Dynamic Complex Emulsions for functional Janus particle design

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The synthesis of nano- to microscale Janus particles with unique functionality or morphology requires creative experimental conditions in opposition to Nature's most efficient surface-to-volume object, the sphere. While many impressive tools exist to generate Janus particles in a bottom-up or top-down approach, these methods are often flexible in their product or easily scalable, but seldom both. To this end, dynamic complex emulsions generated from two liquids miscible above a specific temperature offer one-step generation of a multi-responsive colloidal template. When we replace one or both droplet phases with a photo-polymerizable monomer, the exposed conditions of the monomer-phase on polymerization allow vast opportunity for particle design at each interface. In this context, interfacial assembly enables the self-organization of droplet phases and interfaces into a precision particle. With a dynamically tunable droplet morphology, droplet molds retain a uniform geometry independent of size at the micro- or nanoscale.[1] In one step utilizing amphiphile self-assembly, temperature, and light facilitates the chemical design and conversion of these droplets to particles; with defined form, functionality, and wettability.[2]

The result of this conceptual freedom is the ability to generate highly uniform Janus particles in one step. Morphological tuning of the liquid colloidal template enables the generation of structurally anisotropic Janus particles, which benefit from shape-controlled interfacial behavior and self-assembly due to intrinsic variation of the inter-particle packing density. Pre-assembled functional surfactants at the droplet interfaces can be locked in position upon polymerization, enabling side-selective post-functionalization schemes. In addition, the ability to tune the hydrophilic-lipophilic balance allows the generation of particles with fine-tuned wettability contrast, capable of stabilizing both water-in-air marbles and air-in-water bubbles. We utilized the unique self-assembly behavior of the amphiphilic Janus particles to enhance gaseous oxygen delivery in a liquid-phase catalytic oxidation reaction, improving the reaction rate twofold. Interfacial organization around dynamic complex emulsions facilitates the simple but powerful ability to design Janus particles with programmable size, shape, functionality, and hydrophilic-lipophilic balance, in one scalable step.[3]

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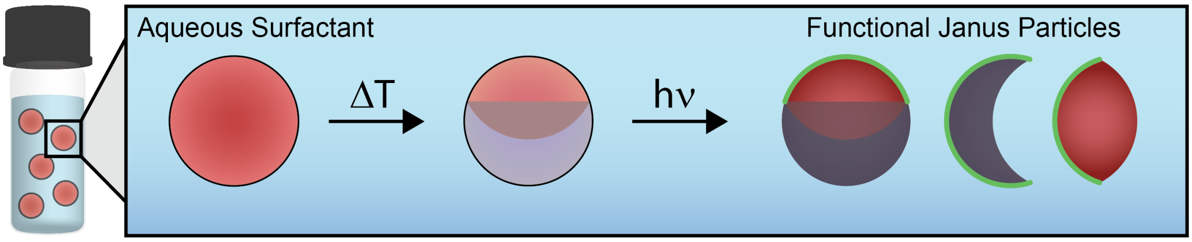

Figure 1. Functional & anisotropic Janus particles generated from complex emulsions, scalebar = 50µm.

Controlled synthesis of poly(ionic liquid) nanovesicles

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Polymer nanovesicles find potential applications in drug delivery, catalyst carriers, and smart nanoreactors, but their controllable synthesis remains a challenge [1-2]. Herein, we report a straightforward, scalable approach towards the fabrication of poly(ionic liquid) (PIL), poly(3-*n*-Decyl-1-vinylimidazolium Bromide, homopolymer nanovesicles with a tunable size of 50-130 nm and shell thickness of 15-68 nm *via* free radical polymerization induced self-assembly. Intriguingly, the overall morphology of PIL nanovesicles has been tuned from hollow to solid vesicles, and finally to directional worms upon increasing the monomer concentration during polymerization as investigated by cryogenic transmission electron microscopy (**Figure 1 a-f**). The monomer concentration, counter anion, and the solvent have been shown to play crucial roles in the morphology transformation of PIL nanovesicles [3].

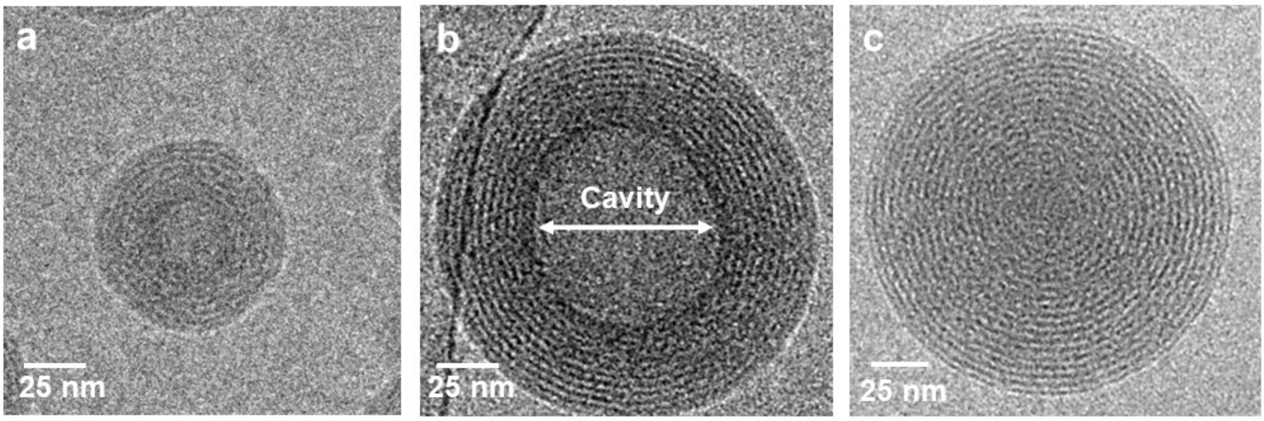

Figure 1. Cryo-TEM images of PIL assemblies prepared at various monomer concentrations: (a) 3 mg/mL, (b, f) 12 mg/mL, (c) 24 mg/mL.

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Dynamic Janus emulsions as foodborne pathogen sensors using stimuli-responsive surfactants

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The development of fast and inexpensive point-of-care sensors is crucial to address the serious public health threat of foodborne pathogenic bacteria. Janus emulsion droplets, composed of hydrocarbon and fluorocarbon oils, are promising liquid sensing devices due to their dynamic nature [1]. The droplets were stabilized using a fluorocarbon surfactant and stimuli-responsive hydrocarbon surfactants, which serve as substrates targeting exoenzymes characteristic for major foodborne pathogenic bacteria, namely *Salmonella enterica, Listeria monocytogenes* and *Escherichia coli*. Upon enzymatic cleavage of the surfactants by extracellular enzymes, their hydrophilic head group is separated from the hydrophobic tail, resulting in a loss of amphiphilicity and therefore an increase of the HC/W interfacial tension at the droplet interface. As a result, rapid, optically detectable changes in the internal droplet morphology occur (Fig.1). We follow such morphological transitions using a customized optical readout platform that is based on a detection of an anisotropic emission signature of dyed complex droplets caused by total internal reflection. To this end, perylene emitters were selectively placed inside the higher refractive index droplet phase, resulting in optical confinement of the perylene emission which transduces changes in the internal droplet morphology. Our system proved to be highly specific, while affording a real-time response with a low detection limit of 10 CFU/mL within 2 h for *Salmonella enterica* and $<10^3$ for *Escherichia coli* and *Listeria monocytogenes*. The implementation of enzyme-cleavable surfactants and Janus emulsions in combination with a novel readout method based on anisotropic light emission both improves the sensitivity of existing liquid sensing platforms, and holds great promise for the sensitive and selective detection of foodborne pathogens.[2]

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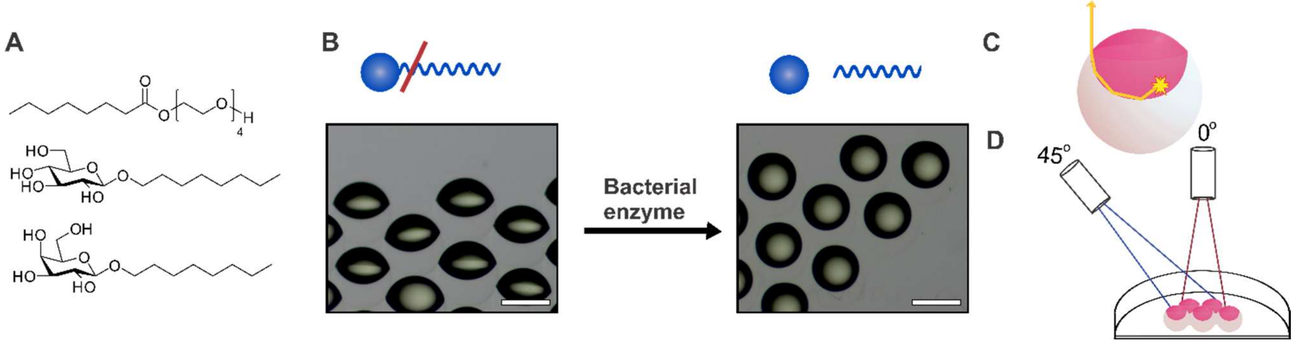
Fig.1 A) Structures of cleavable surfactants. B) Droplet morphology change caused by enzymatic cleavage (scale bar 100µm). C) Total internal reflection in Janus emulsions. D) Our state-of-the art optical ratiometric readout.



Structural and optical properties of (2+1)D colloidal crystals produced by a layer-by-layer approach

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In the natural world, some of the most fascinating colors – i.e. the blue wings of the Morpho butterflies or the brilliant white of the Cyphochilus beetle – are based on tiny layers of complex, hierarchical micro- and nanostructured materials [1], [2]. To mimic these materials, self-assembly of colloidal particles with a few hundred nanometer in size is commonly used [3]. As a result of interactions between the particles, so called colloidal crystals can be formed which show a color based on Bragg diffraction. Commonly, these materials are produced by letting a suspension of colloids evaporate in a controlled manner. Finally, the structures will resemble an fcc lattice, as can be found in metals [3].

One drawback of this technique is the limited control over the colloidal crystal, i.e. controlling the number of layers precisely is difficult and the internal structure is mostly uniform. In this work, we entrap the colloids at the air/water-interface to assemble a monolayer – or 2D colloidal crystal – of particles and transfer it to a glass substrate via the Langmuir-Blodgett technique. By repeating this step, we can precisely control the number of layers. Additionally, it opens the possibility to incorporate absorbing or emitting species at specific positions in the crystal. One method reported in literature is a layer of absorbing material coated onto each particle [4]. But this also changes the parameters of the assembly and influences the order, which in turn has a great influence on the optical appearance [4].

We investigated the order of a layer-by-layer colloidal crystal by calculating the pair correlation function for every layer and compared it to a colloidal crystal produced by evaporative assembly. We found that the orientation of the particles does not translate between layers and the colloidal crystal can be referred to as a (2+1)D colloidal crystal instead of a 3D colloidal crystal [5]. The layer-by-layer colloidal crystal possesses multiple small defects and partial disorder in each monolayer, while the conventional colloidal crystal shows large cracks as grain boundaries. The optical analysis shows that the layer-by-layer colloidal crystal – despite its partial disorder – shows a higher reflection peak for a limited number of layers but the maximum achievable reflection with the layer-by-layer approach is limited due to the accumulation of defects.

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Polyol-assisted synthesis of Copper microparticles and its size-dependent applications

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Colloidal copper particles exhibit excellent catalytic and optoelectronic characteristics, but their synthetic strategies are less common compared to other noble metal particles like gold, silver, or platinum. We proposed a simple additive-based polyol method to synthesize Cu microparticles.[1] Phthalonitrile employed as an additive, influenced the size and properties of the resulting copper particles.

Copper is known to have contraceptive properties and has been clinically used as a non-hormonal intrauterine contraceptive device (IUD) for decades. The spermicidal effect of copper has not been extensively explored and thus we studied the size, concentration, and time-dependent *in vitro* inhibition of bovine spermatozoa by these synthesized copper microparticles.[2]

Additionally, these particles were partially oxidized to $Cu_xO@Cu$ in low concentrations of peroxide. These synthesized colloids displayed outstanding photocatalytic properties and taking advantage of their distinct behavior we investigated the size-dependent (photo)catalytic degradation using rhodamine B (RhB) as a model organic pollutant. Further, followed by an asymmetrization step via deposition of a thin Au layer on one hemisphere, these particles demonstrated their applicability as a photocatalytic micromotor.[1]

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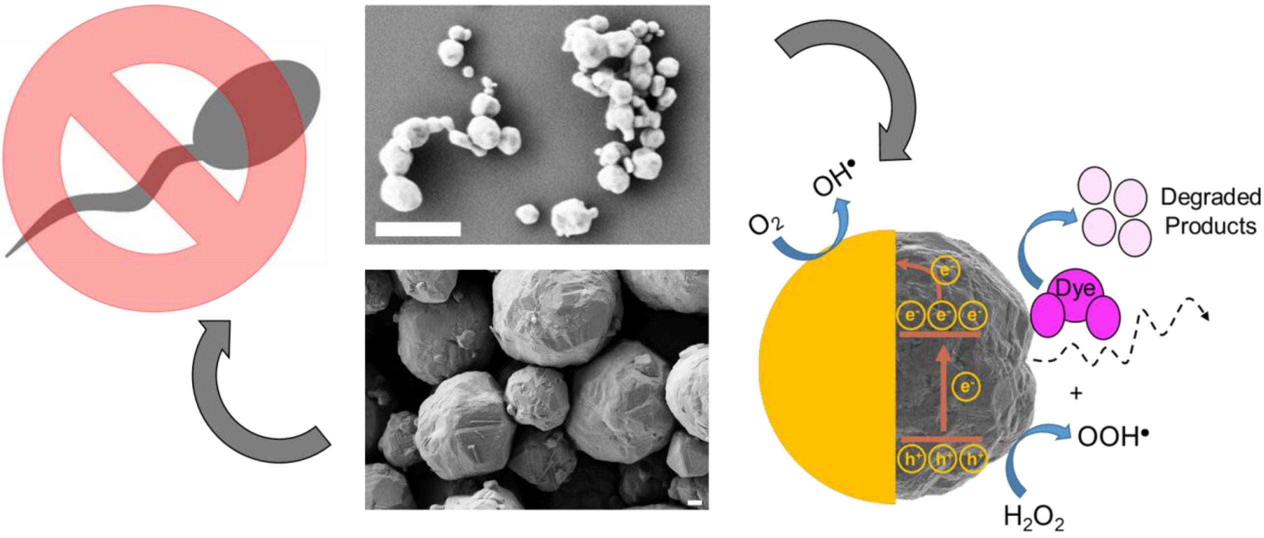

Figure 1. Two different sized copper particles synthesized by assisted polyol method and its application as photocatalytic micromotor and as sperm inhibitor. Scale bar: 1 µm.

Ionization equilibria and swelling behaviour of weak polyampholyte core-shell microgels: A Monte Carlo study

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For polyampholyte microgels, their charge can be tuned by varying the pH and a charge reversal from a positively charged microgel at low pH to a negatively charged microgel at high pH can be achieved. Therefore, a swelling transition from a collapsed to a swollen state occurs when, starting from an average pH value and this value is increased or decreased. Experimental studies indicated an independent ionization of acidic and basic groups in a core-shell microgel, while in a random distribution, there is a mutual influence[1]. Building on our earlier work on alternating polyampholyte microgels, we now investigated the pH-dependent ionization and the swelling behaviour of polyampholyte core-shell microgels with Metropolis Monte Carlo simulations and using the constant-pH method in a bead-spring model[2,3].

As in our previous study on alternating microgels the width of the U-shaped transition in the swelling of the microgels depends on the relative dissociation constants of acid and base[2]. Due to the spatial separation of acid and base, the ionization is less enhanced compared to a microgel with an alternating distribution of the species. However, an independent ionization behaviour cannot be observed. Furthermore, we saw a shift of the isoelectric point towards higher pH caused by a higher charge distribution in the core. Added salt screens the charges within the network, and the U-shape transition becomes more narrow. Radial distribution functions show a clear core-shell structure at low and high pH and a complete interpenetration of the shell in the core at intermediate pH values[4].

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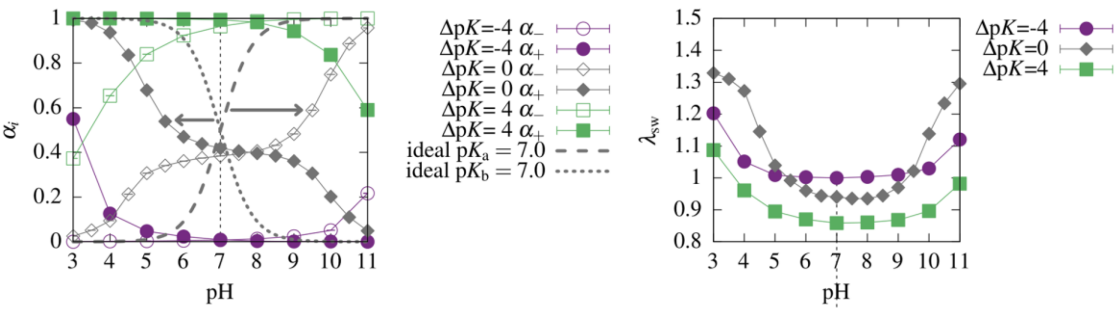

Figure 1. Degree of ionization as a function of pH and different ΔpK (ΔpK=-4: pK_a =9.0, pK_b=5.0; ΔpK=0: pK_a =7.0, pK_b=7.0; ΔpK=+4: pK_a =5.0, pK_b=9.0). Dotted lines represent the ionization of a system without interactions for pK_a=7.0 and pK_b=7.0 (left). Degree of swelling as a function of pH (right).

Reversible structure formation by magnetic nanocubes

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Superparamagnetic iron oxide nanoparticles find wide application in biomedicine [1,2] and materials science, including sensor technologies [3] or ferrofluids [4]. The self-organization of iron oxide nanocubes by evaporation-guided approaches typically leads to mesocrystals with a high structural diversity induced by particle size and shape [5-7]. Similar superstructure formation has been observed in dispersions of magnetic nanoparticles upon application of a magnetic field [8,9]. We have recently observed a clear indication of a reversible, field-induced aggregate formation by the magnetization behavior of concentrated dispersions of iron oxide nanocubes, depending on the particle size [10].

In this contribution we will present our recent SAXS study on the field-induced structure formation of these iron oxide nanocubes. Two different structure factors are revealed, indicating the presence of elongated aggregates and highly symmetric mesocrystals. We will emphasize the field- and time-resolved evolution of the mesocrystal structure and its orientation towards the applied magnetic field [11].

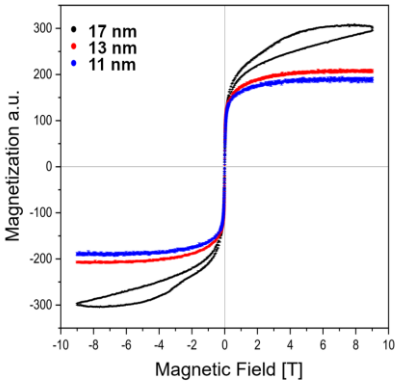

Figure 1. Field-dependent magnetization behavior of highly concentrated nanocube dispersions.

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In situ and ex situ characterization of self assembled colloidal monolayers at air-water interfaces

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Self-assembly at interfaces is an effective and versatile strategy for the fabrication of highly ordered two dimensional colloidal films. Studies on the self-assembly of hard colloidal spheres are typically done with silica and polystyrene particles as building blocks, where the film formation is assisted by various techniques such as a Langmuir-Blodgett trough, spin-coating or self-assembly during solvent evaporation [1-2]. In general, rigid spheres tend to self-assemble into close-packed particle films due to capillary forces at the interface and therefore have only one length scale in interparticle distance [3]. In contrast to that, soft colloidal spheres such as microgels can have a range of interparticle distances due to their deformable nature [4]. In the past few years, core-shell hybrid microgels have received a lot of attentions as they possess properties from both hard and soft spheres [5-6]. However, not much is known about binary systems containing hard and soft spheres. Mixing both types of colloids could introduce controllable defects in assembled colloidal films.

In this study, we investigate binary mixtures of hard and soft colloids at the air-water interface. Previously, we observed strong attractive interactions between both types of colloids in bulk, which led to clustering and gelation of the dispersion. This attraction, already reported in the literature, is a challenge that must be overcome [7]. We tackled this by introducing a thin polymer layer covering the surface of the hard sphere colloids. By means of light microscopy and Langmuir-Blodgett deposition the system was investigated in terms of number ratio under various surface pressures both in and ex situ.

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Direct Measurement of the Forces Acting Between Colloidal Silica Particles

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Natural colloidal dispersions have accompanied mankind in the form of blood or milk ever since. Besides this, artificial systems have gained a significant importance for our daily life during the last decades. From the production of many cosmetics or the water purification and sewage water treatment to the medical field, colloidal systems are widely used nowadays.

For all these applications, it is of special interest to gain an understanding of which interparticle forces govern the stability of colloidal dispersions and how this stability can be tailored. In electrolyte solutions, the classical DLVO theory describes these interactions as a superposition of van der Waals and electrostatic double layer forces. While the simplest description based on the Debye-Hückel superposition approximation provides a good agreement with experimental data for low concentrations and 1:1 electrolytes, larger deviations appear for systems of higher valency [1,2]. For a detailed examination of the van der Waals and electrostatically dominated regimes, we directly measure the forces between a colloidal silica particle and a flat substrate in aqueous solutions by the colloidal probe AFM (atomic force microscopy) technique (Fig. 1 A).

Varying the concentration of sodium chloride solutions allows us to demonstrate the transition from the double layer to the van der Waals dominated regime and the good agreement with the predictions of the DLVO theory for a simple 1:1 electrolyte. Similar measurements for phosphotungstic acid (a 1:3 system with a nanometer-sized anion of the Keggin type) can still be described with the DLVO theory, but reveal significant deviations between the calculated and measured ionic strength (Fig. 1 B). These might be attributed to the decomposition of PTA at pH values above 1.5 described in literature and to the large size of the Keggin ions [3].

