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Sonochemical growth of antimony sulfoiodide in multiwalled carbon nanotube

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ABSTRACT

This paper presents for the first time the nanocrystalline, semiconducting ferroelectrics antimony sulfoiodide (SbSI) grown in multiwalled carbon nanotubes (CNTs). It was prepared sonochemically using elemental Sb, S and I in the presence of methanol under ultrasonic irradiation (35 kHz, 2.6 W/cm^2) at 323 K for 3 h. The CNTs filled with SbSI were characterized by using techniques such as powder X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, high-resolution transmission electron microscopy, selected area electron diffraction, and optical diffuse reflection spectroscopy. These investigations exhibit that the SbSI filling the CNTs is single crystalline in nature and in the form of nanowires. It has indirect forbidden energy band gap E_{gIf} = 1.871(1) eV.

1. Introduction

Since their discovery by [1] various potential applications have been proposed for carbon nanotubes (CNTs): sensors, field emission displays, nanometer-sized semiconductor devices and hydrogen storage media. There is a huge literature stream related to nanotube research. On a fundamental level, there are still challenges to mass-produce controlled nanostructures at reasonable cost and new features. One strategy is to use the CNTs themselves, controlling useful properties *via* their radii and morphologies. An alternative approach leading to new features of CNTs, i.e., directional action on their versatile electronic characteristics, is based on filling them with condensed substances from a wide range of materials. CNTs are sp^2 graphene carbon cylinders capable of hosting a variety of species, including 1D crystals of metals, metal salts and oxides; semiconductors; superconductors; helical iodine chains; and chains of fullerene or endofullerene molecules (see e.g., literature cited in [2–4]). Among crystals grown within CNTs there are halogenides: BaI_2 [4], KI [5], LaI_2 [6], LaI_3 [7], CoI_2 [8], $LaCl_3$ [9], UCl_4 [10], $(KCl)_x(UCl_4)_{1-x}$ [10], and $AgCl_{1-x}I_x$ [3]. Such objects are distinguished in their properties from both hollow nanotubes and the encapsulated substances, which permits one to purpose-tailor "nanowires" and "nanocables" with unique physical and chemical properties [2,7].

These studies have been prompted by a desire to synthesize a new hybrid material on the nanometric scale: the antimony sulfoiodide (SbSI) within CNTs. Recently [11] a novel sonochemical method for direct preparation of semiconducting and ferroelectric SbSI nanowires has been established. The determined [11] value of the indirect forbidden energy band gap of SbSI gel E_{gIf} = 1.829(27) eV is well compared to the bulk value of band gap of SbSI reported in the literature (see Refs. in [11]). The maximum of dielectric constant $\varepsilon = 1.6 \times 10^4$ of SbSI nanowires was observed at Curie temperature T_c = 292(1) K [12] that well corresponds with the phase transition in bulk SbSI crystals. It should be underlined that the bulk SbSI has an unusually large number of very interesting properties. Among them there are the photoferroelectricity, pyroelectric, pyrooptic, piezoelectric, electromechanical, electrooptic, photorefractive and nonlinear optical effects. Therefore SbSI is taken into consideration as a valuable material for many applications (see the literature cited in [11]).

The current status of research in sorption properties of CNTs was reviewed in [2]. There are known a few methods for filling CNTs with different substances [2]: catalytic synthesis of nanotubes using the metals as catalysts, capillary drawing-in of molten

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materials or materials dissolved in solvents having a low surface tension, saturation with metal vapor as well as electrochemical methods based on passing the electrical current through an electrolyte containing dissolved metal atoms. In this paper we used another method for inserting materials into the inner cavity of a nanotube. Our method is based on sonochemistry. It is well known [13–16] that ultrasound can induce new reactivities leading to the formation of unexpected chemical species, what makes sonochemistry unique is the remarkable phenomenon of cavitation [16,17]. Comparing sonochemical method of preparing materials with the traditional ones, it can be seen that ultrasound irradiation can be used at room temperature and ambient pressure to promote heterogeneous reactions that normally occur only under extreme conditions of hundreds of atmospheres and degrees (see e.g., [13,18]).

2. Experiment

The SbSI was prepared in CNTs ultrasonically from the constituents (the elements Sb, S and I). Methanol served as the solvent for this reaction. All the reagents used in our experiments were of analytical purity and were used without further purification. Antimony (99.95%) and multiwalled CNTs (90+%) were purchased from Sigma–Aldrich. Sublimated sulfur (pure p.a.), iodine (pure p.a.) and absolute methanol (pure p.a.) were purchased from POCH SA (Gliwice, Poland). In a typical procedure, the elemental mixture with stoichiometric ratio of e.g., 0.380 g Sb, 0.099 g S and 0.394 g I, was immersed with 0.282 g of CNTs in 40 ml absolute methanol, which was contained in a 54 ml Pyrex glass cylinder of 20 mm inside diameter. The cylinder was partly submerged in water in an ultrasonic reactor (InterSonic IS-UZP-2, frequency 35 kHz, with 75 W electrical power and 2.6 W/cm^2 power density guaranteed by the manufacturer). The used experimental set up and the applied procedure were the same as the described in [11]. The sonochemical process was continued 3 h at 323 K temperature of the water in the ultrasonic reactor. When the sonification process was finished a dark sol was obtained. It was centrifuged using the MPW-223e centrifuge, MPW Med. Instruments (Poland), to extract the products. Then the liquid above the sediment was replaced with pure methanol to wash the precipitates. The centrifugation and washing were performed 5 times. At the end methanol was evaporated from the sample during the drying in air at room temperature, so a brown-purple substance was obtained.

