Morphological Studies of Bismuth Nanostructures Prepared by Hydrothermal Microwave Heating.

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ABSTRACT

Elemental bismuth nanoparticles and nanotubes were obtained via microwave hydrothermal synthesis starting from bismuth oxide (Bi_2O_3) in the range of temperatures 200-220^{o}C for 10-45 min. The formed nanostructures were studied by scanning electronic microscopy (SEM) and transmission electronic microscopy (TEM). Relationship between reaction parameters and shape of the formed nanostructures is discussed.

Keywords: bismuth, nanotubes, truncated nanospheres, microwave hydrothermal synthesis.

1 INTRODUCTION

Metallic bismuth is an important element, having a lot of distinct industrial applications as a component of low-melting alloys, catalysts, for production of polonium in nuclear reactors and tetrafluorhydrazine, among others. High-purity metal is used, in particular, for measuring super-strong magnetic fields. Bismuth in nanostructurized forms has been mentioned in some recent monographs [1-4], reviews [5-7], patents [6-7], and a lot of experimental articles. Bismuth nanoparticles, nanopowders, nanowires, nanofilms and other nanostructurized forms have been produced by a host of methods, among which, microwave heating (MW) has been also used to obtain bismuth nanostructures [8]. Thus, microwave treatment of bulk bismuth in air in a domestic MW-oven (power 800 W and frequency 2.45 GHz) led to formation of bismuth nanoparticles (60-70 nm) with Bi_2O_3 impurities [9], in a difference of a similar treatment in vacuum [10, 11], when Bi nanotubes formed for 5-15 min. The optimal MW-heating process time was 60 min; the process was found to be highly reproducible and easy. The ***objective*** of this report is the study and comparison of various bismuth nanostructures, observed as a result of the synthesis in the conditions of microwave hydrothermal procedure.

2 EXPERIMENTAL

The reactions were carried out in a Teflon autoclave (equipment MARS-5), using bismuth(III) oxide as a precursor and ethyleneglycol (EG) as a reductant. Due to the necessity to exceed boiling point of EG (187^{o}C) and security limits of the equipment, the syntheses were made in the range 200-220°C, reaching pressure close to 300 psi. The reaction times were 10, 15, 30 and 45 min. The formed nanostructures were studied by scanning electronic microscopy (SEM, equipment Hitachi S-5500) and transmission electronic microscopy (TEM, equipment JEOL 2010-F).

3 RESULTS AND DISCUSSION

The samples, heated for 10-15 min at 200°C, were analyzed by high-resolution TEM, where 5 nm nanoparticles were observed (Fig. 1a). Fig. 1b shows a nanostructure having 5 nm diameter and length of 58 nm, constituted of various aligned more thin structures. It can be affirmed that these nanoparticles grow accordingly to the bottom-up type: the nucleation process takes place, in which, meanwhile the reduction of bismuth oxide occurs, the bismuth atoms are being added to the particle constructing different nanoforms.

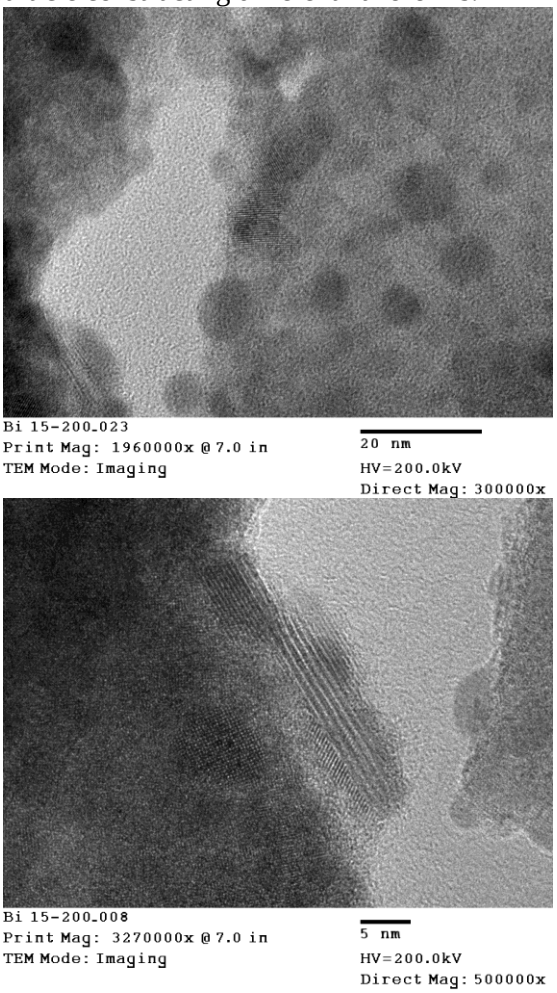


Fig. 1. TEM images of the formed nanostructures (15 min heating at 200°C). The image a) shows nanoparticles with <10 nm size; the image b) shows the growth of nanotube agglomerates.

Fig. 2 (in this case, the heating time was 10 min and temperature 220°C) shows high-resolution TEM images of nanoparticles with 15-20 nm diameters, one of which is shown in a larger scale in Fig. 3. The nanoparticles are of a spherical or truncated-spherical form. No nanotubes were observed for 10 min heating.

