

Quantum Chemistry Research of Interaction between 3D-Transition Metal Ions and a Defective Graphene on the Supercomputer Base

*Nikolai V. Khokhriakov*¹, *Santiago Melchor*²

© The Authors 2018. This paper is published with open access at SuperFri.org

Quantum chemistry research is presented in the article, and it concerns the interaction within the complexes formed by the defective graphene clusters and ions of 3d-transition metals *V, Cr, Mn, Fe, Co, Ni, Cu*. The charges of all regarded ions were +1. All calculations were made at UDFT B3LYP/6-31G level of theory with the BSSE error taken into account. The strongest interaction with the defective clusters is observed in the case of *Co*⁺ ion. At the same time, this ion has demonstrated rather weak interaction with the defect-free graphene. Thus, the presence of *Co*⁺ in the reaction media increases probability of defect formation with the further forming of short nanotubes and curved carbon clusters with complex topology of their own.

Keywords: graphene, transition metals, quantum chemistry, density functional.

In the last thirty years, properties of nanoparticles and nanostructured media have been attracting unremitting interest in scientific community. Computer experiments are necessary to search for synthesis conditions to obtain the particles with predetermined structures and properties because of their complexity and possible formation of short-lived states influencing a synthesis process. The characteristic size of a nanoparticle can reach tens of nanometers, and the model system may include millions of atoms in order to reflect correctly its geometrical features and chemical behavior. The computing complexity of the classical algorithms of quantum chemistry based on calculation of nanoparticles electronic Hamiltonian eigenfunctions begins from $O(N^3)$ for the simplest semi-empirical tight-binding model (where N is the quantity of atomic orbitals in a basis set). Computing demands increase dramatically with improving of quantum chemistry model. The problem becomes NP-complete at accurate accounting of electronic exchange and correlation. Since the end of the 20th century quantum chemistry algorithms with complexity $O(N)$ have been developing, but the coefficient of proportionality for similar algorithms is rather large. Thus, the advantage of linear-scaling algorithms is reached only for the systems with a large amount of atoms. Therefore, the quantum chemistry research studies in the field of nanotechnologies are possible only when using the capacities of supercomputers.

The interaction of transition metal ions with a defective graphene is considered in the article. An ideal graphene is a plane packed by hexagons with the carbon atoms in their corners. Replacement of one of the hexagons with a pentagon during the growth of the graphene plane leads to formation of conic surface, and replacing with a heptagon results in formation of saddle surface. The system of topological defects can be constructed to obtain a junction of several carbon nanotubes of various types, or a closed shell of fullerene. The defective areas in a graphene structure demonstrate higher chemical activity; therefore, the defective graphene nanostructures are perspective in chemical technologies. Understanding of interaction in complexes formed by the graphene and transition metal ions is of special interest for some practical applications. Such situation is implemented, for instance, when using graphene for cleaning water off ions of

