewhat. (c-f) TEM images product showing regions near the junction. In all these images, the tendency of the graphene sheet to seamlessly merge with the CNT is apparent.

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8. R.K. Garg, S.S. Kim, D.B. Hash, J.P. Gore, T.S. Fisher, *J. Nanosci. Nanotechnol.* **2008**, 8, 3068.

9. M.Y. Zhu, J.J. Wang, B.C. Holloway, R.A. Outlaw, X. Zhao, K. Hou,V. Shutthananhdan, D.M. Manos, Carbon, 2007, 45, 2229.

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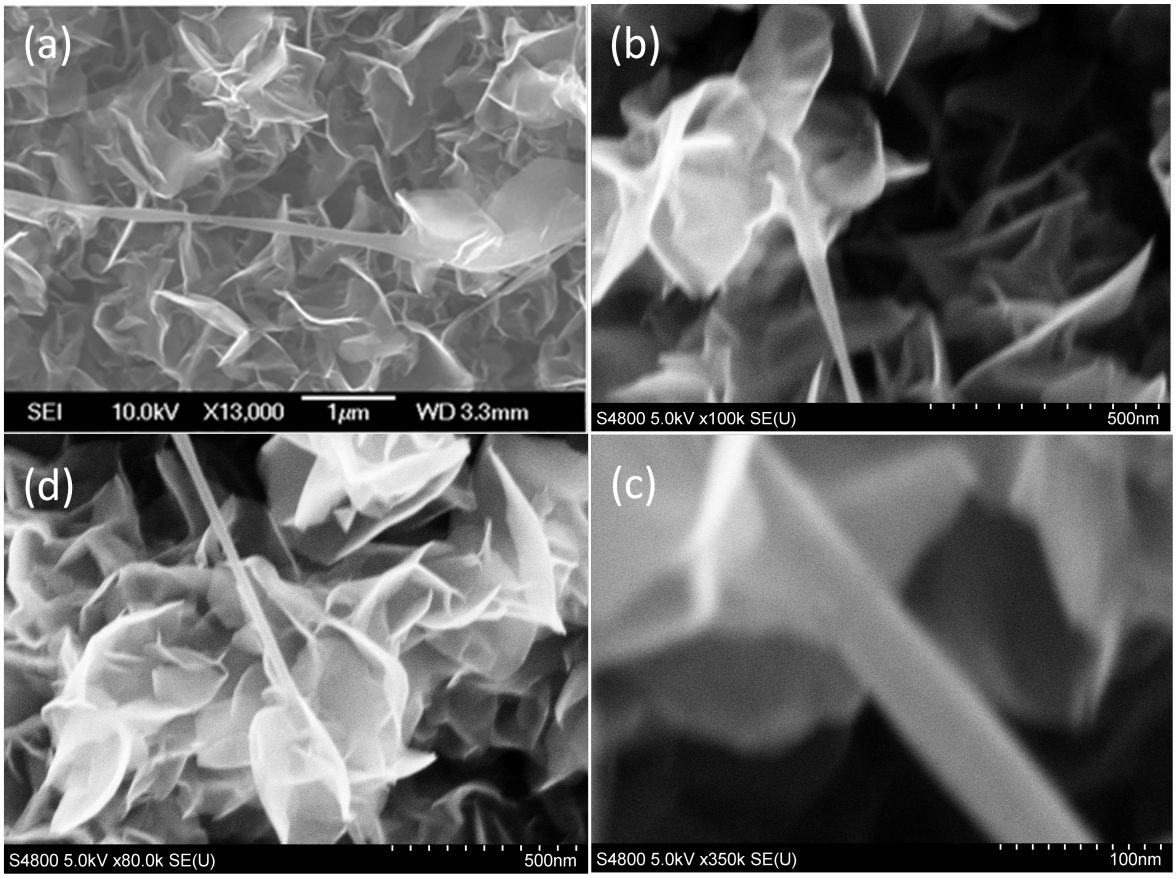

Figure S6: SEM images showing growth of graphene layers from CNTs