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Graphene-like carbon nanosheet field emitters using metal particle catalysts for miniature X-ray tubes

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1. Introduction

Two-dimensional (2D) carbon nanostructures such as carbon nanosheets have attracted great attention of researchers due to their excellent electrical, optical, thermal, and mechanical properties [1-5]. Carbon nanosheets have freestanding graphitic nanostructures with subnanometer thickness typically consisting of 1 ~ 10 graphene layers and open surfaces and edges [4-6]. The sharp edges and open structures of the carbon nanosheets provide a high surface-to-volume ratio, which is attractive for the electronic applications such as gas detection, gas storage, and catalyst support in fuel cells and batteries [2-6]. In particular, vertically-oriented carbon nanosheets have been highlighted as an ideal candidate for electron field-emission sources because of their geometries with high aspect ratios and good electrical properties [7-11]. Therefore, various techniques have been developed for the synthesis of the vertically-oriented carbon nanosheets, including chemical vapor deposition (CVD) [7-9], electrophoretic deposion [10], vapor-solid process [11], and salt-templating methods [4]. However, practical application of the carbon nanosheets for field emitters is still limited due to the difficulties in the preparation of large-scale, dense, and vertically-aligned carbon nanosheets [7-11].

Here, we present a simple and convenient route to graphene-like carbon nanosheets by thermal annealing of metal particles and carbon nanotubes (CNTs) mixture. The carbon nanosheets exhibited excellent field-emission performance due to high-density edges and furthermore good emission stability due to strong adhesion to a substrate.

2. Methods

The fabrication process of the graphene-like carbon nanosheets is schematically displayed in Figure 1. A single-walled CNT (model: carbon nano-materials Technology Co., LTD, CNT SP95) solution consisting of 0.3 wt% CNT and 99.7 wt% 1, 2-dichlorobenzene (Sigma Aldrich) was sonicated at room temperature for 2 h. The CNT solution (3 μl) was mixed with a metal mixture (0.025g) composed of 61.5 w% silver, 24 w% copper, and 14.5 w% indium micro- and nano-particles. A copper wire with diameter of 0.8 mm was used as a substrate. One end of the copper wire was mechanically polished to have a flat surface and then washed using acetone (Sigma Aldrich). Around 1.0 μl of the CNT/metal mixture was put on the copper tip substrate. The CNT/metal mixture dried out very quickly in ~1 min using a heater. Subsequently, an annealing process was carried out under vacuum at ~4 × 10^{-6} torr at different temperature of higher than 900 ° C for 1 ~ 2 h after a preheating step. For comparison, a CNT emitter was prepared without the metal mixture under similar conditions.

The fabricated carbon nanosheets were characterized by field emission scanning electron microscope (FESEM; Hitachi S–4800), field emission transmission electron microscope (FETEM; JEM-2100F, Jeol) and a Raman spectroscopy (514.5 nm laser, ARAMIS, Horiba Jobin Yvon). Field emission properties of the fabricated carbon nanosheets were characterized in a vacuum chamber. A diode type with a copper disc (diameter: 30 mm) acting as an anode was employed for the field emission test. Negative high voltage of 0 ~ -50 kV was applied to the emitter while the copper anode was grounded. The distance between the emitter and the anode was fixed to 15 mm. Before field emission tests, electrical conditioning processes were carried out for stable operation of the emitters.

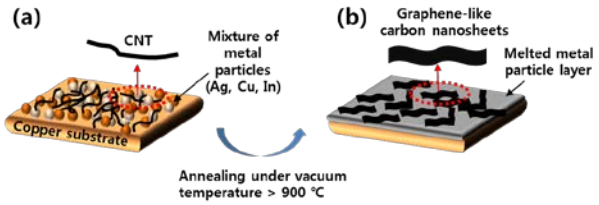

Figure 1. Schematics of the fabrication process for the carbon nanosheets using thermal annealing of metal particles and CNT mixture.

3. Results and discussion

In this research, the metal mixture can play two important roles: synthesis of carbon nanosheets and strongly attachment of carbon nanosheets to a substrate after an annealing process. The morphologies of CNTs were analyzed at the each step of fabrication processes (Figure 2). Raw CNTs were not purified using any treatments. Therefore, pristine CNTs were excessively aggregated each other and with amorphous carbons (Figure 2a). After sonication with 1, 2-dichlorobenzene during 2h, CNTs were little dispersed; however, most CNTs were still agglomerated together and the tube shape was maintained (Figure 2b). Figure 2c shows the FESEM images of the CNTs with the metal mixture after the annealing process at the temperature of 925 ºC.

