Novel tubular graphene synthesized via chemical vapor deposition process

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Abstract. In this work, we prepared a novel nanoscale tubular graphene (TG) by depositing it on the surface of nickel nanowires (Ni-NWs). This method allowed us to synthesize Ni-NWs by a chemical reduction process carried out under water-bath heat and magnetic field. The TG was subsequently deposited on the as-prepared Ni-NWs through a chemical vapor deposition (CVD) process under atmospheric pressure. Scanning electron microscopy (SEM) and Raman spectroscopy revealed the presence of Ni-NWs and TG/Ni-NW composites containing a few layers of graphene. The diameters of the Ni-NWs and TG/Ni-NW composites were ca. 300–500 and 500–1000 nm, respectively. The novel tubular structure of graphene provided this material with large specific surface area and excellent electrical conductivity, making it an ideal for sensor applications.

1. Introduction
Graphene is a flat monolayer of carbon atoms packed in a two-dimensional (2D) honeycomb lattice. This material was prepared by Andre Geim and Konstantin Novoselov by mechanical exfoliation in 2004 [1]. Graphene has received significant research attention owing to its excellent performance. In subsequent years, a whole range of carbon materials including 2D graphene, zero-dimensional (0D) fullerene, one-dimensional (1D) carbon nanotubes, and three-dimensional (3D) graphite and diamond materials have been developed. As revealed in the past decade, single-layer graphene possesses a number of interesting characteristics including extremely high charge (electrons and holes) mobility (230000 cm²/Vs), superior thermal conductivity (3000 W/mK), a visible light absorption as low as 2.3, and ultrahigh specific surface area (2600 m²/g) [2–4]. Owing to these excellent properties, graphene has been widely used in many areas including electronic devices, information, energy, materials, and biomedicine, among others [5].

Following the pioneer production of graphene by mechanical stripping of graphite crystals, many other preparation methods have been developed including epitaxial growth on SiC [6], chemical reduction of graphite oxide [7], chemical vapor deposition (CVD) growth on copper or nickel substrates [8], and unzipping carbon nanotubes (CNTs) [9]. Chemically derived graphene is widely...
used in combination with other materials (e.g., metal oxides) and self-assembled into 3D macroporous structures owing to its convenient preparation and processing characteristics [10]. However, as a result of the redox process, a large number of defects appears on the surface graphene, which alters greatly its conductivity. Large-area and high-quality graphene materials can be prepared by CVD [11]. CVD achieves materials with significantly higher charge mobility compared to chemically reduced graphene sheets. A large number of studies have recently focused on growing 2D graphene sheets and macroscopic 3D graphene foams by CVD [12–15]. However, despite these advances, the preparation of high-quality graphene with microscopic tubular structure by CVD has not been targeted yet.

Herein, we report a simple method for synthesizing microscopic 3D foam-like tubular graphene (TG). The simple flowchart of this experiment was described in figure 1. Nickel nanowires (Ni-NWs) prepared by chemical reduction under water-bath heat and magnetic field conditions were used as substrates for depositing this TG. The TG was grown by ambient-pressure CVD on Ni-NWs. As revealed by scanning electron microscopy (SEM) and Raman spectroscopy, the Ni-NWs and TG/Ni-NW composites contained graphene with a few layers. The resulting TG showed excellent specific surface area, making it a promising sensor material.

2. Experimental

2.1. Materials
Nickel chloride hexahydrate (NiCl₂·6H₂O) and hydrazine hydrate (N₂H₄·H₂O, 85 wt%) were purchased from Sinopharm Chemical Reagents Co.Ltd (China). Ethylene glycol (EG) and sodium hydroxide (NaOH) were obtained from J&K Scientific Ltd (Shanghai). All organic solvents were analytical grade and were used without further purification.

2.2. Preparation of Ni-NWs
Ni-NWs were synthesized by chemical reduction under a magnetic field [16]. Briefly, 0.7 g of NiCl₂·6H₂O and 100 mL of EG were added to a 200 mL beaker, and the mixture was magnetically stirred for 1 h at room temperature to ensure uniform dispersion of Ni²⁺ ions in the solution. 2 g of NaOH were dissolved in 100 mL of EG to obtain a NaOH solution in EG. After adding 20 mL of a N₂H₄·H₂O solution to the above mixture solutions, the reaction mixture was continually sonicated until a homogeneous blue solution was obtained. This solution was subsequently poured into a 500 mL flask. The flask was placed in a water bath under a 0.5 T magnetic field and subsequently heated at 70 °C for 45 min, after which fluffy black products were formed. The solid product was separated from the solution by a magnet and cleaned three times with deionized water, ethanol, and acetone (one time each). Finally, the as-cleaned Ni-NWs were placed in a vacuum oven and dried at 60 °C.

