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# Highly improved field emission from vertical graphene–carbon nanotube composites

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ABSTRACT

Few-layer vertical graphene (VG) was prepared on arrayed carbon nanotubes (CNTs) without a catalyst by using radio frequency sputtering deposition and microwave plasma enhanced chemical vapor deposition, and the field emission (FE) performance of VG–CNT composites was tested and optimized. The FE performance is found to be strongly dependent on the heights (but not the actual heights) and densities of CNTs, the shapes of VG, and the diameters of VG–CNT composites. The optimal shapes for FE are demonstrated to be CNTs with middle densities and small diameters and VG with high densities and small sizes. The optimal FE performance from our large area VG–CNT composites is found to have a low threshold field of 1.28 V/μm (at 10 mA/cm$^2$), a high maximum emission current density of 87.63 mA/cm$^2$ (4.28 times higher than that from our previously prepared graphene–CNT composites), and excellent stability at an extremely high mean emission current density of 36.28 mA/cm$^2$ over a period of 50 h, far better than those of pristine CNTs, pure VG, and shape non-optimized VG–CNT composites.



## 1. Introduction

Graphene has proved to drastically influence the futuristic technology and even our daily lives due to its fascinating thermal, electrical, and mechanical properties [1–4]. It has aroused intensive interest in many applications such as energy storage [5], field effect transistors [6], and memory devices [7]. Graphene has also been demonstrated as a highly efficient field emission (FE) cathode material and the FE performance from single-, few-, and multi-layer graphene has been well reported over the last few years [8–11]. The sharp edge of graphene could serve as high-efficiency emission sites during FE and its unique two-dimensional surface is advantageous for faster heat dispersion and could greatly weaken Joule heating induced FE degradation [12]. In comparison with carbon nanotubes (CNTs), which have been demonstrated as an excellent FE cathode material in the past two decades [13–16], however, pure graphene emitters usually have higher operation voltages and lower current densities. This has aroused a need for the preparation of graphene–CNT composites, which are expected to have both the low working voltage of CNTs and the excellent FE stability of graphene. Two types of graphene–CNT composites are reported. (1) Graphene is flat-lying serving as a substrate for loading CNT emitters [17–19], but the FE capability from the sharp-edged graphene in this regime is totally buried. (2) Aligned CNTs are used as a substrate for growing vertical graphene (VG), which could fit our needs readily. As an example, Nayak et al. fabricated highly protruded graphene wrapped CNTs and ascribed the improved FE properties to the combined advantages of high aspect ratio and protruded graphene layers [20]. Kaushik et al. prepared graphene–CNT hybrids by using microwave plasma enhanced chemical vapor deposition (PECVD) and the hybrids were found to have a high field enhancement factor of ~6500 [21]. We also prepared VG on CNTs by using radio frequency (rf) sputtering deposition and microwave PECVD [22–24]. The FE performance of VG–CNT composites was found to outperform that of bare CNTs and VG. However, the VG–CNT composites we prepared have relatively low maximum emission current densities ($J_{max}$) [20–22] and poor FE stability at high current densities [24], and the underlying relationship between the FE response of emitters and the geometry of CNTs and VG needs to be further understood, which is

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helpful for optimizing the morphology of VG–CNT emitters and achieving highly efficient field electron emission.

Here, we adopted rf sputtering deposition and microwave PECVD to prepare differently shaped VG–CNT composites and optimized their FE properties. The influence from the shapes of VG–CNT composites (CNT: height and density; VG: size and density; VG–CNT: diameter) on their FE performance is discussed. VG with high densities and small sizes, CNTs with good alignment and well-preserved tube-tube spaces, and VG–CNT composites with small diameters are demonstrated to be the optimal shapes for high-efficiency FE. The optimal FE performance is found to have a high $J_{max}$ of 87.63 mA/cm$^2$ at 1.85 V/μm and excellent stability at a high mean emission current density ($J_{mean}$) of 36.28 mA/cm$^2$ over a period of 50 h, far better than those reported in previous studies [20–24].

## 2. Experimental details

### 2.1. Preparation of VG–CNT composites

The influence of experimental parameters (the concentration of carbon source, microwave power, and the growth time) on the growth of VG has been discussed in our previous studies [22,23]. Herein, we mainly discuss the influence of CNT shapes (heights and densities) on the FE performance of VG–CNT composites. The preparation of CNTs were performed on n-(100) Si wafers (resistivity: 1–10 Ω m; thickness: 505–545 μm; area: ~2 × 2 cm$^2$) by using the classical thermal CVD [22]. The Si wafers were pre-bombarded by iron ions at ~10 kV for 15 min using a metal vapor vacuum arc ion source followed by the deposition of a 5-nm-thick iron film as a catalyst using magnetron sputtering. The CNT growth was carried out in a tubular furnace under 600 sccm $H_2$ and 87 sccm $C_2H_2$ at 750 °C. The geometry of CNTs was controlled by changing the thickness of catalyst and the growth time. The resultant CNTs were further annealed at 1000 °C for 5 h. Both the iron ion pre-bombardment and the post-annealing are helpful for improving the adhesion of CNTs to substrates [24]. Microwave (2.45 GHz) PECVD and rf (13.56 MHz) sputtering deposition were employed to prepare the VG [22–24], and the VG shapes were mainly determined by changing the experimental methods. VG prepared by using microwave PECVD is densely distributed and has large sizes [23], while VG prepared by using rf sputtering is sparsely distributed and small-sized [22].

