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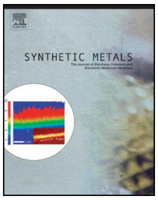

Rapid thermal annealing of nickel-carbon nanowires for graphene nanoribbons formation

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ABSTRACT

In this paper, we present a novel method for graphene nanoribbons formation using nickel nanowires as templates. Modification of electrochemical procedure for nickel nanowires synthesis was introduced by implementing graphene quantum dots as a carbon source. Thus, nickel nanowires with graphene quantum dots were prepared. These wires were exposed to rapid thermal annealing at high temperatures (500 °C, 700 °C and 800 °C). During this process carbon atoms dissolve in metal and precipitate to the nickel surface forming nickel-carbon nanowires. Atomic force microscopy, scanning electron microscopy and Raman spectroscopy were characterization methods used for analysis of changes in nickel-carbon nanowires properties depending on the different annealing temperatures. After etching nickel with nitric acid, graphene nanoribbons with average diameters of 32 nm and average lengths of 4 μm were obtained.

1. Introduction

Graphene, a monolayer of sp^2—hybridized carbon atoms organized in honeycomb lattice, is a semi metal (zero gap semiconductor) [1]. Graphene nanoribbons (GNRs), as quasi one dimensional graphene nanostructures, represent thin strips of graphene whose widths are of the order of nanometers. Due to the quantum confinement effect, they exhibit unique electrical properties different from two-dimensional graphene sheet [2]. Finite termination of graphene sheet results in opening a band gap in graphene nanoribbon structures, that is inversely proportional to the width [3]. Depending on the edge configuration (zigzag or armchair) and width, graphene nanoribbons show different electronic properties [4]. However, it has been experimentally shown that all GNRs with widths less than 10 nm, show semiconducting behavior, regardless of their edge structure and can be used as room-temperature field effect transistors [5].

Different methods for GNRs synthesis have been developed, including chemical [6–8], sonochemical [3,5,9], lithographic [10–14] methods and the unzipping of carbon nanotubes [15–19]. In previous publications, we had shown a unique method which we have developed for GNRs synthesis by gamma irradiation of graphene [20]. Although it is a simple procedure, its disadvantage is a very high cost of production. Accordingly, we have continued to explore new ways of GNRs fabrication and developed a more cost-effective approach.

In this work, we present a novel template based method for graphene nanoribbons synthesis. Alumina membranes were used as templates, as pore diameter in membrane predetermines diameter of deposited nanowires and membrane itself can be easily removed. Well-known electrochemical procedure for synthesis of nickel nanowires [21] was modified by adding graphene quantum dots (GQDs) which will be implemented in nickel nanowires and serve as a carbon source. GQDs represent 0D nanomaterial that consists of 10 graphene sheets, or less, with lateral size below 100 nm [22]. Carbon nanomaterials, graphene and carbon nanotubes, are grown from different solid carbon sources such as polymer films or small molecules [23]. For this research, original method for application of graphene quantum dots as a carbon source was developed. GQDs were chosen as an ideal precursor material for GNR formation because of their good stability and solubility in a nickel bath [24]. After the electrodeposition and formation of nickel-carbon nanowires (Ni-C NWs), rapid thermal annealing process led to formation of thin uniform graphene layer on the surface of nickel nanowires. Nickel core was

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etched with nitric acid (HNO_3) and graphene nanoribbons were obtained. Average diameter of GNRs was 32 nm, with heights of 3 nm.

2. Experimental

Graphene quantum dots were synthesized using a modified alkali-assisted electrochemical procedure [25]. Firstly, spectroscopic graphitic electrodes (Ringsdorff Werke GmbH, Bonn, Germany, 99.999% purity), with 3.05 mm in diameter, were rinsed with MiliQ water and ethanol (98%) and used both as anode and cathode. The current intensity was set to 20 mA. NaOH/EtOH solution in concentration 3% was used as electrolyte. After that, ethanol solution of GQDs was neutralized with hydrogen chloride (HCl), filtrated in order to remove sodium chloride (NaCl) and then evaporated to obtain GQD powder.

The alumina membranes (Whatman, Inc), with 0.2 μm pore diameter, were used in the process of nickel electroplating as templates for obtaining Ni-C nanowires. One side of alumina membrane was painted with gallium indium (GaIn) eutectic alloy (75.5% Ga—24.5% In), which forms a conductive layer that serves as the cathode, while nickel wire served as the anode. Watts nickel platting solution (0.4 M ($NiCl_2 \cdot 6H_2O$); 0.28 M (H_3BO_3); 0.32 M ($NiSO_4 \cdot 6H_2O$)) was used as an electrolyte in the process of electrodeposition. GQD powder, in concentration of 0.2 g/l, was added to Watts solution and used as a carbon source. GQDs have carboxyl groups which are base condition deprotonated (COO^- groups) and during the process of electrodeposition GQDs move with all other negative ions towards the cathode. Electrical circuit was established by KEITHLEY 220 programmable current source. Electrodeposition of nickel and GQDs in the pores of alumina membrane was carried out during 15 min. After the process of electrodeposition, GaIn alloy was removed with concentrated nitric acid. Ni-C nanowires were freed from the filter by dissolving alumina in 6 M sodium hydroxide and afterwards suspended in water.

