The electrochemical decoration of multi-walled carbon nanotubes with nickel oxide coating

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Abstract. In this paper, nickel coatings have been deposited on the multi-walled carbon nanotubes (MWCNT). In the first stage, MWCNT powder was ultra-wave mixed in the acid bath (H₂SO₄ and HNO₃). The acid treating activates inert carbon surface introducing functional –OH and –COOH groups on the MWCNT surface. The mixture was diluted with distilled water and filtered for several times. The filtered sediment was dried in a plasma cleaner. The powder of such cleaned functionalized MWCNTs (fMWCNTs) was ultrasonicated with deionized water to produce stable colloid. Nickel atoms were injected into the colloid from a positive nickel electrode (with a negative graphite one). The Ni containing tubular nanostructures decorated the fMWCNTs at the specified regulated conditions (temperature, colloid concentration, electric current density). The electrochemically treated colloid was filtered and dried to a powder state (Ni-containing-fMWCNT powder). Hollow NiO nanotubes were produced by the annealing of the powder at 600°C (tubular nanostructured NiO powder). Both powders were examined by the Raman spectroscopy (RS), high-temperature X-ray diffraction (HTXRD), scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA). The estimated high specific surface area of the nanostructured NiO powder is up to 97 m²/g at least and may be varied by time and the electric current of the electrochemical process.

1. Introduction

Carbon nanotubes (CNTs) feature remarkable thermal, mechanical, and electric properties because of their unique nanostructural geometry. These properties have attracted considerable interest since their discovery in 1952 [1]. The tubular geometry of CNTs provides diverse possibilities for the design of promising nanodevices in various fields [2]. Some chemical properties of the CNTs hinder their applications. The CNTs are inert and chemically stable. They are highly hydrophobic tending to self-entangle in water and in other polar liquids. There are treatments that change and improve the properties of CNTs. The CNTs may be functionalized [3,4] coated [5] and filled [6]. External coating (decorative) and the internal filling of CNTs usually become possible only after their functionalization (surface chemical modification) [7]. In this study, MWCNTs are functionalized by their ultrasonication in a mixture of nitric and sulfuric acids. The processing results in surface modification of MWCNTs by hydroxyl (−OH), aldehyde (−COH), and carboxylic acid (−COOH) groups. The oxygen-containing groups make MWCNTs polar and highly dispersible in polar solvents. The as-made fMWCNTs are chemically active. Metal and metal oxide coating and/or filling inside the fMWCNTs produce new nanostructured materials with excellent electrochemical properties [7–9].
The zinc oxide (ZnO) spheres were grown in a chemical process on the external surface of the carbon spheres (CCSs) dispersed in water [10]. Hollow ZnO spheres were produced by subsequent annealing in the air of the ZnO-CCSs composite. The similar approach was successfully applied for the production of other hollow metal oxide micro- and nanospheres [11–13]. Hollow micro- and nanostructures have lower density and higher surface area than the corresponding bulk materials. Such structures show distinct electric and optical properties [14]. In this paper, a general electrochemical method for the synthesis of metal oxide crystal tubular nanostructures is reported. We used the method earlier for CuO growing on the fMWCNTs surfaces and production of hollow CuO nanotubes after subsequent air annealing [14]. Our present study shows the applicability of the method for production of Ni containing coated fMWCNTs and of hollow NiO nanotubes. As a source of the nickel atoms, we use a positive nickel electrode (with a negative graphite one) placed in a water dispersion of the fMWCNTs. Nickel ions deposit onto surfaces of the fMWCNTs, take oxygen and –OH groups and form NiO and nickel hydroxide nanocrystals. The following air annealing at 600°C produced hollow NiO nanotubes.

2. Materials and experimental methods

The used MWCNTs were manufactured by Nanocyl SA (the chemical vapor deposition method). The MWCNTs were 1-5 μm in length, with 12 nm of mean outer diameter, more than 90% of purity. The 60% sulfuric and 70% nitric acids were analytically graded. Pure nickel (99.9%, Ural Mining and Metallurgical Company) plates were used for nickel electrodes. The MWCNT were functionalized according to [15, 16] by ultrasonication in a mixture of nitric and sulfuric acids for 5 hs (with mass ratio 3:1), and at the temperature of up to 42°C. The as-functionalized MWCNTs (fMWCNTs) were diluted with distilled water and filtered for several times. The functionalizing results in MWCNT surface modification [7] (Figure 1).

![Figure 1](image-url) A sketch of the MWCNT and fMWCNT geometries.

The filtered sediment was finally dried in a plasma cleaner. The powder of such cleaned functionalized MWCNTs (fMWCNTs) was ultrasonicated during 2 hs with deionized water (0.012 g of fMWCNTs in 250 ml of water) to produce stable colloid. A high enough level of surface oxidation of the fMWCNTs was verified by the Fourier transform infrared spectroscopy. Nickel anode electrodes were 6×6×0.4 mm3 plates. Working surfaces of the electrodes were mechanically polished and chemically polished, in succession. The nickel anode electrode was fixed parallel to a graphite cathode (10×10×100 mm3 plate) in a bath of the water/fMWCNTs colloid. The distance between electrodes was 15 mm. The electrochemical process was sustained by the electric current between electrodes of 2 mA during some time (t). Then, colloid was filtered, and sediment was dried to a powder state in plasma cleaner. The powder sample was air annealed during the high-temperature X-ray diffraction studies. Raman spectroscopy, thermal gravimetric analysis, and scanning electron microscopy were used to study powder samples of the NiO coated fMWCNTs and of the hollow NiO nanotubes.

