



Selective fabrication of carbon nanowires, carbon nanotubes, and graphene by catalytic chemical liquid deposition

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ABSTRACT

Large quantities of graphene sheets, carbon nanotubes, and ultra-long carbon nanowires can be selectively fabricated at a high rate in ethanol by catalytic chemical liquid deposition under atmospheric pressure at room temperature. Synthesis of the carbon nanostructures can be achieved through the following procedural changes: (a) by manipulating the H₂O content, carbon nanostructures can be tailored from carbon nanotubes (CNTs) with various inner diameters to carbon nanowires (CNWs). (b) By adding an organic precursor containing S, graphene can be selectively fabricated. The simplicity and scalability of our method provides a high potential for mass growth, and the inherent cleanliness of the procedure offers a perfect starting point for straightforward, contamination-free synthetic processes without the use of expensive equipment. We also provide clear pictures of the growth process of these materials, where the pressure difference across the graphene surface results in the formation of bubbles that leads to the growth of CNTs, CNWs, or graphene.

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1. Introduction

Carbon nanotubes (CNTs), carbon nanowires (CNWs), and graphene are members of the carbon allotrope family with different structures and have been the source of substantial research efforts among scientists and engineers [1–4]. A single-walled carbon nanotube (SWCNT) is a hollow cylindrical tube with a sidewall of sp² hybridized carbon atoms that exhibit similar (but strained) bonding and structure to graphite. Graphene is a single atomic sheet of carbon atoms arranged in a honeycomb. In contrast to the hollow structured CNTs and mono- or few layer sp² graphene, CNWs are composed of both sp² (graphite, fullerenes, and nanotubes) and sp (C chain and carbyne) bonds. Theoretical calculations demonstrate that the inserted C chain within the CNWs can modify the electronic structure by increasing the density of states at the Fermi energy level. They also show an increase in the Young's modulus, strength and toughness compared to CNTs and graphene [5]. CNTs, CNWs, and graphene

possess many intriguing electrical and mechanical properties, such as a wide electrochemical stability window, excellent biocompatibility and high thermal conductivity [6–10]. Due to the aforementioned properties, CNTs, CNWs, and graphene have been studied for use in many different fields, including electronic switching [11,12], heat exchangers [6], various lab-on-a-chip systems [8], molecular sensors [13,14], fuel cells [15], and biomedical purposes, where they have been implanted over a million times in heart valves and orthopedic joints [16].

Despite the huge amount of research effort that has been dedicated to the synthesis of these materials, controllable growth of these materials remains the bottleneck, and mass production of the CNTs, CNWs, and graphene with the desired structures has been a long-standing challenge. Currently, catalytic chemical vapor deposition (CCVD) [17] remains the most employed method to produce these materials. However, it requires stringent growth parameters (such as high temperature) [18] and requires changing the experimental setup and conditions to grow CNTs, CNWs, and graphene. For example, specific substrates or porous membranes are required to grow CNWs [19–22], while copper foils are employed for graphene production [23]. As a result, the length of CNWs is limited by the mold, and the catalyst or the mold may

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remain as undesired impurities [18]. In recent years, more attention has been paid to electrochemical deposition technique for manufacturing thin films and devices due to its simplicity, its low capital equipment cost, and its ability to be scaled up for large production. An electrochemical deposition technique has been employed to produce carbon nanotubes from organic solvents at room temperature [24]. However, the potential difference applied between the anode and cathode was kept nominally at 1000 V.

In this work, we develop a novel and efficient protocol to produce CNWs, CNTs, and graphene directly in liquid ethanol under atmospheric pressure. The growth of the different nanocarbon forms can be conducted in one simple reactor under mild conditions. Here we also propose a growth model that couples the chemical and physical properties surrounding the growth of the CNWs, CNTs, and graphene. This model allows us to understand the growth mechanism, with the ultimate goal of engineering the synthesis of CNW, CNT, and graphene in large quantities.

2. Experimental

2.1. Synthesis of CNT, CNW, and graphene

All chemicals were analytical reagent grade and were used without any further purification. The growth of CNTs, CNWs, and graphene took place on mono-crystalline silicon (Si 111) substrate pieces (n-type with a root-mean-square roughness of ~ 0.2 nm, a diameter of 76.2 mm and a thickness 0.37 mm) purchased from Shanghai Yiyang Electron Material Co., Ltd., China and cut to the desired size before use in the experiments. Before the growth reaction, the mono-crystalline silicon chip was ultrasonically (Kunshan Hechuang Ultrasonic Instruments Co., Ltd.) cleaned in ethanol for 20 min, washed in a 2 M hydrofluoric acid (HF) solution for 10 s and washed again in ethanol. Thereafter, the pretreated silicon chip was dried in Ar gas at room temperature and then coated with a 5 nm uniform Fe film by electron beam evaporation in a DZS-500 vacuum coater (Chinese Academy of Science, Shenyang Instrument Research Center, $\sim 2 \times 10^{-6}$ Torr pressure during deposition).

