<table>
<thead>
<tr>
<th>Poster No.</th>
<th>Poster Details</th>
</tr>
</thead>
</table>
| 1 | Imaging the calcium carbonate - organic interfaces in sea urchin spines  
M. Albéric, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany |
| 2 | Towards atomic resolution imaging of zeolites  
G. Algara-Siller, Fritz-Haber-Institut der MPG, Berlin, Germany |
| 3 | Bio-inspired surface modification based on artificial glue proteins with tunable adhesion and cohesion properties  
S. Arias, Humboldt-Universität zu Berlin, Germany |
| 4 | New insights into the role of the osteocyte network in the stage of early mineralization of human cortical bone  
M. Ayoubi, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany |
| 5 | Characterization of ASR products by STEM  
S. Barbotin, EPFL, Lausanne, Switzerland |
| 6 | Nanobiolasmonic catalysts: The study of the nano-bio interface of enzyme-gold nanoparticles structures for light-driven reactions  
H.R. Barros, São Paulo University, Brazil |
| 7 | In situ electrochemical liquid-cell transmission electron microscopy studies of nanoparticle catalysts  
V. Beermann, Technical University Berlin, Germany |
| 8 | Electron microscopy of virus composites  
A.M. Bittner, CIC nanoGUNE, Donostia-San Sebastián, Spain |
| 9 | Observation of charge density waves in free-standing 1T- TaSe2 monolayers by transmission electron microscopy  
P. Börner, Ulm University, Germany |
| 10 | Imaging dynamic processes with high spatial & temporal resolution by scanning transmission electron microscopy  
N.D. Browning, University of Liverpool, United Kingdom |
| 11 | Optimization of electron-beam parameters for adequate cathodoluminescence characterization of hybrid halide perovskites  
S. Caicedo-Dávila, Helmholtz-Zentrum Berlin for Materials and Energy, Germany |
| 12 | Dynamics of dirhenium molecule containing multiple bonds  
K. Cao, Ulm University, Germany |
| 13 | Comparison of low-dose imaging using simultaneous iDPC- and ADF STEM for beam-sensitive crystals  
<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>Authors</th>
<th>Institution/Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>Interfacial Design through Poly-Ionic Liquid Surface Modification in Efficient pin Perovskite Solar cells</td>
<td>S.D. Cruz, Max-Planck-Institute of Colloids and Interfaces, Potsdam, Germany</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>TEM imaging on micro-channels directed hierarchical nanocrystal structures</td>
<td>X. Deng, Queen Mary University of London, United Kingdom</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Surface atomic structure and growth mechanism of monodisperse (100)-faceted strontium titanate zirconate nanocubes</td>
<td>H. Du, Forschungszentrum Juelich GmbH, Germany</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>In situ liquid cell microscopy: An essential tool for studying dynamic processes at the nanoscale</td>
<td>M.J. Dukes, Protochips Inc., Morrisville, NC USA</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Organic ice resist lithography for the nanofabrication of bio-hybrid devices</td>
<td>A. Elsukova, DTU Nanolab, Denmark</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Influence of the antimicrobial modified polymers microstructure on the bacteria cell wall</td>
<td>M. Er-Rafik, DTU Nanolab, Denmark</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>3d visualisation and characterisation of microporous polymer coatings for controlled drug release</td>
<td>C. Fager, Chalmers University of Technology, Gothenburg, Sweden</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Fluoride treatment of hydroxyapatite – mechanisms and effects</td>
<td>T. Faidt, Saarland University, Saarbrücken, Germany</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Microstructure diagnostics of ophthalmic lens coatings</td>
<td>R. Feder, Fraunhofer Institute for Microstructure of Materials and Systems IMWS, Germany</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Early stages of biomineral formation by STEM-EELS spectromicroscopy</td>
<td>M. de Frutos, Université Paris Sud, Orsay, France</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>TEM analysis and sample preparation of inorganic cesium-lead-halide perovskites</td>
<td>H. Funk, Helmholtz-Zentrum Berlin, Germany</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>Crystallinity, texture and nanomorphology of organic bulk heterojunction solar cells studied by electron microscopy</td>
<td>C. Harreiß, Center for Nanoanalysis and Electron Microscopy, Erlangen, Germany</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Reduction of systematic and excessive noise in charge-coupled device measurements</td>
<td>T. Heil, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>Nanoscale characterisation of ultrathin gold films deposited on silica with organosilane adhesion layers</td>
<td>M.F. Heinig, DTU Nanolab, Denmark</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Title</td>
<td>Author(s), Institution, Country</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----------------------------------------------------------------------</td>
<td>--------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>In-situ transmission electron microscopy on reversible lithium loading of bilayer graphene</td>
<td>U. Kaiser, Ulm University, Germany</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>Structural characteristics of biological objects visualized by TEM techniques</td>
<td>B.P. Kaltschmidt, Bielefeld University, Germany</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>In situ SEM characterization of materials</td>
<td>I. Kaplan-Ashiri, Weizmann Institute of Science, Rehovot, Israel</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>2D and 3D electron microscopy imaging in tissue engineering</td>
<td>J. Karbowniczek, AGH University of Science and Technology, Poland</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Reduced radiation damage in transmission electron microscopy of proteins in graphene liquid cells</td>
<td>S. Keskin, INM - Leibniz Institute for New Materials, Saarbrücken, Germany</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>Novel lattice-rotation nanostructures formed in TEM by crystallization of amorphous films</td>
<td>V.Yu. Kolosov, Ural Federal University, Ekaterinburg, Russia</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>Characterising chemical composition of perovskite solar cells with multivariate statistical analysis</td>
<td>F.U. Kosasih, University of Cambridge, United Kingdom</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>Poly arginine intervening in the crystallization pathway of magnetite</td>
<td>L. Kuhrs, Max Planck Institute of Colloids and Interfaces, Germany</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>Liquid cell electron microscopy for observing colloidal self-assembly of low-z material</td>
<td>P. Kunnas, Leibniz Institute for New Materials, Saarbrücken, Germany</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>Grain boundary structures in 2d polyimine by low-dose HRTEM</td>
<td>B. Liang, Ulm University, Germany</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>Cryo-electron microscopy of colloidal nanoparticles</td>
<td>W.L. Ling, University Grenoble Alpes, France</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>Towards tunable near-obstruction-free phase plates</td>
<td>P.-H. Lu, Forschungszentrum Jülich, Germany</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Mineral and organic matrix interaction in calcifying avian tendons: A transmission electron microscopy study</td>
<td>E. Macías-Sánchez, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>M1-phase (Mo,V)Oₓ – Probing the local metal distribution</td>
<td>L. Masliuk, Fritz-Haber-Institut der Max Planck Gesellschaft, Berlin, Germany</td>
<td></td>
</tr>
</tbody>
</table>
### Poster List

<table>
<thead>
<tr>
<th>Page</th>
<th>Title</th>
<th>Author(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>Black carbon nanoparticles on the Greenland ice sheet: Where do they come from and how do they contribute to melting?</td>
<td>J. McCutcheon, University of Leeds, United Kingdom</td>
</tr>
<tr>
<td>43</td>
<td>Seeing between the cells: Highlighting extracellular biofilm structure and mineral nucleation processes</td>
<td>J. McCutcheon, University of Leeds, United Kingdom</td>
</tr>
<tr>
<td>44</td>
<td>Mapping structure and morphology of amorphous organic thin films by STEM pair distribution function analysis</td>
<td>X. Mu, Karlsruhe Institute of Technology, Germany</td>
</tr>
<tr>
<td>45</td>
<td>Triple and quintuple ordering in the perovskite-type solid oxides $\text{Ln}<em>{0.4-\delta}\text{Ba}</em>{0.6+\delta}\text{Fe}<em>{1-\gamma}\text{Co}</em>{\gamma}\text{O}_3$ ($\text{Ln}=\text{Gd, Sm}$; $\gamma=0-0.035$; $\delta=0-0.4$)</td>
<td>M.Yu. Mychinko, Ural Federal University, Ekaterinburg, Russia</td>
</tr>
<tr>
<td>46</td>
<td>Atomic resolution imaging and analysis of nanomaterials in cells and tissue</td>
<td>H.C. Nerl, Trinity College Dublin, Ireland</td>
</tr>
<tr>
<td>47</td>
<td>Supercooled water in ESEM</td>
<td>E. Nikulina, CIC nanoGUNE, Donostia-San Sebastián, Spain</td>
</tr>
<tr>
<td>48</td>
<td>Interaction between ‘green rust’ and redox-sensitive oxyanions revealed by STEM-EELS</td>
<td>J.P.H. Perez, GFZ German Research Centre for Geosciences, Potsdam, Germany</td>
</tr>
<tr>
<td>49</td>
<td>Enhancing the photocatalytic activity of calcium and strontium-based molybdates</td>
<td>D.V. Piankova, Ural Federal University, Ekaterinburg, Russia</td>
</tr>
<tr>
<td>50</td>
<td>Operando transmission electron microscopy to study catalysts under reaction conditions</td>
<td>C. Pratsch, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany</td>
</tr>
<tr>
<td>51</td>
<td>Cryo Volume Imaging: From cell nucleus to extracellular structure</td>
<td>K. Rechav, Weizmann Institute of Science, Rehovot, Israel</td>
</tr>
<tr>
<td>52</td>
<td>Electron beam induced amorphisation of polypropylene particles</td>
<td>C. Rohner, Fritz-Haber-Institut der MPG, Berlin, Germany</td>
</tr>
<tr>
<td>53</td>
<td>Crystallisation and orientational behaviour of nylon on inorganic nanoplatelets in nanocomposite fibres</td>
<td>W.F.C. Sager, Forschungszentrum Jülich, Germany</td>
</tr>
<tr>
<td>54</td>
<td>Low dose scanning transmission electron microscopy of organic crystals by scanning moiré fringes</td>
<td>M. S’ari, University of Leeds, United Kingdom</td>
</tr>
<tr>
<td>55</td>
<td>Correction of motion aberration in liquid-cell TEM imaging with MotionCor2</td>
<td>J. Seto, UCSF, San Francisco, USA</td>
</tr>
</tbody>
</table>
56 Sub-cellular elemental mapping by combined STEM-EDX-EELS
A.A. Sheader, University of Oxford, United Kingdom

57 Copper canister for spent nuclear fuel storage: Gamma-radiation induced corrosion
I.L. Soroka, KTH Royal Institute of Technology, Stockholm, Sweden

58 Nano-crystallography structure solution of organic and inorganic crystals
A.A. Stewart, University of Limerick, Ireland

59 Mineral and organic matrix interaction in calcifying avian leg tendons: A focused ion beam – scanning electron microscopy study
T. Tang, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

60 Synthesis and characterization of nanosized metal nanoparticles in a disulfide matrix polymer
M. Wagner, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany

61 In situ electrochemical liquid-cell transmission electron microscopy studies of CuOx nanosheets for CO2 electroreduction
X. Wang, Technical University Berlin, Germany

62 Degradable Mg-based implants: Impact on the ultrastructure of bone
D.C.F. Wieland, Helmholtz Zentrum Geesthacht, Germany

63 Measurement of the mean inner potential of PMMA and its electron beam induced charging using off-axis electron holography
F. Zheng, Forschungszentrum Jülich, Germany
Two poster prizes – on general topics and on in-situ studies – are kindly sponsored by Protochips.
Imaging the calcium carbonate - organic interfaces in sea urchin spines

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Sea urchin spines are formed via the deposition of amorphous calcium carbonate (ACC) that further crystallizes into calcite in the presence of organic molecules (proteins, glycoproteins, saccharides, pigments) [1,2]. They comprise about 1.5 wt.% of intra-crystalline organic molecules and 10 wt.% of remnant anhydrous and stable ACC [3]. In order to further understand the biomineralization mechanisms leading to the formation of macro-size single crystals with complex shapes, it is essential to determine the role of organic molecules in the biologically controlled continuous deposition of mineralized layers.

Figure 1. Polished section of a sea urchin spine observed under A) and C) SEM-BSE, B) and D) CRM (Fluorescence maps: 1800-3900 cm⁻¹) and E) AFM.

