

Preparation and Characterization of Cobalt Nanoparticle-Decorated Multi-Walled Carbon Nanotubes

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Abstract

In order to increase gas storage capacity such as hydrogen and methane, various wt% of cobalt were decorated on the surface of MWCNTs which was already treated nitric and sulfuric acids to provide functional groups on the surface of MWCNTs. The characteristic peak of SO_4^{2-} in FT-IR spectrum was at 1220 cm^{-1} , which was resulting from sulfuric acid treatment. This peak implies that acid treatment containing sulfuric acid can give rise to the incorporation of sulfur onto the surface of MWCNTs. According to the results of XRD, cobalt were thoroughly reduced under hydrogen around 673 K. This indicates that cobalt oxides need the temperature of 673 K to be reduced under hydrogen. In case of 15 wt% cobalt decoration on the surface of MWCNTs, cobalt particle size was around 10 nm.

Keywords; Carbon nanotubes, Chemically modified carbons, Gas storage

Instruction

Hydrogen fuel is one of the cleanest and idealized energy sources. In order to use hydrogen fuel efficiently, hydrogen storage is an essential condition for widespread utilization all over the world. In recent years, there has been considerable experimental and theoretical interest in the use of nano-structured carbon materials, especially in the form of tubes [1-4] and fibers [5,6] as potential hydrogen sorbents [7]. Unfortunately, these materials do not meet the DOE targets. The DOE has asked for achievable hydrogen storage capacity to reach 4.5 wt% by the FY 2005, 6.0 wt% by the FY 2010, and 9.0 wt% by the FY 2015 [8].

Carbon nanotubes (CNTs), having high surface-to-volume ratios, are ideal for fast kinetics because of their reversible characteristics during hydrogenation and dehydrogenation. Dillon [9] et al. first reported the reversible hydrogen storage properties of carbon soot containing 0.1-0.2 wt% single-walled carbon nanotubes (SWCNTs) at 300 Torr. The hydrogen storage capacity of pure SWCNTs could be extrapolated to reach 5-10 wt% after calculating their purity. An overview of experimental data on hydrogen adsorption in carbon nanotubes (CNTs) was given in the literature by Ding et al. [10]. In additional, it was found that multi-walled carbon nanotubes can have a hydrogen storage capacity at room temperature of 1.97 wt% H_2 at 4 MPa [11], 3.7 wt% H_2 at 6.9 MPa [12], 4 wt% H_2 at 10 MPa [13], and 6.3 wt% H_2 at 14.8 MPa [14]. These high values, however, have not so far been verified independently. The storage values are dependent on many parameters of the carbon nanotubes, including their structure, structure defects, pretreatment, purification, geometry (surface area, tube diameter, and length), arrangement of tubes in bundles and/or 'ropes', storage pressure, temperature, etc. The nature of the factors that influence the level of hydrogen storage is still disputed [7]. However, recent studies [15, 16] have shown that the hydrogen storage capacity on a pristine CNTs is less than 0.01 wt% at room temperature. Also, Lawrence and Xu [17] also reported that hydrogen only 0.6 wt% was adsorbed on the CNT bundle at 294 K and 10 MPa. Ni supported activated carbon reported by Zieliński et al. [7] stored up to 0.53 % at 3 MPa against 0.1 % for as-received activated carbon. More recently, it was reported by Kim et al. that 6 wt% Ni nanoparticle-dispersed multi-walled carbon nanotubes released hydrogen of 2.8 wt% in the range of 340 – 520 K [18]. As described above, the important point for hydrogen storage is the use of transition metals such as Fe, Co, Ni, Cu, etc.

In this study, prior to hydrogen storage study using cobalt-decorated MWCNTs, Co-MWCNTs were investigated by various analysis tools. Also, the optimum condition of cobalt dispersion on the surface of MWCNTs is provided.

Experimental

Cobalt decoration on MWCNTs

In order to decorate cobalt particles on MWCNTs, 0.5 g of MWCNTs treated with acids was immersed into 6.5, 65 and 110 mM cobalt nitrate solutions of 20 ml, respectively. These solutions were sonicated for 1 h at room temperature for good dispersion. Each sonicated solution was evaporated in oil evaporator until solution was perfectly vaporized. After vaporization, vaporized powder was dried at 383 K overnight. And then, the sample containing 15 wt% cobalt was reduced in flowing 5 % H₂/Ar as the reducing gas, during which reduction conditions were first heated at 5 K/min, and kept at 523, 673, 823 and 973 K for 3 h, respectively.

Characterization and analysis

In order to estimate the crystallinity of the samples, X-ray diffraction (XRD, Rigaku, D/Max III) analysis was used. The specific surface area and pore volume were measured by the BET specific surface analyzer (Micromeritics Co., ASAP 2020) using nitrogen adsorption at 77 K. The changes of chemical species on the surface of MWCNTs before and after cobalt decoration were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB MK II, VG Scientific LTD). Monochromised AlK α (1486.7 eV) was used as X-ray source. The binding energy (BE) was referred to the C 1s signal (284.6 eV). The XPS spectrum was fitted using Gaussian function.

