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Improved field emission of few-layer graphene–carbon nanotube composites by high-temperature processing

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ABSTRACT

Self-assembled few-layer graphene–carbon nanotube (FLG–CNT) composites were prepared and their field emission (FE) properties before and after high-temperature (H-T) processing were investigated. It was found that their FE performance deteriorated slightly when they were processed at 1273 K for 5 h before the FE tests; the applied field increased ~0.05 V/μm at 10 mA/cm^2. X-ray photoelectron spectroscopy analysis indicates that the decreased amount of SP^3-hybridized defects from 39.91% to 23.87% after the H-T processing directly leads to this FE degradation. However, the largest emission current density (J_{max}) of the FLG–CNT composites increased from 33.48 to 64.00 mA/cm^2 after the H-T processing. This improved FE performance was attributed to the enhanced adhesion between the CNT and substrates. We consider that the catalyst wrapping at the CNT foot after the H-T processing is responsible for this CNT–substrate reinforcement.

1. Introduction

Carbon nanotubes (CNTs) can serve as high-performance field emitters due to their high aspect ratio and excellent conductivity [1–3]. Various strategies have been used to improve the field emission (FE) properties of CNTs, such as element doping [4], ion irradiation [5], and chemical processing [6]. We have demonstrated a promising approach to fabricating high-performance field emitters by compositing CNT with vertical graphenes in our previous studies [7,8]. These self-assembled composites, having both the large aspect ratio of CNTs and the outstanding FE stability of graphenes, were found to have excellent FE properties. However, the largest emission current density (J_{max}) of these composites was no more than 30 mA/cm^2 in most cases, which is detrimental for applications requiring large current FE.

In the present study, we fabricated few-layer graphene–carbon nanotube (FLG–CNT) composites, employed a simple high-temperature (H-T) processing method to improve their J_{max}, and proposed a possible mechanism to illustrate this FE enhancement.

2. Experimental

The CNTs were fabricated by using thermal chemical vapor deposition, and FLGs were prepared by using radio frequency sputtering deposition. The composites were then annealed at 1273 K for 5 h in H_2 ambient. All the experimental details are shown in *Methods* of the Supplementary material (pages S1–S4), and the corresponding images are shown in Figs. S1 and S2.

The samples were characterized by a scanning electron microscope (SEM), a transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), and a photoelectron spectrometer for structural information. The FE tests were carried out by using a traditional diode setup in vacuum ($\sim 1.0 \times 10^{-7}$ Pa) at room temperature. Details for the sample characterizations and the FE tests are shown in *Methods* of the Supplementary material (pages S4–S6), and the corresponding image is shown in Fig. S3.

3. Results and discussion

Fig. 1(a) shows the SEM image of FLG–CNT composites. It can be seen that the CNTs are densely packed and well aligned, and FLGs are sparsely distributed on the tips of CNTs (inset of Fig. 1(a)). We have found in our previous study that this sparse distribution of FLGs on the CNT tips, which not only introduces a great amount of sharp FLG edges but also preserves the field enhancement from

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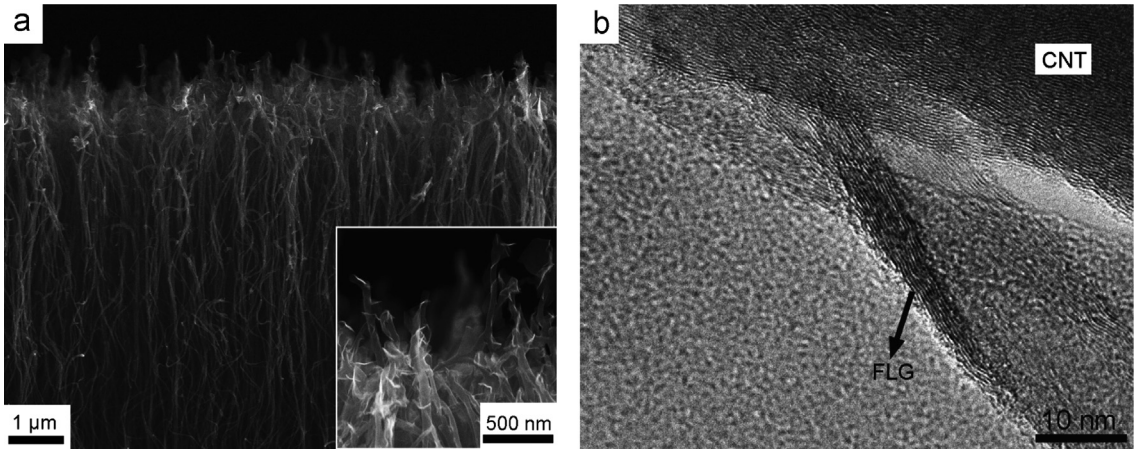

Fig. 1. (a) SEM image of the FLG–CNT composites. (Inset) Enlarged image showing the distribution of FLGs on the CNT tips. (b) High-resolution TEM image showing a FLG–CNT hybrid.

