Electrochimica Acta 56 (2011) 5205–5209

Contents lists available at ScienceDirect

Electrochimica Acta

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

Preparation and characterization of a graphite electrode containing carbon nanotubes grown in situ by flame synthesis

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ARTICLE INFO

Article history:
Received 4 February 2011
Received in revised form 10 March 2011
Accepted 11 March 2011
Available online 21 March 2011

Keywords:
Carbon nanotubes
Chemically modified electrode
Flame synthesis

ABSTRACT

A crystalline flake graphite electrode (GE) was impregnated with nickel particles using direct current electrochemical deposition. The particles were used for in situ growth of carbon nanotubes (CNTs) by flame synthesis with a liquid ethanol flame. The obtained electrode was characterized by X-ray diffraction, and scanning and transmission electron microscopy. The results showed that the deposited Ni catalyst crystal face was mainly (1 1 1). CNTs with a diameter of about 40 nm were uniformly grown on the GE surface. The electrochemical performance of the CNT–GE was characterized by cyclic voltammetry using a $[Fe(CN)6]^{3-}/[Fe(CN)6]^{4-}$ solution, and showed a much greater electrochemical response than that obtained using a material in which CNTs were grown by catalytic chemical vapor deposition.

1. Introduction

Carbon nanotubes (CNTs) have attracted extensive attention in many science and technology fields since they were discovered [1,2]. Due to their unique structure and physical properties, CNTs have been considered as one of the best candidate for fabricating nano-electronic devices [3], composite materials [4,5], gas storage materials [6] and catalyst support materials [7]. Regular methods such as arc-discharge [8], laser ablation [9], and catalytic chemical vapor deposition (CCVD) [10] have been successfully used to synthesize CNTs. Flame synthesis is a new developing method to grow CNTs compared with the methods mentioned above [11–15], and its prominent advantages are energy saving up and simple operation. In flame synthesis, some fuel provides heat while the remainder serves as carbon source for CNT growth. Recently, liquid ethanol had been developed as carbon source for CNT growth by a common ethanol burner [16,17]. In comparison with the regular methods mentioned above, flame synthesis was much simpler and more cost-effective.

In electrochemical field, CNT novel characteristics including high aspect ratio, nano-scale dimensions and good electrical conductivity have indicated that CNTs are a type of potential modified materials for chemically modified electrode (CME) [18,19]. According to the literatures, five ways were developed to prepare CNT–CME [20–24], which are listed as follows: The first is mixing the CNTs, bromoform, mineral oil and liquid paraffin carefully and stuffing the mixture into the glass capillary to prepare electrode. The next is filling the CNTs into the corration platinum electrode to prepare CNT powder microelectrode. The third is embedding the CNTs into the graphite electrode (GE) to prepare embedding modified electrode. The fourth is "abrasive immobilization" (simply rubbing the CNTs onto an electrode surface to prepare electrode). The last is dispersing the CNTs into the H_2SO_4 solution, H_2O solvent, dimethyl formamide solvent and coating directly on the surface of the electrode to prepare CNT–CME. Following these ways, CNT–CMEs were done as two steps: firstly, CNTs were prepared by the CNT growth methods mentioned above and then the CNTs were fixed on the electrode surface by some physical ways, for example, using binder. However, the binder could reduce the CNT utilization efficiency by enhancing the resistance or changing the CNT novel nanometer hollow tube structure. In order to avoid these defects, we have introduced a new method to prepare CNT–CME by growing CNTs in situ (named as GSCNT–CME) in our previous work [25]. The GSCNT–CME was obtained by directly growing CNT on a crystalline flake graphite electrode (GE) surface, namely one-step method. The obtained GSCNT–CME can hold the CNT pristine nanometer structure and has showed excellent potential application value. In that report, CNTs were grown by CCVD and CNT catalyst on the electrode was prepared by immersion. However, the operation is relative complicated and inefficient (the operation process is over 4 h and in vacuum).

In order to enhance the GSCNT–CME preparation process practicability and maneuverability, flame synthesis and catalyst direct current electrochemical deposition were used to replace CCVD and

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doi:10.1016/j.electacta.2011.03.038

catalyst immersion in this paper. And a liquid ethanol was used as the carbon resource. With these improvements, the GSCNT–CME can be prepared in a few minutes and without vacuum condition. Therefore, the operation is much simpler and safer. The CNTs with a diameter of about 40 nm are uniformly grown on the GE surface. All these show that the way used here is of much more practicability and maneuverability.

2. Experimental

2.1. Electrochemical deposition nickel catalyst

To prepare Ni catalyst, a galvanostatic – voltage instrument (ZF-9, Shanghai, China) was used. Ni slice (99.99%) with 1 cm × 3 cm size was used as the anode. A crystalline flake graphite disk (5.3 mm in diameter, 7.0 mm in length) was used as the electrode. The graphite disk was polished to a mirror surface with the metallographic abrasive paper (W 7-05). Then, it was sealed by fixing into a teflon housing with the polished surface out. The obtained electrode was named as GE. The electrochemical deposition solution was composed of nickel sulfate ($NiSO_4{\cdot}7H_2O$, 300 g L^{-1}), nickel chloride ($NiCl_2{\cdot}6H_2O$, 45 g L^{-1}), boric acid (H_3BO_3, 40 g L^{-1}), saccharin sodium ($C_6H_4COSO_2NNa{\cdot}2H_2O$, 5 g L^{-1}), sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$, 0.1 g L^{-1}) and redistilled water. The direct current electrochemical deposition was carried out for 1.5 min using a current of 20 mA. The deposited Ni catalyst GE was named as Ni/GE and used to grow CNT.

