Journal of Molecular Structure 1074 (2014) 250–254

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

# Growth and microstructural investigation of multiwall carbon nanotubes fabricated using electrodeposited nickel nanodeposits and chemical vapor deposition method

Navid Zanganeh [a], Armin Rajabi [b], Morteza Torabi [c], Masoud Allahkarami [d], Arshak Moghaddas [c], S.K. Sadrnezhaad [c,*]

[a] *Mississippi State University, School of Chemical, Engineering, Mississippi State, MS 39762, USA*
[b] *Department of Materials Science and Engineering, Karaj Islamic Azad University (KIAU), Iran*
[c] *Department of Materials Science and Engineering, Sharif University, Tehran, Iran*
[d] *Mechanical and Aerospace Engineering, Oklahoma State University, Tulsa, OK, USA*

## HIGHLIGHTS

- Nickel nanodeposits were electrodeposited on n-Si(1 1 1):H substrate with a morphology of polygonal.
- The diffusion of carbon atoms in nano-particles Ni was acquired through decomposition of $C_2H_2$ at 700 °C.
- We were able to grow MWCNTs on nickel nanodeposits by CVD method.

## ARTICLE INFO

*Article history:*
Received 7 March 2014
Received in revised form 4 June 2014
Accepted 4 June 2014
Available online 14 June 2014

*Keywords:*
Multiwall carbon nanotubes
Electrodeposition
Nickel nanodeposits
Chemical vapor deposition

## ABSTRACT

This study proposes a common approach for growing multiwall carbon nanotubes (MWCNTs) on nickel nanodeposits. MWCNT growth was performed in two separate stages. In the first stage, nickel nanodeposits were electrodeposited on n-Si(1 1 1):H substrate in the presence of sulfuric acid. Based on atomic force microscopy (AFM) observations, the nickel deposits had a fairly polygonal morphology and were distributed on the prepared n-Si(1 1 1):H substrate. In the second stage, acetylene gas was decomposed on the surfaces of the nickel nanodeposits using chemical vapor deposition method at 700 °C. When carbon is saturated in a catalyst, it acts as a primary nucleating element for MWCNT growth. The structure of the MWCNTs was also investigated using scanning electron microscopy, high-resolution transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. Results showed that the synthesized MWCNTs had a small wall thickness and were formed under the experimental conditions applied to the system.

## Introduction

Although primary studies in the nanotechnology field have started since 1980, interest in nanoscience continues to grow because of various technological applications. These materials may bring significant innovation with their unique properties [1–4]. Carbon nanotubes (CNTs) are a group of relatively new nanomaterials made of carbon with a nanotubular structure and graphitic lattice [5]. CNTs possess attractive features, namely, electronic properties [6] and unique dimensions with a structural stability, because of efficient sp2 hybridization and p bonding [7]. These properties make them the best potential candidates in various fields of science and technology [8]. CNTs have potential applications in composite reinforcement [9], transistors [10], logic circuits [11], field emission sources [12], nano-biotechnology [13], and hydrogen storage nanodevices [14]. CNTs can be grown through different methods. The most common methods are direct current arc-discharge between electrodes [15], laser ablation of carbon rods [16], and chemical vapor deposition (CVD) [17]. CVD is preferred over the other techniques because of its high yield [18], high purity [19], low cost [20], and performance in irregular-shaped substrates and multiple-substrate coatings [21,22]. The main parameters for CNT growth via CVD are hydrocarbon sources, catalyst type, and growth temperature [22]. CNT growth mechanisms involve the dissociation of hydrocarbons catalyzed

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* Corresponding author. Tel.: +98 21 66165215; fax: +98 21 66013126.
*E-mail address:* nanomaterialgroup@hotmail.com (S.K. Sadrnezhaad).

http://dx.doi.org/10.1016/j.molstruc.2014.06.012
0022-2860/

by transition metals and the saturation of carbon in a metal nanoparticle. Carbon precipitates from saturated metal nanoparticles and forms nano tubes [23]. The most effective catalysts for growing of CNTs known so far include iron, cobalt, and nickel [24]. The peculiar abilities of these metals are reportedly related to their catalytic activity for the carbon precursor decomposition, meta-stable carbide formation, carbon diffusion, and graphitic sheet formation [25,26]. Based on investigations on the average growth rate of CNTs in Fe, Co, and Ni catalysts through CVD, Ni catalysts have shown maximum growth rates [27]. The diffusion coefficients of carbon in bulk Fe, Co, and Ni metals are reported to be $1.1 \times 10^{-7}$, $8 \times 10^{-8}$, and $1.6 \times 10^{-7}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ at 950 °C, respectively. The diffusion rate of carbon follows the order of Ni > Fe > Co because it is usually proportional to the aforementioned metal diffusion coefficients [28]. Significant efforts have been devoted for growing CNTs on the Ni particles through chemical vapor deposition (CVD). It might be due to the fact that the survival of Ni nano particles associated with their size in the plasma method during CNT growth, i.e., small particles of Ni (<50 nm) were removed [29]. Generally, CNTs consist of two main groups': single-wall carbon nanotube (SWCNT) and multi-wall-carbon nanotube (MWCNT). In the present work, we highlight a common method (CVD) to grow MWCNTs on nickel nanodeposits that are electrochemically synthesized on well-defined n-Si(1 1 1):H electrode as catalyst through CVD.

