Ivano Eligio Castelli - Research outputs - DTU Orbit (14/05/2019)

Functional Role of Fe-Doping in Co-Based Perovskite Oxide Catalysts for Oxygen Evolution Reaction

Perovskite oxides have been at the forefront among catalysts for the oxygen evolution reaction (OER) in alkaline media offering a higher degree of freedom in cation arrangement. Several highly OER active Co-based perovskites have been known to show extraordinary activities and stabilities when the B-site is partially occupied by Fe. At the current stage, the role of Fe in enhancing the OER activity and stability is still unclear. In order to elucidate the roles of Co and Fe in the OER mechanism of cubic perovskites, two prospective perovskite oxides, La0.2Sr0.8Co1-xFe xO3-δ and Ba0.5Sr0.5Co1-xFe xO3-δ with x = 0 and 0.2, were prepared by flame spray synthesis as nanoparticles. This study highlights the importance of Fe in order to achieve high OER activity and stability by drawing relations between their physicochemical and electrochemical properties. Ex situ and operando X-ray absorption spectroscopy (XAS) was used to study the local electronic and geometric structure under oxygen evolving conditions. In parallel, density function theory computational studies were conducted to provide theoretical insights into our findings. Our findings show that the incorporation of Fe into Co-based perovskite oxides alters intrinsic properties rendering efficient OER activity and prolonged stability.

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Fe-Doping in Double Perovskite PrBaCo2(1-x)Fe2xO6-δ: Insights into Structural and Electronic Effects to Enhance Oxygen Evolution Catalyst Stability

Perovskite oxides have been gaining attention for its capability to be designed as an ideal electrocatalyst for oxygen evolution reaction (OER). Among promising candidates, the layered double perovskitePrBaCo(2)O(6-) (PBC)has been identified as the most active perovskite electrocatalyst for OER in alkaline media. For a single transition metal oxide catalyst, the addition of Fe enhances its electrocatalytic performance towards OER. To understand the role of Fe, herein, Fe is incorporated in PBC in different ratios, which yielded PrBaCo2(1-x)Fe2xCo6- (x = 0, 0.2 and 0.5). Fe-doped PBCF’s demonstrate enhanced OER activities and stabilities. Operando X-ray absorption spectroscopy (XAS) revealed that Co is more stable in a lower oxidation state upon Fe incorporation by establishing charge stability. Hence, the degradation of Co is inhibited such that the perovskite structure is prolonged under the OER conditions, which allows it to serve as a platform for the oxy(hydroxide) layer formation. Overall, our findings underline synergetic effects of incorporating Fe into Co-based layered double perovskite in achieving a higher activity and stability during oxygen evolution reaction.

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High-Entropy Alloys as a Discovery Platform for Electrocatalysis
A theoretical method for finding active alloy electrocatalysts is proposed, and the method is applied to the electrochemical half-cell reaction of reducing oxygen to water, which is vital for improving the efficiency of, for example, hydrogen fuel cells. Our method predicts adsorption energies between reaction intermediates and the alloy surface to discover which sites on the surface are the most active. Starting from the multicomponent alloy IrPdPtRhRu, the alloy composition with best predicted catalytic activity is found.

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Computational Screening of Light-absorbing Materials for Photoelectrochemical Water Splitting
Efficient conversion of solar energy into electricity or fuels requires the identification of new semiconductors with optimal optical and electronic properties. We discuss the current and future role that computational screening is expected to play in this challenge. We discuss the identification of new computable descriptors characterising optimal materials performance, and we outline different search strategies in the materials screening. Finally, we describe some of the screening results obtained for perovskites, 2D materials, and for materials extracted from crystallographic databases.

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Effects of the cooperative interaction on the diffusion of hydrogen on MgO(100)

Understanding hydrogen diffusion is important for applications such as hydrogen storage and spillover materials. On semiconductors, where paired electron acceptors and donors stabilize each other, the hydrogen diffusion depends on the number of adsorbed fragments. Using density functional theory, we investigate the effects of preadsorbed hydrogens on activation energy and reaction path for hydrogen diffusion on MgO(100): the presence of an unpaired hydrogen causes a diffusion, on O-sites, above the surface with a lower activation energy compared to the case of paired hydrogens where the diffusion distorts the surface. This effect is missing for diffusion on Mg-sites. Published by AIP Publishing.

