One-step Synthesis of Carbon Nanotubes Network with Rich Oxygenated Functional Groups via Microwave Plasma in Atmospheric Pressure

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Abstract

An atmospheric pressure microwave plasma tubular furnace apparatus (MPTF) for the rapid synthesis of carbon nanotubes (CNTs) has been developed. CNTs have been synthesized by an Argon-Hydrogen microwave plasma using ethanol vapor as carbon source with the furnace temperature of 800 °C at the atmospheric pressure. The synthesized CNTs have been analyzed by scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), and are shown to be multi-walled and tangled and chemically connected to form a high-density network with the diameter at the range of 25-70 nm. The measurement of X-ray photoelectron spectroscopy (XPS) indicates that a large number of oxygenated functional groups grown on the surface of CNTs. These properties proved that the CNTs could be utilized as nanoscale templates for various applications.

INTRODUCTION

Over the past decade, the application of plasma in nanomaterials synthesis has attracted more interest, like diamond-like carbon, CNTs, graphene, and so on. However, the plasma used in the CVD process is generally working under low pressure, which leads to low electron density and electron energy. It can activate reaction and reduce the reaction temperature. The potential of microwave plasma in molecular deposition has not been realized. The atmospheric pressure microwave plasma has the advantages of high electron density, high electron activity, high temperature, and strong molecular decomposition ability, which is very powerful in the synthesis of nanomaterials. Using atmospheric pressure microwave plasma torch (AMPT), CNTs [1], graphene [2], metal oxide nanoparticles [3], and so on were obtained. But the atmospheric pressure microwave plasma has not been widely used in the field of nanomaterials synthesis due

to the characteristics of the excitation difficulty, open space, and stability of atmospheric pressure microwave plasma.

The CNTs have attracted considerable attention due to their unique physical and chemical properties [4,5]. Various methods, such as arc discharge [4], laser ablation [5,6], thermal chemical vapor deposition (CVD) [7], plasma-enhanced chemical vapor deposition (PECVD) [8], or microwave plasma [9], etc. have been developed to synthesis CNTs. Numerous applications of CNTs as a sensor for nanoscale platforms [10], transparent electrode [11], the template of the catalytic surface for fuel cell [12], were proposed. In order to improve the proficiency of CNTs as the nanoscale platform, it is highly preferable to form the high-density network structure with chemically connected CNTs [13].

In this study, we developed a novel apparatus for the production of nanostructured material. This apparatus combined the keen ability to the decomposition of microwave plasma with the advantages of a clean atmosphere, high precision of temperature control and temperature stability, etc. in a tubular furnace. Using the MPTF, we synthesized 30 mg network structured CNTs powder using ethanol vapor as the carbon source in 30 min.

The MPTF is based on atmospheric pressure microwave plasma technology and CVD. Compared with the direct synthesis of CNTs by AMPT, the MPTF have the advantages of high atmosphere purity, controllable growth of materials and low power. Compared with the CVD synthesis of CNTs, the MPTF have the advantages of fast growth rate and low temperature of tubular furnace. And compared with the PECVD synthesis of CNTs, the MPTF have the advantages of fast growth rate, high atmospheric pressure range, and plasma separate from material.
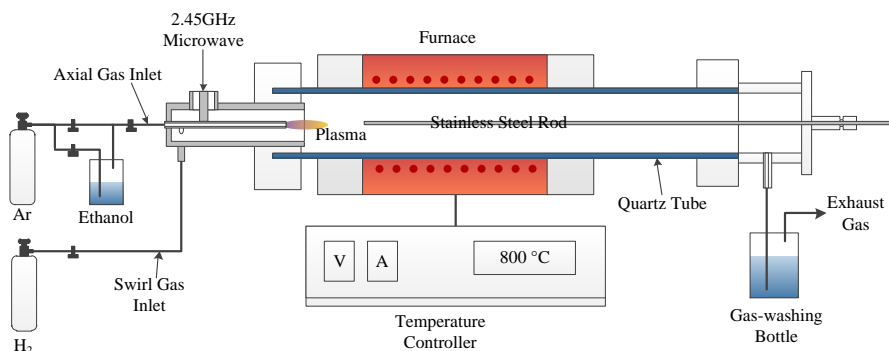

Figure 1. The schematic diagram of the MPTF used for CNTs synthesis.