Results and discussion

Fig. 1 shows the XRD patterns of cobalt-decorated MWCNTs, from which it can be seen that the diffraction peak of the plane (111) of the fcc cobalt phase ($a = 3.544 \text{ \AA}$, JCPDS No.15-0806) is strong in terms of reduction temperature from 523 to 973 K. However, there is no distinctive peak corresponding to cobalt nitrate hydrate or other cobalt oxides such as Co₃O₄ or CoO on the diffractogram reduced at 673 K. It clearly means that cobalt was thoroughly reduced by hydrogen to metal cobalt over 673 K. Zhang et al. [19] reported that, in the case of Co/CNTs reduced by hydrogen at 623 K, there are two phases on CNTs, which are Co₃O₄ and Co, respectively. This result suggests that the effective reduction temperature of cobalt oxides by hydrogen is around 673 K.

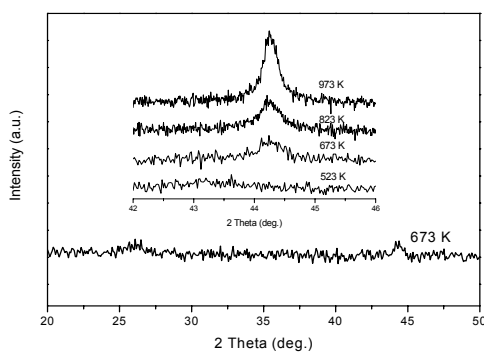


Figure 1. XRD patterns of 15 wt% Co-MWCNTs reduced at 673 K under hydrogen, inset: various reduction temperatures of 15 wt% Co-MWCNTs.

BET specific surface areas were listed in Table 1. Among these data, the result of 25 wt% Co-MWCNTs is the lowest. This implies that, in case of 25 wt% Co-MWCNTs, the decrease of specific surface area is resulting from the increase of the cobalt content. It can be explained that small cobalt particle increases specific surface area of samples, whereas the aggregation of cobalt particles and the coverage of MWCNTs surface is resulting in the decrease of surface area. From these results, in order to make high specific surface area on MWCNTs, it is important independently to disperse nanoparticles on the surface.

Table 1. BET specific surface areas of various MWCNTs.

Samples	BET specific surface area (m ² /g) ^a
Acid-treated MWCNTs	85.04
1.5 wt% Co-MWCNTs	92.02
15 wt% Co-MWCNTs	92.87
25 wt% Co-MWCNTs	78.07

As can be seen in Fig. 2 (a) and (b), it was clearly shown that cobalt peaks were decorated on the surface of MWCNTs. It can be known that the relative peak intensity of 25 wt% Co-MWCNTs are higher than that of 15 wt% Co-MWCNTs. On the other hand, the peak shown around 2 keV indicates sulfur compounds, which were derived from sulfuric acid treatment. This result is in good agreement with the fact obtained from XPS spectrum.

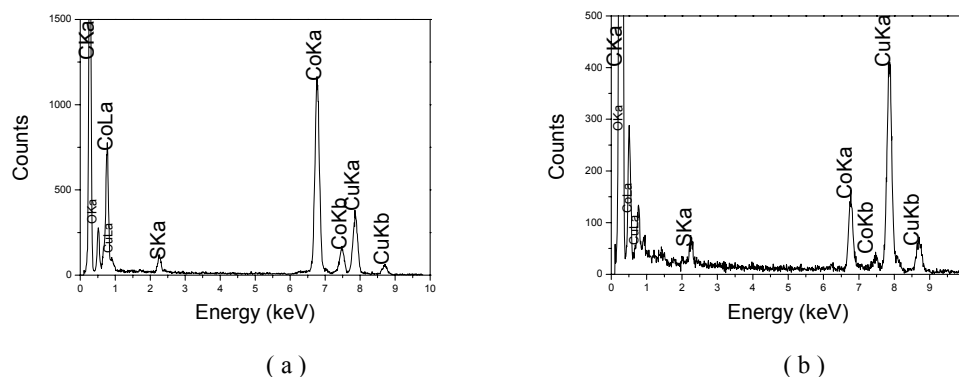


Figure 2. EDS spectra of (a) 15 wt% Co-MWCNTs; (b) 25 wt% Co-MWCNTs.

In order to confirm further the XRD results, the phase and composition of cobalt were investigated by X-ray photoelectron spectroscopy (XPS) measurement. Fig. 3 (a) shows the full survey of XPS spectra of Cobalt-decorated MWCNTs. As shown in Fig. 3 (c) and (d), the broad peaks around 700 eV indicate Auger electron peaks of cobalt.

