CHIMIA

CHIMIA 2017, Volume 71
ISSN 0009-4293
www. chimia.ch
Supplementa to Issue 7-8/2017

SCS
Swiss Chemical
Society

SCS Fall Meeting 2017
Future Leaders on Stage, Lecture Abstracts

Session Physical Chemistry, Theoretical Chemistry and Materials

August 21-22, 2017
University of Bern, Areal vonRoll
http://scg.ch/fallmeeting/2017

Swiss Chemical Society
Haus der Akademien
Postfach
3001 Bern
Switzerland
info@scg.ch
www.scg.ch

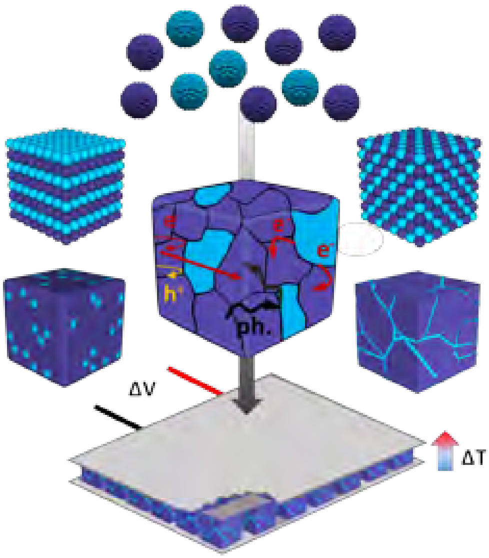
High-Performance Thermoelectric Nanocomposites from Nanocrystal Building Blocks

M. Ibáñez[1,2], M. V. Kovalenko[1]*

[1]ETH Zürich, [2]EMPA

The efficient conversion of thermal energy to electricity and vice versa by means of solid-state thermoelectric devices has been a long-standing goal. However, its cost-effectiveness is hampered by the relatively low efficiency and high production cost of current thermoelectric materials. Therefore, materials with significantly improved performance need to be developed to enable a successful deployment of thermoelectric systems in their wide application range. The efficiency of TE devices depends on three interrelated material parameters: the electrical conductivity, *s*, the Seebeck coefficient, *S*, and the thermal conductivity, *k*. These parameters are grouped into a dimensionless figure of merit, *ZT*, defined as $ZT=sS^2Tk^{-1}$ where *T* is the absolute temperature.

Nanostructuration has been proven helpful to reach the very particular group of properties required to achieve high thermoelectric performances: high *s*, high *S*, and low *k* (*Chem. Soc. Rev.* **2017**, DOI: 10.1039/C6CS00567E). Nanodomains within a crystalline matrix can inject large charge carrier concentrations without significant influence on their mobility, thus reaching high electrical conductivities. Moreover, nanostructured materials contain high density of interfaces that efficiently scatter mid- and long-wavelength phonons hence reducing the thermal conductivity. Finally, nanocrystalline domains can increase the Seebeck coefficient by modifying the density of states and/or providing type- and energy-dependent charge carrier scattering. All these advantages can only be reached when engineering a complex type of material, nanocomposites, with exquisite control over structural and chemical parameters at multiple length scales. Current conventional nanomaterial production technologies lack such level of control, thus alternative strategies need to be developed and adjusted to the specifics of the field. A particularly suitable approach to produce nanocomposites with unique level of control over their structural and compositional parameters is their bottom-up engineering from solution-processed nanoparticles. Herein, we present the synthesis of nanoparticles of suitable materials with precisely engineered composition and surface chemistry, their combination and consolidation into nanostructured materials, and the strategies to electronically dope such materials to overall produce high performance thermoelectric materials.

