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Facile synthesis and enhanced field emission properties of Cu nanoparticles decorated graphene-based emitters

X.D. Hong, D. Liang *, P.Z. Wu, H.R. Zheng

Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Institute of Biomedical and Health Engineering, Paul C. Lauterbur Research Center for Biomedical Imaging, Shenzhen 518055, PR China

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ABSTRACT

Cu nanoparticles (Cu NPs) were decorated on the surface of graphene films to form composite emitters. The graphene films were deposited by electrophoretic deposition and subsequently coated with Cu NPs via electrochemical reduction. The Cu NPs decorated graphene films exhibited lower turn-on field, lower threshold field and larger field enhancement factor compared with those of the pristine films. The Cu NPs decorated graphene films also showed good emission stability. The field emission properties of Cu NPs decorated graphene films were tunable through adjusting decoration time. This graphene-based composite could be used as a possible candidate for vacuum electron source.

1. Introduction

Since its discovery in 2004, graphene, a two-dimensional carbon-based nanomaterial, has attracted much attention from both academic and commercial communities in recent years [1–5]. Graphene is a monoatomic layer of graphite with carbon atoms arranged into a hexagons honeycomb structure. Due to its unique properties such as high electrical and thermal conductivity, superior mechanical strength as well as good chemical properties, graphene is considered as a promising candidate for different electronic devices application [6–12]. Particularly, the abundant sharp edge structures make graphene as an efficient electron emitter for various field emission applications such as X-ray tubes, flat panel display devices and microwave amplifiers [13–16]. Graphene as field emitters exhibits a high density of effective emission sites, low turn-on/threshold voltages, large field enhancement and high emission current.

Although graphene displays potential of being excellent field emitters, practical fabrication of graphene emitter with high current density and good emission stability is challenging work. It is because that the graphene sheets tend to flatly lay on the substrates and aggregate, leading to limited protruding structures for field emission. This results in a high current from each active emitter even under a moderate extraction current density, which leads to failure of the emission structures of graphene within a relatively short time. Thus, the microstructure and field emission properties of graphene-based emitters still need to be improved.

Recently, some research groups reported their study that decorated low work function metal/metal oxide/metal halide nanoparticles on the surface of graphene sheets to increase density of emission tips as well as modulate band structures of graphene. For example, Kaushik et al. [17] deposited graphene films on Si wafers by microwave plasma enhanced chemical vapor deposition. Subsequently, the graphene films were grafted with metal nanoparticles (Ti, Pd, Ag, Au) via thermal evaporation. Long et al. [18] fabricated graphene films by electrophoretic deposition (EPD) then coated the films with MgO though radio frequency magnetron sputtering. Liu et al. [19] deposited graphene sheets on the substrate by EPD. After that, the graphene sheets were coated with CsI by drop coating. It has been demonstrated that these heterostructures exhibited lower turn-on field, larger emission current and improved emission stability compared with pristine graphene, which indicated decoration of graphene is an effective method for the enhancement of field emission properties from graphene-based emitters.

Cu nanostructures have many advantages, such as high electrical conductivity, low work function, ease of fabrication and low cost. Previous study reported that the field emission properties of carbon nanotube emitters were significantly improved by decoration Cu NPs [20]. Moreover, some researchers recently have reported the graphene-based composites combined with different copper nanostructures via complicated approaches for various applications such as transparent electrodes [21], photocurrent generation [22], electrochemical sensing [23]. These copper/graphene composites displayed greatly enhanced performance compared with the pristine graphene. Motivated by these, in the present work, Cu NPs are decorated on the top surface of the graphene films to form Cu/graphene composite emitters. Due to its advantages of simple and facile, high deposition rate, high throughput, good homogeneity, and controllable morphology, electrophoretic deposition (EPD) technique were employed to fabricate graphene

* Corresponding author.
E-mail address: dong.liang@siat.ac.cn (D. Liang).

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films on ITO-coated glass. After that, Cu NPs were coated on the surface of graphene films by facile electrochemical reduction process. The field emission characteristics of Cu NPs decorated graphene were studied. The Cu NPs decorated graphene showed outstanding field emission properties with low turn-on and threshold field, large field enhancement factor and good emission stability, which were much better than those of the pristine graphene fabricated under the same deposition condition. Furthermore, the effect of decoration time on the field emission properties of Cu NPs decorated graphene was also discussed.

2. Experiment

2.1. Fabrication of Cu/graphene composites

The graphene sheets in the present work were acquired from Chengdu Organic Chemicals Co., Ltd. (China). They had a thickness between 0.55 and 3.74 nm and a lateral size ranging from 0.5–3 μm. The fabrication process of Cu/graphene composites was comprised of two key steps: (i) the EPD process of graphene films. (ii) The coating process of graphene films by Cu NPs. In the EPD process, the stable suspension of graphene was produced firstly. 25 mg of graphene sheets were dispersed into 100 ml of ethanol using the sonication of 200 W for 2 h. After that, 12 mg of $MgCl_2$ were added into the suspension to render the graphene sheets positively charged. Subsequently, a stainless steel plate and an ITO-coated conductive glass, which were used as positive and negative electrode respectively, were submerged into the graphene suspension. The distance between the two electrodes was set to 1 cm. Under a DC voltage of 120 V for 6 min, the positively charged graphene sheets were deposited onto the surface of the ITO glass, forming graphene films.