2.3. Deposition of the TG
The TG was grown on Ni-NWs by CVD to obtain TG/Ni-NW composites. Specifically, the prepared Ni-NWs were placed in a tubular furnace and the pressure was decreased to 8 Pa. Ar (300 sccm) was then introduced into the tube furnace until the pressure in the furnace reached 1 atm. Then, the temperature inside the furnace was increased to 850 °C under flowing Ar (300 sccm) and the material was annealed for 5 min to clean the Ni-NWs surface. After that, H₂(50 sccm) and CH₄(3–15 sccm) were introduced into the tube furnace for 10 min. The number of graphene layers of the TG increased with the concentration of CH₄. Finally, the samples were cooled down to room temperature at a rate of 10 °C/min under flowing Ar (300 sccm) and H₂(50 sccm) after 10 min of the reaction-gas mixture flow. Thus, TG deposited on Ni-NWs substrate was successfully synthesized.

2.4. Characterization
Field-emission SEM (FE-SEM, Sigma 300, Carl Zeiss, Germany) was employed to study the morphologies of the samples. The structure of the samples was investigated by Raman spectroscopy (HR-800, HORIBA JobinYvon, France) with a 632.8 nm He-Ne laser. X-ray diffraction (XRD, X Pert-Pro MPD, Panalytical, Holland) was used to determine the crystalline structure of the samples.
Figure 1. Simple flow chart showing the method used for preparing Ni-NWs and TG.

3. Results and discussion

The morphologies and microstructures of the Ni-NWs and the TG/Ni-NW composites are shown in figure 2. Low- and high-magnification images revealed that Ni-NWs with a diameter of 300 nm were successfully prepared (figures 2a and b). The Ni-NWs grown under a magnetic field contained numerous surface spikes. After depositing graphene on Ni-NWs by CVD, the surface protrusion disappeared and a fraction of the NWs melted at high temperature, which resulted in the diameter of the NWs increasing to 500 nm (figures 2c and d). By comparing pictures before and after the CVD process, the successful synthesis of graphene was clearly revealed by the surface morphology and color change of the material.

Figure 2. SEM images of: (a) Ni-NWs, (b) high-magnification SEM images of: Ni-NWs and (c) TG/Ni-NW composites, (d) high-magnification SEM image of the TG/Ni-NW composites.

Raman spectroscopy further revealed the presence of graphene on the Ni-NWs. As shown in figure 3, the Raman spectrum of Ni-NWs contained three characteristic peaks at 1323, 1579, and ca. 2670 cm\(^{-1}\) [17]. The G band is produced by the first-order scattering of the \(E_{2g}\) phonon plane vibration on the sp\(^2\) domain. Therefore, this band provides an indication of the degree of crystallization of graphene. The D band is produced by the discontinuity of the crystal plane of the graphene or the doping of foreign atoms. The intensity of the D band reflects the defect density of graphene. The most intense peak for graphene is the G' peak produced by the double phonon resonance Raman peak of graphene. The appearance of this G' peak is the main indicative of the presence of graphene. The intensity of this peak indicates the degree of stacking of the material. Figure 3 shows the Raman spectra of few-layers and multi-layers graphene materials. The ratio of G'/G decreases as the number of graphene layers increases. As can be seen in figure 3, the ratio of G'/G decreased from 0.94 to 0.42, indicating that the
number of graphene layers changed from a few layer (2~3) to multilayer (>3). The peak of D is very low, which indicates that the synthesized graphene has a very high quality, which is consistent with previous reports[18, 19].

Figure 3. Raman spectra of the TG deposited on Ni-NWs.

4. Conclusions
In conclusion, graphene with a novel tubular structure was easily synthesized by CVD over Ni-NW substrates. Ni-NWs were prepared by chemical reduction under water-bath heat and magnetic field. Graphene was deposited on the surface of Ni-NWs by CVD using H2 and Ar as carrier gases and CH4 as a carbon source. The number of graphene layers was found to depend on the concentration of the carbon source, the growth time, and the cooling rate. This particular tubular structure of graphene provided this material with higher specific surface area compared to ordinary 2D graphene materials. As a result, the resulting material can have potential applications in the sensor and energy-storage fields.

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