In order to do so, we investigate the spatial distribution of organic molecules, ACC and calcite in sea urchin spines by using a variety of high-resolution imaging and spectroscopic techniques, such as Back Scattered Electron - Scanning Electron Microscopy (BSE-SEM), Confocal Raman Microscopy (CRM) and Atomic Force Microscopy (AFM) (Figure 1).


Keywords: Microscopies, calcium carbonate-organic interface.
Towards atomic resolution imaging of zeolites

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Zeolites are of great importance for scientific purposes or industrial processes such as catalysis, purification, structural templates, etc. These materials are known to be sensitive to the electron beam. This sensitivity can be related to the Si/Al ratio, type of cations, water content, etc. [1-3]. In this work we present a TEM characterisation of zeolite A (LTA framework). The zeolites used in this work have a Si/Al ratio of one, and contain K or Na cations in the channels, rendering them highly sensitive to electron irradiation. HRTEM characterisation was performed in an aberration-corrected JEOL ARM 200F and FEI Titan 80-300 operated, both, at 200 kV under low dose rate imaging conditions (<10\textsuperscript{3} e/nm\textsuperscript{2}s). Even under these conditions the structure of zeolite A could be obtained by digital processing. Firstly, a set of low dose images was drift corrected using a combination of cross correlation based template matching, and secondly the resulted set was then processed by hierarchical clustering. The average image from the stack is an atomically resolved image with specific features such as crystal misorientation and structural defects are discernible and interpretable. These results demonstrate that the imaging limitation caused by radiation damage can be lessened by applying an image processing methodology that does not use a priori knowledge of the structure.


Keywords: Microscopy, zeolite, radiation damage, image processing.
Bio-inspired surface modification based on artificial glue proteins with tunable adhesion and cohesion properties

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High performance wet adhesives are technologically and scientifically of interest as they promise applications such as under water glues, anti-fouling or anti-corrosive coatings as well as biomedical glues for tissue sealing or surgical adhesion. The mussel-inspired adhesives will be generated in an enzyme activated polymerization process of peptide-based macromonomers and mimic the adhesive behavior through cystenyl-Dopa-connectivities that are produced in the polymerization process. Most importantly, cohesion will be controlled and modulated by incorporation of switchable β-sheet segments that complement the adhesive behavior by inducing inner secondary structure formation to generate cohesion control and contribute to under water gluing performance.

Figure 1. Graphic concept of enzyme-mediated polymerization principle.


Keywords: Adhesives, tyrosinase activation, mussel glue, QCM, colloidal probe atomic force microscopy (CP-AFM).
Bone as a hierarchically structured biomaterial has various functions such as locomotion of body, protection of organs, calcium homeostasis, etc. Some of these functions are due to its unique mechanical properties which are mirrored from a combination of collagenous matrix and crystals of carbonated hydroxyapatite. Biomineralization of bone, the process in which these crystals are formed, has been vastly studied [1]. However the role of Osteocytes - the most abundant cells in bone - on the mineralization of non-mineralized bone (osteoid) is still unclear.

In the presented study, we investigated this early mineralization process in a polymethylmethacrylate embedded post-mortem sample of human osteonal bone. We established a 3D imaging routine based on FIB-SEM (focused ion beam-scanning electron microscopy) to image the bone structure with a resolution of 30 nm after staining the collagenous matrix with iodine vapor.

Our measurements show newly mineralized foci of less than 200 nm in diameter at the mineralization front. Because of the iodine staining, we could distinguish the collagenous matrix from the osteocyte network which, therefore, could be segmented out from the imaged volumes. Thanks to this, we were able to obtain a correlation between the grey scale values of the backscattered electron images (which can be interpreted as degree of mineralization) and the shortest distance to the nearest canaliculus. Our preliminary data show that early bone mineralization is happening usually more than ~0.4 µm away from the canaliculi. With our results we aim to create a model to understand if or how the osteocytes mediate the mineralization process.


**Keywords:** Osteoid mineralization, Osteocyte network, FIB/SEM.
Characterization of ASR products by STEM

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Alkali-Silica Reaction (ASR) happening in concrete structures is one of the main issues regarding concrete durability. Metastable silicates present in aggregates are dissolved by hydroxyl groups OH⁻ in the alkaline pore solution. The degrading silica structure then bonds mainly to water, calcium and alkali ions. Due to the water uptake, the reaction products expand, leading to stress in the aggregates and subsequent cracking. The composition and structures of ASR products located in aggregates and cement paste can vary substantially. In a novel approach using SEM and TEM [1], two different stages in the product formation could be identified, namely initial and “second-stage” products. The small volume of initial ASR product makes its analysis with classical techniques difficult. “Second-stage” ASR product occurring in larger volume has been analyzed and characterized in several studies [2,3,4,5]. Data on initial ASR are needed to improve our knowledge on ASR evolution. The aim of the project is to improve the understanding of initial product formation and its relation to the “second-stage” product. Transmission Electron Microscopy (TEM) analysis is performed to assess the morphology, the chemical composition as analyzed by EDX and the structure of the product. Two sample types are studied and compared to characterize ASR products: (1) concrete from a structure affected by ASR, and (2) laboratory concrete in accelerated conditions.


Keywords: Microscopy, ASR, FIB, TEM.
Nanobioplasmonic catalysts: The study of the nano-bio interface of enzyme-gold nanoparticles structures for light-driven reactions

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Nanobioplasmonic catalysts are designed by the association of nanocatalysts and biocatalysts with controlled catalytic properties under illumination since the stimulus of localized surface plasmon resonance (LSPR) of plasmonic nanoparticles.¹ In this work, enzyme-gold nanoparticles structures were built up as nanobioplasmonic model system. The goal is to study the effect on the enzymatic activity of lipase from Candida sp. (CALB) when associated with gold nanoparticles (AuNPs) under illumination. The nanobioplasmonic catalysts were designed by different approaches (Figure 1). The enzymatic activity was controlled and enhanced by the light incidence with an increase around 30%. The enzymatic activity under illumination depends on the different CALB-AuNPs structures (as seen by the images in Figure 1) and it is further correlated with their biophysicochemical properties. Finally, the CALB-AuNPs structures acted as great nanobioplasmonic catalyst, with control and enhancement of enzymatic activity under illumination; paving the way for novel approaches of designed materials for green chemistry, biocatalysis and nanocatalysis.

Figure 1. TEM images of the CALB-AuNPs nanobioplasmonic catalysts structures prepared by covalently coupling (A), adsorption (B) and adsorption on AuNPs supported on SiO₂ spheres (C). Scale bars: 100 nm.


Keywords: Nano-bio interface; enzyme; plasmonic nanoparticles.
In situ electrochemical liquid-cell Transmission Electron Microscopy studies of nanoparticle catalysts

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Nanoparticles have attracted much attention as electrocatalysts for applications like fuel cells or electrolyzers in the last years. To understand their growth and degradation behaviour, this group of materials has been studied extensively including methods like XPS, TEM, EDX and EELS¹-⁶. However, nanoscale analysis of their formation and degradation behavior has not been observed in real time.

Here, we present an in situ electrochemical liquid-cell transmission electron microscopy (TEM) approach which offers the opportunity to real-time image nanoparticles in their original environment during formation and degradation. We introduce the setup and its assembly as well as challenges, opportunities and limitations of in situ liquid TEM. The systematic evaluation of system parameters and the resulting data are presented.

Finally, we present a scanning TEM (STEM) study on the electrochemical degradation behaviour of PtNi octahedral nanoparticles during electrochemical potential cycling, and investigated the possible influence of beam damage. We were able to track structural and morphological changes of particles and facets, monitor carbon corrosion, translational particle motion and coalescence, and investigate electrochemical dissolution/redeposition processes of the nanocatalyst under working conditions.


Keywords: in situ liquid STEM, setup evaluation, octahedral Pt-Ni nanoparticles.
One of the earliest TEM images of biological objects [1] shows a composite of two microscopy classics: The filamentous Tobacco mosaic virus (TMV), the first and best characterised virus, covered by gold nanoparticles (see Figure 1). Today’s techniques allow for a more detailed view, including chemical analysis by EELS, for example of alloys and oxides on TMV, and inside its 4 nm cylindrical channel [2-4].

Only recently environmental SEM and wetSTEM™ offer sufficient resolution, at minimal beam damage, to investigate layers of water and of ionic liquids on viruses [5-7]. These EM techniques differ substantially from cryoEM, and allow for new insights on virus “survival”. Future challenges comprise correlative AFM-EM imaging with nm resolution.

Figure 1, left to right: Gold nanoparticles on the best known virus (Tobacco mosaic) 1940 (TEM [1]) and today (STEM [4]); wetSTEM™ of viruses and water [6].


Keywords: SEM, ESEM, wetSTEM, viruses, nanoparticles, thin layers, water.
Observation of charge density waves in free-standing 1T-TaSe$_2$ monolayers by Transmission Electron Microscopy

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Metallic TMDs like 1T-TaSe$_2$ can produce charge density waves (CDWs) depending on temperature, doping and pressure [1]. This periodic modulation of the charge density is accompanied by a periodic lattice distortion (PLD). Bulk 1T-TaSe$_2$ shows a commensurate CDW (CCDW)/PLD at temperatures below 473 K [1], which are characterized by a $\sqrt{13} \times \sqrt{13} a_0$ superstructure, but does this exist also in a single layer and at room temperature? Our room temperature high-resolution aberration-corrected TEM - and selected area electron diffraction (SAED) experiments show a PLD in mechanical exfoliated single-layer 1T-TaSe$_2$, in good agreement to our image simulations based on atom coordinates obtained from density functional theory (DFT) calculations [2]. In order to reduce radiation damage effects the experiments were performed in the graphene/1T-TaSe$_2$ heterostructure configuration [3] at an accelerating voltage of 80 kV.

Further experiments for detailed defect characterization in monolayer 2H-MoTe$_2$ were conducted with the unique 20 – 80 kV spherical and chromatic aberration-corrected SALVE [4,5] instrument with a resolution of 0.76 Å at 80 kV and 1.39 Å at 20 kV. Strongly improved resolution and contrast in this instrument allow precise identification of atomic defect structures, differentiation between double and single Te-vacancy and the associated Jahn-Teller distortion.


Keywords: AC-HRTEM, charge density wave, single-layer, heterostructure, SALVE.
Imaging dynamic processes with high spatial & temporal resolution by Scanning Transmission Electron Microscopy

B. L. Mehdi$^{1,2}$, A. J. Stevens$^{3}$, H. Amari$^{1}$, D. Nicholls$^{1}$, N. Johnson$^{1}$, K. Dawson$^{1}$, M. Bilton$^{1}$, N. D. Browning$^{1,2,3}$

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Many processes in materials science, chemistry and biology take place at interfaces in a liquid environment – such as chemical conversions, the synthesis of nanoparticles, the operation of Li-ion or next generation batteries, and cellular functions. Often the final desired outcome is a result of a series of complicated transients, where a change in the order, magnitude or location in each of the steps in the process can lead to a radically different result. Understanding and subsequently controlling the process therefore requires the ability to directly observe the transients as they happen. Aberration Corrected (Scanning) Transmission Electron Microscopy ((S)TEM) has the spatial resolution to directly visualize these transient processes on the atomic scale. However, the increased current densities caused by the correctors have made beam damage more prevalent and the limitation to imaging in many cases is now the sample rather than microscope. The aim now is therefore to more efficiently use the dose that is supplied to the sample and to extract the most information from each image. Optimizing the dose/data content in non-traditional ways (i.e. not just simply lowering the beam current) involves two main strategies to achieve dose fractionation – reducing the number of pixels being sampled in STEM mode, or increasing the acquisition speed of the images in TEM mode. For the case of the STEM, inpainting methods allow a dose reduction of an order of magnitude or more, allowing data to be automatically recorded in a compressed form. For the TEM mode of operation, an increase in speed increases the number of images and means that compressive sensing and automated methods of tracking changes in the structure need to be developed so that only the important changes are automatically detected and recorded. In this presentation, the basic approach to dose control using both conventional and unconventional sampling methods will be described. Results demonstrating these methods to study metal-organic frameworks (MOFs) and using in-situ liquid stages to study nanoscale dynamic processes involving electrochemical driving forces will be presented.