The FESEM images exhibit that the CNTs were completely disappeared and many wrinkled ribbon-like nanosheets were newly formed on the substrate.

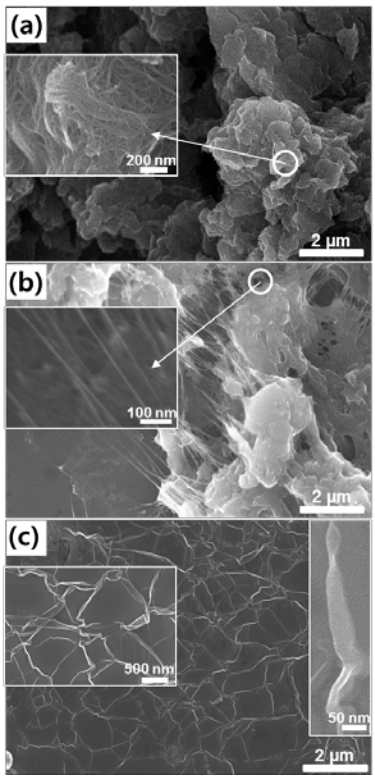

Figure 2. FESEM image of the CNTs and carbon nanosheets at the each step of fabrication processes: (a) pristine CNTs, (b) CNTs sonicated with 1,2-dichlorobenzene during 2 h, and (c) carbon nanosheets after an annealing process with metal particles and CNT mixture. Inset: Magnified FESEM images.

Furthermore, FETEM images show that the nanosheets have a strip-shaped morphology with width of 40 ~ 100 nm and length of 2 ~ 100 μm (Figure 3a). Moreover, Raman spectra of the nanosheets display three main peaks at 1345 cm-1, 1578 cm-1, and 2689 cm-1 (Figure 3b), which correspond to D, G, and 2D peak of graphene. The presence of D+G peak at 2914 cm-1 in the Raman spectra is attributed to the defects in graphene layers, twisted morphologies, and edges of the carbon nanosheets. Raman intensity ratio of I_{2D}/I_G is ~0.4, which corresponds to a characteristic of multi-layer graphene. Consequently, FETEM images and Raman spectra confirm that the nanosheets are a graphene-like carbon material.

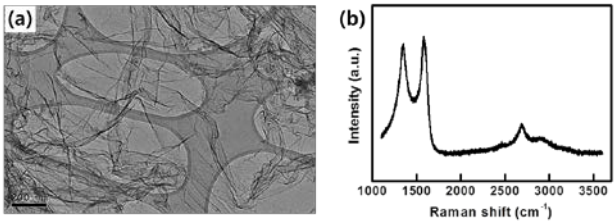

Figure 3. (a) FETEM image and (b) Raman spectra of the carbon nanosheets.

Figure 4a shows that the side-view FESEM images of carbon nanosheets prepared on the copper substrate after an annealing process with the metal mixture (copper, silver, and indium) at 925 ° C. The FESEM image indicates that the sheets were randomly oriented, and some of them are almost normal to the substrate, exhibiting numerous sharp edges. These vertically-standing carbon sheets can act as active emission sites to enhance the electron field emission due to their high aspect ratio. Moreover, a uniform film of carbon nanosheets/metal mixture was fabricated on the copper tip after an annealing process at 925 ° C (the inset of Figure 5c). To investigate the adhesive force between u-CNTs/metal mixture film and the copper substrate quantitatively, the adhesive force of the CNT/metal binder coating on a substrate was measured by a pencil hardness test, which is described in ASTM D 3363. For the characterization, the metal mixture was annealed with CNTs on a copper sheet (10 x 10 mm^2) at 925 ° C. The pencil hardness of the carbon nanosheets/metal binder film attached to the copper sheet was 5H, which is indicates that the films were very strongly attached to the substrate.

