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Site-selective silica rod-like colloids

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Abstract

Over the last two decades, researchers have been able to create increasingly complex colloids in terms of their shape and chemical composition. Anisotropic particles have been one of the fundamental focuses of materials research since their introduction, because they possess directional and configurable interactions, unlike their isotropic counterparts. Specifically, Janus colloids have received great attention in the search for the next generation of functional materials. Named after the two-faced Roman god, Janus particles possess unique asymmetry and combine two separate functions at their opposite sides, allowing them to access complex self-assembled architectures. However, obtaining the ideal biphasic Janus feature is still limited due to various synthetic difficulties and challenges. Because of this, scientific research has steadily focused towards the generation of asymmetric colloidal structures without ideal biphasic topologies, such as single and multi-patchy Janus particles. Among a wide variety of materials chosen to synthesize patchy particles, silica has been widely used over the years. The ease of adjustment of the structural properties of silica makes it possible to introduce various types of functional groups on its surface.

In this thesis, we describe the synthesis of hybrid organic-inorganic Janus particles by utilizing different synthetic approaches. In the first part of the work, we have drawn our attention to the optimization of the synthetic procedures concerning the preparation of bullet shaped anisotropic silica particles with tunable dimensions. The growth mechanism of these rods involves emulsion droplets, inside of which silica condensation takes place. Due to an anisotropic supply of reactants, the nucleus develops exclusively to one side only, resulting in anisotropic rod formation. In the second part, the synthesis of amine terminated Janus patchy particles was conducted. By introducing an organo-silica precursor with amine functionality, further anisotropic growth of the silica rods was observed. Therefore, the hydrophilic silica rods were used as seeds, with the growth starting at the boundary of the seed rod and the water emulsion. Furthermore, the assembly of the functional rod-shaped particles was investigated depending on the nature of the surrounding media. It was found that, under specific conditions, the Janus particles formed aggregated structures in solution, which were not observed in the case of the homogeneous particle mixtures. In the third part, functionalized silica particles were used as

stabilizers for the synthesis of poly(methyl methacrylate) in dispersion polymerization. The polymer was found to anchor exclusively at the flat tip of the rods, rather than at the other surfaces with a higher curvature. The anisotropy of the particles along the length direction could provide rich self-assembly phase diagrams. In the last part of the thesis, a different approach was examined for the synthesis of Janus particles. Silica rods of different aspect ratios were self-assembled by exploiting a Pickering emulsion based strategy. This technique takes advantage of the large surface area provided by spherical polystyrene particles to immobilize anisotropic silica particles at the polystyrene-solvent interphase, providing protection to one hemisphere of the colloidal particle, while allowing the exposed silica surface to be chemically modified as required. The resulting hybrid polymer-silica Janus particles could be further examined for their self-assembly behavior.

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Chapter 1 – Introduction

1.1 Colloid particles

Colloidal particles are characterized by their small size, ranging at least in one dimension between a few nanometers and several micrometers. The fine control of their size and interactions plays a key role in their behavior. On the one hand, colloidal particles are small enough, so their thermodynamic properties can be compared to that of atoms and molecules, and their thermal energy drives their dynamics and ensures equilibration with the suspending fluid.¹ On the other side, they are large enough to be measured precisely using advanced optical methods, such as laser-scanning confocal microscopy.¹ Their position can be visualized and their motion can be followed in real-space and time, thus allowing for detailed investigations of both their structure and dynamics on the single particle level. Moreover, their size allows for guided assembly by external fields, generating a large number of mesotropic phases, which are distinguished by various translation and orientation order states.²

The simplest and most symmetric shape (isotropic) is the sphere, as nature tends to enforce spherical interfaces to minimize surface energy. It is the most traditional shape in theoretical studies, due to its lack of orientation degrees of freedom and its ease of description. In fact, a number of distinct atomic crystalline phases have been discovered using model colloidal particles, which behave like hard spheres or interact with isotropic potentials. However, the development of novel colloidal systems that have non-isotropic, directional interactions opens the possibility to examine molecular interactions and phase behavior in considerably more complex situations. The preparation of asymmetric particles, such as rods, disks, cylinders and dumbbell shaped has been realized by a variety of different fabrication processes.² Stretching techniques, micro-molding, microfluidic techniques and seeded polymerization have all been proven very effective for the generation of well-defined anisotropic particle morphologies.³ ⁴ Beside the shape anisotropy, new synthetic strategies have been developed to impart colloidal particles with chemical and morphological anisotropy.⁵ Surface functionalization can promote colloids to directional interactions and aggregation strategies, thus expanding the opportunities to investigate self-assembly at greater degrees of complexity. This is accomplished via chemically

designed Janus and patchy particles produced by inhomogeneous surface coatings. Figure 1 illustrates these particles, classified by means of their geometric properties and the nature of physical or chemical functionalization of their surfaces.³



Figure 1: Classification of colloidal particles with respect to symmetry and chemistry, shifting from isotropic to anisotropic.³

1.2 Geometry-anisotropic colloidal particles

Shape anisotropy can generally be conceptualized as a particle feature that imparts a difference from that of a sphere's uniform composition, but this guideline can be generalized to a particle having a variation in curvature along its surface.² A wide variety of anisotropic particles can be found in nature or be man-made and are exploited in colloidal research. Particles with cylindrical morphology constitute a great example of anisotropic shapes that deviate from a sphere. Both the bacteriophage FD (FD-virus) and the Tobacco Mosaic Virus (TMV) are colloidal rod-like particles that can be used as a hard rod model, due to their monodispersity and high aspect ratio. Their property to assemble into liquid crystal phases creates beautiful isotropic-nematic phase transitions that were observed by Fraden and colleagues using suspensions of these viruses. ⁶ The use of an external force, often in the form of an electric, magnetic, or shear field to confine the

particle location, is yet another property that distinguishes their properties in comparison to their spherical counterparts. These techniques can frequently accomplish high levels of alignment in an easy way, with CdS or CdSe nanorods serving as a suitable example. Such nanorods have been shown to possess a dipole moment and can be particularly well organized through the application of a DC electric field, as there is no need to polarize the particle.⁷

Different strategies have been developed to synthesize anisotropic colloidal particles with adjustable aspect ratios and narrow size distribution. Typically, a bottom-up technique is used to create spherical particles by an even material growth from all sides. The anisotropic addition, however, can produce particles with broken symmetry such as gold nanorods, that can be grow in aqueous solutions by using a directing agent.⁸ By utilizing the characteristics of the emulsions, we can effectively remove or add material to shape colloidal particles in an asymmetric manner. In a respective work, Yang and coworkers, asymmetrically etched trapped colloidal silica particles at a Pickering emulsion interface made of solidified wax, to obtain particles with tunable shapes.⁹ To prepare a larger amount of particles, a versatile modified sol-gel strategy is widely used to produce silica rods, due to its ability to control the particle size, size distribution and morphology through a systematic monitoring of the reaction parameters. For instance, by altering the surrounding environment during growth, and especially the temperature, a step change in the width of the silica rods was observed.¹⁰ This adaptable system has opened the path to many explorations into the effects of particle shape anisotropy, for example, on the colloidal phase behavior. While there are countless different synthetic procedures, the examples described in the following will focus on systems of rod-like or cylindrical particles, similar to the model systems studied in this work.

1.2.1 Silica rods - Emulsion stabilization and rod growth

Since their first report by Kuijk et al. colloidal silica particles of controlled morphology, and especially silica rods, have attracted widespread attention due to their high surface area, tunable length, diameter and ease of fabrication.¹¹. Depending on the chemical concentration of the precursors used in the synthetic procedure, the rods can be developed having a diameter ranging from 300 to 500 nm and a length that ranges from 300 nm to 3µm, corresponding to the aspect

ratios from 1 to 10.⁸ ¹¹ Figure 2 depicts the synthetic system employed in the generation of silica rods, their growth over time and final morphology.