Fundamental Atomic Insight in Electrocatalysis

Electrochemical energy conversion reactions depend on the atomic structure of the interface between the electrode and the electrolyte. In order to make advances in technology, atomic-scale simulations are needed to provide insight and fundamental understanding of the electrocatalytic reactions. Thus electronic structure calculations relevant for electrocatalysis have attracted a lot of attention in the last decade. However, it is not straightforward to translate state of the art simulations into electrocatalysis. As the simulations normally are done at constant number of ions and electrons rather than at constant potential and constant pH, which represent the real physical conditions. In fact, due to this, the electrochemical interface presents one of the frontiers for electronic structure simulations.

In this chapter we describe how standard simulations can provide atomic-scale understanding of electrocatalytic reactions. We introduce the computational version of reference electrodes, which are key in the interpretation of simulations. Furthermore, the reference electrodes are used to create phase diagrams and reaction free energy diagrams for electrocatalytic reactions. The chapter will focus on simulations which can be done without any special implementation of the electronic structure method. This means that we focus on explicit solvent and charge-neutral interfaces. The connection to the electrode potential is introduced in the analysis of the simulations rather than in the simulations themselves.
Highly Active Nanoperovskite Catalysts for Oxygen Evolution Reaction: Insights into Activity and Stability of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{2+δ}$ and PrBaCo$_2$O$_{5+δ}$

It is shown that producing PrBaCo$_2$O$_{5+δ}$ and Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{2+δ}$ nanoparticle by a scalable synthesis method leads to high mass activities for the oxygen evolution reaction (OER) with outstanding improvements by 10× and 50×, respectively, compared to those prepared via the state-of-the-art synthesis method. Here, detailed comparisons at both laboratory and industrial scales show that Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{2+δ}$ appears to be the most active and stable perovskite catalyst under alkaline conditions, while PrBaCo$_2$O$_{5+δ}$ reveals thermodynamic instability described by the density-functional theory based Pourbaix diagrams highlighting cation dissolution under OER conditions. Operando X-ray absorption spectroscopy is used in parallel to monitor electronic and structural changes of the catalysts during OER. The exceptional BSCF functional stability can be correlated to its thermodynamic meta-stability under OER conditions as highlighted by Pourbaix diagram analysis. BSCF is able to dynamically self-reconstruct its surface, leading to formation of Co-based oxy(hydroxide) layers while retaining its structural stability. Differently, PBCO demonstrates a high initial OER activity while it undergoes a degradation process considering its thermodynamic instability under OER conditions as anticipated by its Pourbaix diagram. Overall, this work demonstrates a synergetic approach of using both experimental and theoretical studies to understand the behavior of perovskite catalysts.
Oxidation of Ethylene Carbonate on Li Metal Oxide Surfaces

Understanding the reactivity of the cathode surface is of key importance to the development of batteries. Here, density functional theory is applied to investigate the oxidative decomposition of the electrolyte component, ethylene carbonate (EC), on layered LixMO(2) oxide surfaces. We compare adsorption energy trends of atoms and small molecules, on both surface oxygen and metal sites, as a function of the Li content of the surface. The oxygen sites are identified as the reactive site for the electrolyte oxidation reaction (EOR). We report reaction energies and NEB-calculated kinetic barriers for the initial oxidative decomposition of EC, and correlate both with the reaction energy of hydrogen adsorption on oxygen. The hydrogen adsorption energy scales with the distance between the Fermi level and the O-2p band center. We expect this model of the EOR to be valid for other organic electrolytes and other Li metal oxide surfaces, due to its simplicity, and the model leads to simple design principles for protective coatings.

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Precision and efficiency in solid-state pseudopotential calculations

Despite the enormous success and popularity of density-functional theory, systematic verification and validation studies are still limited in number and scope. Here, we propose a protocol to test publicly available pseudopotential libraries, based on several independent criteria including verification against all-electron equations of state and plane-wave convergence tests for phonon frequencies, band structure, cohesive energy and pressure. Adopting these criteria we obtain curated pseudopotential libraries (named SSSP or standard solid-state pseudopotential libraries), that we target for high-throughput materials screening ("SSSP efficiency") and high-precision materials modelling ("SSSP precision"). This latter scores highest among open-source pseudopotential libraries available in the.-factor test of equations of states of elemental solids.

