Hollow boron nitride spherical nanoparticles: synthesis, structure and applications.

Andrey Kovalskii *, Andrei Matveev *, Oleg Lebedev **, Irina Sukhorukova *, Konstantin Firestein *, Alexander Steinman *, Dmitry Shtansky *, Dmitri Golberg ***

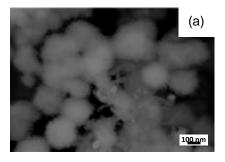
- * National University of Science and Technology "MISIS", Leninskiy prospect 4, Moscow 119049, Russia
- ** CRISMAT, UMR 6508, CNRS-ENSICAEN, 6Bd Marechal Juin, Caen 14050, France
- *** National Institute for Materials Science (NIMS), Namiki 1, Ibaraki, Tsukuba 3050044, Japan andreykovalskii@gmail.com

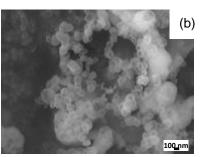
Nanoparticles of spherical morphology find many areas of application now, significant usages are at the moment are actively developing in biological, medical and ecological fields. Due to excellent physical-chemical properties of boron nitride, applications of its nanospheres can significantly expand areas of utilization. The question of present interest in regards of such nanoparticles is the development of high yield synthetic method which may produce particles of homogenous size. In the present work the new nanomaterial consisting of hollow spherical BN nanostructures with smooth and petal-like surfaces was obtained for possible applications in composite materials and as drug delivery containers.

Synthesis of BN nanospheres with an external diameter of 80-250 nm was carried out by CVD method using boron oxide vapor and flowing ammonia in a BN ceramic reactor placed in a vertical induction furnace. Three types chemical compound powders with a different ratio of constituents were used as a source of B₂O₃ vapor: FeO+MgO+B, SnO+MgO+B and H₃BO₃+MgO+B. The temperature in a location area of the precursor was varied over the range of 1200-1430°C. Synthesis was carried out for 200-420 min. Products of syntheses were collected on the walls of BN crucible in a low temperature zone out of BN reactor as a thick light snow-white material. Typically, using 10 g of the precursor was enough to synthesize about 250-400 mg of the material in 420 min.

The morphology of synthesized products and their elemental composition were studied using a scanning electron microscope JEOL JSM-7600F equipped with the EDX detector. As was revealed by SEM analysis, the synthesized powders obtained in all experimental conditions consist of agglomerates of spherical nanoparticles with a hollow core and an average size 80-200 nm (Fig. 1a, b), and a petal-like surface made of nanosheet-like flakes. After some syntheses hollow spherical particles with smooth surface were also observed. The synthesized products were proved to be of the BN phase with a hexagonal structure using EDX, XRD and FTIR methods. It was shown that the experimental conditions mostly affected the impurity content and the yield of the nanomaterial product.

Low-magnification (Fig. 1c, Fig. 2a, b), and high-resolution TEM investigations of synthesized nanoparticles were carried out and it was demonstrated that agglomerates consist of round shape nanoparticles. The corresponding SAED pattern taken from the number of BN nanoparticles contains two diffuse rings with d-spacings roughly corresponding to the BN interplanar spacings (d_{002} and d_{100}). TEM analysis shows (Fig. 2b) that nanoparticles exhibit a hollow spherical central part and a petal-like surface due to exposed BN layers at the side area. On the HRTEM image of surface area (Fig. 2c) one can observe nanospheres build up from exposed BN layers with typically two to six stacked sheets.





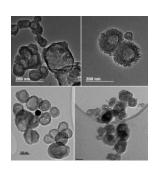
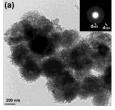
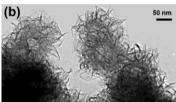


Fig. 1 SEM image of agglomerates of (a) petal-like and (b) smooth spherical BN nanoparticles with an average size 100-200 nm. (c) LM-TEM image of petal-like and smooth BN nanospheres.





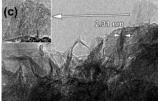


Fig. 2 (a, b) BF LM-TEM image of petal-like BN nanospheres; (c) HRTEM image of the side region of a BN nanosphere.

(c)

The applications of obtained spherical BN nanoparticles for the reinforcement of composite materials and as a drug delivery containers are demonstrated.