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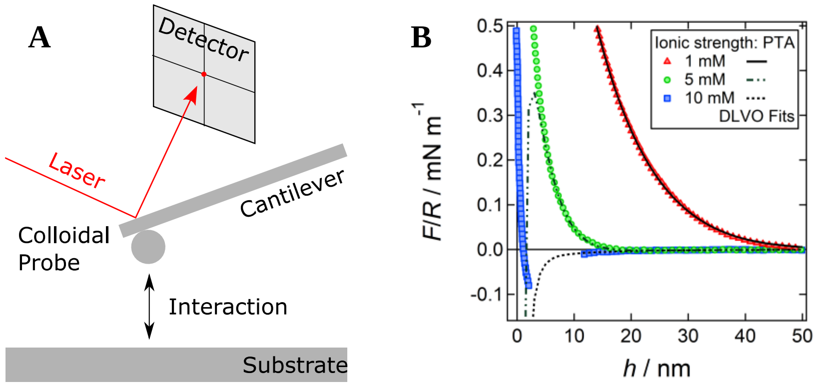

Figure 1. A) Schematic depiction of the colloidal probe technique, where a reflected laser beam records the bending of a cantilever with a colloidal silica sphere attached to it. **B)** Force versus separation curves for phosphotungstic acid (PTA, ionic strength calculated assuming a full dissociation) with the corresponding fits according to the DLVO theory.

Evolution of Magnetization in Sequentially Grown Ferrite Nanoparticles

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Magnetic nanoparticles are technologically relevant for catalysis, high density magnetic data storage, ferrofluids and medical applications [1-2]. A drastically reduced magnetization to the bulk material is commonly observed and attributed to spin disorder in magnetic nanoparticles. Such spin disorder is typically considered confined to the nanoparticle surface but has also been observed in the nanoparticle interior as a result of atomic scale structural defects [3]. Structural defects and the associated spin disorder in nanoparticles have recently been suggested to be beneficial for magnetic heating such as in intracellular magnetic hyperthermia [4]. A key challenge in magnetic nanoparticle research is therefore in the quantitative description and control of the nanoscale distribution of magnetization and spin disorder. Magnetic SANS provides the nanoscale spatial sensitivity to monitor the intraparticle distribution of magnetization and spin disorder [5-6].

In this contribution, we will present our approach to the systematic variation of spin disorder in ferrite nanoparticles upon sequential growth. Our aim is to follow the surface near spin disorder in nanoparticles when the initial surface becomes the interior of the grown particle. Cobalt ferrite and manganese ferrite nanoparticles of varying growth stages are synthesized following an optimized thermal decomposition method involving a seeded growth technique [7]. Structural and magnetic characterization using electron microscopy, SAXS, and magnetization measurements confirms a systematic particle growth (Figure 1) that is accompanied by a significant evolution of the nanoparticle magnetization upon the first growth stages. In the long term, the sequential growth technique might contribute to the engineering of nanoparticles with a tunable surface spin disorder thickness [8].

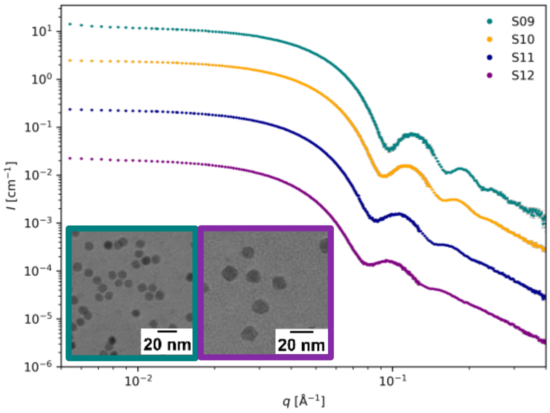

Figure 1. TEM and SAXS by sequentially grown cobalt ferrite nanoparticles.

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How to make a surface act as a micropump

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In this work we investigated the phenomenon of *local* light driven diffusioosmotic (*l*-LDDO) long-range attractive[1] and repulsive[2] interactions between micro-sized objects trapped near a solid wall. The range of the DO flow extends several times the size of microparticles and can be adjusted to point towards or away of the particle by varying irradiation parameters such as intensity or wavelength of light. The “fuel” of the light driven DO flow is a photosensitive surfactant (Figure 1a) which can be photo-isomerized from a more hydrophobic *trans*-state to a rather hydrophilic *cis*-state.[3] The *trans*-isomer tends to accumulate at the interface, while the *cis*-isomer prefers to stay in solution. In combination with a dissimilar photo-isomerization rate at the interface[4] and in bulk solution[5] (Figure 1b), this yields into a concentration gradient of the isomers around single particles resulting in generation of *l*-LDDO flow (Figure 1c).[6] Here we present the extended analysis of the *l*-LDDO flow as a function of irradiation parameters by introducing time dependent development of the concentration excess of isomers near the particle surface and bulk solution. With this we demonstrate that the *l*-LDDO can be generated at any solid/liquid interface being more pronounced in the case of strongly absorbing material likewise human hair and dust particles (Figure 1d,e). This phenomenon has plenty of potential applications since it makes any type of surface to act as a micropump under right illumination conditions.

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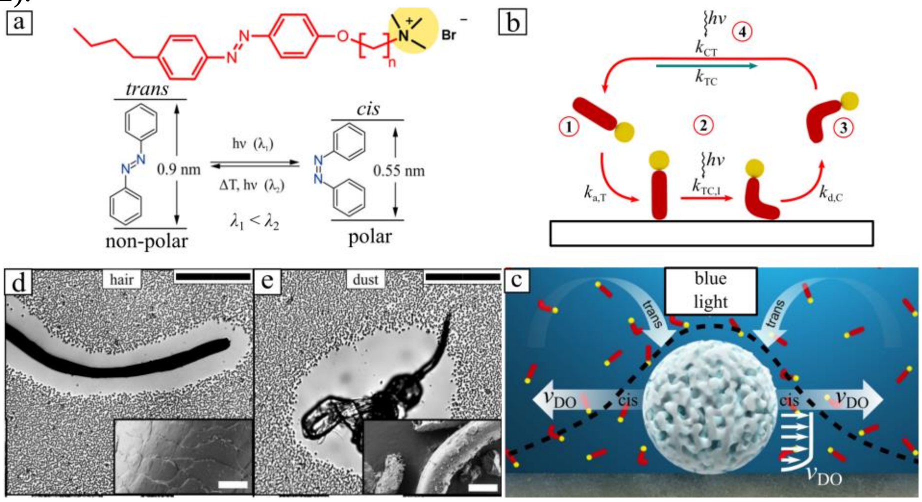

Figure 1. (a) Chemical structure of the photo-sensitive surfactant and the two isomers of the azobenzene group. (b) Cartoon of effective dynamic exchange of both isomers under illumination at bulk and interface, which induces a gradient and a local light driven diffusioosmotic flow illustrated in (c). Optical micrographs of human hair (d) and dust (e) mixed with tracer particles under irradiation with blue light. SEM micrographs of the corresponding surfaces are inserted. Black scale bar is 100 µm, white scale bar is 2 µm.

Impact of ionic strength in the melting temperature of DNA coated colloids

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Microparticles can assemble into superstructures creating colloidal materials with unique properties arising from this structuration [1]. Surface functionalization is an appealing route to program the assembly pathways because it provides a way to encode affinity, specificity and directionality through selection of suitable motifs onto the colloids. A particularly powerful surface functionalization is DNA. Both the affinity and selectivity of hybridization of complementary single DNA strands is modular and to a large extent predictable, such that it can be used to program particles to assemble into a wide range of superstructures [2]. It has been shown that the total coverage of DNA on the particles will determine if particles can roll over each other to anneal into crystalline structures or not [3,4]. Thus, to be able to form crystalline structures and circumvent kinetic traps in assembly pathways the DNA coverage should be maximized. Here, we studied to what extent salt concentration/ionic strength can be used as control parameter to modulate the density of DNA strands covalently attached to polymer-coated polystyrene particles through click chemistry (see cartoon Figure 1). We check the DNA coverage via the melting temperature (Tm), as it has been shown that Tm of the colloidal suspension is a good indicators of DNA coverage [2]. We find that as more salt is added to the click chemistry step, Tm shift to higher values (Figure 1), thus indicating that more DNA is grafted onto the particles and salt is a crucial parameter in controlling DNA coverage of a particle.

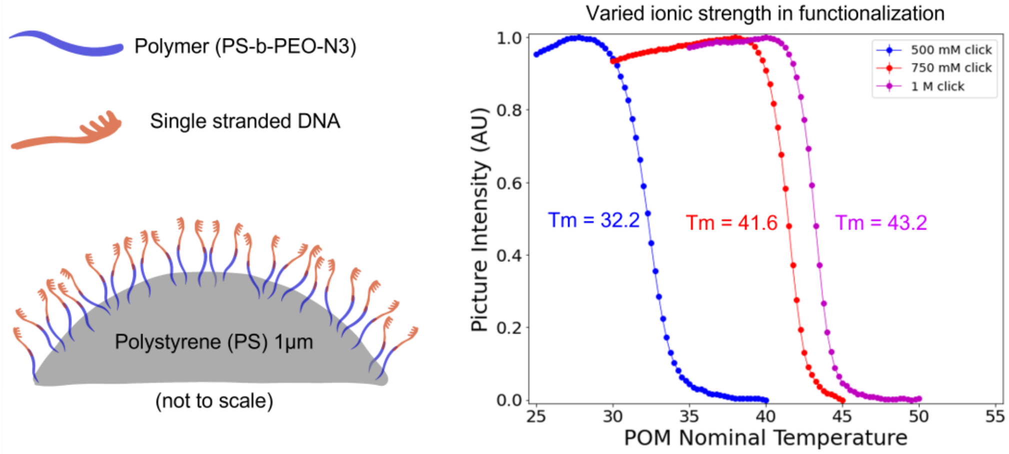

Figure 1. Cartoon of the studied system (left) and measured Tm of colloidal suspensions functionalized at varied ionic strength (right).

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Study on the Mechanical Properties of Interfacial Nanobubbles and Their Interaction with Different Hydrophobic Surfaces

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Due to the unique physical and chemical properties, interfacial nanobubbles (INBs) are widely used in minerals flotation, aquaculture oxygen enrichment, medicine delivery, etc. It is of great significance to understand the special physicochemical characteristics of INBs and the interaction with hydrophilic and hydrophobic surfaces. The morphology of INBs and the interaction between INBs and solid surfaces were investigated by AFM probe tips with different wettability. With hydrophilic probes, it is found that the distance between the first inflection point and the zero point of the approach force curve is equal to the vertical height of the nanobubble [1,2]. There is a positive correlation between the INBs vertical height and the applied force of the tip, i.e., the higher the position of the INBs, the greater is the applied force when reaching the bottom of the INBs. For instance, point a (7.4 nm) and point d (65.4 nm) require 0.7 nN and 6.5 nN, respectively (Figure 1 (a)) [3]. The shapes of INBs are deformed by the medium hydrophobic probe in the horizontal direction, but seriously deformed by the strongly hydrophobic probe. Moreover, the characteristics of the approach force curve show that the dimensions of INBs are underestimated by the medium hydrophobic probe (Figure 1 (b)), however, it cannot be calculated from the force curve tested by the strong hydrophobic probe (Figure 1 (c)). Besides, the maximum attraction and adhesion obtained by the strongly hydrophobic probes are significantly higher than those obtained with the hydrophilic and medium hydrophobic probes.

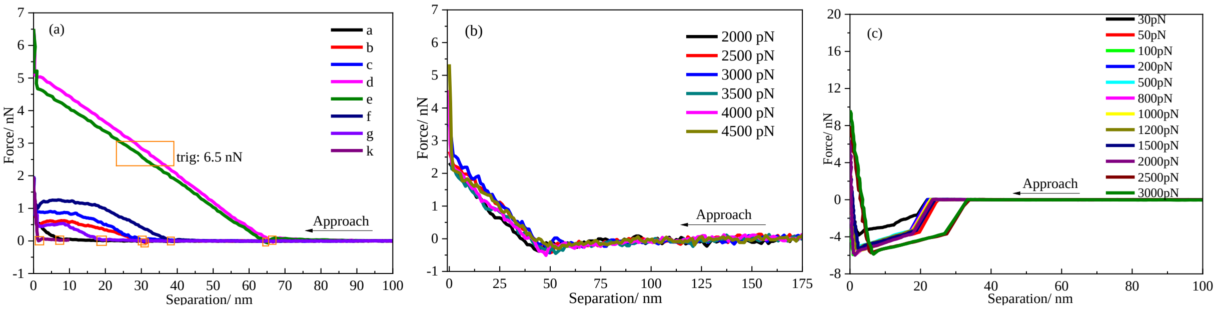

Figure 1. Interaction between INBs and AFM probes with different wettability: (a) interaction of an INB with the hydrophilic probe at its different positions; (b) interaction of an INB with the medium hydrophobic probe at its center; (c) interaction of an INB with the strong hydrophobic probe.

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Microcube Self-Assembly at the Water / Air Interface to Fabricate Multifunctional Microwells for Cell Studies

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Self-assembled objects have been recently identified as an important subclass of smart materials [1]. Unlike the self–assembly of homogenous spherical particles, which possess only one orientation at e.g., the liquid/air interface, the self-assembly of anisotropic, e.g., cubic particles may lead to different structures of aggregates due to different particle orientations at the liquid/air interface [2-5]. Concomitantly, the structure of the aggregates obtained by the self-assembly of cubes (Fig. 1) opens interesting possibility to form combinatorial 3D microwells for systematic cell-environment studies. In particular, the hexagonal aggregates generated by cubes possess different surface properties in an individual microwell. Here we discuss recent progress in the assembly process and the engineering novel 3D microenvironments, which are rendered functional by introducing versatile poly(di(ethylene glycol) methyl ether methacrylate) (PDEGMA) brushes for controlling the interfacial functionalities. Such microenvironments are beneficial to better understand the interactions of individual cells and cell clusters with their surroundings in 3D.

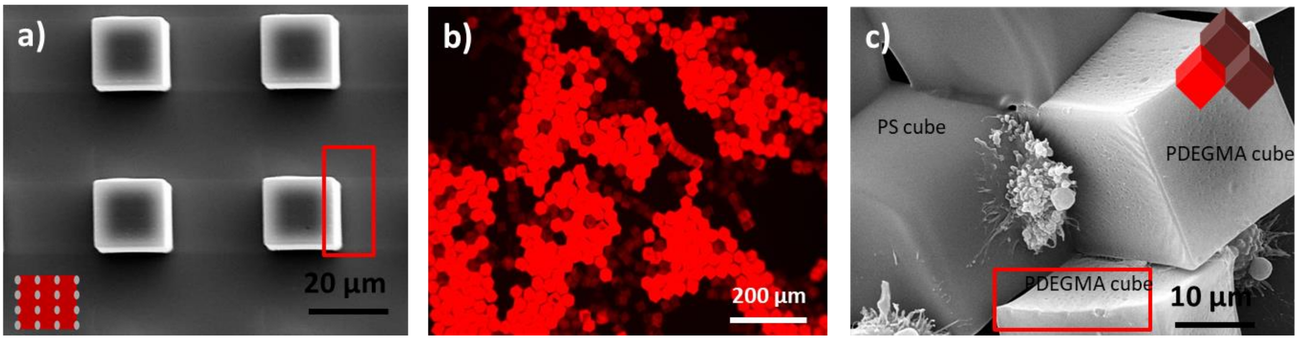

Figure 1. a) Scanning electron microscopy (SEM) image hydrophobic cubes fabricated by the hot embossing technique (top surface labeled with nanopoint patterns), the cube surfaces were pre-modified with a ~30 nm thin Au layer. b) Fluorescence microscope image of co-assembly of non-coated PS cubes and functionalized cubes at the water/air interface (all the cubes were labelled with Nile red). The dark red cubes represent the functionalized cubes and the bright red cubes represent the non-coated polystyrene cubes. c) SEM image of PaTu 8988t cells cultured inside the multifunctional microwells, consisting of 25 nm thick PDEGMA brush and non-coated PS surfaces.

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Generation of local diffusioosmotic flow by light responsive microgels

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Our study shows that microgels trapped at a solid wall can issue liquid flow and transport over distances several times larger than the particle size. The microgel consists of crosslinked poly(*N*-isopropylacrylamide-co-acrylic acid) (PNIPAM-AA) polymer chains loaded with cationic azobenzene-containing photosensitive surfactant, which can assume either a *trans*- or a *cis*-state depending on the wavelength of the applied irradiation.

The microgel, being a selective absorber of *trans*-isomers, responds by changing its volume under irradiation with light of appropriate wavelength at which the *cis*-isomers of the surfactant molecules diffuse out of the particle interior [1]. Together with the change in particle size, the expelled *cis*-isomers form an excess of the concentration and subsequent gradient in osmotic pressure generating a halo of local light-driven diffusioosmotic (*l*-LDDO) flow. The direction and the strength of the *l*-LDDO depends on the intensity and irradiation wavelength, as well as on amount of surfactant absorbed by the microgel. The flow pattern around a microgel is directed radially outward and can be maintained quasi-indefinitely under exposure to blue light when the *trans-/cis-* ratio is 2/1, establishing a photo-stationary state. Irradiation with UV light, on the other hand, generates a radially transient flow pattern, which inverts from inwards to outwards over time at low intensities. By measuring the displacement of tracer particles around neutral microgels during a temperature-induced collapse, we can exclude that a change in particle shape itself causes the flow, i.e., just by expulsion or uptake of water. Ultimately, it is its ability to selectively absorb two isomers of photo-sensitive surfactant under different irradiation conditions that leads to an effective pumping caused by a self-induced diffusioosmotic flow [2].

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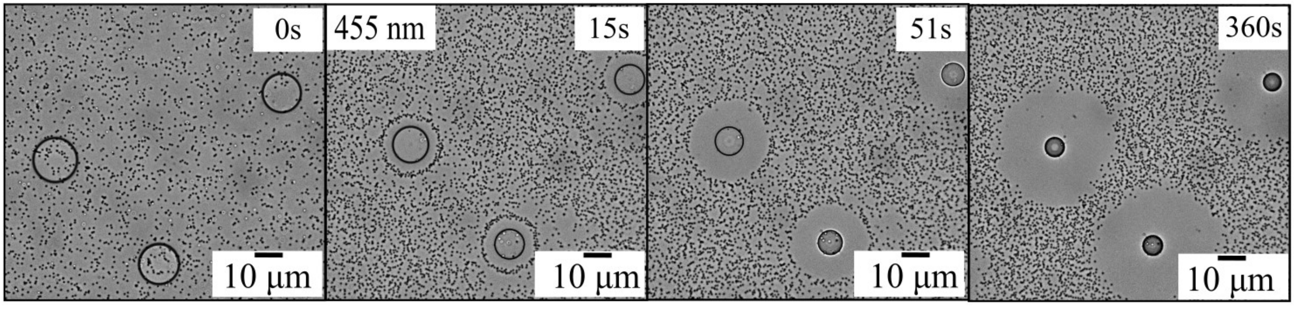

Figure 1. Optical micrographs of the microgel and the tracer particles before irradiation (at 0s) and during exposure to blue light (irradiation time is indicated on the micrographs).

Thermo- and pH-responsive Pickering-emulsions stabilized by NnPAM and NIPMAM core-shell-microgels

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Using thermoresponsive microgels as an emulgator for Pickering-emulsions results in an emulsion that can be broken on demand by varying the temperature. By copolymerizing an acid-function, the emulsion gains an additional pH-responsiveness and can be destabilized by lowering the pH-value.[1] Therefore, these emulsions represent an interesting medium for chemical reactions that involve both water and organic soluble components.[2]

The stabilizing effect of microgels differs from that of rigid particles that are conventionally used to stabilize Pickering-emulsions. Microgels strongly deform at the liquid-liquid-interface to cover a wider area while they adsorb irreversibly. Therefore, the deformability of the microgel is a key parameter for the stabilizing effect.[3]

Usually *N*-isopropylacrylamide (NIPAM) or *N*-isopropylmethacrylamide (NIPMAM) based microgels are used as an emulgator for these emulsions. In this work *N*-*n*-propylacrylamide (NnPAM) and NIPMAM based core-shell microgels copolymerized with methacrylicacid (MAA) containing an NnPAM-co-MAA core, an NIPMAM shell and an additional layer of non-crosslinked NIPMAM dangling ends were used to stabilize emulsions that can by broken by varying the pH and the temperature. By varying the organic phase, it was possible to stabilize both water in oil and oil in water emulsions.

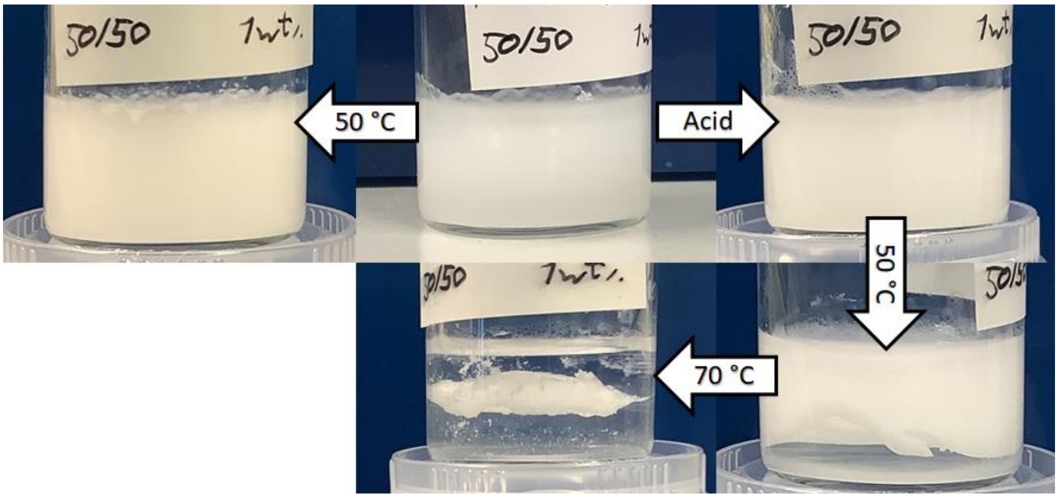

Figure 1. Phase separation behavior of an microgel based Pickering-emulsion under variation of the temperature and the pH-Value.