3. Results and discussion

The electrochemical crystallization (ECC) of nickel compounds on the fMWCNTs surfaces was performed for various durations (t=2–8 hs). Results for t=4 and 6 hs are presented.
3.1. High-temperature X-ray diffraction (HTXRD)
The HTXRD results demonstrate (Figure 2) that annealing at 600°C transforms possible compounds of NiO, NiCO₃·Ni(OH)₂, and 2NiCO₃·Ni(OH)₂ (peaks labeled X) into NiO powder:

\[
\begin{align*}
\text{NiCO}_3 \rightarrow & \text{NiO} + \text{CO}_2 \uparrow \quad \text{(at t=300°C),} \\
\text{Ni(OH)}_2 \rightarrow & \text{NiO} + \text{H}_2\text{O} \uparrow \quad \text{(at t=230–360°C).}
\end{align*}
\]

![Figure 2. HTXRD of the samples before annealing (25-250°C) and after annealing (600°C). (left) ECC for t = 4 hs and (right) ECC for t = 6 hs. ▼ NiO – nickel oxide peaks, ★ X – chemical intermediates.](image)

3.2. Raman spectroscopy (RS)
RS results demonstrate that air annealing has burnt MWCNTs (Figure 3,4). Characteristic for MWCNTs lines disappear (D = 1336 – 1353 cm⁻¹, G = 1567 – 1600 cm⁻¹, intensities ID > IG) disappear. There are one and two phonon modes for nanocrystal NiO in region 200 – 1100 cm⁻¹ [17].

![Figure 3. RS of the samples (ECC for t = 4 hs) before and after annealing (600°C).](image)
3.3. Thermal gravimetric analysis (TGA)

The TGA (Figure 5,6) graphs show exit of volatile components up to $\approx 550^\circ$C confirming HTXRD results. There is a significant weight loss at 400 – 500$^\circ$C interval corresponding to the MWCNTs burning according to the RS results.

**Figure 4.** RS of the samples (ECC for $t = 6$ hs) before and after annealing (600$^\circ$C).

**Figure 5.** The TGA graph of the samples, ECC for $t = 4$ hs.
3.4. Scanning electron microscopy (SEM)
The results SEM for the samples show the tubular geometry of the nanostructures before and after annealing (Figures 7, 8). Diameters of the structure vary from 14 nm to 34 nm. Structures are entangled but not entangled parts are long (hundreds of nanometers) and may be separated for following studies.

Figure 6. The TGA graph of the samples, ECC for t = 6 hs.

Figure 7. SEM image of the sample before annealing. ECC for t = 4 hs.
3.5. Specific surface area

We present an evaluation of the specific surface area of the NiO nanostructured powder produced with ECC for four hs. Mass fractions of the burnt carbon and of the NiO structures after annealing were $m_C \approx 8.19\%$ and $m_{NiO} \approx 38.27\%$ correspondingly. Therefore, $m_{NiO}/m_C \approx 4.7$. According to SEM results (Figure 7, 8), the coaxial hollow cylindrical form of the NiO nanostructures is assumed. Outer cylinder mean diameter $<D> \approx 22.5$ nm, and root mean square diameter $<D^2>^{1/2} \approx 23.4$ nm. From mass ratio

$$\frac{m_{NiO}}{m_C} = \left( \frac{D^2}{d^2} - 1 \right) \rho_{NiO} / \rho_C,$$

where $<d> = (d^2/\gamma)^{1/2} \approx 16.3$ nm, $\gamma = (m_{NiO} \rho_C / m_C \rho_{NiO}) + 1$, with densities $\rho_{NiO} \approx 6.67$ g/cm$^3$ and $\rho_C \approx 1.5$ g/cm$^3$). The specific surface area of the NiO tubular nanostructures:

$$S_{ud} = \frac{4}{<D - d>} \rho_{NiO} \approx 97 \text{ m}^2/\text{g}$$

4. Summary

In summary, the coating of MWCNTs with nanocrystals of nickel (II) oxide by the electrochemical method was performed. SEM demonstrates a form of the coated MWCNTs and the microstructures after annealing. The form does not change during annealing. TGA demonstrates exit of volatile components, and RS data show burning of the MWCNTs after annealing. The wet and amorphous substance resulting from the electrochemical crystallization at 25°C is complex, and its precise composition is not clear. Possible compounds are NiO, NiCO$_3$·Ni(OH)$_2$, and 2NiCO$_3$·Ni(OH)$_2$. Changes of XRD at different temperatures show that only at about 600°C the NiO composition of the microstructures manifests itself (111, 200, and 220 peaks). The electrochemical method of nickel (II) – fMWCNTs nanocomposite (Ni/fMWCNT) formation may be used to tune the catalytic and physical properties of the nanocomposite. The nickel (II) oxide hollow nanotubes (NiO hNTs) produced by the Ni/fMWCNT annealing is new material. NiO is an excellent catalyst for various oxidation processes including combustion of methane [18]. The catalyzing ability grows with the specific surface area. We performed ECC for durations of $t=2$, 4, 6, and 8 hs. From the general considerations, it seems clear that the thickness of the Ni-containing coating of the fMWCNT must grow with time. Not thick enough Ni-containing coating may degrade with the fMWCNT burning, whereas growth of the thickness leads to a decrease of the specific area. The powder of the NiO nanotubes has a specific surface area up to 97 m$^2$/g (for $t=4$ hs). Other physical and chemical properties of the Ni/fMWCNT and NiO hNTs are being studied.

Figure 8. SEM image of the annealed sample. ECC for $t = 4$ hs.
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