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Effect of purification treatment on adsorption characteristics of carbon nanotubes

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Abstract

Carbon nanotubes are novel materials with porous-rich structures and superior adsorption characteristics. In this report, multi-walled carbon nanotubes with different diameter were synthesized by thermal chemical vapor deposition. Amorphous carbon particles were highly removed by thermal oxidation process. Microwave digestion acidic procedure was used to dissolve metal catalysts and open tip of carbon nanotubes. The opened-end multi-walled carbon nanotubes are expected to be much more porous with more gas adsorption sites. The results indicated that the BET surface area decreases with their increasing of diameter of MWCNTs. The effective surface area of carbon nanotubes processed by thermal annealing treatment can increase with the increasing temperatures of 300 °C, 400 °C and 450 °C. Similarly, effective surface area of carbon nanotubes processed by microwave digestion acidic treatment can also increase with increasing processing time. Nitric acid can effectively absorb microwave energy and rapidly dissolve impurities in the carbon nanotubes during digestion process. The surface area increased about 30% with 20 min microwave digestion treatment time. However, microwave digestion acidic and thermal annealing treatments not only remove metallic catalysts and amorphous carbon particles and also increase effective surface area and the extent of purification of carbon nanotubes.

Keywords: Nanotubes; Purification; Multi-walled carbon nanotubes; Microwave digestion; Adsorption

1. Introduction

Carbon nanotubes (CNTs) have excellent properties and versatile application. [1–3]. Carbon is well known as one of better adsorbents for hydrogen gas. The amount of hydrogen storage depended on the surface area of the electrode material. In recent years, carbon materials such as carbon nanofibers, milled graphites and carbon nanotubes have attracted attention due to the available hydrogen storage material. Dillon et al. [4] reported that single-walled carbon nanotubes can store hydrogen 5–10 wt % at 133 K and 300 torr. Several researcher groups are also devoted to investigate the physical adsorption of gas on carbon nanotubes [5–7]. They reported that the inner hollow cavities of carbon nanotubes can hold molecules or atoms through adsorption and capillarity. It signified that the unique possibility of using carbon nanotubes as singular adsorbents for hydrogen gas storage materials [8,9]. Talaparta et al. [10] reported a contrary sentiment that gas molecules do not absorb on the interstitial channels of closed-end single-walled carbon nanotubes bundles. The pores of multi-walled carbon nanotubes are formed by the isolated multi-walled carbon nanotubes. Yang et al. [11] reported that aggregated multi-walled carbon nanotubes with high purity can hold nitrogen gas as extremely high as 750 mg/g. They suggested that two types of pore determined nitrogen capillarity process under different pressures. Then, they concluded that the aggregated pores of the multi-walled CNTs were important than inner cavities for adsorption and capillarity.

Some groups [12–15] have reported that atomic hydrogen can be stored at defect sites on carbon materials. Orimo et al. [12] have investigated that nanostructured graphite can store hydrogen up to 7.4 wt% by ball milling at hydrogen atmosphere. They reported that hydrogen storage capacity varies depending on the number of defects because the defects should have dangling bonds. Various methods for forming defects in carbon materials include mechanical milling [12,15], chemical oxidation using HCl, HNO_3 and H_2O_2 [16–18], alkali-metal addition [19] and oxidation by O_2 at 800 K [20]. Hou et al. [14] have

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studied the hydrogen adsorption/desorption behavior of multi-walled carbon nanotubes with different diameter. They found that the hydrogen storage capacity of the MWCNTs was proportional to their diameter. Yang et al. [21] have postulated that the spacing between the wavy adjacent graphene layer of carbon island in which N_2 can enter and may provide an important adsorption site for hydrogen adsorption in MWCNTs.

In this report, multi-walled carbon nanotubes (MWCNTs) were annealed in air at various temperatures to remove the amorphous carbon nanoparticles and an acidic treatment in microwave digestion system was used to dissolve metallic catalysts. In microwave digestion, acidic solution can rapidly absorb heat energy and completely dissolve metallic catalysts. Some carbon nanotubes are laid open cap end after acidic treatment. Purification of MWCNTs by microwave-assisted digestion method have reported in our previous studies [22–24]. The opened-end multi-walled carbon nanotubes are expected to be much more porous with more gas adsorption sites. Here, the effect of purification treatment on adsorption characteristics of MWCNTs will be furthermore investigated. The amount of nitrogen storage and absorption behavior of MWCNTs will be carried by volumetric adsorption apparatus.

