Poster Abstracts



52nd Biennial Assembly of the **German Colloid Society**

September 30 - October 2, 2024 Zentrum Regenerative Therapien Dresden – CRTD in Dresden, Germany

https://cfaed.tu-dresden.de/kolloidtagung2024







Posters

P1: Nanoparticle formation utilizing simple PAA-Cation coacervates as template

<u>Bastian Rödig</u>¹, Patrick Denk², Phillip Polzer³, Matthias Kellermeier⁵ and Werner Kunz⁴

¹⁻⁴ University of Regensburg, Institute of Physical and Theoretical Chemistry, Regensburg, Germany ⁵ BASF SE, Material Physics, Ludwigshafen, Germany

Coacervates are of two types, simple, meaning they consist only of one type of molecule at certain environmental conditions, and complex, consisting of two polymeric, surface-active compounds. [1] Simple Coacervate formation of polyelectrolytes is known to be dependent on salt concentration, alcohol, or a change in pH or temperature. [2] The liquid-liquid phase separation results in one diluted and one concentrated phase. [3] Scattering experiments and cryo-TEM measurements have shown the hollow, spongelike structure inside the coacervate droplets [4], which can be utilized as template for nanoparticle synthesis.

Coacervates of polyacrylic acid (PAA) with divalent transition-metal cations can be formed in the pH range of 5.5 to 6. Typical coacervate droplet sizes are in the range of 100 to 1000 nm. The best concentration of cation, for the smallest coacervate drop size, was to be found at one-half of the concentration of the concentration of deprotonated carboxylic groups. The addition of sulfide/carbonate, resulting in the formation of insoluble transition-metal salts leads to the precipitation of nanometric-sized particles in the range of 30 to 300 nm. Transition metal oxide nanoparticles can be produced by the calcination of the carbonate samples.



Figure 1. Co₃O₄ particles derived from CoCO₃ after calcination at 500 °C.

[1] Moulik, S.P., Rakshit, A.K., Pan, A., and Naskar, B. (2022) An Overview of Coacervates: The Special Disperse State of Amphiphilic and Polymeric Materials in Solution. *Colloids and Interfaces*, **6** (3).

[2] Veis, A. (2011) A review of the early development of the thermodynamics of the complex coacervation phase separation. *Adv Colloid Interface Sci*, **167** (1–2), 2–11.

[3] Bungenberg De Jong, H.G., and Kruyt, H.R. (1929) Coacervation (partial miscibility in colloid systems). *Proc. K. Ned. Akad. Wet.*, **32**, 849–856.

[4] Fan, Y., and Wang, Y. (2019) Applications of small-angle X-ray scattering/small-angle neutron scattering and cryogenic transmission electron microscopy to understand self-assembly of surfactants. *Curr Opin Colloid Interface Sci*, **42**, 1–16.

P2: Preparation of Polyelectrolyte Complexes and Their Application as Adsorbent Material for Heavy Metal Ions

<u>Rahma Boughanmi</u>, Marina Oelmann, Christine Steinbach, and Simona Schwarz

Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany

Recently, due to industrial growth, there has been an increase in industrial wastewater containing a range of toxic and non-biodegradable heavy metal ions [1]. To solve this problem, we combined two biopolymers: chitosan as a polycation (n+) and pectin as a polyanion (n-), to prepare polyelectrolyte complexes (PECs). We chose biopolymers for their biodegradability, non-toxicity, high availability in nature, and low cost [2][3]. We prepared a series of PECs with varying molar charge ratios (n-/n+). Pectin, varying in concentration, was gradually added to continuously stirred chitosan solutions using a peristaltic pump to form PECs according to the desired molar charge ratio (n-/n+).

The prepared PECs were used for the adsorption of Cd^{2+} , Ni^{2+} , $Fe^{2+/3+}$, Mn^{2+} , and Cu^{2+} from their respective sulfate salt solutions. The adsorption rates are in the order of $Cu^{2+} > Fe^{2+/3+} > Cd^{2+} > Ni^{2+} > Mn^{2+}$.

To characterize the PECs, methods such as dynamic light scattering, scanning electron microscopy, streaming potential, charge density, and Fourier-transform infrared spectroscopy were applied.

[1] K. B. L. Borchert et al., "Removal of Lead, Cadmium, and Aluminum Sulfate from Simulated and Real Water with Native and Oxidized Starches," Polysaccharides, vol. 2, no. 2, pp. 429–453, **2021**, doi: 10.3390/polysaccharides2020027.

[2] R. Boughanmi, C. Steinbach, N. Gerlach, M. Oelmann, C. Beutner, and S. Schwarz, "Ecological Sorption of Iron and Sulfate Ions onto Starch and Chitosan Biopolymer Blend," Polysaccharides, vol. 4, no. 3, pp. 325–342, **2023**, doi: 10.3390/polysaccharides4030019.

[3] R. Boughanmi et al., "Native and Oxidized Starch for Adsorption of Nickel, Iron, and Manganese lons from Water," Polysaccharides, vol. 3, no. 3, pp. 556–573, **2022**, doi: 10.3390/polysaccharides3030033.

P3: Model particles to study interaction of microplastic particles

Kai Gossen, Thomas Witzmann, Andreas Fery and Günter K. Auernhammer

Leibniz-Institut für Polymerforschung Dresden e.V., Institute of Physical Chemistry and Polymer Physics, Dresden, Germany

The increase in the production, processing and improper disposal of plastic has led to global plastic pollution. In the environment micron-sized microplastic particles are covered by an ecocorona that consists of biopolymers from the environment. In order to describe the interaction of microplastics in the environment and the ecocorona has to be considered [1].

In this contribution, we present an approach to model this ecocorona with well-defined polymers, synthetic and derived from natural polymers. Four fluorescent polystyrene multilayer systems, PS(Chitosan/Hyaluronic acid)_{2/4} and PS(Poly(dimethyldiallylammonium chloride) /Polystyrene sulfonate)_{2/4}, were synthesized by layer-by-layer methodology [2]. The surface charge and pH-dependent fluorescence of these systems were examined more closely. It was found that the zeta-potentials of the PS(Chi/HS)_{2/4} systems assume values (-20 mV to -35 mV) that are similar to those of PS-ecocorona (-40 mV to -5 mV) particles.

For the investigation, the pH-dependent fluorescence of particle suspensions and individual particles were measured. Fluorescence spectra of the individual particle systems were recorded using fluorescence spectrometry at pH values between pH 3 and pH 8. A well measurable pH dependence between pH 4.5 and 8 for the PS(Chi/HS)_{2/4} systems and the PS(PDADMAC/PSS)₂ system could be measured. Individual particles of the PS(Chi/HS)₄ system were examined with a confocal microscope for their fluorescence spectra at pH 3 and pH 8. A strong correlation between pH value and fluorescence spectrum was found. In the future, the model systems should provide information on the influence of microplastic on their environment.

[1] Witzmann, Thomas, et al., *Langmuir 38.29* (2022): 8748-8756.

[2] Hartmann, Raimo, et al., Angewandte Chemie International Edition 54.4 (2015): 1365-1368.

[3] This work was supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – project number 391977956 – SFB 1357.

P4: Interpolyelectrolyte complexes of guanidine-based polyelectrolytes

Patricia Montes¹, Tania,¹ Vladimír Raus² and <u>Miroslav Štěpánek²</u>

¹ Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic²

² Institute of Macromolecular Chemistry, Heyrovský sq. 2, 162 00 Prague 6, Czech Republic

It is generally assumed that properties of polyelectrolytes (PEs) in solution, including their electrostatic complexation, are dictated mostly by Coulombic interactions between charges on the PE backbones and on small ions (counterions, co-ions) in the solution. This means that two PEs differing only in charged groups should have the same properties as long as the charges of the groups and their mutual distances remain the same.

A few recent studies stressed the difference in the behavior of interpolyelectrolyte complexes (IPECs) formed by PEs with ammonium groups and by a PE with guanidinium (Gnd+) groups [1,2]. From the structural point of view, Gnd+ is an intriguing chemical species belonging to the class of planar Y-conjugated quasi-aromatic structures [3]. The ion is partly hydrophobic as water molecules can form hydrogen bonds only from the sides of the planar ion. Therefore Gnd+ sticks to hydrophobic surfaces or proteins and forms like-charge contact ion pairs despite the obvious electrostatic repulsion.



Figure 1. Structures of guanidine based polyelectrolytes.

This communication reports a study of guanidine-based PE (GPE) obtained either by postpolymerization modification of polyallylamine (Figure 1a) or by condensation of biguanide derivatives with formaldehyde (Figure 1b). Formation of IPECs of GPE with poly(methacrylic acid)*block*-poly(ethylene oxide) (PMAA-PEO) yielding core-shell nanoparticles with PEO coronas and cores of the GPE/PMAA complexes was studied by light scattering and SANS. Results suggest that in the case of biguanide GPEs, their binding to PMAA is cooperative because of attractive interactions between guanidine moieties.

[1] K. Sadman, Q. Wang, K. R. Shull, ACS Macro Lett. **2019**, *8*, 117.

[2] S. Kim, M. Lee, W.B. Lee, S.-H. Choi, *Macromolecules* 2021, 54, 7572.

[3] M. Vazdar, J. Heyda, P. E. Mason, G. Tesei, C. Allolio, M. Lund, P. Jungwirth, Acc. Chem. Res. 2018, 51, 1455.

P5: Stimuli-responsive self-immolative copolymer surfactants for droplet-based liquid sensing applications

Semira Bener and Lukas Zeininger

Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Am Muehlenberg 1, 14476 Potsdam

Janus emulsions, known for their rich optical properties, are versatile transducers in liquid sensing. Due to their intrinsic thermodynamic out-of-equilibrium nature, gravity-aligned biphasic droplets offer a programmable, chemically triggerable alternative for highly sensitive optical sensing layers. [1] Self-immolative polymers (SIPs) have recently gained attention for their capacity to undergo endto-end depolymerization triggered by an external stimulus [2].

In this study, amphiphilic block copolymers comprising a SIP unit were employed and their triggerable nature is investigated in response to external stimuli such as light, pH, and reactive oxygen species. Sensitization of Janus droplets with degradable surfactants selectively at one of the interfaces of Janus droplets enables to induce substantial changes in droplet shape in response to marginal changes in the droplets' chemical environment. We utilize the gravitational alignment of Janus droplet optical elements to transduce surfactant depolymerization, yielding detectable optical read-outs. This introduces a versatile liquid chemo- and biosensing paradigm for various platforms [3].

[1] L. Zeininger, Analytical and Bioanalytical Chemistry, 2023 (21), 5205.

[2] J. Gong, B Tavsanli, E. R. Gillies, Annual Review of Materials Research, 2024, 54.

[3] The authors acknowledge funding from the the Max-Planck Society and the Emily-Noether program of the German Research Foundation.

P6: Janus Emulsion Droplets Containing Liquid Sensing Platform Achieving Automated Real-Time Morphology Monitoring and Surfactant Characterization

Yuzi Hong, Bradley D. Frank, and Lukas Zeininger

Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Potsdam, Germany

Liquid sensing platforms are essential for environmental protection, product quality assurance, and scientific innovation. Traditional methods for detecting aqueous pollutants, such as HPLC and GC-MS, are often time-consuming, expensive, and confined to laboratories. As an alternative, liquid-liquid chemo- and biosensors offer a promising on-site pre-monitoring solution that mirrors natural recognition environments, complementing existing techniques.

Oil-in-water emulsion droplets are highly effective for environmental monitoring due to their ease of preparation in diverse settings. Their hydrophobic-hydrophilic interfaces facilitate reactions between synthetic surfactants, which are often organo-soluble, and analytes in aqueous environments. These droplets, stabilized by surfactants, exist in dynamic, thermodynamic out-of-equilibrium states, with molecules continually exchanging between the droplets and their surroundings. Interface-selective sensitization allows for programmed up- and down-regulation capabilities. Dynamic interfacial host-guest complexation can trigger morphological changes resembling cell surface environments. As messenger colloids, emulsion droplets visualize and report chemical changes with exceptional sensitivity, detecting levels as low as femtomolar [1].

While previous studies have succeeded in analyzing individual droplet shapes, they have been limited to producing repeatable results and analyze specific signatures of targets [2]. To address this, we developed a rapid analytical tool for multiplexed high-throughput screening using Janus emulsions containing hydrocarbon and fluorocarbon oils, stabilized by both inert and stimuli-responsive surfactants. These Janus droplets have demonstrated significant potential as liquid sensing materials, capable of detecting a range of analytes, including small molecules, metal ions, viruses, and bacteria. We analyzed droplet morphologies using customized side-view microscopy, coupled with a real-time droplet morphology monitoring system, following the addition of analytes. Key parameters such as contact angles, snowman angles, surface area ratios, and volume ratios were extracted and calculated through MATLAB algorithms, generating calibration curves for further analysis. Our results demonstrate that this sensing machine can accurately differentiate between analytes rapidly and efficiently. At the same time, Critical Micelle Concentrations (CMC) of active surfactants in the complex environment can be extracted, giving the sensing system more potential for surfactant characterization,

Automated complex Janus droplet-based sensing devices offer significant advantages, including low cost, short response times, and high accuracy, making them ideal for rapid monitoring of environmental pollution, diagnostic markers, and water quality.

[1] Zeininger, L., Responsive Janus droplets as modular sensory layers for the optical detection of bacteria. Anal Bioanal Chem, 2023. 415(21): p. 5205-5219.

[2] Barua, B., et al., Multiplexed and continuous microfluidic sensors using dynamic complex droplets. Soft Matter, 2023. 19(10): p. 1930-1940.

P7: Electrochemical Modulation of Redox-Responsive Copolymer Systems

Vincent Schildknecht¹, Quirin Prasser¹, Richard Neubert¹ and Felix Plamper¹

¹Institute of Physical Chemistry, TU Bergakademie Freiberg, 09599 Freiberg, Germany

Beyond classical stimuli like temperature, we introduce an electrochemical approach to change the aggregation state of block copolymers [1]. Aqueous solutions of the nonionic-cationic block copolymer poly(ethylene oxide)₁₁₄-b-poly{[2-(methacryloyloxy)ethyl]diisopropylmethylammonium chloride}₁₇₁ (i.e., PEO₁₁₄.b-PDPAEMA₁₇₁ with a quaternized poly(diisopropylaminoethyl methacrylate) block) [2] were investigated by dynamic light scattering and small angle x-ray scattering, analysing the micellization of PEO₁₁₄-b-qPDPAEMA₁₇₁ in the aqueous medium. Potassium hexacyanoferrates (HCFs) were used as electroactive complexants for the charged block, which convert the bishydrophilic copolymer into amphiphilic species. Ferricyanides ([Fe(CN)₆]³⁻) act as stronger complexants than ferrocyanides ([Fe(CN)₆]⁴⁻), leading to an insoluble qPDPAEMA block in the presence of ferricyanides. In the next step, an electrochemical switching of the micelles was investigated. Hereby, the open-circuit potential (OCP) was changed by electrolysis to vary the ratio between ferricyanides and ferrocyanides in the aqueous solution to induce micelle formation or deformation. Besides the electrochemical oxidation/reduction as a soft trigger, also experiments with chemical oxidation/reduction as a hard trigger were conducted. These two different pathways lead to different (non-equilibrium) aggregate sizes, but can be reversed to the same unimolecular state of the polymer.