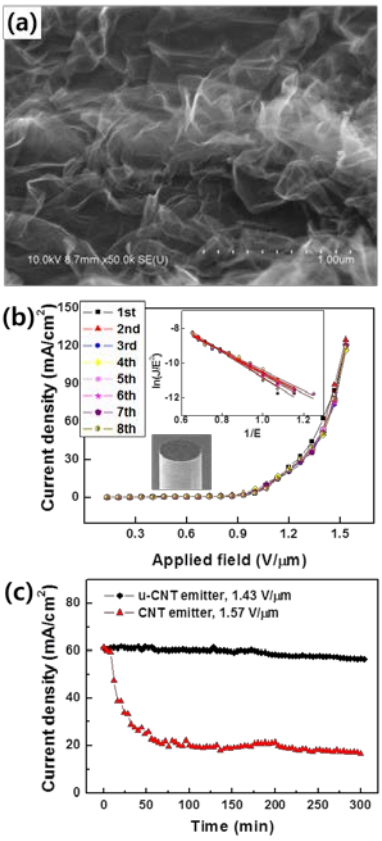

Figure 4. (a) Tilted FESEM images of the carbon nanosheets: randomly oriented or normal to substrate. (b) Field emission characteristics of the carbon nanosheet emitters after the conditioning process. Inset graph and image in (b) are the FN plots of the J-E curves of the emitter and the wettability of metal mixture on the copper tip substrate after annealign at 925 ° C, respectively. (c) Emission stability of the carbon nanosheet and CNT emitters at different electric fields.

Figure 5b exhibits typical field emission characteristics of the fabricated emitters on the copper tip after the conditioning processes. Current density vs. electric field (J-E) curves were repeatedly measured. The maximum current densities of the carbon nanosheet emitters were over ~120 mA/cm^2 and the J-E curves kept almost constant at the repeated field emission tests, exhibiting a threshold electric field corresponding to 10 mA/cm^2 was ~1.07 V/m. The J-E curves follow well the Fowler-Nordheim (FN) equation (inset of Figure 5b) with a comparatively high field enhancement factor of about 13,000, assuming that the work function of carbon nanosheets is the same as that of CNTs (~5 eV). Especially, the carbon nanosheet emitters using metal mixture had a remarkable advantage for field emission stability compared to CNT emitters, as shown in Figure 5c. The carbon nanosheet emitters exhibited excellent emission stability without degradation, which were measured at a medium vacuum of ~10^{-5} torr. The constant current densities at high values of ~60 mA/cm^2 were stably emitted over 5 h under a field of 1.43 V/m. For the comparison, CNT emitters were prepared without the metal mixture under similar conditions and then were treated with the electrical conditioning processes. Even after same conditioning processes with carbon nanosheet emitters, the CNT emitters show very poor stability. Electron current density emitted from the emitter was initially 61.3 mA/cm^2 at the field of 1.57 V/m; however, the current density was dramatically reduced to 16.7 mA/cm^2 for 300 min operation. FESEM images before and after stability tests of the CNT emitters (Figure 5c and d) clearly show that most CNTs on the substrate were almost removed after the test. However, due to the strong binding of carbon nanosheets to the substrate using the metal mixture film, carbon nanosheets were still adhered to the tip substrate without seriously damaging the carbon nanosheets even after over 5 h emission tests (Figure 5a and b).

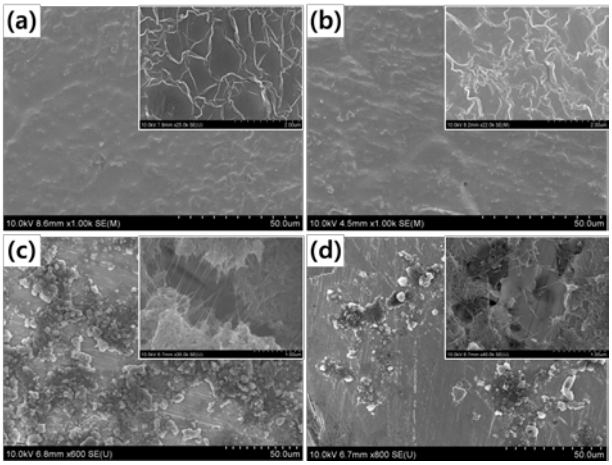

Figure 5. (a, b) FESEM images of the carbon nanosheet emitters before and after field emission tests, respectively. (c, d) FESEM images of the CNT emitters before and after field emission tests, respectively.

4. Conclusions

Graphene-like carbon nanosheets were fabricated by thermal annealing of metal particles and CNT mixture. Excessively aggregated raw CNTs with amorphous carbons were completely disappeared and vertically standing carbon nanosheets were newly formed after an annealing process. In addition, the metal mixture was totally melted and uniform mixture films were formed on a sharp copper tip substrate. The uniform films could strongly attach the carbon nanosheets to the substrate and the fabricated carbon nanosheets were embedded in the films. As a result, the carbon nanosheet emitters show excellent field emission properties and good emission stability compared to CNT emitters.

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