Figure 2: (A) Schematic representation of the reagent species used for the synthesis of the silica rods. (B) TEM and Cryo-TEM images showing the step-by-step growth of the silica rods: (a) Water droplet in the pentanol solution. (b) - (f) Water droplet attached on the rod and the growth of the rod-like particles after TEOS enters the droplet to fuel the growth. (C) TEM images of rod-shaped silica particles after synthesis and size-separation to improve their size uniformity.¹¹

Silica rods are prepared by a simple one-pot synthesis by mixing water, ethanol, sodium citrate, ammonia, tetraethyl orthosilicate (TEOS) and polyvinylpyrolidone (PVP) in 1-pentanol, as shown in Figure 2A.^{8,12} The bullet shaped particles emerge out of a rich water-in-oil emulsion droplet that contains PVP, sodium citrate and ammonia. The addition of PVP and citrate is necessary for the formation of the emulsion droplets. In the absence of either one of them, droplet formation was prevented, resulting in spherical silica particles synthesized according to the "standard" nucleation-and-growth model. Silica rods are synthesized with one rounded end where the silica growth started and progressed, and one flat end to which the droplet remained

stably attached. Within the droplet, hydrolysis and condensation reactions of the silica precursor converts it into amorphous silica clusters, inducing the directional growth of silica particles. While TEOS molecules are hydrophobic and dissolve well in the pentanol phase, upon reaction with the surface of the water droplet they are hydrolyzed and become hydrophilic, migrating into the droplet. Then the hydrolyzed TEOS undergoes a condensation reaction and a nucleus of silica forms at the interface of the emulsion droplet. By further addition of the silica precursor the rods become elongated. As a result of this one-sided supply of TEOS the nucleus is grown in one direction, while the water droplet stays affixed to the end (Figure 3).¹¹ Additional steps take place such as the diffusion and agglomeration of primary particles into silica aggregates, interfacial adsorption of the aggregate and termination of growth once all TEOS has reacted. At this stage, the emulsion droplet that is still attached to the rod's end can be rinsed away, generating a flat rod end.



Figure 3: TEOS addition in a water-in-oil emulsion, results in the primary growth along the particle length axis and significantly less growth in the diameter. Bare silica rods are produced, containing residual organics such as PVP after washing and size separation.

While the size of the water emulsion droplets determines the rods' diameter, the length can be controlled via different routes such as the reagents' concentration and seeded growth.⁸ ¹³ Generally, by varying the reaction conditions the length of the particles can be varied, yet there is a critical concentration in which the rods can become curly or spherical.⁸ In specific, by increasing the reaction time or the volume of TEOS, the growth rate in length gets significantly higher compared to the increase in the diameter. Longer particles can also be obtained by reducing the water or ammonia content, switching to a shorter chain alcohol or minimizing the PVP content.⁸ The application of bath sonication during the reaction can produce multi-modal distributions of rods. On the other hand, an increased stirring has been also shown to have a negative effect during the growth of the rods as the droplet can shrink or can be completely disrupted. As a result, these critical parameters can affect the size or polydispersity of the emulsion droplets and the resulting particle size.¹⁴

Furthermore, several unique geometrical features of these particles are noteworthy. First, the asymmetry created by the distinct flat part on one end of the rod is an intriguing aspect. The majority of the rods collected can be identified as bullet shaped rods due to the round end indicating the growth of the particle and the flat end from which the emulsion droplet was detached. The planar design of the rod's flat end introduces a larger contact area for attractive colloidal systems, potentially enabling substantially stronger attractions than the hemispherical end. However, the rods occasionally lacked the flat end while a pointed tip with smaller diameter occurred. It is believed that rod tapering results from the terminal water droplet's gradual shrinkage.¹⁴ For this reason, the particle sizing reports the diameter at the midpoint along the length axis to average the tapering effect. Beside this effect, various others were observed such as tailing at one end, sphere shaped particles (failure to initiate), curving and fiber formation. These different features are not desired and a better understanding that ideally favors simultaneous initiation and sustained propagation, while obstructing droplet termination paths, is mandatory.

A variety of anisotropic silica colloids have been synthesized using this method. For example hollow inorganic particles¹⁵, cone-shaped¹², segmented rods¹⁰, bend-shaped¹⁶ and Janus particles comprising silica rods coated with gold tips¹⁷, The self-assembly of these particles is of great interest, due to their shape anisotropy which enables shape selective interactions producing

therefore rich phase diagrams. Essential to self-assembly is the ability of spontaneity, occurring without external intervention or guidance through the inherent properties (shape, polarity or surface properties) of the individual particles and their resulting interactions by enthalpic and entropic forces. However, the self-assembly process can also be guided or enhanced by external fields to create richer phase diagrams.

1.3 Liquid Crystal phases

Before the discovery of liquid crystals by Reinitzer and Lehmann ¹⁸, three fundamental states of matter were known to exist for material with roughly spherical shape: a solid, a liquid and a gas phase. Amongst them the degree of ordering is different. Gases and liquids lack transitional and rotational order, in contrast to crystals that are almost precisely ordered to form a tightly packed lattice.¹⁹ However systems with less symmetrical shape, such as elongated particles in one or more directions, form richer phases owing to their additional rotational degree of freedom. This fourth state is observed between the crystalline and liquid states and is known as liquid crystalline phases. The classification of these phases was set out a few decades later, by George Friedel in 1922.²⁰

As their name implies, liquid crystals are exquisite combinations of the ordering properties of crystalline formations and fluid-like motion which is typically connected with isotropic liquids.²¹ ²² Liquids being isotropic, means that the arrangement of molecules is disordered in all directions. However, the anisotropic nature of the liquid crystalline phases sets them apart from regular liquid phases as a result of the significant directionality in the electrical, optical, magnetic and mechanical properties of liquid crystals.¹⁹ This extreme sensitivity to the external stimuli is crucial for the formation of mesophases. Figure 4 shows schematic representations of the most common phases formed by rod-like particles including the isotropic, nematic, smectic and crystalline phases, in increasing order of ordering.²³ For instance in the nematic phase, particles have positional freedom but are all oriented in a common direction. In the smectic phases, molecules are also aligned with the main axis while ordered into layers. A variety of smectic phases exists, that range from smectic-A to smectic-L, depending on the types and the intensity of positional and orientational order.²⁴ Crystal phases form if there is long-range connection

between the hexagonal smectic-B layers. As seen in Figure 4 this can either be an ABC crystal or a AAA crystal, depending on how the layers are stacked.²⁴



Figure 4: Graphic representation of various phases exhibited by rod shaped particles

Figure 5 shows the packing fraction in relation to the aspect ratio phase diagram of a hard spherocylinder system obtained via computer simulations by Bolhuis and Frenkel. ²⁵ The shape of the particle plays a significant role in the formation of mesogens. For example the isotropic-nematic transition arises in high aspect ratios such as L/D > 3.7, and the isotropic-smectic transition requires L/D > 3.1.²⁵ In these simulations, the aspect ratio L/D was defined as the cylinder length over the diameter. The particles utilized in the experiments described in the following chapters are not completely identical to sphero cylinder particles, but exhibit a more bullet-like morphology. For this reason, we define the end-to-end aspect ratio L'/D', with L' being the average end-to-end length and D' the diameter of the particle.



Figure 5: Phase diagram for a system of rod-like particles obtained from computer simulations. The system's density and the particle aspect ratio both affect the formation of liquid crystalline phases. The gray areas indicate coexistence regions.²⁵

In addition to the structures that liquid crystals can form, we can further describe them by their response to environmental conditions.²⁶ They can be broadly categorized into two classes: thermotropic and lyophobic liquid crystals. Thermotropic liquid crystals exhibit phase transitions as a function of temperature. Typically, they show mesophases when a material is heated from its crystalline solid state or when it is cooled from its isotropic liquid state. On the other hand, lyotropic liquid crystals do not require a change in temperature but instead they exhibit a phase transition as a function of concentration, i.e. when the concentration of amphiphilic molecules scattered in an isotropic medium changes.¹⁹

1.3.1 Nematic liquid crystals

Nematic liquid crystals are considered the most ideal phase towards the observation of both the liquid and crystalline features of this state, because they display director alignment yet they can flow due to the lack of positional order.²² Although the particle distribution in the bulk nematic liquid crystal is homogenous, the orientation of the particles is no longer isotropically

distributed. A preferred axis known as the nematic director, which is represented by the unit vector n, shows the direction and is aligned along the long body axis vector u_i of the particles labeled by i.²⁷ Since the phase has cylindrical and inversion symmetry, the thermodynamics are unaffected by inverting the unit vector n to -n or by rotating the rod particles along their main body axis, This inversion symmetry of the nematic phase is crucial to determine the order parameter. However this ideal situation of rotational invariance may be challenging to achieve in experiments due to constant presence of anchoring effects that often compel a certain direction for vector n.²⁷

Significant results were achieved from Onsager and coworkers, in the demonstration of an entropy-driven phase change in hard particle dispersions.²⁸ Onsager demonstrated that an isotropic fluid of hard rods gets shifted to a nematic phase upon increasing the concentration of the rods. According to Onsager, the aligned rods in the nematic phase reserve more free volume per particle than the randomly oriented rods in the isotropic phase. Therefore, the decrease in excluded volume between pairs of rods makes up for the entropy loss associated with the orientational ordering in the nematic phase, which becomes the thermodynamically stable phase.²⁹ This work inspired computational simulation studies that led to the discovery of highly organized smectic phases in concentrated suspensions of hard rods.

