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Electronic Supplementary Information (ESI)

Self-assembled growth of multi-layer graphene on planar and nano-structured substrates and its field emission properties

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Experimental section

The preparation of Si wafers

n (100) Si wafers with a resistivity of 1–10 Ω·m and a thickness of 505–545 μm were chosen as the substrates. We followed a process of sonication (50 W, similarly hereafter) in deionized water for 5 min, sonication in acetone (99.5%) for 10 min, sonication in alcohol (99.7%) for 10 min, and then immersing the thus prepared Si wafers into diluted hydrofluoric acid (4%, volume fraction) for 5 min to remove the organic contaminant and the SiO_2 termination on the surface of Si wafers. The thus prepared Si wafers were taken out air stand-by without any other treatment.

The preparation of diamond-like carbon films

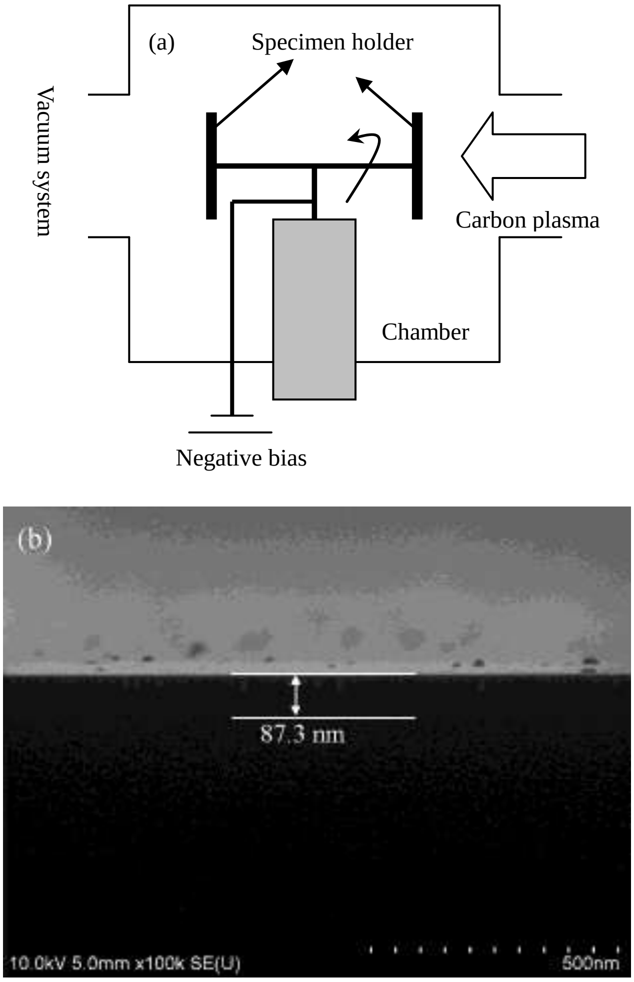

Fig. S1 (a) Schematic diagram of the MEVVA system used for the deposition of DLC films. (b) SEM side view image of an 87.3 nm-thick DLC film. An ultrathin Pt coating of about 2 nm was deposited on the cross-section of the DLC sample before SEM imaging to prevent the electron accumulation.

The diamond-like carbon (DLC) films were deposited by using a metal vapor vacuum arc (MEVVA) ion source deposition system at room temperature. Fig. S1a shows the schematic diagram of the deposition chamber. We first fixated the thus prepared Si wafers on a stainless specimen holder, which rolls during the DLC deposition to increase the uniformity of the deposited films. The Si wafers were placed facing the carbon plasma during the DLC deposition. The chamber was pre-vacuumed to 5×10^{-4} Pa. The carbon plasma used for DLC deposition was generated by an arc discharge system. A negative bias of ~150 V was applied on the Si wafers to obtain the DLC films we needed. The depositing time was 40 min. The thus prepared DLC films are about 85 nm in thickness, as shown in Fig. S1b.

