Applied Surface Science 324 (2015) 174–178

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Field emission properties of the graphenated carbon nanotube electrode

H. Zanin[a,b,*], H.J. Ceragioli[b], A.C. Peterlevitz[b], Vitor Baranauskas[b], F.R. Marciano[c], A.O. Lobo[c]

[a] School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom
[b] Faculdade de Engenharia Elétrica e Computação, Departamento de Semicondutores, Instrumentos e Fotônica, Universidade Estadual de Campinas, UNICAMP, Av. Albert Einstein N. 400, CEP 13 083-852 Campinas, São Paulo, Brazil
[c] Laboratory of Biomedical Nanotechnology/Institute of Research and Development at UNIVAP, Av. Shishima Hifumi, 2911, CEP 12244-000 Sao Jose dos Campos, SP, Brazil

ARTICLE INFO

Article history:
Received 31 July 2014
Received in revised form 14 October 2014
Accepted 19 October 2014
Available online 24 October 2014

Keywords:
Carbon–carbon composites
Graphenated nanotubes
Field emission
Current stability

ABSTRACT

Reduced graphene oxide-coated carbon nanotubes (RGO-CNT) electrodes have been prepared by hot filament chemical vapour deposition system in one-step growth process. We studied RGO-CNT electrodes behaviour as cold cathode in field emission test. Our results show that RGO-CNT retain the low threshold voltage typical of CNTs, but with greatly improved emission current stability. The field emission enhancement value is significantly higher than that expected being caused by geometric effect (height divided by the radius of nanotube). This suggested that the field emission of this hybrid structure is not only from a single tip, but eventually it is from several tips with contribution of graphene nanosheets at CNT's walls. This phenomenon explains why the graphenated carbon nanotubes do not burn out as quickly as CNT does until emission ceases completely. These preliminaries results make nanocarbon materials good candidates for applications as electron sources for several devices.

1. Introduction

Field emission efficiency is determined by a combination of factors such as conductivity, surface work function and geometry of the emitter [1]. An ideal field emitter must be a good electrical conductor with low work function, high enhancement factor (β) and be stable at fairly high emission current density. Carbon-based materials are suitable for use as cold cathode emitters, because of the low voltages required to extract electrons from its surface. Among carbon-based materials, diamond (mainly sp^3 hybridized state of carbon), carbon nanotubes (CNTs) and graphene (both sp^2 hybridized state of carbon) have low power consumption, potential for miniaturization, and outstanding field emission behaviour. All these properties make attractive candidates for applications as electron sources for several devices [2].

The emission of electrons from diamond in vacuum occurs readily as a result of the negative electron affinity (NEA) the hydrogenated surface due to features with nanoscale dimensions, which can concentrate electric fields high enough to induce electron emission from them [3,4]. It has been direct measured by Chatterjee et al. [4] that the emission came from the grain boundaries (sp^2-rich region) and not the protruding regions. In contrast, excellent electron emission behaviour of CNTs is related to high-aspect-ratio geometry [1]. To date, very good results from both carbon hybridizations have been reported with currents of 1 mA cm^{-2} for threshold fields as low as 2 V μm^{-1} [5].

The NEA and chemical stability of doped diamond and nanocrystalline diamond make them highly stable field emitter material [2], however with higher threshold field than high-aspect-ratio geometry emitters. The field-emission properties of diamond emitters depend upon the thickness, density, microstructure and sp^3/sp^2 carbon ratio in the films with typical threshold field values ranging from 5 to 50 V μm^{-1} [7–10]. Lower threshold field from diamond electrodes were reported from samples with high β values, which could require complex and expensive micro-fabrication [6,8]. High β values are usually required to pattern and etch the diamond into suitable pyramids or needle shapes, although recently diamond nanocones or microstructured have been made using CVD process and show promising field-emission characteristics [7,9]. Xiao et al. reported low threshold field emission ~2.5 V μm^{-1} to nested cones of graphitically bonded carbon (graphene sheets) covered with

* Corresponding author at: School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom. Tel.: +44 7462529137.
E-mail address: hudson.zanin@bristol.ac.uk (H. Zanin).

http://dx.doi.org/10.1016/j.apsusc.2014.10.102
0169-4332/

nitrogen-doped ultrananocrystalline diamond (N-UNCD), however no current transient was showed [8].

Zou et al. [9] and Zanin et al. [7] recently showed field emission studies of microstructured diamond films deposited onto a densely packed "forest" of vertically aligned multiwalled carbon nanotubes (VACNT). On both works, field-emission tests of diamond/carbon nanotube composite show the typical low threshold voltages for carbon nanotube structures ($2\,V\,\mu m^{-1}$) but with better stability and longer lifetime up to 35 h [9] and 75 h [7].

Getty et al. reported a field emission study of N-UNCD films grown on polished Si and contrast with N-UNCD films grown on sharpened Si tip arrays and Si ridges [2]. Authors showed the electron emission from planar N-UNCD films are fairly comparable to the emission from films grown on sharpened Si tip arrays and Si ridges, indicating that field emission in these materials is dominated by electron emission from nanoscale grain boundaries [2]. However, it was not clear why the planar N-UNCD film exhibits lower field emission threshold voltages compared to sharp emitters tested, which is unexpected. It is remarkable the life testing of electron emission from N-UNCD films, which showed the emission with low current degradation over 1000 h. Although with considerable fluctuation, emission stability of these diamond electrodes has been proved better than CNTs or graphene.

