Understanding Chemical Reactions Triggered by Defects on Energetic Materials and Interfaces. Insight from Quantum Chemistry.

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 Understanding, predicting, and controlling the materials response to external stimuli, such as heat, impact, spark, shock, and radiation continues to represent an outstanding challenge for both experimental and theoretical studies. Of a special interest are multifunctional materials and interfaces designed to achieve targeted properties. In this presentation, *ab initio* modeling of chemical reactions in solids will be highlighted. The role defects play in materials ranging from advanced perovskites to molecular crystals to energetic oxide interfaces will be discussed.

A stubborn challenge in the field of energetic materials (EM) is in gaining a reliable control over explosive chemistry. EM store large amounts of chemical energy, which can be rapidly transferred into thermal energy. The lack of understanding of microscale mechanisms of such a transfer leads to our inability to use an enormous potential of EM. We demonstrate that optical (laser) excitation of EM-metal oxide interface enables control of both the energy absorption and release. We show how surface defects (e.g., oxygen vacancies, F-centers) and charge transfer present new opportunities to ensure highly controllable photo-initiation of chemistry at the interfaces.

In the field of energy conversion, solid oxide fuel cells (SOFC) open the way of ecologically clean direct conversion of the chemical energy into electricity. However, the practical development of SOFC faces unresolved fundamental problems, in particular, concerning mechanisms of the electrode reactions. We illustrate how the crystal structure and morphology of materials (including defects and deformations) can be correlated with their stability mechanisms relevant to energy conversion and release. In particular, it will be revealed why (Ba,Sr)(Co,Fe)O3 (BSCF) perovskites, which show the best cathode kinetics known for oxides, turned out to be unstable and hence lead to a reduced cathode performance under SOFC operating conditions, while (La,Sr)(Co,Fe)O3 (LSCF) should offer a better alternative.

We recently applied the similar approach to understand interactions of toxic chemical warfare agents (CWAs) with existing filter materials. We explore various physical and chemical properties of CWAs including their reactivity in the gas phase, liquid solutions and interfaces to improve practical filtering systems.