The CNT, CNW, and graphene growth process with catalytic chemical liquid deposition (CCLD) in liquid ethanol was carried out in a reactor consisting of the main reaction apparatus, a recycling-cooling system for the organic liquid and a gas purging system, as shown schematically in Fig. 1.

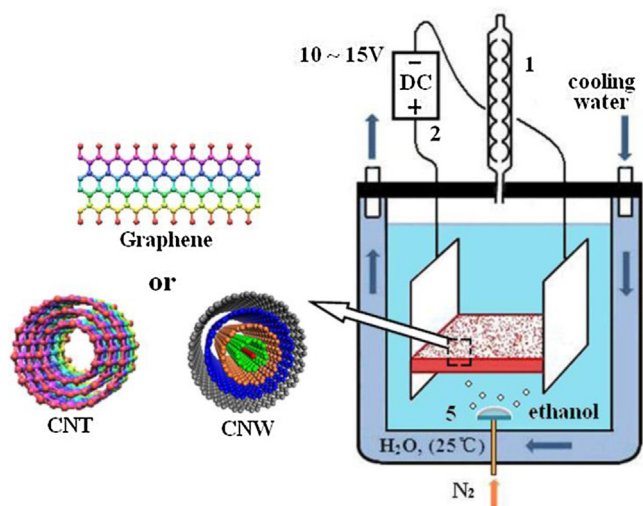


Fig. 1. Schematic setup of the experimental process: (1) cooling-regurgitated pipe; (2) DC electric power supply; (3) graphite electrode; (4) silicon chip coated with Fe membrane; (5) gas diffuser.

In the main reaction apparatus ($R^2 \times H = 95^2 \times 100$ mm), a silicon chip coated with Fe film (60×15 mm) was situated transversely at the center of the chamber in the liquid and was anchored between two graphite chips (Shanghai Carbon Co., Ltd.). The graphite chips were connected to the DC electric power supply (Shanghai Liyou Electrification Co., Ltd., China) for controlling the current and voltage (10–15 V). N₂ gas was pumped into the chamber by an air-pump (Guangdong Chuangxing Electrical Appliance Co., Ltd.) in the experiments. The silicon chip was heated by applying a voltage to the electrodes. Various growth condition parameters, such as the voltage, types of organic liquid, organic liquid-to-water ratio, reaction time, and sweep gas flow rate were adjusted to achieve high-purity CNTs, CNWs, and graphene. The temperature of the liquid in the reaction chamber was controlled by cooling water (25 °C) recycle system using a peristaltic pump (Baoding Longer Precision Pump Co., Ltd., China), as shown in Fig. 1.

2.2. Characterization of CNT, CNW, and graphene

The morphology and composition of the CNWs and CNTs on the silicon chip were observed by scanning electron microscopy (SEM) and energy dispersion X-ray (EDX) using a ZEISS ULTRA-55 instrument (Carl Zeiss, Germany). High-resolution transmission electron microscopy (HRTEM, JEOL Ltd., Japan, operated at 400 kV acceleration voltage) was used to investigate the near-surface region. Resonance Raman spectra of the CNWs and CNTs were taken with a Senterra R200-L (Bruker Optics, Inc., Germany) at 532 nm excitation. The laser power was 20 mW, and the spot size was ~ 25 μ m at 50 \times magnification.

3. Results and discussion

3.1. Growth of CNTs, CNWs, and graphene

Most of commercial applications demand the efficient production of large quantities of nanostructured carbon arrays as well as high standards of purity, length, and structural quality. To achieve these, a big challenge of the synthetic method is to control the competing reaction pathways that lead to desirably high growth rates but with the formation of amorphous carbon, which undesirably coats the catalyst and the already-grown sidewalls of the nanostructured carbon arrays. In our experiments, initially only CNTs, instead of CNWs or graphene, were produced at high selectivity in pure liquid ethanol. A SEM image (Fig. 2(a1)) reveals that large quantities of CNTs displaying hollow, cylindrical shapes were embedded on the silicon chip coated with Fe film. A transmission electron microscope (TEM) image provides more direct evidence of the SWCNT structural quality and is shown in Fig. 2(a2). The diameter of the SWCNT ranges from 20 to 30 nm, and the length is on the order of a few micrometers. Furthermore, the TEM images show that the SWCNTs exhibit significantly little amorphous carbon on their sidewalls and have good crystallinity, indicating that the proposed process improves both the purity and structural quality of the produced CNTs.

H₂O could play an important role in the synthesis of CNTs, a well-known example of the role of H₂O is the synthetic route developed by Hata et al. [25,26]. They demonstrated that small additions of H₂O vapor to the buffer gas during CCVD yielded highly pure, super-dense and vertically aligned ultra-long SWCNTs. It was postulated that the involvement of H₂O in the synthesis conditions not only removed amorphous carbon species but also played an additional indirect role in the growth of the SWCNT by promoting the graphitization of carbon at the root of a growing tube. Thereafter, various amounts of H₂O were introduced in the liquid ethanol to examine their effect on SWCNT growth. In pure

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