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MFM and gas adsorption isotherm analysis of proton beam irradiated multi-walled carbon nanotubes

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ABSTRACT

To enhance the gas adsorption properties and modify the physical properties of carbon nanotubes, multi-walled carbon nanotubes (MWCNTs) were irradiated by high-energy proton beams, and the physical properties including morphology and local surface structure were investigated by using a transmission electron microscope (TEM), magnetic force microscope (MFM) and a gas adsorption isotherm apparatus which can deeply probe the fine structure of surface. Interestingly, clearer MFM images were obtained from the proton irradiated samples which supports that carbon exhibits magnetism under proton bombardments, although the intrinsic magnetic property is not understood. The layering properties of argon on MWCNTs were measured from 59 to 69 K and the interaction of argon on the surface was analyzed. The calculated values of isosteric heat of adsorption demonstrated that higher interaction of gas molecules with surface is found from the proton irradiated MWCNTs. This result strongly supports that the local surface modification, partial defects, for example, were created due to the external high energy impacts. Our results are worthy to note that gas adsorption technique can provide the fine atomic resolution which beyond the one of TEM and MFM.

1. Introduction

Since the first discovery of carbon nanotubes (CNTs) by Iijima in 1991 [1], studies on physical, chemical, and mechanical properties of CNTs have contributed to deepen the knowledge of physics, chemistry and material sciences. Although CNTs exhibit a superior structural and physical properties such as well-defined nanodimensional structure, high electrical and thermal conductivity, good mechanical stability, etc. [2,3], many researches have been limited to the mechanical properties [4,5] and their potential applications [6,7].

One of the strong features of CNTs is that well-defined nanodimensional structure provides a large specific surface area per unit weight, indeed, higher than that of graphite, although the density is lower due to the hollow interiors. This suggests that CNTs are excellent candidate materials for gas storage, purification, and separation. In fact, there have been a large number of experimental investigations of gas adsorption on CNTs, such as, nitrogen [8] methane [9] and butane [10] adsorption isotherms on MWCNTs. Researches of hydrogen adsorption on CNTs were largely carried at both cryogenic and ambient temperatures aims at developing vehicles driven by the pollution-free fuel cell [11–15].

Molecular simulations, first-principles quantum mechanics methods, and their combinations, have been applied to understand the mechanisms of gas adsorption on nanotubes. Extensive theoretical and experimental studies have shown that gas adsorption on CNTs is characterized by the presence of large specific surface areas and the availability of different groups of adsorption sites having different binding energies on the nanotubes. It is known that ad(de)sorptive properties of the nanotubes can be altered significantly by subjecting them to treatments. Procedures opening the interior of the tubes result in CNTs became a potential material for gas absorption applications [16–24]. Purification of nanotubes with acids leads to the enhancement of the available specific surface area for adsorption [25].

Recently, many experimental techniques have developed to modify the surface of the CNTs using intense irradiations of proton beams, because proton irradiation on CNTs is known to induced the chemical and structural modification of polymer-CNT composite [26,27]. Very recently Esquinazi et al. [28], reported that the proton irradiated graphite exhibits the inducement of magnetic ordering. It is believed that the proton irradiation on CNTs mostly resulted in morphological damage, such as welding, curve and fraction of small pieces, and chemical modification forming C–H bonding [26,29,30]. However, no direct evidence of such damage

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was noted by using a gas-adsorption technique which can probe the local surface modification in an atomic scale.

The aim of this paper, therefore, is to investigate the effects of high-energy proton beam irradiation onto CNTs in terms of the gas adsorption and modification of physical properties of MWCNTs. For an adsorption experiments, Ar gas was used because it adsorbs reversibly on MWCNTs bundles and is thus well suited for thermodynamic measurements. In addition, the Ar isotope is known to have a large coherent neutron cross section of 77.9 barn giving rise to clear neutron-diffraction patterns that can be analyzed for structural analysis [31–35].

2. Experiment

The MWCNTs, prepared by an arc-discharge method, were purchased from ILJIN Nanotech Co. Ltd. The electron microscopy studies including TEM and SEM have shown that the diameters of MWCNTs were 10–15 nm, and have a purity of higher than 90 of volume%. The 0.5772 g of non-surface treated MWCNTs were irradiated with proton beams of energy which was tuned to 38 MeV by a cyclotron adjustment at the Korea Atomic Energy Research Institute. The morphologies of unirradiated and irradiated MWCNTs were examined by using a transmission electron microscope (TEM) operated at 200 kV (see Fig. 1).

Magnetic force gradient images and topography were simultaneously obtained at room temperature with a Nanoscope IV scanning probe microscope from Digital Instruments. The magnetic images were taken with a standard magnetic-etched-silicon probe (MESP) with tip coercivity (H_c) of $\sim$300 Oe. The MFM (magnetic force microscope) measurements were performed in the "tapping/lift TM" scanning mode with the phase detection system. The first scan of the surface is made in the intermittent contact mode to determine the topography (Tapping mode). During the second scan the tip follows a constant height pathway determined from the topography scan and senses the magnetic forces (Interleave mode).