The field emission of CNTs is problematic because they burn out during emission, ceasing the emission completely. Significant research efforts have been performed to improve field emission stability of carbon nanotubes. Chen et al. [10] improved field emission stability of thin film of MWCNT using a tip sonication treatment. Authors showed field emission current of thin-MWCNT film at high current density was quite stable up to 19 h and after tip sonication treatment that stability showed to be longer ~30 h. Field emission stability was significantly improved during a long period of operation probably because many shortened thin-MWCNTs could then participate of the emission after the treatment. Pandey et al. [11] showed strontium titanate coated carbon nanotube matrices with low emission thresholds of $0.8\,V\,\mu m^{-1}$ and very stable electron field emission for 40 h. Authors claimed low emission threshold was obtained due to tunnelling width as a function of the $SrTiO_3$ thickness.

Recently, significant research efforts have been centred on graphene due its electronic properties, which are very similar or even better than CNTs [12–15]. Consequently, much effort has been made to prepare and to apply reduced graphene as a field emission material. The electric field emission from graphene is challenging especially when the sheets lay on the substrate surface, resulting in low field enhancement [16]. Nevertheless, Malesevic et al. [17] showed that graphene could be deposited vertically aligned to substrate, which increased the field enhancement factor. Quian et al. [18] showed that the field emission from graphene oxide (GO) nanosheets prepared by Hummer method have excellent and stable field emission properties with a low threshold field ($\sim 1.5\,V\,\mu m^{-1}$).

Huang et al. [19] showed the field emission properties of GO are found to be a non-monotonic function of the C/O ratio in a wide range of 2.06–14.80. Samples with C/O ratio of 6.98 show the lowest turn-on ($\sim 1.8\,V\,\mu m^{-1}$) and longest-time (10 h) current stability. In agreement with Huang, Kung et al. showed the emission current of vertically aligned (VA) CNT array increased ~800% along with a decrease of the onset field emission voltage from 0.8 to $0.6\,V/\mu m$, when treated by oxygen or ozone compared to as-grown samples [20]. Mathur et al. showed that oxygen plasma treatment opens VACNTs' tips enhancing its field emission behaviour [22]. Authors measured the turn-on electric field $\sim 0.80\,V\,\mu m^{-1}$ from untreated VACNTs and $\sim 0.60\,V\,\mu m^{-1}$ from open ended VACNTs samples. These open VACNTs have more defects sites such as edge defects from the edge planes of the graphene sheet [21]. Kurt et al. [22] reported, for the first time, carbon nanotubes decorated with graphene nanosheets growing radial to the tube axis and Parker et al. [23] proposed a model that involves the build-up of residual strain followed by buckling to nucleate a graphitic-edge protrusion from the CNTs' sidewall.

All these literature have inspired us to prepare and study field emission behaviour of graphenated CNTs samples. Herein we demonstrate that the major advantage of these hybrid structures is their significant improvement in emission current stability due to multiple-graphene edges covering CNTs.

2. Experimental

Reduced graphene oxide-coated CNTs (RGO-CNT) samples were prepared on titanium 10 mm × 10 mm × 1 mm substrates by hot filament chemical deposition vapour system (HFCVD) reactor. Prior to the deposition, 250 mg of nickel nitrate were diluted in 80 ml of acetone and 0.2 ml were dropped on the substrate with polyaniline and dried at room temperature for 2 h. For sample growth, the HFCVD chamber is maintained at 10 Torr with a constant flow of nitrogen (65 sccm) and oxygen (20 sccm). The carbon source was a mixture of propanone (acetone), camphor, and citric acid. This carbon source is dragged to HFCVD by hydrogen gas flux (15 sccm). A hot spiral tungsten filament heated to ~1500 °C dissociates gases and vapours into radicals, depositing RGO-CNT thin films on Ti substrates over a 30 min period.

The MWCNT were prepared using a mixture of camphor (90% w) and ferrocene in a thermal chemical vapour deposition (CVD) furnace [24] for use as control samples. The mixture was vapourized at 220 °C in an antechamber, and then the vapour was carried by an argon gas flow at atmospheric pressure to the chamber of the CVD furnace set at 850 °C. The CVD growth took only a few minutes and produced black powder, which consisted of CNT with 20–50 nm diameter and up to 40 μm length [25]. 5 mg of this black powder was dispersed in ethanol and dropped on 10 mm × 10 mm × 1 mm titanium substrates to form a cold emission electrode.

Micrographs were performed by high-resolution scanning and transmission electron microscopy (HR-SEM, FEI Inspect F50; and HR-TEM, JEOL 3010, respectively) to characterize the morphological and structural properties of samples. Raman spectrum was carried out using a Renishaw 2000 system with $\lambda = 514.5$ nm. X-ray photoelectron spectra were performed using VSW H100 system to identify oxygen-functional groups on the sample surface. The wettability of samples was evaluated by the sessile-drop method using a Krüss Easy-Drop system to measure the contact angle (CA) of water on the samples.

A parallel-plates electrodes configuration for field emission measurements with prepared sample acting as the cathode and a phosphor screen acting as the anode was employed [7]. Briefly, a silica spacer kept a fixed separation of $d = 500\,\mu m$ between the two electrodes. The vacuum chamber pressure ranges from 5×10^{-7} to 1×10^{-7} Torr. To normalize the data, we plotted emission current density, J ($mA\,cm^{-2}$), versus electric field, E ($V\,\mu m^{-1}$), as well as the form of a Fowler–Nordheim (F–N) plot ($\ln(J/E^2)$ versus $1/E$).

3. Results and discussion

Fig. 1 shows the morphology and structure of the RGO-CNT onto titanium substrates. Fig. 1(a) shows top view SEM image, revealing porous microstructure composed of entangled tubes. Fig. 1(b)–(d) shows details of reduced graphene oxide nanosheets coating CNT radially to the tube axis. From these images, we also can see the outer diameter range from 200 nm to 600 nm. Fig. 1(e) presents a transmission electron micrograph of RGO-CNT, revealing