Keywords: STEM, In-situ Liquids and Gases, MOFs, Low Dose, Compressive sensing.
Optimization of electron-beam parameters for adequate cathodoluminescence characterization of hybrid halide perovskites

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Hybrid organic-inorganic lead-halide perovskites (Pb-HPs) are promising materials for optoelectronic and photovoltaic applications. They have raised great interest among the research community [1] because of the rapid increase in power conversion efficiency of corresponding solar cells, from 3.8% in 2009 [2] to over 22% in 2018 [3], and low-cost processing. Cathodoluminescence (CL) imaging and spectroscopy are important tools for microscopic characterization of photovoltaic materials, since they provide optoelectronic information correlated to the microstructure, with spatial resolution below the optical diffraction limit. However, when used on halide perovskites, CL characterization and correct interpretation of its results are still challenging tasks due to the intrinsic “softness” of the material, and the electron-beam induced effects [4]. In the present contribution, we report the mechanistic optimization of the electron-beam parameters for CL characterization of formamidinium-lead-bromide (FAPbBr₃) thin films. We found that a critical dose between 1.5 and 2.0 × 10²⁰ cm⁻² minimizes the electron-beam-induced damage on the film, quantified via the integrated CL intensity prior and after exposure to the beam. We compare and validate our CL results with those reported in the literature for similar Pb-HP films [4,5] and discuss the validity of such measurements. Finally, we propose some guidelines to reduce electron-beam-damage during CL measurements and discuss how the beam conditions and instrument sensitivity impose limitations on the spatial resolution of both CL imaging and spectroscopy.


Keywords: Halide perovskite, cathodoluminescence, microscopy, spectroscopy.
Dynamics of dirhenium molecule containing multiple bonds

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Metallic homonuclear diatomic molecule has been predicted by theoretical calculations. Understanding the multiple bonds in metallic diatomic molecule is important for studying the compounds with metal-metal core and related relations. By applying the Cₐ/Cₛ-corrected SALVE (Sub-Ångström Low-Voltage Electron microscopy) instrument, we directly observed with atomic resolution the dirhenium molecules containing multiple bonds confined in a single walled carbon nanotube. Utilizing the electron beam both as stimulus and probe, the dynamics and the bond order changing of dirhenium molecule are monitored. Direct imaging of the Re-Re bond breaking process reveals a high amplitude vibrational stretch of Re-Re, once the bond order decreases below 1, preceding the bond dissociation.

Figure 1. Dirhenium molecule movement under 80 keV electron beam irradiation.

Keywords: diatomic molecule, AC-HRTEM.
Comparison of low-dose imaging using simultaneous iDPC- and ADF STEM for beam-sensitive crystals

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Imaging of structures such as zeolites or metal organic frameworks (MOFs) are limited in resolution by their beam sensitivity. Therefore, imaging techniques which make use of all the available electrons during acquisition are preferred to increase the S/N ratio to increase sensitivity and resolution. The Integrated Differential Phase Contrast STEM (iDPC-STEM) technique [1, 2] uses the full diffraction pattern to reduce the noise or electron dose required and offers phase contrast information to boost the signal on delicate low contrast samples. Simultaneous Annular Dark Field (ADF) STEM imaging with iDPC shows the benefit of the method in MOF samples (figure 1).

Thanks to the sensitivity of iDPC-STEM imaging we were able to obtain images of the zeolite ZSM-5 at a dose of 1000 e/Å² that reliably represents the structure down to 1.1 Å resolution.

MOFs are typically more beam sensitive than zeolites, but by reducing the dose to 140 e/Å², we could obtain images at 1.6 Å resolution of the MOF MIL-53 (Al).

Figure 1. Comparison of simultaneously recorded ADF and iDPC images with corresponding FFTs of MIL-53 (Al) recorded at a dose of 140 e/Å².


Keywords: Microscopy, zeolite, MOF.
Interfacial design through poly-ionic liquid surface modification in efficient pin perovskite solar cells

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Effective design of interfacial solution-processing of electron transporting layers (ETL) or hole-blocking layers are a promising tool in modern electronic devices, e.g. to improve performance, cost and stability of perovskite-based solar cells. Herein, we introduce a facile ionic polymer surface modification on perovskite triple cation (Cs5(MA0.17FA0.83)95)95Pb(I0.83Br0.17)3 in p-i-n solar cell architecture. We show that this enables electronic interface enhancement via suppression of charge recombination, achieving 21% PCE and 82.5% of FF, suggesting the first successful implementation of ionic polymers to enhanced boost charge extraction from perovskite toward the electron transport layers.

Figure 1. Perovskite interface modification with Polyinoic Liquid(PIls) : a) SEM imagen b) EDX carbon distribution c) EDX oxigen distribution, d) SEM transversal profile e) EDX-transversal carbon distribution f)EDX-transversal oxygen distribution g) Perovskite reference cathodoluminescence h) Perovskite+PIls cathodoluminescence i) PIls reference cathodoluminescence.

Keywords: pin Perovskite solar cells, PiLs poly(ionic)liquids, hybrid organic-inorganic interfaces, CAFM, cathodoluminescence.
TEM imaging on micro-channels directed hierarchical nanocrystal structures

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Biomineralization occurs mostly around restricted corners on organic matrices, therefore, developing a novel templated strategy based on directed biomineralization of hydroxyapatite (HAp) by controlling organic/inorganic molecular interactions may help to control the assembly, directionality, and the structure hierarchy of both the cluster crystals phase and the single crystal phase. Our research is focused on investigating the nanocrystals growing direction with spatiotemporal variations guided by a biomineralized organic matrix patterned with micro-scale structural features.

Figure 1. TEM overview of HAp crystal bundles inside micro-channel & HRTEM of two single HAp nanocrystal and corresponding FFT indexing patterns

Elastin-like peptides (ELP) membranes were successfully microfabricated with precise micro-scale channels. Upon exposure to the biomineralization solution, hierarchically ordered HAp nanocrystalline structures were formed. Transmission electron microscopy (TEM) is an effective technique to observe the cross-section at the interface of the organic matrix and the inorganic hierarchical nanocrystal structures. Figure 1 shows that with a limited growing space, the nanocrystals tend to rotate at the corners along the grids which suggesting that micro-channels patterned organic matrix has the potential to direct the growth of nanocrystals.


Keywords: TEM microscopy, hybrid organic-inorganic interfaces, biomineralization.
Surface atomic structure and growth mechanism of monodisperse \{100\}-faceted strontium titanate zirconate nanocubes

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The highly sensitive and selective properties of monodisperse faceted nanocrystals inherently stem from the atomic and electronic structures on the faceted surfaces. For elemental nanocrystals, the atomic structure on the surfaces is merely determined by the geometric shape itself. However, for compound materials such as alloys and complex oxides, atomic details on the faceted surfaces need to be studied on the atomic level. Here, we demonstrate that the surface atomic structure of faceted nanocrystals of complex oxides, \{100\}-faceted strontium titanate zirconate nanocubes, can be unambiguously resolved by aberration-corrected scanning transmission electron microscopy. The resolved surface atomic details reveal an epitaxial or layerwise growth process of the nanocubes, thereby allowing an in-depth understanding of the growth mechanism.

![Image of epitaxial / layerwise growth process of the nanocubes]

Figure 1. Epitaxial / layerwise growth process of the nanocubes. (a) Sketch of a layerwise growth process for a \{100\} facet of the perovskite ABO\textsubscript{3} structure presuming a faster growth rate for the AO layer (green) than that for the BO\textsubscript{2} layer (blue). The gray, yellow, and red symbols indicate the possible atom sites for the BO\textsubscript{2} layer growth in the order of increasing preference. Oxygen was omitted in the model for clarity. (b) HAADF-STEM image of a SrTi\textsubscript{0.75}Zr\textsubscript{0.25}O\textsubscript{3} nanocube with a growth step, averaged from 2 frames and denoised by a nonlinear filter. (c) HAADF-STEM image overlaid with color-scale two-dimensional Gaussian peaks from fitting the intensity distribution of each column. (d) Magnified image of the growth step. (e) Magnified image of the growth step overlaid with structural model.


Keywords: Microscopy, nanocrystal surfaces.
In situ liquid cell microscopy: An essential tool for studying dynamic processes at the nanoscale

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Liquid-cell transmission electron microscopy (LC-TEM), is now a fundamental tool in the repertoire of materials and life sciences research. LC-TEM enables direct imaging of hydrated and liquid samples using a TEM. In a liquid environment, samples are able to move and react freely, enabling real-time processes such as growth, degradation, interaction and fine movements to be observed at a resolution of a few nanometers [1]. Samples are sandwiched between microchips containing electron transparent membranes and secured in dedicated sample holders (Figure 1a). Thus samples ranging from soft materials such as liposomes (Figure 1b) to colloidal nanoparticles such as titanium dioxide (Figure 1c) can be imaged in different liquid environments.

Stimuli such as heat and electrical signals can be delivered to the sample via specially designed microchips enabling a wide range of experiments to performed for observation with the electron microscope, and careful design of the holder penumbra can enable collection of x-rays for energy dispersive x-ray spectroscopy (EDS) (Figure 1d).
In addition to nanomaterial movement and interaction, the intrinsic movements of enzymatically active rotavirus particles in buffer solution were recorded in situ, demonstrating that fragile, beam sensitive particles can be studied using in situ liquid techniques [2]. Virion particles were tethered to the surface of the viewing membrane using a targeted antibody affinity coating to prevent long range diffusion. A series of low-dose TEM images were recorded and the series of images was recorded [2]. From this image series, the intrinsic movement of viral genome could be observed and quantified (Figure 2).

Figure 2. Dynamic movements of active virus assemblies (DLPs). (2a) LC-TEM images, density threshold measurements, and contour maps were used to determine pixel displacements in mobile units over a 10 second interval of 3 different virions. (2b) 3D reconstruction of DLPs in liquid display greater internal disorder compared to (2c) the 3D construction of DLPs in ice.

These results demonstrate that LC-TEM enables the direct observation of material and biological assemblies in a native liquid environment at the nanoscale.


**Keywords:** Microscopy, in-situ, LC-TEM, virus, liquid TEM.
Integration of biomatter into artificially fabricated components is an exciting trend in modern engineering [1]. Potential applications of such bio-hybrid devices include new sustainable energy solutions, robotics and remedies for industrial waste [2]. A crucial need in this highly interdisciplinary field is the development of nanofabrication methods that can produce biocompatible structures with well-defined 3D architectures.

We have recently introduced Organic Ice Resist Lithography (OIRL) [3,4] – a novel nanofabrication technique based on electron-beam patterning of frozen organic materials (Fig. 1). Key advantages of OIRL are: the use biocompatible organic materials with no additional chemicals; effective fabrication of 3D structures; easy handling of substrates with complex morphologies. In our poster we will show OIRL-fabricated structures, discuss organic materials used for patterning and the physical transformation of the organic ice exposed to an e-beam. We will also introduce the concept of bio-OIRL – an approach we are developing for the direct patterning of biocompatible media with embedded microorganisms.

Figure 1. Basic steps of OIRL. a) Condensation of organic vapours on a cold substrate. b) E-beam patterning. c) Upon heating, the unexposed ice sublimates, while the exposed ice is becomes non-volatile and remains on the substrate.

Keywords: nanofabrication, bio-hybrid devices, lithography.
Influence of the antimicrobial modified polymers microstructure on the bacteria cell wall

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Antimicrobial synthetic polymers are in demand for industrial applications like disinfection and antimicrobial coatings. Ultimately antimicrobial polymers may be useful antibiotics even in pharmaceutical applications, depending on the range of targeted organisms, and the absence of haemolytic activity (destruction of mammalian red blood cells).

