Assembling anisotropic colloidal building blocks

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CHAPTER 2

SPHERICAL, DIMPLED AND CRUMPLED COLLOIDS WITH TUNABLE SURFACE MORPHOLOGY

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Abstract

Surface morphology is a tool to tune physical properties of colloidal suspensions such as the wettability, viscoelasticity and depletion attractions. Existing synthesis methods to obtain colloids with a rough surface morphology often result in colloids with non-tunable surface properties. Here, we developed a synthetic approach to obtain both spherical and shape-anisotropic hybrid colloids with tunable surface morphology. With our approach monodisperse linear polystyrene colloids, obtained in large quantities using a dispersion polymerization method, are swollen and crosslinked with styrene and 3-(Trimethoxysilyl)propyl methacrylate (TPM) in the presence of the polymerization inhibitor hydroquinone. We show that by varying only two experimental parameters, the concentration of the inhibitor and of TPM during swelling linear polystyrene colloids, three different types of particles can be synthesized. At low TPM concentration spherical colloids are obtained where the surface roughness can be tuned by varying the hydroquinone concentration. At intermediate TPM concentrations single-dimpled colloids are formed with tunable dimple size. High TPM concentrations yield crumpled colloids of various shapes. Additionally, we demonstrate that all particles can be used as templates for silica coating, resulting in electrostatically stabilized silica-coated hybrid colloids or silica shells with rough, smooth, dimpled or crumbled surface morphology.

2.1 Introduction

The surface morphology of colloidal particles plays a crucial role in many physical phenomena. For instance, theory predicts that the surface roughness of colloids is of major influence on the interactions between particles at liquid-liquid interfaces, due to nanoscopic deformations of the interface.[40–42] Recently, it has also been proposed that shear thickening behavior of colloidal suspensions is mainly governed by frictional forces.[43–45] Since frictional forces in dispersions depend on the surface morphology of the colloids, the viscoelastic properties of rough particle suspensions are expected to differ from suspensions of particles with a smooth surface.

Surface morphology can also be used as a tool to induce directional interactions between particles by tuning the strength of depletion forces through the site-specific overlap volume.[46] Using depletion interactions, rod-like, micellar or tubular structures can be assembled from anisotropic particles with smooth and a rough surface depending on whether particles with a platelet, snowman or mickey-mouse shape are employed.[29,32,46–48] Likewise, depletion forces enable the formation of lock-and-key structures from particles with an extreme degree of surface roughness, that is colloids with a dimpled surface.[11] These lock-and-key structures were assembled from dimpled particles and spheres that precisely fit the dimple and therefore are strongly attracted to it in the presence of a depletant.

Colloids with rough surfaces and dimples have been prepared by several methods. Dimpled and crumpled colloids can be obtained by inducing buckling of a rigid shell in core-shell structures, typically by dissolution or volume reduction of the core.[6,49] The rigidity and thickness of the shell and rate of deformation play a crucial role in the buckling process.[12,50–52]

Surface roughness can be achieved by depositing or growing a second type of smaller particle, for instance, inorganic nanoparticles[53], polystyrene[54] or silica spheres[55–57]. Rough polymer colloids, for example from poly(methylmethacrylate) or polystyrene, can be synthesized from linear seed particles by tuning the crosslink density, molecular weight of the polymer and type of apolar solvent during shell growth.[58–60] We recently found that hybrid colloids with a rough surface morphology can be achieved by swelling linear polystyrene colloids functionalized with poly(vinyl alcohol) (PVA) with a mixture of styrene and 3-(trimethoxysilyl)propyl methacrylate. During polymerization, secondary nucleated particles adsorbed onto the seed particles thereby yielding rough crosslinked polystyrene spheres, which we employed to create snowman particles with smooth and rough sides.[29]