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Hierarchical Self-Assembly of Triblock Terpolymers into Water-Soluble Multicompartment Micelles[1]

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In nature, compartmentalization into operating regions often functions as a barrier in order to increase efficiency and selectivity of biological reactions. Inspired by that, many scientists focus on the design of multicompartment micelle (MCM) architectures with phase separated nanodomains with applications in cascade catalysis,[2] in nanomedicine as nanocarriers,[3] or to receive stimuli-responsivity. For the design of complex nanostructured MCMs we chose triblock terpolymers as material and a hierarchical self-assembly process as method. Consecutively, in this work we demonstrate the synthesis of amphiphilic PEO-*b*-PS-*b*-PMA triblock terpolymers and their self-assembly into water-soluble spherically patched MCMs on the nanoscale. The synthesis of the triblock terpolymers was achieved by ATRP to receive different degrees of polymerization of the PS and PMA blocks. With control over the block chain length, we obtained terpolymers with systematically varied block weight fractions to research the transformation of the MCMs patch and core morphology. Hierarchical self-assembly was achieved by a stepwise dialysis process using different solvent mixtures. Firstly, spherical Janus precursor micelles were formed, which assemble in a further step to water-soluble MCMs equipped with spherical patches on the surface (**Figure 1**). By means of this strategy, we selectively achieved spheres-on-sphere, spheres-on-cylinder, spheres-on-sheet, and spheres-on-vesicle morphologies, which were confirmed by cryo-TEM.

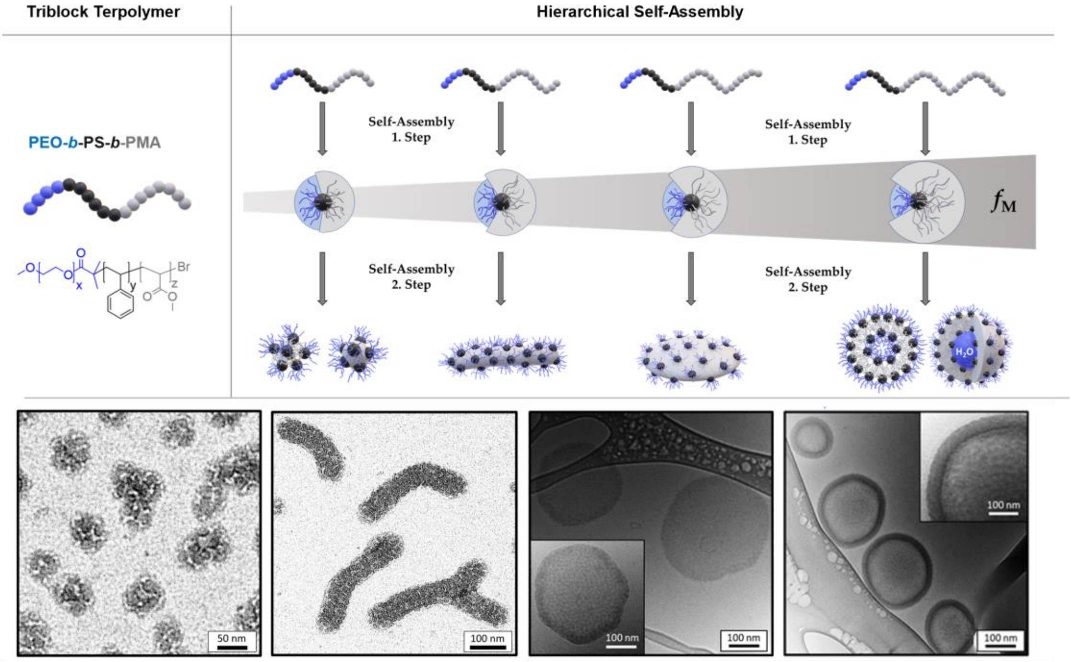

Figure 1. (A) Assembly of triblock terpolymers to spherical Janus precursor micelles followed by the formation to diverse MCMs. PEO (blue), PS (black), PMA (grey).[1]

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Pre-programmed rod-shaped microgels to create multi-directional Anisogels for 3D tissue engineering.

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Microscale anisotropic building blocks have been receiving increasing attention in respect to their use as model systems to study complex phase diagrams, dynamics and self-assembly processes and for their biomedical applications. Tissue engineering is one of them, where rod-like magnetic microgels loaded with superparamagnetic iron oxide nanoparticles (SPIONs) were found to direct cell growth when aligned under a homogeneous magnetic field [1].

We are currently aiming at controlling the magnetic orientation and actuation of such microgels using ferrimagnetic maghemite spindles as anisotropic magnetic fillers instead of SPIONS [2]. Polyethyleneglycol based rod-shaped microgels were designed produced using particle replication in non-wetting templates (PRINT). The maghemite spindles were pre-aligned and self-assembled into dipolar chains during the microgel synthesis as evidenced by the examination of the resulting composite microgels by scanning electron microscopy (SEM) (Figure 1A). This procedure allows us to pre-program the orientation of the composite microgels parallel or perpendicular to the applied magnetic field as shown in Fig. 1B,C. The actuation of these systems by an external rotating magnetic field further offers the possibility to dynamically align the microgels rods with an orthogonal magnetic moment in the third dimension (Figure 1D). When embedded in Anisogels for cell culture, cell growth can be directed in the direction of the pre-programmed microgel rods. (Figure 1E).

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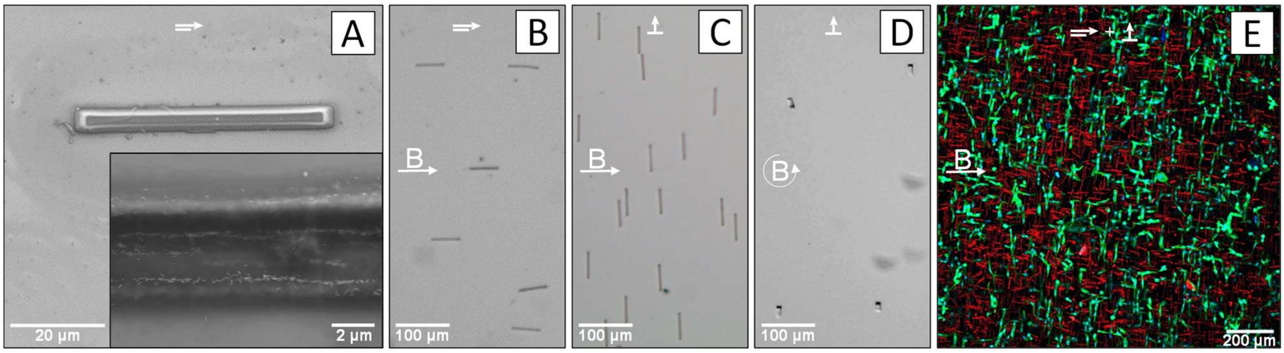

Figure 1. (A) SEM image of incorporated maghemite nanoparticles inside a rod-like microgel. (B,C) Bright field micrographs of the composite microgel alignment parallel and perpendicular to the applied magnetic field. (D) Vertical alignment of the composite microgels with an orthogonal magnetic moment under rotating field (70 mT, 10 rpm). (E) Mouse fibroblast cells growing along parallelly and perpendicularly aligned rod-shaped microgels.

Percolation in binary colloidal systems – introducing direction-dependent thermal properties

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Predicting the properties of a binary mixture of colloids is essential to design new materials for various applications selectively. Several studies exist investigating the behavior of such particle mixtures, investigating full spheres, hollow spheres, and different arrangements of the particles. With these findings, it is possible to predict the thermal and mechanical properties of a material concerning the volume content of its components[1]. The results can be attributed to percolation effects. For particular systems consisting of two particles with various volume fractions, percolation occurs when a continuous connection between the components of one type is formed. Predicting the so-called percolation threshold can be challenging, as it is influenced by the arrangement of the particles and their individual properties. For homogeneous systems, the challenge has been extensively met. But what happens when introducing particles with non-homogenous properties? Does the percolation threshold shift to a higher or lower amount of the anisotropic particles? How does the introduction of direction-dependent properties influence the network behavior?

To study this effect systematically, COMSOL Multiphysics simulations are the tool of choice. This enables the investigation of a vast amount of particle arrangements while changing the particle's properties and vice versa. Furthermore, different particle structures (ordered, disordered) and particle shapes are accessible for statistical analysis. The presented study focuses on the thermal properties of binary mixtures, which can be extended to other mixtures' properties. Therefore, the property of choice to introduce direction-dependency in the system is the thermal conductivity of the single particles. Evaluating the resulting heat flux of the binary colloidal mixture opens the way to establish correlations between structure and the number of anisotropic particles. The final goal is to predict the resulting thermal properties of binary colloidal assemblies containing one or two species of thermally anisotropic components[2].

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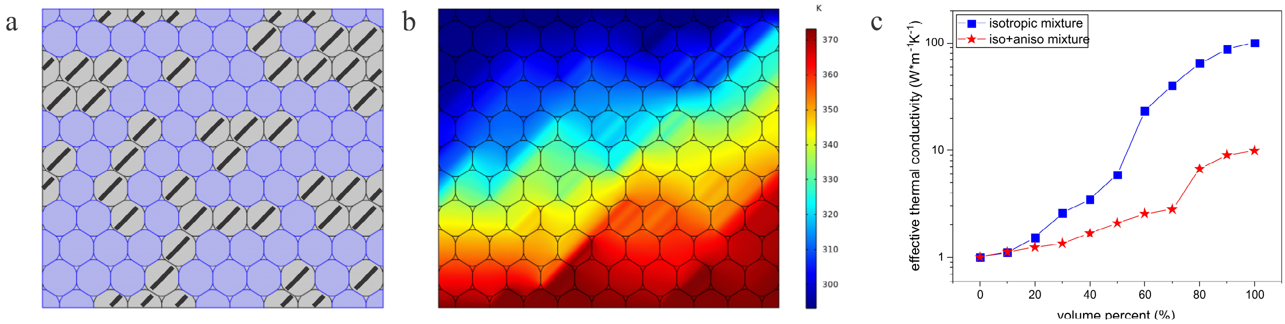

Figure 1. a) 2D-view of a mixture of 50 % isotropic particles (blue) and 50 % thermally anisotropic particles (grey). The preferred way of heat conduction is given by the black lines. b) Resulting steady-state temperature distribution for a temperature gradient of 80 K from bottom to top. c) Effective thermal conductivities for different mixing ratios of a system consisting of two isotropic materials (blue) and a system like in a) (red).

Phase behaviour and percolation of Red Blood Cells

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In the mixture of colloidal particles and polymers, the range and magnitude of the interaction potential can be tuned by the size and volume fraction of the polymers. Depending on the volume fraction of the particles and the interaction potential, colloidal particles and polymers can form a percolated gel-like network.

Similar to colloidal particles, Red Blood Cells (RBCs) exhibit a transition to a solid phase at a sufficiently high enough volume fraction and strong attraction. Depletion and bridging interactions are the two mechanisms for RBC aggregation, underlying the formation of a 3-D network of rouleaux similar to a weak physical gel. Understanding the dynamics of formation and break-up of the 3-D network of RBCs plays an important role in different phenomena, such as RBCs sedimentation or increased hydrodynamic resistance at low shear rates.

In this project, we induce the attraction between RBCs by adding rod-like particles with a high length-to-diameter ratio, as well as small Dextran polymers. The different nature of interaction results in different percolated networks of RBCs. We investigated the phase diagram of the mixture of RBCs and these macromolecules from the gas phase up to percolation using confocal images. To this end, we developed an algorithm to directly determine percolation in 3 dimensions from confocal images of RBCs.

Control of the light-driven flow direction by the irradiation intensity

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We report on interplay of two surface bound flows emanating from thermo-osmotic and diffusio-osmotic mechanisms. The orthogonally directed flows are generated at the gold surface immersed into an aqueous solution containing photo-sensitive surfactant during irradiation with focused light. At low power of incoming UV light, the diffusio-osmotic mechanism generated due to local photo-isomerization of the surfactant dominates resulting in the flow directed out of the irradiated area (**Figure 1a**).[1,2] While at larger power thermo-osmotic flow takes over due to local heating of the gold surface and the flow points towards the hot spot.[3] To image flows, we utilize colloids as tracer particles which can be visualized in an optical microscope.
By simple turning the power one can reversibly sweep the liquid flow between outwards and inwards with an intermittent range of zero flow at which tracer particles undergo only thermal motion (**Figure 1b**). Our work demonstrates an optofluidic type of flow generation enabling a high degree of the net motion control necessary to transport particles precisely on desired locations, which opens a new possibility to generate novel and advanced microfluidic applications.

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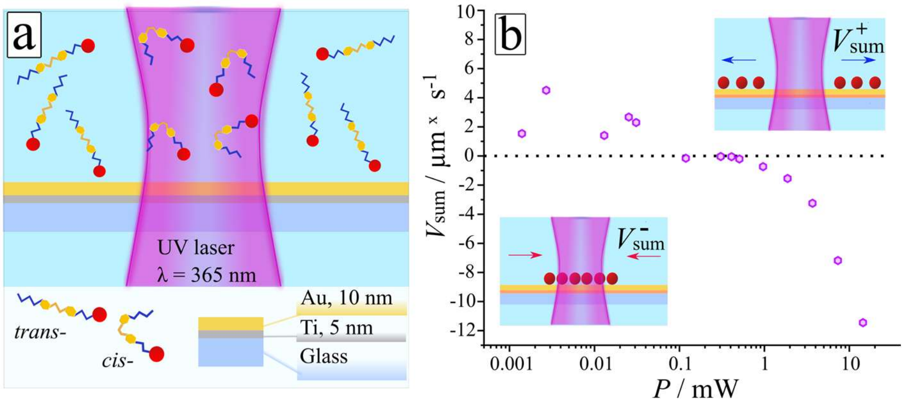

Figure 1. (a) Schemes of the sample: a glass surface is covered by gold layer; the solution above contains tracer particles (red spheres) and photo-sensitive surfactant (cis- and trans- isomers). (b) The average velocity of silica particles as a function of the laser intensity. Inset in the upper right corner representing positive velocities are related to outwards flow, while the negative velocities are assigned to flows pointing towards the laser beam. The laser (λ=375nm) is focused at the Au/liquid interface.

Near-infrared reflective coatings

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The sun's rays hitting the Earth's have a wide spectrum of wavelengths, from ultraviolet to infrared. The absorption of near-infrared (NIR) rays, which constitute 53% of the sun's total rays, is responsible for the heating of objects [1, 2]. The amount of NIR rays increases during the summer season, causing the walls and roofs of buildings to overheat. To reduce the discomfort felt in warm buildings, the usage of air conditioning increased. Buildings coated with a NIR reflective paint absorb less energy, resulting in a 20% - 40% energy savaging through reduced use of air conditioning systems [3, 4].

In this study, different NIR reflective coatings have been prepared by sol-gel reaction of tetraethoxysilane, methyltrimethoxysilane, and TiO_2 based inorganic NIR reflective pigments. The coatings morphology and spectral reflectance were investigated by SEM and UV-VIS-NIR spectrophotometry, respectively. NIR solar reflectance (%) performance of coatings was calculated to examine the effect of pigment concentration on reflectance performance. The coatings showed a maximum of 89% NIR solar reflectance.

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Poly (ionic liquids) templated molybdenum nitride nanoparticles

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The incoming novel approach of hybrid materials has made possible to fulfill various function in a nanoscale range. Among them, molybdenum-based hybrid materials are highly desired for their tunable crystal structure, tunable composition, high temperature and pressure window usage [1-2]. Herein, it is reported a facile method to synthesize templated molybdenum nanoparticles (Mo-NPs) within poly(ionic liquids) (PILs) as main carbon source. Poly(3-*n*-Decyl-1-vinylimidazolium Bromide) was coated with polydopamine (PDA), subsequently coordinated with ammonium orthomolybdate ($(NH_4)_2MoO_4$), followed by calcination in argon atmosphere at 600 °C. Overall, the morphology of PILs after calcination resembles that of porous particles formed by the absorbed Mo-crystal, according to TEM images (Figure 1 a-b). In addition, Mo_2N nanoparticles have been successfully obtained and confirmed by X-ray diffraction (XRD) (Figure 1 c). [3]

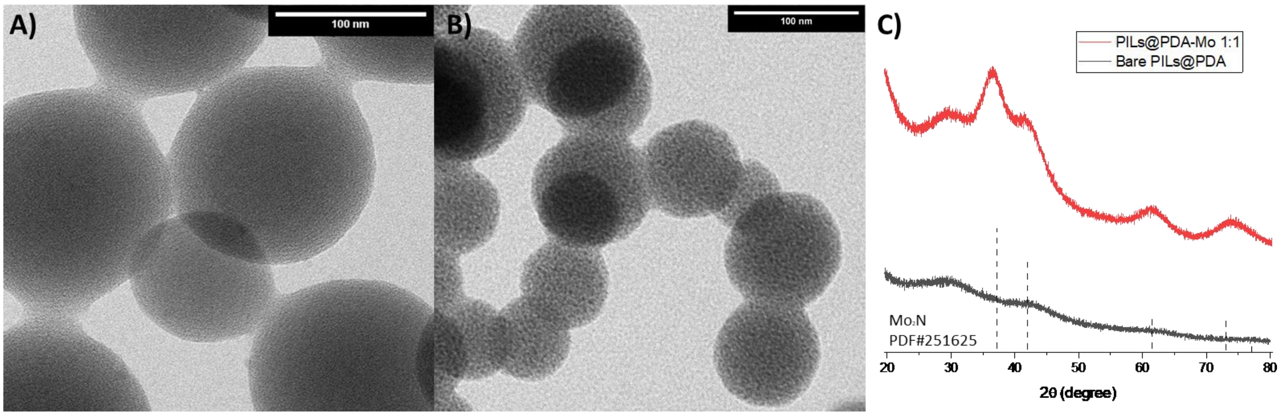

Figure 1. PILs template TEM images, a) after $(NH_4)_2MoO_4$ coordination, b) after calcination, and c) XRD of templated Mo-NPs after calcination

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[2] Y. Zhong, X. Xia, F. Shi, J. Zhan, J. Tu, and H. J. Fan, Advanced Science, vol. 3, no. 5, 2016.
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Towards rapid prototyping of graded macroporous polymer foams

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Graded polymer foams (GPFs) confer substantial mechanical stability in a lightweight form to various natural and technical materials. Their versatile properties are particularly sought after in applications such as energy absorption, insulation, or tissue engineering. For example, ideal bone mimics for tissue engineering recapitulate the solid skin as well as the density gradient towards its center in a way that allows cells and fluids to move freely within. GPFs can be produced using microfluidics (MFs), 3D printing or reaction injection molding. The resulting polymer foam properties can be tuned by using different polymers or by varying their morphology.

Foam templating using microfluidics allows one to adjust GPF parameters like the pore size, the degree of polydispersity and even the window size of the interconnection between pores with ease. Moreover, it can be scaled to liter per hour production rates [1-3]. However, attainable bubble sizes remain usually limited to roughly 100 – 1000 µm and only spherical structures can be produced. Costantini et al. [4] introduced a PDMS chip to formulate gradient foams (Fig. 1 (left)) with controlled bubble sizes spanning one order of magnitude in real time. Conversely, additive manufacturing of GPFs using two-photon-polymerization (2PP) or stereolithography (SLA) offers tantalizing avenues. Fused filament deposition molding allowed Bates et al. [5] to create density gradient scaffolds of ~1 cm honeycombs (Fig. 1 (right)). Improved energy absorption and damping profiles were observed for the graded honeycombs compared to their uniform counterparts. While freeform additive manufacturing usually covers extensive design space freedom, their sequential fabrication puts stringent limits on suitable fabrication volumes, especially for highest resolutions.

This work seeks to establish a combined microfluidic SLA 3D-printing approach for the synthesis of GPFs to combine the advantages of both techniques. For this purpose, ultracompact 3D microfluidic engineering [6] will be tailored for rapid foam production rates, increased bubble size ranges, as well as precise local foam property control. The morphology and the mechanical properties of the resulting GPFs are studied and compared. Our approach will expand the scope of designing innovative gradient and graded materials for tissue engineering, energy absorption, or insulation applications in the future.

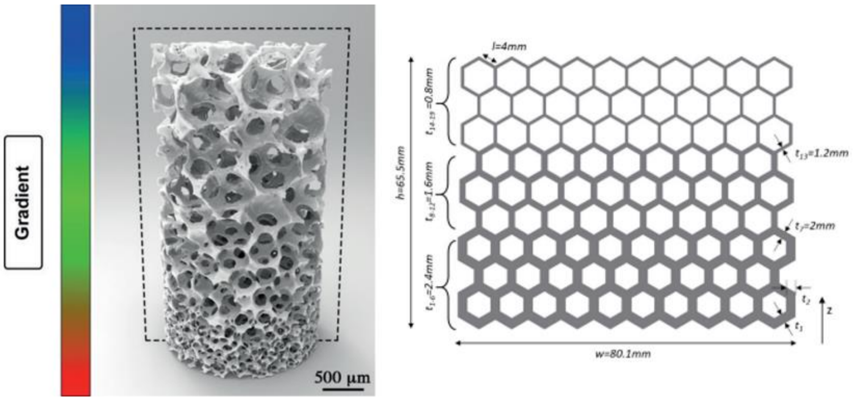

Figure 1: (left) 3D reconstruction of graded porous material [4]. (right) Density graded honeycombs [5].

