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Theoretical Study of Metal Composite on the Monolayer PPAN Basis, Containing Pair Metal Atoms Cu-Co and Cu-Ni

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Abstract - In this work PPAN monolayer containing pair of atoms of metals Cu-Co, Cu-Ni is considered. The structure of the metal complex system was investigated. Single-electron spectra were constructed; the width of the energy gap was analyzed and compared with the similar characteristic of PPAN, which does not contain metal atoms. Binding energy is calculated and metal charges are carried out. Influence of copper atom on basic characteristics of metal complex is determined. The studies were performed using the DFT method with B3LYP functionality and cc-pvdz basis.

***Keywords*:** Metallocarbon nanocomposite, Carbon-containing matrix, Pyrolized polyacrylonitrile, Paired metal atoms, DFT.

1. Introduction

At present, in view of the specific properties that appear when substances transition to a nanoscale state, composite materials consisting of a polymer matrix and a filler are of particular interest to researchers. Introduction of metal nanoparticles into the matrix enables to obtain materials with improved physical and chemical properties. For example, the inclusion of ferromagnetic metals in polymer matrices allows the use of such metal composites in various fields of technology: magnetic recording systems [1], high-frequency devices [2, 3], magnetic resonance tomography [4], biomedical [5], radiation protection systems [6], electronics and others. Theoretical investigation of metal composites is an important problem, the solution of which will allow controlling the process of their production in order to obtain the specified structure and necessary characteristics. [7-9].

One polymer that can be used as a matrix for introducing metallic nanoparticles is a carbonaceous material, pyrolized polyacrylonitrile (PPAN), obtained by IR heating polyacrylonitrile [10-15]. PPAN is a graphite-like layer structure. The addition of copper, nickel and cobalt (Cu, Ni and Co) nanoparticles to this structure will produce magnetically soft composites that effectively absorb radio waves in a wide range of radiation.

For theoretical investigation of the structure of PPAN-based metallocarbon nanocomposites with introduced metal atom pairs, calculations were made using the molecular cluster model and the Density Functional Theory (DFT) method. The hybrid functionality is a B3LYP functionality using the base set cc-pvdz. This functionality is preferable for calculations of systems with transition metals. The cc-pvdz basis refers to a group of correlation-matched basis sets. Such a set includes polarization functions [16]. This basis is analogue of 6-31G basis (d) [17].

2. Formulation of the problem

We investigated the model of a PPAN monolayer containing selected metals. The original structure is a monolayer cluster with a defect in the centre (Figure 1). The defect is formed by removing 6 carbon atoms from the centre of the cluster. The resulting molecular cluster contained atoms in the following proportions: carbon - 70%, nitrogen - 19%, hydrogen - 11%. Then the defect was filled with pairs of atoms with metals: Cu-Co, Cu-Ni.

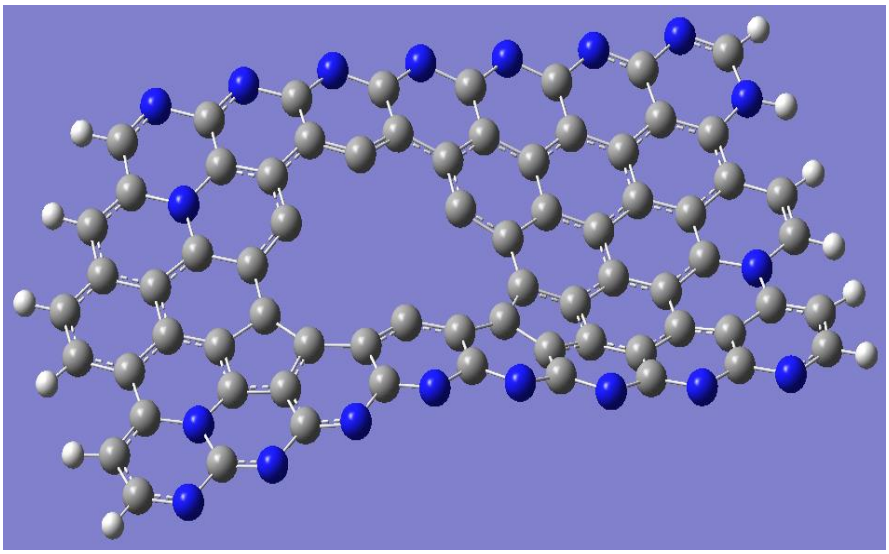


Fig. 1: Optimized structure of PPAN nanocomposite without metal atoms.