In this paper, we focus on controlling the degree of surface roughness by employing the inhibitor hydroquinone (HQ) and the overall particle shape of the polymer particles after crosslinking by systematically varying the synthesis parameters. We find that this approach not only is able to produce spherical particles with a tunable coverage with asperities, but also particles with a dimpled and crumpled morphology. Since our synthesis procedure is based on a dispersion polymerization method, we obtain monodisperse colloids in high yields. We show that by varying only two experimental parameters, that is the concentration of the polymerization inhibitor hydroquinone (HQ) in the aqueous phase and the volume ratio of styrene : 3-(trimethoxysilyl) propyl methacrylate (TPM) of the swelling solution, rough, semi-rough, smooth, dimpled and crumpled colloids with different material composition (polystyrene, polystyrene-TPM) can be obtained.

Furthermore, we demonstrate that silica coating can be achieved without loss of the particle morphology.[61–63] Silica colloids with a rough surface morphology are particularly interesting for their photoresponsive and superhydrophobic properties[53,64–67] but also as model dispersions for studying the hypothesized roughness induced shear thickening[43–45]. We provide evidence from zetapotential measurements that the silica coating changed the stabilization mechanism of the colloids from steric to electrostatic stabilization. Finally, we show that by removing the organic core hollow silica shells of different morphologies are obtained as well.

2.2 Experimental Methods

Materials

Styrene (≥99%, contains 4-tert-butylcatechol as stabilizer), divinylbenzene (DVB, technical grade 55%), sodium dodecyl sulfate (SDS, ≥98.5%), hydroquinone (HQ, ≥99.5%), poly(vinyl alcohol) (PVA, Mw 72,000, 88% hydrolyzed), azobisisobutyronitril (AIBN, ≥98%), ammonium hydroxide(ACS reagent, 28.0–30.0% NH3 basis), Ethanol (EtOH, puriss., 96%) and 3-(Trimethoxysilyl)propyl methacrylate (TPM, 98%) were purchased from Sigma-Aldrich. Poly(vinylpyrrolidone) (PVP-40, K30, Mw 40,000) and Poly(vinylpyrrolidone) (PVP-360, K90, Mw 360,000) were purchased from Fluka, Germany. The tetraethyl orthosilicate (TEOS, 98%) was supplied by Acros Organics. All chemicals were used as received and all solutions were prepared from deionized water with 18.2MΩ·cm resistivity, using a Millipore Filtration System (Milli-Q® Gradient A10), unless stated otherwise

Methods

Linear polystryene synthesis Linear polystyrene spheres were synthesized by a dispersion polymerization method performed in ethanol.[68] Here, 20 g of PVP-40 was dissolved in 545 mL EtOH and 56 mL of water by shaking and ultrasonication. To the PVP-solution a swelling solution containing 554.26 mg of AIBN in 40 mL styrene was added under magnetic stirring. The reaction mixture was flushed with N_2(g) for 20 min and transferred to a preheated oil bath (75°C) where it was stirred magnetically at 320 rpm for 24h. A high yield of monodisperse linear polystyrene colloids of 910 ± 30 nm in diameter (as measured from scanning electron micrographs) was obtained.

Crosslinked polystryene synthesis Crosslinked polystyrene colloids with tunable surface morphology were obtained by swelling and crosslinking the PVP-functionalized linear polystyrene particles with a mixture of styrene and TPM including 2% wt AIBN and 1.5% v/v DVB. Before swelling, the linear seeds were washed twice with water, and subsequently they were transferred to a 1% wt PVA-solution. The final particle concentration of this dispersion was 15.1% wt. A mixture containing 4.4 mL of 1% wt PVA-solution in water, 0.88 mL of swelling solution and no, 0.0029 or 0.0185% wt HQ with respect to the total volume, was emulsified for 2 min at 8000 rpm followed by 10 s at 10,000 rpm using an IKA T18 Ultra Turrax emulsifier. Immediately after emulsification the emulsion was transferred to a 20 mL glass flask containing 1.32 g of linear polystyrene dispersion (15.1% wt). The flask was shaken gently by hand for 30-60 s, flushed with N_2(g) for 10 s, sealed with Teflon tape and placed on a tumbler covered in aluminium-foil to avoid UV-light exposure at 13 rpm. After 24h of swelling the flasks were transferred to a preheated oilbath (72°C) and rotated under a 45○ angle at 60 rpm for 24h. The following styrene:TPM v/v ratios were used: 100:0, 98:2, 94:6, 90:10, 70:30, 50:50, 30:70, 25:75, 20:80, 0:100.