Characterization of the multiwalled CNTs filled with SbSI was accomplished using different techniques, such as powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and optical diffuse reflection spectroscopy (DRS). Description of the used equipments and the applied procedures were given in [11].

3. Results

The powder XRD pattern of the CNTs filled with SbSI is shown in Fig. 1. The well-defined, sharp diffraction lines suggest the well-crystallized substance. It was found that the diffraction lines can be divided into three groups. In the first group, containing most of the lines, the peaks can be indexed to be a pure orthorhombic phase for SbSI with the cell constants $a = 0.858$ nm, $b = 1.017$ nm, and $c = 0.414$ nm. The identification was done using the PCSIWIN computer program and the data from JCPDS-International Centre for Diffraction Data 2000. The intensities and positions of the peaks are in good agreement with literature values for SbSI [19]. The second group of diffraction lines can be indexed to be a carbon phase

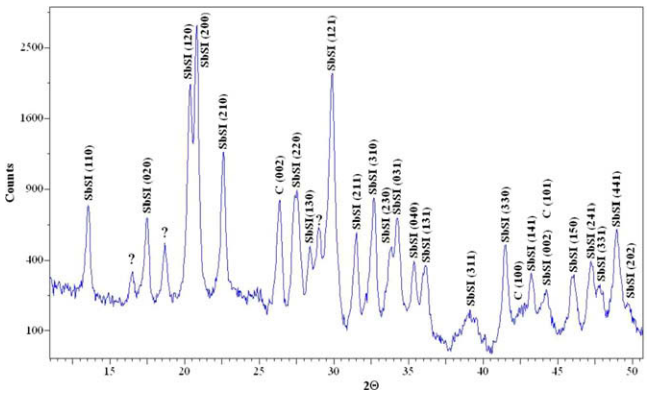

Fig. 1. The powder XRD pattern of dried multiwalled CNTs filled with SbSI ultrasonically in methanol.

Table 1
Positions of the unidentified X-ray diffraction peaks in the powder XRD pattern of dried multiwalled CNTs filled with SbSI ultrasonically in methanol.

2θ (°)	d_{hkl} (nm)
16.51	0.536
18.66	0.475
29.00	0.308

$P6_3mc$ with the cell constants $a = 0.2470$ nm and $c = 0.6790$ nm [20]. The third group of a few additional X-ray diffraction lines is presented in Table 1. They are discussed in the next section.

The typical SEM micrograph of dried CNTs filled with SbSI prepared ultrasonically in methanol is shown in Fig. 2. The EDAX analysis of this material was also done, and only characteristic peaks for carbon, antimony, sulfur and iodide were observed (Fig. 3). The measured atomic concentrations of Sb, S, I and C are presented in Table 2 and discussed in the next section.

The TEM (Figs. 4 and 5) and HRTEM (Fig. 6) of an individual CNTs sonochemically filled with SbSI reveals that the product consists of coaxial nanocables. The lateral dimension of the nanocables (see the representative SEM and TEM images in Figs. 2, 4 and 5) is

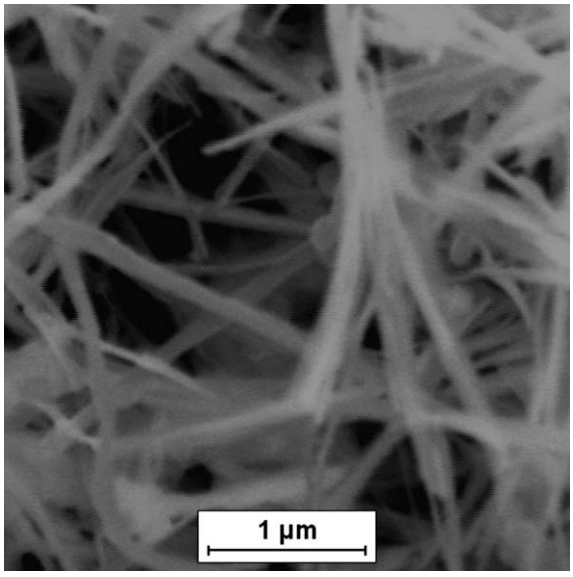

Fig. 2. The typical SEM micrographs of dried multiwalled CNTs filled with SbSI ultrasonically in methanol.