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Design and synthesis of nanoparticles for biotechnology and medicine

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Core-shell nanoparticles smaller than 100 nm are in demand for biomedical applications, e.g., as imaging contrast agents, for hyperthermia and in drug delivery, as well as for biotechnological applications such as separation and purification. They employ nanoscale inorganic cores, such as superparamagnetic iron oxide nanocrystals and nanoplasmonic gold particles, to interact strongly with electromagnetic fields and achieve their unique functions. For all biomedical and biotechnological uses, the functional core of the nanoparticle must be protected from the environment and targeted to specific disease markers or other biomolecules. The first and most critical step to achieve this is to design a biocompatible polymer shell around the nanoparticle core that repels biomolecules, e.g., proteins, and enables dispersion of the nanoparticles in biofluids. If serum proteins, especially opsonins, adsorb on the nanoparticles, they will lose their function and be cleared from the blood by the immune system. The next step is to bind, e.g., antibodies to the nanoparticle shell that enable specific binding of the nanoparticles to biomarkers. The resulting so-called core-shell nanoparticle structure is a general platform for creating theranostic nanoparticles for biomedicine that perform novel functions at desired biological sites. I will step-wise describe the state-of-the-art of this design approach and how to characterize it using superparamagnetic iron oxide nanoparticles as an example. I will focus on how the nanoscale geometry imposed by the core influences the properties of molecules grafted to its surface, and how a magnetic core can be used to control the interactions of molecules on its surface. Examples of magnetothermally actuated nanoparticle systems combining polymers, lipids, and iron oxide nanocrystals that allow magnetic imaging and triggered release of drugs will be described.
Co-existing Ferromagnetic-Antiferromagnetic Order in a Metamaterial

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Square artificial spin ice (ASI) are systems of bistable coupled single-domain nanomagnets arranged on a square lattice, with four adjacent magnets aligned head-on at each vertex point. The magnets are dipolar-coupled so that the macrospins at each vertex point obey ice rules, minimizing the magnetic charge. The square ASI systems have been extensively studied and found to exhibit stable demagnetized antiferromagnetic ordering. By rotating each nanomagnet some angle $\alpha$ around its center the pinwheel ASI variant is created. In our work, we have observed a new phase of stable ferromagnetic ordering for pinwheel ASI where $\alpha$ is near 45°. Furthermore, close to the transition angle ($\alpha = 30°–40°$), the systems show co-existing ferromagnetic and anti-ferromagnetic phases. The co-existence, and seeming degeneracy, of magnetized and demagnetized phases in ASI are interesting both through a metamaterial perspective and as use in a computational device.
Ice adhesion and wettability at nanoscale

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Low ice adhesion surfaces are a promising strategy for anti-icing surfaces. However, successful anti-icing surfaces need to be tested in all relevant environmental conditions, including extremely low temperatures. Such temperatures are costly and difficult to incorporate during testing. Although there has been proposed several room temperature correlations with ice adhesion strength for potential low ice adhesion surfaces, results diverge widely due to experimental factors.

Through molecular dynamics simulations, the behaviour of the ice itself and the adhesion mechanisms can be investigated. Thermodynamic theory describes a theoretical relation between the work of adhesion and contact angle on a given surface. Here, atomistic modelling and simulations are utilized to probe the correlation of contact angle and ice adhesion strength at the nanoscale. The results give a correlation close to the theoretical model, indicating that the behaviour of water at room temperature might be used to predict ice adhesion strength under certain conditions.
NIL Metasurfaces for miniaturized optics

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In vivo imaging by use of miniature cameras has a wide range of clinical applications but is today limited in imaging quality due to the strict size and weight constraints involved. Trade-offs between transverse resolution and depth of focus must typically be made. At SINTEF MiNaLab we are currently pursuing imaging by utilizing a recent development within nanophotonics known as metasurfaces. Metasurface lenses (metalenses) offer dramatic miniaturization without compromise on imaging resolution, and have the potential to outperform conventional refractive and diffractive optics. This is achieved through tailor-made nanostructures acting as pointwise phase shifters for the transmitted field (Figure 1a-b).

Figure 1 a) An illustration of a simple metalens consisting of cylindrical dielectric pillars of varying diameters. The structure focuses light by radially shifting the phase of the transmitted field, so that all the light rays originating at some object point will arrive at the focal point in-phase despite travelling different trajectories (Fermat’s principle) b) SEM image of patterned resist for a metalens manufactured at SINTEF MiNaLab.

