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Synthesis of Carbon Nanotubes by Catalytic Chemical Vapor Deposition Using Hydrogen Storage Alloy as A Catalyst

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Abstract: Carbon nanotubes (CNTs) were synthesized by catalytic chemical vapor deposition and using the alkali-reducing pretreated hydrogen storage alloy ($MlNi_{4.0}Co_{0.6}Al_{0.4}$) powder as a catalyst. It was found that the surface modification of the alloy was effective to provide the catalytic active sites for CNTs growth. The Ni- and Co-clusters on the surface of the treated alloy were dominant for the growth of CNTs. The composite of CNTs with the hydrogen storage alloy has the potential to be used as a new type of hydrogen storage material without further purification.

Keywords: Carbon nanotubes, hydrogen storage alloy, catalytic chemical vapor deposotion, surface modification.

Carbon nanotubes, which was discovered by Iijima[1] in 1991, is the most typical one-dimensional nano-material with the micrometers order in length and nanometers order in diameter. CNTs are composed of graphitic sheets rolled into closed concentric cylinders, and classed into single wall nanotubes and multi-wall nanotubes. CNTs can offer many significant advantages over most existing materials. Since its discovery, unprecedented interest has been stimulated because of its significance both in the fundamental and applied perspective. The potential applications of CNTs investigated include use for nanoscale electronic devices[2], new type hydrogen storage material[3, 4], electrochemical storage energy material[5] and novel composites[6].

Several strategies such as catalytic chemical vapor deposition, arc-discharge and laser ablations have been developed to synthesize CNTs. The production of CNTs by the catalytic chemical vapor deposition (CCVD) is much simpler than other method. Although, up to now, the growth mechanism of CNTs is not well understood, it is well known that metallic catalysis is necessary to sustain CNTs growth. The catalysts were usually selected from Ni, Co, Fe metallic particle[7] and Co-Ni, Fe-Ni and Y-Ni alloy supported by a substrate[8]. More recently, Liang *et al.*[9] reported the growth of CNTs by catalytic disproportionation of CO over Ni nanoparticles prepared by reducing La_2NiO_4. They claimed that the rare earth oxides can prevent transition metal from agglomerating and promote dispersion of nano-scale Ni particles, which is advantageous for CNTs growth.

On the other hand, CNTs were reported to be very attractive materials for hydrogen storage[3, 4], but it has not the catalytic activity for hydrogen uptake. Metal Pd powder was employed to improve the electrochemical hydrogen storage property of CNTs as reported by Nutzenadel *et al*[10]. It is well known that the hydrogen storage alloys have a high capacity as well as excellent catalytic activity for hydrogen uptake in gas-solid and electrochemical reaction reactions. In this paper, CNTs were directly grown over the alkali-treated $MlNi_{4.0}Co_{0.6}Al_{0.4}$ hydrogen storage alloy powders by catalytic decom-position of acetylene, to prepare the composite of CNTs with hydrogen storage alloy. This composite does not contain the catalysts carrier such as SiO_2 and Al_2O_3, so it can be potentially used as the hydrogen storage material without further purification.

The hydrogen storage alloy powders with compositions of $MlNi_{4.0}Co_{0.6}Al_{0.4}$ (Ml = La-rich mischmetal with composition in atom percent: La: 64.6%; Ce: 5.9%; Pr: 26.6%; Nd: 2.2%) were treated by immersing in 6 M KOH +0.02 M KBH_4 solution at 80°C for 6h. The surface compositions of the untreated and treated alloy powders were analyzed by energy-dispersive X-ray (EDX). It was found that after treating the content of Al on the alloy surface is greatly decreased from 23.6 at% to 4.24 at%, while Ni and Co on the alloy surface were increased from 54.7 at% and 7.7 at% to 66.6 at% and 10.2%, respectively. The results of ICP showed that the Al on the alloy surface was preferentially dissolved in the alkaline solution, but the Ni and Co in the treating solution were hardly found as shown in **Table 1**. Therefore, the Ni-rich alloy surface was produced because of preferential dissolution during in treating. The cobalt oxide or hydroxide on the alloy surface can be firstly dissolved in hot alkaline solution, which exists in the form of $[Co(OH)_4]^{2-}$. This complex ion could be reduced to metallic Co to be deposited on the alloy surface[11, 12]. The Ni and Co on the treated alloy surface have been demonstrated to be in the form of clusters[13,14], which have a very high electrocatalytic activity for hydrogen electrode reaction[11,12]. We think that the Ni- and Co-clusters could be used as a new catalyst for CNTs growth.

