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Large-scale template-free synthesis of N-doped graphene nanotubes and N-doped SiO_2-coated graphene nanotubes: Growth mechanism and field-emission property

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ABSTRACT

The use of dopants and other functional materials has been proven to be an effective approach in tailoring the electronic properties of the composition of graphene nanosheets. However, investigations into doping and compositing of tubular graphene are still at an early stage. Herein, the first large-scale synthesis of N-doped graphene nanotubes (GNTs) and the N-doped graphene coaxial nanotubes with amorphous SiO_2 coating layer (GNTs@SiO_2) have been performed in a facile free-template, one-step chemical vapor deposition method, and the growth mechanism was investigated in detail. This approach both simplifies the synthetic process and protects the nanotubes from destruction caused by template removal. Moreover, a high ratio of graphitic-N to pyridinic-N doping (~6.5:1) was achieved, which is an important factor required to improve the various properties of graphene. The N-doped GNTs and GNTs@SiO_2 displayed excellent field emission properties, with E_{to} of 1.2 and 0.5 V/μm and E_{thr} of 3.4 and 4 V/μm, respectively, and a synergistic effect mechanism has been proposed to interpret the enhanced FE properties. This present research not only offers a new route for large-scale synthesis of N-doped tubular graphene and its nanocomposite, along with excellent field emission properties and electroconductivity, but also establishes a foundation for their application in various fields.

1. Introduction

Tubular nanostructures have unique internal hollow channels, which provide opportunities for studying nanoscale fluid flow [1], chemical reactions [2,3], electrochemical energy storage [4,5], biomedical drugs delivery [6]. Graphene is a rising star in material science that has many remarkable properties and numerous potential applications [7–13]. Combining the unique advantages of tubular nanostructures with the properties of graphene suggests that tubular graphene would be an attractive nanostructure for study and design. And it would be a promising material in a variety of scientific and engineering applications, for example, it will be used as a catalyst support material, as a core material for biosensors, as storage/delivery containers for biomedicine, as energy conversion and storage material, as mechanical reinforcement agents of composites. However, there have been few studies focusing on graphene nanotubes (GNTs), which may be partially due to limited synthesis methods. To the best of our knowledge, only the template method has been utilized for synthesizing graphene nanotubes. Wang et al. [14] reported that GNTs were synthesized by CVD method using Ni nanowires as templates, and the GNTs collapsed when the Ni nanowires core were removed by chemical etching; Li et al. [15,16] synthesized graphene/graphene-tube nanocomposites using a specially-designed Cage-Containing Metal-Organic Framework as the template. It is not to be neglected that this template method is complex and requires special template designing and growth of the desired product on/around the template, as well as selective removal of the template from the composite structure. The template-free method for synthesizing GNTs remains unexplored. Due to being free from the templates, this method possesses the inherent advantages: simple process, low-cost, easier operation and potential application for the

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industrialization and production. And more importantly, the template-free method can completely protect the desired nanotubes from destruction and contamination caused by template removal.

Incorporation of guest atoms, such as nitrogen, into the graphene lattice has been demonstrated to be reliable in tailoring the electronic band structure, which is important for potential applications in nanoelectronics, opto-electrochemistry, enzymatic biosensor and green energy technology [17–22]. The nitrogen atoms incorporated into the graphene matrix usually exist in different bonding configurations: e.g., pyridinic nitrogen (p-N doped) and graphitic nitrogen (g-N doped). The impact of N-doping on graphene properties largely depends on the nitrogen bonding configurations. It has been reported that g-N doping plays an important role in enhancing the various properties of the graphene among the various N bonding configurations. Li et al. [15] reported that the oxygen reduction reaction activity of N-doped graphene was commensurately enhanced as the relative extent of g-N doping went up. Soin [23] reported that N-doped graphene nanoflakes that had a high g-N/p-N ratio (2:1) had significantly improved field emission (FE) properties. Usachov [24] developed an efficient method in transforming p-N to g-N doped graphene by the post growth annealing N-graphene nanoflake on a gold monolayer. A higher g-N/p-N ratio(4:1) was achieved by this transformation method. However, challenging work remains in directly obtaining N-doped graphene at high g-N/p-N ratios by a one-step synthesis.

Apart from doping, fabrication of graphene-based nanocomposites has been demonstrated to be another feasible approach to improve graphene properties for a variety of applications. To date, various nanomaterials have been explored as the functional material to composite with graphene nanosheets. For instance, graphene-Mn_3O_4, graphene-metal nanoparticles (Ag, Pd and Pt), graphene-SnO_2, ZnO/graphene/Ag, graphene-MoS_2, chitosan-graphene nanocomposites and graphene/copper have been fabricated. These graphene-based nanocomposites exhibit excellent oxygen reduction reaction performance [25], FE properties [26,27], enhanced photocatalytic performance [28], good electron transport characteristics [29,30], enhanced sensitivity as a cholesterol biosensor [31,32] and enhanced mechanical properties [33]. Recently, due to the relatively small positive electron affinity and superior chemical inertness, SiO_2 has been explored in fabricating graphene-based nanocomposites. For example, graphene@SiO_2@PMMA [34], Ag-graphene@SiO_2 [35], Ag/graphene@SiO_2-$NaLuF_4$ [36] and graphene oxide-SiO_2-C=C [37] have been synthesized and their different properties have been explored. Motivated by these results, GNTs@SiO_2 should be investigated as a promising graphene nanocomposite.