## Experimental details

The nickel nanodeposits used as catalyst for the growth of nano tubes were electrochemically prepared on an n-Si(1 1 1):H substrate. The n-Si(1 1 1):H substrate cleaned using the RCA procedure [30] before the electrodeposition process. During this process, degreasing in 2-propanol under reflux for 2 h was followed by alternate boiling in basic and acidic $H_2O_2$ solutions ($NH_3$:$H_2O_2$:$H_2O$ = 1:1:5 and HCl:$H_2O_2$:$H_2O$ = 1:1:5) for 15 min. The samples were etched for 1 min in 50% HF to remove the oxide layer and for 3 min in 40% NH4F. The last step led to the formation of well-defined monohydride-terminated Si(1 1 1) [Si(1 1 1):H] surfaces with large and atomically flat terraces [30]. The electrochemical measurements and deposition were performed in a typical three-electrode cell using a platinum plate as counter electrode [31]. Nickel was electrodeposited from 0.1 M $H_2SO_4 + 10^{-4}$ M $NiSO_4$ (Merck, Germany). Electrochemical experiments were performed using an Autolab potentiostat/galvanostat model PGSTAT30. The potentiostatic transients were recorded at time intervals of 10 seconds. The morphology of the electrodeposited nickel nanodeposits was observed under a scanning electron microscope. The resultant catalyst was placed in a horizontal furnace and heated up to the growth temperature (700 °C) under nitrogen and hydrogen flow at 10:1 ratio. Then, acetylene was injected at a flow rate of 60 ml/min for 30 min. The MWCNTs growth on Ni-deposited n-Si(1 1 1):H substrate analyzed using scanning electron microscopy (SEM; Hitachi S-4800 with bruker EDX system), High-resolution transmission electron microscopy (HRTEM; JEOL JEM-2010) and X-ray diffraction (XRD; Philips X'Pert diffractometer Endhoven). Room-temperature Raman spectroscopy (Thermo Nicolet) was used to obtain the overall information on the synthesized carbon materials.

## Results and discussions

A potentiostatic method was utilized to investigate the mechanism of the electrodeposition of nickel nanodeposits. Fig. 1 shows the potentiostatic current transient curves in a wide range of cathodic potentials from −0.7 V to −1.3 V for the electrodeposition of nickel nanodeposits. The currents reached well-defined recognizable maxima observed as clear peaks because of the double layer capacitance. Then, a sharp fall and posterior growth occurred. The current densities of each transient increased with increasing overpotential.

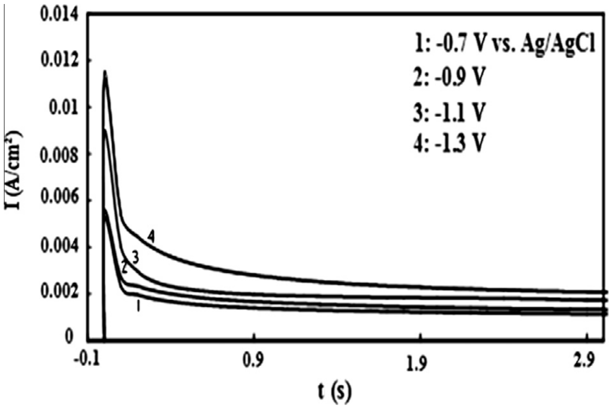

**Fig. 1.** Potentiostatic *I*–*t* transients for deposition of the nickel electrodeposition [31].

According to the Pourbaix diagram of nickel [32], Ni is stable at this potential and pH range. The partial current related to $Ni^{2+}$ reduction was lower than 1/1000 because of the low concentration of $Ni^{2+}$ ions in the solution and the acidic pH. Moreover, the total current mainly increased from the proton reduction which simultaneously occurred. Therefore, inferring anything reliable on the nucleation and growth mechanism of the nickel electrodeposition from these transients is not possible. The surface morphology of the nickel deposits was observed under AFM. The AFM image of the nickel nanodeposits in Fig. 2 shows that the electrodeposition process is not preferential and the particles are distributed on n-Si(1 1 1). The morphology of the deposits was polygonal-like, and these deposits seemingly grew epitaxially.

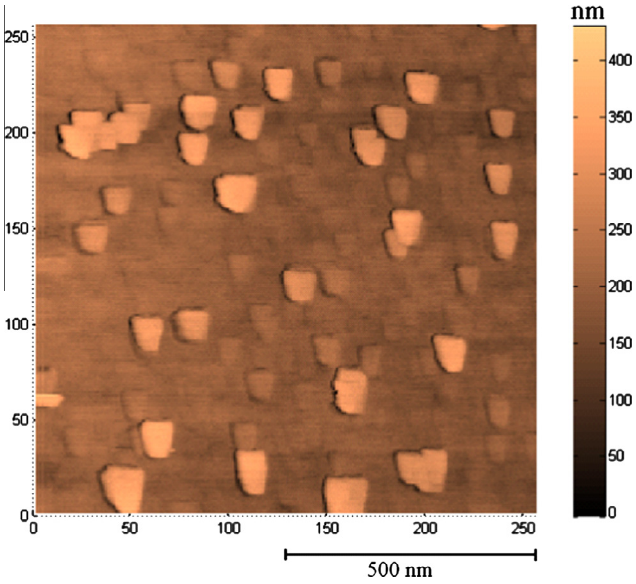

**Fig. 2.** AFM image of nickel nanodeposits electrodeposited on well-defined n-Si(1 1 1):H substrate.

### *Carbon nanotubes*

Fig. 3 shows a typical SEM image of the MWCNTs grown on electrodeposited nickel nanodeposits using the CVD method