[1] Felix A. Plamper et al., *Macromolecules* **2009**, 42, 19, 7254–7257.
[2] Quirin Prasser et al., *Langmuir* **2021**, 37, 3, 1073–1081.

P8: Pressure-induced phase transition in polymer brushes

<u>Leonardo Chiappisi</u>¹, Samantha Micciulla¹, Philipp Gutfreund¹, Matej Kanduč²

¹ Institut Max von Laue - Paul Langevin, 71 avenue des Martyrs 38042 Grenoble Cedex 9, France, ² Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

Polymers are key elements in modern material science, and, since the first polymer synthesis in 1907, tremendous progress in polymer chemistry were made. Today, an endless assortment of polymers – whose properties are adapted to specific needs – is available. In many cases, a thin polymer film, the coating, is sufficient to impart desired properties to the material.

One of the most employed stimuli to tune phase transition in polymer coatings is temperature. Since the first reports of the thermo-responsive behaviour of poly(N-isopropylacrylamide) (PNIPAM) in an aqueous environment in the late sixties, PNIPAM has become the most studied model for non-ionic polymer systems. However, temperature is not the only physical parameter to tune the phase behaviour of polymeric systems. Pressure can be similarly used to control the phase behaviour of polymer solutions and thin films.

Herein, we provide an extensive overview of the phase behaviour of end-grafted PNIPAM brushes as a function of pressure and temperature. The phase behaviour, extracted from the neutron reflectometry curves, is compared with the phase behaviour of semi-dilute solutions. Further, we show that the coexistence line as a function of pressure and temperature can be predicted assuming a two-state model – swollen and collapsed – knowing the different derivatives of the free energy of collapse as a function of pressure and temperature. These quantities can be precisely accessed using calorimetric and densitometric measurements.

The results evidenced that the pressure-temperature phase behaviour of polymer solutions and coatings can be predicted from simple, laboratory-scale experiments, paving the way for the rational design of smart coatings with pressure and thermo-responsive behaviour.

[1] Micciulla, Gutfreund, Kanduc, Chiappisi, Macromolecules 2023, 56, 3, 1177–1188

P9: Structure formation in polymer brush/gold nanoparticle composite materials

Elias Hallenbach, Philipp Ritzert, and Regine von Klitzing

Technical University of Darmstadt, Department of Physics, Soft Matter at Interfaces, Darmstadt, Germany

Metal/polymer nanocomposites are versatile hybrid materials and find use in many fields such as photonics, biomedical engineering and catalysis. A promising realization of this type of hybrid material is the controlled self-assembly of gold nanoparticles inside a polymer brush, which induces color changes upon exposure to environmental changes enabling sensor applications. Therefore, we aim to gain insights into and control over the manufacturing process leading to more elaborate nanocomposite fabrication.

The polymer brushes serve as a matrix for the immobilization of gold nanoparticles (AuNPs). Particle uptake into the brush matrix is affected by parameters such as brush thickness, particle size and the brush grafting density [1,2]. Polymer brushes are synthesized by Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) directly from a silicon substrate. As has been shown earlier by our group, the grafting density has a strong impact on the distribution of nanoparticles [2]. Therefore, the focus of this work is to evaluate the grafting densities of synthesized thermoresponsive brushes, such as Poly(N-isopropylacrylamide) (PNIPAM) or Poly(oligo(ethyleneglycol)methacrylate) (POEGMA) brushes. Two different methods, namely surface cleavage of polymers and single-molecule force spectroscopy (SMFS) by AFM, are used to characterize the molecular weight distribution (MWD) of the polymer chains.

Surface cleavage of the grafted polymers is achieved by incubation of the polymer brush in a solution of tetrabutylammonium fluoride (TBAF) in THF [3]. Subsequently, the polymers degraft into solution and can be analyzed by size exclusion chromatography. For comparison, SMFS is used. In a typical SMFS experiment, the AFM tip approaches the surface, indenting the polymer brush. Then, the tip is withdrawn from the surface, and the polymer chains adhered to the tip experience a gradually increasing force. The polymer chains are stretched until they subsequently detach ("pull-off event"). The acting force on the cantilever can then be fitted by the worm-like chain model, yielding the contour length and a molecular weight. From the MWD, grafting densities are calculated.[4]

[1] S. Christau et al., Polymers 2014, 6 (7), 1877-1896.

[2] S. Christau et al., *Langmuir* **2014**, 30 (43), 13033-13041.

[3] R. R. Patil et al., *Langmuir* **2015**, 31 (8), 2372-2381.

[4] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG) through GRK2516, Grant Number 405552959.

P10: Interactions of colloidal materials with wrinkle-structured surfaces

Fabian Kopsch¹, Andre Knapp¹, Ralf Helbig², Mirko Nitschke², Anett Müller¹ and Andreas Fery^{1,3}

¹ Institute of Physical Chemistry and Polymer Physics, Leibniz Institute of Polymer Research Dresden e. V., Hohe Str. 6, 01069 Dresden, Germany

² Max Bergmann Center of Biomaterials, Leibniz Institute of Polymer Research Dresden e. V., Hohe Str. 6, 01069 Dresden, Germany

³ Chair for Physical Chemistry of Polymeric Materials, Technical University Dresden, Mommsenstr. 4, 01062 Dresden, Germany

Colloidal materials concepts based on particulate building blocks allow the integration as a sensor or optoelectronic components for biotechnology, biomedicine and environmental applications. Structured polymeric surfaces using controlled mechanical instabilities, called wrinkling, provide template-assisted colloidal self-assembly on large areas based on the effect of arranged colloids following the given wrinkle structure.[1,2] The interactions of colloidal materials with wrinklestructured surfaces are of particular interest concerning the adhesion properties between the wrinkled structure and the colloids. Typical wrinkle features, such as the wavelength, amplitude and wrinkle shape, result in contact with different-sized colloids to localized, the wrinkle structure following contact zones, with changed adhesion properties across the surface.[3] Theoretical investigations allow the systematic characterization of different measured wrinkled surfaces based on the contact match or mismatch of selected silica diameters with the wrinkle-formed cavities (figure 1). Analyzing the localized wrinkle curvature and comparing it with the sphere curvature allows the detection of areas of contact and non-contact along the wrinkle shape. Summarizing these contact points of a wrinkled surface provides different-sized line-like contact areas and the real contact area. AFM measurements, using colloidal probe, provide adhesion maps that show the influence of the wrinkle structure. Rigid silica spheres, synthesized with Stöber process, are used at different sizes to validate different average wrinkle-induced adhesion values.



Figure 1: Schematic illustration of the theoretical consideration of the contact area between a colloid and a wrinkle-structured surface (top) and the experimental proof of concept using of a colloid-probe AFM measurement (bottom).

[1] Y. Yu et al., *Langmuir* **2019**, 35 (26), 8629-8645.

- [2] M. Müller et al., *Nanoscale* **2019**, 4 (7), 2491-2499.
- [3] C. Spengler et al., Soft Matter 2024, 20 (3), 484-494.

P11: Reorientation of surface bound nanocrystals of rhodium coordination polymers in the light of GISAXS and GIWAXS

<u>Richard Neubert</u>¹, Daniel Steinbach², Florian Mertens¹ and Felix Plamper¹

¹ Institute of Physical Chemistry, TU Bergakademie Freiberg, Freiberg, Germany ² Hydrogenious LOHC Technologies GmbH, Oberaurach, Germany

Understanding crystal growth and the resulting crystal morphology is crucial for developing functional surfaces, such as those used in catalysis and sensing. [1] Rhodium coordination polymers exhibit promising properties in these fields. These polymers can be grown stepwise on a selfassembled monolayer at a gold surface using a dip-coating procedure. [2] The common structural analysis regarding the morphology of these polymers were complemented by GIWAXS and GISAXS. GIWAXS revealed their preferred orientation. It turned out that the automated dipping procedure does not lead to a strong alignment of crystallites along the dipping direction for the pyrazine-based [Rh(ac)₄(pyz)]_n polymers. However, these nanocrystals exhibit a preferential orientation with respect to the substrate normal direction. The crystallographic direction and the degree of the alignment depend on the number of deposition cycles. In the early phases of the deposition process, predominantly "lying" crystals were detected. With increasing number of the deposition cycles, the fraction of "standing" crystals became dominant. These crystals are oriented with their {010} directions perpendicular to the surface of the substrate. Still, "lying" and some tilted crystals were detected additionally. The study gives a deeper structural understanding of crystallite assemblies and suggests an evolvement of more anisotropic orientations of the crystallites with increasing deposition cycles (leading to the prevalence of crystals having the preferred {010} orientation with respect to the surface normal direction). [3]



Figure 1. left: GIWAXS pattern at 0.23° inclination angle (sample after 100 dipping cycles | right: SEM image of crystals of [Rh(ac)₄(pyz)]_n after 100 dipping cycles.

[1] Xuanjun. Zhang et al., *Coordination Chemistry Reviews* **2015**, 284, 206–235.

[2] Daniel Steinbach et al., J. Phys. Chem. C 2022, 126, 16421.

[3] Daniel Steinbach and Richard Neubert et al., CrystEngComm 2023, 25, 4568-4581.

[4] The authors acknowledge funding from the DFG (e.g. PL 571/5-1). F.A.P. and the public funds from State of Saxony for the GISAXS/GIWAXS instrument "SAXsONIA".

P12: Linear Assembly of Gold Nanoparticles with Improved Refractive Index Sensitivity for Biosensing Applications

<u>Taufhik Hossain Tonmoy</u>¹, Marisa Hoffmann², Sezer Seçkin², Isli Çela¹, Gyusang Yi², Christian Roßner², Tobias König², Andreas Fery², and Larysa Baraban¹

¹Institute of Radiopharmaceutical Cancer Research, Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany ²Leibniz Institut für Dehmarforschung Dreader o. V. DE 120411, 01005 Dreader, Correspond

²Leibniz-Institut für Polymerforschung Dresden e. V., PF 120411, 01005 Dresden, Germany

The unique optical features of gold nanoparticles (AuNPs), such as localized surface plasmon resonance (LSPR), have attracted substantial attention in biosensing applications. In closely spaced nanoparticle assemblies, the electromagnetic fields of neighboring particles interact strongly, leading to significant near-field coupling which influence the LSPR signature. Therefore the collective plasmonic characteristics in ordered arrangements of AuNPs are more sensitive to variations in the local refractive index (RI) than in individual particles. Such local RI modifications also take place when biomolecules bind to the AuNP surfaces. Therefore, by increasing RI sensitivity, AuNP assemblies have the potential to detect biomolecules of interest with much higher accuracy.

In this study, a comprehensive investigation is presented comparing the plasmonic spectra of linear periodic assemblies of AuNPs against individual particles (50 nm diameter) for biosensing applications. Simulations using the Finite-Difference Time-Domain (FTDT) method suggested that longitudinal coupling along the AuNP lines were more sensitive to RI changes than transversal coupling. Practical experiments supported the simulation results through an exemplary attachment of the biomolecules to AuNP assemblies. A pro-inflammatory cytokine- Tumor Necrosis Factor Alpha (TNF- α), which is an important marker in cancer research influencing various aspects of tumorigenesis, tumor progression, and therapeutic response was chosen for the biofunctionalization process. Polydimethylsiloxane (PDMS) templates were used to confine large arrays (cm²) of amine-functionalized AuNPs into linear assemblies on glass substrates. RI sensitivity of the AuNP assemblies during various steps of the functionalization process were investigated using UV-Vis spectrometry. Promising experimental results exhibited enhanced RI sensitivity of the linear assemblies as compared to individual or randomly ordered AuNPs, offering a favorable approach towards plasmonic biosensing applications.

[1] The authors acknowledge the financial support of the project ImmunoChip which has received funding from the European Research Council (ERC) under the European Union's Horizon Europe research and innovation programme grant agreement No 101045415. Furthermore, they thank DFG for the financial support in the project GRK2767 'Supracolloidal Structures'.

P13: Antibacterial coatings based on polyelectrolytes and bacteriophages

L. Wirth^{1,2}, M. Müller^{1,2}, B. Urban¹, G. M. Mannala³, V. Alt³

¹Leibniz-Institut für Polymerforschung Dresden e.V., Dpt. Func. Coll. Materials, Dresden, Germany ²Technische Universität Dresden, Faculty of Chemistry and Food Chemistry, Dresden, Germany ³Universitätsklinikum Regensburg, Dpt. Trauma Surgery, Regensburg, Germany

Based on previous work focusing on low molecular bioactive compounds, [1, 2, 3] soft coatings based on polyelectrolytes (PEL) were prepared on relevant surgical biomaterials and loaded with specific bacteriophages (PHAG). This approach is intended as a novel antibacterial coating concept to replace low-molecular antibiotics and solve the problem of multidrug resistance in connection with implant-associated infections. [4]

PEL coatings can be built up on planar model substrates, agar plates or surgical Kirschner wires (Kwires). The alternating deposition of polycations and polyanions from solution forms PEL multilayers (PEM), as described by Decher. [5] PHAG can be either preloaded or postloaded into PEM coatings. Synthetic and biorelated PEL and both *Staphylococcus aureus* (S.a.) bacteria and S.a. PHAG were utilized. Analytical methods include FTIR, UV-Vis, DLS and AFM.

Defined PEM coatings were prepared from poly(ethyleneimine) (PEI) and lactic acid grafted hyaluronic acid (DAC[®]), with the outermost layer consisting of either PEI or DAC[®], so that the surface charge is either cationic or anionic. S.a. PHAG showed higher binding at PEI compared to DAC[®] terminated PEM. PEM/PHAG coatings at agar plates showed plaque formation towards S.a. bacterial cultures, which was dependent on both the final layer and the corresponding number of bound PHAG. K-wires with respective PEM/PHAG coatings were implanted into *Galleria mellonella* larvae and infected by S.a. bacteria. Generally, K-wires with PEM/PHAG coatings showed higher larvae survival rates compared to blank K-wire controls. Both outermost layer nature and bound PHAG amount affected larvae survival rate, which supports the agar experiments.

