Research Article

Synthesis of Co Filled Carbon Nanotubes by In Situ Reduction of CoCl_2 Filled Nanotubes by NaBH_4

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An alternative process of filling the multiwall nanotubes (MWCNTs) with cobalt metal was developed. Empty core of nanotubes was first filled with CoCl_2 by stirring with CoCl_2 and alcohol at room temperature for six hours. CoCl_2 filling inside MWCNTs was then converted into Co after treating with NaBH_4 at room temperature. High resolution transmission electron microscope (HRTEM) studies showed the filling of the CoCl_2 and Co inside the nanotubes before and after the treatment. EDX studies show the nonexistence of chlorine after the reduction with NaBH_4 . Amount of filling was also reduced after the treatment. Paper describes the possible mechanism of filling CoCl_2 inside nanotube and its reduction by NaBH_4 .

1. Introduction

Exceptional properties of carbon nanotubes, like high strength, discrete electronic states, and so forth, make them highly suitable for the applications in nanodevices. They are the most appropriate material for using in devices like AFM probes [1], FE transistors [2, 3] display devices [4–6], and so forth. Filling of carbon nanotubes with materials enhances their physical and chemical properties and their potential applications in different areas [7–9]. They show interesting physical and structural properties which are different than their parent materials [7, 10].

Magnetic metal nanoparticles (such as Fe, Co, and Ni) have applications such as high-density magnetic data storage, magnetic separation of biomolecules, and treatment of cancer [11, 12]. However, the poor oxidation resistance of the metal nanoparticles is a great hindrance for their applications. Encapsulation of nanoparticles in carbon nanotubes may be highly useful with the combination of properties of magnetic nanoparticles and carbon nanotubes [13–16]. Ferromagnetic metals filled carbon nanotubes have significant potential in data storage technology [17]. Additionally, the walls of carbon nanotubes provide an effective shelter against oxidation of magnetic nanoparticles and thus ensure a long-term stability of the ferromagnetic core [17].

Various methods are employed for the filling of carbon nanotubes, such as arc discharge [18, 19], high-temperature heat treatment [20], capillary induced [21], ion-beam sputtering [22], and chemical vapor deposition (CVD) [23, 24]. Although arc discharge technique is a better method, low yield is a problem for commercial applications. CVD method is a simple and low cost method and can produce filled carbon nanotubes in large quantities. However, all these methods are the in situ synthesis of metal filled nanotubes. There are very few studies for the filling the CNTs using after their preparation [9, 10]. The present paper describes an easy method of the filling of the carbon nanotubes using first CoCl_2 and then reducing the CoCl_2 into Co using NaBH_4 .

2. Materials and Methods

MWCNTs obtained from ASI, open from both ends, having a diameter in the range from 150 to 200 nm, were taken in a flask and mixed with CoCl_2 in alcohol in equal molar ratio. The mixture was stirred for 6 hours at room temperature in air. After stirring, the sample was washed with alcohol for the removal of unreacted CoCl_2 . CoCl_2 filled MWCNTs were then mixed with NaBH_4 in alcohol, and the mixture was cooled down to 273 K. The reaction between CoCl_2 filled MWCNTs and NaBH_4 was carried out in inert atmosphere of

FIGURE 1: HRTEM micrographs showing the (a) and (b) CoCl_2 filled nanotubes in low magnifications where the filling appears darker than the empty part in the hole of the nanotubes.

argon. The mixture was then stirred for 6 hours. Once the treatment time were over, nanotubes were taken out from flask, washed with alcohol, and characterized.

Structural investigation of the products was done using high resolution transmission electron microscope (HRTEM) operating at 150 KV with a point resolution of 3 Å. Contrast was enhanced by adding an 8 nm large aperture in the back focal plane on the objective lens. Electron dispersive X-ray spectroscopy was used to characterize the elemental analysis.

