Review Report on PhD Thesis

Faculty: **Central European Institute of Technology**
Brno University of Technology in Brno

Academic year: **2020/2021**

Student: **Ing. Lukáš Kormoš**

Doctoral study program: **Advanced Materials and Nanosciences**

Field of study: **Advanced nanotechnologies and microtechnologies**

Supervisor: **Assoc. prof. Jan Čechal, Ph.D.**

Reviewer**:** **Assoc. prof. Josef Mysliveček, Ph.D.**

PhD thesis title: **2D molecular systems at surfaces**

Topicality of doctoral thesis: The Thesis of Ing. Kormoš deals with a highly relevant topic of two-dimensional (2D) supported molecular structures. Motivated by the expected applications of ordered molecular structures in electronics, spintronics, and heterogeneous catalysis, studies of 2D molecular structures represent a vividly growing research field offering numerous open questions and new material combinations for detailed investigations.

Meeting the goals set: The goals are not formulated explicitly in the Thesis. Rather, the Thesis represents a collection of scientific studies dealing with open issues in the field of 2D supported molecular structures, particularly

1) the influence of the presence and of the chemical state of carboxyl functional groups on the arrangement of molecular structures on metal substrates studied on the example of 4,4-biphenyl dicarboxylic acid (BDA) adsorbed on Cu(100) and Ag(100) surfaces,
2) the possibility of synthesizing metal-organic molecular networks coordinated via metal single atoms on metal supported graphene studied on the example of BDA and 7,7,8,8-tetracyanoquinodimethane (TCNQ) molecules coordinated via Fe or Ni atoms on graphene/Ir(111),
3) the possibility of synthesizing graphene nanoribbons from a molecular precursor studied on the example of dibromo-bianthracene (DBBA) molecules on a nanostructured surface Au(16 14 15).

The presented studies are complete, bringing clearly formulated new findings, and, within the topics 1) and 3), yielding publications in international peer-reviewed scientific journals. The majority of the discussed experimental data has been obtained using a newly installed ultra-high-vacuum cluster of surface science experimental tools in the CEITEC Institute. The Thesis of Ing. Kormoš clearly illustrates that the new cluster is providing state-of-the-art experimental data.

Problem solving and dissertation results: In his Thesis, Ing. Kormoš is fully exploiting the possibilities offered by the unique combination of surface science experimental tools – scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM), low energy electron microscopy and diffraction (LEEM/LEED), and laboratory photoelectron spectroscopy (XPS). Particularly strong is the combination of the employed microscopic techniques yielding information on the morphology of the investigated molecular systems on the scales from units of Angstroms (0.1 nm, atomic resolution) in STM and nc-AFM to units of μm in LEEM, complemented with the measurements of LEED from areas as small as 200 nm. The combined microscopic techniques yield a complex information on the structure, morphology and crystallographic arrangement of the investigated molecular structures including the information on their evolution in real time (LEEM, LEED). Finally, XPS is complementing the information on the chemical state.

Results presented in the Thesis represent a range of new basic research findings, particularly

1 a) determining the chemical state of the BDA molecule on Cu(100), determining the 2D crystallographic structure of the BDA monolayer on Cu(100), and of the homogeneous character of BDA nucleation after passivation of Cu step edges by the BDA molecules,

1 b) observation of gradual deprotonation of the BDA molecule on Ag(100) upon increasing the substrate temperature, determining the changing 2D crystallographic structure of the BDA monolayer on Ag(100) as a function of the degree of BDA deprotonation, and determining the microscopic mechanisms governing the transitions of the BDA monolayer between different crystallographic phases,

2) confirming the possibility of synthesizing the metal-organic molecular network of TCNQ coordinated by single Ni atoms on the surface of graphene/Ir(111),

3) confirming the possibility of synthesizing graphene nanoribbons from a molecular precursor DBBA on Au(16 14 15) surface and determining the electronic structure of the nanoribbons determined by their 1D character.

Importance for practice or development of the discipline: The relevance of the results presented in the Thesis of Ing. Kormoš for the progress within the research field of supported 2D molecular structures is demonstrated by publication of results 1a, 1b, and 3 in leading international scientific journals in the fields of physical chemistry and nanotechnology (J. Phys. Chem. C, ACS Nano), and in a leading multidisciplinary journal Nature Communications. Of particular interest is the identification of 2D crystallographic phases of BDA on Ag(100) in terms of the mathematical formalism of k-uniform tilings.

Result 2 is potentially of a high interest in the field of spintronics; the relevance of the system Ni/TCNQ/graphene/Ir(111) for spintronics must be however confirmed by further studies.

Formal adjustment of the thesis and language level: The Thesis is written in sound English and it is clearly presented and informative. The Author is clearly formulating the motivation for his research and he is introducing the state of the art in the field based on a broad selection of up-to-date scientific literature. Further the Author is presenting the employed experimental methods with an accent on the LEEM/LEED techniques, and, in the following Sections, he is laying out the investigated topics.

The Thesis presented by Ing. Kormoš fulfills the conditions summarized in the §47, Section 4 of the Higher Education Law 111/1998 Sb:

(4) The study is duly completed by a state doctoral examination and the defense of a dissertation, which proves the ability and readiness for independent activity in research or development or for independent theoretical and creative artistic activity. The dissertation must include original and published results or results accepted for publication.

Questions and comments:

On Pages 58-60 and in the images 5.15-5.17 you are describing the detailed structure of BDA β-phase on Ag(100). You are showing that the structure contains three types of molecules – 0H-BDA, 1H-BDA, and 2H-BDA randomly occupying the elementary unit cells of a 2D lattice. How it can be justified that random combinations of molecules with different bonding properties give rise to a regular 2D grid?

On Page 93 you are discussing the chemical structure of a test sample of an Fe-coordinated BDA metal organic molecular network on graphene/Ir(111). In the Fe 2p spectra on Fig. 6. 10 b you are identifying an asymmetric peak indicating the presence of metallic Fe. Can this peak be interpreted as Fe atoms intercalated between Ir and graphene, or as Fe atoms nucleating into Fe clusters?

On Page 98 you are showing that on graphene/Ir(111) substrate it is possible to synthesize patches of Ni-coordinated TCNQ metal organic molecular network. Are you planning to continue research of this intriguing system, and, eventually, what are the proposed research directions? In Section 6.6.2 it becomes apparent that the research of this system within your Thesis was limited by the insufficient sensitivity of the laboratory XPS.

Conclusion: I consider the Thesis of Ing. Kormoš as very well-done. Ing. Kormoš has clearly demonstrated his experimental skills, his ability to work in a scientific team, and his ability of independent and creative scientific work. Ing. Kormoš has acquainted an indispensable experience in the international scientific research working out one of the presented research topics during a visit to a foreign laboratory.

In my opinion, the reviewed Thesis fulfills all requirements posed on Theses aimed for obtaining PhD degree. This Thesis is ready to be defended orally, in front of respective committee.

In Prague, 10th December 2020

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Assoc. prof. Josef Mysliveček, Ph.D.

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