PHAG/PEL functionalization of bone substitute materials based on aqueous systems is a sustainable technology for combating implant-associated infections.



Figure 1. Polyelectrolyte multilayer deposited on a substrate. Bacteriophages bound to the outermost layer, can infect approaching bacteria.

- [1] M.Müller et al., *Langmuir* **2018**, 34 (28), 8129-8144.
- [2] M. Müller et al., Colloid and Polymer Science 2017, 295, 1187-1199.
- [3] D. Vehlow et al., *Pharmaceutics* **2020**, 12 (9), 799.
- [4] V. Alt et al., *Injury* **2017**, 48 (3), 599-607.
- [5] G. Decher et al., Thin Solid Films 1992, 210-211 (2), 831-835.
- [6] M. Müller et al., ACS Applied Polymer Materials **2021**, 3 (12), 6230-6237.

P14: Bio-Inspired Design of Tunable Hybrid Colloids with Star and Surfactant-like Architectures

<u>Alan Francisco¹</u>, Anna Kharlamova², Eric Grelet², Jérôme Crassous¹

¹Institute of Physical Chemistry, RWTH Aachen University, 52074 Aachen, Germany. ²Centre de Recherche Paul Pascal, Université de Bordeaux, 33600 Pessac, France

This study explores the design of bio-inspired hybrid colloids mimicking star-shaped and surfactantlike architectures. We achieve this by conjugating thermos-responsive poly(N-isopropylacrylamide) (PNIPAM) microgels with various functional groups on their surface with bioengineered filamentous viruses (fd viruses).

This approach offers remarkable flexibility, enabling targeted coupling with gold nanoparticles (AuNPs) and the fd virus tip [1,2], leading to well-defined hybrid structures. We investigate how microgel properties, including the type of incorporated functional groups, affect the conjugation efficiency with AuNPs. AuNPs serve as bridging elements due to their affinity for both the functional groups on the microgel and the modified virus tip, enabling covalent linkage. The conjugation yield and temperature-dependent behaviour of the assemblies will be evaluated using multiple microscopy and light scattering techniques.



Figure1. Bio-conjugated PNIPAM microgel with fd viruses trough Au-S bond.

[1] Zavala-Martínez, A. B., & Grelet, E. ACS nano , 18(1), 281-287(2023). [2] Alexis de la Cotte, Cheng Wu & Eric Grelet, ACS nano, 11, 10616-10622 (2017).

P15: Water-based biomedically relevant polyelectrolyte coatings studied by in-situ ATR-FTIR spectroscopy

<u>M. Müller^{1,2}</u>, L. Wirth^{1,2}, B. Urban¹, S. Schwarz¹, V. Alt³

¹Leibniz-Institut für Polymerforschung Dresden e.V., Dpt. Func. Coll. Materials, Dresden, Germany ²Technische Universität Dresden, Faculty of Chemistry and Food Chemistry, Dresden, Germany ³Universitätsklinikum Regensburg, Dpt. Trauma Surgery, Regensburg, Germany

Three water-based deposition concepts of polyelectrolyte (PEL) coatings at planar substrates (Fig. 1) for biomedical applications mainly studied by in-situ-ATR-FTIR spectroscopy are reviewed [1]. At first, adsorption from cationic PEL solutions in dependence of charge density q_m is shown [1]. Epoxy-propyl-trimethylammonium (EPTA) modified amylose is treated. The adsorbed polycation amount decreased with increasing q_m according to a known relation [2].

Secondly, sequential adsorption from cationic and anionic PEL solutions in dependence of salt concentration is dealt with. Poly(L-lysine) (PLL) and sulfated cellulose (CS) were used. Expo-nentially increasing adsorbed amounts with adsorption step and part pull out of the outermost PEL layer by the actual PEL in solution was found with a maximum at medium salt concentration [3]. Thirdly, deposition of preformed colloidal PEL complex (PEC) coacervates is outlined. Solutions of ethylenediamine modified cellulose (EDAC) and CS were mixed under variation of the molar mixing ratio n-/n+ of anionic and cationic repeating units and the turbid coacervate phase casted and dried. With increasing deviation from n-/n+ = 1.0 (charge compensation) the respective excess PEL could be increasingly rinsed out by water from the PEC coating [1].

All three water- and adsorption-based PEL coating types featured high surface integrity after water rinsing, if interfacial PEL related excess charge is kept low. For non-binary PEL coatings this can be achieved by minimizing linear charge density, while for binary PEL coatings (PEM, PEC) by maximizing opposite charge compensation close to 1:1 stoichiometry.

As biomedical applications, PEM coatings terminated by cationic or anionic PEL featured attraction or repulsion of respective basic or acidic proteins [4] as well as bacteriophages addressing implant associated infections [5]. PEC coatings slightly excessed by cationic or anionic PEL showed sustainable delivery of low molecular drugs and protein growth factors to address local bone healing [6]. Actual funding of antibacterial PEL coatings is acknowledged [7].



Figure 1. PEL deposition concepts (a; from [1])

- [1] M.M. et al. Langmuir **2018**, 34 (28), 8129.
- [2] N.G. Hoogeveen et al. J. Coll. Interf. Sci. 1996, 182, 133.
- [3] M.M. et al. Molecules **2020**, 25, 2336.
- [4] M.M. et al. Biomacromolecules **2006**, 7, 1285.
- [5] M.M. et al. ACS Appl. Polym. Mat. **2021**, 3, 12, 6230.
- [6] M.M. et al. Curr. Pharm. Des. **2018**, 24(13), 1341.
- [7] Acknowledgements: This work is partly sponsored by DFG (PN 491517909).

P16: Zwitterionic polymer and particle based surfaces for antifouling application

<u>Ola Diring^{1,2}</u>, Jens Friedrichs¹, Carsten Werner^{1,2} and Alla Synytska^{1,3}

¹ Leibniz Institute of Polymer Research Dresden e. V., Germany

² Technical University Dresden, 01062 Dresden, Germany

³ University of Bayreuth, 95447 Bayreuth, Germany

Besides gold standard-polymer Poly(ethylene glycol) with well examined anti-biofouling properties, both polyacrylamide-derivates and zwitterionic polymers show high potential for antibacterial applications [1]. In aqueous solutions zwitterions demonstrate a higher swelling degree with increasing salt concentration and thereby offer a further antifouling mechanism compared to temperature responsive polymers, such as Poly(N-isopropylacrylamide) (PNIPAM) [2]. Amongst zwitterionic polymers with antifouling properties, Poly(sulfobetaine), grafted by atom transfer radical polymerization (ATRP), shows promising protein- and bacteria-repelling properties [2,3]. The combination of polymers with different antifouling mechanisms, for example depending on temperature and ionic strength, promises a higher antifouling effect in challenging biological environments. A coating based on core shell particles with an antifouling polymer shell provides a easy solution for industrial applications.

The present work investigates the influence of the heterogeneity of the polymer shell by comparing the antibacterial properties of mixed fully each PNIPAM and Poly(sulfobetaine methacrylate) (PSBMA) covered core-shell particles and their corresponding inhomogeneous Janus type.



Figure 1. Schematic illustration of a) mixed and b) Janaus core-shell particle based coatings and their antibacterial properties.

[1] Hong Chen et al., *Langmuir* **2016**, 32 (14), 3315-3330.

- [2] Fabian Kopsch, et al., Macromol. Chem. Phys. 2023, 224, 2200454.
- [3] Zheng Zhang et al., J. Phys. Chem. B 2006, 110 (22), 10799-10804.

The authors acknowledge funding from the German Research Foundation (DFG project Number Grant SY 125/11-1).

P17: DNA mold-based fabrication of silver nanostructures

Christoph Hadlich, Ulrich Kemper and Ralf Seidel

Peter-Debye-Institut für Physik der weichen Materie/Universität Leipzig, Leipzig, Germany

A challenge for the bottom-up fabrication of nanoelectronic devices is the accurate spatially resolved material deposition on the nanometer scale. In the field of biomolecular materials, DNA nanotechnology overcomes this challenge by being highly precise at building DNA structures of nearly any desired form. To exploit this concept for other materials, we recently developed a DNA origami mold-based nanoparticle synthesis scheme that allows the fabrication of metallic

nanoparticles with DNA-programmable shape. Particularly, we demonstrated the fabrication of gold nanostructures with aspect ratios of up to 7 grown from single seeds [1] as well as the fabrication of rolling-pin-, dumbbell-, loop- and T-shaped gold nanoparticles [2].

Now, we expanded the mold-based fabrication method to silver, pictured in Figure 1. First, gold nanoparticles were introduced inside the mold cavity to work as nucleation centers for a subsequent silver growth. Since silver ions can bind with the DNA bases causing unwanted nucleation spots, we carefully tuned the reaction conditions to favor silver growth on the gold nanoparticles. As a result, we have established new assembly and growth protocols that take place under complete exclusion of light below 600 nm. The resulting silver wires are grown exclusively inside the DNA molds and are up to 700 nm long. By using silver, we can create nanowires with better conducting properties and meet more diverse requirements in nanoelectronics, for example altering the Schottky barrier. Additionally, combining different materials in one DNA superstructure will allow us in the future to create multi-metallic structures with unique electrical properties [3].



Figure 1. Scheme of the seeded growth protocol: presynthesized gold nanoparticles are functionalized with ssDNA oligos and loaded inside of DNA origami molds. Due to specific interfaces the molds can form superstructures of controlled lengths. A subsequent growth step allows for the synthesis of silver metal nanostructures of defined shapes.

[1] Jingjing Ye, Richard Weichelt, Ulrich Kemper, Vaibhav Gupta, Tobias A. F. König, Alexander Eychmüller, and Ralf Seidel, *Small*, **2020**, 16(39), 2003662.

[2] Jingjing Ye, Olha Aftenieva, Türkan Bayrak, Archa Jain, Tobias A. F. König, Artur Erbe, and Ralf Seidel, *Advanced Materials*, **2021**, 33 (29), 2100381.

[3] The authors acknowledge funding from GRK 2767 (Project No. 451785257) by the Deutsche Forschungsgemeinschaft.

P18: Plasmon-induced RAFT polymerization

<u>Anahita Heraji Esfahani¹</u>, Ilko Bald¹ and Matthias Hartlieb^{1,2}

¹ University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Straße 24-25, 14476, Potsdam, Germany ² Fraunhofer Institute for Applied Polymer Research (IAP), Geiselbergstraße 69, 14476, Potsdam, Germany

Plasmonic nanoparticles (NP) exhibit distinct optical properties due to localized surface plasmon resonance (LSPR), which can be tuned through alterations in particle shape and size. They have been exploited for various applications, particularly due to their ability to exhibit intense electric fields, known as hot spots, in assemblies [1].

Surface modification of these NPs with macromolecules influences their interaction with each other and their surroundings and enhances colloidal stability. Specifically, when this modification involves the precise placement of polymers, it further tunes their optical characteristics [2].

To synthesize defined polymers with predictable chain lengths and narrow dispersity, reversible addition–fragmentation chain transfer (RAFT) polymerization is a valuable tool. Moreover, to locally direct and confine polymerization activity, photopolymerization can be employed [3].

Among various photo-controlled RAFT polymerization methods, photoinduced electron/energy transfer (PET)-RAFT polymerization has gained attention. Here, light excites a photocatalyst (PC), which interacts with the chain transfer agent (CTA) that controls the polymerization process. Through electron or energy transfer, the CTA is fragmented and produces a propagating radical. The back reaction deactivates growing chains resulting in an overall low radical concentration and respective diminished termination. However, while the PET-RAFT process is well established and investigated for small molecule PC, there are limited examples for plasmonically activated polymerizations, and the mechanism is not fully understood. In particular, whether the excited state PC interacts with the CTA through electron transfer or energy transfer remains unclear [3,4].

This work presents the first steps on the way to understand this mechanism. We investigated PET-RAFT polymerization using citrate stabilized Au NP as PC and explored various CTAs to elucidate the underlying mechanisms of plasmonically triggered, catalyzed, and directed RAFT polymerization on NPs. Future research will use the insight gained from this study to design localized structures on plasmonic NPs [5].

- [1] C. Hamon, L. M. Liz-Marzán, Chemistry A European Journal 2015, 21 (28), 9956–9963.
- [2] X. Jing, Y. Zhang, M. Li, X. Zuo, C. Fan, J. Zheng, *Mater Horiz* **2023**, 10 (4), 1185–1209.

[3] Y. Lee, C. Boyer, M. S. Kwon, *Chem Soc Rev* 2023, 52 (9), 3035–3097.

[4] J. Jiang, G. Ye, F. Lorandi, Z. Liu, Y. Liu, T. Hu, J. Chen, Y. Lu, K. Matyjaszewski, *Angewandte Chemie* **2019**, 131 (35), 12224–12229.

[5] Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – CRC/SFB 1636 –Project ID 510943930: Project No. B03

P19: Zig-zag assembly of nanoparticles based on 2D wrinkles

<u>Ziwen Yu</u>¹, Anik Kumar Ghosh², Ningwei Sun³, Sven Wießner^{1,4}, Ziwei Zhou² and Andreas Fery^{2,5,6}

¹ Technische Universität Dresden, Institute of Materials Science, Dresden, Germany

² Leibniz-Institut für Polymerforschung Dresden e.V., Institute of Physical Chemistry and Polymer Physics, Dresden, Germany

³ Leibniz-Institut für Polymerforschung Dresden e.V., Institute of Macromolecular Chemistry, Dresden, Germany

⁴ Leibniz-Institut für Polymerforschung Dresden e.V., Institute of Polymer Materials, Dresden, Germany

⁵ Technische Universität Dresden, Cluster of Excellence Centre for Advancing Electronics Dresden(cfaed), Dresden, Germany

⁶ Technische Universität Dresden, Department of Physical Chemistry of Polymeric Materials, Dresden, Germany

Template-assisted colloidal self-assembly has attracted much attention due to its flexibility and versatility.[1] By controlling the shape of the template, one can easily get designed nanoparticle assembly. The difficulty lies in how to prepare the templates in large area with low cost.[2] Recently, 1D nano-wrinkle structures have been well used for linear assemblies of single-chain or multi-chain nanoparticles, which are rich of interparticle nanogaps to enable efficient plasmonic coupling. Furthermore, to integrate sharp tips into the conventional linear assembly, in this paper, we developed the 2D zig-zag wrinkles, with which the nanoparticles can be successfully assembled into zig-zag chains. Through the microspectral measurements and lumerical simulations, we saw that the sharp-tip excited stronger plasmonic coupling compared with the linear part, which could be advantageous for sensing applications.



Figure 1. Sketch of assembly of 1D and 2D wrinkles.

