Catalysis at nanoscale from DFT calculations

Z. I. Popov[1,2] A. S. Konopatsky[1] P. B. Sorokin[1] D. V. Golberg[3,4]
D. V. Shtansky[1]

[1]National University of Science and Technology "MISIS", Moscow 119049, Russian Federation
[2]Emanuel Institute of Biochemical Physics RAS, Moscow 199339, Russian Federation
[3]World Premier International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Namiki 1, Ibaraki 3050044, Japan
[4]Science and Engineering Faculty, Queensland University of Technology, 2nd George st., Brisbane, QLD 4000, Australia

Catalytic processes are important for many areas of our daily lives. One of the main aspects is the processing and storage of energy in the form of chemical compounds, which is an alternative to energy storage using lithium-ion batteries. Another interesting application is the reduction of harmful gases such as CO generated in industrial processes. In this regard, there is an increasing interest in the study of catalytic processes at the nanoscale. The solution for many complex problems in the field of catalysis depends on the smart implementation of novel advanced nanomaterials. One of the promising directions is the utilization of hybrid nanomaterials, i.e. nanohybrids. Such hybrids, consisting of various nanostructures, have intensively been studied and successfully been used in many different areas because of the unique combination of properties. Primarily, the catalyst nanohybrid development is based on the right selection of a nanocarrier and a catalyst agent. While t he agents have a dominant role in the catalysis, the nanocarriers are also crucially important with respect to the material synthesis and following catalytic reactions. Hexagonal boron nitride (BN) is an attractive material due to its outstanding mechanical, chemical and physical properties. BN nanoparticles could be used as novel nanocarriers for different catalysts. Metallic nanoparticles supported by BN nanostructures demonstrated higher aggregative stability leading to superb catalytic properties. The catalytic activity of Ag nanoparticles (AgNPs) was under the spotlight for many years. In this study, the calculation of intermediate compound of methanol oxidation at Ag surface was made in order to investigate thermodynamic of this process [1] as well as CO oxidation thermodynamic and kinetic at Ag surface in Ag/BN hybrid structure [2]. In the area of photoinduced processes, the formation of a dipole on the interface of nanohybrid structures (Pt-Au-ZnO and Au-ZnO) as a co nsequenc e of the charge redistribution due to the difference in the electronegativity of the constituent parts of the interface leads to the increased of the efficiency at Toluidine blue photoreduction [3]. The inhomogeneity in the charge distribution in the defect region, as well as the contribution to the bottom of the conduction band from the embedding atoms,

leads to a significant increase in the HER activity of the base plane of the 2D MoS_2 crystal [4]. The importance of the binding energy for HER activity is also shown for H2O dissociation on a carbon-coated Ni_3N (110) surface [5]. This result is in accordance with the experimentally observed enhancement of HER activities in Ni_3N@CQDs and suggests that the enhanced catalytic activity is largely governed by the more energy-favored water dissociation process. A set of factors such as binding energy, electronic structure, and charge distribution which is important for the explanation of catalysis processes at the nanosca le that can be obtained through DFT calculations will be discussed.

[1] A. Konopatsky, K. L. Firestein, D. V. Leybo, Z. I. Popov, K. Larionov, A. E. Steinman, A. M. Kovalskii, A. Matveev, A. Manakhov, P. B. Sorokin, D. Golberg, D. Shtansky, *Catalysis Science & Technology* **8**, 1652 (2018).

[2] A. S. Konopatsky, D. V. Leybo, K. L. Firestein, Z. I. Popov, A. V. Bondarev, A. M. Manakhov, E. S. Permyakova, D. V. Shtansky, D. V. Golberg, *Journal of Catalysis* **368**, 217 (2018).

[3] J. F. S. Fernando, M. P. Shortell, K. L. Firestein, C. Zhang, K. Larionov, Z. I. Popov, P. B. Sorokin, L. Bourgeois, E. R. Waclawik, D. Golberg, *Langmuir* **34**, 7334 (2018).

[4] J. Pető, T. Ollóar, P. Vancsó, Z. I. Popov, G. Zsolt Magda, G. Dobrik, C. Hwang, P. B. Sorokin, L. Tapasztó , *Nature chemistry* **10**, 1246 (2018).

[5] M. Zhou, Q. Weng, Z. I. Popov, Y. Yang, L. Yu. Antipina, P. B. Sorokin, X. Wang, Y. Bando, D. Golberg, *ACS Nano* **12**, 4148 (2018).