While conventional lenses are made through cost intensive methods such as cutting, polishing and grinding, metalenses can be made using cost effective silicon batch processing tools. Currently, however, high-resolution metalenses for VIS and NIR are fabricated using direct writing methods, in particular Electron Beam Lithography (EBL), which are slow and unsuited for entire wafer patterning. There is now a need for development of methods which permit low cost, high throughput, large area, good reproducibility, and high resolution fabrication. This talk will discuss the operation principle of metasurfaces, the challenges we face with NIL and how we plan to overcome them.

References
The future of Materials: Smart, Functional, Sustainable

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Friction vs. area scaling of superlubric NaCl particles on graphite

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Structural superlubricity is the extremely low friction that appears between two surfaces that do not share the same lattice structure. One challenge in such achieving such low friction in practical conditions is the presence of molecules from that atmosphere, that enter into the interface and break the superlubric contact. Here, we introduce a new material combination, namely NaCl-particles on highly oriented pyrolithic graphite (HOPG), where the nanoparticles coalesce under the influence of ambient humidity. Our experiments reveal that the interfacial friction can be described by the concept of structural superlubricity despite the seemingly unavoidable contamination of the interface. We systematically analyze the friction versus area scaling, and explain the experimental results by a model that considers the influence of nanoparticle preparation on the interface conditions, specifically the inevitable water layer at the interface between particle and substrate.

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Working with NorFab:
The Norwegian Infrastructure for Micro- and Nanofabrication

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Point defects in semiconductors as quantum contenders

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Quantum technologies (QT) have recently become a top research priority, where exciting applications are envisioned within computing, communication, and metrology, and where systems based on superconductors and trapped ions are already demonstrated. However, point defects in semiconductors and insulators have recently emerged as an alternative technology and gained tremendous research interest, since they provide a wafer based platform that combines the environmental isolation necessary to maintain the coherence of quantum states with the ability to perform electrical and optical manipulation.

In this contribution, spin defects in wide band gap semiconductors will be discussed. In particular, silicon carbide (SiC) has become a leading contender accommodating several promising point defects, including the silicon vacancy $V_{\text{Si}}$, that act as single-photon sources and show promise for qubit applications. Selective population and efficient switching between charge states are essential for preparing the $V_{\text{Si}}$ as a building block for QT, and can, interestingly, be achieved through electrical manipulation, as will be shown in this contribution.
Chasing hydrogen with photons and neutrons

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Hydrogen-rich solids, or hydrides, are versatile systems with a wide range of exciting properties. They can store hydrogen with high energy density that is very compelling if compared to that of battery,\(^1,2\) and also possess other fascinating properties potentially interesting for applications within a wide range of solutions for energy technology. The numerous potential applications owe in part to an astonishing chemical bonding flexibility of hydrogen, which can be ionic (H\(^-\), H\(^+\)), covalent (H\(^{\text{cov}}\)), neutral for the atoms at interstitial sites, or intermediate between these. Balance between the different contributions defines thermodynamic\(^3\) and electric\(^4\) properties of hydrides. On the other hand, many of the properties can be controlled and tuned by introducing nanostructures. Understanding the structure and dynamics in hydrogen-rich solids is not an easy task. This presentation overviews the recent progress in functional hydrides for energy-related applications, effects of nanosizing for the material properties, and the efforts in the state-of-the-art advanced characterisation of hydrogen-rich solids.

References

Synthesis and application of core-shell nanostructures of graphene-wrapped CdS nanoparticles and TiO$_2$ for photocatalytic H$_2$ generation

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To overcome the issues related to low photocatalytic efficiency for H$_2$ generation due to less light absorption by the semiconductor materials, cadmium sulphide (CdS) having a bandgap of $\sim$2.4 eV is applied. The formation of core-shell nanostructures of CdS with TiO$_2$ has been shown to enhance the photocatalytic activity and stability for H$_2$ generation from water. The presence of TiO$_2$ over CdS nanoparticles increase the charge separation efficiency which eventually leads to enhanced activity and stability. Motivated to improve the photocatalytic activity of our previous core-shell nanostructure of CdS@TiO$_2$ [1] and to utilize the conductor role of graphene (G), we report a new core-shell structure of CdS@G@TiO$_2$. The graphene layer present in between the CdS core and TiO$_2$ shell acts as a conductive layer, which promotes the charge separation efficiency (fig 1) even more than the CdS@TiO$_2$ nanostructure alone.