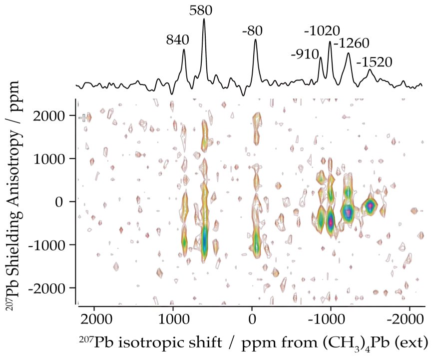


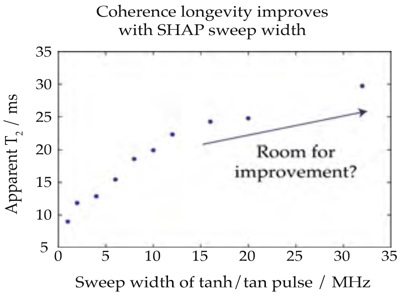
^{207}Pb NMR of Perovskite Ferroelectrics at Variable Temperatures using Frequency-Swept Pulses

C. E. Avalos[1], B. J. Walder[1], J. Viger-Gravel[1], L. Emsley[1]*

[1]Ecole polytechnique fédérale de Lausanne

Ferroelectric materials exhibit spontaneous electric polarization along a crystallographic axis where the direction and strength of the spontaneous electric field is dependent on the structure and composition of the material. The bulk piezoelectric and ferroelectric properties of these materials make them useful for applications in optics, microelectronics and additionally fundamental physics applications where lead ferroelectrics have been proposed for a search of a P,T-violating Schiff moment of the ^{207}Pb nucleus [1]. The properties of these materials depend strongly on microscopic displacements of the metal cations within the material. As has been demonstrated in the past [2], ^{207}Pb NMR yields information about the structure and magnetic anisotropy of lead sites in ferroelectric materials. These experiments are often challenging due to a combination of chemical and positional disorder present in these materials which leads to broadened and low-resolution NMR spectra. As such, exciting the full magnetic resonance bandwidth requires proper implementation of broadband pulses [3].





Using short, high-power adiabatic pulses (SHAP) [4] in combination with state-of-the-art NMR pulse sequences [5, 6] we investigate changes in the chemical shift anisotropy (CSA) parameters and spin relaxation behaviour at ^{207}Pb sites in three ferroelectric materials: $PbTiO_3$, $Pb_5Ge_3O_{11}$ and PMN-PT. We observe the first site resolved spectra of $Pb_5Ge_3O_{11}$ and we measure a T_2' for $PbTiO_3$ that is one order of magnitude longer than previously reported [7]. We present variable temperature ^{207}Pb NMR data and discuss how changes in the NMR spectra relate to changes in the local and bulk structure of these materials.

[1] D. Budker, S. K. Lamoreaux, A. O. Sushkov and O. P. Sushkov, *Physical Review A*, **2006**, 73, 022107.
[2] D. H. Zhou, G. L. Hoatson, R. L. Vold and F. Fayon, *Physical Review B*, **2004**, 69, 134104.
[3] A. J. Pell and G. Pintacuda, *Progress in Nuclear Magnetic Resonance Spectroscopy*, **2015**, 84, 33-72.
[4] G. Kervern, G. Pintacuda and L. Emsley, *Chemical Physics Letters*, **2007**, 435, 147-162.
[5] B. J. Walder, K. K. Dey, D. C. Kaseman, J. H. Baltisberger and P. J. Grandinetti, *The Journal of Chemical Physics*, **2013**, 138, 174203.
[6] S. L. Gann, J. H. Baltisberger and A. Pines, *Chemical Physics Letters,* **1993**, 210, 405-410.
[7] L. S. Bouchard, A. O. Sushkov, D. Budker, J. J. Ford and A. S. Lipton, *Physical Review A*, **2008**, 77, 022102.

