



Short Communication

Porous multi-walled carbon nanotubes by using catalytic oxidation via transition metal oxide

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ABSTRACT

Porous carbon materials are attractive due to their wide applications in gas separation, water purification, catalyst support, and electrodes for energy system. Especially, it is interesting to create a porous structure on nano-carbon material. In this work, we report an easy method to create porous multi-walled carbon nanotubes (MWCNTs) by using the catalytic oxidation via transition metal oxide ($C + O_2 = CO$ or CO_2). We selected Co and Fe elements as catalyst sources for transition metal oxide. Under different oxidation time conditions (2 and 3 h), Co and Fe precursor-impregnated MWCNTs were oxidized at 300 and 350 °C in air, respectively. In transmission electron microscopy analysis, we observed various shapes of porous structures such as pits and thinned walls, and nanoparticles (NPs) were present around the porous structures on MWCNTs. In addition, a tubular structure and the original crystallinity of MWCNTs were maintained even after creating a porous structure on MWCNTs. X-ray diffraction measurements confirmed the crystal structure of NPs, indicating that Co and Fe elements were converted into Co_3O_4 and $\gamma-Fe_2O_3$ after oxidation, respectively. Especially, X-ray photoelectron spectroscopy was used to confirm the oxidation state of $\gamma-Fe_2O_3$. Eventually, the porous structures resulted in the increase of specific surface area and mesopore volume of MWCNTs. We think that porous MWCNTs can be applied in the fields which require an active surface as well as a porous structure of MWCNTs.

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1. Introduction

Porous carbon materials are attracting widespread interest in fields such as gas separation [1], water purification [2], catalyst support [3], and electrode for supercapacitors [4] and fuel cells [5]. Among diverse carbon materials, carbon nanotubes (CNTs) have been one of the promising carbon materials since the discovery by Iijima in 1991 [6] due to their superior electrical [7], thermal [8], and mechanical properties [9]. Unfortunately, a porous structure of CNTs has not been investigated in spite of the great concerns on CNTs. On the other hand, various methods such as chemical and physical activation [10], catalytic activation [11], carbonization [12,13] have been studied to create porous carbon materials. This motivated us to develop an easy way to create a porous structure of CNTs.

In this study, we show that porous multi-walled carbon nanotubes (MWCNTs) can be easily attained by the catalytic oxidation

using transition metal oxide. Literally, MWCNTs have a unique structure which is composed of a number of graphene cylinders having different diameters. Hence, to create a porous structure on MWCNTs, it is necessary to locally generate nano-scale pores on walls by removing carbon atoms through several walls of MWCNTs. At this moment, the most important thing is to maintain a tubular structure of MWCNTs in spite of the introduction of nano-pores on MWCNTs. To realize this porous structure on MWCNTs, we adopted the catalytic oxidation of carbon by using transition metal oxide. It has been reported that transition metal oxides such as NiO, Co_3O_4 , CuO, and Fe_2O_3 work as a catalyst to gasify carbon with oxygen ($C + O_2 = CO$ or CO_2) [14]. Based on this fact, our idea was realized by two steps: (a) preparation of transition metal precursor-impregnated MWCNTs to form transition metal oxide nanoparticles (NPs) on MWCNTs and (b) oxidation of MWCNTs with the NPs to occur the catalytic oxidation between carbon of MWCNTs and the oxygen in air. During this oxidation process, NPs are formed by thermal calcination of the precursors, and the NPs play a role as a catalyst. MWCNTs have been shown to be thermally stable up to 400 °C in air atmosphere and to start

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to lose their weight by the oxidation in the range from 410 to 490 °C [15]. Therefore, in order to obtain a porous structure on MWCNTs without losing a tubular shape, the creation of nano-pores should be performed by oxidizing MWCNTs below 400 °C under air atmosphere. The presence of transition metal oxide NPs on MWCNTs enables us to create a porous structure below 400 °C by partially oxidizing a local part around NPs ($C + O_2 = CO$ or CO_2). In other words, if we heat MWCNTs with catalyst NPs below 400 °C under air atmosphere, catalytic oxidation of carbon occurs only around the catalyst NPs on MWCNTs. This feature of a localized oxidation is the main idea of our work to create porous MWCNTs.

Also, porous MWCNTs can be considered in a different viewpoint of the surface modification of MWCNTs. The nano-pores which are formed on MWCNTs through several layers of mono-layer carbon sheets are multi-carbon vacancies on a tubular structure of MWCNTs. In the viewpoint of surface modification, these vacancies on MWCNTs are active sites for functionalization [16], metal decoration [17], sensor [18], and drug delivery system [19] since active sites of MWCNTs are essential in the applications. Consequentially, the creation of a porous structure on MWCNTs has more chance to be applied to diverse fields, apart from the porous structure itself. Therefore, we think that porous MWCNTs can be applied in the fields which require an active surface as well as a porous structure of MWCNTs.

2. Experimental

MWCNTs were purchased from Nanocyl (NC 7000, average length: 1.5 μm , average diameter: 9.5 nm, purity: 90%) and used as received to create a porous structure. Co and Fe precursor solutions were prepared by separately dissolving 0.05 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma–Aldrich, 98%) and 0.08 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma–Aldrich, 98%) in 100 ml of ethanol. The weights were determined for metal elements to be about 10 wt.% when each metal salt is mixed with the following amount of MWCNTs. 0.1 g of MWCNTs was added to each solution and the mixtures were sonicated for 15 min for good dispersion of MWCNTs. Then, the mixtures were heated at 80 °C under stirring until ethanol was totally evaporated. This step was to obtain Co precursor-impregnated MWCNTs (hereafter, Co-impregnated MWCNTs) and Fe precursor-impregnated MWCNTs (hereafter, Fe-impregnated MWCNTs). Then, Co- and Fe-impregnated MWCNTs were ground into fine powder. The powders were carried to a furnace to create a porous structure on MWCNTs, and Co- and Fe-impregnated MWCNTs were oxidized at 300 and 350 °C in air for 2 h, respectively. After analysis, both samples were further oxidized for 1 h under the same condition to investigate the effect of oxidation time on a porous structure.