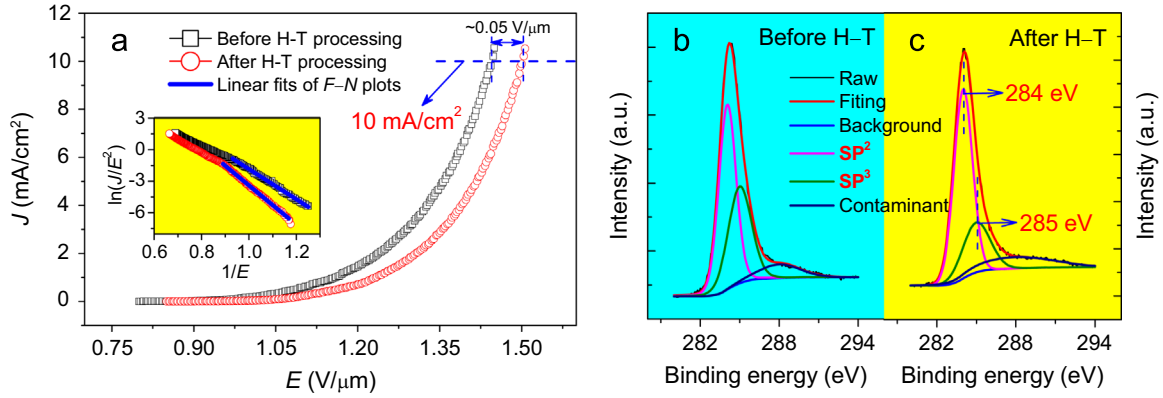

Fig. 2. (a) FE *J*–*E* curves of FLG–CNT composites. (Inset) Corresponding *F*–*N* plots given in terms of $\ln(J/E^2)$ and $1/E$. XPS spectra of FLG–CNT composites (b) before and (c) after the H-T processing.

the CNTs, is beneficial for high-performance FE [8]. Fig. 1(b) shows the high-resolution TEM image of a FLG–CNT hybrid, indicating that the FLG growth is self-assembled. We have observed 8 FLG edges, the high-resolution TEM images of which are shown in Fig. S4 of the Supplementary material, which show that our FLGs have 5 layers on average. The sharp FLG edges are believed to facilitate the electron tunneling during FE [9].

Fig. 2(a) shows the FE properties of FLG–CNT composites before and after the H-T processing presented in terms of emission current density (J) *versus* applied field (E), *i.e.*, the *J*–*E* curves. These two *J*–*E* curves were obtained right after an aging process took place. In this process, continuous FE from our composites was performed at a constant E when J was around 10 mA/cm^2 for 5 h to remove any absorbate on the emitters [10]. It can be seen that the FE performance of FLG–CNT composites deteriorates slightly after the H-T processing, as seen from the right-shift of the *J*–*E* curves. For example, the threshold field (E_{th}, E at 10 mA/cm^2) increases ~0.05 V/μm after the H-T processing. Replotting of the data as $\ln(J/E^2)$ *versus* $1/E$, *i.e.*, the *F*–*N* plots, as shown in the inset of Fig. 2(a), indicates typical *F*–*N* type FE behavior [11]. By using a photoelectron spectrometer, the work function (Φ) of the FLG–CNT composites is obtained. It increases slightly from 4.67 to 4.71 eV after the H-T processing. With Φ and the constant *F*–*N* slopes in the low-current regions, the field enhancement factor (β) of the FLG–CNT composites before and after the H-T processing can be determined as 4794 and 3733, respectively. In comparison with the little change of Φ, the great change of β indicates that the structure of our emitters changes dramatically after H-T processing. We attribute this structural change to decrease of SP^3-hybridized defects, which can be evidenced by the XPS spectra shown in Fig. 2(b) and (c); the fraction of SP^3-hybridized carbon (centered at 285 eV) decreases from 39.91% to 23.87% after the H-T processing [12]. In comparison with the planar SP^2-hybridized defects, the distorted SP^3-hybridized defects can improve FE properties of emitters by means of introducing new active emission sites [13]. The H-T processing decreases the amount of SP^3-hybridized defects and thus deteriorates the FE performance of the FLG–CNT composites.