Fig. 1 Photocatalytic H$_2$ generation by utilizing CdS@G@TiO$_2$ samples and proposed reaction mechanism.
Perspectives on costs and development of nano-materials for energy conversion processes

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This work presents a perspective on economics of the process as the main driver for development of nano-structured materials for energy conversion processes. A multi-scale modeling framework connecting models from atomic to plant scale (Figure 1), is also proposed and applied to design a efficient and cost effective gas-fired power production process integrated with chemical looping reforming (CLR) and CO2 capture. CLR uses oxygen carrier material to convert natural gas into syngas, and hence this material is crucial to techno-economic performance of the process. However, it is observed that for power production process, the cost of electricity is less sensitive to reactivity of the oxygen carrier material (nano to micro scale) and more sensitive to lifetime. Therefore, this work aims to provide the scientific community with an approach to integrate the material development with the market (economics) and environment driven indicators (for example cost of electricity and CO2 avoided). The goal is to minimize the time, costs, risks and efforts in developing novel materials and processes to reduce greenhouse gas emissions.

![Figure 1: Schematic of different scales and related scientific and engineering aspects](image-url)
Engineering approaches for Perovskite solar cell materials

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Lead halogen perovskite materials have recently build up a significant research interest for applications in low cost solar cells with high efficiencies and low fabrication cost. They have been referred as “the next big thing in photovoltaics”, where their spectacular physical properties at nanoscale makes them promising candidates for thin film and tandem solar cell device applications. Herein, the basic principles, benefits and drawbacks of perovskite solar cells would be summarized and approaches for engineering/enhancing the device based on the new perovskite materials will be discussed. Specifically, the topic of controlling the defect migration in the solar cell and novel ways to investigate the ionic movement by Stark spectroscopy will be shortly presented.
Core-Shell Electrocatalysts for Energy Applications

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Electrochemistry deals with the relation between electrical current and chemical reactions. These reactions take place in a cell containing an electrolyte and two electrodes across which a cell voltage is applied to provide the current. Electrochemical technology is a critical component of modern society, and many metals, including copper, zinc, nickel and aluminium are produced in electrochemical plants. The production of important chemicals such as chlorine, critical to the production of plastics, desinfectants, and household chemicals, and to the pulp and paper industry, is also inherently electrochemical.

Electrochemistry is also a cornerstone of a number technologies upon which the transition to a greener society rests, including fuel cells, batteries, and water electrolysis for the production of hydrogen and other fuels from renewable energy. The electrification of the energy and transport sectors imposes new demands on the materials needed to build storage (for example batteries for cars), charging facilities, and the associated infrastructure (grids).

In a special subset of electrochemical reactions — so-called electrocatalytic reactions — the rates of the electrochemical reactions (at a given electrode potential) depend strongly on the characteristics of the electrode material, such as its chemical composition. Electrocatalysis is particularly important in electrochemical energy storage and conversion such as in fuel cells and water electrolysis [1, 2]. Many electrocatalysts consist of particles with diameters in the order of a few nanometers. For such catalysts particle size and catalyst architecture on the atomic level are also important in determining the electrocatalytic activity. Much of the research on electrocatalytic reactions pursues rational design of catalysts so that these can be engineered to suit a particular application under the constraints of cost and availability [3-7].

In this presentation, we will review briefly current theories of electrocatalysis, and on this basis, provide a motivation for the design of so-called core-shell electrocatalysts [8, 9]. These are nanometer-sized particles consisting of a core made of one metal covered by another metal (the shell). Such catalysts are, among other things, relevant for the electrochemical oxidation of methanol in fuel cells that employ methanol as a fuel (direct methanol fuel cells, DMFCs). We will describe the synthesis and

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1 For example, copper is pivotal wiring and transmission of electrical energy and signals in anything from high-voltage lines to its use in printed circuit boards in hand-held devices associated with the current digitalization of advanced societies. Nickel and cobalt are essential elements in modern batteries and other applications, notably the lithium-ion batteries on which portable electronics and electric vehicles are based. A recent report estimates that as early as 2020 electric vehicles (EV) will impose an additional demand of 390 000 tons of copper, 85 000 tons of nickel, and 24 000 tons of cobalt over current consumption. In 2030 the annual requirements are projected to be 4.1 million tons of copper (corresponding to 18 % of the global supply in 2016), 1.1 million tons of nickel (56 % of the global supply in 2016), and 314 000 tons of cobalt (314 % of the 2016 supply). The Nobel prize for chemistry 2019 went to scientist behind the development of the ubiquitous Li-ion battery.
structural and electrochemical characterization of such core-shell catalysts. Finally, we will review their performance in view of the theory, and discuss their practical applications in DMFCs.