Versatility of perovskite semiconductors as detectors for visible and high energy photons

S. Yakunin[1,2], D. N. Dirin[1,2], Y. Shynkarenko[1,2], V. Morad[1], I. Cherniuh[1], O. Nazarenko[1,2], M. V. Kovalenko[1,2]*

[1]ETH Zürich, [2]Empa – Swiss Federal Laboratories for Materials Science and Technology

Lead halide perovskites emerged as excellent absorber materials in photovoltaic research a few years ago. Thereafter they were demonstrated as versatile photonic sources [1] and photon detecting materials [2]. As to the latter, detecting capability has been reported in two distinct spectral ranges: visible light and high energy photons (X-ray and gamma-rays). Detectors of such hard radiation that are low-cost, are highly-sensitive and operate at ambient temperatures are highly desired for numerous applications such as in defence, medicine, as well as in research. Recently we have shown that $MAPbI_3$ polycrystalline films work as sensitive detectors of soft X-ray radiation [2]. We also demonstrated that 0.3-1 cm, solution-grown single crystals (SCs) of semiconducting hybrid lead halide perovskites ($MAPbI_3$, $FAPbI_3$ and I^-treated $MAPbBr_3$, where MA=methylammonium, FA=formamidinium) can serve as solid-state gamma-detecting materials [3]. This possibility arises from a high mobility(μ)-lifetime(τ) product of 1.0-1.8 10^{-2} cm^2 V^{-1}, the low dark carrier density of 10^9 - 10^{11} cm^{-3} and low density of charge traps of 10^9 - 10^{10} cm^{-3}, and a high absorptivity of hard radiation by the lead and iodine atoms.

Lead halide perovskites are highly compelling materials for the detectors operated in the visible spectral range, as they feature high optical absorption coefficients and excellent compositional tunability of their bandgaps, easily achievable via inexpensive solution growth. This allowed as constructing a full-colour sensor with three layers, complimentary detecting blue, green and red photons [4]. We find that this prototype detector could faithfully reproduce simple one-dimensional images and realistic two-dimensional images with excellent colour resolution. Such vertically layered detectors offer several advantages over traditional Bayer-type dissipative and subtractive optically filtered detectors: a potentially higher spatial resolution improves optical efficiency suppresses the occurrence of colour moiré and de-mosaicing artefacts.

[1] S. Yakunin, L. Protesescu, F. Krieg, M. I. Bodnarchuk, G. Nedelcu, M. Humer, G. De Luca, M. Fiebig, W. Heiss, and M. V. Kovalenko. Nature Communications, **2015**, 9, 8056.
[2] S. Yakunin, M. Sytnyk, D. Kriegner, S. Shrestha, M. Richter, G. Matt, H. Azimi, C. J. Brabec, J. Stangl, M. Kovalenko and W. Heiss. Nature Photonics, **2015**, 9, 444-449.
[3] S. Yakunin, D. Dirin, Y. Shynkarenko, V. Morad, I. Cherniuh, O. Nazarenko, D. Kreil, T. Nauser and M. Kovalenko. Nature Photonics, **2016**, 10, 585–589.
[4] S. Yakunin, Y. Shynkarenko, D.N. Dirin, I. Cherniukh and M.V. Kovalenko (submited).

Towards hybrid trapping of cold molecules and cold molecular ions

D. Zhang[1], D. Haas[1], C. von Planta[1], S. Willitsch[1]

[1]Department of Chemistry, University of Basel, Basel, Switzerland

Hybrid systems of cold atoms and ions have been studied insensitively in recent years. The simultaneous trapping of atoms with ions has opened up new possibilities for the investigation of interactions between the two species and has greatly contributed to the understanding of collisional and chemical processes at low temperatures [1]. Here, we report on the development of an advanced hybrid trapping technique which aims at trapping neutral molecules and molecular ions simultaneously. A translationally cold package of neutral molecules is produced by means of either Stark deceleration or Zeeman deceleration. With the deceleration technique, a molecular package at translational temperature in the mK regime can be produced [2]. During the last deceleration stage, the molecular package is loaded into a magnetic trap, which is incorporated into an RF ion trap. With this set-up, the superposition of cold neutral molecules with molecular ions allows for quantum-state selective investigations of elastic, inelastic and reactive collisions at low translational energies. Initial experiments will focus on $OH + Ca^+$, $OH + N_2^+$ and $OH + H_2O^+$ as collision systems.