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The preparation of carbon nanotube arrays

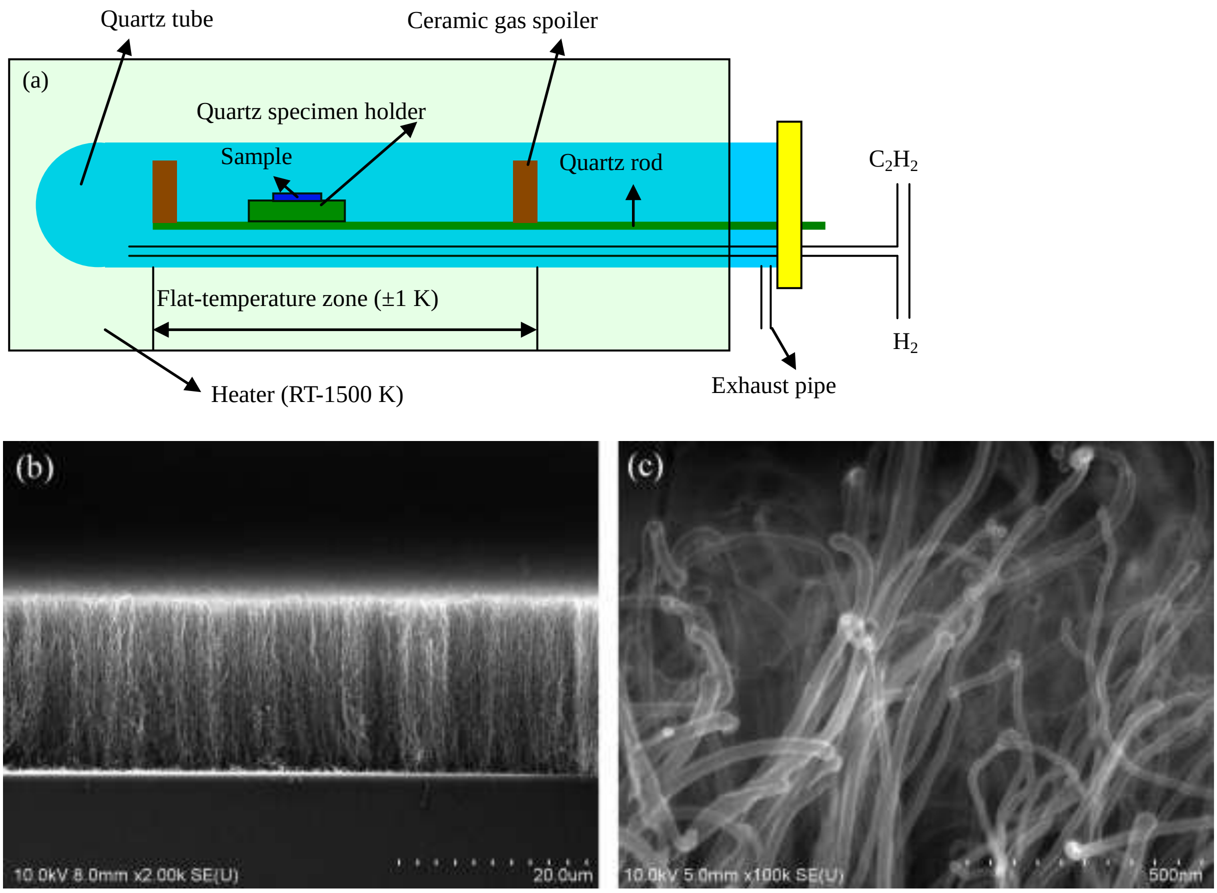

Fig. S2 (a) Schematic diagram of the thermal CVD system used for the CNT array fabrication. (b) Low- and (c) high-resolution SEM images of the CNT array.

The carbon nanotube (CNT) arrays were prepared by using a traditional chemical vapour deposition (CVD) method. We first followed the same process above mentioned to prepare the Si wafers. And then, a 5 nm-thick iron film was deposited on the Si wafers as a catalyst by using a magnetron sputtering system. The CNT growth was carried out in a tubular furnace at atmospheric pressure, as schematically shown in Fig. S2a. Before the CNT growth, the catalyst was first annealed at 580 °C for 1 hour under 400 sccm H_2, and then etched in 150 sccm NH_3 for 10 min at 750 °C. The growth was then carried out at 750 °C for 30 min under a gas mixture of 600 sccm H_2 and 87 sccm C_2H_2. After then, the sample was rapidly cooled to room temperature in H_2 ambient (600 sccm).