1.3.2 Smectic Liquid Crystals

Another distinct mesophase of liquid crystals is the smectic state. In contrast to the nematic, molecules in the smectic phase exhibit a degree of translational order. The molecules continue to organize themselves in layers or planes, while maintaining the general orientational order of the nematic phase.¹⁹ The motion is limited within these planes and the spacing can be measured by X-ray diffraction, similar to crystals. Smectic phases can be further categorized according both to the arrangement of the mesogens in each smectic phase and the tilt angle between the long axes of mesogens and the plane. For instance, Friedel first identified a type of smectic liquid crystal, currently known as smectic A. While the layer spacing inside the Smectic A is consistent, irregular spacing within each layer is observed. In fact, within each layer the long axes of the

molecules are on average oriented in the same direction perpendicular to the layer and thus to the director n, although the molecules are loosely positioned into the layers.²⁴ By significantly altering the tilting angle of the molecules within the layer plane, the smectic C phase is obtained. As an alternative, the smectic B phase can be created by adding hexagonal symmetry to the layer and slightly increasing the order so that the molecules are positioned in fixed positions in the hexagonal. Many more smectic phases have been discovered to date, with the determining characteristics being the amount of positional order inside a layer and the direction of the director axis.²⁶

1.4 Chemically anisotropic particles

Despite the shaped anisotropic particles discussed above, the idea of chemically anisotropic particles is of great scientific interest as such systems exhibit unique behavior. Breakthroughs in the synthesis of different particles has led to a variety of techniques that allow for the precise chemical and physical patterning of colloidal particle surfaces³⁰ Typically, this patterning is in the form of precisely controlled patches on their surface, which determine the interactions between them, as well as with their environment, and ultimately render possible the desired assemble of the colloidal structures. Particles with a single protrusion make up the most basic subclass of patchy colloids.³¹

Janus particles are a unique class among homogenous and multi-functional patchy particles, combining two distinct functionalities at their opposite sides. These particles were named after the two faced Roman god, Janus, first indicated by Casagrande et al. in 1988, by describing glass spherical particles with one hydrophilic and one hydrophobic hemisphere.³² Later, Pierre-Gilles de Genes mentioned the Janus particles in his Nobel lecture, pointing out their significance and potential. Indeed, this unique asymmetry of these particles offers the ability to target unreachable self-assembled structures.³³ The development of new synthetic techniques, deep comprehension of their new novel physical properties, and perspective fields of use, has all contributed to significant advancements in the design and synthesis of Janus particles in the last years. However, obtaining the ideal biphasic Janus feature is still limited due to synthetic difficulties and challenges. As a result, scientific research has steadily focused towards the generation of

asymmetric colloidal structures without ideal biphasic topologies, such as single and multipatchy Janus particles.³⁴

In general these particles can be divided into three different categories defined by the type of functionalization.³⁴ In details, the compartmentalization of these particles can occur throughout the whole particle core (core-compartmentalized), only at the surface through different surface modifiers (polymers etc.) and finally to the whole particle including its surface and the core. Figure 6 summarizes the chemically anisotropy of particle's architectures that have been achieved up to this point.³⁵ This includes Janus particles functionalized in the core or the surface, multi-compartment particles in the core domain and finally patchy particles. The combination of these categories is illustrated by a beautiful example of isotropic micelles in Figure 6b, showing how challenging it is to define each sort of particle due to structural similarities. Finally, compartmentalization has been also shown for particles of more complex morphologies such as cylindrical, cubic and disk particles



Figure 6 : Schematic representation of anisotropic particles in A: (A) Janus particles, (B) multicompartment particles, (C) patchy particles, (D) patchy Janus particles, (E) patchy multicompartment particles. An example of anisotropic micelles is used to demonstrate the structural similarity of all three types of anisotropic particles B: (1-3) Janus micelles, (4) Janus multi compartment micelles, (5) patchy Janus micelles, (6) multi-compartment micelles, (7) patchy multi-compartment micelles, (8) patchy micelles.³⁵

1.4.1 Preparation pathways of Janus particles

After the introduction of Janus particles by de Gennes in 1991, numerous techniques have been used to synthesize "Janus" particles that exhibit remarkable features with a variety of sizes, materials, forms, and functions. According to the physical characteristics of the Janus particles, their main synthetic pathways can be classified into three categories: masking techniques, self-assembly and phase separation.³⁶ The asymmetric particles fabricated with these techniques can be soft organic Janus particles, hard inorganic or metallic particles and a combination of organic-inorganic materials named hybrid particles. In all cases, in order for a fabrication procedure to be considered successful, three important criteria must be met. In specific, the size and the geometry of the particles need to be carefully and efficiently controlled, while the capacity of synthesized particles has to be in sufficiently large quantities.

1.4.1.1 Synthetic methods for the preparation of Janus particles based on isotropic particles

The most reliable method for the preparation of Janus particles, and in particular inorganic hybrid ones, relies on employing interfaces as a desymmetrization tool, by modifying the accessible exposed surfaces of particle monolayers fixed on planar substrates.³⁴ In a typical approach shown in Figure 7, Yang and Composto et al. suggested a straightforward method to make optically adjustable silica-gold patchy and multi-region Janus particles of various sizes.³⁷ Briefly, amine-modified silica particles of different sizes and diameters were covalently bonded, through the creation of amide bonds, to a styrene-acrylic acid copolymer film. The particles were then partially sunk into the polymeric film via its swelling in an appropriate solvent. By altering the swelling time, the immersion depth and consequently the Janus ratio of the particles was carefully tuned. Next, Janus particles partially coated with gold were prepared by assembling negatively charged gold nanoparticles onto the positively charged silica surfaces. By varying the surface energy of the silica particles, the dewetting of the gold nanoparticles can be controlled to form patches or hemispherical caps via a thermal annealing process. Whereas desymmetrization at planar surfaces is a very simple method for the fabrication of Janus particles, this method

normally yields very limited amounts of particles, due to the confined interface and limitations in the particle size used.



Figure 7: Schematic representation of the self-assembled formation of patchy and multi-region Janus particles.³⁷

To overcome the problem of low Janus particle yields during desymmetrization at planar surfaces, more efficient routes have been realized, employing systems with high internal interfaces, including particle-stabilized foams and emulsions. Pickering emulsions in particular, are very promising candidates as they provide high internal interfaces, a property of great value for particle immobilization, leading to significant improvements in the preparation of Janus particles. Described for the first time by S.U. Pickering, Pickering emulsions consist of a two phase system, oil and water, while the interface of these two is stabilized by solid particles, for example colloidal silica spheres, adhering to the interphase by physical interactions.³⁸ The formation of Pickering emulsions is challenging with particles of small size, but it is greatly favored for larger size particles, while the strong interaction of the particles with the interphase is beneficial. Based on this principle, Falireas et al. proposed a very elegant way of preparing Janus particles by using polymer as the core of the colloidosomes, as shown in Figure 8.39 In this process, spherical colloidosomes were prepared by immobilizing amine functionalized spherical silica particles onto positively charged polystyrene microspheres. After the modification of the exposed amine groups on the silica surface by an isothiocyanate ATRP initiator, polymer brushes of poly(tert-butyl acrylate) (Pt-BA) and poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) were grafted by a multi-step surface initiated ATRP. Before the polymerization of DMAEMA from the uncovered surface of the Pt-BA-g-SiO2-g-APTES nanoparticles, it was necessary to eliminate the bromide end-groups of the polymer. In this way, the chain growth of the Pt-BA chains with DMAEMA could be avoided on the first hemisphere of the silica nanoparticles. After the removal of the Br atom, the amine groups on the second hemisphere were coupled with the ATRP initiator, followed by the surface initiated ATRP of DMAEMA. In this way, the asymmetry decoration of the nanoparticles via polymer brushes was achieved.



Figure 8: Schematic illustration of the synthetic procedure followed for the preparation of Janus silica particles, bearing Pt-BA and PDMAEMA polymer brushes on their two opposite sides. ³⁹

Another envisaged strategy to realize Janus particles is by a controlled surface nucleation of colloidal particles. Duguet et al. reported a controlled number of polystyrene patches grew onto the surface of silica particles via a seeded-growth emulsion polymerization of styrene, as shown in Figure 9.⁴⁰ The silica surface was treated with a silane at low surface density, in order to promote the surface capture of the growing polystyrene molecules and therefore, the nucleation of the latex particles. By increasing the silane surface density, more encapsulated polystyrene nodules occurred. However, a very high density rendered the silica seed too organophilic, leading to its complete embedding in a single nodule. By this method an extensive range of colloidal particles were produced, ranging from a single to twelve nodules. Next, their conversion into dimpled silica particles was achieved by first re-growing the silica core and then removing the polystyrene by simple dissolution. In addition to sharing the same characteristics as the template satellites in terms of number, size, and location, the as-created dimples also bore anchored polystyrene residues at the bottom of the dimples. The successful functionalization of both the non-protected surface of the grown silica core and of the organic residues, remaining at

the bottom of each dimple, was also demonstrated, thereby providing the possibility of obtaining particles with patches combining both an enthalpic and entropic character.