2.2. GSCNT–CME preparation

A liquid anhydrous ethanol flame was used to grow CNT. The flame height and middle width were about 20 and 60 mm, respectively. The wick height was about 10 mm. In order to grow CNTs, the Ni/GE was placed about 8 mm over the wick for 4 min, where the flame color was blue and the temperature was about 610 °C (tested by an electronic sensor). After that, a layer of black sample appeared on the Ni/GE surface. Then the obtained electrode was treated by concentrated sulfuric acid, supersonic and redistilled water for removing the impurities (including amorphous carbon, catalyst and so on). As this, the GSCNT–CME was prepared.

2.3. Morphology and microstructure characterization

The GE and the Ni/GE surfaces were characterized by scanning electron microscopy (SEM, QUANTA 200). The crystal structure of the deposited Ni was characterized by X-ray diffraction (XRD) (XRD, PWI 3040/60). The morphology and microstructure of the CNTs were also characterized by SEM and transmission electron microscopy (TEM, HITACHI H-700H).

2.4. Electrochemical performance testing

Cyclic voltammetry (CV) with three-electrode-system was used to test the obtained GSCNT–CME electrochemical performance. A platinum wire was used as the counter electrode, the saturated calomel electrode (SCE) was used as the reference electrode and the obtained GSCNT–CME was used as the working electrode in the testing system.

3. Results and discussion

3.1. SEM, XRD and TEM study

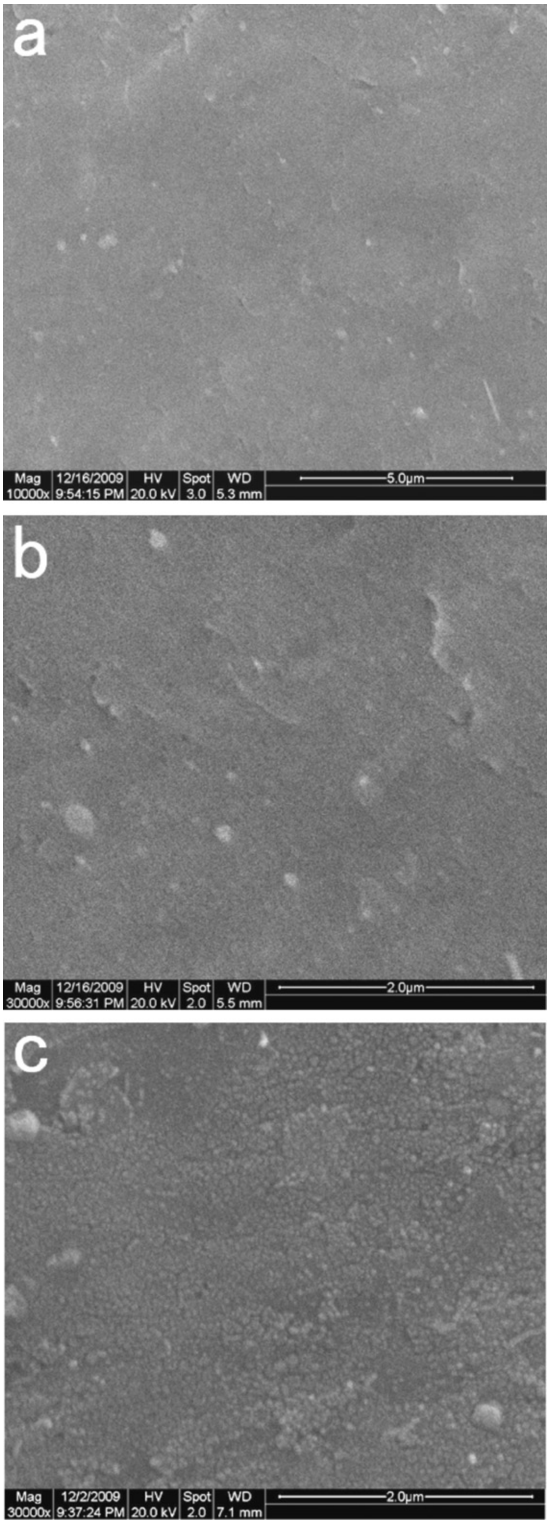

Fig. 1. SEM images of GE before (a and b) and after (c) the catalyst deposition.

Fig. 1 shows SEM images of the GE surface after being polished (a and b) and the Ni/GE surface after the electrochemical deposition (c). It can be seen from Fig. 1a that the GE surface after being polished is very smooth and flat. Fig. 1b shows SEM images with higher amplification (3 times higher) of the GE after being polished. Fig. 1c shows SEM images at the same amplification (30,000) of the Ni/GE surface after electrochemical deposition. Comparing Fig. 1b with c, it is found that there are lots of grains in Fig. 1c, and the average grain diameter is about 35 nm. These grains are the result of direct current electrochemical deposition. In order to characterize the grain component and structure, XRD analysis was used.