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Anisotropic Proton and Oxygen Ion Conductivity in Epitaxial Ba$_2$In$_2$O$_5$ Thin Films

Solid oxide oxygen ion and proton conductors are a highly important class of materials for renewable energy conversion devices like solid oxide fuel cells. Ba$_2$In$_2$O$_5$ (BIO) exhibits both oxygen ion and proton conduction, in a dry and humid environment, respectively. In a dry environment, the brownmillerite crystal structure of BIO exhibits an ordered oxygen ion sublattice, which has been speculated to result in anisotropic oxygen ion conduction. The hydrated structure of BIO, however, resembles a perovskite and the protons in it were predicted to be ordered in layers. To complement the significant theoretical and experimental efforts recently reported on the potentially anisotropic conductive properties in BIO, we measure here both the proton and oxygen ion conductivity along different crystallographic directions. Using epitaxial thin films with different crystallographic orientations, the charge transport for both charge carriers is shown to be anisotropic. The anisotropy of the oxygen ion conduction can indeed be explained by the layered structure of the oxygen sublattice of BIO. The anisotropic proton conduction, however, further supports the suggested ordering of the protonic defects in the material. The differences in proton conduction along different crystallographic directions attributed to proton ordering in BIO are of a similar extent as those observed along different crystallographic directions in materials where proton ordering is not present but where protons find preferential conduction pathways through chainlike or layered structures.

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Computational High-throughput Screening for Solar Energy Materials

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Defect Chemistry and Electrical Conductivity of Sm-Doped La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ for Solid Oxide Fuel Cells

We have calculated the electrical conductivity of the solid oxide fuel cell (SOFC) cathode contact material La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ at 900 K. Experimental trends in conductivity against x, and against δ for fixed x, are correctly reproduced for x $\leq$ 0.8. Furthermore, we have studied the chemistry of neutral and charged intrinsic and extrinsic defects (dopants) in La$_{0.5}$Sr$_{0.5}$CoO$_3$ and have calculated the conductivity of the doped systems. In particular, we find that doping with Sm on the La site should enhance the conductivity, a prediction that is subsequently confirmed by electrical conductivity measurements.

Band-gap engineering of functional perovskites through quantum confinement and tunneling

An optimal band gap that allows for a high solar-to-fuel energy conversion efficiency is one of the key factors to achieve sustainability. We investigate computationally the band gaps and optical spectra of functional perovskites composed of layers of the two cubic perovskite semiconductors BaSnO$_3$ and BaTaO$_2$N. Starting from an indirect gap of around 3.3 eV for BaSnO$_3$ and a direct gap of 1.8 eV for BaTaO$_2$N, different layerings can be used to design a direct gap of the functional perovskite between 2.3 and 1.2 eV. The variations of the band gap can be understood in terms of quantum confinement and tunneling. We also calculate the light absorption of the different heterostructures and demonstrate a large sensitivity to the detailed layering.
Calculated optical absorption of different perovskite phases

We present calculations of the optical properties of a set of around 80 oxides, oxynitrides, and organometal halide cubic and layered perovskites (Ruddlesden-Popper and Dion-Jacobson phases) with a bandgap in the visible part of the solar spectrum. The calculations show that for different classes of perovskites the solar light absorption efficiency varies greatly depending not only on bandgap size and character (direct/indirect) but also on the dipole matrix elements. The oxides exhibit generally a fairly weak absorption efficiency due to indirect bandgaps while the most efficient absorbers are found in the classes of oxynitride and organometal halide perovskites with strong direct transitions.

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Strain sensitivity of band gaps of Sn-containing semiconductors

Tuning of band gaps of semiconductors is a way to optimize materials for applications within photovoltaics or as photocatalysts. One way to achieve this is through applying strain to the materials. We investigate the effect of strain on a range of Sn-containing semiconductors using density functional theory and many-body perturbation theory calculations. We find that the band gaps of bulk Sn oxides with SnO2 octahedra are highly sensitive to volumetric strain. By applying a small isotropic strain of 2% (-2%), a decrease (increase) of band gaps as large as 0.8 to 1.0 eV are obtained. We attribute the ultrahigh strain sensitivity to the pure Sn s-state character of the conduction-band edges. Other Sn-containing...
compounds may show both increasing and decreasing gaps under tensile strain and we show that the behavior can be understood by analyzing the role of the Sn s states in both the valence and the conduction bands.