¹Izhevsk State Agricultural Academy, Izhevsk, Russian Federation

²Universidad de Granada, Granada, Spain

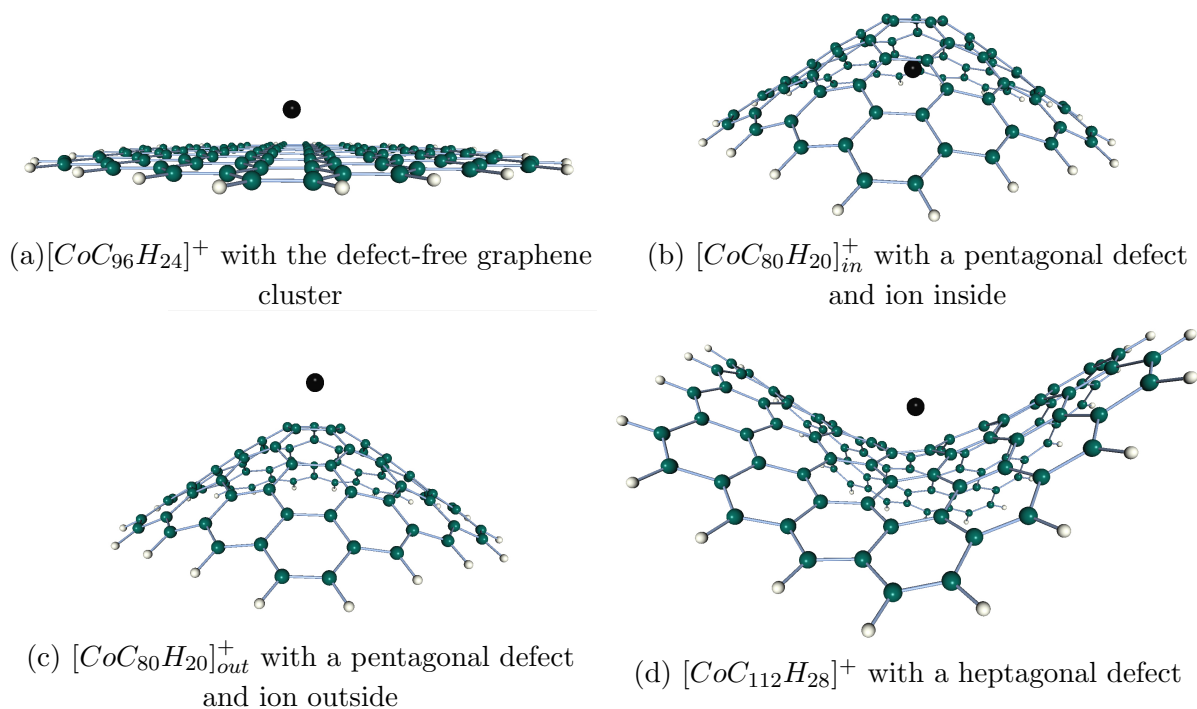


Figure 1. Optimized complexes of cobalt ion with graphene clusters

transition metals [9]; when using graphene clusters as sensors for definition of transition metals in water environment [2]; during synthesis of carbon nanostructures in molten salts of transition metals [5]; at contact of a graphene with oxide of transition metal in the anode of a lithium ion battery [10]. And, probably what is of most interest, the matrix of a defective graphene with metal atoms fixed on the defects is considered as promising single-atom catalyst [3].

All calculations were made at the UDFT B3LYP/6-31G level of theory. Minimal basic set m6-31G was used adapted for compounds of transition metals [6]. The method was examined by calculation of chemically similar systems formed by transition metal ions and benzene [4]. Calculation results for the interaction energies between ions and a molecule of benzene are in complete accordance with the available experimental data.

An infinite graphene leaf with a single defect polygon was modelled by a finite size cluster constructed from the defect polygon in the center, the latter surrounded by three strips of carbon hexagons. Dangling bonds on the boundaries were compensated by hydrogen atoms. Further on, such graphene clusters have been considered. Including the cluster with pentagonal defect of a cone form, a saddle-like cluster with heptagonal defect, and a plane defect-free cluster with a carbon hexagon in the center. The complexes were considered formed by each graphene cluster and ions of 3d-transition metals *V, Cr, Mn, Fe, Co, Ni, Cu*. The charges of all ions were +1.

Initially, every ion was placed above the center of every graphene cluster. For a cluster with a pentagonal defect, two situations had been considered: a case when the ion of metal lies inside the cone (such systems are designated further by the index “in”), and the case when the ion is located outside (designated further by the index “out”). Further, the geometry optimization of the complex was completed. Optimized complexes with the cobalt ion are shown in Fig. 1. Green spheres designate carbon atoms, the light ones hydrogens, and cobalt ion is black.

Interaction energy E_{int} between metal ion and a carbon cluster has been estimated by the formula

$$E_{int} = E_{Me} + E_{Gr} - E_{MeGr}, \quad (1)$$

where E_{MeGr} is the energy of the complex after optimization, E_{Me} is the energy of the isolated ion, E_{Gr} is the energy of the isolated carbon cluster. E_{int} was calculated taking into account the BSSE correction.

Table 1. Interaction energy between transition metal ions and graphene clusters (in kJ/mol)

Transition metal ion	Spin multiplicity	$C_{96}H_{24}$	$[C_{80}H_{20}]_{out}$	$[C_{80}H_{20}]_{in}$	$C_{112}H_{28}$
Co^+	3	222	403	281	407
Cr^+	6	216	254	185	262
Cu^+	1	273	346	218	348
Fe^+	4	327	342	300	386
Mn^+	7	206	242	158	241
Ni^+	2	253	346	248	345
V^+	5	238	270	216	291