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Synthesis of Plasmonic Silver Nanowires and Their Surface Modification with Organic Emitters

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Hybrid inorganic-organic plasmonic nanostructures coupled to organic emitters are interesting building blocks for future nanophotonic devices. For example, dye-modified silver nanowires can be used for sub diffractional waveguides (to localise light to nanoscale and guide them to a certain direction) and for chiral sensing (where the organic dyes facilitate detection of the directional, propagating plasmons) [1]. Here I show recent works on our hybrid nanostructure, which consists of modified perylene diimide (mPDI) embedded in a thin silica shell (~8 nm) around the colloidal silver nanowires. I will cover the synthesis of these nanowires and their surface modification [1]. Then I will briefly discuss their use as a chiral sensor and share our latest findings on the photo-bleaching process of the embedded emitters.

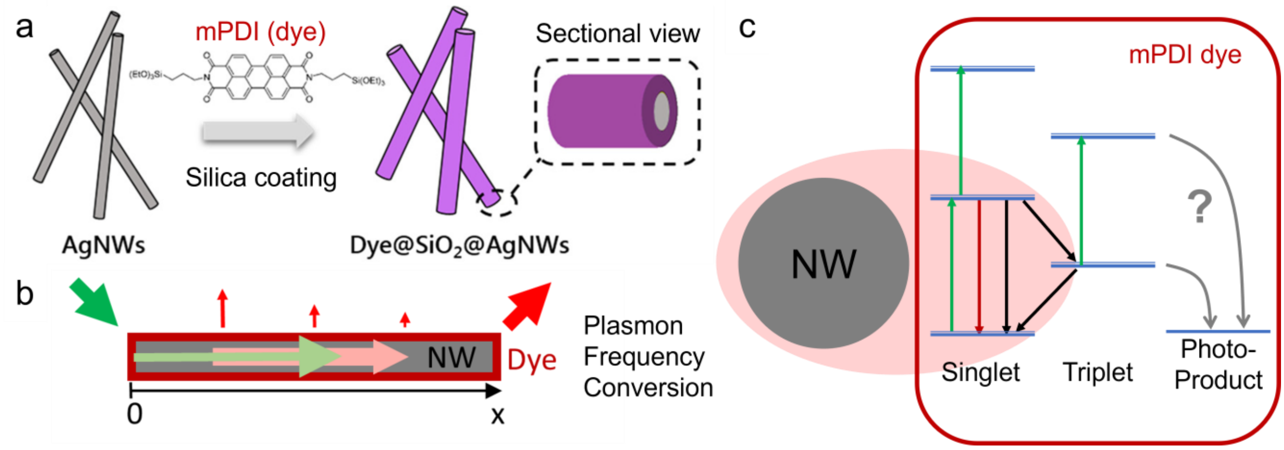

Figure 1. a) Schematic of embedding organic dyes to the silica shell of silver nanowires (NW) to form the metal-organic plasmon converter [1]. b) Schematic of the photobleaching experiment [2]. A single nanowire is excited by a 532 nm continuous wave laser on one end (green arrow). The energy from the laser excites the propagating plasmons (light green arrow) and is also frequency converted (light red arrow). The fluorescence emitted from the dyes are measured (red arrows). c) Simplified Jablonski diagram of the embedded mPDI dye molecules. Green arrows represent excitation, red arrow fluorescence, black arrows non-radiative decay and grey arrows as the irreversible bleaching of the mPDI.

[1] M. Rothe et al. *ACS Nano* **2021** *15* (1), 351-361
[2] M. Rothe et al. *Optics Express* **2022** *submitted*
[3] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG), Sonderforschungsbereich 951 (SFB 951), Hybrid Inorganic/Organic Systems for Opto-Electronics (HIOS)

Duo-stimuli microgels for the control of cell adhesion

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One of the major difficulties in the treatment of cancer is the formation of metastases. Since metastases are often caused by circulating tumor cells (CTCs), their early detection is of great importance. Strategies to isolate and detect CTCs include specific targeting via ligand-receptor interactions, e.g. by using cancer-related receptors like CD44 and their natural ligand hyaluronic acid [1, 2]. Our aim was to create a gentle isolation method for CTCs with hyaluronic acid -functionalized switchable microgels.

For this purpose, HA-functionalized thermoresponsive microgels based on poly-(N-isopropylacrylamide) were prepared and coated on glass surfaces. The prepared microgels were evaluated for size, degree of swelling, surface charge, and ligand functionalization, all parameters that were shown to affect cell attachment. We expected that when the temperature was increased above the lower critical solution temperature (LCST) of 32°C, the cells would show increased binding to the microgels due to an increase in hyaluronic acid density at the microgel surface. When the temperature was lowered below the LCST, the cells would detach due to the lower hyaluronic acid density and the brush-like conformation of the microgels. Therefore, extensive cell adhesion studies were performed on the microgel surfaces at 37°C and 20°C using microscopy and automated cell counting. To enable even more effective detachment of adhered cells, a dual- switchable microgel surface was developed. For this purpose, the hyaluronic acid was coupled to the microgel via a UV-labile linker, which was cleaved off under UV irradiation. Overall, moderately selective adhesion of cells to hyaluronic acid -functionalized microgels was observed, and detachment of cells below LCST was demonstrated as intended. Additionally, it was shown that the adhered cancer cells could be released more efficiently when the UV-labile linker was used. [3]

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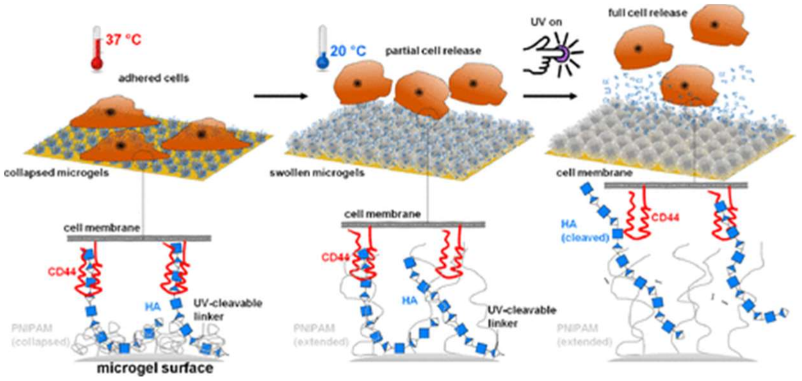

Figure 1. Illustration of the surfaces coated with dual-stimuli responsive HA-functionalized microgels and the expected cell release by temperature and light stimulus.

Effect of surface conductivity on zeta potential of latices in electroacoustic measurements.

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The measurement of electroacoustic colloidal vibration current (CVI) can be used to determine zeta potential of particles even in highly concentrated dispersions without dilution [1]. Most publications analyzing zeta potential with the CVI method have studied concentrated inorganic dispersions. Publications dealing with concentrated polymer latices are quite rare [2].

Surface conductivity effects can often be neglected for the evaluation of CVI experiments. This has considerable advantage because the evaluation of CVI results is associated with significantly less effort. However, our current results indicate that for most of the latex samples we have studied, the consideration of surface conductivity effects is mandatory. Neglecting this would lead to measurement errors of nearly up to 50% in case of very high particle volume fractions, as can be seen in Fig. 1 right side. Surface conductivity effects can be taken into account by determining the Dukhin number $Du = K^{\sigma}/(a \cdot K_{\mathrm{m}})$, which relates surface conductivity K^{σ} to conductivity of the medium K_{m} and particle radius a [3]. The Dukhin number itself was determined by measuring the conductivities of dispersion and medium, K_{s} and K_{m} respectively at different particle volume fractions φ. For this purpose, relative conductivity $K_{\mathrm{s}} \cdot K_{\mathrm{m}}^{-1}$at different particle volume fractions has to be fitted by means of Maxwell-Wagner-O'Konski theory (Eq.1) [4].

$$\frac{K_{\mathrm{s}}}{K_{\mathrm{m}}} = \frac{1 + Du - \varphi(1 - 2Du)}{1 + Du + 0{,}5\varphi(1 - 2Du)} \tag{1}$$

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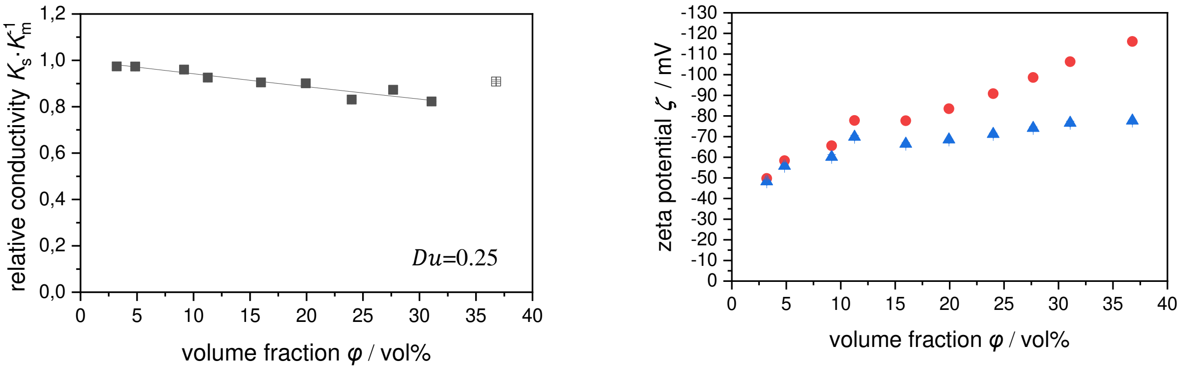

Figure 1. Results of an PVC latex with a d_{50}=0,79 µm. Left side diagram shows relative conductivity data (■). By fitting data to Maxwell-Wagner-O'Konski theory, a Dukhin number of 0.25 was obtained (solid line). The diagram on the right shows the zeta potential without taking surface conductivity into account (●) and taking surface conductivity into account (▲).

Interface Driven Atomically Oriented 2D Assembly of Colloidal Gold Nanodisks Leads to Tunable Plasmonic Resonance

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[1]Surface Physics and Materials Science Division, Saha Institute of Nuclear Physics, Kolkata, India
[2]Institute of Applied Physics, University of Tübingen, Tübingen, Germany
[3]Jülich Centre of Neutron Science (JCNS-1), Forschungszentrum Jülich GmbH, Jülich, Germany
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Colloidal Nanoparticles (NPs) are broadly used to produce self-assembled superstructures, however, a little have been achieved on the 2D assembly of NPs with anisotropic shapes[1]. A key challenge with the anisotropic NPs is to assemble them into long-range positional and orientational order. We synthesize disk-shaped colloidal gold nanocrystals (AuNDs) and assemble them into two-dimensional iso-oriented ordered superlattices at the air-liquid interface using Langmuir method[2-3]. *In-situ* structural and optical properties of the ND assemblies have been monitored using grazing incidence small-angle X-ray scattering (GISAXS), X-ray reflectivity (XRR), grazing incidence X-ray diffraction (GIXD) and UV-vis spectroscopy. Au NDs assemble into a highly ordered 2D hexagonal superlattice and align preferentially with a specific atomic orientation at the air-liquid interface. A continuous blue shift of the plasmonic peak has been observed from the coherent ND assembles with increasing surface pressure[4]. Such preferentially oriented anisotropic NCs is expected to lead to novel optoelectronic properties, which have promising prospects for future applications.

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[3] S. Maiti, S. Maiti, A. Maier, J. Hagenlocher, A. Chumakov, F. Schreiber, M. Scheele, J Phys Chem C 123, (2019), 1519.
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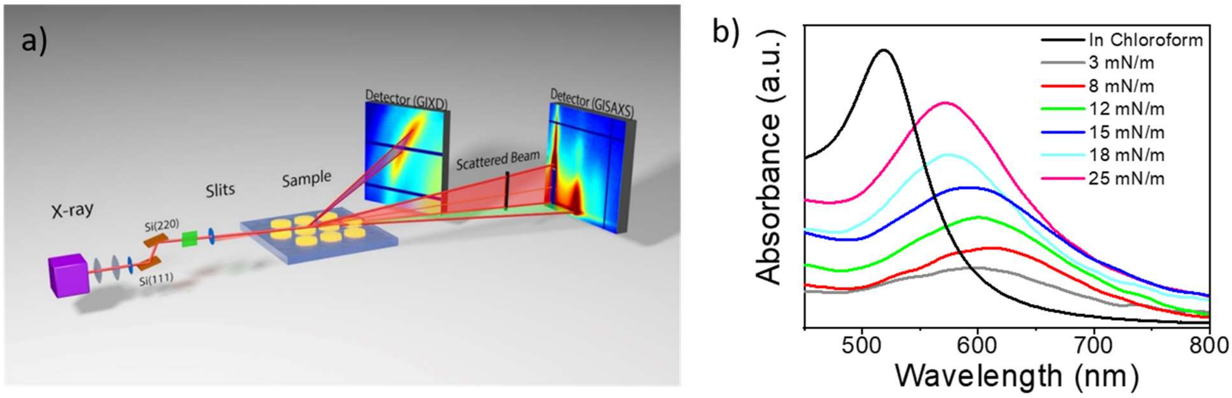

Figure 1. a) A schematic of simultaneous GISAXS, GIXD geometry to study *in-situ* self-assembly at the air-water interface. b) UV-vis absorption spectra of AuND superstructure films.

Cloud point, auto-coacervation, and nematic ordering of micelles formed by ethylene oxide containing carboxylate surfactants

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Independently of temperature and concentration, only spherical or slightly prolate micelles are formed in binary solutions of octyl ether octaethylene oxide carboxylic acid ($[H^+][C_8E_8c^-]$, Akypo™ LF2) in acidic, sodium and calcium forms, due to the surfactant's strong packing constraint. In the presence of sodium or calcium ions, the micelles cannot only be negatively charged, but also intermicellar cross-linking is made feasible by divalent calcium ions or by two monovalent sodium ions. Even in the presence of multivalent ions, the micelles are stable only in two morphologies: the classical core-shell state (L_1) and the water-poor state with partially interdigitated head-groups ($L_1^{'}$). At the borderline of these two regimes, the 'flocculated' micellar regime ($L_1/L_1^{'}$), probably a new wormlike hexagonal (WH) phase made from linear chains of charged prolate micelles is found. The peak shift in SAXS/SANS suggests that the WH phase is an unusual lyotropic liquid crystalline phase because the hydrocarbon cores have the same shape as in the micelles. The WH phase of $[X^+][C_8E_8c^-]$ shares some characteristics with a proposed transition from a classical hexagonal phase of infinite cylinders (H_1) to a cubic Im3m phase by Sakya et al. [1] in binary mixtures of $C_{12}E_{12}OH$ and water. Sakya et al. proposed that undulations form in the hexagonally packed cylinders with the cylinders subsequently being 'pinched' at regular intervals to form the isotropic cubic phase made of spherical micelles. In the case of $[X^+][C_8E_8c^-]$, however, neither a H_1 nor a cubic phase are observed. Instead of a cubic phase made of spherical micelles, a hexagonal phase made of prolate micelles is found. An increase in temperature leads to a decrease of the average number of micelles per chain, 'melting' the hexagonal phase into a nematic phase (N) and eventually into an isotropic micellar phase. While there are some examples of nematic phases made of prolate or oblate micelles made of charged surfactants and a co-surfactant in literature [2,3], they always involve a micellar shape transition through the right ratio between surfactant and co-surfactant. Thus, they are intermediate states between lamellar or H_1 phases and do not form a hexagonal phase made of the same prolate or oblate micelles but have a shape transition to cylinders. In the present case, there is no shape transition involved and all phases are made of the same prolate micelles. The presence or absence of a lower critical solution temperature (LCST) located on the clouding line is related to intermicellar interactions between small spherical or prolate micelles. Clouding is driven by intermicellar attraction and impeded by electrostatic repulsion. If electrostatics are screened, ion bridging can enhance intermicellar attraction especially well at higher concentrations (in the $L_1/L_1^{'}$ phase), thus lowering the LCST and shifting it to higher concentrations. Auto-coacervation triggered by polar head-group heterogeneity occurs as equilibrium between a sub-critical micelle concentration bulk phase and small quantities of a coacervate that is made of macroscopically observable droplets formed by flocculated, partially head-group interdigitated micelles.

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Multicompartment Micelles and Cubosomes from Redispersion of Triblock Terpolymer Bulk Films

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Compartmentalization is ubiquitous in nature, considering for example the working principle of cells and organelles. Despite nature complexity, synthetic counterparts, that could mimic their compartmentalized character, represent an emerging trend. ABC triblock terpolymers are the ideal candidates for the formation of multicompartment micelles (MCMs), due to the possibility to synthesize building blocks, with different chemistries, which can microphase separate in nanocompartments.

In the present work, we investigate the formation of MCMs out of ABC triblock terpolymers, *i.e.*, through redispersion of polymeric bulk films in selective solvents. In particular, we employ polystyrene-*block*-polybutadiene-*block*-poly(*tert* butyl methacrylate) (SBT) triblock terpolymers in acetone/isopropanol solvent mixtures of varying composition (). The largely different block compositions result in diverse morphologies, including spheres-on-spheres, -cylinders, -bilayer sheets and -vesicles, helix-on-cylinders, striped sheets and vesicles, as well as sheets and vesicles with a bicontinuous membrane. Interestingly, below a critical PT corona length (f_{PT} = 5-7 wt%), we were able to identify the first reported example of a multicompartment cubosome (MCC), which in our case consist of a lamella-lamella membrane morphology. We modified these MCCs for catalytical applications by first crosslinking of the PB middle block (outer wall of the membrane) followed by loading with catalysts (*e.g.*, metal nanoparticles such as Pt NPs). Hydrolysis of the PT corona block further converts the MCCs into water-soluble and porous catalyst scaffolds, while the PS inner walls maintain structural stability. Hybrid MCCs loaded with Pt NPs (MCC@Pt) were employed for reduction of methylene blue (MB) to leuco MB, which resulted in enhancement of reaction time. We foresee that such MCCs will serve as platform for catalytical applications due to their larger surface area, porous structure, and overall chemical and mechanical stability.

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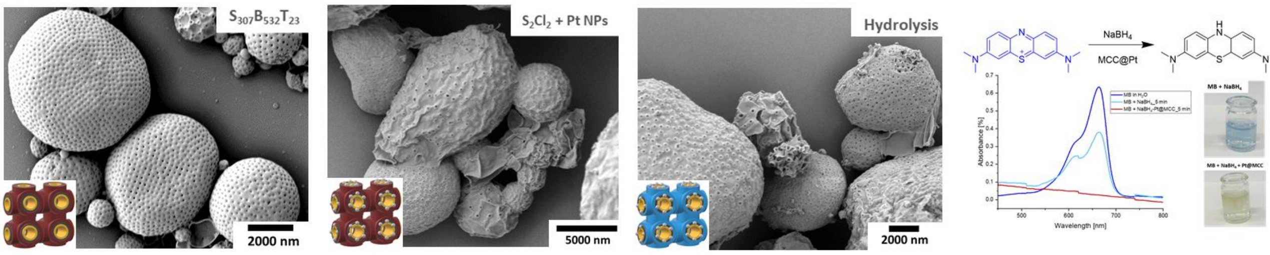

Figure 1. Multicompartment Cubosomes (MCCs) for catalysis application. a) Schematic of formation of water soluble MCCs@Pt; b) $S_{307}B_{532}T_{23}$ in acetone/isopropanol 30:70 v/v; c) MCCs crosslinked with S_2Cl_2 and loaded with Pt NPs; d) Hydrolysis and redispersion in H_2O; e) Reduction of methylene blue to leuco methylene blue catalysed by MCC@Pt.

Janus particles: Challenges in the preparation process and self-thermophoretic propulsion

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Inspired by biological microswimmers (e.g., sperm or flagellated bacteria), scientists began creating artificial microswimmers in the early 21st century. Active colloidal particles with different functionalities at their opposite sides are named Janus particles - motivated by the Roman mythological god. The anisotropy in the particle architecture enables them to generate an out of equilibrium condition around the particle under the right environment, which is a precondition to induce self-propulsion. One possible propulsion mechanism is thermophoretic self-propulsion. When laser light (λ = 532 nm) illuminates a gold-capped particle, a local temperature gradient is generated along the particle surface due to surface plasmon excitation of the gold cap. This gradient perturbs the equilibrium conditions of the surrounding medium and finally leads to particle self-propulsion.

This contribution focuses on various preparation processes of self-thermophoretic gold-polystyrene (Au-PS) microswimmers. The influence of the preparation technique on the gold cap size and the resulting self-thermophoretic behavior of the Janus particle will be presented. For this purpose, Janus particles are prepared either by metal sputtering or thermal evaporation or by a combination of gel trapping technique and metal sputtering. With scanning electron microscopy (SEM), the dimension of the gold cap was investigated. Dark-field microscopy (DFM) combined with a LabView program enables real-time tracking of the Janus particles. The study shows that the preparation method of the Janus particle has a strong effect on the size of the gold cap.

[1] The SEM images were recorded in the materials department at GSI Helmholtzzentrum für Schwerionenforschung GmbH.

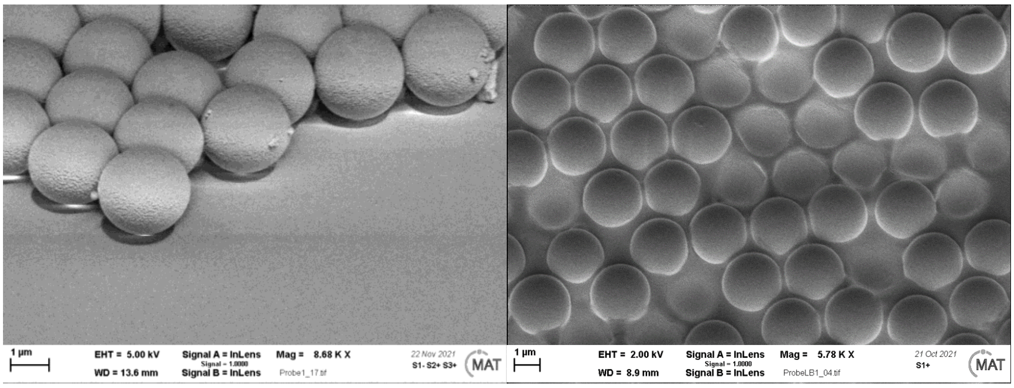

Figure 1. SEM images of Au-PS Janus particles after thermal evaporation (left) and particle embedding + metal sputtering (right). The scale bar represents a length of 1 µm in both images [1].

