DISSERTATION REVIEW

Structural, electronic, and magnetic properties of nanomaterials for potential magnetic, energy storage, and catalytic applications

By Mgr. Rostislav Langer
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Reviewed by Prof. RNDr. Mojmír Šob, DrSc.

Exploring connections between macroscopic characteristics of materials and their microscopic structure in atomistic dimensions has been an important topic in contemporary materials science as well as in solid-state physics and chemistry. A better understanding of the relations between macroscopic properties of solids and their structure yields new knowledge needed for development of materials with better technological properties.

The present Thesis fits perfectly into this trend. Its goal is to advance our fundamental understanding of properties of nanomaterials and to explore their technological potential for magnetic, energy storage and catalytic applications. To obtain relevant characteristics of the materials studied, the state-of-the-art first principles electronic structure methods based on the density functional theory are used.

The Thesis itself has 175 pages and apart of Preface and Introduction, it is divided into 10 numbered chapters. The bibliography contains 440 items. Additionally, in the Appendix (60 pages), the Thesis contains 6 papers published in leading international journals within the years 2020-2022, where the candidate is the first author in three of them. As a whole, the Thesis represents a comprehensively written and well researched work. I was surprised how many new significant results are contained there. In most cases, the results of calculations were compared with experimental results, which further enhances the scientific level of the Thesis. The main scientific contributions of the Thesis may be characterized as follows:

1. **New information on the structure, electronic and magnetic properties of graphene doped by phosphorus, transition metals Cr, M and Fe as well as by nitrogen.** The electronic structure calculations revealed that the magnetic ordering of P-doped graphene can be attributed to a combined direct coupling in an antiparallel fashion of an electron cloud of partially filled π-orbitals of neighboring carbon atoms that extends over a large distance from the P dopant, and the RKKY interaction. These theoretical results were supported by an experimental reconstruction of the 3D geometry of the single P substitution. As to transition-metal doping, it was found that doping of graphene with two different transition-metal atoms and the formation of upright transition-metal dimers leads to a huge increase in magnetic anisotropy energy, Namely, the combination of graphene-mediated RKKY-like superexchange interactions between transition-metal dopants and the presence of partially occupied degenerate states at the Fermi level favors a large magnetic anisotropy energy, which for some systems can reach ~120 meV. And, in the investigations of graphene doped by nitrogen, a new class of carbon-based materials was discovered (denoted as GN3 in the dissertation), comprising nitrogen-doped graphene with diamond-like tetrahedral bonds formed between carbon-centered radicals that emerged near the nitrogen dopants and high

mass density. This may stimulate further research of other high-density conductive carbon-based materials for advanced technological applications.

2. Graphene acid was identified as a highly efficient anode material for lithium-ion batteries. It exhibits excellent redox and intercalation properties and low charge transfer resistance, resulting from the conductive and selectively carboxylated graphene backbone.

3. An extended analysis of the possibilities of anchoring the Pt single atoms onto graphene functionalized by –H, -F and the groups –OH and –CN. It was found that on the one hand the Pt adatom cleaved the -F, -OH and -H bonds to graphene leading to the formation of graphene-Pt-F, Pt-OH or Pt-H complexes, on the other hand the -CN group remained attached to the graphene lattice and anchored the Pt adatom with high energy barrier against -CN-Pt diffusion. The effective immobilization of Pt ions on nitrilated graphene, g-CN, was also confirmed experimentally. Thus, the nitrilated graphene g-CN is as a suitable candidate for Pt single-atom catalysis, enabling the efficient use of rare and expensive noble metals.

4. Investigation of conformational changes of one-dimensional metal-porphyrin wires on Au(111) due to sample annealing. Considerable changes in magnetic properties were found, in particular the reduction of magnetic anisotropy energy related to the planarization of the porphyrin units. It turns out that, upon planarization, the magnetic anisotropy energy of the triplet ground state of the central Fe ion dropped down due to the reduction of the ligand field symmetry and the subsequent change in the occupancy of the 3d Fe electronic states. These findings indicate new possibilities in the design of on-surface one-dimensional organic magnets with tailored magnetic properties.

I would like to stress again that the present Thesis contains a lot of new and interesting results that substantially advance our understanding of properties of selected nanomaterials. The Thesis is written clearly and comprehensibly. It achieves a high level of competence and offers valuable information. All the objectives, problems and ways of solution are concisely described. The author has clearly demonstrated his abilities for a systematic scientific work. Most of the findings obtained in the Thesis have an important impact in the field of computational materials science. And all the results from the Thesis have already been published in high-impacted international scientific journals. I do not have any formal or scientific objections.

In conclusion, the present Thesis fulfils very well all the necessary academic and legal requirements needed for a PhD Thesis at most European universities. Certainly, the candidate is capable of producing new scientific results. His methodological approaches are scientifically sound and flawless. His papers have already advanced the field of computational materials science and, without any doubts, it may be supposed that, with increasing experience, he will be delivering further important results in the field. Therefore, I suggest the continuation of the graduation procedure of Mgr. Rostislav Langer at the Palacký University and, after a successful defense of the Thesis, I recommend the awarding of the degree of Doctor of Philosophy.

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