The physicochemical principles by which antimicrobial peptides adhere to the cell envelope and finally destroy its integrity might be implemented in the design of synthetic macromolecules. Although the structure-property relationships yielding an antimicrobial polymer, three elements are obviously beyond any doubt: (i) the polymer must be available in the aqueous medium, in which microbes proliferate; (ii) the polymer must contain hydrophobic elements to be attached on or integrated in the cell membrane, and (iii) cationic charges promote attack of the cell envelope and selectivity for microbes. Here water-soluble amphiphilic hyperbranched PEI polymers can be expected to provide a readily available alternative to design amphipathic structures, mimicking some of the features discussed for antimicrobial peptides [1]. Electron microscopy coupled to cryogenic allow investigating in native state their antimicrobial activity in relation to the ratio of alkyl/cationic groups, length of the alkyl chains, the molecular weight of the PEI against E. coli, their permeability potential and the effect on the ultrastructure of E. coli (Fig. 1) [2].

![Figure 1. Effect on antimicrobial amphiphilic PEI polymer on E. coli cell wall](image)


**Keywords:** Biomimetic antimicrobial polymer, permeability, microstructure.
3D visualisation and characterisation of microporous polymer coatings for controlled drug release

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FIB-SEM tomography on ion and electron beam sensitive, porous and poorly conductive soft materials is challenging. Common challenges are cross-sectioning artefacts, shadowing-effects, charging and sub-surface information due to the pores [1]. We present a general protocol for optimisation of FIB-SEM tomography parameters for porous and poorly conductive soft materials. We illustrate the protocol using phase separated polymer films used for controlled drug release [2]. The films are used at room temperature, hence the FIBSEM analysis is performed at room temperature. The optimised parameters include the energies and currents of the ion and electron beams, reduction of shadowing-effects, choice of electron detector and selection of method for charge neutralisation. A new self-learning segmentation algorithm is introduced to enable an automatic separation between pores and matrix. The binary data has been used to visualise individual transport paths in 3D through phase separated polymer films used for controlled drug release, see Figure 1. In addition, determination of pore size distribution, tortuosity, morphology and diffusion simulations have been done.

Figure 1. Shows a transparent SEM BSE 3D image stack of a phase separated polymer film for controlled drug release with an individual pore path marked in red.


Keywords: focused ion beam, scanning electron microscopy, tomography, 3D, beam sensitive material, interconnectivity, polymer film.
Fluoride treatment of hydroxyapatite – mechanisms and effects

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Tooth enamel consists by more than 95 % of hydroxyapatite. Since decades, fluoride treatment of teeth is used due to its caries-prophylactic effect, be it in the form of fluoridated toothpastes, mouthwashes or other fluoride containing dental care products. However, the exact mechanisms of the fluoride uptake are yet to be explored.

We used sintered hydroxyapatite pellets as a model system for a tooth surface and treated it with a NaF-solution. XPS-measurements in combination with Ar-ion-etching revealed that the thickness of the fluoridated layer which forms on the hydroxyapatite surface is in the range of only a few nanometers [1]. By using different application times of the NaF-solution, we found that both the thickness of the fluoridated layer and the overall amount of fluoride taken up start to become constant on a timescale of about 3 min [1].

Etching experiments with pure and fluoridated hydroxyapatite surfaces showed a very strong effect of the fluoridation. Although the fluoridated layer is extremely thin and contains only minute amounts of fluoride, AFM-measurements showed a complete inhibition of etching on the fluoridated surface for at least 5 min. The major part of the surface withstood etching even for more than 23 min [2].

These findings give new insight into the mechanisms and especially the timescale of fluoride uptake by hydroxyapatite and show how the incorporated fluoride in hydroxyapatite correlates with its protective impact.


Keywords: hydroxyapatite, fluoridation, acid resistance, etching, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM).
Microstructure diagnostics of ophthalmic lens coatings

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More than 80\% of the ophthalmic lenses sold nowadays are based on plastics/polymeric substrates. These materials offer excellent optical properties in combination with a comparable low weight, but are very sensitive to being scratched and cause unintended reflections that decrease the visual comfort.

Therefore, a complex coating system is used to solve these challenges by adding a hard coating layer (polymer matrix containing inorganic nanoparticles) and an anti-reflection multilayer-stack of alternating oxides (Fig. 1). Additionally, an anti-static layer as well as an easy-to-clean surface layer are applied. Besides a high durability under comparably rough environmental conditions upon wearing, the coating techniques used must be flexible and adaptable to other systems, production sites, and substrates.

![Figure 1. SEM micrograph of a FIB cross section of the anti-reflective and hard coating.](image)

For future coatings development and the understanding of failure patterns caused by test procedures as well as field-return samples, commonly used defect-characterization techniques (mainly optical microscopy) are no longer sufficient. The capabilities of advanced microstructure diagnostics, namely SEM/FIB and TEM/STEM/EDX, are presented on selected tasks and results.

**Keywords:** SEM, FIB, TEM, ophthalmic lenses.
Early stages of biomineral formation by STEM-EELS spectromicroscopy

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Biominerals are naturally occurring biomaterials combining organic and inorganic compounds organized in a multi-scale structure, ranging from the macroscopic level down to nanometer. They are found to constitute physiological hard tissues (bones and teeth of vertebrates and shells of invertebrates) but also pathological calcifications. To understand the early stages of the biomineral genesis one needs data on their chemical composition and structure at the nanoscale. Of particular relevance is the characterisation of the interface between the mineral and the organic compounds. Conventional TEM cannot achieve this, since it cannot easily distinguish the different compounds present. Compared to other spectroscopic approaches, EELS spectro-microscopy offers the advantage of an outstanding spatial resolution in both imaging and chemical analysis. By coupling STEM imaging to EELS (electron energy-loss spectroscopy), one can map the elements composing the sample with a resolution defined by the diameter of the electron probe (typically better than a nanometer). Beyond elemental identification, the fingerprint of the elemental edges provides information on the chemical bonding and makes possible the identification of the chemical compounds. For sensitive samples such as organic materials, it is essential to limit the radiation damage induced by the electron beam. The measurements are obtained using a nitrogen-cooled sample stage and with the minimum electron dose. Under these conditions, EELS signals are extremely noisy and difficult to analyze using the raw data. The use of multivariate analysis methods (principal component analysis, PCA) significantly improves the detection limit and the signal-to-noise ratio. To illustrate the interest of this approach for biomaterial studies, we will present selected results concerning some biominerals (kidney calcifications, bone, shells).

**Keywords:** Scanning transmission electron microscopy, Electron energy loss spectroscopy, biomineralization.
TEM analysis and sample preparation of inorganic cesium-lead-halide perovskites

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With power conversion efficiencies surpassing 22% in 2018, hybrid organic-inorganic lead-halide perovskites solar cells attract ever more interest in the photovoltaics community [1]. Inorganic Cs-Pb-X (X=Cl,I,Br) compounds have been investigated as more stable wide-gap absorbers for photovoltaics [2], but also as light emitting diodes [3]. Due to temperature-dependent phase transformations, secondary phases, as well as due to local fluctuations in composition, the determination of the CsPbX₃ phases is often not unambiguous and demands careful microscopic analysis [4]. Furthermore, electron beam sensitivity of materials is an important issue. In the present work, we report about the analysis of the phase distribution in different Cs-Pb-Br thin films on various scales by means of correlative electron microscopy. We also show first results of phase transformations in CsPb(Brₓ,I₁₋ₓ)₃ induced by the electron beam in TEM. Finally, we give details on our experiences with specimen preparation of the beam-sensitive Cs-Pb-X materials for TEM analyses.


Keywords: Electron Microscopy, TEM, inorganic perovskites, phase identification, phase transformation, specimen preparation.
Crystallinity, texture and nanomorphology of organic bulk heterojunction solar cells studied by electron microscopy

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The power conversion efficiency of solution-processed bulk heterojunction (BHJ) solar cells has seen a dramatic increase in the last decades due to the introduction of new donor and acceptor materials, as well as the development of new processing conditions. A systematic understanding of the processing-structure-property relationship is still on high demand to develop new processing routes. While the crystallinity and texture of the donor/acceptor components determines the efficiency of exciton generation and mobility, the nanomorphology of the BHJ dictates the charge separation and transport properties.

In this work, we study the crystallinity, texture and nanomorphology of BHJ solar cells by using electron microscopy techniques including energy-filtered TEM (EFTEM) imaging and diffraction, low-energy transmission SEM (tSEM) imaging, diffractive mapping (4D-STEM), as well as tomographic diffraction (e.g. Figure 1). Technical and strategical methods to study these beam sensitive samples will be shown and discussed.

Figure 1. (a) EFTEM Elemental map revealing the nanomorphology of DRCN5T:PC70BM, (b) EF diffraction of DRCN5T:PC70BM fresh and after e-beam illumination for 1s at a dose of 0.68 e/Å²s, (c) STEM-BF image of PIDTTQ:Si-PCPDDBT:PC70BM.

Keywords: Organic bulk heterojunction solar cells, energy-filtered transmission electron microscopy, electron diffraction, nanomorphology, crystallinity.
Reduction of systematic and excessive noise in charge-coupled device measurements

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When dealing with low-signal TEM measurements, usually neglected systematic and x-ray noise can become an important factor in the signal-to-noise ratio of charge-coupled devices (CCD) [1,2]. For example, x-ray spikes in the dark-reference image, which are applied to correct flaws of the CCD chip, can become an issue in drift-corrected multi-frame images (figure 1a) or in measurements integrated over many pixels, like EELS spectra (figure 1b). Eliminating the influence of x-ray events can therefore improve the quality of low-signal measurements.

Having access to a stack of images offers the possibility to apply routines to separate intense outlier noise like x-ray spikes from wanted features like hot pixels and to remove their influence on the merged image altogether, instead of only diminishing it by merging only [3]. This approach is not limited to dark-reference images, but can be used for any suitable multi-frame measurement.

Figure 1. a) Artefacts in a drift-corrected multi-frame EFTEM image caused by x-ray noise in the dark-reference image. b) EELS spectrum with artefacts caused by x-ray noise in the dark-reference image (dark pointers) and during the signal acquisition (bright pointers).


**Keywords:** Charge-Coupled Device, TEM, X-ray Noise, Noise Reduction.
Nanoscale characterisation of ultrathin gold films deposited on silica with organosilane adhesion layers

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Fabrication of thin metallic films on dielectric or semiconductor substrates is central to the plasmonics research field. Here, gold is the most used material, but due to its chemical inertness typically require an adhesion promoter to bind to the substrate. Metals such as Ti and Cr are often used for this purpose. However, they are known to degrade the plasmonic response of the metallic layer [1]. In this study, we investigate the adhesion mechanism between gold and SiO₂ substrates, using Ti, Cr and organosilanes as adhesion layers [2, 3]. In particular, surface roughness, grain size, grain orientation and interdiffusion of the adhesion material into the gold film are analysed. Transmission and scanning electron microscopy, transmission Kikuchi diffraction and electron energy-loss spectroscopy (EELS) are used to understand and compare the morphology, microstructure and chemistry of the different thin film interfaces.


Keywords: adhesion layer, metal thin film, microstructure.
In-situ Transmission Electron Microscopy on reversible lithium loading of bi-layer graphene

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Lithium ion batteries are the subject of vibrant research nowadays. To enhance their performance, the microscopic mechanisms when charging or uncharging a battery need to be understood. Previously the lithium dynamics when charging or discharging the bilayer graphene, the most reduced graphite electrode, has been studied by time-dependent transport measurements [1]. But how lithium atoms are incorporated between two layers of graphene was completely unknown; thus we designed and conducted an in-situ TEM experiment. Because of the extremely low interaction cross-section of lithium, we use the geometrical and chromatic aberration-corrected SALVE instrument [2]. The use of 80 kV electron acceleration voltage ensures that the bilayer graphene stays intact and the chromatic aberration correction offers sufficient contrast for imaging lithium at atomic resolution. We find a dense lithium crystal growing reversibly between the graphene sheets, controllable by electrical biasing.

Figure 1. HRTEM image of an intermediate state of bilayer graphene with a crystalline lithium load. left—raw image, middle—graphene lattice filtered away, right—the lithium grain orientations indicated by different colors.