### 2.2. Structural characterizations

Scanning electron microscope (SEM, S–4800, Hitachi, Japan) was used to characterize the surface morphology of the as-received VG–CNT composites under an acceleration voltage of 10 kV. Their fine structure was observed by using a high-resolution transmission electron microscope (HRTEM, JEM–2010) operated at 200 kV. For TEM observation, the samples were prepared by following a process of scraping off from Si wafers, ultrasonicating in an ethanol bath for 15 min, and dropping the as-received solution onto a copper grid. Raman spectroscopy with a He–Ne laser (laser wavelength: 633 nm) was used to evaluate the perfection of our carbonaceous materials and roughly determine the number of layers of VG. The defect analysis was also performed by using X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM) with Al Kα irradiation (~1486.6 eV).

### 2.3. FE measurements

FE measurements of the resultant VG–CNT composites were performed at room temperature by using a diode-type setup under an ultrahigh vacuum condition (~1.0 × 10$^{-7}$ Pa), using our samples (sample area: ~2 × 2 mm$^2$) as the cathode against a stainless steel plate (~10 cm in diameter) as the anode. The surfaces of the cathode and anode were kept perfectly parallel to avoid inhomogeneous electric field. The cathode–anode gap was 1 mm. During FE tests, a DC bias voltage (0–10 kV) was applied to the anode at a constant rate of 500 V/min while grounding the cathode. The FE results were recorded in terms of emission current *versus* voltage by a computer.

## 3. Results and discussion

### 3.1. FE from VG–CNT composites with differently heighted CNTs

We first investigated the influence of CNT heights on the FE performance of VG–CNT composites. Fig. 1a–c shows side-view SEM images of CNTs with heights of 26, 17, and 10 μm, respectively. The height of CNTs was controlled by adjusting the growth time: 40, 25, and 15 min for the 26, 17, and 10 μm samples, respectively. All the CNTs are densely arrayed with their tips randomly distributed. VG was prepared on the CNTs by using rf sputtering deposition (parameters: 320 W, 300 Pa, 750 °C, 2.5 sccm $H_2$, and 10 h) and microwave PECVD (parameters: 100 W, 1 kPa, 800 °C, 4 sccm $C_2H_2$, 10 sccm $H_2$, and 4 h). The VG prepared by using rf sputtering is sparsely distributed on the top section of CNTs and is less than 200 nm in width (Fig. 1d), and the spaces among adjacent CNTs are well preserved (Fig. 1e). Upon the VG prepared by using PECVD, it reaches ~1 μm in width and is densely grown on CNTs forming a flower-like appearance (Fig. 1f), and the spaces among adjacent CNTs are fully filled by the large-size VG (Fig. 1g). This difference of the shapes of VG is mainly attributed to the fact that the concentration of carbon source in the rf system is much lower than that in the microwave PECVD system, resulting in that the VG grows much slower in the rf system [22,23]. Fig. 1h and i shows typical HRTEM images of these two types of VG–CNT composites and the insets are the corresponding TEM images. The VG prepared by using rf sputtering exhibits a folded edge of ~2 layers, while that for the VG prepared by using PECVD is ~10 layers.

Raman spectra analysis was performed in order to analyze the vibrational characteristics of our VG–CNT composites. Pure VG was prepared on Si wafers under the same growth conditions to eliminate the influence of CNTs on the Raman characterization of VG. Fig. 2a represents the Raman spectra of pure VG prepared by using rf sputtering and microwave PECVD. For both types of samples, two peaks corresponding to D band (~1327 cm$^{-1}$) and G band (~1575 cm$^{-1}$) appear [25]. The D band is sensitive to defects in graphitic structure, while the G band is associated with the $E_{2g}$ vibration mode of graphitic carbon and is common in almost all kinds of graphitic materials [26,27]. The ratio of the intensity of the D band to G band ($I_D/I_G$) could be used as a measure to scale the defects in our carbon materials. The $I_D/I_G$ values for the rf sputtering and microwave PECVD prepared VG are calculated to be 1.60 and 1.82, respectively, suggesting that (1) these two types of VG are rich in defects and (2) VG prepared by rf sputtering has more defects. The distinct peak centered at ~2643 cm$^{-1}$ is the 2D peak, which arises from the two-phonon scattering process [28]. The ratio of the intensity of the 2D peak to G peak ($I_{2D}/I_G$) could be used to roughly evaluate the number of layers of graphene. For example, a single-layer graphene has an $I_{2D}/I_G$ value up to ~4 [26]; few-layer (<10 layers) graphene has $I_{2D}/I_G$ values approximate or larger than 1.00 [22,29]. The $I_{2D}/I_G$ values for the rf sputtering and microwave PECVD prepared VG are calculated to be 1.61 and 1.00, respectively, indicating that all the VG is few-layer graphene and the VG prepared by using rf sputtering has less layers. The chemical bonding information of VG was further characterized by using XPS spectroscopy. Fig. 2b shows the C1s peak of the pure VG prepared by using rf sputtering and microwave PECVD. Peak