Ten microliters of this suspension were deposited on freshly cleaned Si substrates. Silicon substrates were then put on a magnetic stirrer to manipulate wires so they are aligned with the magnetic field, and held for 5 min at the temperature of 100 °C to evaporate water. Samples were then annealed in the process of rapid thermal annealing at different temperatures (500 °C, 700 °C, 800 °C) in vacuum for 30 min, followed by rapid cooling in order to segregate carbon on nickel surface. After that, nickel was etched with nitric acid (HNO_3) and graphene nanoribbons on Si substrates were obtained.

In order to etch nickel, first the bubbling transfer process was used to detach nanowires from the silicon substrate [26]. 10 μl of polymethyl methacrylate (PMMA) was deposited over the sample and dried at 160 °C during 5 min. Then, in the process of electrolysis PMMA/nanowires layer was detached from the silicon substrate. In the electrolysis procedure the solution of NaOH was used as an electrolyte, while PMMA/nanowires/silicon served as the cathode and nickel wire as the anode. After rinsing it with MiliQ water, floating PMMA/nanowires layer was captured and immersed in nickel etching solution ($HCl:HNO_3 = 4:1$) for 5 min. Finally, the PMMA was removed by acetone vapor.

Morphological features of Ni-C NWs and GNRs were investigated by Quesant/Ambios atomic force microscopy (AFM) system. Premounted standard silicon probes Q-WM300 (purchased from Nano and more) with a force constant of 40 N/m and resonant frequency of 300 kHz were used. All images were recorded in AFM tapping mode, in the air and at the room temperature conditions. For AFM image analysis, Gwyddion software was used [27]. Tip convolution artifact (a convolution of the shape of the probe, and the shape of the sample) is always present on AFM images. Accurate values for the diameters of particles were calculated from equation for the larger dimension of particles: $r_c = r\ (\cos\theta_0 + (\cos^2\theta_0 + (1 + \sin\theta_0)(-1 + (tg\theta_0/\cos\theta_0) + tg^2\theta_0))^{1/2})$ [28]. Samples were deposited on Si substrates as described above.

Transmission electron microscope (TEM) observations were carried out on TEM JEOL Jem 1210 Electron microscope operating at 120 kV. Samples were prepared by drop casting of nanowire dispersion on carbon coated copper grid with 300 mesh.

Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) recordings were carried out on a QUANTA FEI 200 FEG-ESEM instrument, at 10–30 kV under high vacuum conditions.

Fourier transform infrared (FT-IR) measurements were recorded on Thermo Scientific Nicolet iN10 FT-IR instrument at the room temperature. Spectral resolution was 4 cm^{-1}.

Raman spectra were recorded on a DXR Raman microscope (Thermo Scientific) using 532 nm excitation line from a diode pumped solid state laser. Laser power was 1 mW. The Raman spectra were recorded with an 1800 lines/mm grating. The spot size of laser beam was 0.7 mm. The spectral resolution was 0.5 cm^{-1}. Acquisition time for all spectra was 100 s (10 × 10 s).

Thermo-gravimetric analysis (TGA) was carried out under nitrogen flow of 30 ml/min using Mettler Toledo TGA/DSC STAR system at a ramp rate of 10 °C/min.

The photoluminescence spectra of graphene nanoribbons on Si/SiO_2 substrate were recorded at room temperature on a Fluorolog-3 Model FL 3-221 spectrofluorometer system (HORIBA Jobin-Yvon S.A.S., Chilly Mazarin, France). Emission spectra were measured utilizing a 450 W Xenon lamp as an excitation source and R928P photomultiplier tube as a detector.

3. Results and discussion

3.1. GQDs as precursors for GNRs formation

Particular novelty of this work is a modification of nickel plating bath by incorporating graphene quantum dots (GQDs) into the bath solution [29]. GQDs have hydrophobic spherical graphene base and hydrophilic oxygen-containing functional groups [30]. GQDs were used as a carbon source and represent basic material for subsequent formation of GNRs. We chose GQDs to be a building block of GNRs on the basis that these two materials share the same fundamental sp^2-hybridized hexagonal lattice structure of graphene.

The morphology of GQDs was examined by atomic force microscopy (AFM) and transmission electron microscopy (TEM) techniques (Fig. 1a). Statistical analysis of AFM images reveals that average height of GQDs is 1.7 nm with average diameter of 20.7 nm. AFM images also reveal uniform surface morphology and spherical shape of GQDs.

Structural properties of GQDs were characterized using Raman spectroscopy. Raman spectra of carbon nanomaterials show two main peaks: G peak which appears around 1580 cm^{-1} and D peak around 1360 cm^{-1} [31]. In Fig. 1b Raman spectra of GQDs with characteristic peaks at 1590 cm^{-1} and 1360 cm^{-1} are presented. Presence of G bands proves graphene structure of GQDs, while high intensity of D band indicates that this structure is very disordered and defective. Defects in Raman spectrum stem from GQDs edges and oxygen-containing functional groups, which are located both at the edges of GQDs or in their graphene core.

Chemical properties of GQDs were analyzed by means of Fourier transform infrared (FTIR) spectroscopy (Fig. 2a). Peaks near 1572 cm^{-1}, 1418 cm^{-1} and 2980 cm^{-1} can be assigned to C=C stretching of graphite. Peak at 1011 cm^{-1} stems from C—O bonds in carboxyl groups and peak at 1365 cm^{-1} stems from symmetric stretching of carboxyl groups. Peak at 1045 cm^{-1} originates from