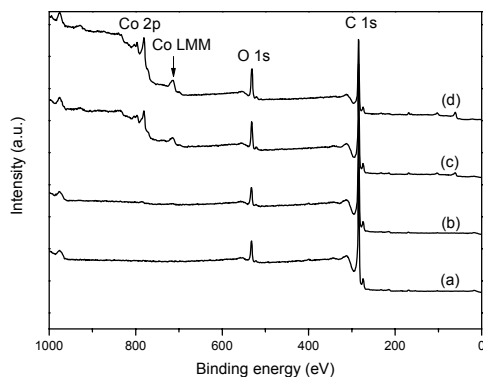


Figure 3. Full range XPS spectra (a) acid-treated; (b) 1.5 wt% Co-MWCNTs; (c) 15 wt% Co-MWCNTs; (d) 25 wt% Co-MWCNTs.

Also, Fig. 4 shows XPS spectra of various cobalt contents. As shown in Fig. 4, the relative intensity of the main Co $2p_{3/2}$ peak may be indicative of the various cobalt contents.

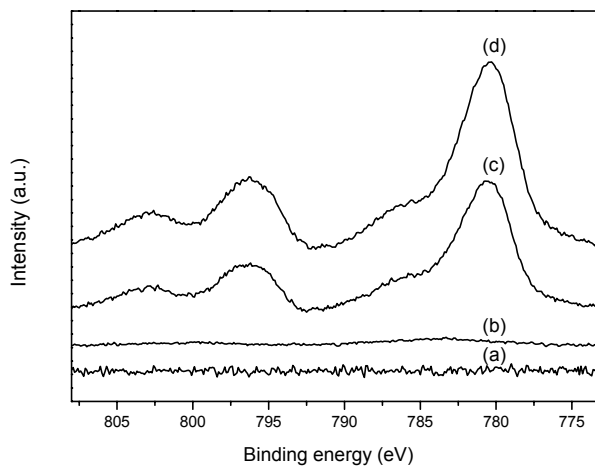


Figure 4. XPS Co 2p spectra (a) acid-treated; (b) 1.5 wt% Co-MWCNTs; (c) 15 wt% Co-MWCNTs; (d) 25 wt% Co-MWCNTs.

In order to characterize the XPS peaks in detail, as can be seen in Fig. 5, the spectrum of 25 wt% Co-MWCNTs was deconvoluted by Gaussian method due to the shape of peaks.

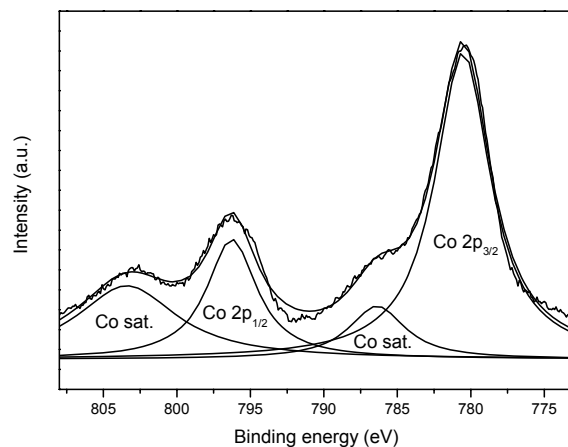


Figure 5. Deconvoluted XPS Co 2p spectra of 25 wt% Co-MWCNTs.

As shown in Fig. 5, the peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$ indicate cobalt metal on MWCNTs. In addition to the main Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks, satellite peaks (spin-orbital splitting) are also shown in the XPS spectra at 786.6 and 803.3, respectively. This result is consistent with XRD patterns shown in Fig. 1. Compared to the results [20], Co $2p_{3/2}$ peak of 25 wt% Co-MWCNTs shown at 780.3 eV is higher than that of 15 wt% Co-MWCNTs, which is resulting from the content of cobalt. Elemental atomic percentage calculated from XPS spectra was summarized in Table 2.

Table 2. Element composition of MWCNTs obtained from XPS spectra.

	Elemental content (at.%)				
	C	O	S	Co	N
Acid-treated MWCNTs	76.6	20.33	3.07	-	-
1.5 wt% Co-MWCNTs	90.31	8.35	0.33	0.31	0.69
15 wt% Co-MWCNTs	84.31	11.41	0.7	3.29	0.3
25 wt% Co-MWCNTs	75.2	17.14	1.43	6.06	0.18

As known from Table XPS, there are no cobalt peaks on only acid-treated MWCNTs. In spite of heat treatment at 673 K, it was founded that acid-treated MWCNTs contained 3.07 at.%. It implies that sulfur compounds formed from sulfuric acid treatment was not thoroughly removed during heat treatment because sulfur compounds were tightly bonded to carbon on the surface of MWCNTs.

Conclusions

In order to decorate the cobalt nanoparticles on MWCNTs, various cobalt concentrations were used. According to EDS, XPS, cobalt was decorated on the surface of MWCNTs in the order of 1.5, 15 and 25 wt%. In case of 15 wt% cobalt decoration, the particle sizes shown in TEM image on MWCNTs were independently around 10 nm. From XRD data, it can be concluded that the reduction temperature of cobalt-decorated MWCNTs is nearly 673 K under hydrogen. In addition, as the results of XRD and XPS, cobalt was thoroughly reduced by hydrogen.

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