2. Experimental

MWCNTs with diameter of 10–20 nm, 40–60 nm and 60–100 nm were synthesized by thermal chemical vapor deposition. The amount of catalysts in primitive MWCNTs samples were about 11.0 wt% of La and Ni. The primitive samples were thermal annealed in air and heated at 300 °C, 400 °C and 450 °C for 50 min by using heating chamber to remove carbonaceous particles. Then, an acidic treatment in microwave digestion system (Milestone Microwave Labstation ETHOSD) was used to remove the metallic catalysts. In this procedure, MWCNTs were placed in a Pyrex digestion tube. The first digestion step run at 100 °C for 5 min with 5 M HNO_3. The second digestion step was carried out at 100 °C for 10 min. After digestion, the suspension was filtered with 0.1 μm PTFE (poly-(tetrafluoroethylene)) membrane in deionized water. After rinsing with alcohol and drying the sample, a black thin mat composed of MWCNTs was obtained.

A scanning electron microscope (Jeol-6700) and high resolution transmission electron microscope (Philips Tecnai-20) were used to examine the morphology of MWCNTs. Nitrogen adsorption measurements at 77 K were carried out using a volumetric adsorption apparatus (Quantachrome NOVA 4200e). The amount of nitrogen adsorption for each measured point was set as 3 cc at 273 K and 760 mmHg. The pore size distribution of carbon nanotubes was analyzed by Barrett–Joyner–Halenda equation at adsorption isothermal [7].

3. Results and discussion

3.1. Effect of preheated treatment on adsorption characteristics of MWCNTs

Fig. 1a shows SEM image of the primitive MWCNTs sample. In this image, there appeared impurities such as amorphous carbons, graphite and metals in multi-walled carbon nanotubes. Furthermore, we can see that metallic particles were evidently embedded in the tip or in tube core of MWCNTs in Fig. 2a. It indicates metallic particles encapsulated tip and defective graphite sheets and amorphous carbon at the outer wall surface. The samples were thermally annealed at 300 °C, 400 °C and 450 °C for 50 min in air to remove the amorphous carbons. The amorphous carbons can be etched away more easily than MWCNTs due to the difference in reactivity between carbon nanotubes and amorphous carbon [25]. Amorphous carbon have faster oxidation reaction rate. The major weight loss of carbon nanotube below 500 °C was amorphous carbon when MWCNTs were significantly oxidized [26]. In Fig. 1b, it is indicated that after preheating at 450 °C for 50 min, amorphous carbon and other carbon particles are apparently decreased with increasing oxidation temperature.

It is well known that nitrogen adsorption at 77 K is a powerful and convenient method to measure the specific surface areas, pore size distribution and pore volumes of porous materials. The adsorption isotherm of N_2 on the primitive

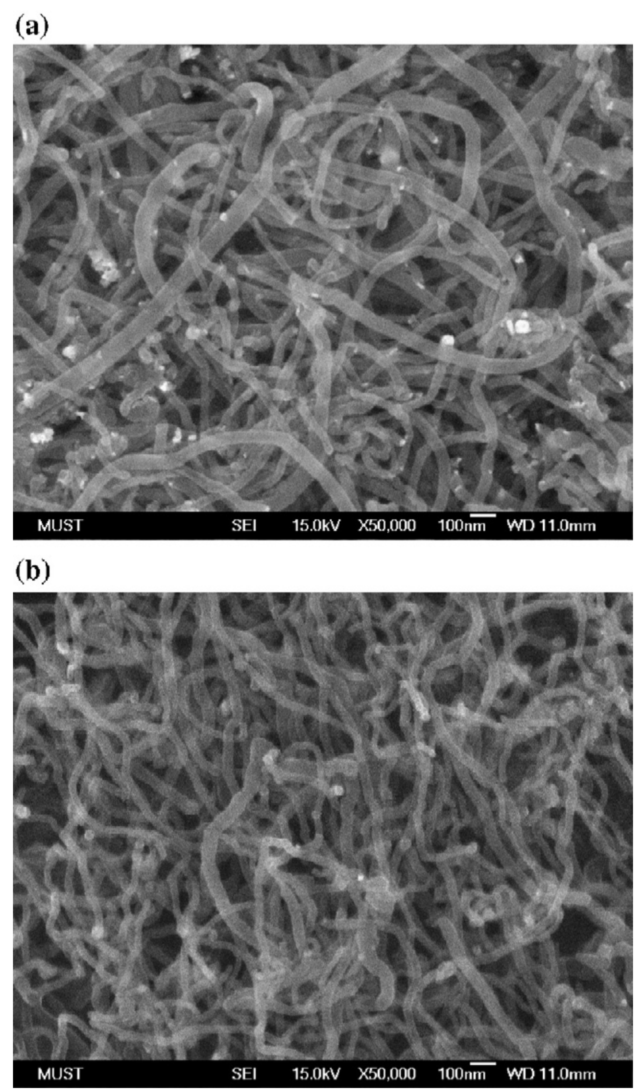

Fig. 1. SEM image of MWCNTs (a) raw sample (b) thermal annealed at 450 °C.