Fig. 3(a) and (b) shows the FE *J*–*E* curves of FLG–CNT composites in different testing circles before and after the H-T processing, respectively. The circular testing method has been clearly illustrated in the *Methods* of the Supplementary material (pages S5 and S6). The right-shift of *J*–*E* curves with the increase of testing circles indicates a Joule heating induced decrease of active emission sites [14,15]. It is interesting that J_{max}, obtained when a breakdown occurs during FE (corresponding with the last testing circle), increases dramatically from 33.48 to 64.00 mA/cm^2 after the H-T processing. The FE breakdown usually occurs when some of the emitters are pulled out from the substrates due to the electrostatic force at the emitters during FE; this increase of J_{max} thus suggests the increase of adhesion between the emitters and substrates. We can roughly evaluate this enhanced adhesion. Assuming that the electric quantity of aggregated electrons at the emission sites is q, which is proportional to J ($q=KJ$, where K is a constant); the critical (largest) electrostatic force, which is firmly related to the adhesion between the emitters and substrates, can

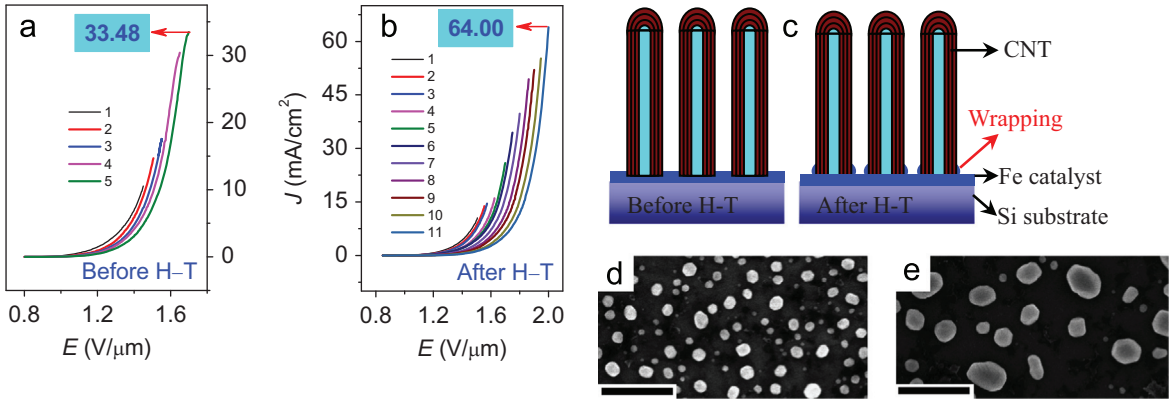

Fig. 3. FE *J–E* curves of FLG–CNT composites in different testing circles (a) before and (b) after the H-T processing. (c) Schematic illustration for the improved adhesion between CNT and substrate. SEM images showing the morphology of catalysts (d) before and (e) after the H-T processing; the scale bars in (d) and (e) are 400 nm.

be obtained: $F=qE=KJE$. According to this rough calculation, the ratio of electrostatic force after and before the H-T processing (F_{after}/F_{before}) is determined to be ~2.25. We ascribe this enhanced adhesion to the changed catalyst morphology, as schematically shown in Fig. 3(c). The H-T processing induced aggregation of catalyst will wrap the CNT foot and thus reinforce the adhesion between the CNT and substrate. The catalyst here plays a role similar to the wetting layer that used to reinforce the adhesion of CNTs to substrates reported previously [16,17]. By reproducing the growth conditions of FLG–CNT composites without carbonaceous gas, this catalyst aggregation can be clearly observed: the average diameter of the catalysts increases dramatically after the H-T processing, as shown in Fig. 3(d) and (e).

4. Conclusions

We have studied the influence of H-T processing on the FE performance of FLG–CNT composites. The right-shift of *J–E* curves indicated that the FE properties deteriorate slightly after the H-T processing. Based on the XPS analysis, this degradation of FE was ascribed to the decrease of SP^3-hybridized defects. In addition, J_{max} of our FLG–CNT composites increased from 33.48 to 64.00 mA/cm^2 after the H-T processing. This increased FE performance was attributed to the enhanced adhesion between the CNT and the substrate after the H-T processing. We consider that the catalyst wrapping at the CNT foot after the H-T processing is responsible for this CNT–substrate reinforcement. Together with the low applied fields (less than 2 V/μm), our H-T processed FLG–CNT composites may find applications requiring large current FE.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2014.03.035.

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