JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **6** No 3, 03035(3pp) (2014)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **6** № 3, 03035(3cc) (2014)

Theoretical Studies of the Structure of the Metal-carbon Composites on the Base of Acryle-nitrile Nanopolimer

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(Received 19 May 2014; published online 15 July 2014)

The presence of the metal compounds in the acryle-nitrile nanopolimer (PPAN) leads to the formation of the metal nanoparticles. The metal-carbon nanocomposites based on PPAN including pair connections with iron and cobalt has been theoretically investigated. The spatial configuration of the nanocomposite for each option of the arrangement of metal atoms has been received. The analysis of the received results for all options of the arrangement of the metal atoms allowed defining the binding energy of the systems and the width of the forbidden gap ΔE_g of the nanocomposite. The analysis of the electronic and energy structures of the system found out that the introduction of the metal atoms leaded to the essential reduction of the width of the forbidden zone of the composite in comparison with the pure PPAN.

Keywords: Metal-carbon nanocomposite, Carbon matrix, Pair connection, Acryle-nitrile nanopolimer.

PACS number: 73.22. – f

1. INTRODUCTION

It is experimentally revealed [1, 2] that processes of chemical transformations in acryle-nitrile nanopolimer (pyrolyzed polyacrylenitrile PPAN) lead to formation of the nanoparticles of the metal evenly distributed and included in structure of a carbon matrix. It is possible to the presence of the metal compounds. The essential interest to the nanostructured materials including a nanoparticle of ferromagnetic metals in its structure, is caused by the specific magnetic properties which are showing in a nanodimensional state: high magnetization, possibility to change the values of coercive force due to the dependence of this quantity from the sizes of nanoparticles, Curie's lower temperature, high anisotropy, etc. Despite the active using and the numerous pilot researches of nanocomposites based on PPAN till our days the geometrical structure (morphology) and the features of the electronic and power structure of metal-carbon materials are not enough studied. The optimum structure of PPAN was defined in the work [3, 4] with the using of the semiempirical MNDO, PM3 methods and the density of functionality theory [5-8] (with functionality of B3LYP, PBE). This work presents the results of the theoretical research of metal-carbon nanocomposites based on PPAN including nanoparticles of the pair connections with the metals of iron and cobalt.

The model of a monolayer of carbon material at which there were two atoms of metal – atoms of iron and cobalt was used for the research of the structure and the calculation of the electronic and power characteristics of metal-carbon nanocomposites based on the PPAN. These atoms were built in the PPAN plane, replaced the atoms of a monolayer in the following options: 1) replaced six next atoms of carbon, 2) replaced 5 atoms of carbon and 1 atom of nitrogen. To make the calculations of a nanocomposite, the cluster containing, besides atoms of carbon, 6,7 % of hydrogen, 8,71 % of nitrogen and 1,34 % of a replacing element (atoms of metals) was got out. The calculations were carried out within the density of the functional theory with the using of the potential of B3LYP. Two options of the arrangement of the metal atoms in the plane of the monolayer PPAN differing with an atomic encirclement, namely, by existence (or absence) atom of nitrogen in the immediate environment were investigated. The considered options are presented in Fig. 1.

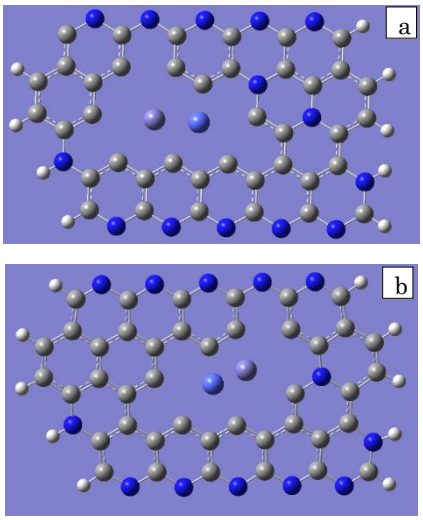

Fig. 1 – a) The option of the 1st arrangement of the atoms of iron and cobalt in the planes of the monolayer of PPAN, atom of N is located at the distance of the second neighbor; b) The option of the 2d arrangements of the atoms of iron and cobalt, atom of nitrogen is in the immediate encirclements

The spatial configuration of the nanocomposite for each option of the arrangement of the metal atoms was received as a result of the calculations executed with full optimization of the geometry of metal-carbon system. And also the analysis of the results discovered that there was a curvature of the plane of the monolayer of the nanocomposite received from initially planar monolayer of PPAN, besides, the atoms of the monolayer and the introduced metal atoms which formed new hexagonal and pentagonal structures (Fig. 2, 3) for all options and for all considered atoms of metals. The

The article was reported at the International Conference «The Advanced Technology, Equipment and Analytical Systems for Materials», Kursk, 13-14 May, 2014

distance between the atoms of iron and cobalt for both options was equal 1,57 Å that corresponded to the interatomic distances in a cubic lattice.