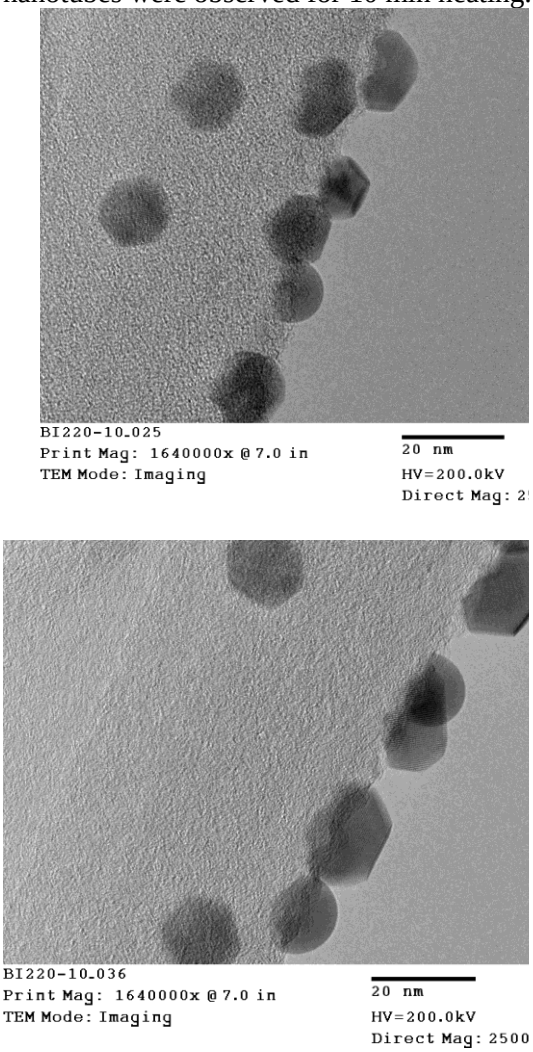
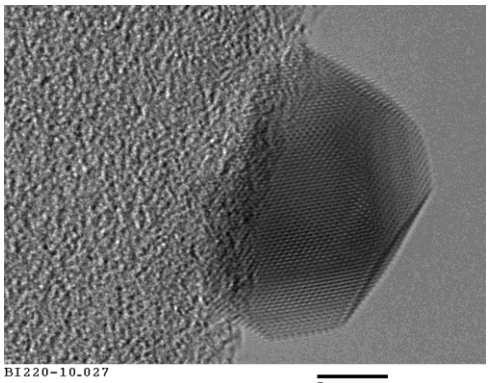
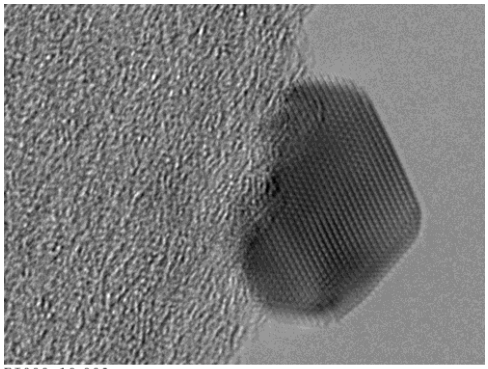


Fig. 2. TEM images of samples, heated for 10 min at 220°C.



a



b

Fig. 3. High-resolution TEM images of the samples, heated for 10 min at 220°C: a) nanoparticle with a visible diameter of 18.8 nm; b) nanoparticle with sizes of 13.52 nm x 17.94 nm and interatomic distance of 3.5 Å

Further increase of heating time to 30-45 min leads to formation of two types of nanostructures, depending on temperature: spherical nanoparticles are observed in the samples heated at 200°C and 220°C (Fig. 4), as well as multi-wall nanotubes (Fig. 5), observed heating at 220°C only. The maximum observed diameter of spherical nanoparticles reaches 500 nm.

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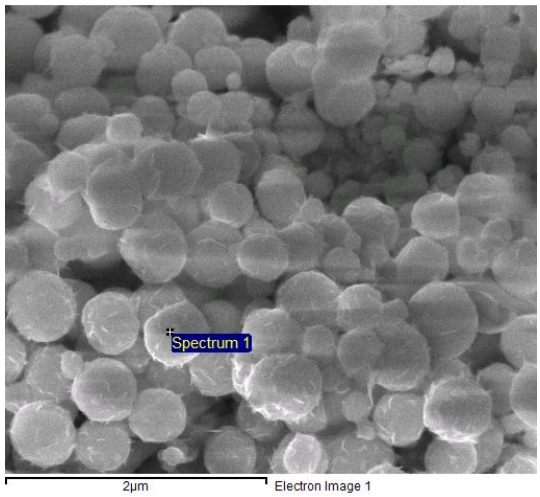

Fig. 4. SEM image of spherical nanoparticles (the sample, heated for 45 min at 220°C).

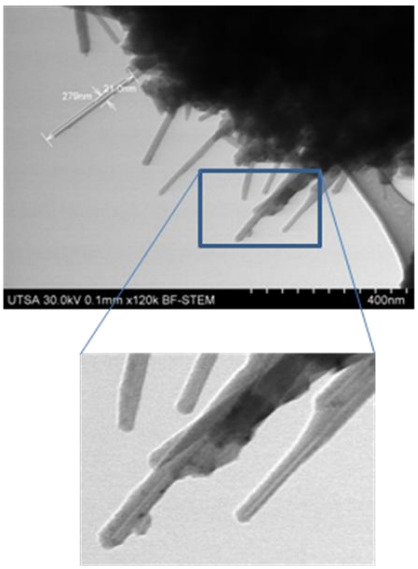

Fig. 5. S-TEM image of nanotubes (the sample, heated for 45 min at 220°C).

4 CONCLUSIONS

Elemental bismuth was obtained in the form of nanoparticles and nanotubes in the conditions of microwave hydrothermal heating. Complete reduction of bismuth oxide to metallic bismuth was observed starting from 10 min of

treatment. Agglomerates and blocks of metallic nanotubes were observed at intermediate heating times (15-30 min), meanwhile short (10 min) and large (45 min) treatment durations led to spherical and truncated spherical nanoparticles. Additionally, multi-wall nanotubes were observed at large heating times and higher temperature.

5 ACKNOWLEDGMENT

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