[1] A.M. Steiner, M. Mayer, M.Seuss, S. Nikolov, K.D. Harris, A. Alexeev, C. Kuttner, T.A.F. König, and A. Fery, ACS Nano 2017, 11, 8871-8880.

[2] L. Pellegrino, S. Khodaparast and J.T. Cabral, Soft Matter, 2020, 16, 595-603.

[3] The author acknowledges support from Prof. Dr. Andreas Fery and Prof. Dr. Ing. Sven Wießner. Dr. Anik Kumar Ghosh is thanked for contribution Animations to this work. Dr. Ningwei Sun is thanked for contribution Gold Nanoparticles to this work.

P20: Conductive microtubule-templated gold nanowires

<u>Brenda Palestina-Romero</u>¹, Borja Rodriguez-Barea², Foram M. Joshi¹, Raghda Abdelfattah², Artur Erbe², Stefan Diez^{1,3,4}

¹ B CUBE - Center for Molecular Bioengineering, TUD Dresden University of Technology, Germany
 ² Institute of Ion Beam Physics und Material Science, Helmholtz-Zentrum Dresden-Rossendorf, Germany
 ³ Max Planck Institute for Molecular Cell Biology and Genetics, 01307 Dresden, Germany
 ⁴ Cluster of Excellence Physics of Life, TUD Dresden University of Technology, 01062 Dresden, Germany

Metallic nanowires (NWs) are considered good connectors in electronic circuits due to their lateral electron confinement [1]. Various methods exist for synthesizing NWs, and bio-templating has emerged as a promising approach to grow nanowires under mild conditions, such as low temperature, neutral pH, and without the need for clean room facilities. Specifically, gold nanowires (AuNWs) have been successfully synthesized using high aspect ratio templates like microtubules [2]. Microtubules (MTs) are cytoskeletal filaments composed of self-assembled beta- and alpha-tubulin proteins, which can be easily polymerized in vitro from porcine brain tubulin. The resulting structure is a hollow cylinder with outer and inner diameters of 25 nm and 15 nm, respectively, and lengths extending up to tens of microns. Their geometry makes MTs ideal templates for casting gold nanowires. The process begins with the attachment of functionalized gold nanoparticles (1.4 nm in diameter) to the MT lumen [2]. These nanoparticles act as seeds and grow upon the addition of a gold precursor (chloroauric acid) and a reducing agent (hydroxylamine), ultimately forming AuNWs shaped by the MT lumen [2]. Using this method, smooth-appearing AuNWs with lengths of a few hundred nanometers were achieved [2]. However, to accurately characterize their electrical properties, the length of the AuNWs needs to exceed 500 nm.

In this study, we report the electrical characterization of AuNWs templated by MTs. We optimized the synthesis process to produce longer nanowires, reaching lengths of up to 900 nm, by fine-tuning the concentrations of the gold precursor and the reducing agent relative to the seed concentration. Subsequently, we characterized the electrical properties of the AuNWs by measuring the changes in electric current in response to varying applied voltages at both room and low temperatures. At room temperature, we observed both linear and non-linear behaviors in the I-V curves, along with an increase in conductivity over multiple measurements, likely due to sintering. Low-temperature measurements provided further insights into the electronic transport properties of these AuNWs. Our results indicate that MT-templated AuNWs have diverse electrical properties, potentially attributed to grain boundaries and the broad distribution of morphologies in each sample. In future studies, we will reduce the length distributions of MT-templated AuNWs include (i) connectors for DNA-origami electronic devices and (ii) novel biosensors capitalizing on their high surface-to-volume ratio.

[1] D. W. Hobson, in Comprehensive Biotechnology (Second Edition), M. Moo-Young, Ed., *Burlington: Academic Press*, 2011, pp. 683–697.

[2] F. M. Joshi, G. A. Viar, G. Pigino, H. Drechsler, and S. Diez, *Nano Lett.*, vol. 22, no. 9, pp. 3659–3667. The authors acknowledge funding from the DFG (GRK 2767 – Project No. 451785257, N.M.)

P21: Self-assembly of tetravalent patchy particles into cubic tetrastack crystals

Łukasz Baran¹, <u>Dariusz Tarasewicz¹</u>, Daniel M. Kamiński², Andrzej Patrykiejew¹, Wojciech Rżysko¹.

¹ Department of Theoretical Chemistry, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Sklodowska University in Lublin.

² Department of Organic and Crystalochemistry, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Sklodowska University in Lublin.

Achieving the formation of target open crystalline lattices from colloidal particles is of paramount importance for their potential applications in photonics. Examples of such desired structures are the diamond, tetrastack, and pyrochlore lattices. Since the spherical colloidal particles usually crystallize into simple face-centered cubic (fcc) and hexagonal close-packed (hcp) lattices [1], a lot of research has focused on the self-assembly of anisotropic colloidal particles. One class of such particles are so-called patchy particles with chemically or physically modified regions on their surfaces. Those particles can form a variety of complex structures and can be used as building blocks for new functional materials [2].

Here we demonstrate that the self-assembly of tetravalent model patchy particles leads to the selective formation of cubic tetrastack (CT) structures in the bulk as well as in the external field. However, the formation of well-ordered crystals in the bulk is hampered by the presence of numerous defects and grain boundaries between nucleating crystals. On the other hand, when "the disordered fluid" of patchy particles is placed in contact with the solid substrate, it forms quite well-ordered crystals via a sequence of layering transitions that occur upon a decrease in temperature [3].



Figure 1: Snapshot demonstrating cubic tetrastack (left) and local environments of the particles with 10 (green) and 12 (red) nearest neighbors (right).

[1] I. Sanchez-Burgos, E.Snaz, C. Vega, and J. R. Espionsa, *Physical Chemistry Chemical Physics* **2021**, 23, 19611-19626.

[2] S. C. Glotzer, and M. J. Solomon, Nature Materials 2007, 6, 557-562.

[3] Ł. Baran, D. Tarasewicz, D. M. Kamiński, A. Patrykiejew, W. Rżysko, *The Jurnal of Chemical Physics* **2024**, 160, 194707.

P22: Highly efficient and reversible chirality transfer between protein and achiral plasmonic assemblies

<u>Ziwei Zhou</u>¹, Ningwei Sun², Nina Tverdokhleb^{3,4}, Franziska Lissel^{2,5}, Olga Guskova^{1,6}, Tobias A. F. König^{1,7}, Nicholas A. Kotov^{8,9,10} and Andreas Fery^{2,5,6}

¹ Leibniz-Institut für Polymerforschung Dresden e.V., Institute of Physical Chemistry and Polymer Physics, Dresden, Germany

² Leibniz-Institut für Polymerforschung Dresden e.V., Institute of Macromolecular Chemistry, Dresden, Germany

³ Institute for Materials Science and Max Bergmann Center for Biomaterials, TU Dresden, Dresden, Germany

⁴ Dresden Center for Computational Materials Science (DCMS), TU Dresden, Dresden, Germany.

⁵ Hamburg University of Technology, Hamburg, Germany

⁶ Technische Universität Dresden, Dresden Center for Computational Materials Science (DCMS), Dresden, Germany

⁷ Technische Universität Dresden, Cluster of Excellence Centre for Advancing Electronics Dresden(cfaed), Dresden, Germany

⁸ Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, USA.

⁹ Biointerfaces Institute, University of Michigan, Ann Arbor, MI, USA.

¹⁰ Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, USA

¹¹ Technische Universität Dresden, Department of Physical Chemistry of Polymeric Materials, Dresden, Germany

Chirality can be transferred spanning multiple length scales[1]. Particularly, the transfer of chirality from abundant biomolecules to nanostructures has garnered increasing interest over the past decade. However, achieving such nanoscale chirality often involves biomolecules serving as structurally chiral templates, irreversibly breaking the mirror symmetry of nanostructures. The pursuit of reversible chirality transfer presents a significant challenge. Accordingly, plasmon-coupled circular dichroism (PCCD) emerges as a potential pathway, facilitating chirality transfer from molecules to plasmonic nanostructures uniquely via Coulomb interactions, rather than relying on shape interactions. Nonetheless, PCCD typically remains weak due to the size mismatch between molecules and nanostructures, even when benefiting from strong plasmonic hotspots [2,3]. In this study, we unveil an effective approach to tremendously enhance PCCD (1.18 degrees with a dissymmetry factor of 0.2) through the straightforward stretching of biomolecules positioned between plasmonic nanoparticles. This method proves more efficient than the creation of robust plasmonic hotspots in creating robust PCCD. Notably, the dynamic stretching and releasing of biomolecules results in the reversible inversion of PCCD over more than 100 cycles.

[1] Hazen, R. & Sholl D. Chiral selection on inorganic crystalline surfaces. Nat. Mater. 2, 367–374 (2003).
[2] Govorov, A. O. Plasmon-induced circular dichroism of a chiral molecule in the vicinity of metal nanocrystals. Application to various geometries. J. Phys. Chem. C 115, 7914-7923 (2011).

[3] Cao, Z., Gao, H., Qiu, M., Jin, W., Deng, S., Wong, K. Y. & Lei, D. Chirality Transfer from Sub - Nanometer Biochemical Molecules to Sub-Micrometer Plasmonic Metastructures: Physiochemical Mechanisms, Biosensing, and Bioimaging Opportunities. Adv. Mater. 32, 1907151 (2020).

P23: Multicompartmentalized micellar structures by gold NPs grafted with diblock copolymers

Marina Sebastian, Andreas Fery, and Christian Rossner

Leibniz-Institut für Polymerforschung Dresden e.V. Institut für Physikalische Chemie und Physik der Polymere, D-01069 Dresden, Germany.

Because of their rich application potential in e.g. energy materials,[1] autonomous motile systems,[2] or as nanocarriers of drugs,[3] colloidal particles with an internal compartmentalized structure are of abiding interest in soft matter research. In this contribution, the synthesis and characterization of such structures assembled from gold nanoparticles grafted with polystyreneblock-poly (methacrylic acid) (PSt-block-PMAA) diblock copolymers is presented. The gold nanoparticles form intrinsically phase separated cores, whereas several segregated PMAA domains are distributed around this core, at a distance defined by the polystyrene spacer (Figure 1a). Dialysis against water leads to re-configuration of the formed structures to unique, kinetically trapped pinned-micelles structures with internal structure (Figure 1b).



Figure 1 : Bright-field TEM images of multicompartmentalized micellar structures (a) and surface-pinned micelle structures with internal, phase separated morphology (b).

[1] Zakia, M.; Yoo, S. II. Core-Satellite Assemblies of Au@polydopamine@Ag Nanoparticles for Photothermal-Mediated Catalytic Reaction. *Soft Matter* **2020**, 16 (45), 10252–10259.

[2] Gompper, G.; Winkler, R. G.; Speck, T.; Solon, A.; Nardini, C.; Peruani, F.; Löwen, H.; Golestanian, R.; Kaupp, U. B.; Alvarez, L.; et al. The 2020 Motile Active Matter Roadmap. J. *Phys. Condens. Matter* **2020**, 32 (19), ab6348.

[3] Rabanel, J. M.; Adibnia, V.; Tehrani, S. F.; Sanche, S.; Hildgen, P.; Banquy, X.; Ramassamy, C. Nanoparticle Heterogeneity: An Emerging Structural Parameter Influencing Particle Fate in Biological Media? *Nanoscale* **2019**, 11 (2), 383–406.

P24: Stable Redox-Active Gold Nanoparticles with *N*-Heterocyclic Carbene/Triphenylamines Surface Ligands for Application in Optoelectronics

H. Zhang^{1, 3}, N. Sun¹, A. Fery^{1, 2}, F. Lissel^{1, 3}

¹ Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Saxony, Germany

² Technische Universität Dresden, Chair for Physical Chemistry of Polymeric Materials, Dresden, Saxony, Germany

³ Technische Universität Hamburg, Hamburg, Hamburg, Germany

Organic-hybrid particle-based materials are crucial in (opto)electronics, sensing, and catalysis due to their synergistic effects, printability, and stretchability. [1] However, poor electronic coupling between organic and metallic parts often limits their functionality. N-heterocyclic carbenes (NHCs) are promising anchors for achieving electronic delocalization across interfaces, forming robust, highly conductive bonds with metals. Here, NHC anchors coupled redox-active gold nanoparticles (AuNPs) with triphenylamines (TPA), are used as hole transporting and electrochromic materials. These AuNPs exhibit remarkable thermal and redox stability due to the robust NHC-gold bond. As electrochromic materials, they show significant color changes, stable cycling (1000 cycles), and rapid response (5.6 s/2.1 s). The work function of TPA-NHC@AuNP is 5.26 eV, making them suitable HTMs for OLEDs and OSCs. The hybrid nanoparticle-based perovskite solar cell has a maximum power conversion efficiency of 8.79%, showing its potential as a hole transport layer in perovskite solar cells. [2] Additionally, we are exploring the connection of poly(triphenylamine)s with AuNP *via* NHC to improve the film formability of the hole transport layer, thereby enhancing the power conversion efficiency.

[1] M. Steiner, F. Lissel, A. Fery, J. Lauth, M. Scheele, Angew. Chem. Int. Ed. 2021, 60, 1152.
 [2] N. Sun, S. Singh, H. Zhang, I. Hermes, Z. Zhou, H. Schlicke, Y. Vaynzof, F. Lissel, A. Fery, Adv. Sci. 2024, DOI: 10.1002/advs.202400752.

P25: Super-Radiant SERS Enhancement by Plasmonic Particle Gratings

<u>Sezer Seçkin¹, Tobias A.F. König^{1,2,3}</u>

 ¹ Leibniz-Institut für Polymerforschung e.V., Hohe Straße 6, 01069 Dresden, Germany
 ² Center for Advancing Electronics Dresden (cfaed), Technische Universität Dresden, Helmholtzstraße 18, 01069 Dresden, Germany
 ³ Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, Bergstraße 66, 01069 Dresden,

Germany,

Despite recent progress, surface-enhanced Raman spectroscopy (SERS) still faces challenges in achieving high sensitivity and uniform Raman signals across a large area. Our research demonstrates a significant 43-fold increase in the SERS signal by employing the directional self-assembly of plasmonic nanoparticles in lattice structures without relying on the photoluminescence of Rhodamine 6G [1]. We specifically selected the lattice constant for an off-resonant case that matches the lattice resonance and super-radiant plasmon mode along the particle chain. Our approach is supported by electromagnetic simulations, where we systematically analyze the radiative components of the plasmon modes by varying the particle size while keeping the lattice periodicity constant. Additionally, we conducted polarization-dependent SERS measurements and compared them with other standard SERS excitation wavelengths. Through our work with the self-assembled plasmonic particle lattice, we have developed an effective SERS substrate that provides a significantly higher signal with 73% less surface coverage. This colloidal approach [2] allows for the cost-effective and scalable fabrication of highly sensitive, uniform, and polarization-dependent SERS substrates. [3]



Figure 1. Optical and SEM images of SERS substrates with their surface coverage and calculated enhancement factors.