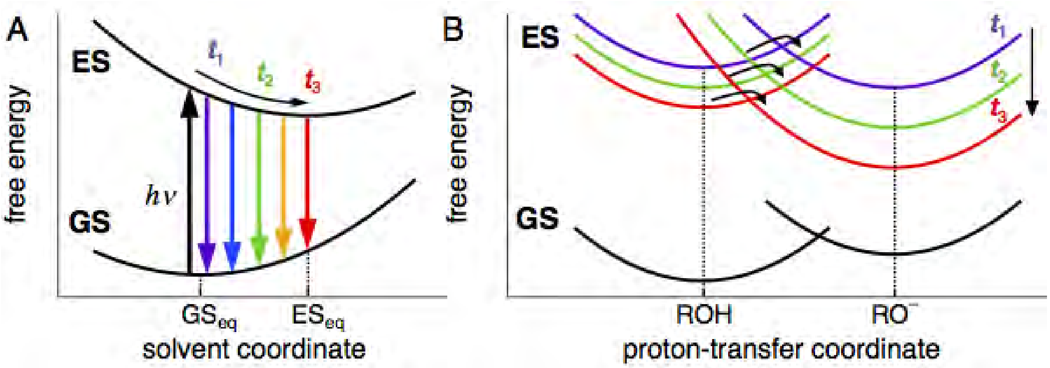
[1] Stefan Willitsch, *Proceedings of the International School of Physics "Enrico Fermi"*, **2015**, 189, 255.
[2] Sebastiaan Y. T. van de Meerakker, Hendrick L. Bethlem, Nicolas Vanhaecke, and Gerard Meijer, *Chemical Reviews*, **2012**, 112, 4828-4878.

Solvent Relaxation and its Influence on Photochemical Reactions

T. Kumpulainen[1], A. Rosspeintner[1], E. Vauthey[1]*

[1]University of Geneva, Department of Physical Chemistry, Sciences II, CH-1211 Geneva, Switzerland

The choice of the solvent can have a dramatic effect on the outcome of a chemical reaction. In addition to specific solvent interactions such as hydrogen bonding, solvent environment can greatly influence equilibrium, reaction rate and driving force by different stabilization of the reactants, transition states or products, especially with reactions involving charged or strongly dipolar species. For example, the activation energy is decreased when solvation energy of the transition state is larger than that of the reactant state, whereas the overall driving force of a reaction is increased upon greater stabilization of the product state relative to the reactant state.[1] All these above effects can be considered as equilibrium effects and can be illustrated by a static energy-level diagram. How about when the rate of a solvent influenced reaction is faster or comparable to the dynamics of the solvent itself? In this case, the situation cannot be illustrated by a static picture and the reaction becomes solvent controlled i.e. both the rate and the yield of the reaction are controlled by the solvent relaxation.[2]



In our communication, we will explain the basic principles of dynamic solvent relaxation: What is its origin and how can we monitor this process?[3] Second, we will demonstrate the effect of solvent relaxation on a photochemical reaction, namely an excited-state proton transfer (ESPT). This reaction consists of the photodissociation of a hydroxylic proton from an aromatic alcohol and results in formation of charged products. The reaction is therefore strongly influenced by the solvent environment making it an ideal candidate to study the dynamic solvent effects.

[1] Christian Reichardt, Thomas Welton (**2010**) *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Weinheim, Germany, pp. 107–357.

[2] T. Kumpulainen, B. Lang, A. Rosspeintner, E. Vauthey, *Chem. Rev.*, **2016**, DOI: 10.1021/acs.chemrev.6b00491.