EXPERIMENT

The system contains a microwave plasma generator and a high-temperature tubular furnace. A solid-state microwave source, provides stable 200W microwave power for the apparatus to produce atmospheric pressure plasma. An axial gas and a swirling gas stabilize the plasma flame. The axial gases are composed of 200 sccm (standard cubic centimeter per minute) argon (Ar) for direct bubbling of ethanol maintained at the temperature of 25 °C as the carbon source and 800 sccm pure Ar. The swirling gas, 200 sccm hydrogen (H_2), pumped into the plasma generator through a tangential injection hole to stabilize the plasma and works as the deoxidizer. The exhaust

gas would be emitted into the air though a gas-washing bottle. The stainless steel rod was used as the trigger for microwave plasma and as the substrate for CNTs, and its location was shown in figure 1.

A vacuum pump was employed to empty the air in the apparatus for 10 min. Then, H_2 swirled into the apparatus with a flow of 200 sccm. The valve of the gas-washing bottle would turn on when the air pressure in the quartz tube raised to the atmosphere. After that, the furnace heated to 800 °C and kept for 20 min to further reduce the oxygen in the apparatus. Before the excitation of the plasma, 800 sccm Ar and 200 sccm mixture gas of Ar and ethanol vapor pumped into the apparatus. The synthesis process of CNTs lasted for 30 min, then, turned the microwave power source, tubular furnace, and axial gas off. After that, the apparatus was cooled down to room temperature under the H_2 environment. The CNTs presented in this paper were taken from the surface of the stainless steel rod in the area of the furnace. The coating on the surface of the stainless steel rod was sonicated in ethanol for 10 min in order to get the ethanol dispersion of CNTs.

A Scanning Electron Micrograph (SEM) (Hitachi S-5000 20 kV) and a High-Resolution Transmission Electron Microscope (HRTEM) (FEI Tecnai G2 F20 200 kV) were used to examine the size-morphology and the microstructure of the CNTs. The composition of the samples was measured by an X-ray photoelectron spectroscopy (XPS) (ThermoFisher Escalab Xi+).
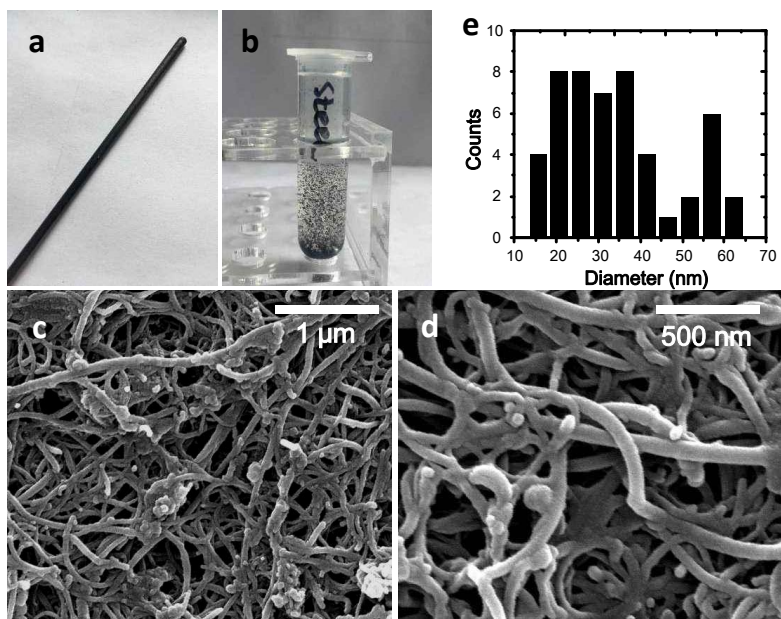

Figure 2. Photographs and SEM micrographs of CNTs synthesis in the microwave plasma tubular furnace. (a) the photograph of the CNTs on the stainless steel rod; (b) the photograph of the ethanol dispersion of the CNTs; the SEM micrographs of the CNTs (in low (c) and high (d) magnification); and (e) the diameter distribution.