[1] Seçkin et al., ACS Applied Materials & Interfaces **2023**, 15(36), 43124-43134.

[2] Gupta et al., Advanced Functional Materials 2021, 31(36) 2105054.

[3] The authors acknowledge funding the Freigeist Fellowship from the Volkswagen Foundation, Grant Number 92 902. Dr. Swagato Sarkar and Dr. Olha Aftenieva are thanked for their contributions to this work's experimental design and FDTD simulations.

P26: Janus Supraparticles by Induced Phase Separation by Gravity

Sayanth Ramachandran¹, Marcel Sperling², Michael Gradzielski², Michael Kappl¹ and Hans-Jürgen Butt¹

¹ Department of Physics at Interfaces, Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

² Stranski-Laboratorium für Physikalische und Theoretische Chemie, Technische Universität Berlin, Straße des 17. Juni 124, D-10623 Berlin

Janus particles have gained the attention of researchers over the last few years due to their anisotropic structure. This anisotropy shows potential for applications in various areas, specifically, but not limited to, the biomedical field [1]. This work unveils a facile method to fabricate Janus supraparticles from a binary colloidal suspension that employs gravity as the means for segregation. Self-assembly of colloidal suspensions confined in an evaporating droplet forms Supraparticles. Using a superhydrophobic surface as a substrate allows one to maintain the spherical shape for the colloidal suspension drop, thereby facilitating drying at a constant contact angle [2]. The effect of gravity on nanoparticles is comparable with their thermal energies [3]. We exploit this property to induce a phase separation between different colloidal species that have different buoyant masses, thereby creating a Janus particle. The buoyant mass can be controlled by changing parameters such as the size and density of the particles. The sedimentation process inside the microdroplet is non-trivial compared to the bulk due to the flow patterns inside the droplet. Careful control of these parameters yields Janus particles of desirable spherical shape [4].



Figure 1. Overview image of Janus Supraparticle with 800nm Polystyrene (pink) and 900nm SiO₂ (white) spheres as individual components.

[1] Walther, Andreas, and Axel HE Muller. Chemical reviews 113.7 (2013): 5194-5261.

[2] Rastogi, Vinayak, et al., Advanced Materials 20.22 (2008): 4263-4268.

[3] Piazza, Roberto. *Reports on Progress in Physics* 77.5 (2014): 056602.

[4] Funding from the German Science Foundation is acknowledged: Hans-Jürgen Butt is member of the RTG 2516 (Grant No. 405552959) and Sayanth Ramachandran is the recipient of a doctoral position within the RTG 2516 program.

P27: Towards the sustainable production of hydraulic sulfate binders via solution-mediated crystallization in the presence of highly specific additives

Selina Reigl¹, Alexander Van Driessche², Werner Kunz¹ and Matthias Kellermeier³

¹ University of Regensburg, Germany

² CSIC - University of Granada, Spain

³ BASF SE Ludwigshafen, Germany

CaSO4 minerals play an important role in both natural and engineered environments. Three different hydrate phases can form in contact with water: anhydrite (CaSO₄·OH₂O), bassanite (CaSO₄·1/2H₂O) and gypsum (CaSO₄·2H₂O). Despite its scarcity, bassanite is the most used CaSO₄ mineral and even one of the most produced inorganic materials worldwide (ca. 150 Mio tons annual). The use of bassanite as hydraulic binder in construction products is based on its reversible hydration process into gypsum producing high-strength cementitious materials.

Currently, bassanite is industrially obtained through thermal dehydration of gypsum at temperatures above 150 °C accompanied by an alarming carbon footprint. Consequently, several alternative routes towards more sustainable bassanite have been proposed during the last years mostly relying on the use of organic solvents or wet dehydration procedures in hot salt solutions. In contrast to that, we developed a potentially even greener and more sustainable process relying on the direct precipitation of bassanite from aqueous calcium chloride and sodium sulfate solutions with the help of suitable, highly specific additives at room temperature.



Figure 1. Overview of the stepwise development of a sustainable bassanite formation process (scale: 20µm).

First, we revisited the role of salinity revealing that relative levels of supersaturation play an important role in CaSO₄ crystallization [1]. Second, we investigated the impact of more specific additive classes, where we observed the general water-withdrawing (and hence dehydration promoting) effect of kosmotropes compared to chaotropes. Most notably, bassanite formation was boosted when additives with CaSO₄ binding heads combined with water withdrawing tails were present [2]. While bassanite precipitation from aqueous salt solutions only proceeds above 100 °C under additive-free conditions and above 70 °C in high salinity (> 4M) media, it was successfully precipitated at 40 °C and very low concentrations of alkyl ether carboxylate (< 0.1M). In a final step, we combined orthogonally operating additives, i.e. the described alkyl ether carboxylate and simple salts, yielding bassanite formation even at room temperature [3].

[1] Selina Reigl et al., CrystEngComm 2022, 24 (8), 1529-1536.

- [2] Selina Reigl et al., ACS Sustain. Chem. Eng. 2023, 11 (23), 8450-8461.
- [3] Selina Reigl et al., Chem. Commun. 2024, 60 (5), 610-613.

P29: Gelatin-based hydrogel particles for controlled sorption and release of model drugs

<u>Omar Abdelaziz Mohamed^{1, 2}</u>, Robin R. Benedix^{1, 2}, Alexander Southan¹, and Cosima Stubenrauch²

¹Max Planck Institute for Intelligent Systems, Stuttgart, Germany ²Institute of Physical Chemistry, University of Stuttgart, Stuttgart, Germany

Hydrogels are three-dimensional hydrophilic polymer networks with a high ability to swell in water. They can be fabricated in different shapes, thus enabling versatile applications. Hydrogels formed by biopolymers such as gelatin have gained significant interest in the field of biomaterials due to their inherent chemical functionality, biodegradability and biocompatibility [1]. This study followsup our previous studies where we synthesized, modified, and applied monodisperse gelatin-based foamed hydrogels [2]. Here we aim at synthesizing monodisperse gelatin-based particles. The objective is to study the effect of the particle size and the isoelectric point (IEP) of the hydrogel on the release kinetics of model drugs.

First, gelatin methacryloyl (GM) was chemically synthesized from gelatin type B as described by Claaßen et al [3], in order to obtain a low viscosity hydrogel precursor with a high cross-linking ability. Synthesis of GM and the degree of modification were confirmed by proton NMR. Second, monodisperse hydrogel particles were prepared with particle diameters ranging from 50 - 250 µm using microfluidics. The continuous oil phase consisted of isopropyl myristate and 3 wt% of Hypermer 2296 as surfactant. The aqueous phase contained 20 wt% of GM with 0.14 wt% lithium phenyl2,4,6-trimethylbenzoylphosphinate as a photo-initiator. The formed water-in-oil (w/o) droplets were subjected to UV light for photo-chemical cross-linking (curing), after which the obtained particles were further swollen in water or dried. We will show first results how the obtained monodisperse GM hydrogel particles can be used as a platform to control sorption and release of model drugs.



Figure 2: (A) Synthesis of gelatin methacryloyl via methacryloylation of amine and hydroxyl residues of gelatin type B. (B) microfluidic fabrication of GM hydrogel particles.

[1] Sheikhi, A. et al. (**2019**) 'Microfluidic-enabled bottom-up hydrogels from annealable naturally-derived protein microbeads', *Biomaterials*, 192, pp. 560–568. doi: 10.1016/j.biomaterials.2018.10.040.
[2] Dehli, F. et al. (**2019**) 'Highly ordered gelatin methacryloyl hydrogel foams with tunable pore size',

Biomacromolecules, 20(7), pp. 2666–2674. doi: 10.1021/acs.biomac.9b00433.

[3] Claaßen, C. et al. (**2017**) 'Quantification of substitution of gelatin methacryloyl: Best practice and current pitfalls', *Biomacromolecules*, 19(1), pp. 42–52. doi: 10.1021/acs.biomac.7b01221

[4] We deeply thank the Deutsche Forschungsgemeinschaft (grant IDs SO 1387/4-1 and STU 287/10-1) and the Landesgraduiertenförderung Baden-Württemberg for their financial support.

P30: Toward controlling transient states in nonequilibrium systems of responsive colloids

<u>S. Groh</u> and J. Dzubiella

Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, Freiburg, Germany

Responsive colloids can undergo substantial changes in states and properties, such as, shape, charge density or electric dipole, in response to an external stimulus. While these transformations are critical at the level of the individual particles, they also influence the collective behavior and dynamics of a large collection of interacting colloids. An important group of responsive colloids is the one for which the particle size is the internal property that couples to the translational degree of freedom. In that scenario, in addition to translational relaxation, particles are also able to relax their size by either swelling or shrinking in response to an external stimulus. Since many interesting behaviors of responsive system occur out of equilibrium, our work focuses on the interplay between size relaxation and translational relaxation resulting from a pressure jump applied to a 2D system of responsive colloids. More particularly, we aim to answer fundamental questions such as: "Can we observe interesting transient states along the relaxation pathway?" and "Can we control the relaxation pathway for the system to visit a transient state?".

To answer these questions, Brownian Dynamics calculations performed in the framework of the responsive colloids model are carried out. While the colloid-colloid interactions are modeled with a hard-sphere type potential, each colloid carries its own energy landscape $\psi(\sigma) = -k_B T ln p(\sigma)$ where $p(\sigma)$ represents the parent size distribution of an isolated colloid, and is assumed to follow an unimodal distribution. Starting from a polydisperse liquid, a pressure jump is applied, and the relaxation pathway in the density-size space is analyzed for different ratio between size and translational translation. When visible, the transient state is analyzed in terms of the radial distribution function and other local order parameters.

P31: Synthesis and Characterization of Microgels Bearing Electroactive Groups

Annika Lehmann, Erik Schumann, Felix Plamper

Institute of Physical Chemistry, TU Bergakademie Freiberg, Freiberg, Germany

Microgels with their both porous and flexible structure provide a fascinating matrix for organic electroactive groups, although the principles of electron transfer within microgels are not yet fully understood.[1,2] Hence, we synthesized microgels consisting of *N*-isopropyl acrylamide NIPAM copolymerized with 11.5 mol% acrylic acid and modified them with electroactive groups, namely a viologen derivate with a propyl and an 3-aminopropyl group as well as 4-amino-2,2,6,6-tetramethylpiperidinyloxyl (TEMPO), using the EDC/ Sulfo-NHS coupling approach.[3,4] We optimized the conditions of the modification reaction leading to up to a 100% transformation of the acrylic acid groups in case of the viologen. This was demonstrated by advanced NMR experiments such as HSQC measurements as well as titration experiments and determination of the zeta potential. The same was done with TEMPO with a conversion extent of 50% leading to novel TEMPO-containing microgels as multi-radical species.

The temperature-responsive properties of the resulting microgels were examined using dynamic light scattering and small angle X-ray scattering as well as differential scanning calorimetry. According to the results, the two microgels depict a different deswelling or aggregation behavior under various salt conditions because of the charge and, therefore, hydrophilicity of their electroactive groups. Since the high charge of viologen-containing microgels greatly impairs their temperature-induced collapse, we investigated also redox active microgels with other compositions, specifically, those consisting of *N*-n-propyl acrylamide and those consisting of a mixture of NIPAM and *tert*-butyl acrylamide. Furthermore, the responsiveness of both electroactive groups within the microgel network was demonstrated by cyclic voltammetry in the swollen as well as the collapsed state of the microgels.

[1] F. A. Plamper, W. Richtering, Acc. Chem. Res. **2017**, 50, 131–140.

[2] O. Mergel, S. Schneider, R. Tiwari, P. T. Kühn, D. Keskin, M. C. A. Stuart, S. Schöttner, M. de Kanter, M. Noyong, T. Caumanns, J. Mayer, C. Janzen, U. Simon, M. Gallei, D. Wöll, P. van Rijn, F. A. Plamper, *Chem. Sci.* **2019**, 10, 1844–1856.

[3] K. Marcisz, M. Sawicka, D. Jagleniec, J. Romanski, M. Karbarz, Z. Stojek, K. Kaniewska, *J. Electroanal.* **2023**, 937, 117418.

[4] E. Yu. Kozhunova, N. A. Gvozdik, M. V. Motyakin, O. V. Vyshivannaya, K. J. Stevenson, D. M. Itkis, A. V. Chertovich, *J. Phys. Chem. Lett.* **2020**, 11, 10561-10565.

P32: Stimuli-controlled interfacial trapping of surface-modified emulsion-templated hydrogel particles

Jinyuan Li and Lukas Zeininger

Responsive Soft Materials Lab, Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

Emulating the inspirational regulatory capabilities of multicompartmentalized natural systems, the construction of multi-compartment microreactors to perform multistep biochemical cascade reactions in one pot has attracted substantial attention. Spatially localizing reaction centers enables a regulation of the diffusion pathways of substrates, intermediates, and products, as well as control over constructive and destructive interference of active reaction centers, such as enzymes. In addition, higher local substrate and catalyst concentrations within the confined space of a microreactor can effectively tune reaction kinetics by overcoming unfavorable thermodynamics of the bulk environment. Consequently, having fine control over the compartmentalization of active reaction centers within multiphasic microreactors constitutes an exciting avenue to impart materials with regulatory capabilities. Biomimetic hydrogel microreactors enable effective transport of reactants, while distinguished compartments offer desirable micro-environments to control and tune reaction product generation in high efficiency, negating mutual interference. To gain insights into the optimization of enzyme cascade reaction kinetics inside artificial soft microreactors we explore new avenues toward the facile batch generation of synthetic hydrogel cascade microreactors.

In this context, simple poly (ethylene glycol) diacrylate (PEGDA) hydrogels received considerable attention because of their hydrophilic nature, microporous structure, biocompatibility, and adjustable composition properties. Granular hydrogels are composed of hydrogel-based microparticles, and are widely used to sensor, drug delivery, 3D printed, and injected or cast into macroscopic structures. Functional components always be encapsulated in microgels and released under specific circumstances. However, functionalization of the microgel surface is more important because of the direct contact between the microgel and the environment.

Herein, we describe a novel, bulk approach to generate surface modified hydrogel particles based on a UV-polymerization of aqueous emulsion droplets. Microfluidic was used to generate droplets, with poly (ethylene glycol) acrylate dissolved in water as dispersed phase. For surface modification, hydrophobic acrylates were introduced in the continuous phase prior to gelation. The droplet templates were polymerized under the UV light, to generate crosslinked hydrogel particles. At the same time, co-polymerization of hydrophobic acrylates yielded hydrogels with distinct surface wettability differences. The surface wettability determined their interfacial behavior and introduction of stimuli-responsive or cleavable functionality served to sensitively detect target analytes. Examples include both covalent and dynamic covalent post-modification, including cleavage by C8-esterase, an extracellular enzyme of bacterial as well as post-polymerization via formation of boronate esters. Such stimuli-responsive, multi-functional microgels have strong potential applications in industry, agriculture, food chemistry, and medicine.