3. Results and Discussion

3.1. CoCl_2 Filled Multiwalled Nanotubes. HRTEM micrographs in Figures 1(a) and 1(b) demonstrate two MWCNTs after stirring with CoCl_2 . Some part of the central hole of nanotubes, shown between two lines, is observed to be darker than the nanotube walls. This dark material is the filling inside the empty core of the nanotubes. Filling appears darker than the nanotubes walls whereas the empty hole appears lighter than the walls. Core of nanotube is observed to be filled at few places whereas other places are seen empty. Material is not filled throughout the nanotube hole. Filling is dense in Figure 1(b) whereas it is slightly transparent in Figure 1(a). This transparency may be due to the entrance of liquid in the nanotubes.

High magnification study in Figure 2(a) shows that some part of the filling is dense, and there is some crystalline nature in the filled material. The filling covers the entire width of the hole. Graphene layers of nanotube walls remain intact. There is no effect of the treatment on the nanotube walls.

Figure 2(b) shows EDX study of the filled material in Figure 2(a). Analysis demonstrates the presence of Cu, Co, and Cl in the filling. Since Cu grids are used for the study, observed Cu is due to the grid. Existence of Co and Cl indicates the presence of CoCl_2 .

3.2. Co Filled Multiwalled Nanotubes. Figure 3(a) shows a CoCl_2 filled nanotube after treatment with NaBH_4 . A quadrilateral size particle of dimensions 100×60 nm is observed

inside the nanotube. Nanoparticle covers the width of the nanotube. However, a slight gap appeared on the both sides between the nanotube wall and nanoparticles. This gap is not visible in the CoCl_2 filled nanotubes (Figure 2(a)).

EDX study in the Figure 3(b) shows the presence of Co. No existence of Cl is observed in the filling. Reduction in size shows the removal of chlorine from the filling CoCl_2 . The nanoparticle is not as dense as the CoCl_2 . Some part is dense whereas the other part is hollow which may be due to the removal of Cl from the inside of crystalline CoCl_2 .

3.3. Mechanism of the Filling of CoCl_2 and Reduction with NaBH_4 . Illustration in Figure 4 depicts the complete process of filling Co metal in multiwalled nanotube. Step 1 of the process is the stirring of nanotubes with CoCl_2 in alcohol at room temperature in air for six hours. Since the nanotubes used are already open, CoCl_2 along with alcohol enters in the empty hole of the nanotubes due to the capillary effect. This leads to the formation of CoCl_2 filled MWCNTs ($\text{CoCl}_2@\text{MWNTs}$), as shown by the following reaction:

In the second step, CoCl_2 MWNTs are treated with NaBH_4 in ethyl alcohol at 273 K in argon atmosphere. This treatment converts $\text{CoCl}_2@\text{MWNTs}$ into $\text{Co}@\text{MWNTs}$ with NaBH_4 , and CoCl_2 get reduced to the Co, as shown in the following reaction:

NaBH_4 is a reducing agent and better known for the reduction of the aldehydes and acids in the organic chemistry. Besides these, it is also used for reducing metal chlorides into metals [25, 26]. Absence of chlorine in the EDX analysis of Co metal in Figure 3 indicates the reduction of CoCl_2 . NaBH_4 may also form the CoB_2 during the reduction [25], as observed in the

FIGURE 2: (a) HRTEM micrographs showing crystallized CoCl_2 in the hole of nanotube, (b) EDX analysis showing the presence of Co and Cl in the filling material inside the nanotube. This indicates the presence of CoCl_2 inside the empty core of the nanotube.

FIGURE 3: (a) TEM micrographs showing the Co nanoparticle in the nanotube, (b) EDX study of the Co nanoparticle showing the absence of Cl. Cu is from the grid used in TEM.

FIGURE 4: Illustrations showing the (1) filling of CoCl_2 inside the nanotubes, (2) conversion of CoCl_2 into Co inside the nanotubes by NaBH_4 .

earlier studies where water was used as a solvent. However, EDX analyses of Co metal in Figure 3 show the nonexistence of boron and oxygen. This shows that the conditions of the reaction (2) are not suitable for forming the CoB_2 or Co_2O_3 and lead to the formation of pure Co metal inside the nanotube.

4. Conclusions

CoCl_2 was successfully filled inside the multiwalled nanotubes after stirring both in alcohol for six hours. CoCl_2

inside the nanotube is converted into Co by NaBH_4 using alcohol as a solvent. Absence of chlorine, boron, and oxygen in the EDX study shows the formation of pure Co inside the nanotubes.

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