The computed results for interaction energies between transition metal ions and carbon clusters are given in Tab. 1. Almost for all atoms, the weakest interaction is observed when placing an ion inside a conic cluster with the pentagonal defect. The strongest interaction is observed for complexes including carbon clusters with a heptagonal defect. The interaction between conic graphene clusters and an ion of metal located outside of the cone is also strong. The negative charge usually has the maximum density near the vertex outside the cone, and that explains the raised attraction of a positive ion. At the same time, inside the cone the density of the negative charge rapidly decreases while departing the vertex. The metal ion located inside the conic cluster is not able to be close to the vertex because of high density of carbon atoms in the internal area and repulsion of their internal electron shells. Therefore, the ion arrangement inside the conic cluster is energetically unfavorable. In case of the heptagonal defect, the saddle surface is being formed with a number of areas, thus having positive and some of them negative charge. Geometrically, the ion of metal is less constrained than inside the cone; therefore, it acquires wide opportunities for the movement in space, thus resulting in energy decrease. In case of a planar defectless graphene cluster weak interaction with a metal ion can be observed and explained by high stability of the graphite structure, that in this case remains safe.

The calculations show that the strongest interaction with the defective graphene clusters is observed for cobalt ion. At the same time, this ion rather weakly interacts with a defect-free graphene fragment. Therefore, presence of cobalt ions in the reaction media can increase probability of the defect formation. As a result, shorter nanotubes are formed as a result of synthesis, and the graphene leaf can get complex and curved topology.

Acknowledgements

The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University supported by the project RFMEFI62117X0011 [7] and the program FireFly QC [1] developed on the basis of GAMESS (US) [8].

This paper is distributed under the terms of the Creative Commons Attribution-Non Commercial 3.0 License which permits non-commercial use, reproduction and distribution of the work without further permission provided the original work is properly cited.

References

1. Granovsky, A.A.: Firefly version 8, <http://classic.chem.msu.su/gran/firefly/index.html>, accessed: 2018-09-30
2. Huang, H., Liao, L., Xu, X., Zou, M., Liu, F., Li, N.: The electron-transfer based interaction between transition metal ions and photoluminescent graphene quantum dots (GQDs): A platform for metal ion sensing. *Talanta* 117, 152–157 (2013), DOI: 10.1016/j.talanta.2013.08.055
3. Jiang, K., Wang, H.: Electrocatalysis over graphene-defect-coordinated transition-metal single-atom catalysts. *Chem* 4(2), 194–195 (2015), DOI: 10.1016/j.chempr.2018.01.013
4. Khokhriakov, N.V., Kodolov, V.I., Karpova, V.S.: Quantum chemistry research of transition metals complexes with aromatic hydrocarbons. *Chemical physics and mesoscopy* 16(4), 622–626 (2014)
5. Kodolov, V.I., Kuznetsov, A.P., Nikolaeva, O.A., Shayakhmetova, E.Sh., Makarova, L.G., Shabanova, I.N., Khokhriakov, N.V., Volkova, E.G.: Investigation of metal-carbon tubulenes by x-ray photoelectron spectroscopy and electron microscopy. *Surface and interface analysis* 32(1), 10–14 (2001), DOI: 10.1002/sia.996
6. Mitin, A.V., Baker, J., Pulay, P.: An Improved 6-31G* Basis Set for first-row transition metals. *The journal of chemical physics* 118(17), 7775–7782 (2003), DOI: 10.1063/1.1563619
7. Sadovnichy, V., Tikhonravov, A., Voevodin, V.I., Opanasenko, V.: “Lomonosov”: Supercomputing at Moscow State University. In *contemporary high performance computing: from petascale toward exascale*. pp. 283–307. Chapman & Hall/CRC Computational Science, CRC Press, Boca Raton, United States (2013)
8. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S., Windus, T.L., Dupuis, M., Montgomery, J.A.: General atomic and molecular electronic structure system. *Journal of computational chemistry* 14(11), 1347–1363 (1993), DOI: 10.1002/jcc.540141112
9. Yu, J.-G., Yu, L.-Y., Yang, H., Liu, Q., Chen, X.-H., Jiang, X.-Y., Chen, X.-Q., Jiao, F.-P.: Graphene nanosheets as novel adsorbents in adsorption, preconcentration and removal of gases, organic compounds and metal ions. *Science of the total environment* 502, 70–79 (2015), DOI: 10.1016/j.scitotenv.2014.08.077
10. Zhu, J., Duan, R., Zhang, S., Jiang, N., Zhang, Y., Zhu, J.: The application of graphene in lithium ion battery electrode materials. *SpringerPlus* 3, 585 (2014), DOI: 10.1186/2193-1801-3-585