Figure 9: Silica-polystyrene colloidal molecules obtained through seeded growth emulsion polymerization of styrene in the presence of modified silica seeds.⁴⁰

Janus particle architectures can also be achieved by self-assembly into a desired structure by means of a programmable recognition and binding scheme (Figure 10). Weck et al. reported colloidal particles with well-defined spherical multi-cavities and demonstrated the spontaneous and reversible lock and key recognition between these particles and smaller monodisperse colloidal spheres.⁴¹ This binding is specific because it is controlled by how closely the size of a spherical colloidal key particle matches the radius of the spherical cavity of the lock particle. During their approach, clusters of silica particles were prepared by an emulsion-encapsulation process, followed by a partial encapsulation with an organo-silane shell. By increasing the silane concentration or reaction time, larger shells were obtained. Next, the silica particles were removed by treating the pre-synthesized patchy particles with hydrofluoric acid to generate particles consisting of multiple spherical cavities. The diameter of the cavities corresponded to the diameter of the silica spheres that constitute the cluster template. Finally, the binding effect of these templates with different spherical particles was investigated, displaying a well-defined three-dimensional symmetry, from spherical to pentagonal bipyramid geometries.



Figure 10: Preparation of colloidal particles with multiple cavities having well-defined symmetries.⁴¹

1.4.1.2 Synthetic methods for the preparation of Janus particles based on anisotropic particles

While spherical particles have been widely employed in the synthesis of Janus particles, their anisotropic analogues have received significantly less scientific attention. Due to their tunable and controllable asymmetry in shape, anisotropic particles are capable of overcoming the limitations of the isotropic particles and can combine different functions within a single particle entity, which drives their remarkable potential in different fields, including stabilizers, catalysts, sensors of biological, optical and electrical signals and so on.⁴² A considerable number of approaches, which include masking techniques, seeded methods and Pickering emulsions have been devised for fabricating anisotropic Janus particles. In the following, the emphasis is placed on rod-like particles and some examples reported in the literature.

Anisotropic colloidal particles comprising two or more components could potentially produce a variety of spectacular structures. An interesting example of Janus nanoparticles has been reported by Nie et al.⁴³ In this case, amphiphilic, rod-like silica particles with a hydrophilic and a hydrophobic part were synthesized. Briefly, the synthetic procedure involved the hydrolysis and condensation process of two silica precursors, specifically tetraethylorthosilicate silane (TEOS) and hexadecyltrimethoxy silane (HDTMOS) in an oil phase in the presence of water/ethanol and PVP. The anisotropic synthesis of silica rods was promoted by the hydrolysis and condensation of TEOS at the interface of the water emulsion. By incorporating the second silane, the rods

served as seeds for further propagation of their anisotropic character. Depending on the average hydrophilic/hydrophobic length, the Janus particles underwent morphological transformations in polar solvents, shifting from flower to bundle micelles, and finally to star micelles upon increasing the length of the hydrophobic segment. Self-assembly in apolar solvents, led from reverse spherical micelles to monolayers by increasing the hydrophilic part, indicating the avoidance of the hydrophilic part to interact with the apolar solvent.

An interesting approach to fabricate compartmentalized Janus particles was proposed by Imhof et al.⁴⁴ Figure 11 shows that bullet shaped silica rods with different aspect ratios were employed as seeds to selectively grow polymer patches on the inorganic particle surface. By carrying out a surface modification approach with a silane coupling agent, followed by a typical dispersion polymerization, the polymer nuclei attracted and grew selectively to the flat end of the silica rods. This could be explained in terms of gradient variations of the PVP concentration, as well as differences in the surface energy between the flat ends and the rounded surface of the silica rods. The site of polymer attachment could be tuned, from an end-on to a side-on attachment, by calcination or addition of more silica layers to the anisotropic rods. The first approach resulted in a homogeneous surface chemistry due to the removal of PVP, while the second in an elimination of the flat end of the rods. This revealed that the position of the polymer attachment is primarily determined by the surface heterogeneity. Furthermore, the silica rods were successfully implemented as steric stabilizers by collectively attaching end-on to the surfaces of growing PMMA particles, creating unique hedgehog assemblies.



Figure 11: Control over the Poly(methyl methacrylate) bulb growth on the surface of silica particle.⁴⁵

In order to further explore the potential chemical functionality and physical properties of polymer–inorganic Janus particles, Kumacheva et al. focused on the conjugation of gold nanorod colloids with a copolymer, creating a two patch particle. ⁴⁶ The nanorods were coated with cetyl trimethyl ammonium bromide (CTAB) and were terminated with polystyrene chains at both ends. Preferential binding of CTAB to the side of the particles, makes the rod ends receptive to the binding of thiol-bearing polystyrene molecules. Self-assembly of the polymer-terminated nanorods was achieved by utilizing organic/water mixtures of different weight ratios, resulting in end-to-end or side-by-side orientations. In a DMF/water mixture, the solvent caused their end-to-end assembly into nanochains due to DMF being a poor solvent for polystyrene. When THF was incorporated in the DMF/water mixture, both orientations were observed. By further increasing the organic solvent ratio, particles dominated by their side-by-side assembly and the formation of planar raft-like structures and nanospheres was observed. The percentage of side-by-side associated particles varied with water concentration. By increasing the concentration of water, a higher degree of branching of the nanochains was observed resulting in the formation of networks and significantly reducing the propensity towards side-to-side aggregation.



Figure 12: Schematic showing the types of structures that can be formed between side to side and end to end assemblies.⁴⁶

Beside isotropic particles confined in a spherical geometry in the form of an emulsion droplet, anisotropic silica rod particles could also arrange themselves at the interface (Figure 13). Motivated by their interesting assembly behavior, Datskos et al. employed a Pickering emulsion

based process in order to self-assemble the rods in spherical structures. ⁴⁷ No covalent or ionic chemical bonding was performed to make the self-assembly robust, while the rods were kept together only by weak van der Waals forces. In addition to the self-assembly of the silica rods, the influence of the morphology of the particles on the process was also demonstrated. Segmented silica particles were synthesized by temperature changes during the rod growth. However, smooth silica rods assembled better than their segmented counterparts. This indicated that smooth rods have increased surface contact that provides sufficient interactions to generate the self-assembled structures. This study could be further exploited by functionalizing the exposed surface of the silica rods towards the synthesis of the hybrid Janus rod particles.



Figure 13: SEM images of self-assembled silica rod structures. ⁴⁷

In a similar approach, Imhof et al. self-assembled hybrid silica/polystyrene particles into supraparticles. ⁴⁸ Briefly, polystyrene particles were synthesized by a surfactant free emulsion polymerization, followed by a coating with a thin layer of silica, prior to being used as seeds for the growth of hybrid particles. By incorporating the standard procedure used for the synthesis of pure silica rod particles, matchstick-shaped silica rods with polystyrene heads were prepared. To ensure singular headed matchstick particles, a reduced initial concentration of polystyrene particles was mandatory. It was found that the matchstick particles could self-assemble into supraparticles by simply emulsifying the aqueous matchstick dispersion into a water-in-oil emulsion, followed by slow evaporation of the solvent in the suspended water droplets. This

increase in the concentration of the matchstick particles, which were held together by van der Waals forces, led to supraparticles structures.

Except for the aforementioned methods of fabrication of organic-inorganic Janus particles, anisotropic particles containing two inorganic compartments have also received increasing attention. In a related approach, Wang and coworkers published a strategy to fabricate Janus particles by the selective growth of a variety of metals on anisotropic gold particles. ⁴⁹ In this work, a region-specific silica coating on the flat or curved edges of gold nanorods guided the deposition of anisotropic metal nanostructures (Figure 14). Silica was first deposited on the gold nanorod ends owing to their higher curvature, followed by metal deposition exclusively on the uncoated flat sides of the nanorods, creating anisotropic gold nanorods with metal sides. On the other hand, the nanorod ends were functionalized with a thiol-terminated methoxy poly(ethylene glycol) and were employed as a starting material. Next, the silica coating was selectively grown on the sides of the rods as the condensation of silica on the nanorods ends was hindered. In this case, silica protected metal deposition led to the formation of anisotropic metal end nanostructures. The thickness of the coated silica was adjusted by varying the amount of silica precursor. However, above a certain concentration, the nanorod ends were also covered with silica, thus hindering the growth of the metal. Finally, the silica layer was etched to obtain pure anisotropic metal nanoparticles that are challenging to produce by other methods.