The performed optimization of the geometry of the system with metal atoms found that the initially planar structure of PPAN is significantly curved. Figure 2 illustrates by way of example the structure of a metal complex with a Cu-Co pair. The distances between the pairs of Cu-Co metal atoms were 2.57 A and Cu-Ni 2.47 A.

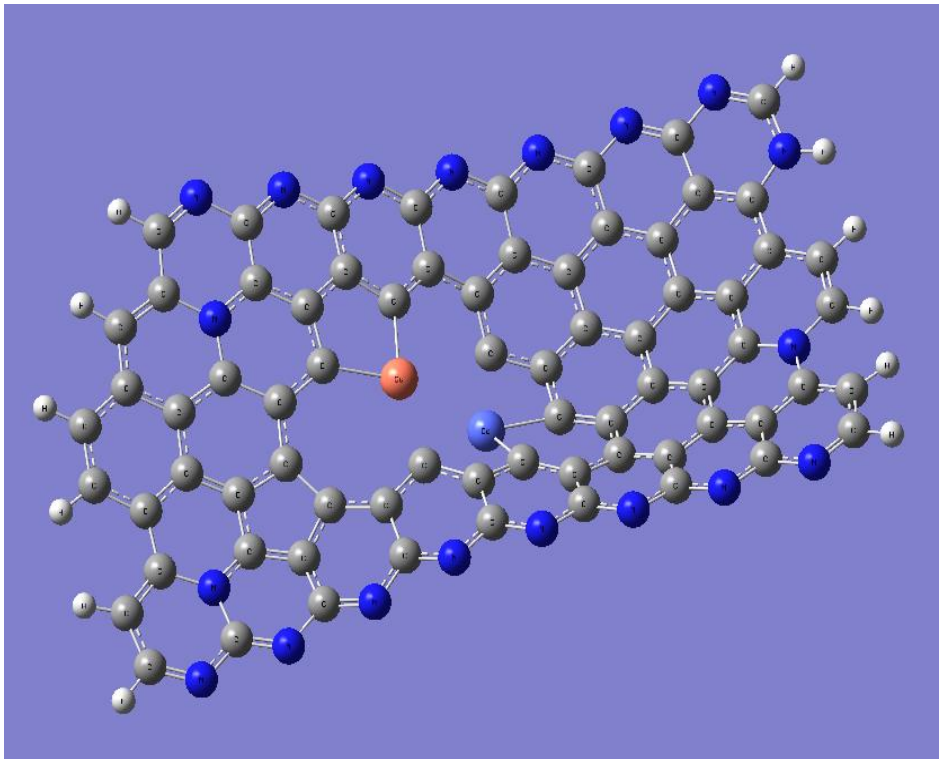
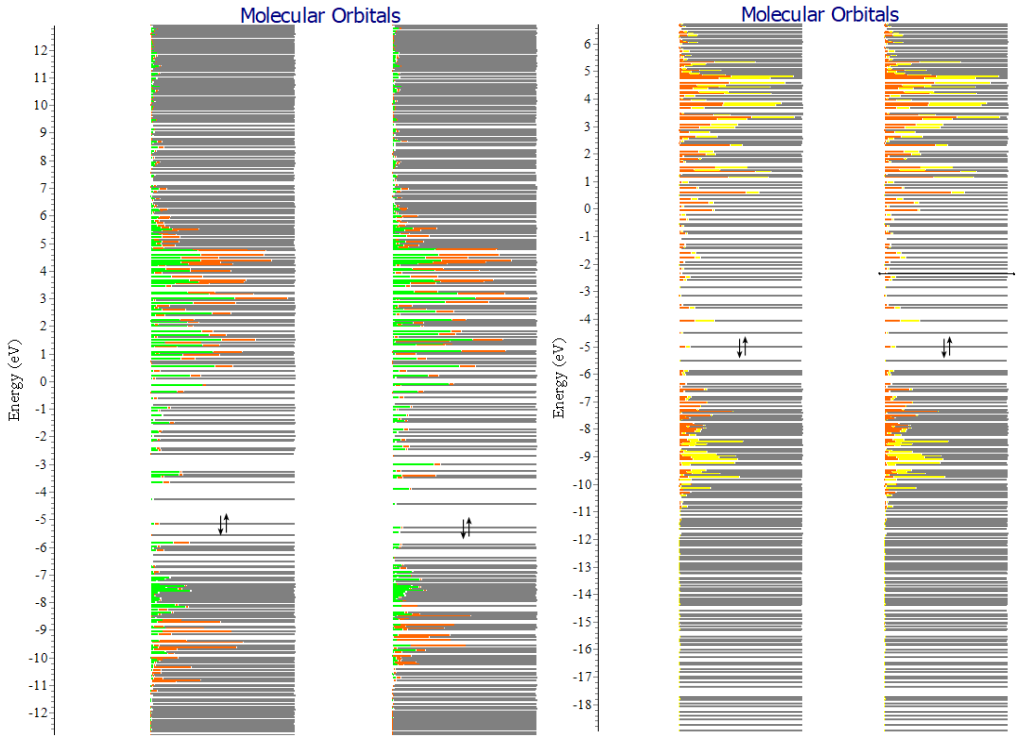


