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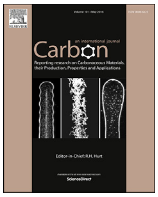

High performance graphene foam emitter

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ABSTRACT

We report a fabrication method for graphene emitter based on simultaneous electrophoretic deposition (EPD) and anodic reduction of graphene oxide (GO). The reduction process of GO employs both copper (Cu) electrodes immersed in well dispersed GO solution. Upon applying DC voltage between electrodes, negatively charged GO platelets are rapidly attracted to an anode, and are simultaneously reduced to graphene (rGO) by the aid of chemically spontaneous oxidation of cuprous to cupric ion and the Kolbe-like decarboxylation. The deposition and reduction processes are accomplished at a low voltage (4 V) in a short period of time (10 s). A rapid vacuum drying process is used after EPD process, which enables to fabricate highly porous rGO structure by vigorous escape of water molecules in an instant. With high electrical conductivity and numerous sharp graphene edges, the rGO emitter shows outstanding field emission properties, such as a low turn-on electric field of 1.06 V μm^{-1}, threshold field of 1.42 V μm^{-1} and long-term emission stability, which are superior to those of graphene emitters previously reported.

1. Introduction

With the superior field emission performance such as low turn-on voltage, high emission current density and long-term emission stability, electron field emissions based on sharp and tapered nanomaterials have been extensively studied as an alternative of thermionic emission [1–4]. In particular, the nature of atomically sharp edges of two-dimensional materials reduces greatly turn-on and applied voltages for electron emission owing to the local amplification of electric field [5–8]. Of these layered materials, graphene and its derivatives have received a great deal of attention with superb emission property and high enhancement factor, stemming from the unique two-dimensional atomic structure and extraordinary electrical property [9–25].

To fabricate graphene emitters with desirable configuration and orientation suitable for field emission, various methods including direct growth [14–17], screen printing [18,19], electrophoretic deposition (EPD) [20–22], filtration [23], spin coating [24], and freeze-drying [25] have been developed. Among the methods the EPD of graphene is cost effective and a versatile processing technique to fabricate a two-dimensional graphene planar emitter. EPD has great advantages in obtaining thin films from charged colloidal suspensions, such as high throughput, precise thickness control and simplicity of scale up.

EPD basically requires charged colloidal particles in a liquid-phase suspension, and the particles are forced to move toward the oppositely charged electrode under an electric field. When adopting negatively charged graphene oxide (GO) suspension for EPD, GO platelets will be deposited to a positive electrode in which the electrochemical reaction is biased toward the oxidation of GO. Therefore, previous EPD studies generally have used the suspension of reduced graphene oxide (rGO) modified with positive charges for deposition on a negative electrode [20,21,26]. To render rGO platelets positively charged, metal salts were introduced to the suspension so that positively charged metal ions are absorbed onto rGO surface. However, the solubility tolerance of metal-absorbed rGO is typically much lower than that of GO due to the lack of oxygen functional groups [27]. Low concentration of rGO solution leads to low deposition rate in EPD process even though a high electric field (~typically 100–320 V cm^{-1}) is applied [20,21], which has hindered the use of electrophoretic deposition of graphene in scalable and productive applications.

However, the oxidation of GO at a positive electrode during EPD process is not always true. Reactive metal electrode, such as copper (Cu) and iron, leads to the reduction of GO instead of oxidation. It implies that direct fabrication of rGO structure from GO colloidal solution could be possible in a single step process with high

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deposition rate. In the present study we report a method to fabricate graphene field emitters based on the anodic reduction of GO at a negative Cu electrode. The process employs both Cu electrodes immersed in highly concentrated GO solution. Upon applying DC voltage between electrodes, negatively charged GO platelets are rapidly attracted to the Cu anode, and are simultaneously reduced to graphene (rGO) by the aid of chemically spontaneous oxidation of cuprous (Cu^{+}) to cupric (Cu^{2+}) ions and the Kolbe-like decarboxylation. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) analysis revealed that the oxygen functional groups of GO, especially C–O bonds in epoxy/ether and C=O bonds in ketone/carboxylic groups, were effectively removed after EPD of GO. It is noteworthy that the deposition and reduction processes are accomplished at a low voltage (4 V) in a short period of time (10 s).

In the present study a rapid vacuum drying process is demonstrated to obtain the porous structure suitable for field emission by vigorous escape of water molecules from graphene hydrogel in a short time.

The fabricated rGO foam on a Cu electrode shows high electrical conductivity and involves numerous sharp edges of graphene, and here we demonstrate its use as a field emitter. The rGO foam emitter shows outstanding field emission properties, such as a low turn-on electric field of 1.06 V μm^{-1}, threshold field of 1.42 V μm^{-1} and long-term emission stability with a current density of 9.2 mA cm^{-2} for 22 h. Our method could be available to various geometries of substrates such as rod, plate, and flexible wire. By employing the flexibility of the electrode, the emitter is applicable to luminescent lighting tube and also provides a winding structure that requires high-current electron sources [28–30].