The preparation of Si nanowire arrays

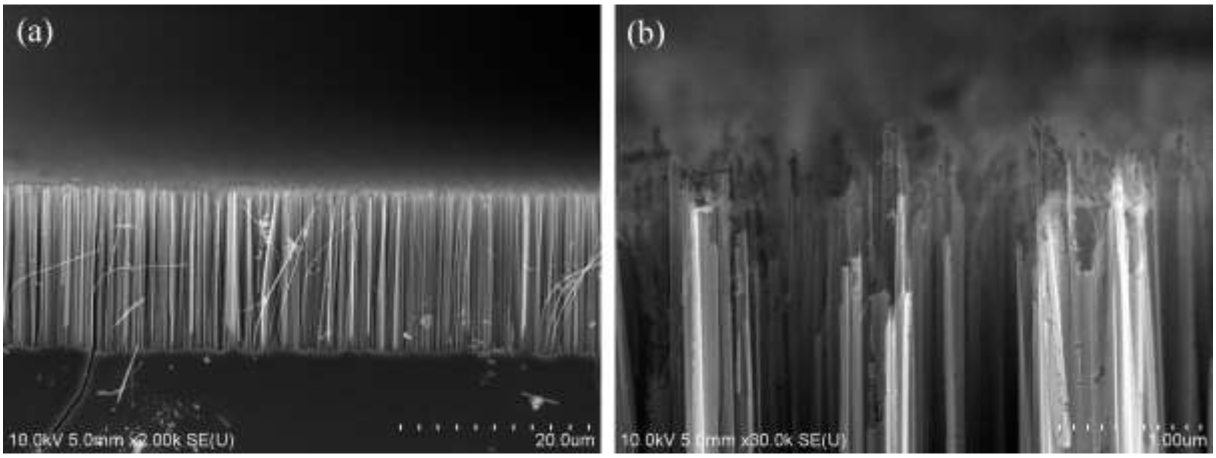

Fig. S3 (a) Low-resolution SEM side-view image of a SiNW array. (b) High-resolution SEM image of a SiNW array, showing the defective surface of the SiNWs.

The Si nanowire (SiNW) arrays were prepared on n-Si (100) wafers in a HF–$AgNO_3$ solution and a HF–H_2O_2 solution with Ag as the etching catalyst. First, we followed the same process above mentioned to prepare the Si wafers. After then, the Si wafers were transferred to a HF–$AgNO_3$ solution for Ag catalyst deposition with a ratio of $AgNO_3$:HF:H_2O = 2:10:38 (Vol%), the deposition time was 1 min. The Ag covered Si wafers were immediately transferred into a HF–H_2O_2 solution for SiNW electroless etching growth with a ratio of

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H_2O_2:HF:H_2O = 1:10:39 (Vol%), and the processing time was 30-60 min. Fig. S3 shows SEM images of a SiNW array etched for 45 min. It can be seen that the SiNW array is about 17 μm in length (Fig. S3a) and the SiNWs have defective surface (Fig. S3b). The concentration of the above reagents are 0.01 ($AgNO_3$), 4 (HF) and 0.176 mol/L (H_2O_2), respectively.