Figure 14: Routes of metal overgrowth. Au nanorod coated with silica at the ends (top) and at the sides (bottom). ⁴⁹

In a pioneering work, Zhao et al. designed dual-mesoporous Janus nanoparticles, containing a one-dimensional mesoporous SiO₂ nanorod and a closely connected mesoporous iron oxide magnetic nanosphere.⁵⁰ First, the Fe₃O₄ nanoparticles were synthesized through a hydrothermal method and were further functionalized by the anisotropic growth of silica rods. Next, the obtained particles were selectively coated with polydopamine, resulting in dual mesoporous Janus nanoparticles after a calcination step. The final asymmetric magnetic Janus nanoparticles, comprising silica and carbon, that are spatially isolated from one another, show complete separation of their hydrophobic and hydrophilic domains. For this reason, the manipulation of the volume ratio between the hydrophilic and hydrophobic domains in every nanoparticle, gave rise to Janus nanoparticles with a surfactant-like ability for emulsion stabilization. This is very important, as different ratios between hydrophilic and hydrophobic moieties can affect the emulsion stability of different emulsion systems. Additionally, the magnetic character of the asymmetric Janus particles enabled the magnetic separation and recycling of the Janus particles, features that are essential for enhancing the effectiveness of biphasic catalysis.

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Chapter 2 - Experimental Section

2.1 Materials and methods

Polyvinylpirrolidone 40 k (PVP, Aldrich), ammonium hydroxide solution (25 wt%, Aldrich), sodium citrate dihydrate (99.0 %, Aldrich), tetraethylorthosilicate (TEOS, 98 %, Aldrich), (3-(APTES, 99%. aminopropyl) triethoxysilane Aldrich), 3-(Methacryloyloxy) propyltrimethoxysilane (MAPTMS, 97%, Thermo Scientific), triethylamine (TEA) (99%, Aldrich) and a-bromoisobutyryl bromide (BiBB, 98%, Aldrich) were used as received. The monomers, methyl methacrylate (MMA, Sigma Aldrich) and styrene (St, Thermo Scientific) were passed through a basic alumina column to remove the inhibitors prior to use. Dry tetrahydrofuran (THF) was refluxed over potassium metal to remove traces of water and was freshly distilled, before use. Ethanol (EtOH, 98 %, absolute, Aldrich), methanol (MeOH, 98 %, Aldrich), tetrahydrofuran (THF, 99.5 %, AppliChem), 1-pentanol (98 %, Alfa aesar) and decane (99 %, Thermo Scientific) were used as received. Milli-Q obtained from a Millipore apparatus with a resistivity of 18.2 M Ω at 298 K (25 °C) was used in all experiments.

2.2 Synthesis of silica rods

The synthesis of rod-shaped silica colloids was adapted from previous reports in the literature ¹¹ ¹⁰. Briefly, 30 g of PVP were mixed with 300 mL of 1-pentanol in a clean 0,5 L round-bottom flask followed by sonication until the complete dissolution of PVP. The solution was further homogenized by stirring with a magnetic stirrer for an hour till the polymer solution reach room temperature. Subsequently, 32 mL of ethanol, 8.1 mL of water and 1.8 mL of 0.18 M aqueous sodium citrate solution were added and the mixture was stirred magnetically for 5 min. Next 6.1 mL of ammonium hydroxide solution (25 wt %) and 2.7 mL of TEOS were added in the reaction flask. The mixture was manually shaken for 30 sec and allowed to react unperturbed without stirring overnight. In order to obtain rods with a higher average aspect ratio, 1.35 ml of TEOS were additionally added 4 hours after the first TEOS addition.

Next the as synthesized silica rods were purified from excess PVP and 1-pentanol by successive centrifugation and re-dispersion cycles with water and ethanol. The silica particles were then size-separated to remove spherical silica particles, as well as shorter and larger silica rods. For this, the suspension of the silica particles were centrifuged at 736g for 12 min, for a total of 15 cycles, and the supernatants were discarded. An additional single fractionation step was performed at 60 g for 12 min to remove very large rods and aggregates. In this final step, the sediment was discarded and the supernatant was collected and dried under vacuum until further use.

2.3 Synthesis of Janus amine functionalized silica rods

The synthesis of amine functionalized Janus rod-like particles was adapted from the procedure described above for the synthesis of silica rods. In a round bottom flask, 30 g of PVP were dissolved in 300 mL of 1-pentanol and sonicated for 2 h. Then, 8.1 mL of Mili-Q water, 1.8 mL of a 0.18 M sodium citrate solution and 32 mL of EtOH were added. The mixture was stirred for 5 min, and 6.1 mL of ammonium hydroxide solution (25 wt%) and 2.7 mL of TEOS were added. After 30 s the stirring was stopped, and the reaction was allowed to proceed for 4 h. Next, 1.35 ml TEOS were added and the spherical flask was gently shaken by hand for 15 sec. The reaction was allowed to proceed overnight. The next day, 1.35 ml APTES were incorporated to the mixture and gently stirred by hand for 15 sec before being left to react overnight. The same purification procedure was used as described above, however the particles were washed and size separated by successive centrifugation and re-dispersion cycles only in ethanol. The obtained particles were dried under vacuum and stored for further use.

2.3.1 Stability of the amine functionalized Janus rods

The stability of the silica rods with the APTES end was studied by firstly dispersing 10 mg of the particles in 7.2 ml ethanol. After mixing the dispersion, 40 ml of Milli-Q water were added and the solution was stirred for 24 h. The stability was monitored by sample collection every 15 min

for the first hour, thereafter, every hour. The particles were washed in ethanol by successive centrifugation and re-dispersion cycles and dried under vacuum until further use. For comparison reasons, stability tests were also conducted under basic solutions using the same procedure as described above. Briefly, 10 mg Janus particles were dispersed in 15 ml of sodium hydroxide solution (1 mM) followed by stirring for 24 h and were washed with ethanol prior to their characterization.

2.3.2 Self-assembly in selective solvents

The segmented Janus silica particles were dispersed in ethanol to obtain a solution with 2 mg mL⁻¹ to 10 mg mL⁻¹ rod concentration. The suspensions were heated to 75 $^{\circ}$ C in a sealed glass vial. The self-assembly of the particles took place via the dropwise addition of decane in the suspension to obtain a final decane volume of 80 vol%, under very gentle stirring. After 30 min, the solution was allowed to cool down to room temperature and was incubated overnight at 40 $^{\circ}$ C to remove the ethanol. A drop of the suspension of the particles was then deposited on glass substrates and was further characterized by microscopy.

2.4 Silica rods as stabilizers in Pickering emulsions

2.4.1 Surface modification of silica rods with MAPTMS

The surface of the silica rods was treated with 3-(methacryloyloxy)propyltrimethoxysilane (MAPTMS). Typically, 0.05 gr of dried silica rod particles were dispersed in 1 ml ethanol by sonication for 1 h. Next, 0.17 ml ammonium hydroxide solution (25 wt %) and 0.5 ml MAPTMS (0.002 mol) were introduced to the mixture and stirred for 3 h at a moderate speed at room temperature. The reaction mixture was then placed in a round bottom flask and the volume of the solution was reduced to ~0.5-1 ml by vacuum distillation. A gel-like suspension was left at the bottom of the flask and was purified by 3 centrifugation/re-dispersion cycles in methanol. The

final suspension of the MAPTMS modified silica rods was dispersed in methanol and was kept in the fridge for no longer than 2 days.



Figure 15: Reaction scheme for the functionalization of the silica particles with methacryloyloxy groups.

2.4.2 Surface modification of silica rods with APTES

Amine functionalized silica rods were also synthesized. For this, 0.05 gr dried silica rods were dispersed in 25 ml dry THF under sonication. Afterwards, the suspension was degassed under a N_2 flow, before the addition of 0.05 ml (0.2 mmol) APTES under nitrogen blanket. The reaction was allowed to proceed for 3 days at room temperature. Finally, the functionalized particles were washed with THF and solvent exchanged to methanol.



Figure 16: Reaction scheme for the functionalization of the silica particles with primary amine group.

