Research Article

Synthesis of Co Filled Carbon Nanotubes by In Situ Reduction of CoCl₂ Filled Nanotubes by NaBH₄

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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 CoCl₂ by stirring with CoCl₂ and alcohol at room temperature for six hours. CoCl₂ filling inside MWCNTs was then converted into Co after treating with NaBH₄ at room temperature. High resolution transmission electron microscope (HRTEM) studies showed the filling of the CoCl₂ and Co inside the nanotubes before and after the treatment. EDX studies show the nonexistence of chlorine after the reduction with NaBH₄. Amount of filling was also reduced after the treatment. Paper describes the possible mechanism of filling CoCl₂ inside nanotube and its reduction by NaBH₄.

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 CoCl₂ and then reducing the CoCl₂ into Co using NaBH₄.

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 CoCl₂ 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 CoCl₂. CoCl₂ filled MWCNTs were then mixed with NaBH₄ in alcohol, and the mixture was cooled down to 273 K. The reaction between CoCl₂ filled MWCNTs and NaBH₄ was carried out in inert atmosphere of...
argon. The mixture was then stirred for 6 hours. Once the treatment time was 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 $100 \times 60$ 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 CI 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 (CoCl$_2$@MWCNTs), as shown by the following reaction:

$$\text{MWNTs} + \text{CoCl}_2 + \text{Alcohol} \xrightarrow{\text{Stirring}} \text{CoCl}_2@\text{MWNTs}$$

(1)

In the second step, CoCl$_2$@MWNTs are treated with NaBH$_4$ in ethyl alcohol at 273 K in argon atmosphere. This treatment converts CoCl$_2$@MWCNTs into Co@MWCNTs with NaBH$_4$, and CoCl$_2$ get reduced to the Co, as shown in the following reaction:

$$\text{CoCl}_2@\text{MWNTs} + \text{NaBH}_4 + \text{Alcohol} \xrightarrow{0^\circ C, \text{Ar}, \text{Stirring}} \text{Co@MWNTs}$$

(2)

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$_2$O$_3$ 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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