Journal of Alloys and Compounds 550 (2013) 353–357

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Synthesis of Sn nanoparticle decorated graphene sheets for enhanced field emission properties

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ARTICLE INFO

Article history:
Received 13 September 2012
Received in revised form 28 October 2012
Accepted 29 October 2012
Available online 3 November 2012

Keywords:
Graphene
Tin
Field-emission

ABSTRACT

The field emission properties of graphene nanosheets were remarkably improved by decorating their surface with tin (Sn) nanoparticles. The Sn nanoparticles were attached effectively on the surface of graphene via a chemical vapor deposition during graphene oxide reduction procedure. The Sn-decorated graphene (Sn-Gr) sheets showed lower turn-on voltage and higher emission stability compared with pristine graphene. The improved field emission properties of Sn-Gr sheets were mainly attributed to the Sn nanoparticles which increased the field enhancement factor and the density of emission sites.

1. Introduction

Field emission is an emission of electron from the surface of a material that is induced by an external electric field. Great efforts have been devoted to the design and fabrication of field emitters for application in electronic devices, such as electron guns, microwave power amplifiers, and flat panel displays. Low-dimension carbon-based materials, such as carbon nanotubes (CNTs), carbon nanofibers, carbon nanowalls, and nanocrystal graphite films, have been proved to be better field emitters [1–4]. As the basic element of carbon-based materials, Graphene (Gr) is a single layer of sp2-hybridized carbon atoms arranged in a two-dimensional hexagonal lattice [5]. Due to its atomic thickness, high-aspect ratio, excellent electrical property, and good mechanical stiffness, Gr has been considered as an ideal candidate for various field emission applications [6–12] such as lamps and flat panel display devices, X-ray tubes, vacuum gauges, and microwave amplifiers. However, field emission from Gr sheets is challenging because they are planar morphological features and tend to aggregation [13,14], which limits the field enhancement.

To achieve high emission performance from Gr emitters, various methods such as surface treatment, utilizing hybrid materials have been fabricated. Zeng et al. [15] improved field emission properties of Gr by Ar plasma treatment. Li et al. [16] reported to deposite zinc oxide nanorods on the surface of Gr sheets for improving the field emission of Gr materials. Eda et al. [17] put the Gr materials in polymer composite and deposited the film by spin-coating and results in good field emission performance. Although the field emission properties of Gr nanosheets have been enhanced by these methods, the performance of these field-emitters should be further improved.

It has been reported that metal nanoparticles decoration of CNTs is an excellent method for tuning the working function and enhancing the stability of CNTs field emitters. It demonstrated the field emission properties enhancement of CNTs by coated with metal nanoparticles or metal oxide, such as Ru, Cs, Hf etc. Liu et al. [18] reported that Ru decorated CNTs with lower turn-on voltage, higher emission current density, and improved emission uniformity compared with pristine CNTs [19,20]. Moreover, the present microstructure of Sn nanoparticles attached on graphene has been proposed as a most promising anode from Li-batteries [21,22]. Motivated by these results, in this work, we report the growth of Sn nanoparticles on the surface of Gr sheets by chemical vapor deposition during the Gr oxide thermal reduction. Effect of field emission property and mechanism on the field emission performance of Sn-decorated graphene (Sn–Gr) are discussed and compared.

2. Experimental

2.1. Growth of Sn nanoparticle decorated graphene sheets

Graphite oxide (GO) was prepared from natural graphite powder by the modified Hummers method. Graphite powder (0.5 g), sodium nitrate (0.55 g) and sulfuric acid (23 ml) were mixed and stirred for 10 min. Then, potassium permanganate (3 g) was added slowly with the temperature maintained below 20 °C. Deionized (DI) water was added slowly and the temperature of the solution was raised to

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http://dx.doi.org/10.1016/j.jallcom.2012.10.169