2.5 Synthesis of hybrid Janus polymer-silica particles

Janus polymer-silica rods were synthesized by the polymerization of MMA in the presence of silane functionalized silica rods in a polar medium. First, 0.4 gr of PVP (90K) were dissolved in 4 ml methanol via sonication, while another 4 ml methanol were used to disperse 0.050 gr of the silane functionalized particles. Next the two mixtures were combined and stirred for 5 min at high speed. Then, MMA (0.125 gr, 0.001mol) containing 1 wt% AIBN initiator was added to the particle suspension, at a silica-MMA mass ratio of 1:2.5. The reaction mixture was deoxygenated for 0.5 h under a N₂ flow and the reaction flask was placed in a pre-heated oil bath at 60 °C and stirred at 200 rpm overnight. The obtained particles were washed extensively with methanol and were stored in methanol for further purification to remove the free polymer particles. To purify the hybrid particles from the free PMMA particles a mixture of glycerin and water (at a weight ratio of 1:4.2) was used in combination with centrifugation and re-dispersion cycles. The separation was carried out at 800g for 5 h, followed by washing the particles with methanol to remove the glycerin/water mixture. Finally, the purified particles were dispersed in methanol for further use.



Figure 17: Reaction scheme of the synthesis of patchy polymer-coated silica particles.

2.6 Synthesis of Polystyrene colloidosomes stabilized by -silica rods

Pickering emulsion polymerization was used to synthesize colloidosome particles. In a glass vial, 0.2 gr silica particles functionalized with APTES were dispersed in 13.4 ml methanol using vortex mixing. Next, 1.46 ml (0.013 mol) styrene monomer, containing 1 wt% AIBN (0.0173 gr, 0.0001 mol) initiator was added to the suspension under stirring at 200 rpm. The reaction mixture was degassed by a N_2 flow for 10 min and was placed in a pre-heated oil bath at 60 °C for 8 h. After 8 h of polymerization, the reaction was cooled at room temperature and the resulting colloidal dispersion was purified by five consecutive centrifugation/re-dispersion cycles in methanol. This procedure was repeated 10 times to remove any free, unattached silica particles.

2.6.1 Immobilization of initiator onto the exposed surface of silica rods

For the preparation of the hybrid Janus silica rods, their exposed surface was first functionalized. In the above synthesized suspension of amine functionalized silica stabilized polystyrene colloidosomes, 150 μ l BIBB were added, in the presence of trimethylamine (100 μ l) in dry methanol (50 mL). The reaction was performed under gentle stirring at 0 °C for 0.5 h, and the reaction mixture was further incubated at room temperature overnight. The purification of the

product was similar to the procedure described above for the amine functionalized silica rods in methanol. To isolate the bromo-functionalized silica rods and dissolve all the traces of polystyrene, successive centrifugation re-dispersion cycles in toluene were conducted.

2.7 Characterization techniques

2.7.1 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission scanning electron microscopy (FESEM) was performed on a FESEM (JEOL JSM 7000F microscope at an accelerating voltage of 10-30 kV to examine the morphology and dimensions of the bare and patchy particles. All samples were prepared by the deposition of a drop of a dilute colloidal suspension directly onto a clean silicon wafer followed by drying in air. Before the measurements, the samples were sputtered with a 10 nm Au coating. The particle dimensions were analyzed with the ImageJ software to obtain the total end-to-end length (L), the midpoint diameter (D, defined at L/2 along the length axis) used for the calculation of the aspect ratio (AR = L/D) of the particles. Approximately 150 particles were analyzed for each sample to determine the particle size statistics and distributions of L, D, and AR.

2.7.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) provides better spatial resolution than SEM. TEM images were obtained on a JEOL 200-CX microscope operating at 200 kV. For this purpose, a drop of the dilute silica particles dispersion was allowed to dry on a carbon-coated copper grid.

2.7.3 Thermogravimetric analysis (TGA)

The amount of organic content of the silica particles was assessed using a Perkin Elmer Pyris Diamond TG/DTA thermogravimetric analyzer. Samples of ~5 mg were used for each

measurement and the measurement was conducted at a heating rate of 10 °C/min from room temperature to 550 °C under a N_2 flow.

2.7.4 Attenuated total reflection-Fourier transform infrared (ATR-FTIR)

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra were recorded on a Nicolet 6700 optical spectrometer (Thermo Fisher Scientific, Waltham, USA). For each spectrum, 128 scans were collected in the range of 400 - 4000 cm⁻¹.

Chapter 3- Results and discussion

3.1 Analysis of particle silica rods size distribution and chemical composition

Since the first introduction of spherical silica particles of well-controlled size and monodispersity by Stober and coworkers, silica colloids constitute one of the most extensively studied model systems in colloid science.⁵¹ Monodisperse silica spheres are produced by the Stober method via the nucleation of siloxane clusters in a surface-limited reaction. Anisotropic addition of the precursor reagents can lead to the synthesis of asymmetric silica particles.¹¹ Herein, we employed a water-in-oil emulsion method in which the silica particles were grown from droplets of water with PVP dispersed in a 1-pentanol phase, to generate anisotropic silica rods with relatively narrow size distributions after size fractionation, and high reproducibility as well as shape adaptability. Towards this direction, the modification in the reaction conditions increased the aspect ratio of the silica particles, by implementing a second addition of TEOS after the initial addition, provided that the emulsion droplet is still attached at the rod end. The rod length is mainly influenced by the stability of the water droplet, the concentration of TEOS, the facile diffusion of the reagents from the organic phase to the aqueous phase and the rate of hydrolysis and condensation processes within the water droplet. The average dimensions and the morphology of the obtained rods were evaluated using SEM, and the respective results are shown in Figure 18.



Figure 18: SEM images of medium silica rods with one addition of TEOS before (a) and after (b) size separation. Synthesis of large silica rods with two successive additions of TEOS before (c) and after (d) size separation. Distributions of (e) length and (f) diameter of the medium and large silica rods.

In specific, particle sizing from the SEM images using the Image J software revealed a consistent average rod diameter D=300-350 nm and a standard deviation $\sigma_{\rm D}$ =30-70 nm, that did not vary significantly with TEOS addition. On the other hand, the average length, L, and standard deviation in length, σ_L , increased considerably by the successive TEOS addition. Rods generated by a single addition of TEOS had an average length of $2.15 \pm 0.2 \mu m$, while with the second addition of TEOS the average length of the rods increased to $L = 3.42 \pm 0.3 \mu m$. As a consequence, the corresponding average aspect ratio of the particles increased from approximately 6.5 to 10 by implementing two successive TEOS additions. The diameter of the rods was found to typically remain constant and was determined by the initial diameter of the emulsion droplet, while it was not greatly influenced by the TEOS concentration. Moreover, the large polydispersity of the as-synthesized silica rods was improved to around 9 %, by successive washing and size separation. This unavoidably resulted in a great loss in material and a final yield of ~ 50 %. The silica rod synthesis with a second addition of TEOS exhibited a higher polydispersity in size and required additional fractionation steps to improve their uniformity in comparison to their analogues obtained with a single TEOS addition. This phenomenon can be attributed to the increased propensity for termination of the rod growth brought on by the additional shaking necessary to mix the reaction medium after the second addition of TEOS.

3.1.1 Chemical composition of silica rods

Next, TGA analysis was performed on the bare silica rods to identify their thermal stability and organic content. A clear weight loss of 2 wt% was observed for the silica rods below 200 °C, which can be attributed to the physisorbed water and residual organic solvent. In addition, a weight loss of approximately 9 wt% at 400 °C was observed, signifying the decomposition of the PVP polymer and suggesting that, after the synthesis and purification processes, the rods retained a fraction of PVP. The silica rods were also characterized by ATR-FTIR, in the 400 to 4000 cm⁻¹ spectral range and the results are presented in Figure 19. The main bands in the 1300–400 cm⁻¹ regions are due to the characteristic vibrations of the silica network. In specific, the band at 440 cm⁻¹ corresponds to the Si-O bending mode, the band at 795 cm⁻¹ to the Si-O-Si bending mode

and the band at 942 cm⁻¹ to the Si-OH bending mode. Accordingly, the bands at 1050 cm⁻¹ can be attributed to the O-Si-O stretching vibration, the band at 1640 cm⁻¹ to the O-H bending vibration and finally, the broad band centered at 3400 cm⁻¹ can be assigned to the O-H stretching vibration.



Figure 19: (a) TGA plot and (b) ATR-FTIR spectrum of the silica rod particles.

