Journal of Materials Science & Technology 31 (2015) 479–483

Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

A Simple Approach to the Fabrication of Graphene-Carbon Nanotube Hybrid Films on Copper Substrate by Chemical Vapor Deposition

Nguyen Van Chuc [1,*], Cao Thi Thanh [1], Nguyen Van Tu [1], Vuong T.Q. Phuong [2], Pham Viet Thang [2], Ngo Thi Thanh Tam [1]

[1] Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam
[2] Hanoi University of Science, Vietnam National University, Hanoi, Vietnam

ARTICLE INFO

Article history:
Received 19 September 2014
Received in revised form
14 November 2014
Accepted 19 November 2014
Available online 15 April 2015

Key words:
Graphene
Carbon nanotube (CNT)
Hybrid films
Copper substrate
Chemical vapor deposition (CVD)

In this study, graphene-carbon nanotube (CNT) hybrid films were directly synthesized on polycrystalline copper (Cu) substrates by thermal chemical vapor deposition (CVD) method. Graphene films were synthesized on Cu substrate at 1000 °C in mixture of gases: argon (Ar), hydrogen (H_2), and methane (CH_4). Then, carbon nanotubes (CNTs) were grown uniformly on the surface of graphene/Cu films at 750 °C in mixture of Ar, H_2, and acetylene (C_2H_2) gases. Ferric salt $FeCl_3$ solution deposited onto the surface of graphene/Cu substrate by spin coating method was used as precursor for the growth of the CNTs. The density and quality of the CNTs on the surface of graphene/Cu films can be controlled by varying the concentration of $FeCl_3$ salt catalyst.

1. Introduction

Owing to its unique electrical, mechanical and optical properties, graphene with two-dimensional (2D) carbon nanostructure has emerged as a new class of promising materials attractive for various applications, such as transparent electrodes[1–3], field-effect transistors[4,5], supercapacitors[6], composites[7], energy storage materials[8–11], chemical and biosensing[12–15]. The combination of 2D graphene of high charge density and one-dimensional (1D) carbon nanotube (CNT) of large surface area generates a flexible three-dimensional (3D) graphene-CNT hybrid network with outstanding properties. Studies proved that graphene-CNT hybrid nanomaterials exhibit higher electrical conductivities, large specific area and catalytic properties compared with either pristine CNT or graphene[16–18]. Graphene-CNT hybrid material has also been applied in many applications including electronics (such as transparent conductors[2,19,20], electron field emitters[21], field effect transistors[20]), supercapacitors[6], Li-ion batters[22,23], sensors[24,25] and biosensors[26–28].

The hybrids were prepared by several approaches including sonication method[16,17], chemical vapor deposition (CVD) method[2,18,29,30], and electrostatic spray technique[31]. In these methods, CVD method has emerged as an appropriate approach to synthesize graphene-CNT hybrid materials. Different transition metal (e.g., iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), gold (Au), palladium (Pd), platinum (Pt), and ruthenium (Ru)[32,33]) have been used to grow graphene and CNTs. Transition metals such as Fe, Co, Ni and Cu are of particular interest, due to their low cost and availability. However, Fe, Co and Ni are not preferred for mono or bilayer graphene growth due to their higher-than-desirable capability to decompose hydrocarbons. On the other hand, the lower decomposition rate of methane on Cu (since Cu cannot form carbide with carbon thereby resulting in low solubility of carbon in Cu) allows the possibility of controlling the number of graphene layers[34], and wet etchant selectivity to graphene[35]. Using a rapid heating and cooling CVD system, Nguyen et al.[2] synthesized thin networks of CNTs with different densities that are controlled by varying the thickness of an iron film sputtered on the graphene/copper substrates. However, this method requires the sputtering equipment to produce iron catalyst on the surface of graphene/copper.

In this study, we present a simple approach to fabricate graphene-CNT hybrid films on polycrystalline Cu substrate. By

* Corresponding author. Ph.D.; Tel.: +84 3 7565763; Fax: +84 3 8360705.
E-mail address: chucnv@ims.vast.ac.vn (N. Van Chuc).

http://dx.doi.org/10.1016/j.jmst.2014.11.027

performing CVD method, graphene layer was synthesized on Cu substrate in mixture of gases Ar, H_2 and CH_4. CNTs were subsequently produced on the surface of graphene/Cu film in mixture of gases Ar, H_2 and C_2H_2. The density and quality of the CNTs in the hybrid materials can be controlled by varying the concentration of $FeCl_3$ salt catalyst.

2. Experimental

2.1. Synthesis of graphene film

The graphene films were synthesized by thermal CVD method of high temperature of 1000 °C in Ar environment (1000 sccm). The polycrystalline Cu with a thickness of 35 μm and a size of 1.0 cm × 1.0 cm were used as substrate for graphene-films synthesis process. To reduce the native copper oxide and to facilitate Cu grain growth on the Cu substrate surface, the samples were annealed at CVD temperature for 30 min in a flow of Ar/hydrogen (1000/300 sccm). After 30 min, a flow of methane (CH_4, 20 sccm) was introduced for growth process. The time for the CVD process was 30 min. After a preset graphene growth time, the samples were cooled rapidly under a flow of Ar (1000 sccm).