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**Using Protection Layers for a 2-Photon Water Splitting Device**
The 2-photon tandem device for photocatalytic water splitting has been theoretically shown to provide a higher efficiency than a single photon device(1). This increased efficiency can be achieved by having one material optimized to absorb high energy photons (large bandgap) and another material optimized to absorb low energy photons (small bandgap). To a large degree this approach has been hindered by corrosion issues. In this talk I will first discuss how our computational screening of 2,400 materials showed that very few materials can efficiently absorb light without corroding in water splitting conditions.(2) I will follow this up by discussing how protection layers bypass the corrosion issue by creating a buffer layer.(3) Finally I will show how we integrated a photocatalyst/protection layer(co-catalyst) scheme to produce highly efficient H2 evolution photocathodes and O2 evolution photoanodes.(3, 4) 1. A. B. Laursen, S. Kegnaes, S. Dahl and I. Chorkendorff, Energy & Environmental Science, 5 (2012). 2. B. Seger, I. E. Castelli, P. C. K. Vesborg, K. W. Jacobsen, O. Hansen and I. Chorkendorff, Energy & Environmental Science, 7, 2397 (2014). 3. B. Seger, T. Pedersen, A. B. Laursen, P. C. K. Vesborg, O. Hansen and I. Chorkendorff, Journal of the American Chemical Society, 135, 1057 (2013). 4. B. Mei, A. A. Permyakova, R. Frydendal, D. Bae, T. Pedersen, P. Malacrida, O. Hansen, I. E. L. Stephens, P. C. K. Vesborg, B. Seger and I. Chorkendorff, The Journal of Physical Chemistry Letters, 5, 3456 (2014).

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2-Photon tandem device for water splitting: comparing photocathode first versus photoanode first designs

Within the field of photocatalytic water splitting there are several strategies to achieve the goal of efficient and cheap photocatalytic water splitting. This work examines one particular strategy by focusing on monolithically stacked, two-photon photoelectrochemical cells. The overall aim of the analysis is to compare the relative merits of two fundamentally different designs: one, where the photoanode is the large bandgap material (light-facing side), and the other, where the photocathode is the large bandgap material. Even though the former design is often shown in the literature, the present analysis shows that the latter design has several advantages. This is particularly true when considering designs that incorporate protection layers to protect the photoabsorbers. A high throughput computational screening was used to filter materials databases in search of candidates with the correct properties. These results show that without protective layers there are scarcely any materials which seem viable as photoabsorbers whereas with protection layers there are significantly more candidates. Since the protection layer (and redox catalysts) on the light facing side should not interfere with light absorption, this is the more difficult side to optimize. Nevertheless, by using TiO2 as a transparent cathode protection layer in conjunction with known H-2 evolution catalysts, protection is clearly feasible for a large bandgap photocathode. This suggests that there may be promising strategies for photocatalytic water splitting by using a large bandgap photocathode and a low bandgap photoanode with attached protection layers.

Bandgap calculations and trends of organometal halide perovskites

Energy production from the Sun requires a stable efficient light absorber. Promising candidates in this respect are organometal halide perovskites (ABX3), which have been intensely investigated during the last years. Here, we have performed electronic structure calculations of 240 perovskites composed of Cs, CH3NH3, and HC(NH2)2 as A-cation, Sn and Pb as B-ion, and a combination of Cl, Br, and I as anions. The calculated gaps span over a region from 0.5 to 5.0 eV. In addition, the trends over bandgaps have been investigated: the bandgap increases with an increase of the electronegativities of the constituent species, while it reduces with an increase of the lattice constants of the system.
Calculated Pourbaix Diagrams of Cubic Perovskites for Water Splitting: Stability Against Corrosion

We use density functional theory calculations to investigate the stability of cubic perovskites for photo-electrochemical water splitting taking both materials in their bulk crystal structure and dissolved phases into account. The method is validated through a detailed comparison of the calculated and experimental Pourbaix diagrams for TiO$_2$ and ZnO. For a class of 23 oxides, oxynitrides, and oxyfluorides, which were recently proposed as candidates for one-photon water splitting, our calculations predict most of the materials to be stable at potentials around the water red-ox level. The oxides become less stable at lower potentials, while the oxynitrides become unstable at higher potentials. We discuss the implications of these findings for the problem of photo-corrosion of water splitting electrodes.
Designing rules and probabilistic weighting for fast materials discovery in the Perovskite structure.