After the EPD process, Cu NPs were coated on the surface of the graphene films via electrochemical reduction method. A copper plate and the prepared graphene/ITO substrate were connected to positive and negative electrode of DC power respectively. The two electrodes were submerged into an ethanol solution of $Cu(NO_3)_2$. Under an applied voltage of 70 V, the copper ions migrated towards the graphene/ITO substrate. Due to the high electrical conductivity of graphene, the copper ions were reduced to metallic Cu coating on the surface of graphene films by gained electron from the negative electrodes. Meanwhile, the atoms of copper plate lost electron to form copper ions in the solution. The decoration time of graphene films varied (1.5, 3.0, and 4.5 min). After finishing the coating process, the Cu NPs decorated graphene films were washed by ethanol carefully and dried at 90 °C for 30 min in the vacuum. For the purpose of comparison, pristine graphene films have also been fabricated under the same deposition condition from the above graphene suspension.

2.2. Characterization

The surface morphologies of all the samples (Cu NPs decorated and pristine graphene films) were characterized by field emission scanning electron microscope (FE-SEM, FEI Nova NanoSEM450) and transmission electron microscope (TEM, FEI Tecnai G2 F20 S-Twin). Energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD, Rigaku D/Max-2500/PC) were employed to analyze the composition of Cu NPs decorated graphene films. In addition, Raman spectroscopy (Renishaw Microraman) was used to acquire structural characteristics of the samples with an excitation wavelength of 532 nm.

The field emission properties of the samples were measured using a diode configuration under a vacuum environment with a pressure of 5×10^{-6} Pa. The samples and ITO-coated glass were used as the cathode and the anode, respectively. The distance between the cathode and the anode was set to 720 μm. All the measurements were carried out using a high-voltage DC power (Keithley 248). The emission current was read out via a current measurement unit combined with the program based on LabVIEW.

3. Results and discussion

Fig. 1 presents the SEM morphologies of pristine graphene films and Cu NPs decorated graphene films at low and high magnifications. In the case of pristine graphene films, it can be seen from the low-magnification image (Fig. 1(a)) that the graphene films possess a homogeneous morphology. The high-magnification image (Fig. 1(b)) reveals that the graphene sheets are randomly stacked and oriented, with some almost perpendicular to the substrate. Moreover, there are large number of sharp edges and wrinkled microstructure of graphene sheets, some of which will act as active emission sites. In the case of Cu NPs decorated graphene films, it can be clearly observed that Cu NPs were successfully deposited on the surface of the graphene sheets, as shown in Fig. 1(c) and (d). Some of these Cu NPs can act as additional emission sites and improve the field enhancement of the graphene-based emitters in the course of field emission. Fig. 2 displays the TEM images of pristine graphene films and Cu NPs decorated graphene films with different magnifications. Graphene nanosheets structure can be obviously observed in Fig. 2(a) and (b). From Fig. 2(c) and (d), it can be seen that large number of Cu NPs were uniformly coated on the surface of graphene sheets. The inset of Fig. 2(d) indicates that most of Cu NPs have a size of below 15 nm.

The compositions of the graphene films before and after Cu NPs decoration have been analyzed by EDS and XRD techniques. Fig. 3(a) shows the energy dispersive spectrum of Cu NPs decorated graphene films. It confirms the presence of Cu element. Fig. 3(b) displays the XRD patterns of pristine and Cu NPs decorated graphene films. The diffraction peak located at 25.6 ° is visible in all the patterns, corresponding to the (002) lattice plane of graphene. The diffraction peak located at 43.3 °, 50.3 ° and 73.9 ° are corresponding to the (111), (200) and (220) plane of Cu NPs, respectively. It can be comfirmed that the Cu NPs possess a face centered cubic crystal structure.

The structural information of pristine and Cu NPs decorated graphene films have also been acquired from Raman spectroscopy, as shown in Fig. 4. The D and G band of graphene, which are respectively located at around 1350 cm^{-1} and 1580 cm^{-1}, are clearly observed for the two samples. The D band is associated with the defects and disorders in the sp^2-bybridized carbon system and the G band indicates the graphitization of graphene [24–26]. 2D band of graphene was not observed, which is consistent with previously published results [27]. Table 1 shows the Raman analysis data of pristine and Cu NPs decorated graphene films. Compared to pristine graphene films, the Cu NPs decorated graphene films exhibit a shift to lower wavenumber in D band. Such shift may be attributed to the interaction between the copper atoms and the carbon atoms that changes the electronic environment of graphene. Furthermore, the I_D/I_G ratio of graphene films shows almost no change after Cu NPs decoration, indicating that this process do not introduce additional defect to the graphene sheets.

The emission current density (J) as a function of the applied electric field (E) for the pristine and Cu NPs decorated graphene emitters is presented in Fig. 5(a). The turn-on field and threshold field are defined as electric fields required to generate a current density of 10 μA/cm^2 and 1 mA/cm^2, respectively. It can be observed that the Cu NPs decorated graphene emitters possess much better field emission properties in comparison to the pristine graphene. After decorating the graphene with Cu NPs for 4.5 min, the turn-on field reduced from 3.5 V/μm to 1.9 V/μm and the threshold field reduced from 6.2 V/μm to 3.4 V/μm.

The field emission properties of pristine and Cu NPs decorated graphene emitters are further investigated by Fowler and Nordheim (F-N) model. F-N model [28] have been widely employed to electron quantum tunneling from various materials under applied electric field. The F-N model is appropriate for sharp single-pointed emitters. However, in case of large-area field emitters comprised of nanostructures, the F-N equation over-predicts the macroscopic emission current density due to the difference of local electric field and average electric field experienced by emitters. Forbes [29] considered such facts and presented