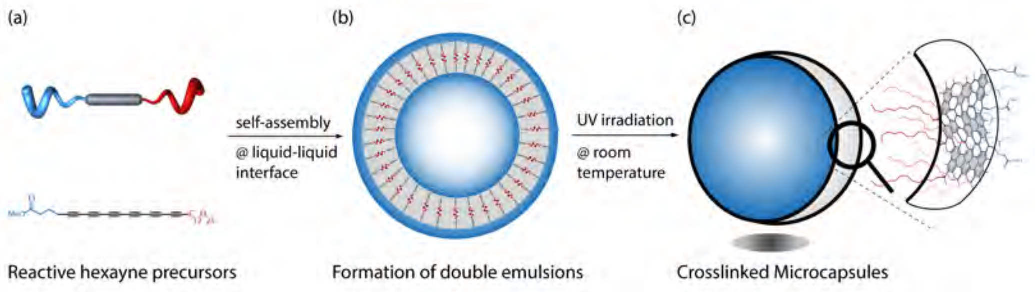
[3] T. Kumpulainen, A. Rosspeintner, E. Vauthey, *Phys. Chem. Chem. Phys.*, **2017**, 19, 8815-8825.

Reactive Hexayne Precursors for Microfluidic Production of Carbon Microcapsules

B. Schulte[1,2], V. Croué[1], E. Bomal[1], E. Amstad[2]*, H. Frauenrath[1]*

[1]Laboratory of Macromolecular and Organic Materials (LMOM), Ecole Polytechnique Fédérale de Lausanne (EPFL), [2]Soft Materials Laboratory (SMaL), Ecole Polytechnique Fédérale de Lausanne (EPFL)

Liposomes are defined vesicular aggregates formed from small amphiphilic organic molecules. The formation of liposomes is an important way to achieve compartmentalization in nature, and synthetic liposomes often serve as simplified model systems to study the behavior of biological membranes with regard to their permeability and their uptake-and-release properties. The work presented here has aimed to prepare “carbosomes” as a novel type of vesicular, synthetic materials that resemble liposomes but have a carbon shell. The "carbosomes" we have prepared represent microcapsules that are fabricated from carbon-rich, amphiphilic precursor molecules (Figure 1).



These precursors have a polar head group, a reactive segment of twelve *sp*-hybridized carbon atoms, and a hydrocarbon tail. Previous investigations of the self-assembly of carbon-rich amphiphiles at the air-water interface showed that flat carbon nanosheets are accessible already under mild conditions, such as UV irradiation at room temperature [1, 2]. We self-assembled these precursor molecules at the oil-water interface using microfluidic drop emulsification, which allows us to create oil-in-water single emulsion or water-in-oil-in-water double emulsion droplets with defined size and composition. The goal is to obtain extensively cross-linked carbon-rich capsules with a diameter on the order of micrometers that have a defined chemical surface functionalization and are constituted from an ultrathin carbon shell with a thickness of 2–4 nm. Such microcapsules are expected to combine a low shell thickness similar to biological cells or synthetic liposomes with the mechanical rigidity and electrical properties of carbon nanomaterials. Thus, the project is expected to deliver insights into the mechanical stability and porosity of these microcapsules. Furthermore, it provides an interesting platform to study fundamental questions of surfactant self-assembly, such as the effect of an ionic or non-ionic precursor on the shell density of the crosslinked microcapsule and the carbon microstructure within the shell.

[1] Stephen Schrettl, Cristina Stefaniu, Christian Schwieger, Guillaume Pasche, Emad Oveisi, Yannik Fontana, Anna Fontcuberta i Morral, Javier Reguera, Riccardo Petraglia, Clémence Corminboeuf, Gerald Brezesinski, Holger Frauenrath, *Nature Chemistry*, **2014**, 6, 468-476.
[2] Stephen Schrettl, Bjoern Schulte, Cristina Stefaniu, Joana Oliveira, Gerald Brezesinski, Holger Frauenrath, *Journal of Visualized Experiments*, **2016**, 109, e53505.