Doctoral dissertation

***"Structural and Surface Modification of Carbon Nano-Onions and Studies Their Physicochemical Properties"***, Olena Butsyk

# ABSTRACT

The main assumption of the doctoral dissertation was structural and surface modification of carbon nano-onions in order to obtain their specific physicochemical properties, including electrochemical and catalytic ones. The modifications were performed in two ways: using physical factors (temperature and the composition of gas atmosphere), and/or using various chemical modifiers (chemical reagents).

In the first section of the dissertation, on the basis of literature data the author describes the structure, synthesis and physicochemical properties of CNOs, with particular consideration of spherical CNOs obtained through the annealing of diamond nanoparticles. A spherical CNO consists of a fullerene core ($C_{60}$) surrounded by graphene layers, with rings mostly arranged in hexagonal (but also pentagonal and heptagonal) pattern. Annealing ND at 1,500-1,900°C leads to the formation of spherical CNOs with the diameter of 5-8 nm, containing 6 to 8 graphene layers. This section also presents literature reports concerning structural and surface modification of CNOs. The author reviews the directions of potential applications of CNOs, especially as regards their use in energy storage systems and in catalytic processes.

In the experimental section, the synthesis of doped CNOs and comprehensive physicochemical characteristics of the modified CNOs are described. A number of research methods were used in the work: transmission and scanning electron microscopy (TEM and SEM), Fourier-transform infrared spectroscopy (FTIR), energy-dispersive X-ray spectroscopy (EDS), Raman spectroscopy, solid state magnetic-angle spinning spectroscopy (MAS NMR), X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), porosimetry, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge measurements. The use of these experimental methods made it possible to determine the relationship between the structure, chemical composition and physicochemical properties of the CNOs. Structural modification was performed via *in situ* synthesis, using varying experimental conditions and doping the carbon

nanostructures with nitrogen or boron atoms. Surface modification involved the modification of CNOs with nitrogen and/or sulfur atoms via post-preparative synthesis.

It was shown that the conditions of CNO synthesis, such as the temperature of annealing (1,650 and 1,750°C) and gas atmosphere (air, $N_2$ or $CO_2$) affected CNOs' structural properties, their shape, and distances between the graphene layers. The process of annealing previously formed spherical CNOs in $CO_2$ atmosphere led to the compression of carbon nanostructure, reducing the distances between carbon layers and changing the shape of the CNOs. In this process, eliptical, polygonal and other irregular nanostructures were formed in addition to spherical carbon nanostructures. Higher degrees of graphitization of CNOs obtained at higher annealing temperatures were confirmed with the use of spectroscopic methods. CNOs obtained in air atmosphere had the highest values of specific surface, pore volume and size, and exhibited optimum electrochemical properties. Structural, textural and electrochemical studies showed that CNOs obtained at 1,650 and 1,750°C and later annealed in air atmosphere had the best electrochemical properties and can be used in the future as electrode materials in capacitors.

Adjusting the amount of modifier, amorphous boron, added to nanodiamond, or annealing temperature of the aminated nanodiamond, two kinds of doped carbon nano-onions were obtained: boron- (B-CNO) or nitrogen-doped (N-CNO) carbon materials. The substitution of some C atoms in CNO graphene layers with B or N atoms was confirmed by spectroscopic methods (XPS, infrared spectroscopy, Raman spectroscopy, and solid state NMR). In addition, detailed physicochemical characterization of B-CNOs and N-CNOs was performed using microscopic methods (TEM and SEM), X-ray powder diffraction, thermogravimetric analysis and porosimetry. Electrochemical activity of the obtained doped carbon materials was characterized by using electrochemical methods, i.e., cyclic voltammetry, galvanostatic charge–discharge measurements, and electrochemical impedance spectroscopy. It was shown that doping CNOs with B atoms improves their electrochemical parameters, including specific capacity, energy density, and power density. The highest values of specific capacity exhibited CNOs with the lowest amount of boron in the starting material. In the case of N-CNOs, increased catalytic efficiency of the materials in non-enzymatic determination of hydrogen peroxide was shown. N-CNOs obtained at 1,650°C showed the highest catalytic activity for detection of $H_2O_2$.

CNOs were doped with N and/or S via post-preparative synthesis in the conditions of thermal and hydrothermal reaction with a number of modifiers, i.e., pyrrole, urea, ammonia base, thiourea and amorphous sulfur. In these experimental conditions, only the outermost graphene layer of a CNO was modified. This type of modification is surface modification. The conducted spectroscopic (Raman, FTIR), microscopic (SEM), X-ray powder diffraction, thermal analysis and low temperature nitrogen adsorption/desorption measurements confirmed changes in the outermost graphene layers of CNOs and the presence of functional groups on their surface. It was proved that S-CNOs had the highest thermal stability in comparison to other modified CNOs, as well as the best textural parameters. N-CNOs, S-CNOs and N-S-CNOs had bigger pores than non-modified CNOs. The presence of oxygen, nitrogen and/or sulfur groups led to the improvement of electrochemical properties of CNOs modified with these elements. In the presence of pyrrole, amorphous sulfur in thermal conditions and thiourea in hydrothermal conditions, specific capacity values of doped carbon nanostructures are almost twice as high as those of non-modified CNOs.

The introduction of heteroatoms of B, N and/or S via structural and surface modification to the spherical structure of CNOs changed their physicochemical properties, improved their ability to store electric charge, and improved their catalytic properties. The results of the experiments confirmed that modified carbon nanostructures can be used in electrochemical sensors and energy storage devices, e.g., capacitors.

Białystok, 05.06.2018r.