Keywords: in-situ TEM, lithium storage, bi-layer graphene.
Structural characteristics of biological objects visualized by TEM techniques

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Supported by the establishment of transmission electron microscopes (TEM) specialized for cryo-microscopy and the improvement of preparation techniques, which e.g. makes staining procedures not mandatory, TEM analysis techniques come into focus in biological research. Numerous studies have utilized Cryo-microscopy for the discovery of e.g. membrane proteins or RNA polymerase transcription (e.g. see [1,2]) and even an observation of conformational changes of proteins come into reach. Recognizing this highly interesting tasks in the field of biology, we have started to analyze biological objects utilizing our JEOL JEM 2200FS.

Different samples have been investigated including e.g. liposomes, polysomes and collagen fibers. Liposomes are nanoscale spherical vesicles, which were prepared by extrusion of phosphatidyl choline from soy bean. The influence of terpenoids on the lamellar structure of liposomes were studied by a Cryo-TEM approach and the effect of terpenoids on the lamellarity can be clearly seen. Whereas a staining procedure with uranyl acetate has been used to check the success of nanoparticle labelling of polysomes. The polysomes are supramolecular structures consisting of a transcript, several ribosomes and nascent peptide chains, where each component can serve as a labelling target using nanoparticles functionalized with different biological probes [3].

Furthermore, a negative staining of dried and vitrified specimen were compared regarding to contrast and visibility of microstructural features on the example of collagen fibers.


Keywords: Cryo-Transmission Electron Microscopy, staining, biological objects.
In situ SEM characterization of materials

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Scanning electron microscopes - SEMs are extensively used in life, chemical and physical sciences. The SEM ability to image surface details and morphology at different length scales, from millimeter to nanometer, together with its remarkable depth of focus makes it an excellent imaging tool for a wide variety of applications. Nevertheless, SEMs can be easily transformed into an advanced laboratory with materials’ synthesis and characterization capabilities (in-situ SEM).

Here we present two different in-situ experiments; the first, study the interaction between a solid and a liquid and the second, study the interaction between two solids at elevated temperatures.

The interaction between single WS$_2$ nanotubes and water was measured in-situ environmental SEM (ESEM) in wet mode. Wetting angles, adhesion forces and capillary forces were measured and found to vary between open-ended and close-ended nanotubes$^1$.

In another experiment we installed a heating stage in the SEM chamber to observe and characterize materials at elevated temperatures. The thermolysis of WS$_2$ nanotubes, which were decorated with gold nanoparticles, was observed in real time. The WS$_2$/Au nanotubes/nanoparticles were heated to 150°C in situ the SEM, the Au nanoparticles migrated along the nanotube and fused into a bigger particle$^2$.

The in situ SEM approach is of great importance to study materials properties and behavior, different set ups can be tailor made for many systems at different environments and temperatures.


Keywords: SEM, ESEM, in-situ, heating, wetting, nanotubes, nanoparticles.
2D and 3D electron microscopy imaging in tissue engineering

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Tissue engineering is a fast developing field employing materials in a form of scaffolds and cells to grow tissues in laboratory conditions. Electrospinning is one of the widely studied method to produce highly porous scaffolds based on polymer fibers. The variety of process parameters during production of electrospun fibers can be optimize to tailor the morphology and surface properties of produced scaffolds. Surface properties of the fibers are critical in regulating cells adhesion, proliferation and differentiation towards a tissue formation. The studies at interface between cells and materials require high resolution imaging, which is often a very challenging, but essential for understanding the cells processes in vitro.

Within this work polymer scaffolds were prepared by electrospinnig using EC-DIC device (IME Technologies) and used for cell culture with osteoblast-like cells line MG-63. Cells and scaffolds were studied in great details by scanning electron microscopy (SEM, Merlin Gemini II, ZEISS) and by focused ion beam (FIB, NEON CrossBeam 40EsB ZEISS) to obtain cross-sections through organic-inorganic interfaces (Fig.1). Additionally the 3D tomography (FIB-SEM) and reconstructions provided the unique view inside the tissue engineering constructs, enabling to relate scaffolds properties with cells morphology and behaviour.

Figure1. Cross-section through cell grown on electrospun fibers and reconstruction after FIB-SEM tomography.

Keywords: SEM, FIB-SEM, cells, polymer fibers, scaffolds

Acknowledgement
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Reduced radiation damage in Transmission Electron Microscopy of proteins in graphene liquid cells

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The tolerance to electron beam irradiation was investigated of microtubule proteins in liquid at room temperature using transmission electron microscopy (TEM) for samples encapsulated in graphene such to keep the proteins hydrated in the microscope vacuum (Figure 1a). Microtubules are micrometers long polymers proteins, composed of alpha- and beta-tubulin monomers helically coiled around a hollow center. This structure exhibits regularly spaced protofilaments showing as lines in their TEM images (Figure 1b). We acquired successive exposures from the same single microtubule and found that its protofilament structure was preserved up to a cumulative electron dose of 720 e\textsuperscript{-}/Å\textsuperscript{2} based on Fast Fourier Transform (FFT) analysis [1].

As a comparison, we imaged flash-frozen microtubules on multi-layer graphene supported by holey carbon coated TEM grids with cryo-electron microscopy (cryo-EM) and observed that the protofilament structures of frozen microtubules completely disintegrated at a cumulative dose of around 70 e\textsuperscript{-}/Å\textsuperscript{2}, which is one order of magnitude lower than that obtained with graphene encapsulated microtubules in liquid.


Keywords: Liquid-phase electron microscopy, microtubule, graphene, cryo-electron microscopy.
Novel lattice-rotation nanostructures formed in TEM by crystallization of amorphous films

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Exotic thin crystals with unexpected transrotational micro-, nanostructures [1] have been discovered by transmission electron microscopy (TEM) for crystal growth in thin (10-100 nm) amorphous films of different chemical nature (oxides, chalcogenides, some metals and alloys) prepared by various methods. The unusual phenomenon can be studied in situ in TEM column during local e-beam heating, Fig.1 a-b: dislocation independent regular internal bending of crystal lattice planes in a growing crystal. Such transrotation (unit cell translation is complicated by small rotation realized round an axis lying in the film plane) can result in strong regular lattice orientation gradients (up to 300 degrees per 1µm) of different geometries: cylindrical, ellipsoidal, toroidal, saddle, etc. Complex skyrmion-like lattice orientation texture is observed in some spherulite crystals, Fig.1b. Atomic model and possible mechanism of the phenomenon are discussed.

Transrotational micro crystals have been eventually recognized by other authors in some vital thin film materials, i.e. PCMs for memory [2-3]. The transrotation phenomenon is the basis for novel lattice-orientation/rotation nanoengineering of smart thin-film materials, templates, surfaces.

Figure 1. Hexagonal Se (a) and α-Fe₂O₃ (b) crystals formed in TEM: micrographs (left), with scheme of lattice orientations (right).


Keywords: in situ TEM, transrotational crystals, amorphous-crystalline transition.
Characterising chemical composition of perovskite solar cells with multivariate statistical analysis

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Organic-inorganic hybrid perovskite is widely used in various optoelectronic devices due to its facile synthesis and many favourable properties. However, the chemical composition of a perovskite active layer in devices is rarely characterised at the nanoscale. Instead, it is usually assumed that the intended perovskite stoichiometry was achieved. In this work, we applied high-angle annular dark field (HAADF) imaging and energy-dispersive X-ray spectroscopy in a scanning transmission electron microscope (STEM-EDX) to analyse the morphology and chemical composition of a perovskite solar cell with a nominal stoichiometry of Cs\textsubscript{0.1}FA\textsubscript{0.9}PbI\textsubscript{2.865}Br\textsubscript{0.135} in a spatially-resolved manner. We used three multivariate statistical analysis algorithms to denoise and decompose the spectrum images, namely principal component analysis, independent component analysis, and non-negative matrix factorisation. These algorithms enabled acquisition of meaningful data with low beam current and dwell time. We show that non-stoichiometric and other parasitic phases occupied a sizeable fraction of the perovskite layer, suggesting incomplete perovskite formation reaction. Moreover, our analysis also revealed halide migration at the interface of perovskite and organic hole transport layer which could cause performance decline over time.

Figure 1. (Left) Cross-sectional HAADF image of a perovskite solar cell with a red rectangle marking the area of EDX scan. (Right) Iodine map showing a hexagonal non-stoichiometric, iodine-rich grain in the perovskite layer. Scale bars are 0.5 μm.

Keywords: scanning transmission electron microscopy, energy-dispersive X-ray spectroscopy, perovskite solar cells, photovoltaics, multivariate statistical analysis
Poly arginine intervening in the crystallization pathway of magnetite

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Magnetotactic bacteria produce chains of stable single domain magnetic particles with an exceptionally narrow size distribution through the protein guided biomineralization of magnetite. Inspired by these bacteria we developed a synthetic route to produce chain-like 1D assembly of polymer scaffolded mesocrystalline magnetic nanoparticles. However, its role on the crystallization pathway of magnetite remains elusive.

To understand the polyelectrolytes influence on the formation process of those mesocrystals we performed \textit{in-situ} SAXS to monitor the formation on different spatiotemporal levels covering early pre-crystallization stages (Fig. 1a) as well as the formation the mesocrystals that organize at later stages, macroscopic chains (Fig. 1b). Complementary, we employ TEM, STEM and related spectroscopy techniques (EDX, EELS) for further structural and chemical characterization of the mesocrystals and their early pre-crystallization counterparts.

From model free analysis of the SAXS data it is evident, that the mesocrystals are formed based on a monomer addition mechanism. Using analytical form factor scattering models, a structural characterization of the monomers becomes accessible showing low density species of \textasciitilde 4nm size from which the mesocrystals seem to grow. Those low crystallinity species are also evident in HAADF-STEM (Fig. 1a). The preliminary chemical characterization of these 4nm aggregates using EELS indicates that magnetite is formed at the core of the particles, remaining still elusive the aggregation process at the interface.

Figure 2. a) HAADF-STEM image of possible pre-crystallization particles and b) TEM image of chain made from mesocrystalline sub-units shown in the inset.

**Keywords:** TEM, Biomimetics, Magnetite, in-situ SAXS.
Our main goal is to observe colloidal self-assembly (SA) of oppositely charged colloidal species and in particular amino-functionalized, 30 nm diameter silica nanoparticles (+) (SiONP) and 100 nm diameter polystyrene microspheres (-) (PMS). In bulk liquid at low values of pH, they spontaneously form binary structures, where the smaller SiONP’s assemble as a shell around the larger PMS. (Fig. 1a). Pre-formed binary structures have been successfully imaged in liquid using scanning transmission electron microscopy (STEM). A series of images was recorded each at a low electron dose and it was tested how many images needed to be averaged such to achieve an optimum between the required spatial resolution need to see the SiONPs and the desired high temporal resolution (Fig. 1b). Monte-Carlo simulations have been conducted for various liquid thicknesses such to support the optimization of the experimental parameters. The sensitivity of the sample to electron beam irradiation was tested. Fig. 1c).

Keywords: Liquid cell electron microscopy, Colloidal self-assembly

Microscopy Characterisation of Organic-Inorganic Interfaces 2019
Grain boundary structures in 2D polyimine by low-dose HRTEM

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In previous studies, a large size two-dimensional (2D) polyimine polymer (fig.1a,b) with high crystallinity was successfully synthesized by the air-water interface method [1,2]. Here we provide a detailed analysis of its structure, in particular of different grain boundaries as seen in the single-exposure low-dose HRTEM images in fig 1c-1f. The average total dose of each image is about 100 e/Å², at a defocus of about 150 nm. We used the Cs-corrected TITAN 80-300 kV operated at 300 kV and achieved a resolution of about 2 Å in single exposure HRTEM images, without complex reconstruction process.

Figure 1. 2D polyimine polymer, a) the chemical structure of the 3 monomers, b) 2D polymer with the unit cell is of 2.5 x 2.5 nm size [1], c-d) HRTEM images of the 2D polyimine with different types of grain boundaries: c) high-angle; d) low-angle; e) antiphase; f) inclusion.


