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

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Abstract

Graphene [1], a two-dimensional (2D) material comprising of covalently bound sp^2 carbon atoms arranged in a hexagonal (honeycomb) lattice sandwiched between two π-electron clouds, has attracted great interest because of its remarkable properties and numerous potential applications [2]–[5]. However, despite extensive research efforts, a limited number of graphene-based products have so far been successfully commercialized. The potential range of graphene applications can be greatly enhanced by covalent modification, including doping of the graphene lattice with foreign atoms [6], [7] and sp^3 functionalization [8]–[12]. And this is the time when theoretical calculations come to demand.

The traditional costly and time-consuming, trial-and-error experimental approaches to develop novel (nano)materials with desired properties are being complemented and often overtaken by new strategies based on a detailed understanding of the materials' properties down to the level of individual atoms with the help of theoretical modeling.

The work presented here concerns modeling and theoretical description of mainly graphene-based materials for potential applications in spintronics and information-storage, single-atom (SA) and molecular magnets, single-atom catalysis (SAC), lithium-ion-batteries (LIBs), and supercapacitors (SCs) **[13]–[18]**. There was a strong synergy between theory and experiments throughout the work.

Annotation

The common denominator of my research is graphene and its derivatives. Fluorinated graphenes (FGs) are key precursors to the synthesis of many graphene derivatives, so a better comprehension of fluorographene (FG) reactivity and the nature of the C-F bond is key to unlocking the application potential of graphene-based materials **[19]**.

Indeed, understanding the mechanism of thermal decomposition of a fully fluorinated graphene in the presence of a reducing hydrogen atmosphere has helped to develop novel electrode materials for SCs aimed at practical applications **[20]**. Further, the radical-based chemistry of FG, which enables the combination of sp^2 and sp^3 carbon bonds in the same network, along with very high nitrogen doping and vacancies, has enabled the discovery of a new class of carbon-based materials comprising nitrogen doped graphene with diamond-like tetrahedral bonds for high energy-density SC electrodes, and with the help of theoretical modeling, the materials' properties has been better understood **[16]**.

Controllable atom substitution and defluorination of FG enables the synthesis of cyanographene (G–CN) [9], which has proven to be a perspective material for anchoring Pt adatoms with potential implications as single-atom catalysts (SACs) **[15],** and the use of complex chemistry of −CN groups makes it possible to synthesize a wide range of graphene derivatives with a very high degree of functionalization, including graphene acid (G–OOH), which emerges as a stable and high-energy organic LIB anode material **[17]**.

The substitution of fluorine atoms in FG with hydroxyl groups **[21], [22]** and simultaneous doping of graphene by phosphorus atoms and its functionalization with P-containing groups **[13]** can lead to materials with magnetic features sustainable up to room temperature (RT), which creates perspectives for the design of metal-free graphene-based spintronic devices.

Doping of the graphene lattice with Fe and Mn atoms results in a high magnetic anisotropy energy (MAE) corresponding to a theoretical blocking temperature of 34 K assuming a relaxation time of 10 years, enhancing the application potential of graphene in spintronics, including data storage in magnets of the size of SAs **[14]**.

Another studied material in this thesis is porphyrin. In porphyrin molecules with coordinated transition metal (TM) atoms, the ligand field coordinated with the central metal atom governs the magnetic anisotropy due to spin-orbit coupling (SOC) in a close analogy to the

TM atoms anchored in N-decorated defects in the graphene lattice **[14],** [23]. The possibility of tailoring the magnetic state in such nanostructures is highly desirable for potential spintronic applications. Theoretical calculations revealed the mechanism of the MAE modification in Au(111) supported one-dimensional (1D) metalloporphyrin polymers depending on the structural conformations of the molecular units **[18]**.

The **Introduction** of the thesis presents the historical timeline of the most important milestones in the development of materials science and gives the main ideas behind the work.

Afterwards, the studied materials that form the basis of our research **[13]–[18]** are introduced in **Chapter 1**.

The magnetism of graphene derivatives is reviewed in **Chapter 2**.

Chapter 3 discusses the theoretical methods applied in my research are described. Besides the description of Schrödinger equation (SE), Hartree-Fock (HF) method, and Thomas-Fermi (TF) model, the focus is on the concept of DFT and its exchange-correlation functionals. Further, the physics behind solid-state calculations is presented.

In **Chapter 4**, the possibilities of establishing magnetic ordering in phosphorus-doped and phosphono-functionalized graphene is discussed. For a single P substitution, the 3D reconstruction of the experimental geometry based on atomic-resolution aberration-corrected scanning transmission electron microscopy (STEM) imaging at multiple sample tilts is compared with the computational results **[13]**.

Chapter 5 deals with the doping of TM atoms (Cr, Mn, and Fe) with vacancy-containing graphene, both bare and nitrogen-decorated, which, based on spin-polarized DFT calculations including spin-orbit coupling, results in a high MAE due to the coupling between TM dopants through graphene. The computational findings are supplemented by an experimental atomic-resolution characterization of a Mn substitution, which may create spots for the formation of atom-sized magnets in graphene **[14]**.

