Electronic structure and thermodynamics of nanostructured 2D materials for energy applications

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Abstract:
Nanostructured two-dimensional materials such as modified graphene, dichalcogenides of transition metals, chalcogenides of p-elements or pniktogens (black phosphorus, arsanene, etc.) have recently become the subject of intensive research due to their unique properties such as (photo) electrocatalytic activity in water decomposition or CO_2 reduction, high mobility of charge carriers usable in semiconductor components or interaction with particles in surrounding media applicable in sensorics.

In the first part of the lecture the results of electronic structure calculations of layered materials by DFT methods will be presented, including the characteristics relevant to their catalytic activity. For the reduction of hydrogen from water (HER), the effective interaction with the material surface related to surface energy, the appropriate position of the Fermi level, sufficient electrical conductivity and, in the case of photocatalysis, the band gap are of primary importance. In addition, due to a considerable anisotropy of layered materials, these properties significantly depend on the surface orientation. It is therefore not surprising that the catalytic activity is much more significant at the edges of the individual layers than on their relatively inert surfaces. For this reason, the lateral nanostructuring is also important apart from the exfoliation (delamination).

The second part of the lecture will be devoted to thermodynamic description of nanostructured materials, whose behavior and stability depend on the surface energy, because, unlike classical bulk materials, the surface valence-unsaturated atoms make up a significant proportion of the total number of atoms. Considering the surface contribution makes the Gibbs energy a homogeneous function of higher order than one with respect to the mole amount, which affects the form of the equations describing the phase equilibrium. The effect of nanostructuring on the thermodynamic stability will be demonstrated on several examples addressing the solubility of nanoparticles in aqueous solutions, oxidation of metal nanoparticles and solubility of individual components in substitutional solid solutions. Finally, the interpretation of the different composition of the solid solution on the surface and in the core of the nanoparticle using a modified Butler's equation will be shown.