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The electrochemical crystallization of the copper (II) oxide on multi-walled carbon nanotubes

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Abstract. Copper (II) oxide (CuO) crystal structures have been grown on multi-walled carbon nanotubes (MWCNT). For this purpose, functional –COOH and –OH groups were introduced on the surface of MWCNTs by ultra-wave mixing in the H2SO4 and HNO3 bath. The functionalized MWCNTs (fMWCNTs) were washed with distilled water and dried in plasma cleaner. Subsequently, the fMWCNTs were ultra-wave mixed with distilled water. CuO crystal structures were formed on the surface of the fMWCNTs during electrochemical dissolving of copper atoms from a copper electrode. The CuO crystal structures coated the fMWCNTs. These structures formed CuO nanotubes on the fMWCNTs at the specified conditions (colloid concentration, temperature, electric current density). The following annealing process at 500°C produced hollow CuO nanotubes preserving the precursor form. We used high-temperature X-ray diffraction (HTXRD), and Raman spectroscopy (RS) to study the chemical structures. Thermal gravimetric analysis (TGA) confirmed results of HTXRD and RS. Scanning electron microscopy (SEM) showed the tubular geometry of the CuO nanostructures. It was shown that powder of the structures features high specific surface area up to 300 m²/g at least. The possible applications of the structures in nanotechnology and of the powder as a catalyst are discussed.

Keywords: Copper (II) oxide, multi-walled carbon nanotubes, CuO nanotubes

1. Introduction
The unique nanostructural geometry and corresponding excellent mechanical, thermal and electric properties have attracted much attention to the MWCNTs since their discovery in 1952 [1]. The tubular structure of MWCNTs provides possibilities for the design of diverse and promising applications on their basis [2]. The MWCNTs are chemically stable, inert; tend to self-entangle in polar liquids (highly hydrophobic). The properties of MWCNTs may be changed and improved by different treatments such as functionalizing [3,4], coating [5] and filling [6]. Functionalizing of MWCNT means its surface chemical modification. In this investigation, the functionalizing implies ultrasonication using a mixture of strong acids and resulting in surfaces of MWCNTs been modified by carboxylic acid (–COOH) and hydroxyl (–OH) groups. The as-made fMWCNTs feature high dispersity in polar solvents. Oxygen-containing groups improve the interaction of fMWCNTs with metal and metal oxide nanoparticles. Therefore the functionalizing of the MWCNTs is usually a
necessary preliminary stage of coating (decoration) of MWCNTs by metals and metal oxides [7]. It was shown earlier [8] that size-tunable zinc oxide (ZnO) spheres might be grown on the surface of the colloidal carbon spheres (CCSs) in a chemical process. Calcination in the air of the ZnO-CCSs produced hollow ZnO spheres. The similar strategy was successful for other nanostructural designs of hollow metal oxide nano- and microspheres [9-11].

In this study, CuO crystal tubular structures have been grown on fMWCNTs as a result of the electrochemical dissolution of copper from a surface of copper positive electrode placed in a water colloid of the fMWCNTs. Copper ions deposited onto surfaces of the fMWCNTs taking oxygen and –OH group and forming CuO and copper (II) hydroxide (Cu(OH)2) nanocrystals. The following annealing process at 500°C produced hollow CuO nanotubes preserving the tubular form of the MWCNTs.

2. Materials and Methods

We purchased the MWCNTs manufactured by Nanocyl SA by the chemical vapor deposition. The MWCNTs were about 10 nm of outer diameter, 1-70% nitric and 60% sulfuric acids were analytically graded. Pure copper (99.996%) plates (PCPs) were purchased from Ural Mining and Metallurgical Company.

Copper anode electrodes were 10×10×0.45 mm3 PCPs. Surfaces of the anode electrodes were in succession polished, annealed, undergone acid-etching in nitric acid and finally chemically polished. The fMWCNT were prepared according to [12,13] by ultra-wave mixing for 5 hs in the H2SO4 and HNO3 bath (with mass ratio 3:1) at the temperature of up to 42°C. The functionalized MWCNTs (fMWCNTs) were washed with distilled water and dried in plasma cleaner (PLASMA SYSTEM FEMTO PCCE). The Fourier transform infrared spectrometer (Nicolet iS50, 0.125 cm−1) showed a high level of surface oxidation of the fMWCNTs. The experimental setup consisted of the copper anode electrode fixed parallel to a flat surface of a graphite cathode plate (10×10×10 mm3). The distance between parallel surfaces of the electrodes was 15 mm. To produce the water/fMWCNTs colloid the fMWCNTs were ultrasonicated with distilled water during 2 hs (0.012 g of fMWCNTs / 250 ml of water). We placed the electrodes into a bath of the water/fMWCNTs colloid. The electric current between electrodes was sustained at 4 mA during some time (t) for all experiments of electrochemical crystallization (ECC) of copper compounds. Then power was turned off, water was drained, sediment was dried in plasma cleaner. The following annealing of the sediment was performed during high-temperature X-ray diffraction studies (GBC αMMA X-Ray Diffractometer).