3.2 Janus anisotropic colloidal particles with different chemical functionalities

By implementing a simple strategy, we then fabricated Janus colloidal rod particles with chemical anisotropy at the tip of the silica rods and in specific a functionality asymmetry at the flat end which is attached to the emulsion droplet.⁴³ After the hydrolysis and condensation of TEOS, which resulted in the generation of silica rods as mentioned above, we exploited the droplet attached silica particles as seeds for the nucleation of a second silica precursor with different chemical functionality. For this, APTES was introduced in the oil phase, after the complete consumption of TEOS, resulting in an anisotropic growth of the silica rod-like particles as can been seen in Figure 20. After the addition of APTES, similar hydrolysis-condensation reactions to TEOS occurred in the water phase, resulting in a continuous inorganic silica matrix with the amine functionalities introduced at the end at which the TEOS-derived silica rod was grown. It is worth mentioning, that a finite amount of water and ammonia can mix completely

with the oil phase until a saturation value has been reached. Hydrolysis and condensation reactions and therefore growth of APTES, can occur from both the oil and the water phases. However, since the amine functionalities (APTES) exhibits higher solubility in water, it is expected that the primary growth will take place at the water droplet.¹²

The SEM and TEM images of the synthesized chemical anisotropic Janus silica particles by implementing the two silane precursors are illustrated in Figure 20. The morphologies of the Janus particles reveal a distinct structural boundary between the two silica precursors, indicating the formation of silanol terminated silica rods with a spherical bulb carrying amine groups on its surface. The sphericity of the APTES "cup" evidenced the presence of the droplet at this location. The average length and diameter of the particles was measured as $L = 2.43 \pm 0.5 \mu m$ and $D = 430 \pm 57$ nm, respectively with an aspect ratio of 5.64 and a polydispersity in length of ~19%. However, it is clear that some of the chemical anisotropic Janus rods lack the amine functionalized spherical end as can be seen in Figure 20 (b), shown with red arrows, indicating the disruption of the emulsion droplet caused by the additional shaking required to mix the reaction medium after the introduction of the APTES silane precursor in the reaction mixture.



Figure 20: Janus particles with anisotropic chemical functionalities, (a-b) SEM images before (a) and after (b) size separation, (c-d) TEM images of particles having the elongated rod-like part made from TEOS and the spherical end comprising APTES. The darker color of the silica rod signifies the condensed TEOS (blue arrow) while the grey part is due to the condensation of APTES (purple arrow).

3.2.1 Stability of Janus particles in water - etching process

In order to ensure that the amine functionalization of the rods was not distributed throughout their whole surface, etching experiments were conducted. First, the etching process in pure water indicated that the APTES segment was partially dissolved in water and was collapsed in 30 min, indicating a porous silica structure for the APTES segment, while the silica part remained intact. It is well-known in the literature, the incomplete condensation of the silane precursors creates

porous structures.¹² The addition of a high APTES volume fraction in the reaction mixture causes the formation of oligomers, which assemble onto less dense silica-based structures. Furthermore, in contrast to the majority of organo-functional silanes, the incorporation of silanes having a primary amino function leads to faster condensation reaction rates, due to the dual role of APTES, which includes its function as a silica precursor, in addition to its function as the base catalyst of the condensation reaction.⁵² By extending the incubation time of the Janus silica rods in water, a higher percentage of the APTES segments was removed, until their complete removal after 24 h. The resulting etched particles were imaged by SEM, as shown in Figure 21 (a-b).

Additionally, etching experiments under basic conditions were also conducted. The different etching rates of the organo-silica and pure silica segments of the Janus rods became apparent, since the APTES segment was completely dissolved in 30 min, whereas the silica compartment remained intact. Figure 21 (c-d), shows the SEM images verifying the complete removal of the APTES segment in basic media. This could be explained by the higher porosity and lower density of the APTES segment, compared to the TEOS segment, discussed above, and it a result of the lower silane condensation yield in the APTES segment.^{12 53} On the other hand, the stability of the TEOS segment is caused by a protective silica surface layer which was introduced during the growth of the rod particles. Due to the finite solubility of water and ammonia in the pentanol phase, hydrolyzed TEOS condenses from the oil phase onto the freshly grown silica rods. This creates a thin, but dense, silica shell around the rods and therefore their dissolution is hindered.¹² The presence of even a very low concentration of sodium hydroxide in water, resulted in a faster etching of the APTES segment, when compared that in pure water medium, rendering the basic environment unsuitable for the selective etching of the APTES layer condensed along the long axis of the silica rods.



Figure 21: Silica rods with etched APTES segments in Milli-Q water (a-b) and in 1 mM NaOH (c-d) after 30 min (a,c) and 24 h (b,d) incubation time.

3.2.2 Self-assembly of Janus anisotropic colloidal particles

The anisotropy of the chemical composition, due to the different polarity between the silanol and amine groups on the surface of the silica rods, could allow their self-assembly in selective solvents. However, due to the collapse of the APTES segments when exposed to water, as described in the previous section, we examined organic solvent mixtures of different nature and in specific, ethanol and decane for the self-assembly studies of the chemically anisotropic Janus silica rods. Discrete Janus particles were observed in pure ethanol which is polar (Figure 18), which tended to agglomerate and form aggregates of no specific shape and structure, after the addition of the apolar solvent in the system, as shown in Figure 22. As the decane concentration increased, aggregates with side-by-side alignment of the rods appeared, as the particles tended to avoid interactions with the surrounding apolar solvent while minimizing the interfacial energy. This effect was identified for 2 mg mL⁻¹ and 10 mg mL⁻¹ of particles in the dispersion. At higher concentration of 10 mg mL⁻¹, an alternate placement of the amine functionalized spherical ends of the silica rods was observed at the tightly packed bundle of the silica particles (see red arrows in Figure 22d). The above observations clearly demonstrate that the polarity of the solvent greatly influences the aggregation behavior of the particles. However, we have to highlight that these results are only indicative and the direct observation of the self-assembled silica rods in the wet state, using other microscopy techniques, would be more representative of their assemblies in the selective solvent media, compared to their observation in the dry state by SEM, described in this work. The latter does not provide accurate information, first due to the absence of the solvent medium and the presence of the substrate, as well as due to the increase of the particle concentration during the drying process.



Figure 22: SEM images of the Janus silica rod particles in an ethanol:decane (1:4) solvent mixture at a rod concentration of 2 mg mL⁻¹ (a) and 10 mg mL⁻¹ (b). The amine functionalized spherical "cup" is indicated with the red arrows in (d).

3.3 Site selective nucleation and growth of polymers on the silica rods

Seeded nucleation and growth has been introduced as a new way to efficiently fabricate anisotropic particles. These techniques give rise to the ability of controlling the location of attachment of organic molecules onto colloidal particles, therefore achieving site specific functionalization/adsorption. In particular, the bullet-shaped silica particles could be used as seeds due to their unique geometrical features discussed in the previous sections. The influence of the geometry can provide a smart way to control the location of the attachment of polymeric materials. Therefore, methyl methacrylate was nucleated and grown using the MAPTMS

functionalized silica rods, and resulted in particles with a matchstick shape, as shown in Figure 23 below. The methacryloxy-silane molecules undergo a hydrolysis reaction, transforming the alkoxy silane groups to the highly reactive silanol species. Condensation of the resultant silanols follows forming siloxane bridges. At the same time the growing silane network interacts with the hydroxyl groups on the inorganic silica surface through the formation of hydrogen bonds, while a second condensation occurs resulting in the production of a covalently attached organosilane layer. At this point, the polymer chains precipitate on the silica surface and grow by addition of the monomer on the attached methacrylate groups.



Figure 23: SEM images of hybrid, organic/inorganic, matchstick-shaped particles obtained at a silica:MMA mass ratio of 1:5 (a,b) and 1:2.5 (c,d), using MAPTMS functionalized silica rods. Bare silica rods without MAPTMS at a silica:MMA mass ratio of 1:5 (e-f) did not promote the attachment of the polymer onto the particle tips.

SEM images of the hybrid, silica/PMMA particles indicated that the polymer particles were formed at the flat end of the rods, where the emulsion water droplet was located. However, small nuclei appeared on the long sides of the particles as well, some of them merging together, probably when the position at the flat end was already occupied by a polymer droplet or due to the lack of a flat end on the rods. The observed attachment could be explained by a combination of the particle geometry and the chemical heterogeneity of the surface of the rods. ⁴⁴ The flat surface has lower surface free energy and therefore provides a more favorable position for the nucleation of the spherical PMMA droplet, compared to the curved surfaces. Another possible explanation can be the favorable contact angle of the spherical cup-shaped droplet on the flat surface. When attached on a flat surface, the droplet assumes a spherical shape with minimal surface area and contact angle determined by the Young's Law. In the case of a curved surface more complex behavior is found. The Young's Law boundary requirements for the contact angle between the fluid interface and the solid surface are no longer satisfied, therefore the shape deviates from a spherical bulb. Because of this, little droplets prefer to adhere at the flat end of the particle, maintaining their spherical shape. Beside these reasons, the surface chemistry of the flat end could also affect the drop attachment. This end was in contact with the water rich droplet during the synthesis procedure and therefore contains a higher concentration of PVP and sodium citrate. TGA analysis performed on the as prepared silica particles, showed that the rods contained 9% PVP. It is conceivable thus, that the flat silica end contains more PVP than the rest of the surface of the silica rods. This quantity is however too small to be detected by analytical methods.