The preparation of multi-layer graphene arrays

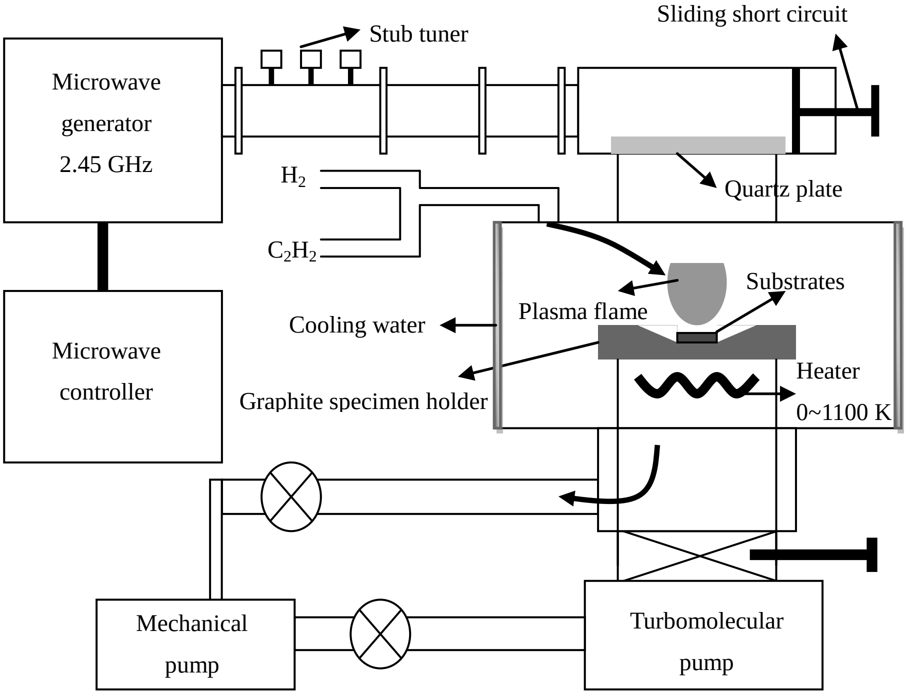

Fig. S4 Schematic diagram of the microwave PECVD system used for the MLG deposition.

The multi-layer graphene (MLG) arrays were synthesized by using microwave (2.45 GHz) plasma enhanced chemical vapor deposition (PECVD), as schematically shown in Fig. S4. C_2H_2 and H_2 were used as the carbon feedback and the assisted gas, respectively. Four types of substrates above mentioned (Si wafers, DLC films, CNT arrays, and SiNW arrays) were adopted to grow MLGs. Contrast to the catalyzed growth of CNTs; the MLG growth is catalyst-free. The MLG growth was carried out in a vacuum chamber. We first vacuumed the chamber to 8.0×10^{-4} Pa and then heated the substrates with an own designed graphite heater to an assigned temperature with an increasing rate of ~60 K/min in hydrogen atmosphere. Glow discharge began when the temperature was stable and a mixed gas, C_2H_2 and H_2 with ratios according to our needs, was led into the chamber, and so started the MLG growth. The substrates were placed about 1 cm away from the plasma flame. The thus prepared MLG samples were cooled to RT in hydrogen atmosphere and were then taken out stand-by.

The structure characterizations of our samples

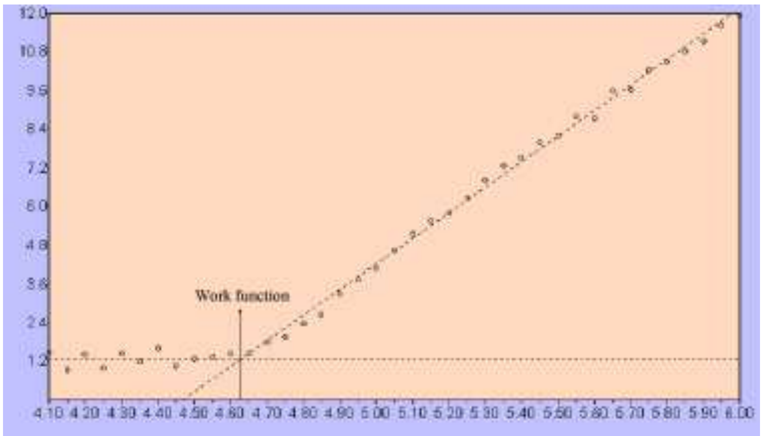

Fig. S5 Work function measuring results given in terms of $(\text{photoemission yield})^{1/3}$ *versus* applied energy, the abscissa of the cross point of the two dashed lines is the work function (marked by an arrow).