P33: Multiresponsive Droplets-Based Optical Logic Gates

Basseem Radwan and Lukas Zeininger

Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Am Muehlenberg 1, 14476 Potsdam, Germany.

Dynamic complex emulsions are colloidal systems characterized by adaptable structures postemulsification. Their internal configurations and interfacial properties can be dynamically adjusted through the control of interfacial tension between the dispersed and continuous phases ^[1]. This enables the tuning of the Janus ratio, which dictates the degree of asymmetry between the two phases. Janus droplets are anisotropic materials with two hemispheres having distinct physical and chemical properties. Their asymmetric surfaces allow controlled manipulation, offering advantages for various applications including their implementation in liquid sensing platforms ^[2].

Biphasic dynamic droplets, comprising immiscible hydrocarbon (H) and fluorocarbon (F) liquids in an aqueous continuous phase, have been shown to act as micro-lenses, focusing or diverging light based on their internal morphology, which in turn could be tuned by altering surfactant effectiveness ^[3]. Therefore, stimuli-responsive surfactants could be employed to sensitize complex droplets to various stimuli. For the first time, we combine different stimuli-responsive surfactants to introduce multiresponsive complex emulsions-based logic gates.

UV-responsive surfactant AzoTAB was used to design UV-responsive Janus droplets. Following UV irradiation, AzoTAB changes to its *cis* isomer, reducing surfactant effectiveness, therefore, altering droplets morphology (reducing the droplet contact angle θ_F). This decreases collimated light transmission through the droplets, creating a droplet-based YES logic gate where UV light input results in reduced light transmittance.

Using natural amphiphilic compounds, such as oleic acid and cholesterol, which change effectiveness as H surfactants based on protonation/deprotonation at different pH values, we designed double pH-responsive droplets. Droplets were designed to assume Janus morphology ($\theta_F \sim 90^\circ$) at neutral pH allowing maximum light transmission. At acidic pH, droplets assume a double emulsion (H/F/W) morphology due to oleic acid protonation, whereas at basic pH the droplets exhibit an F/H/W configuration due to deprotonation of oleic acid and cholesterol. In both cases light transmittance is reduced, constituting an XNOR logic gate.

Moreover, combining AzoTAB and oleic acid, we designed a multiresponsive droplet-based halfadder logic circuit. In this system, neutral pH and no UV irradiation result in maximum light transmittance, either pH change or UV stimuli cause a reduction, and both stimuli together result in minimal light transmittance. This work highlights the potential of multiresponsive complex emulsions in various sensing applications ^[4].

[1] L. D. Zarzar, V. Sresht, E. M. Sletten, J. A. Kalow, D. Blankschtein, T. M. Swager, *Nature* **2015**, *518*, 520–524.

[2] L. Zeininger, Anal. Bioanal. Chem. 2023, 415, 5205–5219.

[3] S. Nagelberg, L. D. Zarzar, N. Nicolas, K. Subramanian, J. A. Kalow, V. Sresht, D. Blankschtein, G. Barbastathis, M. Kreysing, T. M. Swager, M. Kolle, *Nat. Commun.* **2017**, *8*, 14673.

[4] This work is supported by the Max-Planck Society and the Emmy-Noether program of the German Research Foundation under grant no. ZE 1121/3-1.

P34: Structure Formation in Supraparticles Composed of Spherical and Elongated Colloidal Particles

Yashraj Manish Wani¹, Melis Yetkin², <u>Kritika</u>^{1,3,4}, Michael Howard⁵, Hans-Jürgen Butt², Michael Kappl², Arash Nikoubashman^{1,3,4}

¹ Institute of Physics, Johannes Gutenberg Universität, Mainz, Germany

² Department of Physics at Interfaces, Max-Planck-Institut für Polymerforschung, Mainz, Germany

³ Institute Theory of Polymers, Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany

⁴ Institut für Theoretische Physik, Technische Universität, Dresden, Germany

⁵ Department of Chemical Engineering, Auburn University, Auburn, U.S.

In the present work, we use experiments and computer simulations to investigate the formation of supraparticles (SPs) through the evaporation-driven assembly of spherical and elongated colloidal particles (CPs). We systematically explore how different aspect ratios (λ =4,6,11) of the CPs and the drying conditions influence the final morphologies of SPs. In the evaporation-limited regime, where the rate of CP advection is much larger than the rate of CP diffusion, we find a short-ranged orientational ordering of the CPs on the SP surface and isotropic packing in the core. In contrast, simulations in the diffusion-limited regime show a long-ranged orientational ordering of the rods on the SP surface and local nematic ordering in the core. Additionally, we explore SPs fabricated from rod-sphere mixtures, where a thin shell of rods was observed for the slowly dried SPs. In all cases, we also observe that the porosity of the SPs increases with increasing aspect ratio of the elongated CPs [1].

[1] Yetkin et al., *Langmuir* **2024** 40 (1), 1096-1108.

P35: Self-assembly of cubic Janus colloids under rest and shear

Takahiro Yokoyama^{1,2}, Yusei Kobayashi³, Noriyoshi Arai¹, and Arash Nikoubashman^{1,2,4}

¹ Department of Mechanical Engineering, Keio University, Yokohama, Japan

² Institut Theorie der Polymere, Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany

³ Faculty of Mechanical Engineering, Kyoto Institute of Technology, Kyoto, Japan

⁴ Institut für Theoretische Physik, Technische Universität Dresden, Dresden, Germany

Janus colloids exhibit rich self-assembly behavior because of their anisotropic features of, e.g., particle shape, interaction potential, patchy size, and number of patches. The size and morphology of the self-assembled aggregates control the rheological and thermal properties of the suspensions [1], and it is therefore important to understand and engineer their self-assembly behavior. In this study, we used kinetic Monte Carlo (KMC) and molecular dynamics (MD) simulations to investigate the self-assembly of cubic colloids under both rest and shear [2,3] (Fig. 1). We considered five types of events in our KMC calculations, i.e., aggregation by Brownian diffusion, shear-induced aggregation, spontaneous breakup, shear-induced breakup, and shear-induced colliding breakup. We investigated the aggregation number of particles and which kinds of events are dominant in the system, by simulating under various conditions: We systematically varied the number and location of patches, the strength of binding energy, and shear-rate, finding aggregate shapes ranging from elongated rods over self-avoiding random walks to compact clusters.



Figure 1. Schematic representation of aggregation/breakup events of cubic colloids[3].

[1] T. Ikeda et al., Mol. Syst. Des. Eng., 2024, 9 (3), 254-263.

- [2] Y. Kobayashi et al., Langmuir, 2022, 38 (34), 10642-10648.
- [3] T. Yokoyama et al., Soft Matter, 2023, 19 (34), 6480-6489.

P36: Optimizing Wetting Properties of Silica Inverse Opal Structures by Controlling Templating Nanoparticle Properties

Natalie Bonakdar and Nicolas Vogel

Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Inverse opals (IOs) are three-dimensional nanoporous networks with fully interconnected, uniform pores aligned in a periodic nature. If the pore size is within the range of wavelengths of visible light, such materials exhibit structural coloration visible to the naked eye by constructive interference of reflected light (Fig 1a). Since structural coloration relies on a refractive index contrast, the wetting of this periodic, nanoporous material eliminates the structural color because the higher refractive index of the infiltrating liquids compared to air suppresses the interference conditions. This principle provides a simple and unambiguous signal readout: if the pores are infiltrated with a liquid, the structural color disappears and the material becomes transparent. To this point, such wettability changes have been triggered by the physical proprieties of the infiltrating liquid, in particular differences in surface tension between liquids to be differentiated. [1-4]



Figure 1. (a) Structural coloration of an IO with a pore diameter of 350 nm. (b) SEM image of the top view of an IO. The neck angle is determined by the ratio of the neck opening diameter and the pore diameter. (c) When the neck angle is larger than the intrinsic contact angle, the meniscus of the liquid takes on a concave shape and the liquid can propagate through the pores. (d) When the neck angle is smaller than the intrinsic contact and convex shape and the liquid can propagate through the pores.

The wetting behavior of inverse opals (IOs) is governed by the intrinsic contact angle of the liquid θ_c relative to the neck angle ϑ : the structure of an IO wets when θ_c of the liquid is smaller than ϑ , and vice versa (Fig. 1b-d). In an ideal IO, where all pores possess identical geometry and interpore neck radius, the wetting behavior remains consistent across the entire structure. However, imperfections such as cracks and surface roughness can disrupt this uniformity. We investigate how such imperfections influence the wetting properties. Beginning with the synthesis of IOs, polystyrene nanoparticles (PS-NPs) act as sacrificial templates through evaporative co-assembly with silica matrix material formed from the polycondensation of tetraethyl orthosilicate. Consequently, the surface characteristics of the PS-NPs are imprinted onto the pore architecture of the resulting inverse opals. We synthesize both monodisperse smooth and rough PS-NPs via surfactant-free emulsion copolymerization with sodium styrene sulfonate and acrylic acid, respectively. Smooth PS-NPs above a diameter of 280 nm are attained by post-synthesis plasticization above their glass transition temperature (Tg) or solvent swelling. These samples enable us to investigate how the wetting properties are affected by surface roughness. Additionally, we investigate how the softness

of the templating colloidal particles, adjusted via the T_g of the monomer, affect the neck openings, and thus the critical contact angle that determines liquid infiltration.

- [1] Ian Burgess et al., J. ACS Nano **2012**, 6 (2), 1427-1437.
- [2] Ian Burgess et al., J. Am. Chem. Soc. 2011, 133, 12430-12432.
- [3] Yanhao Yu et al., ACS Appl. Mater. Interfaces **2020**, 12, 1924-1929.
- [4] Natalie J. Nicolas et al., *Adv. Healthcare Mater.* **2021**, 10, 2001326.

P37: Organically Modified Silica Based Transparent and Hydrophobic Coatings for Easy-to-Clean Solar Panels with Drop Friction Analysis

Tarik Karakaya, Franziska Sabath, Sa'id Albarqawi, Hans-Jürgen Butt, Emre Yavuz, and Doris Vollmer

Max Planck Institute for Polymer Research, Department of Physics at Interfaces, Mainz Germany

The advancement of renewable energies is crucial in an age in which we are confronted with growing climate and environmental challenges. Solar energy is considered a highly promising, efficient and environmentally friendly source of energy. However, solar panels lose a significant amount of efficiency due to soiling [1]. Thus, a lot of water (more than 35 billion liters per year) is required to keep the panels clean [2]. Hydrophobic coatings that reduce water consumption by promoting selfcleaning via natural rainfall are of high interest. Further desired properties for solar panel coatings are high transparency and mechanical robustness. Our approach is to prepare a hydrophobic, transparent and mechanically stable prototype material by a sol-gel process based on tetraethyl orthosilicate (TEOS) and an alkyl trimethoxysilane (alkylTMS). Here, we vary the alkyl chain lengths (methyl, propyl and hexyl) and precursors' solid weight ratios. The resulting coatings have a transparency of around 90%, comparable to those of plain glass. With increasing alkyl chain length and concentration, we obtain increasing hydrophobicity with contact angles higher than 90° and hysteresis of around 10°. For the evaluation of self-cleaning features, scanning drop friction force microscopy (sDoFFI) was utilized. Here, lower drop friction force correlates to better self-cleaning properties. Drop friction decreased with increasing alkyl chain length and concentration. For fixed methyITMS/TEOS and hexyITMS/TEOS ratios, a respective average friction force of 41±2 µN and 23±2 µN was observed at a drop volume of 5 µL. Moreover, this technique enables the characterization of coating homogeneity. A thoroughly uniform frictional force was observed on the respective surfaces (Figure 1). Our methods thus enable the production of transparent, uniform and hydrophobic surfaces whose suitability as solar cell coatings can be investigated by sDoFFI.



Figure 3. Scanning Drop Friction Microscopy of a glass substrate coated with methylTMS/TEOS (left) and hexylTMS/TEOS (right) sol gels.

[1] Chandler, D. L. (2022, March 15), *This is how solar panels can be kept clean - without using water*. Weforum. Retrieved June 20, 2024, from https://www.weforum.org/agenda/2022/03/solar-panels-waterless-clean/

[2] (a) Borah et al., Sustainability 2023, 15, 16669. (b) Najmi et al., Energies 2023, 16, 7960.

P38: Dynamic adsorption layer and flow within liquid meniscus in forced dewetting

V.I. Kovalchuk¹ and G.K. Auernhammer²

¹ Institute of Biocolloid Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine ² Institute of Physical Chemistry and Polymer Physics, Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany

In surfactant solutions the surface of the dewetting meniscus can be retarded (fully or partially) because of the appearance of surface tension gradients opposing the flow in the adjacent liquid, i.e., because of the Marangoni stresses within the dynamic adsorption layer. In the presence of non-uniform adsorption layers, the calculation of the flow characteristics in the meniscus becomes much more challenging because it requires to consider convective-diffusion surfactant transfer in the bulk and at the surface with account for surfactant adsorption and desorption. In surfactant solutions a non-uniform retardation of the meniscus surface is expected, where the available analytical solutions are not applicable. With increasing flow velocity, the non-uniformity of the meniscus surface retardation becomes stronger, and a separation of the surface on a mobile and an immobile part with a sharp transition between them is possible. A very similar separation of the surface on a mobile and an immobile part is observed also on the surface of rising bubbles or rising/falling drops in surfactant solutions and in other surfactants containing systems with similar flow conditions.

In this study, the liquid velocity profiles in a steady dewetting meniscus have been analyzed from the hydrodynamic and convective diffusion points of view by taking into account possible viscous stresses variations and non-uniform retardation of the meniscus surface due to presence of a dynamic adsorption layer [1]. The numerical calculations of the flow profiles allow to obtain a logarithmic decrement for the surface tension variation with increasing distance from the contact line. This decrement is close to that calculated by using known analytical solutions, except of a small region near the transition point, where the surface tension has a small initial decrease. With this decrement the surface tension difference required to immobilize the surface can be calculated [2].

[1] V.I. Kovalchuk and G.K. Auernhammer, *Curr. Opin. Colloid Interface Sci.* **2023**, 67, 101723.