Fig. 2: Example of optimized structure of PPAN nanocomposite with copper and cobalt metal atoms.

The calculations made it possible to construct single-electron spectra of the obtained composite systems, shown in Figure 3. Analysis of these spectra of metal composites has shown that atomic orbitals (AOs) are grouped into some formations, which conditionally can be called a valence zone and a conduction zone similar to solid bodies separated by the energy gap. Metal atoms provide major contributions to the conduction zone, while participating in the creation of additional molecular orbitals (MOs) in the forbidden zone (Figure 3). The upper occupied molecular orbital in the figure is marked with arrows notionally denoting the spines of electrons. Values of width of prohibited slot ΔEg, defined as difference of energies of upper occupied and lower vacant molecular orbitals, are given in Table 1. Analysis of ΔEg values showed that the presence of a Co atom in the Cu-Co pair reduces the width of the energy gap slightly. The influence of the nickel atom (in the Cu-Ni pair) reduces ΔEg more markedly.

Table 1: Width of prohibited gap of PPAN with and without metals.

System name	Width of prohibited slot
Clean PPAN	0,85
Cu-Co	0,72
Cu-Ni	0,51



a) b)

Fig. 3: Single-electron spectra of metal complex cluster based on PPAN monolayer with embedded metal pairs: a) PPAN with Cu-Co, b) PPAN with Cu-Ni; Nickel levels are highlighted in yellow, cobalt in green, nickel in red, and the remaining PPAN atoms in grey.

Also for all structures, the binding energy was calculated (Table 2). Energy values prove that all systems are quite stable.

Table 2: Charges on metal atoms in molecular cluster.

Metall\Strucrure	Cu-Co	Cu-Ni
Ni		-0,006
Co	0,363	
Cu	0,097	0,652

These calculations are consistent with the concepts of interaction processes between metals and the system of conjugated bonds in PPAN with formation of complexes causing displacement of electronic clouds of metal to the nearest atoms of PPAN monolayer.

3. Conclusion

Thus, the pyrolized polyacrylonitrile metal composites with Cu-Co and Cu-Ni metal pairs are stable formations. The introduction of metals into PPAN results in a reduction in the gap width compared to pure PPAN due to the appearance of additional metal atom levels near the gap boundaries. Such pyrolized polyacrylonitrile matrix-based metal composites can be used as novel magnetically soft compounds having the ability to absorb electromagnetic radiation by possible electron transitions using emerging levels of metal atoms.

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