Keywords: 2D polymer, HRTEM, grain boundaries.
Cryo-electron microscopy of colloidal nanoparticles

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Size, internal structure, and dispersion are important parameters that determine the properties in functional semi-conductor nanoparticles such as colloidal quantum dots. X-ray diffraction techniques, commonly used to characterize nanoparticles, are limited to global averaged information and do not allow local sampling of the nanoparticles in the submicron scale. Transmission electron microscopy plays a complementary role to this limitation and is able to probe individual particles. Nevertheless, because of the nanometer size of the quantum dots and the presence of organic components for certain applications, these colloidal nanoparticles are sensitive to radiation damage by the electron beam. Here, we preserve aqueous quantum dots in their solution state by rapid freezing in ethane and eliminate the use of a support film by suspending the quantum dots in vitreous ice. The specimen is then imaged at liquid nitrogen temperature in low dose mode to reduce the beam damage.

Figure 1. Preparation of colloidal nanoparticles for cryo-electron microscopy.

Keywords: Cryo-electron microscopy, Quantum dots.
Towards tunable near-obstruction-free phase plates

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Approximately 70 years ago, Boersch proposed several devices that could produce a desired phase shift between a direct beam and scattered electrons to enhance phase contrast [1]. One of these devices, which later became known as a Zernike phase plate (PP), makes use of a thin film to introduce a phase shift to scattered electrons, while the direct beam passes through a central hole without undergoing a phase change. As they are charged particles, electrons can also be manipulated using external electromagnetic fields. This is the principle of other arrangements that Boersch proposed [1] and has led to a number of conceptually new PP designs [2]. However, most of these designs suffer from unwanted electrostatic charging, even when self-charging is used to produce the phase shift, e.g., in a Volta PP [3]. The imparted phase shift may then deviate from the optimal value and the lifetime of the device is usually limited. In order to address most of these issues, we introduce a tunable near-obstruction-free PP design based on a magnetic field circulating around a vertical segment of current-carrying wire, which imparts a position-dependent phase shift onto an incident electron wave [4]. The design, implementation and proof-of-concept tests of this device will be presented [5].

[5] The authors acknowledge a Deutsch-Israelische Projektkooperation grant from the Deutsche Forschungsgemeinschaft and funding from the European Research Council under grant agreement No. 766970.

\textbf{Keywords:} Phase plate, contrast enhancement.
Mineral and organic matrix interaction in calcifying avian tendons: a Transmission Electron Microscopic study

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Bone has been extensively studied as a material [1] and as an organ [2]. Nevertheless, its ultrastructure and mineralization of its collagen fibrils still remain unclear, principally because of difficulties deriving from its complex hierarchical organization and the fact that bone formation occurs throughout development. To circumvent these difficulties, the initiation of mineralization has been studied in an avian (turkey) leg tendon model whose uniaxial distribution of collagen fibrils and precise temporal and spatial mineralization pattern correlated with animal age make it a simplified but equivalent counterpart for the study of bone mineralization [3].

Study aims were to increase understanding of collagen fibril mineralization and to compare resulting data with recently described bone mineral patterns [4]. Earlier mineralization investigations used traditional bright field transmission electron microscopy (TEM) imaging, but overlapping crystallites throughout sample thickness precluded proper interpretation of crystal distribution and orientation. The present work combines TEM, scanning transmission electron microscopy, selected area electron diffraction, and 3D focused ion beam/scanning electron microscopy to create a more comprehensive picture of mineralization events.

Results show that mineral crystals in avian tendon are small platelets arranged along slightly curved trajectories, first found outside collagen fibrils and along fibril contoured surfaces. Crystals then appear within fibrils at sites where mineral is also outside the same sites. Mineral subsequently propagates within fibrils and ultimately forms a continuous crystalline network within and outside collagen. Crystal shape and deposition in tendon resemble certain aspects of the lacy mineralization pattern described for bone [4].


Keywords: Mineralization, turkey leg tendon, collagen, analytical microscopy
M1-phase (Mo,V)Oₓ – Probing the local metal distribution

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Properties of functional materials can be crucially influenced by local alterations of their structure and composition, such as promoters in heterogeneous catalysts. These alterations can be easily overseen by common bulk or surface averaging methods, but can be detected by (scanning) transmission electron microscopy ((S)TEM).[1] The analytical power of STEM can be enhanced when coupled with electron energy loss spectroscopy (EELS).

Here we use beam sensitive M1-phase (Mo,V)Oₓ as an example to probe local compositional differences using STEM-EELS line scans (Figure 1). For instance, our local analyses of extended defects suggest a relation between morphology and composition or indicate a preferential Mo enrichment of the surface that is partially interrupted by V-enriched surface facets. The present study can be considered as a background for prospective composition-activity correlations.

Figure 1. a) HAADF-STEM image of a (Mo,V)Oₓ rod, colour lines indicate line scan positions. b) Qualitative Mo/V ratio based on STEM-EELS line scans.


Keywords: Electron energy loss spectroscopy, mixed metal oxides, local structure.
Black carbon nanoparticles on the greenland ice sheet: Where do they come from and how do they contribute to melting?

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Surface melting and net mass loss of the Greenland Ice Sheet (GrIS) has increased measurably in the last two decades. Melt rates are predominantly determined by incoming solar radiation and albedo, which is the measure of the ice surface reflectivity. Albedo is controlled by physical properties of the ice, and the presence of light absorbing impurities (LAI). LAI contributing to darkening of the GrIS include atmospherically delivered black carbon (BC), as well as pigmented microorganisms and mineral dust. BC nanoparticles are the amorphous carbonaceous product of hydrocarbon fuel combustion, and are proficient at absorbing UV radiation. The proportion of surface melting of the GrIS due to BC, compared to other LAI, is ill defined. In this study, BC nanoparticles collected over Greenland during the 2016 and 2017 melt seasons were characterized using transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), and scanning transmission X-ray microscopy (STXM) in terms of particle abundance, size distribution, and chemical properties. The results highlight the variability of the structural and spectral properties of the BC particles being delivered to the surface of the GrIS, thereby providing information about the source of these combustion products. These properties, in turn, alter the photoabsorption characteristics of BC, thus influencing the ability of BC particles to absorb UV radiation, and lower albedo.


Keywords: black carbon, nanoparticles, Greenland Ice Sheet, albedo.
Seeing between the cells: Highlighting extracellular biofilm structure and mineral nucleation processes

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Microorganisms mediate mineral nucleation reactions in a variety of natural and industrial environments. Mineral nucleation processes typically occur within microbial mats and biofilms hosting a diverse microbial community. The organisms in these communities are often spatially organized within the biofilm based on their respective metabolic processes. As a result, biofilms present complex three-dimensional structures hosting chemically stratified microorganisms, among which minerals can precipitate. The precise location of extracellular mineral nucleation, which is more common than its intracellular counterpart, is often unknown. The tendency of microbial mats and biofilms to contain both biological and lithological components makes it difficult to maintain sample structure during preparation for transmission electron microscopy. This challenge can be overcome by preparing microbial mats using staining and fixation techniques developed for eukaryotic tissue samples\textsuperscript{1}. These methods enable visualization of biofilm architecture, particularly the framework of extracellular polymeric substances that surrounds microbial cells. Once biofilm structure can be visualized, it becomes possible to identify where mineral nucleation is occurring within the biofilm. These results have implications for geomicrobiological studies targeting microbial mineral precipitation reactions and fossilization of microbial life preserved in the rock record\textsuperscript{2}.


\textbf{Keywords:} microbial mats, mineral nucleation, biofilm architecture, extracellular polymeric substances.
Mapping structure and morphology of amorphous organic thin films by STEM pair distribution function analysis

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We propose a new approach for imaging the phase distribution and for analysing the local structure of amorphous or partially crystalline organic materials based on scanning transmission electron diffraction (4D-STEM) pair distribution function analysis (PDF) [1]. We show that PDF analysis of electron diffraction [2,3] can be used to characterize the short- and medium-range order in aperiodically packed organic molecules. It allows to decode the complex structural information encoded in the amorphous features of the diffraction pattern. Moreover, we show that, as illustrated in figure 1, STEM-PDF does not only provide local structural information with a resolution of a few nanometers, but can also be used to image the phase distribution of organic composites. The distinct and thickness independent contrast is generated by utilizing the structural difference between the different types of molecules and taking advantage of the dose efficiency due to use of the full scattering signal. Therefore, this approach is particularly interesting for imaging unstained organic or polymer composites without distinct valence states for electron energy loss spectroscopy. In addition, we will also demonstrate the 4D-STEM data can help us to optimise the conditions of convergence/scattering angle in conventional STEM-BF/DF to image phase distribution of organic molecules with low dose.

We explore the possibilities of this new approach using [6,6]-phenyl C61-butyric acid methyl ester (PCBM) and poly(3-hexylthiophene-2,5-diyl) (P3HT) as the archetypical and best-investigated semiconductor blend used in organic solar cells, compare our phase distribution with virtual dark-field analysis and validate our approach by electron energy loss spectroscopy.
Figure 1. (a) A typical (HR)TEM bright field image of the blend film. (b) Virtual STEM HAADF image. (c) Procedure for STEM-PDF analysis. (d) PDF maps of PCBM and (e) the P3HT phase at the same location as in b. (f) RGB color mix of d (green) and e (red). (g) A typical EFTEM map of the blend film. (h) PDFs of the P3HT-rich (red solid line) and PCBM-rich (green solid line) phases of the blend extracted from the STEM-PDF cube. PDFs of the neat P3HT (red dashed line) and PCBM (green dashed line) films obtained by using the SAED microscope setup. Black solid line is the PDF of the neat P3HT film obtained using the STEM-PDF microscope setup. All scale bars are 100 nm.


Keywords: Pair distribution function, 4DSTEM, Organic solar cell.
Triple and quintuple ordering in the perovskite-type solid oxides Ln$_{0.4-y}$Ba$_{0.6+y}$Fe$_{1-x}$Co$_x$O$_{3-\delta}$ (Ln= Gd, Sm; y= 0 – 0.035; x = 0 – 0.4)


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The investigations of Ln-Ba-M-O systems, where Ln is a lanthanide and M is a transition element, such as Co and Fe have discovered an existence of different types of layered structures with promising oxygen-ion and electron transport properties. Recent studies have revealed nanoscale «Ln–Ba–Ba/Ln–Ba/Ln–Ba–Ln» ordering in quintuple perovskites Ln$_2$Ba$_3$Fe$_{5-x}$Co$_x$O$_{15-\delta}$. In order to understand both effect of the size of the Ln$^{3+}$ cation and concentration ratios Ln/Ba and Fe/Co upon the ordering of the layers, oxygen nonstoichiometry and transport properties the crystal and defect structure of the Ln$_{0.4-y}$Ba$_{0.6+y}$Fe$_{1-x}$Co$_x$O$_{3-\delta}$ (Ln= Gd, Sm; y= 0 – 0.035; x = 0 – 0.4) was studied in this work.

The samples were synthesized via glycerin-nitrate method. Phase composition and crystal structure were investigated using X-ray diffraction analysis and transmission electron microscopy. XRD patterns have shown no indication of impurities for all samples. All samples possess cubic structure (sp. gr. Pm3m).

In order to study superstructure ordering TEM techniques (SAED, HRTEM) was used. Quintuple ordering is shown to exist in all Sm-containing samples regardless oxygen content or Co and Ba substitution. Meanwhile, structure of Gd-containing compounds strongly depends on Co content, which in turn effects on oxygen nonstoichiometry. Thus quintuple ordering is observed in samples with the cobalt concentration x = 0.3 and 0.4, triple ordering – for x = 0.1. At the same time there are randomly mixed triple and quintuple ordering in the sample with cobalt content x = 0.2. In spite of strong influence of oxygen content on structure further in-situ investigations of structure in different conditions (temperature, oxygen partial pressure) are required.

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Keywords: Transmission electron microscopy, quintuple perovskites, SOFC.
Recent technological advances in transmission electron microscopy (TEM) allow us to image and analyse materials atom-by-atom with spatial resolutions of ~1 Angstrom or better in high-end aberration corrected microscopes. To-date, these developments have largely been limited to the realm of materials science research.