So far, the research on the template-free synthesis of N-doped tubular graphene and its nanocomposite has not been reported. It is a challenging and meaningful work. Herein, a facile template-free, one-step CVD method has been developed for synthesizing large-scale N-doped GNTs and N-doped GNTs@SiO_2 with an 8-10 nm-thick amorphous SiO_2-coating using a novel self-designed raw materials system. The as-prepared N-doped GNTs and GNTs@SiO_2 exhibited periodic compartmentalized morphology with uniform separation distance along the nanotube axis. And both the sidewalls and the inside compartment layers revealed distorted and cross-like structures. The doped nitrogen was predominantly observed in a graphitic-N bonding configuration, which is the first reported high ratio (6.5:1) of g-N/p-N in N-doped graphene materials. The unique morphology, composition and N-doped bonding configuration endowed the resulting products with excellent FE properties and electroconductivity. Moreover, the reasonable mechanisms of growth and enhanced field emission properties have been discussed in detail. This study reveals a new method for preparing N-doped GNTs and N-doped GNTs@SiO_2 that have excellent FE properties and electroconductivity, while also offering a general reference for synthesizing tubular nanostructures from a variety of materials.

2. Experimental section

2.1. Materials synthesis

The synthesis of N-doped GNTs and N-doped GNTs@SiO2 was carried out using a conventional high-temperature vertical vacuum furnace. The preparation process is detailed in Supporting Information Fig. S1. A polished graphite wafer served as the substrate. The 0.01 mol L^{-1} $Ni(NO_3)_2$ ethanol solution was used as the catalyst. For N-doped GNTs, Si-SiO_2 mixed powder (molar ratio of 1.5:1) and melamine were ground together at a 0.5:1 M ratio, forming a uniform mixture. The mixed material powders covered by a substrate with catalyst were placed in a homemade graphite reaction chamber, which was placed within the center of a vertical vacuum furnace. Before heating, the furnace was purged three times with high purity argon using a rotary vacuum pump to reduce the O_2 concentration to a negligible level. Then the temperature was increased to 1250 °C at an average rate of 15 °C/min, which was then maintained for 20–30 min. Subsequently, methane (purity > 99.99%) was introduced from the bottom of the graphite reaction cell at a 0.10 sccm flow rate for 10 min, after which the power was switched off and the furnace allowed to naturally cool to room temperature. For N-doped GNTs@SiO_2, the preparation process was similar to that of the N-doped GNTs, except in two details: 1) the molar ratio of the Si-SiO_2 mixed powder to melamine was increased to 1:1 and 2) 20 min heat preservation period was utilized after aerating the methane and ensuring the full growth of the SiO_2-coating.

2.2. Materials characterizations

SEM and elemental mapping were performed on a JEOL JSM-6 field emission scanning electron microscope equipped with an EDS unit. TEM, SAED and HR-TEM images were recorded using a Hitachi (Tokyo, Japan) H-8100 transmission electron microscope. X-ray diffraction (XRD) pattern were recorded using a Rigaku D/max-2400 X-ray diffractometer at room temperature. Raman spectra were recorded using a Renishaw2000 micro-Raman system with an excitation wavelength of 514 nm. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Scientific Escalab 250Xi X-ray photoelectron spectrometer system equipped using Al radiation as the probe. Infrared absorbance spectrum measurements were performed using a Nicolet FT-IR spectrophotometer.

The field emission studies were performed in a high-vacuum chamber with a base pressure of 1.0×10^{-6} Torr. The anode was a copper rod with a 3 mm-diameter. The distance between the anode and cathode was adjusted to 500 μm using a micrometer screw. For field emission stability measurements, 1440 data points were collected, each 5 s apart for 120 min.

3. Results and discussion

The X-ray diffraction (XRD) patterns of as-prepared N-doped GNTs and GNTs@SiO_2 had the same characteristic diffraction peak around 26.5°, which matched well with the (002) diffraction of the graphitic layer-by-layer structure, having an interlayer spacing of 0.34 nm (JCPDS card no.00-001-0640), indicating that the main products of the two samples were graphene (Fig. 1). The amorphous broad peak at a low diffraction angle (~20°) was observed in the patterns of N-doped GNTs@SiO_2, which may be attributed to