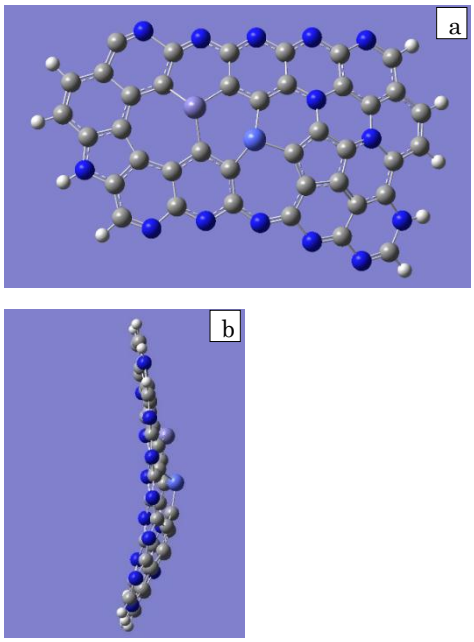

Fig. 2 – Clusters of a metal-carbon nanocomposite based on PPAN for option of the 1st arrangement of the metal atoms of in the monolayer plane: a) top view, b) side view

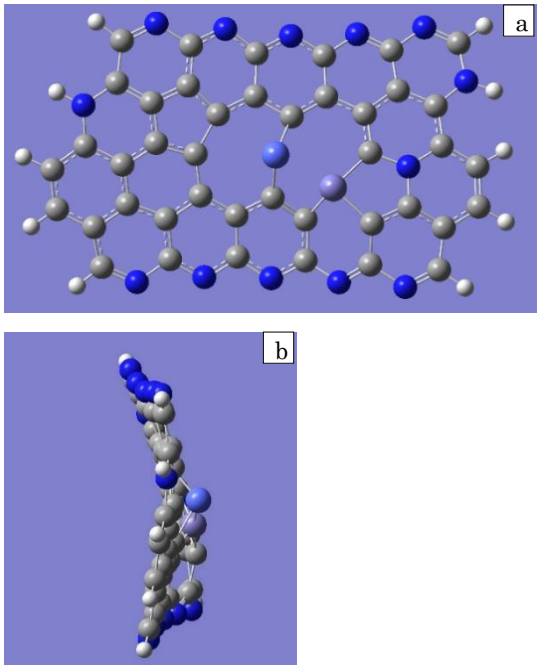

Fig. 3 – Clusters of a metal-carbon nanocomposite based on PPAN for option of the 2nd arrangements of the metal atoms in the monolayer plane: a) top view, b) side view

The analysis of the received results for all options of the arrangement of the metal atoms allowed defining the binding energy of the systems and the width of the forbidden gap ΔE_g the nanocomposite, represented in Table 1. The values of the binding energy, comparable with the values of the energy for the pure PPAN, proved that the received metal-composites were stable. It is established that the introduction of the metal atoms in the monolayer of PPAN leads to the reduction of the width of the forbidden gap in comparison with the width ΔE_g of the pure PPAN.

The analysis of the electronic and energy structures of the nanocomposite showed that levels of the molecular orbitals (MO) were being grouped in zones. MO were responsible for the conditions of the valency zone 2*s*- and 2*p*-atomic orbitals (AO) of carbon and nitrogen atoms of PPAN made an important contribution to these conditions. The bottom of the conductivity zone was composed of atomic orbital, the energy levels corresponding 2*p*-AO of the carbon atoms gave the main contribution in this one. For PPAN with the introduced metal atoms of side by side with the deposits of atoms of C and N the orbitals were found. The main contribution was bringing by 2*s*-and 2*p*-orbitals of iron and cobalt atoms and their levels were located in the border of the conductivity zone (give the contribution to the bottom of the conductivity zone). That leaded to reduce the bottom of the conductivity zone in comparison with the pure PPAN and leaded to the corresponding reduction of the width of the forbidden gap in both cases of the arrangement of the metal atoms in the plane of the monolayer of PPAN.

Table 1 – Electronic and energy characteristics of metal-carbon nanocomposites based on PPAN with the introduced pair atoms of iron and cobalt: E_b – binding energy, ΔE_g – width of the forbidden gap

Options number	E_b, eV	ΔE_g, eV
1	7,48	0,05
2	7,49	0,07
Pure PPAN	E_b = 7,69 eV ΔE_g = 3,40 eV	

So, the realized researches allowed to define the features of the geometry of the received metal-phase composites based on PPAN monolayer with the introduced pair atoms of iron and cobalt, and the found distances between the atoms of Fe and Co permitted to conclude that they corresponded to the interatomic distances in the cubic lattice. In addition, this model is the first approach to the further learning of the features how to form the metal clusters in PPAN structure. Besides, the analysis of the electronic and power condition of this system found out that the introduction of the metal atoms leaded to the essential reduction of the width of the forbidden gap of the composite in comparison with the pure PPAN. That allowed to certainly change the conductive characteristics of the metal-composite. And it can also have impact, in its turn, on the magnetic properties of the system.

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