Here, it will be shown that by using these ultra-high-resolution (non-cryo) techniques in a cross-disciplinary manner it is possible to study materials in soft biological matter at the level of individual atoms.[1-4] Technique-specific highlights are presented for studying the physical and chemical properties of a range of carbon- and non-carbon based nanomaterials exposed to different cells from culture and tissue. An example is shown in Fig.1, where scanning TEM electron energy-loss spectroscopy (STEM EELS) was used to study clusters of Cu biometals in the mouse brain (a&b) and TEM imaging was used to identify Ferritin (c&d) generated during a reactive oxygen species response as a result of exposure to carbon nanotubes (CNTs).

Figure 1. a) TEM image and b) STEM EELS of Cu L2,3 edge of clusters of Cu biometals in the mouse brain as well as c) STEM image and d) TEM image of Ferritin generated during a reactive oxygen species response as a result of exposure to carbon nanotubes (CNTs).( [3] and unpublished work)


Keywords: STEM EELS, CNTs, graphene, MoS2, TEM, tomography.
Supercooled water in ESEM

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Water is the main ingredient of life, but it is very challenging to investigate biomolecules (e.g. proteins) in their natural hydrated state at high spatial resolution. One approach is liquid phase transmission electron microscopy (LPTEM), which has attracted significant interest in recent years [1-2]. Subnanometer resolution is possible, and dynamical processes have been revealed [3-5]. However, LPTEM suffers from significant beam damage. This is especially critical for soft matter, which easily degrades in an electron beam, and which is specifically sensitive to radiolysis products. We present ESEM as an alternative method for wet ambient conditions. ESEM provides sufficient spatial resolution and relatively low radiation damage. We will show that our set-up allows for the condensation of supercooled water (Figure 1), which is usually rapidly freezing at defect sites. We demonstrate the interaction of supercooled water droplets with protein cages (ferritin, apoferritin). Our findings are of relevance to environmental science (cloud formation at biomatter).

Figure 1. ESEM image. Supercooled water droplets of round shape (orange) on a copper surface, and of irregular shape (yellow) on an apoferritin-covered area, T=-20°C, P=130Pa water vapour pressure, HV=5kV


Keywords: ESEM, supercooled water, protein cages.
Interaction between ‘green rust’ and redox-sensitive oxyanions revealed by STEM-EELS

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‘Green rust’ (GR), a highly redox-active Fe(II)-Fe(III) layered double hydroxide (LDH), has been used to removed oxyanions in contaminated groundwater. To date, TEM has been used in previous studies to investigate the morphology, crystal structure, chemical composition and oxidation state of the end-products of these reactions [1-3]. However, the conditions under which TEM analysis does not induce beam damage in these interacted samples were unclear. Our goal was to determine the electron fluence threshold for beam-induced oxidation to enable quantitative determination of Fe oxidation state in pure and contaminant-interacted GR samples. We examined the chemical and structural stability of GRSO4 samples by acquiring an electron fluence series between ca. 40 eÅ⁻² and 10,000 eÅ⁻². TEM imaging and electron diffraction showed that the hexagonal plate-like GR morphology and crystal structure remained largely unaffected. However, quantitative analysis of a series of monochromated Fe L₃,₂-edge electron energy loss spectra (EELS) showed that electron irradiation induced Fe(II) oxidation. We measured an Fe(II)/Fe(III) ratio of 1.93 (as expected for GRSO4) at 50 eÅ⁻². However, above this fluence, the ratio logarithmically decreased, and dropped to ca. 0.5 after 1000 eÅ⁻². With this work, we demonstrated that using combinations of conventional drop-cast and cryo-sample preparation and analyses approaches, we can accurately quantify the Fe oxidation state in GR and the effects that redox-sensitive oxyanions (e.g., As, Cr) have using mono-EELS provided electron dose is kept at minimum [3]. Such data helps us elucidate the role and effects of contaminant elements on reaction kinetics and molecular mechanisms during GR formation and transformations in the subsurface.


Keywords: green rust, cryo, monochromated EELS, Fe oxidation, low dose TEM.
Enhancing the photocatalytic activity of calcium and strontium-based molybdates

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Oxides with scheelite type of crystal structure are widely used as materials for scintillators, lasers, ionic conductors, phosphors, photocatalysts, and microwave dielectrics. This broad variety of applications arises from the ability of the crystal structure to accommodate different cations in the lattice, forming various structural modifications and compositions. The main goal of the present work is to understand how the structure, morphology and microstructure of Bi-doped CaMoO₄ and SrMoO₄ influence their photocatalytic activity and propose ways to further improve catalytic properties. Complex oxides with formula (Ca/Sr)₁₋₃ₓBi₂ₓMoO₄ (x=0-0.225) were prepared by solid state reaction in the temperature range 500-700°C. The homogeneity range of (Ca/Sr)₁₋₃ₓBi₂ₓMoO₄ was found to be 0.025≤x≤0.2125 (sp. gr. I41/a). Superstructure ordering was observed for samples with x>0.15. Electron diffraction and HRTEM study are in progress, and will allow us to propose a model for performing a crystal structure refinement. The average diameter of Ca₀.₇Bi₀.₂MoO₄ particles measured by laser diffraction is 20±6 µm. The surface area determined by the BET method was ~4 m²/g. The typical morphology of the powders is shown in Figure 1.

Photocatalytic activity of Bi-doped (Ca/Sr)MoO₄ was measured under UV light irradiation using RhB as a model organic pollutant. It was shown that these oxides demonstrate photocatalytic activity comparable to TiO₂ (Degussa, surface area of 25 m²/g). Substitution by bismuth as (Ca/Sr)₁₋₃ₓBi₂ₓMoO₄ to increase the concentration of cationic vacancies, enhanced the photocatalytic activity of oxides.

Keywords: Photocatalytic activity, scheelite-type oxides.
Operando Transmission Electron Microscopy to study catalysts under reaction conditions

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The development of in situ/operando techniques that allow characterization of active catalysts and associated dynamic processes under relevant catalytic conditions has become an important research topic in heterogeneous catalysis. Up to now, there are only a few reports, which focus on in situ TEM studies and could simultaneously correlate the catalytic activity with structural and morphological changes of the catalysts.[1] In our department, we have recently implemented a home-built gas-feeding setup combined with a mass spectrometer (MS) for in situ experiments inside the column of a conventional FEI Titan transmission electron microscope (TEM) using commercially available gas-flow TEM holders (Figure 1a). Herein, we will report on the capabilities of the home-built in situ setup to monitor in real time structural changes of Pt nanoparticles (Figure 1b) under controlled reaction conditions, pressures up to 1 bar and temperatures up to 1000 °C. Moreover, during the experiment gas-phase composition is simultaneously analysed, proving the ability to detect the catalytic conversion by MS (response time less than 20, Figure 1c).

Figure 1. a) Experimental setup for operando TEM, b) Atomic resolution imaging of Pt nanoparticle in gas feed CO:O₂=1:5 at 700 mbar and 200 °C, c) Response time of MS at 20 mbar pressure and flow rate 2 μl/min.


Keywords: in situ transmission electron microscopy, mass spectrometry, gas-feeding setup.
Cryo Volume Imaging: From cell nucleus to extracellular structure

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Biological structures have been probed for more than 300 years, and a diverse array of instruments and methods are currently available including optical, electron and X-ray imaging techniques. However, deciphering these high-resolution structures at high resolution in their in vivo or as close as possible to the in vivo conditions, is still challenging to say the least.

Here we describe one of the newest methods for biological structural analysis that integrates the enormous benefits of cryo-imaging and analyzing large volumes, in 3 dimensions. Cryo-FIB-SEM (Focused Ion Beam-SEM) technique [1] allows three-dimensional imaging of high pressure frozen or plunge-frozen biological samples under conditions that are very close to their native state, without any chemical treatment. The cryo-FIB-SEM can produce 3D image stacks of a volume of thousands of micrometers cubed at an image pixel size down to 5 nm, while keeping the sample in a hydrated state in vitreous ice. This method thus fills a valuable niche in biological cryo-imaging by closing the gap between light microscopy and TEM tomography.

Despite the Cryo FIB-SEM workflow is extremely fast, with compare to the traditional, room temperature, FIB-SEM technique, this method is still rarely used.

We demonstrate here this methodology applying to objects, which we are actively investigating: mammalian cells, unicellular algae, tissues; we also discuss the advantages and challenges of this cutting-edge technique.


Keywords: Cryo FIB-SEM, Biomineralization, Cryo-EDS.
Electron beam induced amorphisation of polypropylene particles

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Microplastic pollution is considered a possible threat to the environment. [1] Electron microscopy can help to structurally identify small size fractions of plastics in the environment. For reliable results, beam induced effects on the materials have to be carefully evaluated first, and subsequently be minimized.

In this study, we examine the beam effect on the structure of individual polypropylene (PP) particles by electron diffraction measurements. Consequently, the electron diffraction patterns were recorded immediately after exposure of the particles to the parallel electron beam (Figure 1). We hypothesize that pair distribution function (PDF) analysis of the diffraction data can prospectively provide information on the degradation mechanisms (melting or radiolysis, crosslinking) of polymers.

Figure 1. A) Preliminary PDF analysis of a PP particle immediately after beam exposure (0-5 s) and after more than 9 s of exposure. B) Time series of electron diffraction measurements of one PP particle. C) The measured PP particle after the diffraction experiment.


Keywords: Polymers, Microplastic particles, Diffraction, Pair distribution function.
Crystallisation and orientational behaviour of nylon on inorganic nanoplatelets in nanocomposite fibres

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Nanocomposite fibres consisting of semicrystalline polyamide 6 (PA6) loaded with up to 5\% organically modified nanoclay platelets (NCPs) or graphite sheets (NGPs) are produced by melt-spinning combined with mechanical off-line drawing and characterised by transmission electron microscopy and wide-angle X-ray diffraction. Different to neat polymer fibres, where shish-like $\gamma$ PA6 crystallites form from elongated and aligned unfolded chain segments that are pulled out in fibre direction, the structural evolution in the nanocomposite fibres is significantly influenced by the exfoliated and axial aligned inorganic nanoplatelets (NPs). Crystallisation of folded-chain PA6 lamellae on the aligning NPs lateral surface sites results in orthogonal lamellar growth perpendicular to the fibre axis. The different NP structures and surface energies evoke the building up of $\gamma$ (NCPs) or $\alpha$ (NGPs) PA6 lamellae. Delamination of the formed lamellae due to mechanical drawing leads to a so far unprecedented microstructural transition from nano-lamellar (kebab-like) to nano-fibrillar (shish-like) structures, which is retarded with increasing NP loadings.

![Figure 1. Model for PA6 recrystallisation emphasising the kebab → shish transition.](image)

**Keywords:** nanohybrid shish-kebab structure, epitaxial growth, TEM, WAXD.
Low dose Scanning Transmission Electron Microscopy of organic crystals by scanning moiré fringes

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In the pharmaceutical industry, it is important to determine the effects of crystallisation and processes, such as milling, on the generation of crystalline defects in formulated products. Conventional transmission electron microscopy (CTEM) and scanning transmission electron microscopy (STEM) can be used to obtain information on length scales unobtainable by other techniques, however, organic crystals are extremely susceptible to electron beam damage.[1-3]

This work demonstrates a bright field (BF) STEM method that can increase the information content per unit specimen damage by the use of scanning moiré fringes (SMFs). SMF imaging essentially provides a magnification of the crystal lattice through the interference between closely aligned lattice fringes and a scanning lattice of similar spacing. The generation of SMFs is shown for three different organic crystals with varying electron beam sensitivity, theophylline, furosemide and felodipine.

The electron fluence used to acquire the BF-STEM for the most sensitive material felodipine was approximately 3.5 e⁻/Å⁴. After one additional scan of felodipine (total fluence of approximately 7.0 e⁻/Å), the SMFs were no longer visible due to extensive damage caused to the crystal. Irregularity in the SMFs suggested the presence of defects in all the organic crystals.

Further effort is required to improve the data analysis and interpretation of the resulting SMF images, slowing more information regarding the crystal structure and defects to be extracted.