Mesoporous multicompartment microparticles consisting of semi-crystalline polystyrene-*block*-polybutadiene-*block*-poly(*L*-lactide) (SBL) triblock terpolymers

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Confinement-Assembly of block copolymers (BCPs) are a powerful tool to design a variety of diverse internal structures of multicompartment microparticles (MMs). In particular, mesoporous MMs are highly beneficial and provide promising applications in catalysis, nanomedicine, or energy storage [1]. Nevertheless, less knowledge is gathered about degradation of individual microdomains domains in order to generate mesoporous microparticles with highly complex morphology.

In this contribution, we show the formation of MMs from SBL triblock terpolymers with a semi-crystalline and degradable P*L*LA block. First, SBL triblock terpolymers with different block compositions were synthesized by anionic vinyl and ring-opening polymerization before transformation into MMs *via* evaporation-induced confinement assembly (EICA). After EICA process, we dominantly achieved hexagonally-packed cylinders with a PS matrix, a P*L*LA core and a PB shell. To obtain control about particle size and narrow distribution, the MMs were fabricated through *Shirasu Porous Glass* (SPG) membrane emulsification technique. Furthermore, the variation of the block composition and the affect of the crystallinity exhibit influence on the inner morphology. Degradation studies were performed under basic conditions for selective removal of the P*L*LA domain and reveal mesoporous SBL MMs with clear surface roughness.

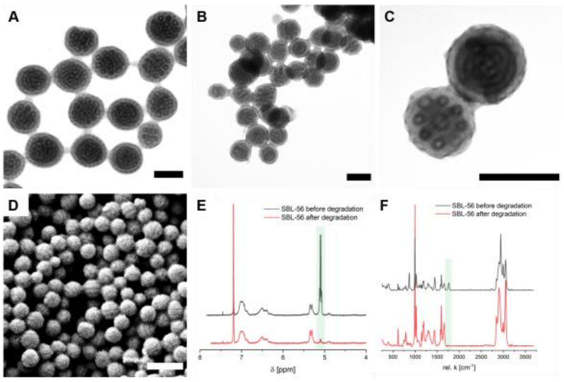

Figure 1. Degradation study of the smallest SBL-56 MMs ($\mathbf{d_{pore} = 0.3\mu m}$) under basic conditions in a course of 5 days. TEM overview before (A) and after (B) degradation experiment (scale bars: 200 nm), C) TEM close-up image and D) SEM images after degradation (scale bars: 500 nm), E) ^{1}H-NMR and F) Raman analysis before (black) and after degradation (red) [2].

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Influence of the hardness on the crystallization behavior of binary polystyrene microgel systems

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Polystyrene (PS) microgel colloids can be used as model systems for hard spheres (HS). Binary mixtures of dispersed small (S) and large (L) PS particles with diameter ratios of S to L close to $\Gamma = 0.8$ have been widely used to investigate glass formation [1]. In purely hard sphere $\Gamma = 0.8$ mixtures the crystallization was found to be kinetically suppressed around the eutectic composition [1,2]. In contrast, simultaneous formation of single component fcc crystals of both components could be enforced at a volume fraction slightly below the glass transition upon addition of a critical amount of free (depletion) PS polymer [3].

Recent investigations of a binary PS microgel system revealed crystallization near the glass transition volume fraction already in case of purely repulsive interactions [4]. Hynninen et al. predicted the so called Laves phases in the investigated region [5]. Static light scattering revealed the crystal structure of the binary system to be $MgZn_2$, a Laves phase of the type AB_2, with an axial ratio consistent with the ideal axial ratio of $c/a = 1.633$. Such Laves phases are of great interest as precursors for the preparation of photonic band gap materials [6,7]. To investigate the crystallization behavior further, we varied the hardness of the PS particles via crosslinking [8]. LaCour et al. predicted that softer particles have a broader region for Laves phases which decreases with higher particle hardness [9]. We prepared and analyzed bimodal systems with different hardness of L and S. By analyzing the crystallization behavior of the different compositions, we found that Laves phases can only be observed if L is the hard and S is the soft component.

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Control of Gold Nanoparticle Suspension Stability by Salt Concentration, Ion-Type and Aging

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Nanocomposite materials based on inorganic inclusions inside an organic matrix are employed in various fields: medical technology, catalysis, materials engineering. Combining the properties of both material classes facilitates high versatility of mechanical, optical and chemical properties, while simultaneously covering obvious drawbacks, e.g. toxicity of many inorganic compounds. One prominent sub-class features gold nanoparticles (AuNPs) in an arbitrary organic matrix (e.g. a polymer brush), since gold provides a distinct set of properties: easy synthesis with variable, well-defined size; versatile surface functionalization via gold-thiol chemistry; antimicrobial behaviour; display of localized surface plasmon resonance (poss. in the visible spectrum) that is sensitive to AuNP parameters (size, shape) and the environment (solvent, neighbouring AuNPs).

To provide the wide range of applications, nanocomposite materials usually require a specific internal structure. Yet, the understanding of the formation of internal structure and control over formation process is still lacking. Therefore, the long-term goal of our project aims to provide an approach to manufacture nanocomposite materials with controlled structure. The model system utilizes salt concentration and ion-specific effects as stimulus to guide the assembly process, since the stimulus is variable and already proven to work [1]. Prior to structure control of the composite materials, the effect of the stimulus on the pure AuNP suspension is necessary. Thus, we investigate AuNP (citrate capping) suspensions with two particles sizes (5 nm, 13 nm) by monitoring their optical response to different sodium salts (anion: F$^-$, Cl$^-$, Br$^-$, I$^-$, SCN$^-$) of different concentration over time. Figure 1 shows photos of AuNP (5 nm) suspensions at various parameter sets [2].

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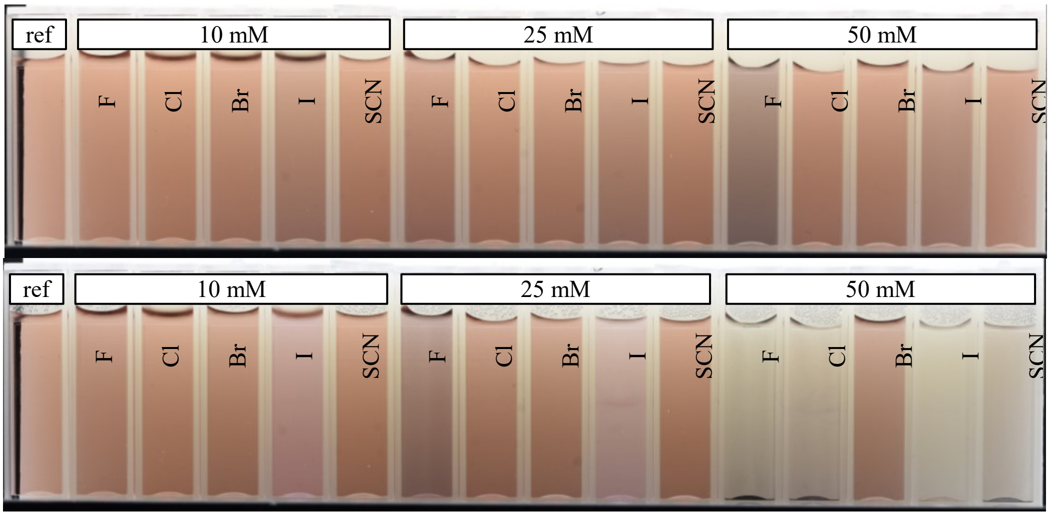

Figure 1: AuNP (5 nm) suspensions with varying salt type and concentration: directly after mixing (upper) and 12 h later (lower). The samples are ordered from left to right with increasing salt concentration and ion size of the sodium salt (F, Cl, Br, I, SCN).

Influence of systematically varied aromatic additive isomers on the phase transition behavior of thermoresponsive Poly(N-isopropylacrylamide) microgels with different cross-linker content

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Thermoresponsive polymers bear a large potential for drug delivery applications, however, the influence of small molecules on the phase transition is a critical issue. Our work investigates the effects of different additives such as benzene derivatives, employed as model drugs, on the phase transition behavior of differently crosslinked Poly(N-isopropylacrylamide)/*N*,*N'*-methylenebis-acrylamide (µ-PNiPAM/x-BIS) microgels. While the homopolymer PNiPAM already has been studied earlier in the presence of aromatic additives, the present work concentrates on a systematic variation of additive isomers and their influence on the phase transition behavior of differently crosslinked microgels[1]. NMR Spectroscopy, Differential Scanning Calorimetry (DSC) and Dynamic Light Scattering (DLS) are employed to determine the Volume Phase Transition Temperatures (VPTT) of polymers in absence and presence of additives. Insights into local dynamics and additive distribution are gained by measuring one dimensional ^{1}H-NMR spectra and transversal relaxation times T_2 in temperature series.

All additives investigated induce a shift ΔT of the VPTT to lower temperatures, consistently determined by all applied methods. It is observed that this shift is depending on the type, position and number of functional groups attached to the aromatic ring. In addition, the crosslinker content influences the sensitivity of the microgel particles towards model drugs considering the same additive in a crosslinker-variation series.. The VPTT depression in dependence on crosslinker content varies somewhat for different parameters considered, which is interpreted as the influence of the network structure.

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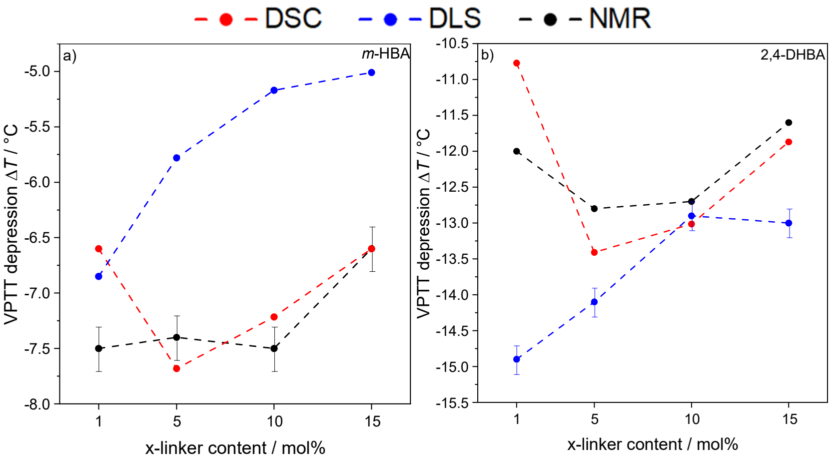

Figure 1. VPTT shifts ΔT of microgels in aqueous solutions with 20 mM *meta*-hydroxy-benzaldehyde (*m*-HBA; (a)) and 20 mM 2,4-Dihydroxybenzaldehyde (2,4-DHBA; (b)) obtained from different methods.

Solid-phase microcontact printing for the preparation of precisely functionalized multi-patch SiO_2 particles

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We present a microcontact printing routine suitable to introduce multiple patches, which are precisely localized at the surface of silicon dioxide (SiO_2) microparticles, and exhibit a well-defined chemical functionality. This method holds great potential for the attachment of functional molecules to up to four different faces at the particles. As a feature of this method, recently introduced solid phase microcontact printing, which contains polymer brush-modified polydimethylsiloxane (PDMS),[1] is adapted in a way to enable addressing SiO_2 particles from multiple sites with certain geometries. Implementing stamps with dimensions, which match the particle size, well-defined particle geometries can be obtained. The presented routine should, therefore, allow the surface modification of particles with the target molecules by keeping the current topography of the aforementioned substrate substantially constant. We anticipate that the advances might stimulate further interest in the anisotropically functionalized particles in the field of directing self-assembly of patchy particles system, or other application fields.[2-4]

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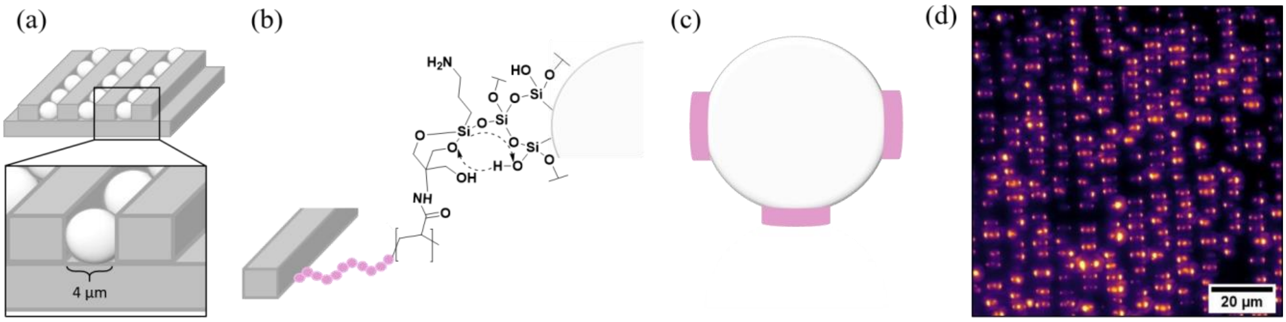

Figure 1. Schematic representation of the microcontact printing process used for the preparation of precisely functionalized multi-patch SiO_2 particles: (a) SiO_2 particles aligned inside the micro channels of PDMS stamp; (b) the transfer of patch material from polymer modified stamp surface to the contact area of the SiO_2 particle; (c) multi-patch SiO_2 particle after microcontact printing; (d) fluorescence microscopy image of the multi-patch SiO_2 particles

Acknowledgement: The authors acknowledge financial support of the European Research Council (ERC) in the framework of the research project Replicoll (Project 648365).

Interaction of microgels with the biomimetic surface

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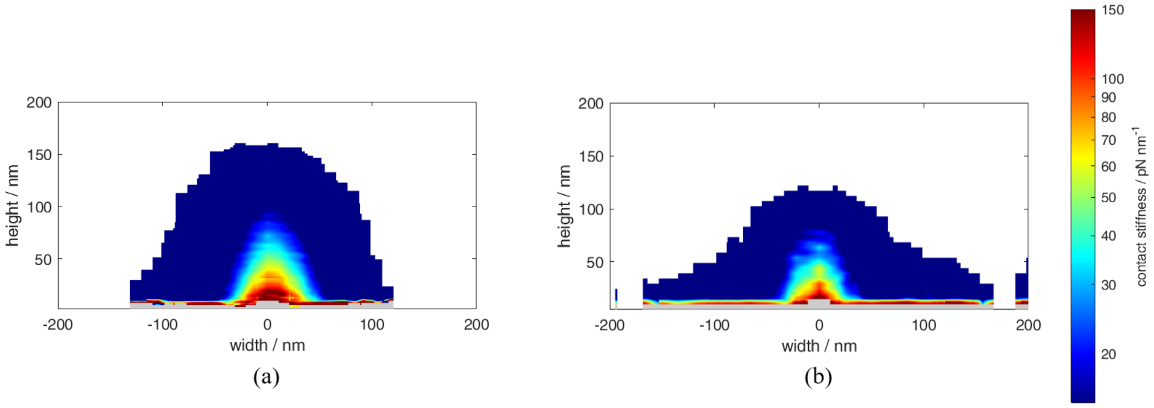
PNIPAM and PNIPMAM microgels are promising agents for various biomedical applications. Though some articles studied how some physicochemical properties of microgels influence their interaction with cells, a detailed understanding is still needed. Important parameters for translocation are microgel softness and its internal structure [1]. Recently it was shown that stiffness and size of the microgels strongly influence their cellular uptake and impact the uptake pathway. [2]. In this work, we investigated how mechanical properties of microgels affect interaction with lipid bilayer.

Atomic force microscopy is a powerful method that allows investigation of mechanical properties, that are related to the internal structure of the material. With this technique we can determine how microgels deform on the interface. Moreover, Force Volume measurements allow determining the stiffness as a function of the three-dimensional position and could be used even for ultra-soft materials [3].

Previously in our group was shown the interaction of microgels with solid-air and solid-liquid interfaces. To continue those findings, we made a first step to the cell membrane surface. We used the simplistic model of the cell surface – supported lipid bilayer (SLB). We prepared SLB based on 1,2-dioleoyl-sn-glycero-3-phosphatidylcholine (DOPC) as model systems for biomimetic surfaces. Then we quantified microgels deformation upon the adsorption to the bilayers (Fig. 1).



(a)

(b)

Figure 1. Average contact stiffness profile of microgels on glass (a) and SLB (b) in water at 27 °C

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Free-Radical Polymerizations in Surfactant-Free Microemulsions

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Today, several systems for polymerizations are known, but especially polymerizations in (micro)emulsion and (micro)suspension comprise an attractive technique. By using microemulsions it is possible to tune the polymer size and morphology, while yields are usually good and temperature control is not a problem. However, the surfactants or auxiliary colloids might have an impact on the latter polymer properties. For example, surfactants have been shown to accelerate the release of small molecules (plasticizers) from a polymeric workpiece into the environment. [1]

Surfactant-free microemulsions (SFME) are ternary, mesostructured liquids consisting of an oil, water, and a hydrotrope. SFMEs were firstly postulated in the late 1970s and found their way to applications as mesostructured reaction systems in the context of enzymatic reactions in the 1980s [2,3]. However, it took until the last two decades that SFMEs were investigated in more detail. [4] In terms of polymerizations, only a limited number of studies in SFME were presented in the last years. All of them present quite special applications. [5,6]

We present a simple system composed of water, the monomer methyl methacrylate as the oil phase, and simple alcohols (iso-propanol, n-propanol, tert-butyl alcohol) as hydrotropes. The alcohols were chosen, as they can be separated simply by distillation after polymerization, if dry polymers are of interest. Polymerizations can be performed using commercial thermal initiators such as peroxodicarbonates, redox-activated systems or UV-activated initiators. By the choice of the exact position to polymerize in the phase diagram, which should be preferably in the pre-Ouzo region close to the phase-border left-hand of the critical point, it is possible to affect the polymer morphology, yield, and mean molar mass. [7]

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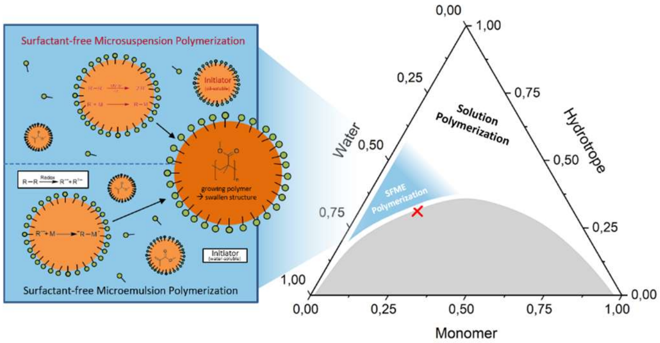

Figure 1. Water – alcohol (as iso-Propanol or tert-Butanol) – (vinyl) monomer structured mixtures (SFME), for which polymerization can be fined-tuned, concerning morphology, yield, and mean molar mass.

Molecular Handedness Detection with Induced Chirality in Plasmonic Lattice Modes

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Plasmonic nanoparticles placed in lattices enable the localised plasmonic resonances (LSPR) to couple to Bragg modes leading to the appearance of surface lattice resonances (SLR). Such resonances can mitigate losses from individual structures and thus show spectrally narrower features (see e.g. white arrows in **Figure 1**, right top inset).[1]

We recently reported the first excitation of surface lattice resonances in arrays of the intrinsic chiral nanocrescent building blocks. These chiral SLRs show the same preference and sign of circular dichroism (CD) as the localised resonances of the metamolecules, while exhibiting a similar narrowing as non-chiral lattice modes.[2] Here, we complete the scene and extend chirality transfer from metamolecules (chiral nanocrescents) to an actual molecular-induced chirality transfer to lattices modes of arrays of achiral gold nanoparticles. We use the synthesis and self-assembly of core-shell gold nanoparticles (AuNPs@PNiPAm) to allow a uniform coverage of substrates over large areas (> cm^2) with hexagonal particle monolayers that have tuneable lattice parameters. The achiral arrays of AuNPs are homogenously covered with randomly oriented chiral molecules of one enaniomer. Illumination with circularly polarized light shows that the chirality of the molecules is not only transferred to LSPRs[3], but also to the lattice modes of the AuNP arrays as revealed by a circular dichroism signal at the wavelength of the SLR (**Figure 1**).[4] This allows to reveal the handedness of a molecule by SLRs. We extend our experiments by numerical and theoretical calculations to examine the underlying transfer mechanism from molecules to plasmonic lattice resonances. Chirality transfer to lattice modes has, to the best of our knowledge, not been observed before.[4]

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European Union's Horizon 2020 grant agreement No 861950 project POSEIDON.

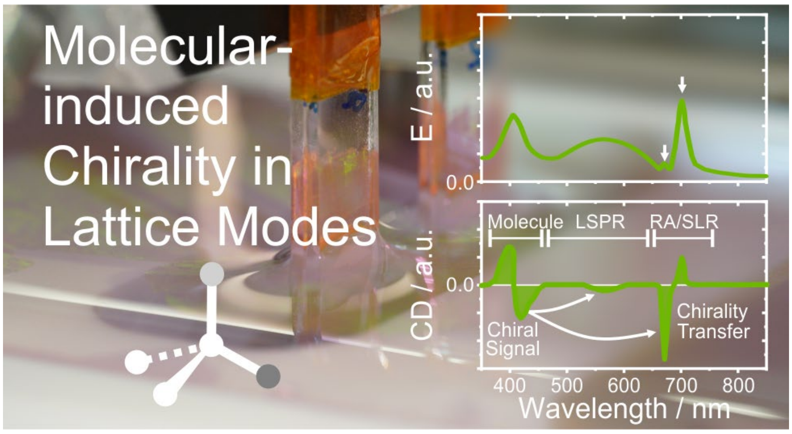

Figure 1. Self-assembly of core-shell AuNPs@PNiPAm) at the air-water interface with a langmuir blodgett trough. Arrays of well-defined AuNPs can reveal the handedness of chiral molecules via induced chirality. This transfers a CD signal from the molecular region to the lattice modes (arrows) of the array, allowing an easy detection in the visible range.

