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Selective synthesis of carbon-nanotubes/graphite or carbon-nanotubes /multi-graphene composites on 3-D nickel foam prepared with different nickel catalyst and pre-treatment

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ABSTRACT

The research is to deposit carbon on porous 3-D nickel foam (NiF) as a gas diffusion electrode (GDE) by chemical vapor deposition (CVD). Effects of three different preparations of the nickel (Ni) catalyst and two pre-treatments of oxidation and reduction for carbon deposition were investigated. In the first method, the carbon was deposited on NiF with and without sputtering a Ni seed layer before the CVD. In the second method, the NiF was oxidized, then reduced by hydrogen into Ni particle as a catalyst and the carbon also was deposited by CVD. In the third method, a thin film of SiO_2 was deposited on the NiF as a separation layer, then the Ni catalyst was deposited and finally, carbon was also deposited by CVD. The results exhibited large grain sizes of Ni catalyst cannot grow carbon nanotube (CNTs) during CVD. Pre-treatment of oxidation and the reduction reduce the grain size of the Ni catalyst, and an oxidation temperature equal or higher than the reduction temperature always makes it easy to grow CNTs. A smooth SiO_2 thin film was used as a separation layer to deposit the Ni catalyst to grow the SWCNTs and a low area ratio of I_D/I_G for a non-crystallized sp^3 graphite microstructure always creates a graphene microstructure. A suitable hydrogen gas could help the amount of growth of CNTs. Anyway, the specified Ni catalysis could promise strategy the selective synthesis of CNTs/graphite or CNTs/multi-graphene composites on NiF.

1. Introduction

Carbon could be synthesized to a lot of structures such as graphene, graphene oxide, graphite, oxided graphite and carbon nanotubes (CNTs). In which graphene and CNTs have good electricity and CNTs could become mature the 3-D structure. Since graphene and CNTs combine a nanoscale size with unique electrical, optical, mechanical, and electrochemical properties, making them ideal candidate materials for high-impact applications in various fields, such as optoelectronics, energy, biomedicine, aerospace and so on [1–3]. With the raising of environmental consciousness on the greenhouse effect and carbon dioxide pollution in recent years, green-energy also catches the attention as a project for our lives. Among these issues, hydrogen energy is also a spotless energy; especially when applied as a fuel battery [4–6]. Its power density is always controlled by the transportation of the proton; a nano-microstructure of the gas diffusion electrode (GDE) plays an important role in enhancing the transportation of the proton. The outstanding performance of graphene and CNTs could be used for the GDE with a 3-D porosity substrate such as metal foam [7,8], metal mesh [9–11], and so on. Metal foam possesses a rich high strength, mechanical stability, high conductivity and thermal dissipation. Simultaneously, the catalyst of Fe, Co, and Ni was easily deposited on metal foam for the deposition of CNTs [12–14]. The response is very enthusiastic on how to grow CNTs on metal foam. CNT deposition methods include laser ablation [15,16], arc discharge [17], and chemical evaporation deposition (CVD) [18,19]. Especially, the method of CVD can be simple and easy to control with a high production of CNTs, becoming the main fabrication process [20].

For this reason, many papers have researched the improvement of gas diffusion on GDE with the base of CNTs [21–23], showing that CNT is better than other carbons, such as carbon black and XC–72 R [24]. Traditional GDE fabrication modulates the content of

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both carbon and polytetrafluoroethene (PTFE) for gas diffusion layers, but as people know PTFE is not a green material for our environment. Since, CNTs maintain a high specific surface area, perfect electricity (large mobility of 10,000 $cm^2/V/s$), stable mechanical properties and are an environmentally friendly material they become a good succedaneum [25–27]. The proposal of this research is to use CNTs + nickel foam (NiF) to substitute for carbon + PTFE on the GDE pole [28]. A total solution of CNTs synthesized on nickel foam by CVD with different Ni catalysts was investigated. These microstructures were checked by scanning electron microscopy (SEM) imaging, X-ray diffraction (XRD) and Raman spectra were used to check the crystal and bond. However, the CNT deposition on 3-D NiF was not only dependent on the flow rate, temperature and time of N_2, H_2, and C_2H_2 gases and the pre-treatment of oxidation and reduction, but also dependent on the microstructure and grain size of the nickel catalyst. However, these results exhibited that the third method could fabricate better single-walled carbon nanotubes (SWCNTs) layers than other methods on NiF. The nanostructure of carbon-nanotubes/graphite (CNTs/graphite) and carbon-nanotubes/multi-graphene (CNTs/M-graphene) composites depended on both the deposition conditions and Ni catalysis preparation.