After MWCNTs were irradiated by proton beams, the samples were loaded into an oxygen free high conductivity (OFHC) copper cell with an indium seal. The sealed cell then was mounted in a vacuum jacket which contains a closed-cycle helium cooling system (Helix Cryogenics). The dead volume (20 mL) of the sample cell was calibrated by expanding a known amount of Ar gas into the cell. The gas adsorption isotherm data were measured while the temperature of the sample was kept at constant temperature. The equilibrium vapor pressure of Ar in our experiment was defined after confirming the vapor pressure difference which was measured every 1 min is less than 0.01% of the dosed amount of the gas.

3. Results and discussion

The possible change of the local surface structure by the proton irradiation was investigated by MFM studies. As shown in Fig. 2, the topography and magnetic images of MWCNTs measured by MFM after irradiating the 38 MeV proton beams were the same as the ones measured before irradiating the beam, suggesting that no significant change of the surface structure was found. It is interesting to note that while MFM images are disappeared when the tip-sample distance is larger than 10 nm for all samples before proton irradiation, clear MFM images are observed even at higher scan height (100 nm) from the samples irradiated by proton beams (see Fig. 3). This result strongly supports Esquinazi et al. 's demonstrations that CNTs exhibits magnetism after proton irradiation.

In order to characterize the physical properties of proton beam irradiated MWCNTs, a series of adsorption isotherms of Ar on irradiated and unirradiated MWCNTs were measured below the triple point of Ar (83.78 K). It is noted that the actual temperature of the sample was calibrated by fitting the saturation vapor pressure (SVP) of Ar measure from 50 to 90 K by 2 K intervals. Fig. 4 shows adsorption isotherms of Ar measured from the unirradiated and irradiated MWCNTs indicating that the amount required to cover the monolayer after the irradiation is almost the same as the amount before the irradiation; approximately 0.002 and 0.004 mol/g are required to form the monolayer and the bilayer, respectively, at 67 K. This observation is confirmed by the calculated results of the 2-dimensional compressibility value, which is used to characterize the response of the argon film to a change in spreading pressure.

An important thermodynamics quantity which is related to probe the local structure including defects on a substrate, is an isosteric heat of adsorption, Q_{st}, and is obtained from the measured isotherm data. It is defined as the energy necessary to bring a molecule from infinity onto the surface, and can be calculated at constant coverage of gas molecule:

$$Q_{st} = RT^2 \cdot \left.\frac{\partial(\ln p)}{\partial T}\right|_x, \qquad (1)$$

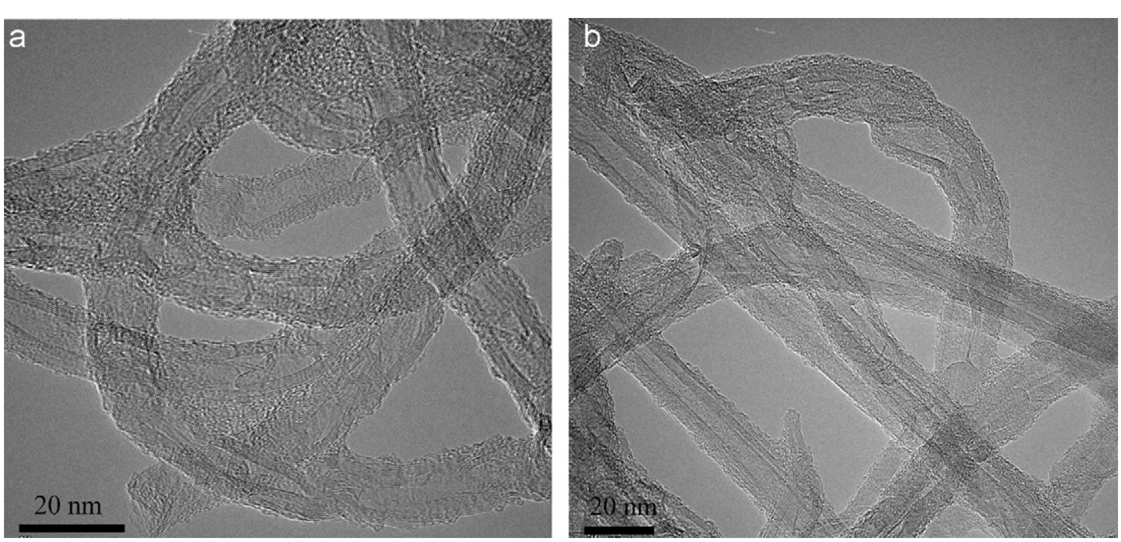

Fig. 1. Morphologies of MWCNTs: (a) before and (b) after irradiated by proton beams.