Grain boundary conductivity in hybrid perovskite crystallite clusters

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Hybrid organic-inorganic perovskite semiconductors, based on the prototype compound methylammonium lead iodide ($MAPbI_3$), are successfully applied as absorber materials in photovoltaic devices reaching power conversion efficiencies of 25.7% as of 2022 [1]. Prepared from solution, perovskite solar cells allow for an inexpensive, low-temperature fabrication. The crystallization of the polycrystalline perovskite thin films ensues from a precursor solution that is viewed as a colloidal dispersion. The colloid chemistry of this dispersion can affect the film morphology by changing the crystal size, orientation and density of the resulting perovskite layer [2]. In this study, we investigated the influence of the film morphology on the electrical transport properties between adjacent $MAPbI_3$ crystallites: By contacting an interconnected crystallite cluster with a gold electrode, we were able to determine the current flow between crystallites via conductive atomic force microscopy (cAFM) and directly correlate the conductivity to the respective grain boundary morphology. While the contact area between adjacent crystallites appeared to have a negligible impact, the grain boundary morphology strongly affected its conductivity. Therefore, a more controlled crystallization from the precursor dispersion could minimize current losses at grain boundaries by increasing crystallite size, orientation and density.

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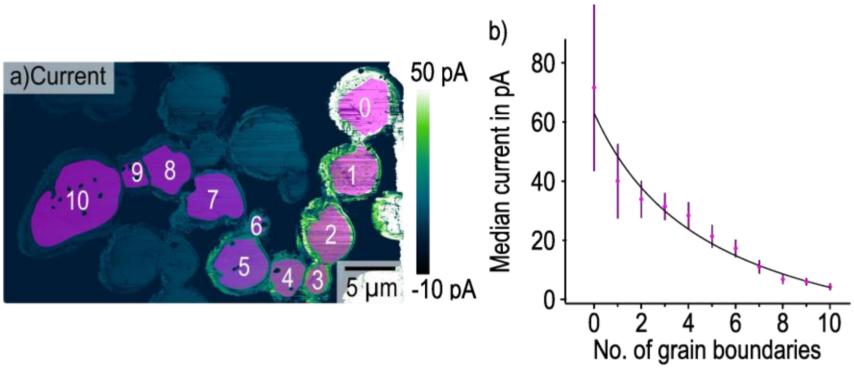

Figure 1. a) CAFM measurement on interconnected $MAPbI_3$ crystallite cluster in contact with gold electrode on the right side of the image. All crystallites are numbered according to the amount of grain boundaries between the gold electrode and the current detection via the conductive AFM tip. b) Median current measured on each of the numbered crystallites.

Cu^{2+} and temperature dual-responsive microgels for smart foams preparation

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Smart foams that can be stabilized and destabilized at will are highly desirable especially for the industrial use of froth flotation in recovering heavy metal ions (e.g. Cu^{2+}) from polluted aqueous environment[1-2]. This study was aimed to developing a Cu^{2+} sensitive foam stabilized by microgels, targeting for selective recovery of Cu^{2+} from competitive ions.

Firstly, a Cu^{2+}-responsive thermo-sensitive poly (N-Isopropylacrylamide-co-Vinyl imidazole) (PNV) microgel was synthesized, and Cu^{2+}-imidazole complexation was demonstrated to enhance the microgel swelling with a softer and more homogenous microstructure and a significant volume phase transition temperature (VPTT) shift to higher temperatures, and the swelling/deswelling was tuneable by Cu^{2+} concentration.

Secondly, temperature responsive foams with a ultra-stability below VPTT of the microgel and a rapid collapse above the VPTT were readily produced based on PNV microgels. Cu^{2+} complexation enabled a modulation of temperature responsiveness of the foams, able to maintain a good foam stability above a critical temperature where foams collapsed for other cations (e.g. Na^+, Mg^{2+}, Zn^{2+}), showing significance for selective recovery of Cu^{2+} from competitive ions.

Furthermore, an interfacial study revealed a better surface activity of Cu^{2+} -complexed PNV microgel with a less temperature dependence, and the responsive foam destabilization was dominated by an abrupt reduction of surface shear viscoelasticity that was avoidable by entanglements between Cu^{2+}-complexed PNV microgels[3].

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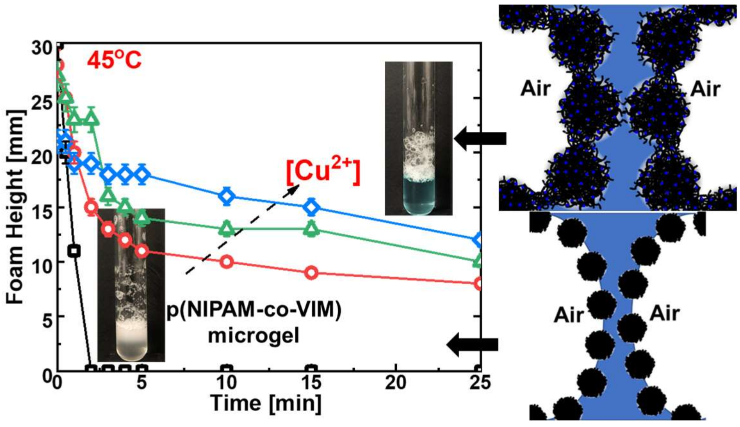

Figure 1. Foam height versus time for PNV microgels with varied Cu^{2+} concentrations and schematics of possible response of the microgel laden air-water interfaces.

Binding of biotin-functionalized and mannose-functionalized, thermosensitive microgels on receptor surfaces: Effect of the volume phase transition

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Almost all biological processes on the cellular scale are mediated by ligand-receptor interactions between biomolecules such as proteins and carbohydrates e.g. cell-cell communication, pathogen invasion, or cell development. To study and mimic these interactions, microgels can be functionalized with bioligands, thus binding of these ligand-presenting polymer scaffolds to receptor systems can be achieved in order to control biological functions. Responsive “smart” microgels could enable a more profound control of these functions. For example, by undergoing a phase transition upon external stimuli, the biomolecular interactions of the ligand-functionalized microgels can be activated and deactivated [1].

Thermoresponsive microgels based on poly *N*-isopropylacrylamide P(NIPAM) exhibit a volume phase transition in a biologically applicable range near the temperature of 32 °C [2]. Two different microgel systems were characterized in terms of their binding properties above and below the volume phase transition temperature (VPTT). For this purpose, mannose- and biotin-functionalized P(NIPAM) microgels and corresponding protein-receptor surfaces were prepared. Inhibition assays were performed below and above the VPTT and the binding of the microgels to the protein surfaces was measured at different inhibitor concentrations by detecting their presence on the receptor surfaces via fluorescence spectroscopy and microscopy. It was found that the biotin-functionalized microgels bind to the avidin surface at temperatures below the VPTT, whereas they do not bind to the surface at 40 °C. We assume that the hydrophobic biotin ligands are located within the polymer network above the VPTT and are thus not available for the specific binding to the surface. In contrast, the mannose-functionalized microgels bind to the ConA surfaces at temperatures above the VPTT. This is presumably due to a higher density of hydrophilic mannose ligands at the microgel-water interface above the VPTT.

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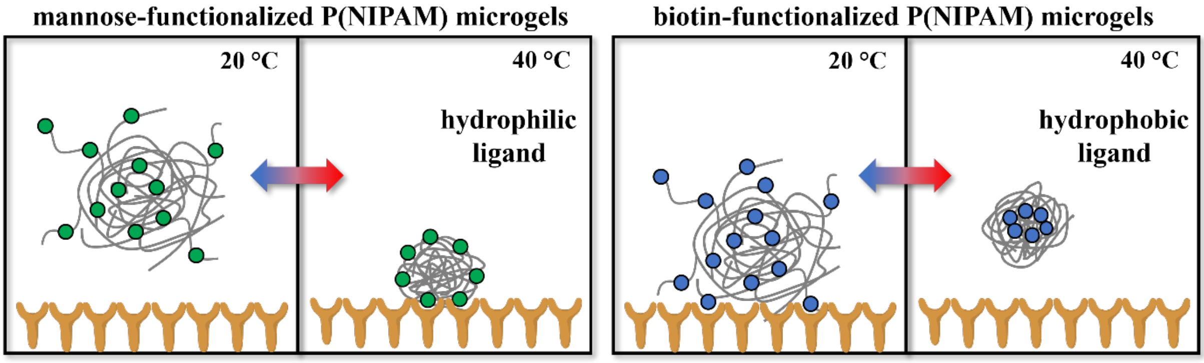

Figure 1. An illustration of mannose- and biotin-functionalized microgels on receptor surfaces. The change in microgel adhesion upon varying the temperature below and above the VPTT is shown. The biotin-functionalized microgels bind to the avidin surface at temperatures below the VPTT, whereas they do not bind to the surface at 40 °C (right). In contrast, the mannose-functionalized microgels bind to the ConA surfaces at temperatures above the VPTT (left).

Buckling and Interfacial Deformation of Fluorescent Poly(*N*-Isopropylacrylamide) Microgel Capsules

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Hollow microgels are fascinating model systems at the crossover be-tween polymer vesicles, emulsions and colloids as they deform, interpenetrate and eventually shrink at higher volume fraction or when subjected to an external stress. Furthermore, their hollow architecture makes them ideal candidates as nanocarriers. Here, we introduce a new system consisting of micron-sized microgels with a large micron-sized cavity enabling a straightforward characterization in situ using fluorescence microscopy techniques. These capsules are found to reversibly buckle above a critical osmotic pressure, conversely to smaller hollow microgels, which were previously reported to deswell at high volume fraction. Simulations performed on monomer-resolved in silico microgel capsules confirm the buckling transition and that the presented capsules can be described with a thin shell model theory leading to a direct estimation of their elasticity. The latter refers to a Young modulus that is experimentally determined to be lower than that of usual polymeric capsules. When brought to the air-water or oil-water interfaces, these microgel capsules strongly deform and we thus propose to utilize them to locally probe interfacial properties within a soft capsule model adapted from the JKR theory.

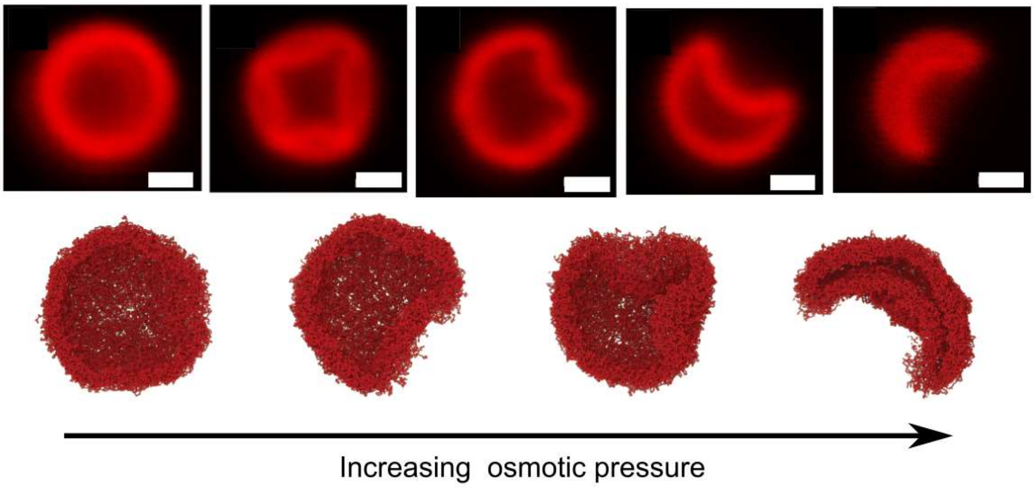

Figure 1. (Top) CLSM micrographs of the microgel capsules obtained from the maximum intensity projection of z-stack highlighting typical configurations observed upon increasing osmotic pressure by addition of PEG 8000. Scale bars: 500 nm. (Bottom) Simulation snapshots of the hollow microgel across the buckling transition.

State Diagram of Soft Dipolar Ellipsoids

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Dispersions of anisotropic ellipsoidal particles are investigated using confocal laser scanning microscopy (CLSM). The particles were obtained by post-processing spherical particles into prolates with an aspect ratio of by mechanical stretching and consist of a polystyrene core surrounded by fluorescent microgel shell [1]. Their phase behavior is explored as function of the volume fraction across the glass transition under deionized conditions at 20 °C. We study the structure and dynamics of dispersions at various volume fractions, the influence of an external electric field on the phase diagram and the metastability of the resulting phases. Our results, supported by Monte Carlo simulations, evidence the organization of the polarized ellipsoids into columnar phases or a face center tetragonal (FCT) crystals with increasing dipolar coupling at high volume fractions with a persisting nematic ordering when the field is turned off at the highest volume fraction.

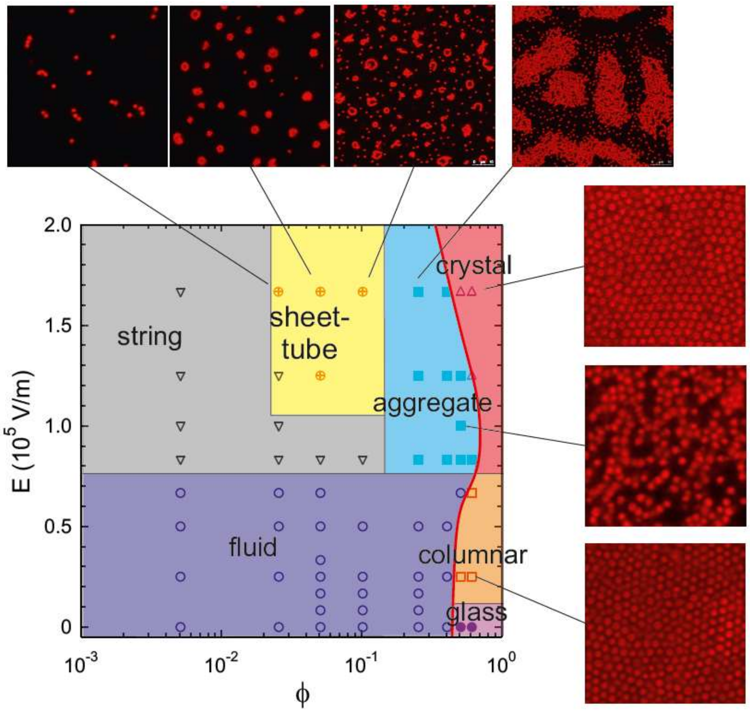

Figure 1. Experimental state diagram of dipolar ellipsoids with an aspect ratio of 3.3 polarized by an alternating electric field determined via confocal microscopy.

Reference

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Drying of Responsive Microgels

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At higher volume fractions, depending on their degree of crosslinking, such soft microgels may further interpenetrate, deform and facet with direct consequences on their collective properties. We discuss how the interplay of molecular and colloidal scales controls drying of microgel dispersions. This is achieved by monitoring the drying at the end of a capillary exposed to a controlled humidity with constant particle feeding ensures by its connection to a reservoir. Hereby, the water evaporation and diffusion set a flow driving the particles at the drying front where they build up crystals. Whether or not the particles are interpenetrable is characterized by the difference of scaling law in the time evolution of the drying front. We evidence an original drying behavior intermediate between colloidal and solution drying, in which a diffusional scaling is observed together with a weak dependence on the air relative humidity. Mapping composition and structuration gradients using Raman spectroscopy and small-angle scattering techniques, we show that this behavior stems from the ability of microgels to both interpenetrate and compact. As a result, water activity and transport is drastically decreased in the vicinity of the air/liquid interface [1]. We further present the influence of the microgel degree of crosslinking down to so-called ultralow crosslinked microgels (ULC) and temperature on the drying process. The described mechanism will be at play in a large diversity of complex colloidal systems and is pivotal for the mastering of drying processes.

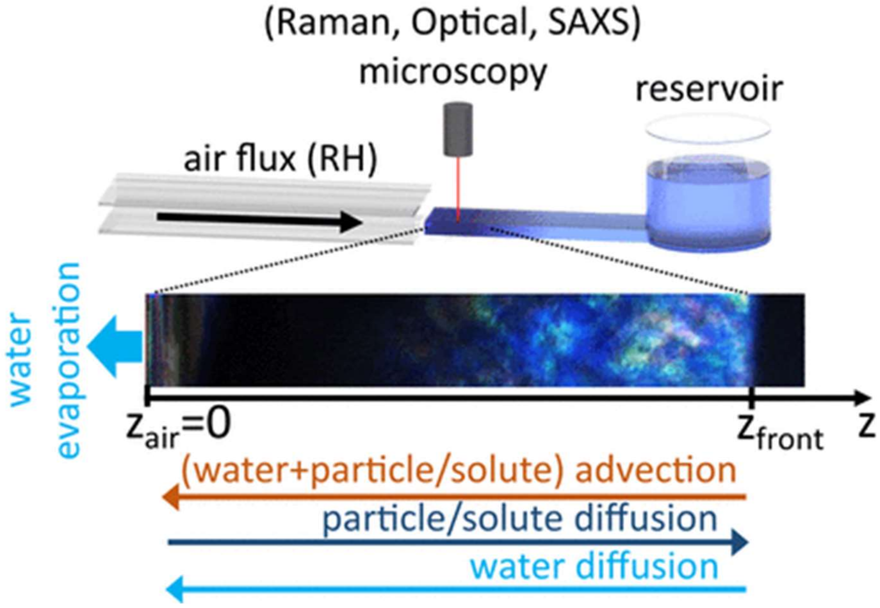

Figure 1. Schematic view of the millifluidic setup, which consists of a rectangular capillary connected on one end to a reservoir containing the microgel dispersion and exposed on its other end to an air flux of controlled RH.

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Working with Nanoparticles and other Hazardous Substances: Challenges for Safety Products

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Although Nanotechnology has been used for centuries and concerns of adverse effects of nanoparticles on human health continue, standard work safety is still not ensured.
In this work we will show the problems that arise from nanoparticle-skin contact and inform about measures that ensure work safety.

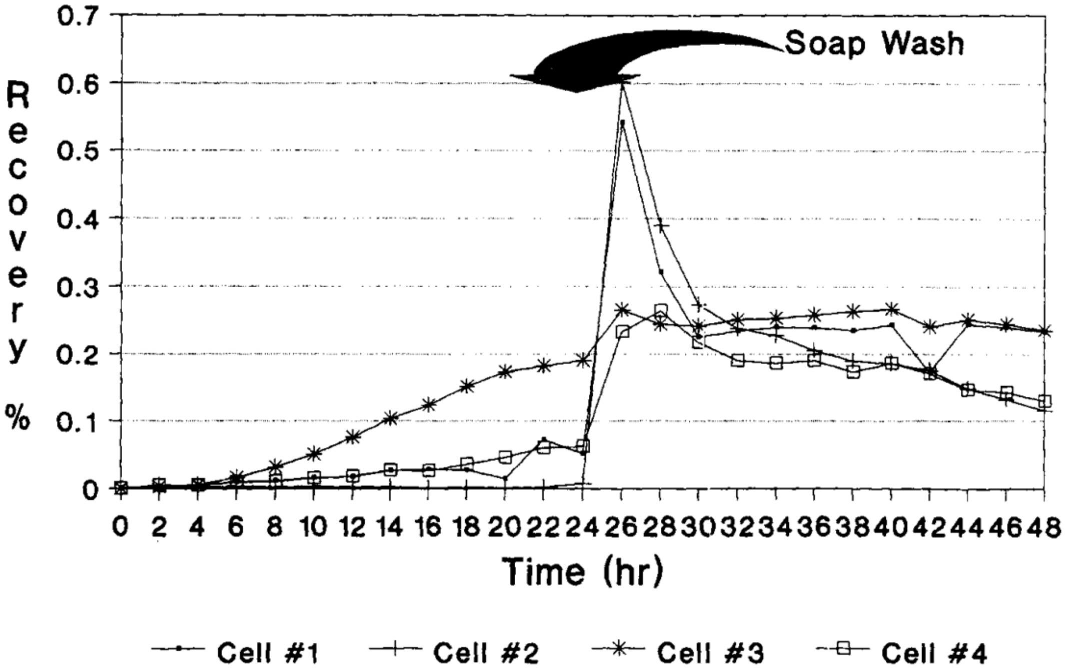

Figure 1. In vitro analysis of “C-B[a]P permeating 32-year-old Q human skin. The % recovery in the receiver solution is shown versus time for each of the four replicate Bronaugh cells. The onset of the 24-h skin wash with Radiac soap and water is shown.

We will concentrate on the problems of the so-called wash-in effect and the ingestion via carry-over contamination. Here a new classification of nanoparticles is shown and how this helps to identify the personal risks. A solution is presented how this risk can be mitigated by modern safety equipment. Finally new insights in the removal of soot particles and the removal of the cancerogenic polycyclic aromatic hydrocarbons will be presented. Firefighters and chimney sweeps are just two groups who constantly work with these hazardous substances. Thus, in the longrun, many suffer from so called chimney sweep cancer. A solution to this problem has long been required. It will be presented in our talk.

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[2] L. Di Cristo, et al., Nanomaterials (2021), 11, 2623.

Colloidal graphene-based inks for screen printed stretchable conductors

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Screen printing presents a suitable manufacturing technique for electronic components, as it is flexible, scalable, cost-effective and prints thick layers, enabling relatively low resistances [1]. Graphene is an ideal conductive component of these inks as it is skin-compatible [2]. We have previously developed conductive inks containing colloidal graphene nanoplatelets (GNPs) for screen printing of flexible conductive tracks [1] and are currently extending their formulation to inks suitable for printing of *stretchable*, skin-compatible conductors combining high conductivity with a high durability over many strain cycles.