It can also be seen in Figure 23 that some particles lacked the polymer bulb indicating that the synthetic procedure was not fully optimized. Furthermore, it was observed that silica particles which lacked the flat end, did not participate as seeds in the polymerization confirming the theories behind the attachment mechanism. To overcome the effect of secondary nucleation of PMMA on the curved rod surface, the mass ratio of MMA to silica was reduced. Figure 23 shows hybrid organic/ inorganic particles at a silica:MMA mass ratio of 1:5, while more optimal results were obtained using an even smaller ratio of silica:MMA ratio of 1:2.5 by mass. The synthesis of those latter particles resulted in a vast amount of free PMMA particles, as identified by SEM. To purify the particles, centrifugation/re-dispersion cycles using a mixture of glycerin and water was used. The higher density of the solvent mixture compared to the PMMA particles

allowed to separate the free polymer, as mentioned in the literature.⁴⁴ Unfortunately, the purification steps removed only to a limited extend the free polymer, while hybrid silica particles were are removed in the discarded supernatant solution, which reduced the amount of hybrid particles obtained as the end product.

It is worth noting, that the surface treatment of the silica rods with MAPTMS promoted the wetting of the silica seed particles by PMMA, while the non-functionalized silica rods did not favor the growth of PMMA on the flat surface of the rods as shown in Figure 23 (e-f) above. However, this does not provide accurate information about the selective attachment location of the polymer as a monolayer of MAPTMS was created on the surface of the silica rods.

Besides methacryloxysilane, APTES, which contains an amino organo-functional group and the same number of alkoxy groups as MAPTMS, was also introduced on the surface of the rod particles, followed by the polymerization of PMMA as mentioned above for the MAPTMS functionalized silica rods. The respective results are shown in Figure 24.



Figure 24: SEM images of the product obtained from the polymerization of MMA in the presence of APTES-functionalized silica rods at a silica:MMA mass ratio of 1:2.5.

As seen in the SEM images, the majority of the polymeric particles were not grown from the flat end of the silica rods, as was observed for the MAPTMS functionalized analogues, instead they were present in the form of free particles. It was assumed that the compatibility between the polymer and the silane organo-functional groups was not sufficiently high to allow the strong adhesion of the polymer on the silica surface. Furthermore, another reason can be attributed to the possible reaction routes of APTES silanization on the silica particles. The general silanization sequence follows the hydrolysis of the alkoxy groups and their condensation with the hydroxyl groups on the silica surface to form siloxane bridges. However, several conformations can be attained, some of which are associated with low silane grafting density and others which result in weakly attached silane molecules, as can be seen in Figure 25.^{54,55} The optimal orientation comprises APTES molecules covalently attached on the substrate with and their amino groups extending away from the interface. Amino groups can then form a weak hydrogen bond with unreactive surface silanol group or with the silanol group of other APTES molecules, minimizing grafting density. The ethoxy groups can be hydrogen bonded with the surface hydroxyl groups can also be protonated retaining their ethoxy groups. As a result of the complexities discussed above, the nature of bonding at the interface and within the aminosilane layer is not clear.



Figure 25: Different types of interactions between APTES molecules and silicon dioxide substrates. (a) Covalently attached APTES molecule with its amine group extending away from the interface. (b-c) Covalently attached APTES molecule with its amine group interacting with a surface silanol group. (d-e) Weakly bounded APTES molecules due to hydrogen bonding interactions.

3.4 Polystyrene-silica rods hybrid colloidosomes

An alternative approach was also exploited for the preparation of Janus particles, which involved the formation of colloidosomes in an emulsion polymerization of styrene in the presence of silica rod particles. This led to the formation of solid polystyrene particles emulsified by the silica rods. The polymerization of styrene in the presence of silica rods of different aspect ratios, using AIBN as the initiator, led to the formation of colloidally stable nanocomposite particles. Adsorption occurred via the well-known Ramsden-Pickering effect, that leads to a minimum in surface free energy upon adsorption of particles at the liquid-liquid droplet interface and takes place only if the particles can be wetted by both liquid phases.⁵⁶ In order to realize the adsorption of the highly hydrophilic silica particles on the styrene droplets, the silica rods were first amine functionalized with APTES to improve the particle-styrene affinity. Figure 26 verifies the synthesis of the hybrid colloidosomes and the adsorption of the silica particles on the surface of the spherical polystyrene particles.



Figure 26: SEM images of the Polystyrene/ silica rods hybrid colloidosomes. Silica rods with aspect ratio of (a,b) 10 and (c,d) 2.8. The perpendicular oriented functionalized silica particles are indicated with the red arrows.

However, the presence of a small fraction of free silica particles was observed, while some areas on the polystyrene surface were not covered by the silica rods. These results can be ascribed to the non-optimized synthetic conditions in terms of the styrene/silica feed ratio. To address this issue and embed more silica particles onto the polymer surface, smaller aspect ratio silica rods were employed. Similarly, a good coverage of the polystyrene surface was achieved, while some inorganic particles were not attached on the polymeric surface. Interestingly, we also observed that some particles preferred to orient themselves perpendicular to the interface, instead of orienting alongside (indicated with red arrows in Figure 26d). This was attributed to the smaller gravimetric effects of the particles with a smaller aspect ratio.

The preparation of Janus particles was exploited by the in-situ modification of the exposed to the continuous phase surface of the silica rod particles, with a bromide initiator. The primary amine groups of the silanized silica rods can undergo a nucleophilic substitution reaction with the acyl bromide groups of BiBB. Once surface modification was complete, the non-crosslinked polymer was dissolved using toluene and the Janus particles were isolated for characterization. Figure 27 shows the silica rods after the purification procedure with toluene. Despite the significant visual weight loss of the sediment, after the purification procedure with toluene, traces of polystyrene were still present in the sample rendering the functionalized silica particles unsuitable for further modifications. These results require further investigation, as the colloidosomes was dispersed in a large excess of toluene during the purification process and were extensively washed with the organic solvent. Perhaps heating of the dispersion could facilitate the dissolution of the polystyrene and the purification of the silica rods.



Figure 27: SEM images of the bromide functionalized Janus silica rods after purification in toluene.

4. Conclusion and Future perspectives

In this thesis, we report the synthesis of Janus rod-like particles utilizing different synthetic approaches. Prior to the preparation of the Janus particles, we present the synthesis of monodisperse bullet shaped rod-like silica colloids with tunable dimensions. The incorporation of additional TEOS during the synthesis led to an increase of the aspect ratio of the rods. By introducing an organo-silica precursor with an amino functionality, the silica rods were exploited towards the preparation of amine functionalized Janus silica particles with a polar head. The latter particles self-assembled in mixtures of ethanol and apolar solvent, and formed clusters to avoid the interactions with the apolar medium. Furthermore, we prepared hybrid silica-polymer particles via a typical dispersion polymerization of MMA in the presence of the bullet-shaped colloidal silica rods, which led to matchstick-shaped silica particles. The selective attachment of the polymer onto the one end of the rods was mainly driven by a difference in the surface chemistry and the geometry at the flat end of the rod colloids. Finally, the preparation of colloidosomes via the adsorption of hydrophobized silica rods onto the surface of polystyrene spheres was achieved via an emulsion polymerization of styrene in the presence of the silica rod particles, although some further work is required to obtain well-defined Janus particles with chemical and physical anisotropy.

In future work, the synthetic procedure for the preparation of the silica rods can be optimized. The reaction conditions strongly influence the shape of the rods resulting in particles with shapes ranging from spherical to rod-like to curly-like. In addition, a tapering effect of the rod diameter and tailing of the flat end of the rods were observed, which are in contrast to the flat end silica rods anticipated from this growth mechanism. This affected the polydispersity of the synthesized Janus particles as the presence of the flat end is crucial for their formation. Furthermore, an initiator could be incorporated at the free surface of the silica rods attached onto the polystyrene-silica colloidosomes, allowing for further modification of the exposed surface. Next, a polymer could be selectively grown from the initiator-immobilized silica surface using the grafting from method. Finally, the self-assembly of these polymer-grafted Janus particles should be studied.

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