The samples were observed by using scanning electron microscope (SEM, S–4800, Hitachi, Japan) to determine their surface morphology. The acceleration voltage during SEM imaging was 5 or 10 kV according to our needs. The fine structure of our samples

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was examined by using transmission electron microscope (TEM, JEM-2010, JEOL, Japan) with an acceleration voltage of 200 kV. The TEM samples were prepared by following a process of scraping off from the substrates, and sonication in alcohol for 45 min. The structure information was further characterized by Raman (LabRAM Aramis, Horiba Jobin Yivon, France) with a wavelength of 633 nm excited by a He–Ne laser in atmosphere. The work function of our samples was measured by using photoelectron spectrometer (AC–2, Riken Keiki, Japan). Fig. S5 shows the measuring results of the work function of one of our samples. The curve is plotted in terms of (photoemission yield)$^{1/3}$ *versus* applied energy. The abscissa of the cross point of the two dashed lines is the work function of this sample. It should be mentioned that the spot area of the photoelectron spectrometer is about 4×4 mm^2, quite larger than the areas of samples used in our field emission measurements (about 2×2 mm^2 in most cases), thus the work function obtained is a statistical value. In fact, we have tried testing a same sample several times but the differences from these multi-time measurements were negligible. Therefore, the work function we obtained can fully express the real work function of the samples used in the field emission measurements.

The field emission measurements of our samples

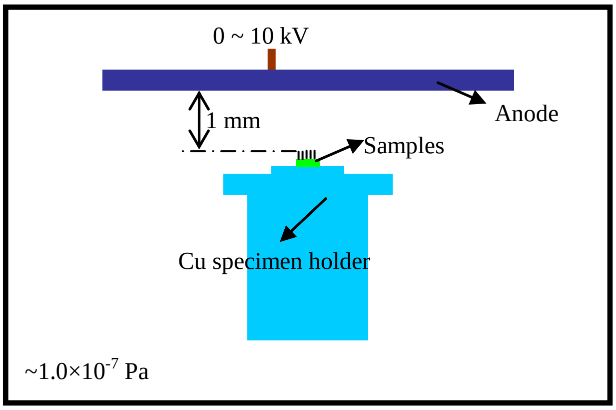

Fig. S6 Schematic diagram of the diode setup used for the field emission measurements.

A diode setup placed in a vacuum chamber with the prepared samples as the cathode and a stainless steel plate as the anode was employed to carry out the field emission measurements, as shown in Fig. S6. The cathode–anode gap was 1 mm. The base pressure was about 1×10^{-7} Pa. The temperature was ~288 K (cooled by water). The field emission results were automatically recorded by a computer in terms of emission current *versus* applied voltage, *i.e.*, *I*–*V*. The applied voltage increased with a rate of 500 V/min during all our tests.