[2] We gratefully acknowledge the financial support by the Deutsche Forschungsgemeinschaft - Project-ID 265191195 - SFB 1194 (GKA), by European Commission within the scope of FP Horizon 2020 (Project "EHAWEDRY", Grant Agreement No. 964524) (VIK) and National Research Foundation of Ukraine (project number 2020.02/0138) (VIK). A fellowship of the DAAD (VIK) is also gratefully acknowledged.

P39: Disjoining pressure and meniscus shape near the contact line at a conducting substrate surface

V.I. Kovalchuk¹, M.P. Bondarenko, E.K. Zholkovskiy¹ and A.E. Yaroshchuk^{2,3}

¹ Institute of Biocolloid Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine

² Department of Chemical Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain

³ ICREA, 08010, Barcelona, Spain

Formation of a stable wetting film behind a receding meniscus depends on the interaction between the liquid and substrate surface. In the case of a conductive substrate surface the situation is non-trivial because, theoretically, van der Waals interaction between the air/liquid and solid/liquid interfaces should be repulsive for water and aqueous solutions that would lead to complete wetting of the substrate surface. However, experimental data show that water can form finite contact angles at conductive surfaces, e.g., at the graphite surface, water forms the wetting contact angle of about 60° [1]. The attraction force in such cases can be a consequence of the attractive electrostatic interaction.

The interaction between the water-air interface and the substrate surface can be characterized by the disjoining pressure which depends on the distance between the surfaces. The dependence of the electrostatic component of disjoining pressure on the distance can be found from the solution of the Poisson-Boltzmann equation with respective boundary conditions that usually impose either constant surface potential or constant surface charge density [2]. In the case of a wetting film on a conductive substrate surface the boundary conditions cannot be the same at the two boundaries. At the substrate surface the electric potential should be constant because of its conductivity. At the same time, the charge at the water-air boundary is formed due to specific adsorption of ions which should not change significantly due to interaction with the second boundary. Thus, the boundary condition should be closer to the constant charge than to the constant potential case. The solution of the Poisson-Boltzmann equation for such asymmetric boundary conditions is presented in the reported study. The obtained solution is used for calculating both the equilibrium film thickness and the meniscus shape [3].

[1] Y. Zhou and E. J. Reed, J. Phys. Chem. C 2018, 122, 18520–18527.

[2] I.V. Kuchin et al., Colloids Interface Sci. Commun. 2014, 1, 18–22.

[3] The authors acknowledge funding from the European Commission within the scope of FP Horizon 2020, Project Acronym "EHAWEDRY", Grant Agreement No. 964524.

P40: Dynamic Wetting of Adaptive Polyelectrolyte Substrates: A multiscale approach

Mona Meltschoch, Mohammad Ali Hormozi, Regine von Klitzing

Soft Matter at Interfaces, Institute for Condensed Matter Physics, TU Darmstadt, Hochschulstraße 8, D-64289 Darmstadt, Germany

Studying wetting phenomena is of great importance across a wide range of scientific disciplines. As a fundamental research area, wettability dynamics of adaptive and responsive substrates gained significant attention. These substrates include polyelectrolyte multilayers (PEM), Poly-Nisopropylacrylamide (PNIPAM) microgels (MG), and Polydimethylsiloxane pseudo-brushes (PDMS brushes), among others. Notably, an interesting property of polyelectrolyte (PE) substrate is their propensity to swell in a liquid environment, yet the complexities like disparity between time and length scales, and surface deformation beyond the three-phase contact line (TPCL) makes experimental investigations to be quite challenging. Here, we prepare PE substrates by the layer-bylayer method invented by Decher and coworkers [1], with a focus on their wettability at the nanoscale. We use atomic force microscopy (AFM) as the main characterization technique at the nanoscale for investigation of layer properties, swelling kinetics, saturation, with an optical contact angle (CA) tensiometry method for measurements at macroscopic scale. The layer thickness is determined by ellipsometry. The results show that the water CA on silicon wafers coated with polystyrene sulfate (PSS) as outermost layer decreases in water-saturated atmosphere as previously described by Hänni-Ciunel et al. [2]. Furthermore, the PDMS brushes CA measurements are compared to these of PEM of different composition and layer thickness. Here fore, the dip protocol was adjusted to fabricate different PEMs consisting of PEI/PSS/PAH with different layer thickness, polyanion or polycation as outermost layer and addition of NaCl. [3]

[1] G. Decher, *Science* **1997**, 1232 – 1237.

[2] K. Hänni-Ciunel, G. H. Findenegg, R. v. Klitzing, Soft Materials 2007, 61 – 73.

[3] The authors acknowledge funding from the DFG, Priority program 2171, KL1165/34, Grant Number 505842923.

P41: Hybrid Au/MOx Nanostructures for Photoactivated Gas Sensing

Gabriele Carelli¹, Andreas Fery^{1,2} and Hendrik Schlicke¹

¹ Leibniz Institut für Polymerforschung Dresden e.V., Dresden, Germany ² TU Dresden, Dresden, Germany

In order to overcome energy-hungry thermal activation, which is common in commercially available metal oxide (MOx) sensors used for chemiresistive detection of gaseous compounds, novel nanomaterial combinations could be decisive. A promising strategy consists in implementing noble metal nanoparticles as efficient light absorber materials into an MOx matrix to make use of their unique optical properties originating from the well-known localized surface plasmon resonance effect. Explicitly, near-field enhancement, hot electron transfer and localized heating are promising phenomena to provide photoactivation with low-energy visible light. [1,2]

The solution-based bottom-up synthesis of nanoparticle building blocks enables controlled adjustment of their size and shape as well as facile ink-based processing and deposition schemes leading to defined nanoparticle solids.

Different approaches are probed for the fabrication of optimized plasmonic metal / MOx hybrid structures, using SnO₂, ZnO and Au as starting materials. Following one approach, the target system consists of Au@SnO2 nanoparticles of different core and shell dimensions. Another approach comprises GNPs randomly embedded a ZnO nanoparticle matrix.

Ultimately, the obtained hybrid material structures were probed regarding photoactivation by monitoring photocurrents under transient illumination, and gas-sensing properties were tested via exposure to ethanol vapor at varying concentrations with and without green light excitation.



Figure 1. TEM images at different magnifications of ZnO, Au and Au@SnO₂ nanoparticles which are used as building blocks for plasmonically photoactivated gas and vapor sensors.

I. Cho, Y. Sym, K. Lee, *Small (2023)*, 19 (27), 2207165.
 S. Linic, P. Christopher, D. Ingram, *Nature Materials* (2011), 10 (12), 911-921.

P42: Integrating 1D and 2D materials to fabricate novel electronic circuit

<u>Madhuri Chennur</u>¹, Borja Rodriguez-Barea^{1,2}, Sayantan Ghosh^{1,2}, Jens Zscharschuch¹, Yordan Georgiev¹ and Artur Erbe^{1,2}

¹ Helmholtz-Zentrum Dresden - Rossendorf, Institute of Ion Beam Physics and Materials Research, 01328 Dresden, Germany ² TUD Dresden University of Technology, 01062 Dresden, Germany

With the increasing demand for energy-efficient, reliable, and compact systems, electronics needs to overcome limitations in conventional silicon-based technologies. In this direction, the integration of 1D and 2D materials provides a plethora of possibilities for exploiting their unique properties. In this study, we explore the synergetic effects of combining low dimensional materials to create structures that exhibit enhanced performance. Firstly, we demonstrate the formation of 1D metallic nanostructures based on the DNA origami technique, which forms the building blocks for an electronic circuit [1]. DNA templates are used as molds to guide the placement and growth of the metallic 1D nanowires (NWs) [2]. This solution-based and high-resolution nanofabrication technique complements traditional top down processes. Later, 2D materials like Graphene, MXenes and other 2D sheets can be mechanically exfoliated onto the NWs to encapsulate them from the external environment [3], act as a gate dielectric [4] or bridge them as interface to facilitate efficient charge transport and improve device scalability. Incorporating such a fusion has displayed reduced hysteresis, increased Ion/Ioff and improved material interaction due to larger surface-volume ratio.

Utilizing different categories of 1D and 2D materials uniquely can lead to novel electronic properties with reduced work-function, tunable-band gap, higher carrier mobility and improved conductivity. They also provide a platform for flexible and wearable electronics due to their mechanical resilience and stretchability. By harnessing the complementary strengths of these hybrid devices, we can pave the way for future technological advancements.



Figure 1. (a) TEM micrograph of a sectioned nanowire device and (b) Corresponding superimposed EDXS-based element distribution maps of the hBN-silicon-nanowire-based device. [4].

- [1] Liu, Jianfei, et al. ACS nano 5.3 (2011): 2240-2247.
- [2] Kemper, Ulrich, et al. Small 19.26 (2023): 2206438.
- [3] Lee, Gwan-Hyoung, et al. ACS nano 9.7 (2015): 7019-7026.
- [4] Ghosh, Sayantan, et al. ACS Applied Materials & Interfaces 15.34 (2023): 40709-40718.

P43: Heading toward Miniature Sensors: Electrical Conductance of Linearly Assembled Gold Nanorods

<u>Marisa Hoffmann^{1,2,3}</u>, Christine Alexandra Schedel⁴, Martin Mayer¹, Christian Roßner^{1,5}, Marcus Scheele⁴, and Andreas Fery^{1,2,3}

¹Institute of Physical Chemistry and Polymer Physics, Department of Functional Colloidal Materials, Leibniz Institut für Polymerforschung Dresden e.V., Germany

² Physical Chemistry of Polymeric Materials, Technische Universität Dresden, Germany

³ Center for Advancing Electronics Dresden, Technische Universität Dresden, Germany

⁴ Institute of Physical and Theoretical Chemistry, Eberhard Karls Universität Tübingen, Germany

⁵ Dresden Center for Intelligent Materials (DCIM), Technische Universität Dresden, Germany

Colloidal metal nanoparticles are increasingly used as key elements in the fabrication and processing of advanced electronic systems and devices. For future device integration, their charge transport properties are essential. This has been exploited, e.g., in the development of goldnanoparticle based conductive inks and chemiresistive sensors. Colloidal wires and metalnanoparticle lines can also be used as interconnection structures to build directional electrical circuits, e.g. for signal transduction. Our scalable bottom-up template-assisted self-assembly creates gold-nanorod (AuNR) lines that feature comparably small widths as well as good conductance. However, the bottom-up approach poses the question about the consistency of charge transport properties between individual lines, as this approach leads to heterogeneities among those lines with regard to AuNR orientation as well as line defects. Therefore, we test the conductance of the AuNR lines and identify requirements for a reliable performance. We reveal that multiple parallel AuNR lines (> 11) are necessary to achieve predictable conductivity properties, defining the level of miniaturization possible in such a setup. With this system, even an active area of only 16 μ m² shows a higher conductance (~10⁻⁵ S) than a monolayer of gold nanospheres with dithiolated conjugated ligands and additionally features the advantage of anisotropic conductance. This proof-of-concept shows that colloidal nanowires are promising candidates for the fabrication of electronic components and miniature sensors of various sizes.



Figure 1. Schematic representation of the colloidal AuNR-lines array (yellow) with anisotropic conductance, self-assembled on a substrate with parallel gold electrodes (light brown). Reliable conductance values are reached for arrays consisting of >11 colloidal nanowires, i.e. an active area of about 16 μ m².

P44: Synthesis & fluorescence characteristics of electrically actuated 6helix bundle DNA origami – gold nanoparticle hybrid structures

T. Jeong^{1,2}, A. Ong³, A. Heerwig², A. Kick², B. Rellinghaus³, M. Mertig^{1,2,3}

1 Physical Chemistry, Technische Universität Dresden, 01062 Dresden, Germany 2 Kurt-Schwabe-Institut für Mess- und Sensortechnik Meinsberg e.V., 04736 Waldheim, Germany 3 Dresden Center for Nanoanalysis, Technische Universität Dresden, 01062 Dresden, Germany

The development of DNA origami nanolevers has opened up new possibilities for the design of nanomechanical devices with unprecedented sensitivity and specificity. Although integration of origami components as functional elements into electro-mechanical devices has an immense potential for novel applications, electrical actuation of origami nanolever - gold nanoparticle (AuNP) hybrid structures has not been established yet. Herein we demonstrate electrical actuation of 100 nm-long 6-helix bundle origami nanolevers with functionalized AuNP attached on one end. DNA origami nanolevers are a novel class of biomolecular machines that utilize the unique structural

properties of DNA molecules to generate mechanical force and motion at the nanoscale [1,2,3]. We use a 6-helix bundle origami nanolever that is attached to a gold electrode with one end and carries a fluorescent dye and a 20 nm AuNP on the other end. By applying an alternating electrical potential, this hybrid structure shows mechanical actuation which can be followed by time-dependent fluorescence intensity [4].



Figure 1. Fluorescence response of an origami – AuNP hybrid in static (a) and dynamic (b) measurement.



Figure 2. TEM image of negatively stained DNA origami – AuNP hybrid structure. (a) TEM image of DNA origami. (b) DNA origami – AuNP hybrid structure.

[1] F. Kroener et al., J Am Chem Soc 2017, 139, 16510 – 16513.

[2] A. Heerwig et al., phys. stat. sol. A 2018, 215, 1700907.

[3] F. Kroener et al., ACS Appl. Mater. Interfaces 2019, 11, 2295 – 2301.

[4] We kindly acknowledge financial support from the "Deutsche Forschungsgemeinschaft" (DFG: RTG 2767).

P45: M(Cu,Ag)InE(S,Se)₂ Semiconductor Nanoparticles for Novel Transistor Structures

Nadia Metzkow, Bjarne-Elias Stern, and Alexander Eychmüller

Technical University Dresden, Physical Chemistry, Dresden, Germany

Smartphones, computers, televisions, radios, power chargers - transistors can be found in almost every electronic device. Nowadays, such electronic components are expected to become smaller, flexible, and more powerful. However, a high-performance, flexible, thin-film transistor technology is still missing.

Semiconductor nanocrystals (NCs) have the potential to achieve a breakthrough in transistor performance, as they are processed solution-based and can overcome the intrinsic low carrier mobility of organic semiconductors. In the last decades, different functional NCs have been successfully fabricated. It is possible to precisely control the physical and electronic properties of NCs via parameters such as size, shape and composition. Using them in different transistor architectures is promising, as studies with CdSe NCs have shown recently.[1]

In this work, we strive to use different NCs for transistors, which allow to easily realize highperformance devices without nanostructuring. Therefore, M(Cu,Ag)InE(S,Se)₂ NCs are synthesized to replace the widely studied but more toxic Cd- or Pb-containing materials. To improve the electronic communication, the insulating organic ligands necessary for the synthesis are exchanged with inorganic ligands (e.g. I⁻, Br⁻, S²⁻, SCN⁻) in simple solution-based phase transition ligand exchanges. The materials are then characterized in terms of their film-forming properties and electronic parameters. [2-4]

[1] Fan, X., J. Phys. Chem. Lett., **2019**, 10(14), 4025–4031.