High-throughput electronic-structure calculations are becoming increasingly popular in materials science and in the design of new compounds. Electronic-structure theory, for example, in the form of density-functional theory, can be used to calculate stabilities and electronic properties as bandgaps of new compounds. However, in practice, the methods are often limited to rather small atomic-scale systems or periodic crystals with only a limited number of atoms in the unit cell. It is therefore of interest to be able to derive generally useful information from simple systems to be applied in other, more complex, crystals. Here, we consider a large database of calculated stabilities and bandgaps of oxides and oxynitrides in the perovskite structure. We use the database as a testing ground for existing ideas about the behavior of these types of compounds and we derive some new simple chemical-based rules which combine structural information, like the ionic radii of the chemical elements, with electronic data, like the number of electrons and the valences of the pure elements. The rules extracted from the ABO₃ cubic perovskite are then tested using the ABO₂N and A₂BO₄ stoichiometry in the cubic and layered perovskite structure, respectively. These rules allow a saving in computer time of around 80%.

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New Light-Harvesting Materials Using Accurate and Efficient Bandgap Calculations

Electronic bandgap calculations are presented for 2400 experimentally known materials from the Materials Project database and the bandgaps, obtained with different types of functionals within density functional theory and (partial) self-consistent GW approximation, are compared for 20 randomly chosen compounds forming an unconventional set of ternary and quaternary materials. It is shown that the computationally cheap GLLB-SC potential gives results in good agreement (around 15%) with the more advanced and demanding eigenvalue-self-consistent GW. This allows for a high-throughput screening of materials for different applications where the bandgaps are used as descriptors for the efficiency of a photoelectrochemical device. Here, new light harvesting materials are proposed to be used in a one-photon photoelectrochemical device for water splitting by combining the estimation of the bandgaps with the stability analysis using Pourbaix diagrams and with the evaluation of the position of the band edges. Using this methodology, 25 candidate materials are obtained and 5 of them appear to have a realistic possibility of being used as photocatalyst in a one-photon water splitting device. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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Bandgap Engineering of Double Perovskites for One- and Two-photon Water Splitting

Computational screening is becoming increasingly useful in the search for new materials. We are interested in the design of new semiconductors to be used for light harvesting in a photoelectrochemical cell. In the present paper, we study the double perovskite structures obtained by combining 46 stable cubic perovskites which was found to have a finite bandgap in a previous screening-study. The four-metal double perovskite space is too large to be investigated completely. For this reason we propose a method for combining different metals to obtain a desired bandgap. We derive some bandgap design rules on how to combine two cubic perovskites to generate a new combination with a larger or smaller bandgap compared with the constituent structures. Those rules are based on the type of orbitals involved in the conduction bands and on the size of the two cubic bandgaps. We also see that a change in the volume has an effect on the size of the bandgap. In addition, we suggest some new candidate materials that can be used as photocatalysts in one- and two-photon water splitting devices.

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Computational Screening of Materials for Water Splitting Applications
Design new materials for energy production in a photoelectrochemical cell, where water is split into hydrogen and oxygen by solar light, is one possible solution to the problem of increasing energy demand and storage. A screening procedure based on ab-initio density functional theory calculations has been applied to guide the search for new materials. The main descriptors of the properties relevant for the screening are: heat of formation, electronic bandgap, and positions of the band edges with respect to the red-ox levels of water. A recently implemented exchange-correlation functional, called GLBB-SC, has been used for the estimation of the bandgaps. Firstly, a screening procedure has been applied to 19000 cubic perovskite structures. These are obtained by combining 52 metals together with oxygen, nitrogen, sulfur and fluorine...
as anions. 32 promising materials have been found for visible light harvesting, 20 for the one-photon and 12 for the two-photon water splitting process. In addition, 16 candidates were suggested for the transparent shielding of the photocatalyst. The problem of corrosion has been addressed for the candidates for the one-photon scheme using Pourbaix diagrams.

Later on, the screening has been extended to more complex structures, like double and layered perovskites and new compounds of interest for the light harvesting problem were found. In addition, the trends in the bandgaps have been studied. The bandgaps can be tuned by an opportune combination of the metal atoms in the B-ion position in the double perovskite, and of the B-metal ion with the thickness of the octahedra in the layered perovskite structure. In the first part, the crystal structure has been kept fixed. Later, the calculations were done using the structures provided by the Materials Project database, which is based on the experimental ICSD database, and the bandgaps were calculated with focus on finding materials with potential as light harvesters. 24 materials have been proposed for the one-photon water splitting and 23 for the two-photon mechanism. Another method to obtain energy from Sun is using a photovoltaic cell that converts solar light into electricity. The absorption spectra of 70 experimentally known compounds, that are expected to be useful for light-to-electricity generation, have been calculated. 17 materials have been predicted to be promising for a single-layer solar cell and 11 for a double-layer device.