2. Experimental

2.1. Deposition of a CNTs/NiF layer and pre-treatment

There are two pre-treatment processes on the 3-D NiF surface: first is the oxidation by oxygen and the second one is the reduction by hydrogen. Then the Ni seed was got on the 3-D NiF surface, and the reaction descriptions are below:

$$2x\mathrm{Ni} + \mathrm{O_2} \rightarrow 2\mathrm{Ni_xO} \quad (1)$$

$$\mathrm{Ni_xO} + \mathrm{H_2} \rightarrow x\mathrm{Ni} + \mathrm{H_2O} \quad (2)$$

CNTs/graphite composite and CNTs/M-graphene come from the synthetized of the acetylene (C_2H_2) by the catalysis of Fe, Co, and Ni to show below:

$$3\mathrm{H} - \mathrm{C} \equiv \mathrm{C} - \mathrm{H} \overset{\mathrm{Fe,Co,Ni}}{\rightarrow} 6\mathrm{C} + 3\mathrm{H_2} \quad (3)$$

Now, there are three methods to prepare the catalyst for deposition of 3-D carbon/NiF by CVD. The deposition processes and parameter conditions of the three methods are described below.

2.1.1. The first method

Carbon was directly deposited on NiF with and without a Ni catalyst during CVD. There were two different processes: one deposited the carbon on the clear NiF by CVD without a Ni catalyst, the other one sputtered the 5 nm Ni catalyst on NiF as a seed layer and then deposited the carbon by CVD. The experimental processes are shown in Fig. 1, and relative fabrication parameters are listed in Table 1. The main working gas was C_2H_2 for carbon growth and hydrogen (H_2) was reduced from the carbon film during the CVD. The deposition temperatures in the furnace were 450 °C and 700 °C for without and with reduction of H_2, respectively.

Table 1
The deposition conditions for the first method.

Pre-treatment (reduction)				Synthesis				
Gas flow (sccm)		Temp (°C)	Time (min)	Gas flow (sccm)			Temp (°C)	Time (min)
N_2	H_2			N_2	H_2	C_2H_2		
0	0	0	0	65	10	25	450	30
80	20	800	5	75			700	

2.1.2. The second method

Nickel foam substrate underwent pre-treatment of oxidization with oxygen and then reduction by hydrogen, and then carbon was deposited on the NiF by CVD. The clean NiF was oxidized and reduced by H_2 and carbon was deposited by CVD in the horizontal furnace. The process involved oxidization, reduction and deposition of carbon by CVD; all were completed in the horizontal furnace. The total experimental processes are shown in Fig. 2, and relative fabrication parameters are listed in Table 2. The oxidation temperature varied from 600 °C, 650 °C to 700 °C, and the reduction temperatures changed from 600 °C, 650 °C to 700 °C. The optimum oxidation and reduction temperatures were all the same at 700 °C. However, the synthesis temperatures of CVD varied from 450 °C, 500 °C, 550 °C, to 650 °C and the synthesis times changed from 5, 30, to 60 min at the same oxidation and reduction temperatures of 700 °C.

2.1.3. The third method

A 50 nm thickness of SiO_2 film was deposited on the NiF by magnetron sputtering as a separation layer, and then 5 nm Ni was deposited on it as a catalytic layer. The catalytic layer was smoother and had a smaller grain size than previous methods. A pre-treatment reduction of H_2 was done and then, the CNTs were synthesized on the substrate in the horizontal furnace. The experimental process is shown in Fig. 3, and relative fabrication parameters are listed in Table 3. The synthesis temperature varied from 700 °C to 800 °C under a hydrogen reduction temperature of 700 °C.The different synthesis times and hydrogen flows changed from 5, 15, to 30 min and from 0, 5, to 40 sccm, respectively, under the hydrogen reduction and deposition temperature of 700 °C.

2.2. Measurements of microstructure, crystallization and bonds

The morphology of all films was analysed with field emission scanning electron microscopy (FESEM, JSM-6701F). The maximum multiple magnifications could reach 100,000 to observe the microstructure of the nickel foam, graphite, multi-graphene, and CNTs. The grain size and surface morphology could be investigated

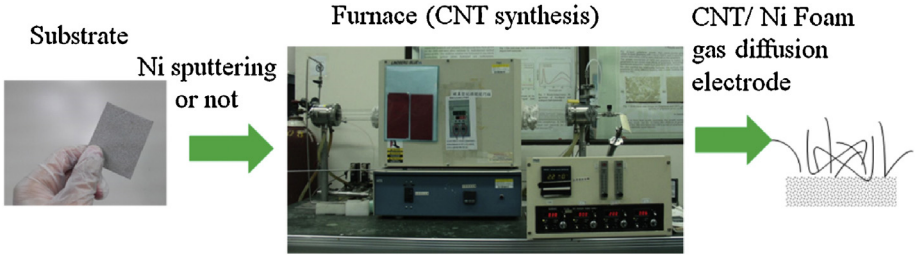

Fig. 1. The experimental process for the first method.