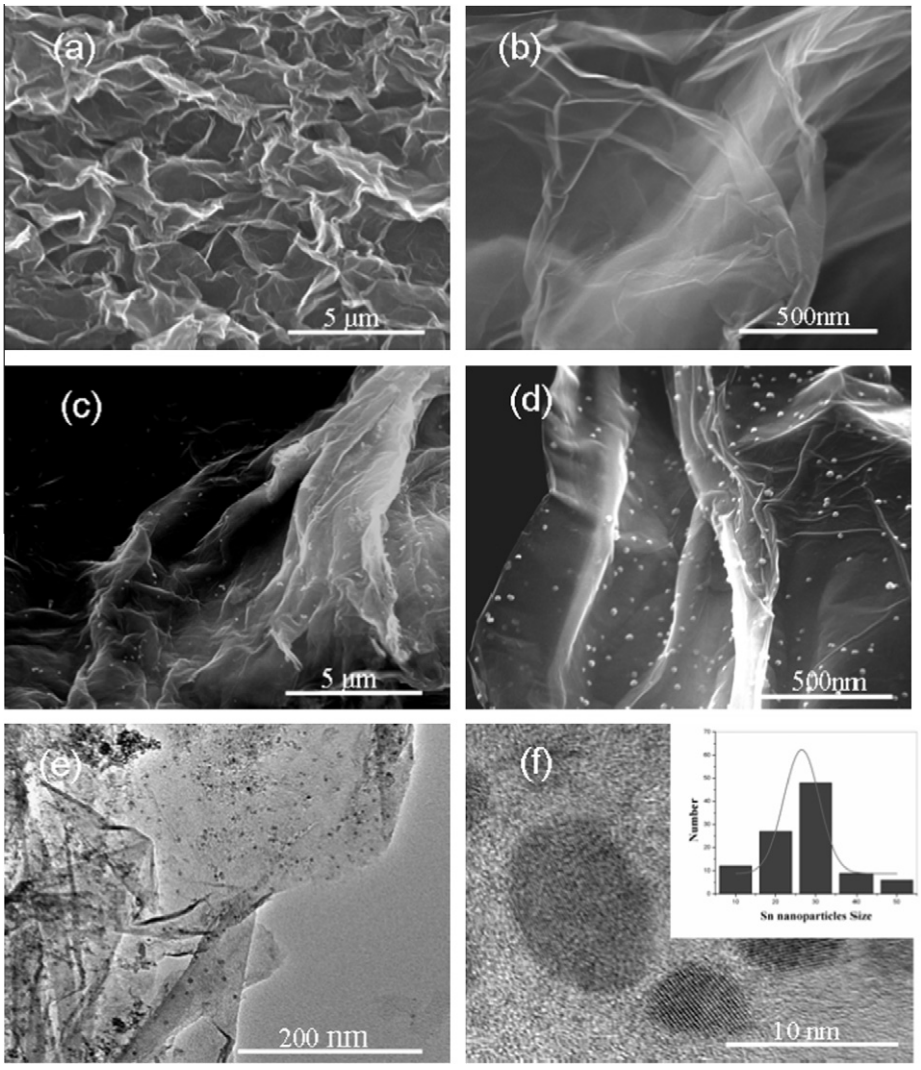

Fig. 1. Low and high-magnification SEM image of graphene sheets before (a and b), and after Sn decorated (c and d), TEM (e) and HRTEM (f) images of the Sn nanoparticle decorated graphene sheets, the inset in Fig. 1(f) is the statistical analysis on the Sn nanoparticle size distribution.

90 °C. The solution turned bright yellow when 3 ml of hydrogen peroxide (30%) was added. The mixture was filtered while warm and washed with warm DI water. The GO was subjected to dialysis to completely remove metal ions and acids. Finally, the product was dried in air at room temperature. The synthesis of Sn-Gr composites was carried out in a horizontal tube furnace. 50 milligram of Sn metal powder was placed at the center of the tube. The GO (0.1 g) was placed in a downstream position from the tin material. After the tube was evacuated to a base pressure of $\sim 1 \times 10^{-3}$ Torr, the Sn and GO materials were heated to 900 °C at a rate of 20 °C min^{-1}, and then maintained at this temperature for 30 min. During the growth process, a carrier gas of argon premixed with 5% hydrogen was fed at a total flow rate of 20 sccm.

2.2. Characterization

Powder X-ray diffraction (XRD) analyses were performed on a Bruker D8 Advance diffractometer with Cu Kα radiation. Raman spectra were obtained from all samples using Renishaw Raman microscope. The morphologies of the as-obtained samples were observed by a field-emission scanning electron microscopy (FESEM, Quanta 250 FEG) and transmission electron microscope (TEM, JEOL JEM-2100). The chemical compositions of the synthesized samples were determined by an Elementar Vario EL CHNS analyzer.

2.3. Field emission measurement

The electron field-emission properties of Sn nanoparticle decorated Gr sheets, and pristine Gr field emitters with a diode structure are measured in a vacuum chamber at a pressure of at a pressure of 1×10^{-5} Pa at room temperature. The silicon substrate with the as-prepared pristine Gr and the Sn nanoparticle decorated Gr materials, served as the cathode. An indium–tin-oxide (ITO) coated glass, which served as the anode. The distance between the cathode and the anode is 150 μm. The field-emission characteristics (current vs. voltage) were measured with a Keithley 237 electrometer. The electric field (E) was estimated by dividing the applied voltage (V) by the anode–cathode separation (d). The emission density (J) was calculated from the quotient of the obtained emission current divided by the cathode surface area ($\sim$0.5 cm^2).

3. Results and discussion

Fig. 1 shows FESEM images of the as-synthesized Gr sheets under low (a) and high (b) magnification. We can see that the Gr was interconnected into a 3D network and some Gr sheets wrinkle at the edges. A high-magnification SEM image of the Gr indicates that the Gr sheet is transparent and some edges are wrinkled with high aspect ration. These edges will act as active emission sites for field emission. Fig. 1(c) and (d) are the typical FESEM images of the Sn nanoparticle decorated Gr sheets at 900 °C for 30 min. The morphology of the Sn nanoparticle decorated Gr was further analyzed by TEM. Fig. 1(e) is the typical low-resolution TEM images of Sn nanoparticle decorated Gr. It can be seen that Sn nanoparticles are uniformly distributed on Gr sheet substrate. Fig. 1(f) is the high-resolution TEM (HRTEM) image of Sn nanoparticle decorated