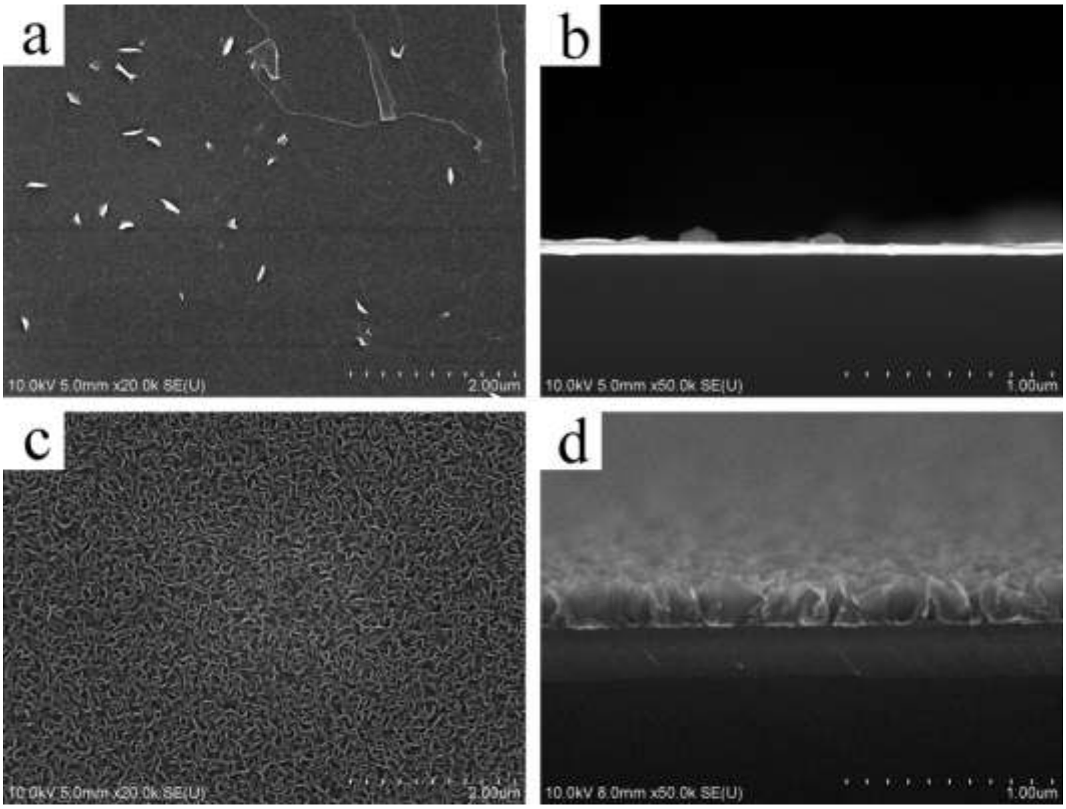

Fig. S7 SEM images of MLGs grown on (a,b) Si wafers and (c,d) DLC films within 1 hour. Other growth conditions: 400 W, 1 kPa, 800 °C, 5 sccm C_2H_2, 10 sccm H_2. It can be seen that the MLGs nucleate more quickly on the DLC films than on the Si wafers.

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Considering the very difference between these two types of substrates is their surface topography, concretely, the distribution of intrinsic defects, we conjecture that the nucleation of MLGs is defect guided.

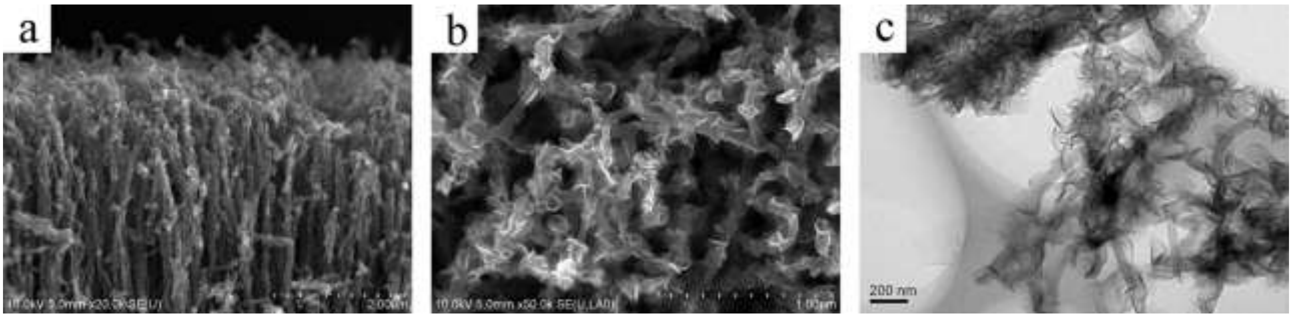

Fig. S8 SEM (a) side-view and (b) top-view images of MLG/CNT composites grown at 100 W. (c) The corresponding low-resolution TEM image showing dispersed MLG/CNT composites. Other growth conditions: 1 kPa, 800 °C, 1 sccm C_2H_2, 10 sccm H_2, and 5 hours. It can be seen that the CNTs reserve their tubular structure and the MLGs are sparsely distributed on the CNTs forming a flower-like appearance. The reason we chose this sample as a comparative sample for the field emission study is that the MLGs of this samples have relatively larger scales than the sample shown in Fig. 1c (MLG/CNT-400W), thus the influence exerted by the MLGs on the field emission of the MLG/CNT composites can be promoted, which has been evidenced in our following field emission study. We find that the MLG/CNT-100W sample has superior field emission properties than the MLG/CNT-400W sample, as shown in Fig. 5b and Table 1.