RESULTS

Figure 2(a) and (b) show the photographs of the CNTs on the stainless steel rod and the ethanol dispersion. SEM micrographs for the CNTs powder grown on the surface of the stainless steel rod in the atmospheric pressure microwave plasma tubular furnace shown in figure 2(c) and (d). The CNTs were tangled with each other formed a CNTs network. A large number of bifurcations and bulges grow on the surface of the coarser CNTs indicates that there are many defects on the surface of CNTs, which provide more specific surface area as a platform for nano-catalysts. The diameter distribution of CNTs was calculated and shown in figure 2(e), which approximates to even distribution in the range of 18-65 nm. The length of CNTs was ups to dozens of micron.
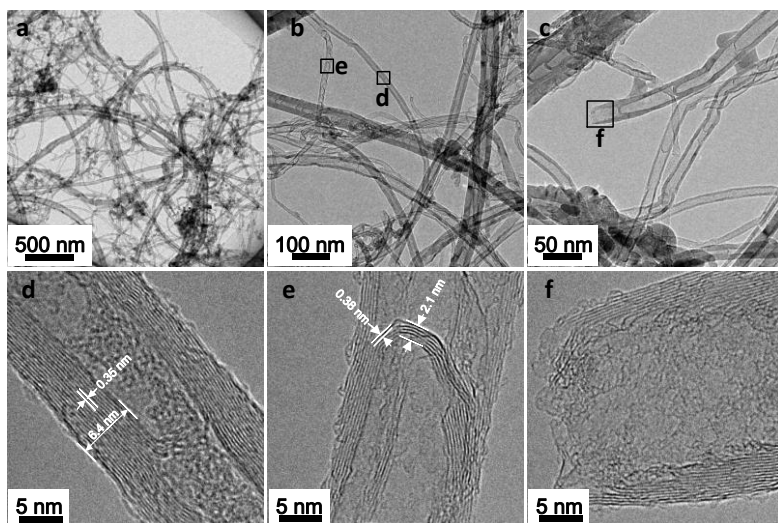

Figure 3. HRTEM images of CNTs synthesis in the microwave plasma tubular furnace.

Figure 3 shows HRTEM micrographs of CNTs, shows that the CNTs network was based on the thick tube with a diameter of ~70 nm as the meridian and the thin tube with a diameter of ~25 nm as the winding connection. Figure 3(b) and (c) is the TEM image showing that the thick CNTs consist of hollow compartments, looking like bamboo. The hollows in the thick tubes were small and intensive, and bigger and sparse in the thin CNTs. The diameter of the hollow was in the range of 10 ~20 nm, and the minimum length of the hollows was ~10 nm in the CNT with a diameter of 66 nm. Figure 3(c) shows that the carbon film acts as an adhesive to chemically bond two adjacent carbon nanotubes together. The walls of the CNTs in figure 3(b) are tightly aligned with a high density of graphite sheets with a thickness of 6.4 nm, and the distance between layers is 0.35 nm, as shown in figure 3(d). Figure 3(e) and (f) show the magnified view of the joint between the wall and the hollow, and the open end structure of the CNTs.
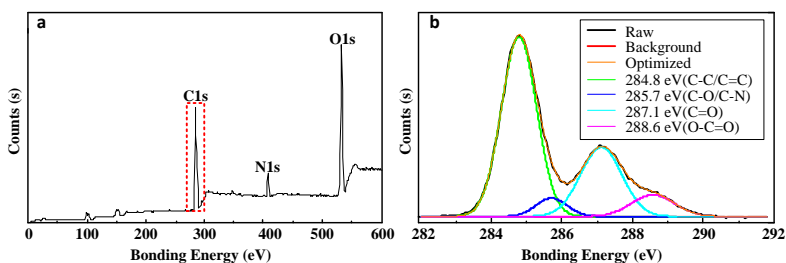
Figure 4. XPS spectra of CNTs, (a) is the global spectra and (b) is the magnification view of C1s.

XPS measurement was carried out to investigate the surface functional groups of the synthesized CNTs. As shown in figure 4, the CNTs contains C, N, and O, and C1s peak indicate that they were mainly composed of the C-C/C=C (284.8 eV) and the surface defects of CNTs as -C-OH/C-N (285.7 eV), -C=O (287.1 eV) and -COOH (288.6 eV). The Oxygen in the functional groups were mainly come from the decomposition of ethanol. These hydrophilic groups play an important role in the dispersion stability of CNTs in water [14]. A large number of surface defects improved the surface roughness and the proficiency of CNTs as the nanoscale platform at the reactions in water.

CONCLUSIONS

The network structured CNTs were synthesized by the microwave plasma tubular furnace using ethanol vapor as carbon source with the furnace temperature of 800 °C at the atmospheric pressure. The synthesized CNTs were tangled and chemically connected to form a network structure with a thick tube with a diameter of ~60 nm as the meridian and the thin tube with a diameter of ~20 nm as the winding connection. Attribute to rich oxygen-containing functional groups on the surface of the CNTs, which got an excellent hydrophilic property and a large number of rough surfaces. The CNTs synthesized in this study can be utilized as nanoscale templates for various applications.

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