Table 1 Results of ICP analysis for the components dissolved in treating solution from the alloy surface during treating (μg/mL)

La	Ni	Co	Al
0.0345	0.350	0.195	125.2

The treated hydrogen storage alloy powders (about 45 mg) in quartz boat were put into the horizontal quartz glass reactor. The reactor was heated to 700°C from room temperature in a flow of hydrogen gas of 200 mL/min and kept for 30 min. Then, the acetylene gas was introduced into the reactor, passing over the hydrogen storage alloy catalyst with 8 mL/min for 6 ~ 15 min. The collected CNTs has been observed by transmission electron microscopy (TEM). A typical TEM image of CNTs is shown in **Figure 1**, in which one can see that a bulk growth of the entangled CNTs on the alloy surface, and the diameter of the most of CNTs ranges from 15 to 20 nm. A thicker CNT with the diameter of 38 nm and a thinner CNT with the diameter of 11 nm are obviously found in **Figure 1**(B). It is well known that the diameter of CNTs grown by CCVD is depended on the size of the catalyst particles. But the diameter of hydrogen storage alloy powder is much larger than that of CNTs as shown in **Figure 1**. It is reasonable that the diameter of CNTs in this study should depend on the size of the Ni- and Co-clusters on the surface on the treated hydrogen storage alloy. For comparison, the untreated hydrogen alloy powder was used as a catalyst for the growth of CNTs. The growth of CNTs as well as in other forms of carbon such as fiber or graphite on the untreated alloy surface was hardly found under the same conditions. The fact indicates that the surface treatment of the hydrogen storage alloy powder is effective to produce catalytic sites for CNTs growth. The Ni- and Co-clusters on the treated alloy surface are dominant for CNTs growth. **Figure 2** shows that the mass of CNTs increases with the growth time increasing. After growing 10 ~ 15 min, the content of CNTs in composite approaches 42~57 wt%. The composite of CNTs with hydrogen storage alloy was prepared by CCVD and using the treated hydrogen storage alloy powder as a catalyst. This composite does not contain the catalyst carrier such as SiO_2, and so can be directly used as a new type of hydrogen storage material without purification.

Figure 1 TEM image of CNTs prepared by CCVD and using the treated hydrogen storage alloy as a catalyst. (A) growing for 15 min, (B) growing for 10 min

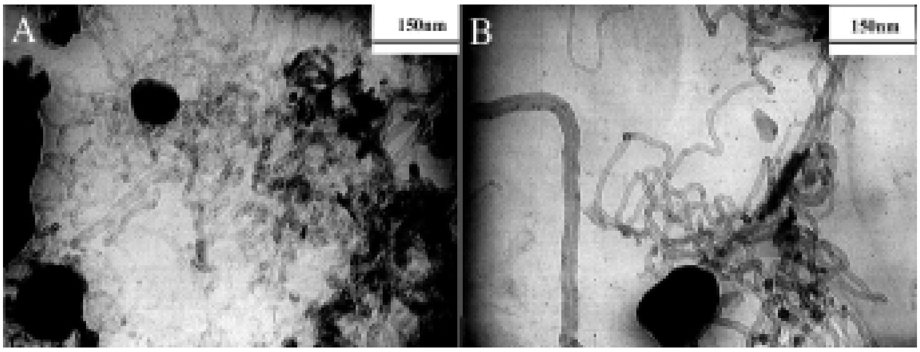
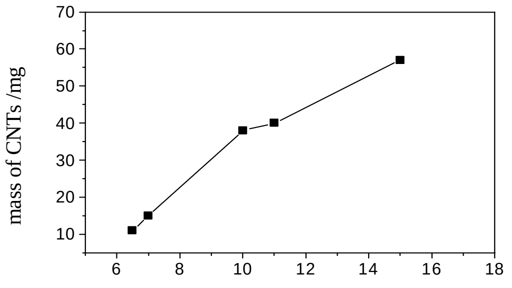


Figure 2 Mass of CNTs as a function of the growth time



(The flow of C_2H_2 and H_2 are 8 mL/min and 200 mL/min, respectively. The treated hydrogen storage alloy powder is about 45 mg, and reacting temperature is 700 ^oC.)

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