Transmission electron microscopy (TEM, Jeol, JEM-4010, 400 kV) analysis was performed to observe the morphology of NPs and a porous structure of MWCNTs. X-ray diffraction (XRD, Philips, XPERT MPD, 30 mA, 40 kV) measurements were performed to confirm the crystal structure of NPs on porous MWCNTs. Also, X-ray photoelectron spectroscopy analysis (XPS, PHI X-tool) was carried out to investigate the oxidation state of transition metal oxide using Al $K\alpha$ (1486.6 eV) at 4.5 W. N_2 adsorption–desorption measurement was conducted at 77 K using Micromeritics ASAP 2020 to examine the porous structure of MWCNTs. The specific surface areas of Co- and Fe-impregnated MWCNTs were calculated by Brunauer–Emmett–Teller (BET) method. The mesopore volume, mesopore surface area, and pore distribution of the samples were obtained by Barrett–Joyner–Halenda (BJH) method, and the t -plot method was used to obtain the volume and surface area of micropore.

3. Results and discussion

TEM analysis is a proper method to confirm the presence and morphology of a porous structure of MWCNTs. Fig. 1 displays TEM images of MWCNTs oxidized by using Co (a, c, and e) and Fe (b, d, and f) precursors, respectively. At first, TEM images were obtained at low magnification to see if a porous structure is evenly created on MWCNTs. Fig. 1(a) and (b) display low magnification TEM images of Co- and Fe-impregnated MWCNTs after oxidation for 2 h, respectively. As shown in the figures, MWCNTs oxidized with both Co and Fe precursors commonly exhibit a porous structure all over the place. Several porous structures on MWCNTs are indicated with arrows in Fig. 1(a) and (b). To observe these structures on MWCNTs distinctly, TEM images were obtained at high magnification as shown in Fig. 1(c) and (d). We can see that regardless of the kind of a catalyst, a common porous structure appears in the shape of a pit, and NPs exist around the porous structure. It is certain that these NPs were produced from the catalyst precursor during oxidation to create a porous structure. The crystal structure of the NPs will be discussed later in XRD analysis section. Another common feature displayed in Fig. 1(c) and (d) is that MWCNTs maintain the original crystallinity of pristine MWCNTs in the part where the reaction between oxygen in air and carbon of MWCNTs did not occur. In addition, we can clearly see that both MWCNTs seen in Fig. 1(c) and (d) still keep a tubular structure in spite of a hole in the walls. This is apparent evidence that carbon atoms were removed through several walls of MWCNTs by the catalytic oxidation of gasifying MWCNTs ($C + O_2 = CO$ or CO_2).

Different from the images mentioned above, Fig. 1(e) displays a different sort of a porous structure which is in the shape of a step, or thinned walls, rather than a pit. This means that NPs moved to the axial direction of MWCNTs while removing carbon atoms from several walls. Unusually, the MWCNT seen in Fig. 1(f) has porous structures in the shape of both a pit and thinned walls on an individual tube.

From these results, we can understand that similar types of porous structures are observed in all cases, regardless of the kind of a catalyst. And, it is obvious that the pore size and the shape of a porous structure are determined by the movement and the direction of NPs on MWCNTs. The pore diameter observed at high magnification was around 10 nm in both cases. Therefore, we can conclude that a porous structure is independent from the kind of a catalyst which is used for carbon gasification of MWCNTs.

Fig. 2(a) presents the XRD patterns obtained after oxidizing metal precursor-impregnated MWCNTs for 2 h to create a porous structure. In Fig. 2(a), the XRD result of Co-impregnated MWCNTs after oxidation is exhibited in (1), while (2) indicates the XRD patterns of Fe-impregnated MWCNTs after the same treatment. As shown in (1) and (2) of Fig. 2(a), several peaks commonly appear at $2\theta = 25.5^\circ$, 43.1° , and 53.4° . The peaks originated from MWCNTs and correspond to (002), (100), and (004) crystal planes of graphite. These peak positions are in good accord with previous reports on the XRD patterns of MWCNTs [20]. In (1) of Fig. 2(a), there are several peaks at $2\theta = 19.0^\circ$, 31.2° , 36.6° , 44.4° , 59.6° , 65.2° , 77.5° in addition to peaks from MWCNTs. The peaks can be assigned to (111), (220), (311), (400), (511), (440), and (533) planes of Co_3O_4 crystal (JCPDS file No. 09-0418). Therefore, it is evident that the oxidation of Co-impregnated MWCNTs at 300 °C in air leads to the formation of Co_3O_4 on MWCNTs with a porous structure. From this, we can demonstrate that NPs showing in the left column of Fig. 1 are Co_3O_4 NPs formed by the oxidation for a porous structure. In the case of the oxidation of Fe-impregnated MWCNTs, Fig. 2(a) (2) displays several peaks which do not originate from MWCNTs. The peaks appearing at $2\theta = 35.4^\circ$, 43.9° , 53.0° , and 63.3° correspond to (311), (400), (422), and (440) planes of $\gamma\text{-Fe}_2\text{O}_3$

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