We have developed an ink based on colloidal GNPs utilizing a skin-compatible thermoplastic polyurethane (TPU) binder with adjustable rheology. We are currently employing small-angle X-ray scattering (SAXS), dynamic light scattering (DLS) and rheological measurements to gain fundamental insights into these complex systems and formulate colloidally stable inks suitable for high resolution printing. Screen printing was used to print stretchable conductors on TPU substrates with high conductivity and excellent feature definition down to 200 µm line width. The conductors tolerate strains up to at least 100% and demonstrate high fatigue resistance to cyclic strains of 20–50%. Post-processing was employed to further reduce the resistances while preserving stretchability and cyclic durability. Its tunable viscosity makes the ink potentially suitable to printing techniques beyond screen printing. This opens a route towards the scalable production of printed sensors, heart rate monitors, athletic garments and artificial skin.

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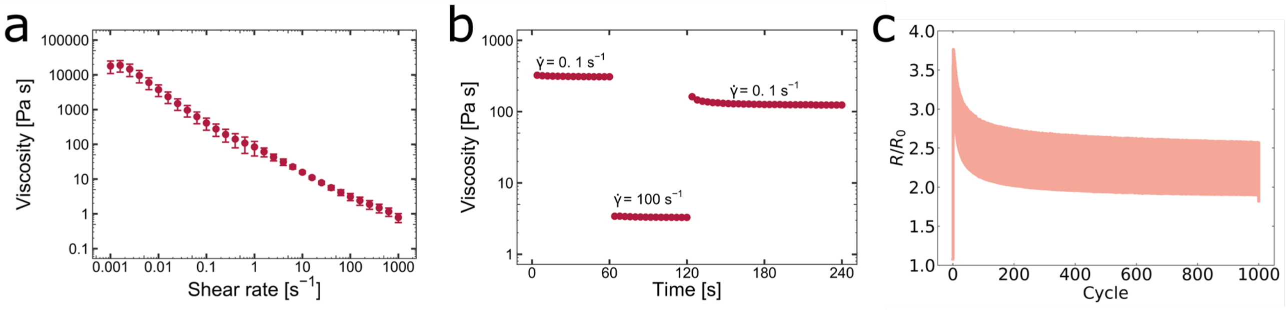

Figure 1. a-b) Ink rheology; a) Flow ramp b) Peak-hold test emulating the screen printing process; c) Electrical resistance response of printed linear tracks submitted to 1000 cycles of 20% strain.

Phase behavior and morphology of cationic/anionic surfactant mixtures

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Cationic surfactants show promising effects in laundry applications, such as an antimicrobial or care effect. However, in such applications anionic surfactants are widely used. Due to their different charge mixtures of cationic and anionic surfactants will not only show a strongly altered phase behavior but can also suffer from aggregation and precipitation of non-soluble complexes. Therefore, there is a great interest in understanding the phase behavior of cationic/anionic mixed systems.

In this study, the phase behavior of the technical, anionic surfactants sodium laureth sulfate (SLES) and sodium dodecylbenzene sulfonate (LAS) and the cationic surfactant didecyldimethylammonium chloride (DDAC) were investigated. Based on turbidity measurements, different aggregates were suspected depending on the mixing ratio. This is in line with changes in conductivity. The charge of the formed objects was characterized through zeta-potential measurements. To identify the morphology of the aggregates, dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS & cryo-TEM) measurements were used.

The figure below shows that mixed micelles can be found at low ratio of oppositely charged surfactant followed by vesicle phases (uni- and multilamellar). Close to stochiometric ratio phase separation occurs and precipitates are formed.

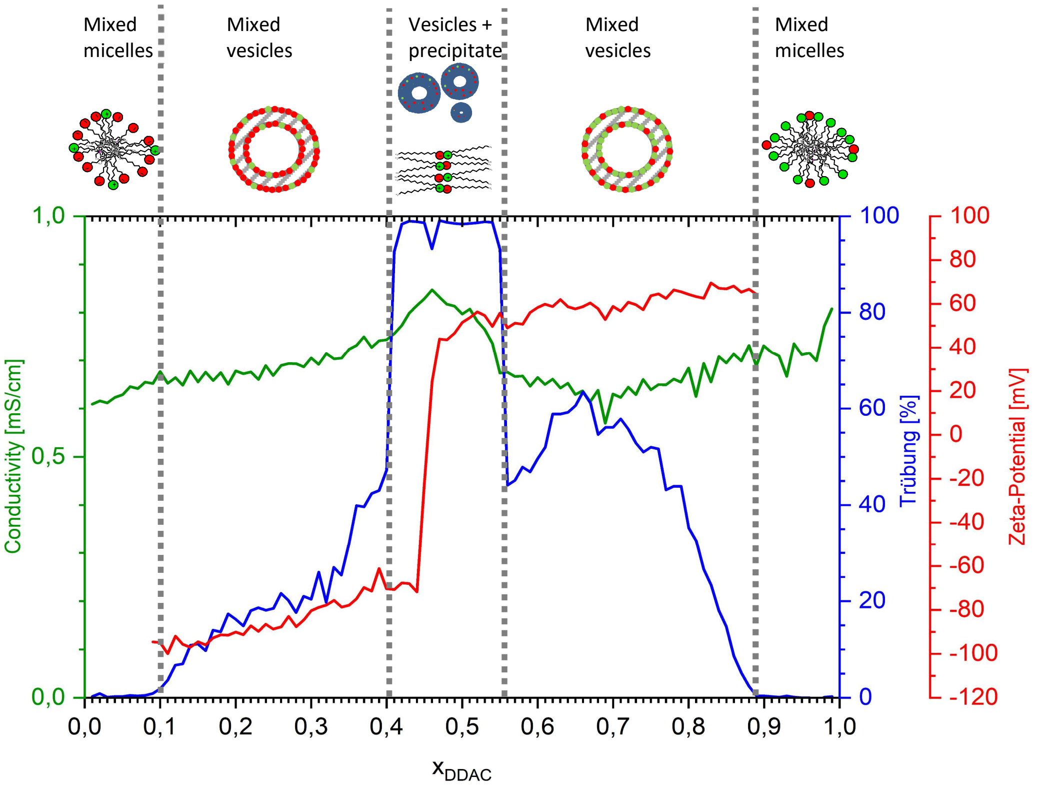

Figure 1. Phase behavior of SLES/DDAC mixtures with the DDAC to SLES molar ratio x_{DDAC} followed by conductivity (green), turbidity (blue) and zeta-potential (red).

Inducing defects in colloidal crystals

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Crystal defects are imperfections that can occur in any crystalline material and can crucially influence the mechanical, structural, and optical properties of the material. Colloidal crystals are useful model systems to study defect phenomena due to their similarities with atomic/molecular crystal systems. Although defect structures in colloidal crystals have been addressed, little is known about how (point) defects interact and the mechanisms of their diffusion in 3D, due to the lack of experimental control over the defect formation.

The aim of this project is to develop a colloidal system in which defect formation in 3D crystals can be controlled *in-situ*. For this the aim was to embed thermo-responsive colloids in a crystal of non-responsive particles. By heating or cooling, the defect particles can collapse or swell, which will induce vacancy-like defects or interstitials, respectively (Figure 1a). To realize this system, we synthesized thermo-responsive colloids with a poly(N-isopropyl acrylamide) microgel shell and non-responsive poly(2,2,2-trifluoroethyl methacrylate) (pFEMA) core [1], and non-responsive core-shell pFEMA particles of the same size that can be refractive index matched. Using a confocal microscope equipped with a temperature-controlled stage, the mixed system can be visualized on a single particle level (Figure 1b) and the dynamical properties of the defects upon switching can be studied. By adopting existing particle tracking and image analysis procedures, local stress- and strain-fields around crystal defects can be visualized [2]. Ultimately, this project will yield fundamental insight into the formation and dynamics of defects in colloidal crystals and in crystalline materials in general.

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[2] N.Y.C. Lin *et al.*, *Nat. Mater.*, **15**, 1172-1176 (2016)

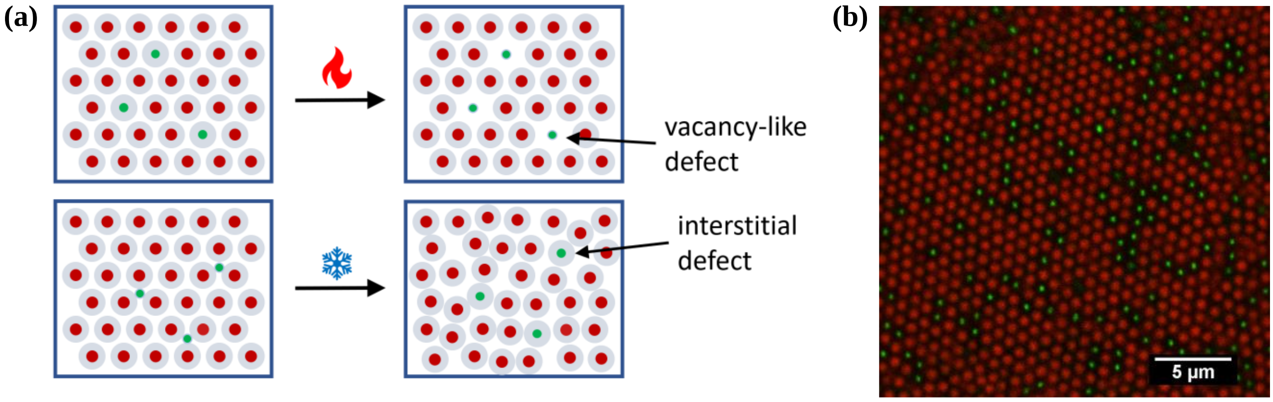

Figure 1. **(a)** Conceptual visualization of inducing vacancy-like and interstitial defects using thermo-responsive particles. **(b)** Confocal image showing swollen thermo-responsive microgels (green) embedded in a crystal of non-responsive particles (red) at 20 °C.

In-situ Investigation of Ca^{2+}-involved Flocculation of Natural Organic Matter (NOM) with Modified Chitosan

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Natural organic matter (NOM) exists ubiquitously in aquatic environments and can negatively affect the quality of drinking water. Its removal typically proceeds via coagulation by means of adding hydrolysing metal cations and cationic polyelectrolytes.[1] To develop a more environmental-friendly and effective chemical regime to remove NOM, natural origin chitosan was chemically modified in our lab and then studied with respect to its interaction with humic acid (HA), which was selected as well-defined model as it is the main component of NOM.[2, 3] In our investigation we concentrated on the phase behavior and the colloidal structures in the dispersed and precipitated state.

The principal aim of our investigation is to understand the interaction of HA (as example for NOM) under different ion conditions with modified chitosan and their formation of larger aggregates that ultimately results in the formation of flocs and precipitates. To gaining comprehensive knowledge about the structural properties. systems with various charge ratio Z, defined here as Z= $[+]_{\text{modified chitosan}} / [-]_{\text{humic acid}}$ were investigated via a series of characterization techniques, such as UV-Vis, static and dynamic light scattering (SLS, DLS), small-angle X-ray scattering (SAXS), and confocal microscopy. In this context we also focused on the role of Ca^{2+} in HA removal in our study to mimic the real condition **(Figure 1)**, and it finally showed the capability to prompt and aid the precipitation process by forming larger/denser complexes. It is worth to mention that in-situ observation via UV-Vis and SAXS were achieved to monitor the transformation of aggregates during the whole process of precipitation of humic acid. With the insights gained on the HA flocculation mechanism, this study is promising in optimizing parameters for NOM water treatment, based on a fundamental colloid chemical investigation.[4]

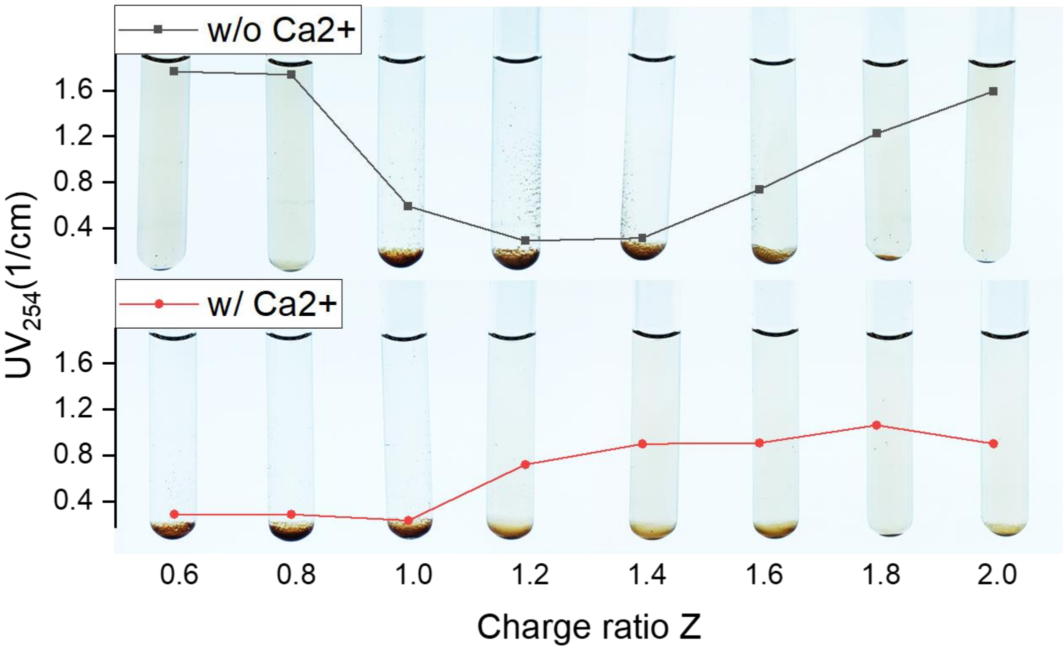

Figure 1. UV absorbance at 254 nm (UV 254) for HA-modified chitosan complexes with charge ratio ranging from 0.6 to 2.0 with the presence of 0 and 75 mg/L Ca^{2+}, respectively.

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Capillary Driven Self-Assembly of Ellipsoidal Composite Microgels at the Air/Water Interface

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In this study, we explored the spontaneous capillary driven self-assembly of composite prolate shaped microgels at air-water interface. The core-shell microgels contain a polystyrene (PS) core surrounded with a cross-linked fluorescently labelled poly(*N*-isopropylmethylacrylamide) (PNIPMAM) shell. The aspect ratios of the composite microgels can be finely adjusted upon uniaxial stretching the particles embedded into polyvinyl alcohol films [1]. The ellipsoidal particles obtain an aspect ratio range ρ varying from 1 to 8.8, measured from confocal laser microscopy (CLSM) in their swollen conformation at 20°C. Using inverted fluorescence microscopy, we investigated their spontaneous interfacial self-assembly at the air-water interface. Comparing with spherical particle ($\rho=1$) with small assembly having weak capillary forces to an apparently random trigonal assembly for $\rho=2.1$ to highly elongated particle ($\rho=8.8$) with a side-to-side assembly into long chains transition is observed. The transition occurs between $\rho=2.6$ and 3.3 for which a trigonal and trigonal/side to side coexistence assembly are respectively identified. The influence of the microgel anisotropy and softness on their interfacial deformation and is further discussed supported by computer simulations.

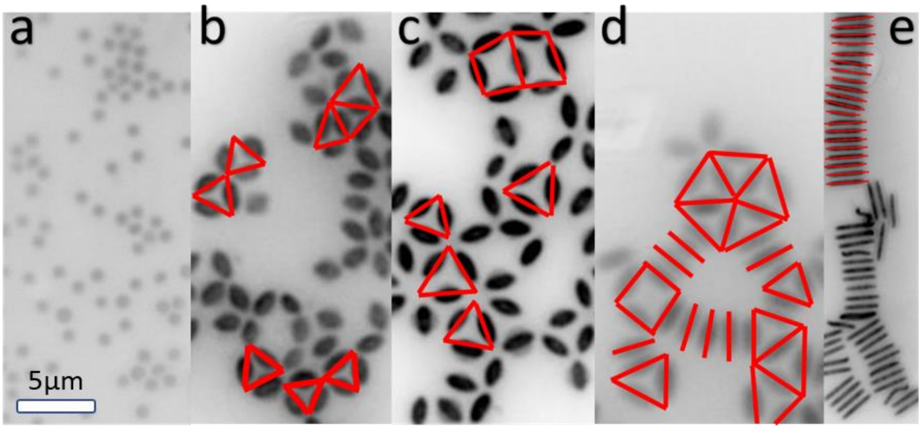

Figure 1. Colour inverted fluorescence micrographs of spherical composite microgels (a) and ellipsoidal composite microgels with an aspect ratio ρ equal to 2.1 (b), 2.6 (c), 3.3 (d) and 8.8 (e) assembled at the air-water interface at 20°C. Some of the typical assemblies are highlighted with red lines.

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Colloidal black gold with broadband absorption for plasmon-driven catalysis and surface-enhanced Raman scattering

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Broadband light absorbers are very attractive for many applications including solar energy, photothermal therapy, and plasmonic nanocatalysis. Colloidal black gold works as an excellent example of the broadband light absorbers in the visible and near-infrared ranges; however, their synthesis procedure typically requires multi-step deposition and/or high temperatures [1-2].

In this study, we report the synthesis of black gold nanowires via a facile, one-step green method using commonly known precursors (chloroauric acid and sodium citrate) performed at room temperature. The formation of the black gold particles is driven by self-assembly of in-situ formed small nanoparticles (~ 5 nm) followed by a fusion step forming extensive networks of nanowires (Figure 1). These assemblies form intense hotspots for enhancing the electric field as well as the local heat. Thus, the nanowires exhibited a strong photothermal effect as well as surface-enhanced Raman scattering (SERS) performance. Upon NIR irradiation, a high temperature up to 47 °C was recorded in the colloidal solution. While the high SERS signal enhancement is used to monitor the plasmon-driven dimerization reaction of 4-nitrothiophenol (4-NTP) in real timescale (milliseconds to seconds).

This work presents the colloidal black gold as a promising candidate for many photo-based applications, as the broadband light absorption enables the use of excitation sources with different wavelengths.

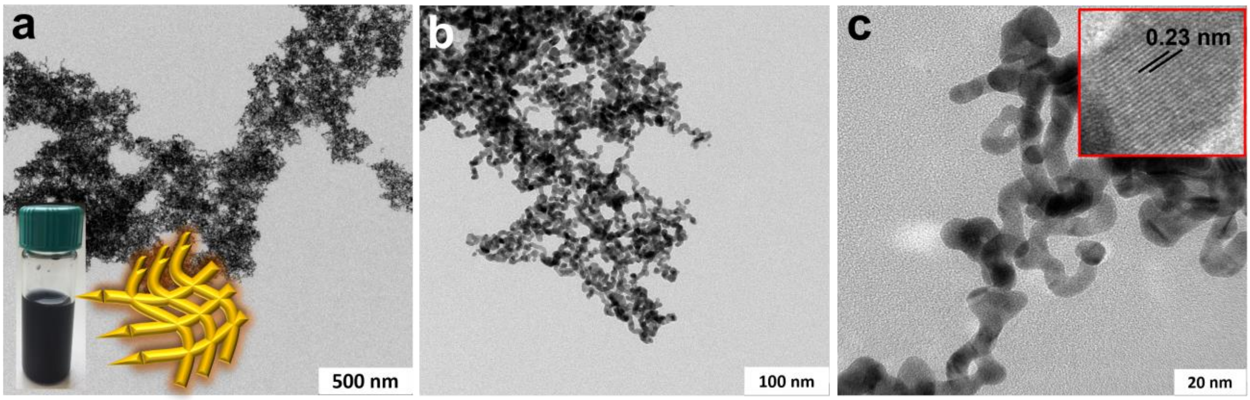

Figure 1. TEM and photo images of the as-prepared black gold showing the network-like morphology of the obtained gold nanowires.

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Gradual, selective, and reversible ionic transport at nanopores by ligand-binding

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Selective binding between different metal ions and their receptors at the cell membranes is essential for the immune reactions, signaling and opening/closing the ion channels.[1] In recent years, such ligand-binding-based pore activities inspired scientists to build ordered and metal-ion-responsive mesoporous films that interact selectively with the metal ions to tune the ionic pore transport. For instance, a chelation reaction between Ca^{2+} ions and phosphate groups of the pH-responsive polymer brushes at the mesopores was recently used to control the transport of anions in on/off states (Fig. 1).[2] For using such mesoporous materials in catalysis, drug release, sensing, and separation applications, their ligand-binding-triggered ionic pore transport needs to be investigated under different application scenarios, such as applications requiring gradual (beyond on/off) transport of both cations and anions under the presence of different amounts and types of metal ions.

Here we show how Ca^{2+} ions interact with phosphate-bearing metal-ion responsive polymer brushes in silica mesopores under different conditions to gradually control the transport of both anions and cations at the pores. First, we explain the growth mechanism of our responsive polymer brushes at silica mesopores in a controlled pore filling. Then we discuss the polymer presence and amount effects on the gradual ionic transport controlled by Ca^{2+} ion amount. Second, we introduce the metal-ion valency number (Ca^{2+} or Al3+) selectivity and reversibility of the Ca^{2+} ion attachment at our (non)functional nanopores and their role on gradual ionic pore transport. We anticipate that the results of our work will be a starting point for the application of hybrid mesoporous films with ligand-binding-triggered ionic pore transport. With (i) reversible and (ii) valency number selective metal-binding and (iii) the detection capability of Ca^{2+} ions even at sub-µM concentrations, the presented hybrid pores will be a suitable platform in challenging nanopore applications.[3]

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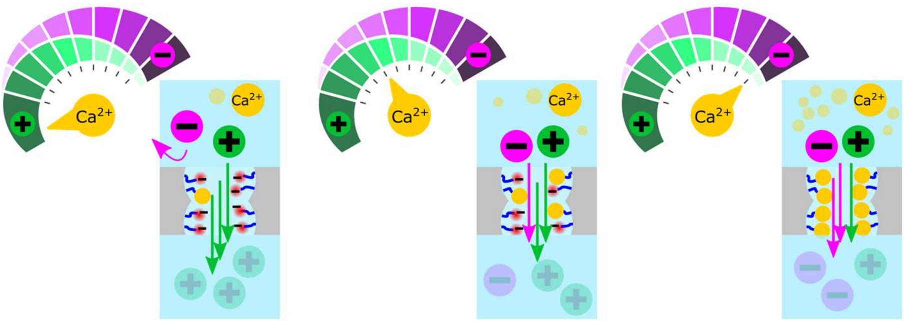

Figure 1. At a fixed pH, transport of anionic (purple) and cationic (green) cargoes gradually be tuned by the Ca2+ ion (ligand) binding at our silica mesopores (grey) functionalized by metal-ion-responsive polymer brushes (curved blue lines).