In **Chapter 6**, the feasibility of adapting the MAE with conformational changes of 1D Au(111)-supported metalloporphyrin polymers is presented. DFT results are discussed in relation to scanning tunneling microscopy and spectroscopy, and high-resolution atomic force microscopy experiments **[18]**.

Chapter 7 discusses the theoretical prospective of graphene and its derivatives as a scaffold for SAC preventing the unwanted migration and agglomeration of SACs. Calculations from first-principles allowed to identify the cyano group as a convenient binding site for Pt adatom, which was additionally supported by the experimental result confirming that the –CN groups act as ligands immobilizing of 3.7 wt.% Pt adatoms **[15]**.

Chapter 8 focuses on the possibility of using G–OOH, a carboxyl derivative of graphene, as the LIB anode. While the experimental measurements showed excellent charge transport, redox activity, and lithium intercalation of the G–OOH anode, theoretical insight was needed into the mechanism underlying energy storage in G–OOH **[17]**. The results of finite (functionalized ovalene) and infinite (periodic) model calculations in the context of experimental data are discussed.

The reaction of FG with azide anions enables the preparation of a material connecting sp^2 layers of the graphene type with tetrahedral carbon-carbon bonds and superdoping with nitrogen. The resulting ultra-high mass density material is an excellent ion host, delivering unprecedented energy densities. Theoretical research allowed for a better understanding of the structural properties of this material, which is discussed in **Chapter 9 [16]**.

Finally, our research is concluded in **Chapter 10**, followed by References, and then Appendices containing reprints of these papers that constitute the basis of my dissertation.

Conclusion

Our calculations within the spin-polarized Density functional theory framework provided an efficient tool to thoroughly characterize both existing and hypothetical graphene-based materials and to a better understand underlying phenomena in spintronics, magnetic data storage, single-atom catalysis, and energy storage. It is amazing that such a broad range of applications of materials based on graphene turned out to be possible thanks to the relatively easy modification and functionalization of graphene layers.

In this dissertation, special emphasis is placed on P-doped graphene, TM-doped graphene, and 1D porphyrin polymer with promise for spintronics and ultra-dens data storage, G-CN binding Pt-SAs for potential applications in SAC, and last but not least, Li-G–OOH and GN3 which may change the contemporary energy-storage landscape.

Due to the ability to tailor the properties of graphene-based materials through doping and sp^3 functionalization, the studied materials can be further optimized and many other applications still to be discovered. The computational design of materials with desired or optimized properties for a given application can be greatly accelerated by machine learning techniques.

For example, catalytic reactions on G-CN with Pt-SAs can be examined in the future. Another direction could be to further optimize the structure and composition of graphene-based towards the desired capacity value, energy density, and power density for SCs. Finally, forthcoming development directions of a wider family of high temperature 2D graphene magnets with application-specific properties must consider aspects of size and morphology with other magnetism sources, *e.g.*, defects, doping, and functionalization. Furthermore, for the practical applications of graphene magnets, the carbon sheet must be deposited on a solid substrate. Finding a suitable solid substrate for graphene magnets that will not compromise or even improve their properties remains one of the goals for the future.

Závěr

Naše výpočty užitím nástrojů spinově polarizované teorie funkcionálu hustoty poskytly účinný nástroj k důkladné charakterizaci a k lepšímu pochopení základních jevů stávajících i hypotetických materiálů na bázi grafenu pro jejich aplikovatelnost ve spintronice, magnetickém ukládání dat, jednoatomové katalýze a ukládání energie. Je obdivuhodné, že tak široká škála aplikací grafenových materiálů je možná díky relativně snadné modifikaci a funkcionalizaci grafenové monovrstvy.

V této disertační práci je zvláštní důraz kladen na grafen dopovaný fosforem, grafen dopovaný přechodnými kovy a 1D polymery na bázi porfyrinu s příslibem pro spintroniku a ukládání dat, cyanografen schopný vázat jeden atom platiny pro potenciální aplikace v jednoatomové katalýze a v neposlední řadě systém Li-grafenová kyselina a dusíkem dopovaný grafen, které mohou změnit současnou scénu ukládání energie.

Díky možnosti ladit vlastnosti grafenu a jeho derivátů pomocí dopování a sp^3 funkcionalizace lze studované materiály dále optimalizovat a mnoho dalších aplikací teprve objevit. Výpočetní návrh materiálů s požadovanými nebo optimalizovanými vlastnostmi pro danou aplikaci lze výrazně urychlit pomocí „machine learningu".

V budoucnu lze například zkoumat katalytické reakce na systému cyanografen-platina. Dalším směrem by mohla být optimalizace struktury a složení grafenových derivátů směrem k požadovaným elektrochemickým pro superkapacitátory. A konečně, budoucí vysokoteplotní 2D grafenové magnety se specifickými vlastnostmi musí zohledňovat aspekty velikosti, morfologie a zdroje magnetismu, jakými jsou například defekty, dopování a funkcionalizaci. Pro praktické aplikace grafenových magnetů musí být grafenová monovrstva nanesena na pevný substrátu. Nalezení vhodného pevného substrátu pro grafenové magnety, který neohrozí nebo dokonce zlepší jejich vlastnosti, zůstává jedním z cílů do budoucna.

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