Keywords: Low dose, Bright field STEM, Organic crystals, Scanning moiré fringes.
Correction of motion aberration in liquid-cell TEM imaging with MotionCor2

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The advent of microfluidics has enabled for the use of in situ High-Resolution TEM (HRTEM) imaging of biologically relevant assemblies and molecules in their native, physiological states. This is especially of interest due to its ability to capture in real-time processes with nm spatial resolution. However, HRTEM imaging in solution introduces motion due to solution-electron beam interactions. With refinements made by MotionCor2, HRTEM imaging in solution can be adjusted to accommodate these artefacts and now fully functional to study biological nanostructures in solution. Here, we demonstrate that a biomineralization protein, SM50 a sea urchin larvae extracellular matrix protein, can stabilize large concentration of amorphous CaCO3 for cellular processing before mineralization events. HRTEM imaging in solution coupled with MotionCor2 can reveal structures and processes at the organic-inorganic interface with unprecedented spatial and temporal resolutions.
Sub-cellular elemental mapping by combined STEM-EDX-EELS

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The scanning transmission electron microscope (STEM) is a powerful instrument for performing quantitative imaging and spectroscopy at extremely high resolution. Powerful techniques in STEM include annular dark-field imaging (which allows heavy elements to be detected and quantified \cite{1}), energy dispersive x-ray (EDX) and electron energy-loss spectroscopy (EELS). Such methods are routinely used in materials science to provide highly localised compositional information, even down to an atomic scale \cite{2,3,4}.

We present simultaneously-acquired high-angle annular dark field STEM, EDX and EELS data, showing ability to detect trace elements such as Ca, which underpin fundamental biological processes. We discuss some specific challenges associated with acquiring such data from biological systems, namely radiation sensitivity and overlap of neighbouring and biologically-relevant elemental peaks. We present multivariate methods as a potential candidate for unwrapping additional information from such combined data sets.

\cite{1} Sheader, AA. et al., Journal of Microscopy, 270(1), pp 92-97. 2018
\cite{2} Aarons, J. et al., Nano Letters, 17(7), pp 4003-4012 (2017)
\cite{3} Kothleitner, G. et al., Physics Review Letters, 112, 085501 (2014)

\textbf{Keywords:} STEM, EDX, EELS.
Copper canister for spent nuclear fuel storage: Gamma-radiation induced corrosion

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The nuclear power plants cover of around 11% of the total energy needs in the world. The nuclear energy production has almost no emission of greenhouse gasses. However, it generates highly radioactive waste, which radioactivity reaches the background level after approximately 100,000 years [1]. Therefore the long term safety of radioactive waste repository needs to be concerned for the countries which use nuclear power. The most developed method of nuclear waste repository in Sweden and Finland is so called KBS-3 method. It implies multi barrier and deep geological disposal concept. The spent nuclear fuel is planned to be stored in copper canisters with cast iron inset. Those canisters will be 5 m long with the diameter of 1 m and the Cu wall thickness of 5 cm. The canisters will be sealed, embedded in bentonite clay and disposed in the granite bedrock at a depth of 500 meters. Thus, copper canisters are used as one of the barriers and provide complete isolation of spent nuclear fuel from the environment. Although the canisters will be stored in anoxic conditions (which favour copper stability), the other parameters such as ionizing radiation, ground water composition (sulphides), increased temperature, microbial activity etc. will contribute to the degradation (corrosion) of the outer copper shell. This may lead to radioactive products release into environment. Understanding the mechanism of the reactions occurring on the copper/water interfaces under the exposure to ionizing radiation will help us to predict and possibly to control the copper canisters’ degradation which this is an important issue in long term safety assessment.


Keywords: Copper corrosion, ionizing radiation.
Nano-crystallography structure solution of organic and inorganic crystals

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Since 2009 electron diffraction tomography has been bringing averaged structure solution of Nano-sized crystals to the field of electron microscopy. The approach has iterated quickly during the last decade with four different flavours of electron diffraction tomography emerging to serve different experimental conditions and microscope setup available to users. These methods have been applied to almost every type of nanocrystal from metals to metal organic framework through to proteins.

We will present data from the newest of these four methods known as MicroED [1] which is mimicking the X-ray crystallography experiment where the crystal under goes continuous rotation of the crystal while a detector with fast read out speed is used to minimise the loss of data during collection. These experiments as extremely efficient taking only a few minutes to collect an entire data set. The data presented will be from a range of nano-crystals from ferroelectric materials to pharmaceutical crystals where the technique is being used to identify new polymorphs for of materials and help explain the physical properties and grow mechanisms of a wide range of materials.

[1] Shi et al., eLife 2013:2e01345 DOI: 10.7554/eLife.01345

Keywords: Electron Diffraction, Electron diffraction Tomography.
Mineral and organic matrix interaction in calcifying avian leg tendons: A Focused Ion Beam – Scanning Electron Microscopy study

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A clear understanding of the cellular organization and spatial relationships between cellular network, collagen fibrils and early deposits of mineral in calcifying avian tendon can provide fundamental information of the mineralization mechanisms in several collagenous tissues. Previous studies investigating extracellular matrix organization have utilized techniques such as X-ray scattering [1], scanning electron microscopy and transmission electron microscopy [2] and faced challenges of providing both nanometer resolution and three-dimensional (3D) volume data in sizes of tens of microns. In this regard, FIB/SEM serial surface imaging is capable of characterizing 3D tissue organization with nanometer resolution and over large volumes. In the present study, tibialis cranialis tendons were obtained from freshly sacrificed domestic turkeys, British United Turkeys, and prepared by high pressure freezing and automatic freeze substitution. FIB/SEM slice-and-view tomographic imaging with a resolution as high as 6 nm was performed at the interface between unmineralized and mineralized zones of the tendons. Reconstruction of the cellular and extracellular matrix organization demonstrates, in the highly mineralized regions, a complex cell network in which primary canaliculi with a diameter of ~100 nm tightly surround each collagen fibril bundle in the circumferential direction to the tendon long axis. More interestingly, high resolution FIB/SEM imaging revealed smaller channels/canaliculi (approximately one-third the diameter of primary canaliculi) that diverge from the primary channels and infiltrate collagen fibril bundles by mainly following the fibril direction. Further, early stage mineral clusters were clearly visualized in extrafibrillar spaces (interfibrillar mineralization), correlated with cell processes. At later stages, mineral deposits appear to propagate both along and into collagen fibrils (intrafibrillar mineralization). Overall, the FIB/SEM study provides a novel view of 3D spatial relationships between tenocytes, extracellular matrices, and minerals and supports the concept that mineral is initially deposited between collagen fibrils, as reported in early TEM studies [2–4]. Such observations could provide invaluable insight into mineralization mechanisms of vertebrates.


Keywords: Avian Leg Tendon, Mineralization, FIB-SEM, Extracellular Matrix.
Synthesis and characterization of nanosized metal nanoparticles in a disulfide matrix polymer

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The synthesis of an organic disulfide polymer was achieved by a nanoprecipitation method providing kinetically stable polymer particles which can be loaded with metal nanoparticles and serve as a novel type of organic-inorganic hybrid catalysts. The polymerization is carried out oxidatively either via hydrogen peroxide or metal salts with high oxidation potential such as hydrochloric acid, hexachloroplatinate and silver nitrate. Due to an affinity to thiols, the corresponding nanoparticles form inside the polymer matrix.

Figure 1. TEM images of platinum and gold nanoparticles in organic-inorganic hybrid structures.

Particles were characterized with dynamic and static light scattering, TEM and AFM. From AFM an impression on the packing and distribution of the nanoparticles within the organic polymer sphere could be gained. Other material classes could be tagged on the polymer nanoparticles leading to unique and versatile composite structures, with excellent catalytic properties. TEM has been of particular importance to characterize the versatile and complex organic-inorganic hybrid structures with different morphologies and properties.

Keywords: Polymers, hybrid organic-inorganic interfaces.
**In situ** electrochemical liquid-cell transmission electron microscopy studies of CuO$_x$ nanosheets for CO$_2$ electroreduction

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Oxidic and oxide-derived nanostructured copper catalysts have been used to promote electrochemical reduction of CO$_2$ (CO2RR) to higher-value products such as ethylene. Restructuring of copper oxides has been suggested to play an important role during the reaction. However, it is still not clear how copper oxides evolve and what structure they form as well as what is the exact active species for CO2RR.

![Figure 1. The morphology change from sheet-like nanoparticles to dendrites during the operating CO2RR condition with in situ electrochemical liquid-cell.](image)

In this poster, we presented a free-standing CuO$_x$ nanosheet with {001} facets exposed which are synthetized by surfactant-free wet-chemistry route. The as-prepared CuO$_x$ shows a stable and selective ethylene formation over 20h. The **in situ** electrochemical liquid-cell was employed for morphology change investigation. We aim at understanding activity-selectivity-morphology under operating conditions. More fundamental knowledge of the shape evolution is needed to guide future catalysts design to access enhanced performance during CO2RR.

**Keywords:** Microscopy, liquid-solid interface, in situ electrochemistry TEM, CO$_2$ electroreduction, morphology change.
Degradable Mg-based implants: Impact on the ultrastructure of bone

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Magnesium with its biodegradable properties can become an alternative to non-degradable metal implants. Still, some question remains to be elucidated, such as: a) how is the material degrading under physiological conditions, b) how is the remodelling of the degradation layer happening and c) how is the healing process changed? There are indications that bone-forming osteoblasts actively change the degradation products. High-resolution two dimensional scanning small angle X-ray scattering (SAXS) and diffraction (XRD) offers a look into the ultrastructure.

Mg-5Gd, Mg-10Gd and PEEK screws were implanted in the femur rats for 4, 8, and 12 weeks. With the help of scattering experiments it is possible to measure the orientation and the crystallinity of the hydroxyapatite platelets. From this, information of the influence of the degradation and mechanical stiffness of the implants on the bone healing and formation can be gained. We have analysed the orientation of the hydroxyapatite plate and their crystallinity. Figure 1 top shows the HA platelet thickness analysed via the stack of cards model along with the orientation of the platelets. The data reveal an inhomogeneous nucleation whereas big particles with 80 Å thicknesses are forming at the screw interface. Comparing the occurrence of the (111) HA diffraction signal, see figure 2 bottom, one observes that crystalline particles only form in the center, whereas the particles forming at the screw interface show an amorphous structure. We will discuss the influence of different Magnesium alloys and healing times on the bone formation.


Keywords: SAXS, bone implant interface, remodelling.
Measurement of the mean inner potential of PMMA and its electron beam induced charging using off-axis electron holography

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Precise measurements of mean inner potential (MIP) in the transmission electron microscope provide valuable information about material properties, such as work function and ionicity [1,2]. However, there are few measurements of the MIPs of organic compounds, in part due to the fact that they often undergo electron beam induced damage and/or charging.

Here, we use off-axis electron holography to measure the MIP of poly methyl methacrylate (PMMA), which is a widely used resist in lithography. The experiments were performed using an FEI Titan 60-300 TEM operated at 300 kV. The electron dose (rate) was recorded using a Gatan K2 camera. Figure 1 shows representative off-axis electron holography results recorded from 200-nm-diameter PMMA nanospheres purchased from the company microParticles. The nanospheres were either supported on continuous C films (top) or placed on holey C films, on which they occasionally protruded into vacuum (bottom). For the nanospheres that extended into vacuum, electron beam induced charging was directly visible. For the nanospheres that were supported on continuous C films, the MIP was measured to be $4.8\pm0.3$ V, regardless of the electron dose or dose rate (which was always kept below 4 electrons per pixel per second), on the assumption that they are perfect spheres are not charged.

The assumption that the nanospheres that are supported on continuous C films are not charged and the observation that nanospheres of PMMA damage more slowly than continuous films of PMMA (not shown here) will be discussed [3].
Figure 1. Measurement of the mean inner potential of PMMA using off-axis electron holography. The upper panel shows (left) a phase image of a PMMA nanosphere supported on a C film and (right) a contoured version of this image. The lower panel shows (left) a phase image of a PMMA nanosphere hanging out into vacuum from the edge of a hole in a C film and (right) a contoured version of this image. The phase contour spacing is $\pi/3$ radians. The electron dose rate is approximately 1 electron per pixel per second. The exposure time is 8s.

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**Keywords:** Mean inner potential, off-axis electron holography, PMMA.