Multicompartment Polymeric Particles from Functional Precursor Microgel: Synthesis in Continuous Process

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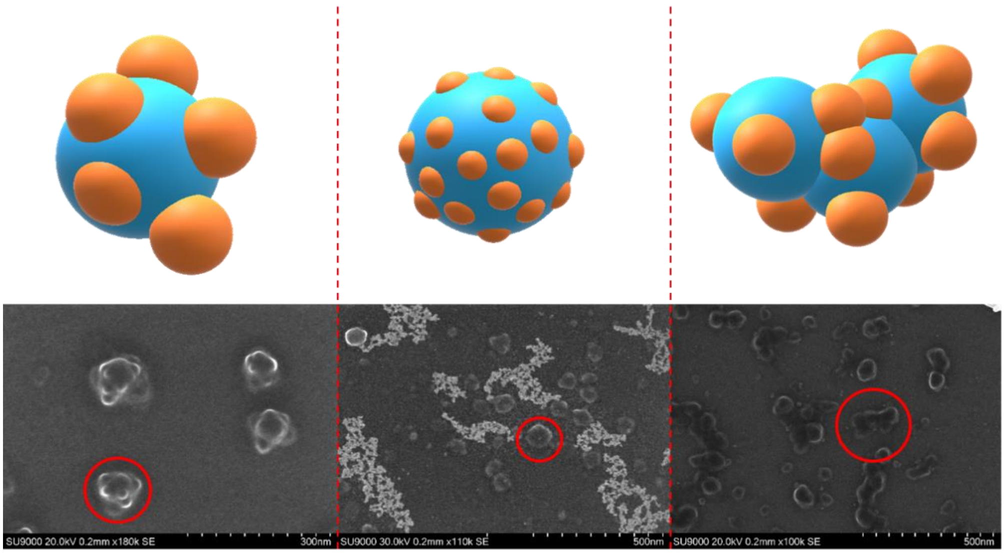
ABSTRACT: Raspberry-like poly(oligoethylene methacrylate-*b*-*N*-vinylcaprolactam)/polystyrene (POEGMA-*b*-PVCL/PS) Janus particles (JPs) and complex colloidal particle clusters (CCPCs) were fabricated in two-, and one-step (cascade) flow process. Surfactant-free, photo-initiated RAFT precipitation polymerization was used to develop internally cross-linked POEGMA-*b*-PVCL microgels with narrow size distribution. Resulting microgel particles were then used to stabilize styrene seed droplets in water, producing raspberry-like JPs. In the cascade process, different hydrophobicity between microgel and PS induced the self-assembly of the first formed raspberry particles that then polymerized continuously in a Pickering emulsion to form the CCPCs. The internal structure as well as the surface morphology of JPs and CCPCs were studied as a function of polymerization conditions such as flow rate/retention time (RT), temperature and the amount of used cross-linker. By performing Photo-PISA in tubular flow-reactor we were able to gained advantages over heat dissipation and homogeneous light distribution in relation to thermally-, and photo-initiated bulk polymerizations. Tubular reactor also enabled detailed studies over morphological evolution of formed particles as a function of flow rate/retention time.



JP: Raspberry - rough JP: Raspberry - smooth CCPC

Figure 1. Resulting raspberry-like JPs and CCPCs with different surface roughness.

High yield synthesis of water-processable donor:acceptor Janus nanoparticles with tuned internal morphology and highly efficient charge separation/transfer

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Here we report, for the first time, high yield (87.6%) robust and facile synthesis of donor-acceptor, water-processable, Janus nano-particles (JNP), that are of high potential for optoelectronic applications. The water-processable JNPs have easily controlled Janus ratios and are of excellent quality, that is shown by energy-filtered transmission electron microscopy (EFTEM). The JNPs exhibit improved charge separation and transfer properties compared to the conventional donor-acceptor nanoparticles that is characterized via both steady-state and transient photoluminescence spectroscopy. The Janus character of particles allows the combination of two materials into one composite and programs morphology of structures, which can be formed on the basis of the particles. Finally, we show outstanding performance of JNP based photovoltaic cells with 53% improvement of efficiency.[1]

[1] Y. Du, Y. Li, O. Aftenieva, T. Tsuda, P. Formanek, T. A. F. König, A. Synytska. High yield synthesis of water-processable donor:acceptor Janus nanoparticles with tuned internal morphology and highly efficient charge separation/transfer. *Advanced Optical Materials*, **2022**, *accepted.*
[2] The authors acknowledge Anja Caspari and Martina Priebs for electrokinetic measurements, Fupeng Wu for steady-state photoluminescence measurements. Y.D. acknowledges the financial support from the China Scholarship Council (CSC). The authors thank Benjamin Kohn for language polishing. This project was financially supported by the Volkswagen Foundation through a Freigeist Fellowship to T.A.F.K. The Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) − 404818834 funded the project for O.A. and T.A.F.K.

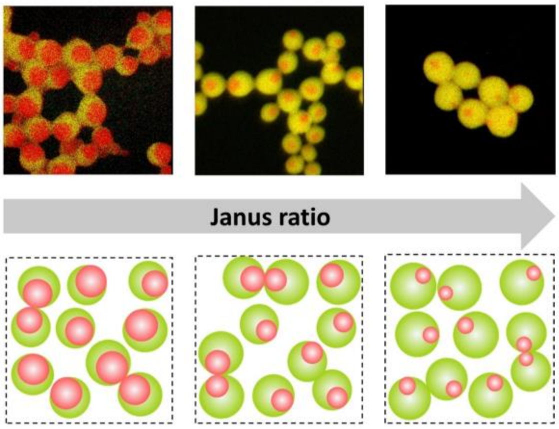

Figure 1. The internal structure of aqueous D:A nanoparticles can be well controlled through a facile route. This strategy is successfully applied to synthesize high-yield and high-quality environmentally friendly D:A Janus nanoparticles with tuned internal morphology. These obtained Janus nanoparticles exhibit efficient charge separation and effective charge transfer properties, that exhibits significant enhancement than traditional core-shell structures in photovoltaics devices.

A Platform for Stop Flow Gradient Generation to Investigate Chemotaxis

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The ability of artificial microswimmers to respond to external stimuli and the mechanistical details of their origins belong to the most disputed challenges in interdisciplinary science [1]. Therein, the creation of chemical gradients is technically challenging, because they quickly level out due to diffusion [2]. Inspired by pivotal stopped flow experiments in chemical kinetics, we show that microfluidics gradient generation combined with a pressure feedback loop for precisely controlling the stop of the flows, can enable us to study mechanistical details of chemotaxis of artificial Janus micromotors, based on a catalytic reaction. We find that these copper Janus particles display a chemotactic motion along the concentration gradient in both, positive and negative direction and we demonstrate the mechanical reaction of the particles to unbalanced drag forces, explaining this behavior [3].

[1] Chao Gao et al., Small (2022) p. 2106263.
[2] Priyanka Sharan et al, Small (2021), 17, p. 2007403.
[3] This project has received funding from the European Union's Horizon 2020 research and innovation pro-gram under the Marie Sklodowska-Curie grant agreement No 812780. J.S. and Z.X. acknowledge a Freigeistgrant (no 91619) from the Volkswagen foundation and a Fulbright Cottrell Award, which partially supported this study. Z.X. acknowledges financial support from China Scholarship Council. All authors ac-knowledge fruitful discussions with Benjamin Friedrich and Mihail Popescu.

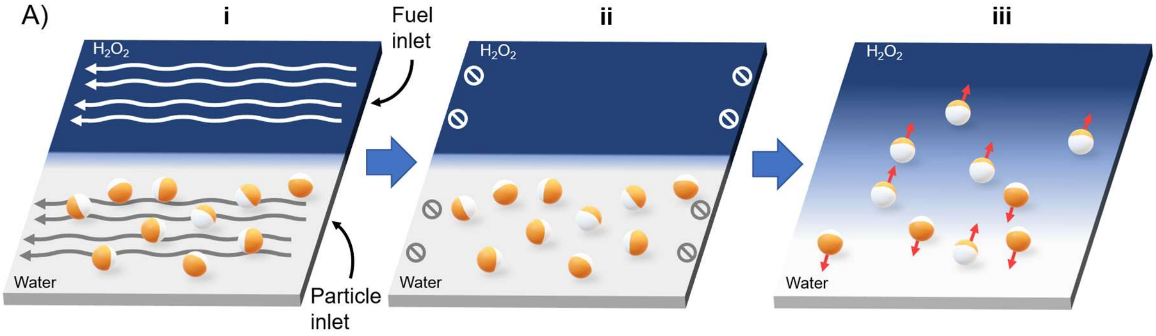

Figure 1. Operating principles of the positive and negative chemotaxis of Cu@SiO_2 micromotors: i sdadas; ii dasdad; iii dadasdas.

Phase behaviour and percolation of Red Blood Cells

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In the mixture of colloidal particles and polymers, the range and magnitude of the interaction potential can be tuned by the size and volume fraction of the polymers. Depending on the volume fraction of the particles and the interaction potential, colloidal particles and polymers can form a percolated gel-like network [1].

Similar to colloidal particles, Red Blood Cells (RBCs) exhibit a transition to a solid phase at a sufficiently high enough volume fraction and strong attraction. Depletion and bridging interactions are the two mechanisms for RBC aggregation, underlying the formation of a 3-D network of rouleaux similar to a weak physical gel. Understanding the dynamics of formation and break-up of the 3-D network of RBCs plays an important role in different phenomena, such as RBCs sedimentation or increased hydrodynamic resistance at low shear rates [2, 3].

In this project, we induce the attraction between RBCs by adding rod-like particles with a high length-to-diameter ratio, as well as small Dextran polymers. The different nature of interaction results in different percolated networks of RBCs. We investigated the phase diagram of the mixture of RBCs and these macromolecules from the gas phase up to percolation using confocal images. To this end, we developed an algorithm to directly determine percolation in 3 dimensions from confocal images of RBCs.

[1] E. Zaccarelli, Journal of Physics: Condensed Matter, 19(32):323101, 2007.
[2] O. Baskurt, and H. J. Meiselman, Hemodynamic effects of red blood cell aggregation, 2007.
[3] A. Darras, A. Kumar Dasanna, T. John, G. Gompper, L. Kaestner, D. A Fedosov, and C. Wagner, arXiv preprint arXiv:2108.13841, 2021.

Crystallization of hollow microgels assisted by regular ones

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Microgels are crosslinked polymer networks in the colloidal size domain swollen in a good solvent. Their swelling degree can be reversibly modified by external stimuli, such as temperature or pH. Advanced synthesis protocols allow for complex architectures, such as hollow microgels with a solvent-filled cavity in the center [1]. The soft and responsive nature of microgels, as well as the variety of internal architectures, makes them an excellent model system to study phase transitions and the behavior of complex fluids.

Here, we focus on mixtures of regular 'neutral' microgels with hollow 'neutral' microgels of the same size. Although the former are well-known to form colloidal crystals similar to hard incompressible colloids, it has been recently shown that hollow microgels fail to do so [2]. The reason for the absence of crystals is that hollow microgels increase their configurational entropy by rearranging the polymer chains into the solvent-filled cavity. By systematically realizing binary mixtures of regular and hollow microgels, we explore the role of hollow microgels as possible 'defects' that suppress the formation of crystals because of a different internal architecture, rather than size mismatch.

First, we confirm the absence of size mismatch and a sufficiently low polydispersity of single microgels using dynamic light scattering, small angle X-ray, and small angle neutron scattering in diluted conditions. In the concentrated binary mixtures, we observe colloidal crystals at fractions of hollow microgels up to 50%, whereby the width of the crystalline region gradually decreases. Small angle X-ray scattering is used to verify the crystal structure of the solutions and to obtain average nearest-neighbor distances in them. We speculate that below this threshold value of 50%, regular microgels can serve as a 'template' that assists the incorporation of hollow microgels into an ordered structure [3].

[1] A. Scotti, A. R. Denton, M. Brugnoni, J. E. Houston, R. Schweins, I. I. Potemkin and W. Richtering, Macromolecules 52 (2019), p. 3995.
[2] A. Scotti, A. R. Denton, M. Brugnoni, R. Schweins and W. Richtering, Physical Review E 103 (2021), p. 022612.
[3] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft within the SFB 985 Functional Microgels and Microgel Systems.

Paradigms for Directional Self-Assembly of Polymer-Functionalized Nanoparticles

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Inorganic Nanoparticles may feature unique size-, shape-, and composition-dependent plasmonic, excitonic, or magnetig properties. From the assembly of these nanoscale entities into ordered supracolloidal clusters, these properties may be further enhanced or completely new phenomena may emerge, as a result of interparticle coupling effects. Therefore, controlling nanoparticle self-assembly is of utmost importance.

This presentation will highlight approaches toward nanoparticle patterning through the recently established approach of constrained de-wetting in polymer grafted nanoparticles.[1] It will be shown how adaptive polymer ligands can be used to achieve surface patterning through distinct stimuli (like solvent environment, temperature, chemical triggers).[2,3] Building on that, it will be demonstrated how diblock copolymers can be employed to achieve colloidally stable, asymmetrical polymer-coated nanoparticles, and their directional self-assembly into supracolloidal clusters (see Figure 1).[3]

Finally, an alternative paradigm for directional nanoparticle self-assembly that does not rely on prior surface patterning with polymer ligands will be discussed. It will be shown that polystyrene-coated gold nanorods can undergo directional tip-to-tip self-assembly, even when they are uniformly coated with a polymer ligand layer.[4] The importance of electrostatic forces for the observed directional colloidal interactions will be discussed.[5]

[1] R.M. Choueiri, E. Galati, H. Thérien-Aubin, A. Klinkova, E.M. Larin, A. Querejeta-Fernández, L. Han, H.L. Xin, O. Gang, E.B. Zhulina, M. Rubinstein, E. Kumacheva, *Nature* 538 (2016) p. 538.
[2] C. Rossner, I. Letofsky-Papst, A. Fery, A. Lederer, G. Kothleitner, *Langmuir* 34 (2018) p. 8622.
[3] C. Rossner, E.B. Zhulina, E. Kumacheva, *Angew. Chem. Int. Ed.* 58 (2019), p. 9269.
[4] S. Vazirieh Lenjani, M. Mayer, R. Wang, A. Fery, J.-U. Sommer, C. Rossner *(submitted).*
[5] The authors acknowledge funding by a Liebig fellowship (Fonds der Chemischen Industrie.)

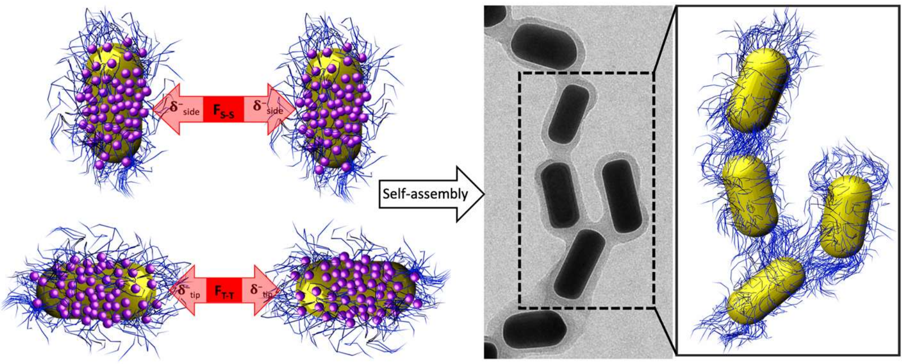

Figure 1. Tip-to-tip self-assembly of gold nanorods coated with a homogeneous polystyrene layer.

Small angle X-ray (SAXS) study of bicontinuous non-ionic microemulsions in confined space

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The widespread use of surfactants in tertiary oil recovery, enabling the recovery of otherwise unreachable oil in porous rock, requires a deeper knowledge of the properties of microemulsions under confinement in pores. Our approach to this problem is to study the phase behaviour of a non-ionic surfactant L_3 phase microemulsion consisting of n-decyltetraoxyethylene($C_{10}E_4$), water, and octane in a controlled porous glass (CPG) as a model system. CPGs are isotropic porous glasses with a bicontinuous pore network.

The stabilising effect of confinement on the single-phase range of a binary liquid from 20°C to lower temperatures has been shown previously [1]. The characterisation of a more complex ternary system, namely the L_3 phase of a $C_{10}E_4$/water/octane microemulsion (CE), is challenging. A theoretical model, together with experimental data, has shown that this system forms a lamellar layer at the solid-liquid interface of a planar glass [2,3]. It is important to note that the thickness of the lamellar layer in this case is equal to the domain size d of the corresponding bulk microemulsion.

To study this system under confinement, the bicontinuous liquid is soaked in a powder of controlled porous glass (CPG) with variable pore diameters. Thus, the confined system can be studied by small angle X-ray scattering (SAXS) to determine the domain size d. Measurements were performed at temperatures from 5°C to 55°C in CPGs with a nominal pore diameter of the CPG from 75 Å to 1000 Å. The SAXS data show a strong temperature-dependent shift in domain sizes of the confined microemulsion in large pore diameters while this shift is suppressed in small pore diameters.

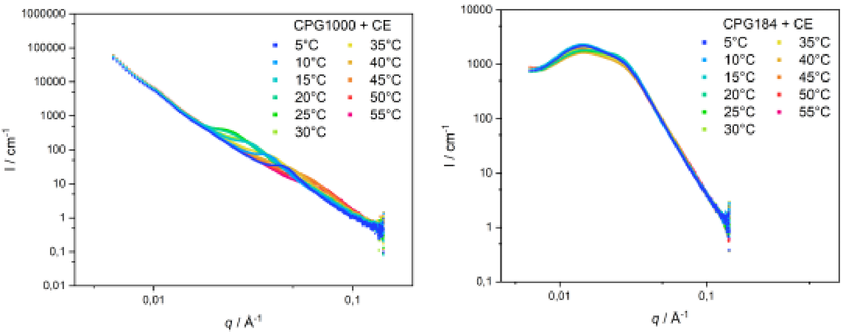

Figure 1. SAXS Graphs of a confined microemulsion in CPG with nominal pore diameter of 1000 Å on the left and 184 Å on the right side.

[1] S. Schemmel et al., Mat. Res. Soc. Symp. Proc. Vol. 790 (2004)
[2] M. Kerscher et al, Physical review (2011)
[3] S. Vargas-Ruiz et al., Langmuir (2016)
[4] The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG), Project number 455432427

Crown ether-functionalized complex emulsions as an artificial adaptive material platform

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In this contribution, we present a material platform based on biphasic, anisotropic double emulsion droplets that can autonomously and reversibly adapt to their chemical environment through different supramolecular recognition events. The recognition mechanism is achieved by the selective assembly of synthetic crown ether surfactants on one hemisphere of the emulsion droplets. [1] The dynamic and reversible host-guest complexation of the crown ether surfactants with different analytes, such as metal and ammonium ions or amino acids, leads to interfacial tension changes at the droplet surface, which in turn results in morphological reconfiguration of the complex emulsion droplets. The newly developed adaptive soft material platform has been used for biomimetic recognition of biomolecules, including amino acids, carbohydrates and antibodies, and for triggered surface-encoded release of payloads, among other applications.
By using the crown ether-functionalized droplets, we observed that different supramolecular host-guest recognition events at the interface can lead to two opposite morphological transitions. After the addition of inorganic metal salts, such as potassium acetate, the droplets transitioned from their initial Janus configuration to an encapsulated double emulsion morphology ($\theta = 0°$). It is known that crown ether units form hydrophobic complexes when coordinated with suitable metal ions, leading to a phase transfer of the metal salts into the organic phase. The reduced effectiveness of the crown ether surfactants thus led to an increase in the interfacial tension between hydrocarbon and water. In contrast, the addition of a hydrophilic ammonium compound, was followed by a further 'opening up' of the Janus droplet morphology towards contact angles of $\theta > 90°$, which corresponds to a decrease of the HC-W interfacial tension. In this scenario, complexation of the hydrophilic ammonium compounds led to an increase of the hydrophilic-lipophilic balance of the surfactant, resulting in a more effective surfactant. Horizontal imaging allowed in-situ visualization of both morphological transitions evoked by the different molecular recognition events.

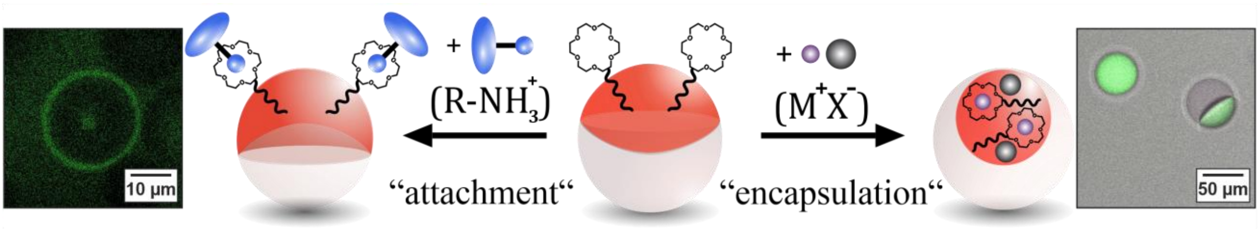

Figure 1. Crown ether-functionalized droplets that can undergo two opposite morphological transitions depending on the supramolecular host-guest recognition event at the interface of the droplets. Attachment of hydrophilic ammonium compounds left and encapsulation of metal ions right.

[1] S. Djalali et al., *Adv. Funct. Mater.* **2021**, 2107688.