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**Performance of genetic algorithms in search for water splitting perovskites**
We examine the performance of genetic algorithms (GAs) in uncovering solar water light splitters over a space of almost 19,000 perovskite materials. The entire search space was previously calculated using density functional theory to determine solutions that fulfill constraints on stability, band gap, and band edge position. Here, we test over 2500 unique GA implementations in finding these solutions to determine whether GA can avoid the need for brute force search, and thereby enable larger chemical spaces to be screened within a given computational budget. We find that the best GAs tested offer almost a 6 times efficiency gain over random search, and are comparable to the performance of a search based on informed chemical rules. In addition, the GA is almost 10 times as efficient as random search in finding half the solutions within the search space. By employing chemical rules, the performance of the GA can be further improved to approximately 12–17 better than random search. We discuss the effect of population size, selection function, crossover function, mutation rate, fitness function, and elitism on the final result, finding that selection function and elitism are especially important to GA performance. In addition, we determine that parameters that perform well in finding solar water splitters can also be applied to discovering transparent photocorrosion shields. Our results indicate that coupling GAs to high-throughput density functional calculations presents a promising method to rapidly search large chemical spaces for technological materials.

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Stability and bandgaps of layered perovskites for one- and two-photon water splitting

Direct production of hydrogen from water and sunlight requires stable and abundantly available semiconductors with well positioned band edges relative to the water red-ox potentials. We have used density functional theory (DFT) calculations to investigate 300 oxides and oxynitrides in the Ruddlesden–Popper phase of the layered perovskite structure. Based on screening criteria for the stability, bandgaps and band edge positions, we suggest 20 new materials for the light harvesting photo-electrode of a one-photon water splitting device and 5 anode materials for a two-photon device with silicon as photo-cathode. In addition, we explore a simple rule relating the bandgap of the perovskite to the number of octahedra in the layered structure and the B-metal ion. Finally, the quality of the GLLB-SC potential used to obtain the bandgaps, including the derivative discontinuity, is validated against \( G_0 W_0 @ \) LDA gaps for 20 previously identified oxides and oxynitrides in the cubic perovskite structure.

Carbon sp chains in graphene nanoholes

Nowadays sp carbon chains terminated by graphene or graphitic-like carbon are synthesized routinely in several nanotech labs. We propose an ab initio study of such carbon-only materials, by computing their structure and stability, as well as their electronic, vibrational and magnetic properties. We adopt a fair compromise of microscopic realism with a certain level of idealization in the model configurations, and predict a number of properties susceptible to comparison with experiment.
Computational screening of perovskite metal oxides for optimal solar light capture

One of the possible solutions to the world’s rapidly increasing energy demand is the development of new photoelectrochemical cells with improved light absorption. This requires development of semiconductor materials which have appropriate bandgaps to absorb a large part of the solar spectrum at the same time as being stable in aqueous environments. Here we demonstrate an efficient, computational screening of relevant oxide and oxynitride materials based on electronic structure calculations resulting in the reduction of a vast space of 5400 different materials to only 15 promising candidates. The screening is based on an efficient and reliable way of calculating semiconductor band gaps. The outcome of the screening includes all already known successful materials of the types investigated plus some new ones which warrant further experimental investigation.

Mechanical properties of carbynes investigated by ab initio total-energy calculations

As sp carbon chains (carbynes) are relatively rigid molecular objects, can we exploit them as construction elements in nanomechanics? To answer this question, we investigate their remarkable mechanical properties by ab initio total-energy simulations. In particular, we evaluate their linear response to small longitudinal and bending deformations and their failure limits for longitudinal compression and elongation.
New cubic perovskites for one- and two-photon water splitting using the computational materials repository