High-temperature X-ray diffraction (HTXRD), Raman spectroscopy (RS), thermal gravimetric analysis (TGA) (STA 8000), and scanning electron microscopy (SEM) (JEOL JSM-66510LV) techniques were used to study properties of the hollow CuO nanotubes.

3. Results and Discussion

The ECC of copper compounds on fMWCNTs was performed for various durations. Here we present results for two durations t=2 and 4 hs as of most demonstrative. Results of HTXRD (Figure 1) demonstrate that annealing at 500°C leads to transformation of possible compounds of CuO, CuCO3·Cu(OH)2, 2CuCO3·Cu(OH)2, Cu(OH)2 (peaks labeled X) into CuO powder: CuCO2→CuO+CO2↑ (at t=290°C), Cu(OH)2→CuO+H2O↑ (at t=150°C). Results of RS show (Figure 2) that annealing has burnt MWCNTs. Lines D = 1336 – 1353 cm−1 and G = 1567 – 1600 cm−1 (with intensities ID >IG) that are characteristic for MWCNT disappear. There are CuO modes in region 200 – 700 cm−1. It is known that A2g+2B1g modes appear at 298, 345, 632 cm−1 for powder and crystal CuO [14, 15]. For nanocrystal CuO structures these peaks move with considerable broadening [16]. Results of TGA (Figure 3) confirm HTXRD results showing exit of volatile components up to ≈ 350°C. Results of TGA also confirm RS showing burning of MWCNTs in 400 – 500°C interval. The SEM results show the tubular geometry of the CuO nanostructures after annealing (Figurs 4, 5). Diameters of the CuO nanotubes grow over time of the ECC. According to the TGA (Figure 3, right) for t = 4 hs mass fraction of the burnt carbon and of CuO after annealing were MC≈ 9.99 % and MCuO≈ 52.93 %
correspondingly. Therefore, $M_C/M_{CuO} = 5.3\%$. We assume the coaxial cylindrical form of the CuO nanostructures ($D$ and $d$ being outer and inner their diameters correspondingly). According to the SEM data (Figure 5) $D = 28.4$ nm, $d = D/\gamma = 20.7$ nm, $\gamma^2 = M_{CuO}P_C/(M_CP_{CuO}) = 1.88$ (from $M_{CuO}/M_C = (D^2/d^2-d^2)^3P_{CuO}/P_C$), where densities $P_{CuO} = 6.31$ g/cm$^3$ and $P_C = 1.35$ g/cm$^3$). The specific surface area of the CuO nanostructures: $S = 4/((D-d)P_{CuO}) = 164$ m$^2$/g.

Figure 1. XRD spectrum of the samples before annealing (25°C) and after annealing (500°C). (a) ECC for $t=2$ hs and (b) ECC for $t=4$ hs.

Figure 2. RS of the samples before annealing and after annealing (500°C). Top – ECC for $t=4$ hs, bottom – ECC for $t=2$ hs.
Figure 3. TGA of the samples after annealing (500°C). Left – ECC for t = 2 hs, right – ECC for t = 4 hs.

Figure 4. SEM image of the annealed sample. ECC for t = 2 hs.
4. Conclusion
In summary, the formation of CuO hollow nanotubes on MWCNTs with the electrochemical method was studied. The electrochemical method of copper oxide nanocomposite formation may be used to tailor chemical and physical properties of the ordered stabilized carbon nanotubes in dependence on various factors. Presented novel technics of copper oxide hollow nanotubes production needs to be refined. Results of the study may be used for the creation of new functional materials. Semiconductive CuO nanotubes may be used in nanoelectronics. The CuO nanostructured powder has big specific surface area up to 164 m$^2$/g according to our evaluation. Therefore it may be used as an active catalyst for various oxidation processes.

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