2. Experimental section

2.1. Synthesis of graphene oxide

GO powders were prepared by a modified Hummer's method [31] from graphite powder (Bay Carbon, SP-1). A solution mixture of graphite powder, sulfuric acid, and potassium permanganate in a beaker was stirred for 6 h at temperature of 45 °C. The solution was neutralized by deionized (DI) water and hydrogen peroxide. The obtained brown solution was subjected to dialysis to completely remove any residual acid and salt in the solution. GO powders in the form of sheet were prepared via a filtration process. This involved vacuum filtering a GO suspension in deionized (DI) water onto a membrane filter (Millipore PTFE filter, 0.2 μm pore size, 47 mm diameter), drying in a vacuum chamber, and removal of the formed sheet from the filter. Afterwards, the GO sheet was redispersed in deionized (DI) water with a controlled concentration of 1.0 mg mL^{-1} by sonication. The resulting suspension yields stable colloidal suspensions of individual GO platelets due to the presence of oxygen functional groups [27].

2.2. Fabrication of reduced graphene oxide foam

After the preparation of GO suspension, two identical Cu wire electrodes were immersed in the suspension as shown in Fig. 1(a). Then, DC voltage was applied between the electrodes with a range from 4 to 10 V for 10 s. The inter-electrode spacing was fixed as 1 cm. The GO platelets in the solution migrated toward the positive electrode due to their negatively charged surface which was induced by oxygen functional groups, such as epoxy, hydroxyl, carbonyl, and carboxyl groups, existing on basal plane and edge of GO platelets. During the EPD process, GO platelets were simultaneously reduced to rGO by the aid of the oxidation process of cuprous (Cu^{+}) to cupric (Cu^{2+}) ion and the Kolbe-like decarboxylation, which will be discussed later. After completing the deposition process, the electrode coated with rGO was dried in two different manners; (1) ambient air drying and (2) rapid vacuum drying at room temperature, as shown in Fig. 1(b) and (c). The inset SEM image of Fig. 1(b) shows that the rGO dried in ambient air had a neatly stacked structure similar to GO paper-like materials prepared by filtration [31]. Surface tension of water between the rGO platelets might attribute to the packing morphology. On the other hand, the rGO electrode dried in a vacuum chamber exhibited highly porous foam structure as shown in Fig. 1(c) and the inset of the figure. Vigorous escape of water molecules from the rGO hydrogel during the drying process does not allow enough time to rearrange rGO platelets, resulting in a porous structure with vertically aligned platelets. It is noteworthy that the rapid vacuum drying process is completed at a chamber pressure of 1.0×10^{-2} Torr in a short time (~10 s).

2.3. Characterization

Scanning electron microscopy (SEM) analysis was performed using a Hitachi S-4800 field-emission electron microscope at an acceleration voltage of 10–15 KeV. X-ray photoemission (XPS) experiments were carried out by using a XPS spectrometer (Kratos, AXIS-HSi). Fourier transform infrared spectroscopy (FT-IR) spectra were measured by a FT-IR spectrometer (Thermo Scientific, Nicolet 6700). The Raman spectra were measured using a micro-Raman system (JY-Horiba, LabRam 300) with excitation wavelength of 532 nm.

2.4. Field emission

A voltage between rGO cathode and molybdenum (Mo) anode was applied using a DC power supply (Matsusada Precision Inc.). Field emission current was measured by a multimeter (KEITHLEY 2000).

3. Results and discussion

Fig. 2(a) shows the optical images of the rGO coated wires before and after drying processes at ambient air and vacuum conditions, respectively. Even under severe bending deformation, the foam-like rGO layer does not show any delamination from a wire electrode and breakage into small pieces of debris (See Fig. 2(b)). It indicates that strong linkages between rGO platelets in the foam as well as high interfacial strength between rGO and electrode were successfully formed. As long as a substrate is electrically conductive, uniform and homogeneous rGO foam could be fabricated regardless of its geometry because EPD process is mainly depending on the electric field around the electrode. The present method was applied to a planar Cu plate in the same manner. rGO foam was also successfully fabricated on the plate as shown in Fig. 2(c) and the SEM image of Fig. 3(d). Thickness of the rGO foam could be controlled by varying the applied voltage and processing time. As shown in Figs. S1 and S2 in the supplementary information, the thickness increases almost linearly with the applied voltage ranging from 4 to 10 V at a fixed processing time of 10 s.

Fig. 3(a)–(d) show SEM images of the rGO foam fabricated with an applied voltage of 5 V for 10 s. Individual rGO platelets were well interconnected each other by forming a highly porous 3-dimensional network. Close observation of rGO foam at an inclined angle (Fig. 3(b)) reveals that rGO platelets with a lateral size of several micrometers stand vertically, providing numerous sharp edges. It is also noteworthy that individual rGO platelets in the foam are spatially separated with distance of several micrometers. We believe that the sharp edges are advantageous by serving as