2.2. Synthesis of graphene-CNT hybrid film

In this work, the ferric salt $FeCl_3$ was used as precursor for the formation of catalytic iron nanoparticles. Firstly, it was dissolved in deionized water. The resultant solution was subsequently deposited on the graphene/Cu substrate. The sample was dried naturally at room temperature to prepare for the growth of CNTs.

The CNTs growth process was performed via "fast-heating" CVD method, using C_2H_2 as carbon source. The graphene/Cu substrates initially placed outside the heating zone were subsequently transferred into the center of CVD chamber when the temperature of the whole system reached to 750 °C in Ar (30 sccm). This step was carried out by moving the CVD chamber to the proper position. The mixture of C_2H_2 (5 sccm), Ar (30 sccm), and H_2 (30 sccm) was simultaneously passed through the tube reactor for 30 min. The whole process was finally followed by cooling the CVD system in Ar to room temperature.

In the growth process, catalyst iron nanoparticles play a crucial role in controlling the structure of CNTs. As mentioned in many previous articles[2,36,37], it is widely accepted that the diameter, which is the main parameter to determine the quality of CNTs, is defined by the size of the catalyst nanoparticles. For that reason, the concentration of the catalyst precursor and its deposition techniques onto the substrates are the key issues for monitoring the shape and size of nanoparticles. To investigate the influence of the formation of surfactant catalytic iron nanoparticle on the growth density and quality of CNTs, the $FeCl_3$ solution was used with four initial different concentrations (0.001, 0.005, 0.01, and 0.05 mol/L). The deposition process of $FeCl_3$ solution onto the graphene/Cu substrate was conducted via spin coating at 5000 r/min for 1 min.

2.3. Sample characterizations

The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the samples were obtained by using Hitachi S-4800 and Jeol JEM-1010 instruments, respectively. The graphene layer structure was studied using a high resolution

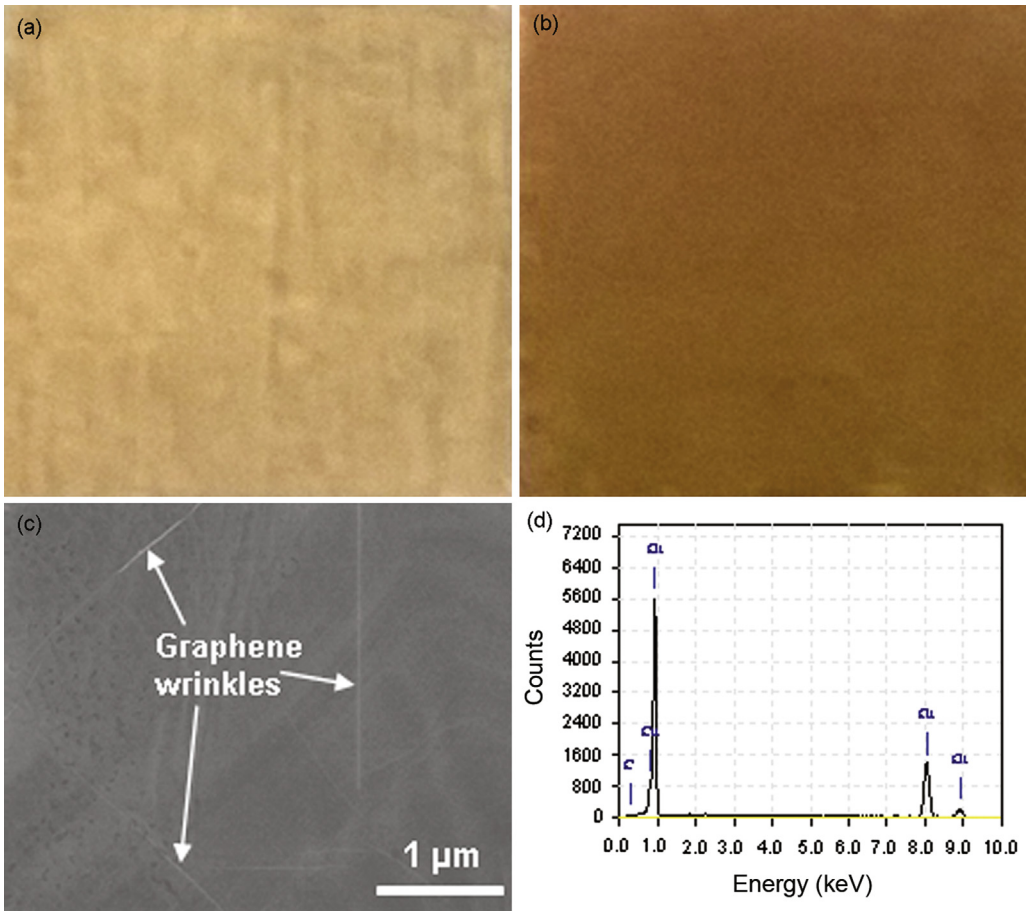

Fig. 1. Photographs of Cu substrate before (a) and after (b) CVD process, typical SEM image (c) and EDX spectrum (d) of Cu substrate after CVD process.