A new efficient photoelectrochemical cell (PEC) is one of the possible solutions to the energy and climate problems of our time. Such a device requires development of new semiconducting materials with tailored properties with respect to stability and light absorption. Here we perform computational screening of around 19 000 oxides, oxynitrides, oxy sulfides, oxyfluorides, and oxyfluoronitrides in the cubic perovskite structure with PEC applications in mind. We address three main applications: light absorbers for one- and two-photon water splitting and high-stability transparent shields to protect against corrosion. We end up with 20, 12, and 15 different combinations of oxides, oxynitrides and oxyfluorides, respectively, inviting further experimental investigation.
Vibrational characterization of dinaphthylpolyynes: A model system for the study of end-capped sp carbon chains

We perform a systematic investigation of the resonance and vibrational properties of naphthylterminated sp carbon chains (dinaphthylpolyynes) by combined multi-wavelength resonant Raman (MWRR) spectroscopy, ultraviolet-visible spectroscopy, and Fourier-transform infrared (FT-IR) spectroscopy, plus ab initio density functional theory (DFT) calculations. We show that the MWWR and FT-IR spectroscopies are particularly suited to identify chains of different lengths and different terminations, respectively. By DFT calculations, we further extend those findings to sp carbon chains end-capped by other organic structures. The present analysis shows that combined MWRR and FT-IR provide a powerful tool to draw a complete picture of chemically stabilized sp carbon chains.

Synthesis, Characterization, and Modeling of Naphthyl-Terminated sp Carbon Chains: Dinaphthylpolyynes

We report a combined study on the synthesis, spectroscopic characterization, and theoretical modeling of a series of α,ω-dinaphthylpolyynes. We synthesized this family of naphthyl-terminated sp carbon chains by reacting diodoacetylene and 1-ethynlnaphthalene under the Cadiot–Chodkiewicz reaction conditions. By means of liquid chromatography (HPLC), we separated the products and recorded their electronic absorption spectra, which enabled us to identify the complete series of dinaphthylpolyynes Ar–C2n–Ar (with Ar = naphthyl group and n = number of acetilenic units) with n ranging from 2 to 6. The longest wavelength transition (LWT) in the electronic spectra of the dinaphthylpolyynes red shifts linearly with n away from the LWT of the bare termination. This result is also supported by DFT-LDA simulations. Finally, we probed the stability of the dinaphthylpolyynes in a solid-state precipitate by Fourier-transform infrared spectroscopy and by differential scanning calorimetry (DSC).
Tribology of the lubricant quantized sliding state

In the framework of Langevin dynamics, we demonstrate clear evidence of the peculiar quantized sliding state, previously found in a simple one-dimensional boundary lubricated model A. Vanossi et al., Phys. Rev. Lett. 97, 056101 2006, for a substantially less idealized two-dimensional description of a confined multilayer solid lubricant under shear. This dynamical state, marked by a nontrivial "quantized" ratio of the averaged lubricant center-of-mass velocity to the externally imposed sliding speed, is recovered, and shown to be robust against the effects of thermal fluctuations, quenched disorder in the confining substrates, and over a wide range of loading forces.

The lubricant softness, setting the width of the propagating solitonic structures, is found to play a major role in promoting in-registry commensurate regions beneficial to this quantized sliding. By evaluating the force instantaneously exerted on the top plate, we find that this quantized sliding represents a dynamical "pinned" state, characterized by significantly low values of the kinetic friction. While the quantized sliding occurs due to solitons being driven gently, the transition to ordinary unpinned sliding regimes can involve lubricant melting due to large shear-induced Joule heating, for example at large speed.

Role of transverse displacements for a quantized-velocity state of a lubricant

Within the idealized scheme of a one-dimensional Frenkel–Kontorova-like model, a special 'quantized' sliding state was found for a solid lubricant confined between two periodic layers (Vanossi et al 2006 Phys. Rev. Lett. 97 056101). This state, characterized by a nontrivial geometrically fixed ratio of the mean lubricant drift velocity and the externally imposed translational velocity vext, was understood as due to the kinks (or solitons) formed by the lubricant due to incommensuracy with one of the substrates, pinning to the other sliding substrate. A quantized sliding state of the same nature is demonstrated here for a substantially less idealized two-dimensional model, where atoms are allowed to move perpendicularly to the sliding direction and interact via Lennard-Jones potentials. Clear evidence for quantized sliding at finite temperature is provided, even with a confined solid lubricant composed of multiple (up to six) lubricant layers.
Characteristic backward lubricant motion produced by the presence of 'anti-kinks' is also shown in this more realistic context.