[2] Stroyuk, O., J. Phys. Chem. C, 2018, 122, 25, 13648–13658.

[3] Sayevich, V., Chem. Mater., **2015**, 27, 12, 4328–4337.

[4] The authors acknowledge funding from the DFG – GRK 2767 – Project number 451785257. Dr. Jörn Vahland is thanked for his expertise in the fabrication of transistors.

P46: Separation of gaseous compounds within stacked nanomaterial films for sensing applications

Lukas Mielke¹, Andreas Fery^{1,2} and Hendrik Schlicke¹

¹ Leibniz Institut für Polymerforschung Dresden e.V., Dresden, Germany ² TU Dresden, Dresden, Germany

The selectivity of gas and vapor sensors remains a significant challenge in recent times. To address this concern, tailored composite materials and their facile fabrication evolve as a promising alternative. It is reported that films made of alkanedithiol cross-linked gold nanoparticles can be used to resolve the sorption kinetics of volatile organic compounds and enable their identification via machine learning based analysis of the chemiresistive sensor signal [1]. Furthermore, variations in the building blocks, viz., organic linkers and nanoparticles, offer tunability of kinetics and sensitivity to analytes [1,2]. The selective permeability of chemiresistive nanocomposite layers can be utilized even more beneficially upon vertical stacking. Here, thin polymer layers are used to separate the sensing layers because they provide electrical insulation, gas diffusion and yet, as a static phase, they show different interactions with gases (Figure 1). We present our current activities focusing on development and characterization of such vertically integrated sensor stacks, aiming at the analysis and evaluation of their response for identifying binary and even more complex gas mixtures. Sensor characterization was carried out using a custom-built modular test system. Ultimately, this opens up a wide range of potential applications, including food monitoring, personal health care via breath analysis and public safety through the detection of explosives and air pollution control [3].



Figure 1. Exposure of vertically stacked, chemiresistive nanoparticle films separated by dielectric layers to a mixture of volatile organic compounds.

- [1] H. Schlicke et al., ACS Appl. Nano Mater. **2021**, 4 (10), 10399–10408.
- [2] C. Liu et al., Adv. Mater. Interfaces 2024, 11, 2301058.
- [3] The authors acknowledge funding from the RTG 2767, Grant Number 451785257.

P47: Novel metallic aerogel electrodes for flexible organic light emitting diodes

<u>N Nandakumar</u>, P Khavlyuk, A Eychmüller, C Murawski

Technische Universität Dresden, Dresden, Germany

In our quest to develop high-performance flexible OLEDs for wearable and implantable uses, we showcase our progress with aerogel electrodes. These aerogels, created via phase-boundary gelation, form ultra-thin layers (4-15 nm) that offer high conductivity (56 Ω / \Box sheet resistance) and exceptional transparency (up to 97%) [1]. As a result, they hold the potential to surpass the limitations of traditional transparent electrodes like transparent conductive oxides and thin metals, which tend to be brittle and less transparent.

Our OLED fabrication process incorporates doped charge transport layers, which optimize charge injection and transport while fine-tuning optical properties. Carefully selecting dopants and their concentrations allows precise control over the electronic characteristics of OLED devices, enhancing overall performance. We thoroughly analyze the aerogels' optical and electrical properties to ensure their seamless integration into the devices.

Additionally, we use flexible substrates made from conformal barrier layers of parylene-C and metal oxides, created through atomic layer deposition, to protect the devices from oxygen and moisture. This protection significantly improves the durability of OLEDs in aqueous environments, making them suitable for biomedical applications [2]. We also investigate the optical properties of these substrates and evaluate the encapsulation efficiency of these barriers.

[1] K. Hiekel et al., Angew.Chem.Int. 2020, 59 (29), 12048.

[2] C. Keum, et al., Nature Communications 2020, 11, 6250.

[3] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – GRK 2767 - Projektnummer 451785257

P48: Liquid Phase (S)TEM of DNA Origami - Gold Nanoparticle Hybrids

<u>Alyna Ong</u>¹, Darius Pohl¹, Taekyu Jeong^{2,3}, Andreas Heerwig³, Michael Mertig^{2,3}, and Bernd Rellinghaus¹

1 Dresden Center for Nanoanalysis (DCN), cfaed, TU Dresden, 01062 Dresden, Germany. 2 Physical Chemistry, TU Dresden, 01062 Dresden, Germany. 3 Kurt-Schwabe-Institut für Mess- und Sensortechnik Meinsberg e.V., 04736 Waldheim, Germany.

DNA origami is a versatile and flexibly adaptable molecular template to control self-assembly of nanoparticles (NPs) and other nanoscopic building blocks [1]. Particle-particle and particle-substrate interactions can be controlled effectively by choosing appropriate functionalization of the NPs. As DNA-based processes require liquid environments, high-resolution microscopy applicable to liquids is needed to characterize, understand, and optimize the underlying physico-chemical mechanisms. Here, we use in-situ (scanning) transmission electron microscopy ((S)TEM) to study Au NPs, which are site-specificly bound to DNA origami structures directly in solution. The study focuses on imaging individual Au NPs adhered to DNA origami, determining the precision, to which particle sizes and positions can be measured in solution, and on imaging the DNA origami to determine their dimensions and shape qualitatively.

Ex-situ (S)TEM and in-situ liquid phase (S)TEM (LP-(S)TEM) were conducted on a JEOL F-200 microscope equipped with a Gatan OneView camera and a HAADF detector at 200 kV. For LP-(S)TEM investigations, a Protochips Poseidon Select holder was used to keep the samples in a liquid environment that was sealed with SiN membranes against the high vacuum of the line tube. The resolution and contrast of the LP-STEM images are reduced by beam-induced crystallization (predominantly of salts from solution). Nonetheless, upon optimizing the scanning parameters, a precision measurement of particle positions and distances is also possible in solution and first measurements indicate a preferred inter-particle distance as intended by the specifically "programmed" DNA pads.

Ex-situ (S)TEM allows to clearly image the hybrid structure of Au NPs and DNA origami dried from solution as well as the mere DNA origami. DNA origami were designed and synthesized by scaffolded self-assembly [1, 3, 4], whereas the DNA origami@AuNPs hybrids were synthesized using freeze-thawed method [2]. In order to visualize both the mere DNA origami and the hybrid structures, staining of both types of specimens on TEM grids with holey carbon carrier films was conducted using 2% uranyl formate solution [4]. Our results show that this staining technique is effective to enhance the contrast of the DNA origami, thereby making it possible to image them using ex-situ (S)TEM. As for the hybrid structure, further contrast enhancement is needed to clearly prove the attachment of the DNA to the AuNPs. The progress towards enhancing the visibility specifically of the hybrid structures, by modifying the staining procedures and imaging strategies will be discussed.

[1] J. Zessin et al., Nano Lett. 17 (2017) 5163.

[2] G. Klös et al., Zenodo (2022), https://doi.org/10.5281/zenodo.6516945.

[3] P.W.K. Rothemund, Nature 440 (2006) 297.

[4] A. Herms et al., Phys. Status Solidi A 214, 9 (2017) 1600957

[5] Financial support by DFG through RTG 2767 and EU's Horizon 2020 Program (grant #964248) is gratefully acknowledged. We thank Gunnar Klös for nanoparticle synthesis and functionalization.

P49: Towards stable CsPbI₃ perovskite quantum dots for photovoltaics

<u>Ruth Pinheiro Muniz</u>,^{1,2} Julius Brunner,^{1,2} Anatol Prudnikau,² Raquel Campos,^{1,2} Yana Vaynzof^{1,2}

¹Chair for Emerging Electronic Technologies, TUD Dresden University of Technology, Nöthnitzer Str. 61, 01187 Dresden, Germany.

² Leibniz-Institute for Solid State and Materials Research Dresden, Helmholtzstraße 20, 01069 Dresden, Germany.

The development of new technologies based on perovskite quantum dots (PQDs) materials have been at the focus of the scientific community due to their excellent optoelectronic properties, ease of fabrication, and multiple possible applications, such as photovoltaic (PV) and light-emitting diodes (LEDs). CsPbl₃ perovskite quantum dots are of particular interest for photovoltaic applications, as their bandgap is favorable to light harvesting across a broad spectral region, leading to power conversion efficiencies surpassing 16% [1]. Despite their excellent performance, these QDs exhibit susceptibility to degradation, limiting the lifetime of the devices [2]. In this work, we focus on developing new routes to passivate the CsPbl₃ PQDs surface to enhance their environmental stability. In particular, we aim to coat the CsPbl₃ PQDs with a thin shell of lead sulfide (PbS), inspired by the excellent match of the atomic lattice parameters between the two materials [3]. We investigate different sulfur precursors as a sulfur source for the formation of the shell and study their effect on the PQDs stability. Our preliminary results show that this strategy can be efficacious in enhancing the stability of the CsPbl₃ PQDs [4].

[1] D. Jia, J. Chen, R. Zhuang, Y. Hua, X. Zhang, Inhibiting lattice distortion of CsPbI3 perovskite quantum dots for solar cells with efficiency over 16.6%, Energy Environ. Sci. 15 (2022) 4201–4212. https://doi.org/10.1039/D2EE02164A.

[2] M. Albaladejo-Siguan, E.C. Baird, D. Becker-Koch, Y. Li, A.L. Rogach, Y. Vaynzof, Stability of Quantum Dot Solar Cells: A Matter of (Life)Time, Adv. Energy Mater. 11 (2021) 2003457. https://doi.org/10.1002/aenm.202003457.

[3] M. Albaladejo-Siguan, D. Becker-Koch, A.D. Taylor, Q. Sun, V. Lami, P.G. Oppenheimer, F. Paulus, Y. Vaynzof, Efficient and Stable PbS Quantum Dot Solar Cells by Triple-Cation Perovskite Passivation, ACS Nano 14 (2020) 384–393. <u>https://doi.org/10.1021/acsnano.9b05848</u>.

[4] The authors thank the DFG for the generous support within the framework of the GRK 2767 (Project A7).

P50: Imidazole-based poly(Ionic Liquid) spheres templating for nanostructured transition metal nitrides as advanced Sulfur hosts in Li-**S** batteries

Yael Rodriguez-Ayllon^{1,2}, Dongjiu Xie¹, Qingping Wu¹ and Yan Lu^{1,2,3}

¹ Helmholtz-Zentrum Berlin für Materialien und Energie, Institute of Electrochemical Energy Storage, Berlin, Germany

² Friedrich-Schiller-Universität Jena, Institute for Technical and Environmental Chemistry, Jena, Germany

³ Helmholtz Institute for Polymers in Energy Applications Jena (HIPOLE Jena), Jena, Germany

Transition metal nitrides (TMNs) are attractive for cutting-edge energy storage technology owing to their unique electronic structure, superior electrical conductivity, chemical, and mechanical stability [1,2]. Nevertheless, the complex synthesis pathway via ammonia-based reduction compromises environmental stewardship and makes large-scale production off-target [3]. Herein, we present a straightforward method to construct nano-structured Mo₂N and VN embedded in carbon spheres via colloidal route using imidazole-based poly(ionic liquid)s (PILs) as an N-rich template [4], eliminating the need for external nitridation (Figure 1).

The resulting nanostructured TMNs exhibit superior catalytic properties against sulfur species generated during the charge-discharge process in Li-S batteries. The incorporation of TMNs significantly enhances the kinetics of redox reactions, reduces overpotentials, and boosts sulfur utilization and retention. This results in higher capacity retention and improved cycling stability of the Li-S batteries. [5]



Synthesis for the of TMN@C nanostructured external

[1] H. Wang, J. Li, and K. Li. Chem. Soc. Rev., 2021,50, 1354-1390.

[2] Y. Zhong, X. Xia, F. Shi, J Zhan, J. Tu, and H. J. Fan. Adv. Sci., 2016,3, 1500286.

[3] Q. Luo, C. Lu, M. Zhu, and L. Liu. Green Energy & Environment., 2023,8, 406-437.

[4] D. Xie, Y. Xu, Y. Wang, X. Pan, E. Härk, Z. Kochovski, A. Eljarrat, J. Müller, C. Koch, J. Yuan, Y. Lu. ACS Nano, 2022, 16 (7), 10554-10565.

[5] The authors acknowledge funding from the German Ministry of Education and Research (BMBF) in the project "SkaLiS" (support code:03XP0398D).

P51: Enhancing Charge Transport in Line Assemblies of Gold/Polyaniline Hybrid Nanoparticles

<u>Gyusang Yi</u>,^{1,2,4} Marisa Hoffmann,^{1,2,4} Sezer Seçkin,^{1,2} Tobias A.F. König,^{1,2,3,4} Ilka Hermes,¹ Christian Rossner,^{1,2,3} and Andreas Fery^{1,2,3,4}

¹ Institut für Physikalische Chemie und Physik der Polymere, Leibniz-Institut für Polymerforschung Dresden e.V., D-01069 Dresden, Germany.

² Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, Bergstraße 66, 01069 Dresden, Germany.

³ Dresden Center for Intelligent Materials (DCIM), Technische Universität Dresden, Hallwachsstraße 3, D-01069 Dresden, Germany.

⁴ Center for Advancing Electronics Dresden (cfaed), Technische Universität Dresden, Helmholtzstraße 18, 01069 Dresden, Germany.

Core–shell-type (hybrid) nanoparticles composed of a metallic core and polymeric shell represent promising building blocks for future electronic materials. These building blocks can be arranged into e.g. line assemblies, providing surfaces with anisotropic conductance of electric current. In addition, the polymeric coating provides responsiveness with regard to strain/bending, [1,2] or other external parameters. To leverage these materials toward applications, control over the coupling chemistry at the metal/polymeric interface is critical. Thus, in this work, [3] different surface anchoring strategies in the synthesis of gold/polyaniline core–shell-type nanoparticles are investigated. Synthesized particles are assembled into lines by confinement assembly on surfaces, and the conductive properties of these line assemblies are compared for different synthetic procedures of depositing the polymeric coating onto the gold-nanoparticle core. In particular, we used conductive AFM experiments to reveal that functionalization of gold nanoparticles with 4-aminothiophenol prior to polyaniline-shell formation leads to enhanced conductive properties of fabricated line assemblies composed of hybrid particles compared with established synthetic routes that lack this pre-functionalization step. This provides new perspectives for flexible, particle-based electronic materials.

Polym Int, **70**, 437 (2021)
 Sci Rep **7**, 41981 (2017)
 Colloid Polym Sci (2024). <u>https://doi.org/10.1007/s00396-024-05262-x</u>