References


Challenges in using nanofabricated structures to study living systems.

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It is suggested that the potential of nanotechnology in biomedical field is almost unlimited. This includes nanotechnology based treatment strategies, sensors & devices used in diagnostics, nanotechnology based drug delivery systems, etc. However, little of this potential has been realized so far, even if this area of science and technology have been researched actively for more than 2 decades. Based on our own work and examples from the literature, I will describe challenges in using nanofabricated structures to study living systems. We focus on surfaces decorated with high aspect ratio nanopillars and apply these to influence and study cells [1]. From this work, we have learnt that reproducibility and throughput of the fabrication process are essential for high quality data in hypothesis driven research. In addition, the competence in nanotechnology needs to be combined with modern cell biology techniques, to allow readout connected to molecular scale events in living cells.

3D orientational imaging of bone using X-ray diffraction computed tomography

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Bone is a hierarchical biological tissue, which needs to be imaged in 3D with material and orientational specific contrast to be able to understand the complex nanoscale structure. In X-ray diffraction computed tomography (XRD-CT)[1], contrast is provided by diffraction rather than beam attenuation, enabling mineral specific 3D imaging. Recorded 2D diffraction patterns contain information about the preferred orientation of the scattering crystallites, allowing orientational information to be reconstructed in 2D and 3D[2,3,4] Here, we demonstrate orientational imaging of porcine subchondral bone, elucidating the bone mineral hydroxyapatite orientation in the vicinity of the ossification front. Non-destructive 2D and 3D imaging of hydroxyapatite orientation provides insights into bone mineralization and growth in the region around the epiphyseal growth plate, which is important to understand the pathology of cartilage- and bone-diseases such as osteochondrosis and osteoarthritis.

Figure 1: A) Volume-rendered CT image of the distal femur and patella from a Landrace piglet. Image adapted from [5]. Abbreviation: LFC., lateral femoral condyle. B) 3D cross-sectional view of bone-cartilage sample studied in a XRD-CT experiment, cut from the LFC of a Landrace piglet. The sample is measured in an ethanol-filled polyimide cylinder to prevent drying. Orange: Polyimide cylinder, blue: ethanol, black: rubber plug, grey: bone, red: cartilage. C) Orientation projection map obtained from the bone region of the sample in B using scanning XRD. The color coding corresponds to the preferred orientation of the bone mineral hydroxyapatite c-axis.

References:
Tantlum Pentaoxide waveguide chip developed directly on thin transparent substrate for fluorescence microscopy of biological cells

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Super-resolution optical microscopy (commonly referred to optical nanoscopy) offers unprecedented opportunities, the rapid adoption of it is presently hindered mainly due to low throughput, complex set-up, high cost, and the need for specialized operators. Recently, photonic chip-based optical nanoscopy was realized that circumvents reduce the cost and complexity of present day nanoscopy. In this research work, we have unleash the true impact chip-based nanoscopy by realizing photonic-chip made of high refractive index material (Ta₂O₅) on top of thin and transparent substrate for high-resolution, large f-o-v, aberration-free bioimaging of thick cells. Waveguide chips on 180um thin transparent Silica substrate enable the imaging of biological sample using an inverted optical microscope which was not possible on opaque silicon (Si) substrate.
Nanomedicine and sonopermeation for treatment of cancer and brain disease

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Cancer treatment with chemotherapy is limited by inadequate delivery to the tumor and severe side-effects due to accumulation in healthy tissue. Encapsulation of drugs in nanoparticles can enable a more targeted delivery, improved efficacy and reduced toxicity. However, delivery of nanoparticles is often insufficient due to various biological barriers in the tumor. Ultrasound in combination with microbubbles has emerged as a promising method to enhance delivery of nanomedicines by sonopermeation. The biomechanical effects from the microbubbles enhance permeability of the vascular wall, improving extravasation and distribution of the nanoparticles in the tumor, resulting in enhanced therapeutic efficacy. The same technique can also be used to open the blood-brain barrier in a non-invasive, localized and reversible manner for drug delivery to the brain. In order to take sonopermeation into clinical practice and to optimize such technology for improved cancer therapy, we are now aiming to understand more of the underlying mechanisms.