Silica coating Rough and smooth colloids swollen with a styrene:TPM v/v ratio of 90:10, dimpled colloids swollen with a styrene:TPM ratio of 20:80 in the presence of 0.0183% wt HQ and crumpled colloids swollen with solely TPM were coated with silica according to a method developed by Graf et al.[61] To remove excess PVA molecules from the surface of the colloids the dispersions were washed twice with water. To coat the colloids with PVP, 1.5 mL of 10 g/L PVP-360 solution, prepared at most 2 days before use, was added to 1.5 mL of colloid dispersion (8% wt). The mixture was magnetically stirred at 250 rpm for 24h to assure adsorption of the PVP-molecules to the colloid surface. The colloids were washed once to remove excess PVP and redispersed in an ethanonl with 4.2% v/v ammonia solution by ultrasonication for 10 min. This was followed by the addition of 900 μL of TEOS in 5-10 s under vigorous magnetic stirring at 400 rpm. The reaction mixture was stirred for 18-24h and finally washed with ethanol or water to remove excess reaction components.

Silica shell formation by decompostion of organic components To obtain silica shells the silica coated colloids were heated for 5h at 450°C in a Nabertherm

B180 oven to decompose the organic polymer core.[69]

Imaging and analysis Bright field microscopy images of colloids swollen with a swelling solution containing 50:50 or 0:100 v/v styrene:TPM were acquired using a Nikon Eclipse Ti microscope with an A1R confocal scan head with a 100x oil immersion objective (NA = 1.4). The polymerized hybrid colloids were imaged using a FEI nanoSEM scanning electron microscope (SEM) at 15 kV and a JEOL JEM-1010 transmission electron microscope at 80 kV. The average diameter of the particles was determined by measuring the circumference of 50-200 particles in the SEM micrographs using ImageJ. For the diameter of the rough and semi-rough colloids the circumference of the spheres without the protruding part of the asperities was measured. The degree of roughness was determined by counting the number of small asperities positioned on the visible hemisphere of 18 representative particles per sample. Zetapotential measurements were performed using a Malvern Zetasizer Nano ZS.

2.3 Results and Discussion

2.3.1 Synthetic approach

To elucidate the formation of the surface roughness during swelling and crosslinking, we performed a systematic set of experiments where linear polystyrene colloids were swollen with several styrene:TPM v/v ratios. The linear polystyrene colloids were prepared by a dispersion polymerization yielding sterically stabilized particles 910 ± 30 nm in diameter. These colloids were swollen with a constant volume of a monomer mixture, which consisted of styrene and TPM at volume ratios ranging from 0:100 to 100:0. To the swelling solution 1.5% v/v divinylbenzene (DVB) was added as a crosslinking agent. The swelling solution was emulsified in an aqueous 1% wt poly(vinyl alcohol) (PVA) solution, before it was added to the linear seed dispersion. After swelling for 24h, we polymerized the particles by the decomposition of the radical initiator AIBN at elevated temperature and analyzed the surface morphologies of the resulting micron-sized hybrid polystyrene-TPM colloids using SEM. It was previously observed, that the surface roughness should originate from the adsorption of secondary nucleated particles during the polymerization step since the size of the asperities on the rough particles was found to be equal to the size of non-adsorbed secondary particles. Therefore, we expected that controlling the nucleation of polymers in the aqueous phase should affect the degree of surface roughness of the resulting particles. We achieved this control by the introduction of an additional component, the aromatic compound HQ, during synthesis. HQ suppresses the polymerization of monomers in the aqueous phase and thus secondary nucleation.[70]

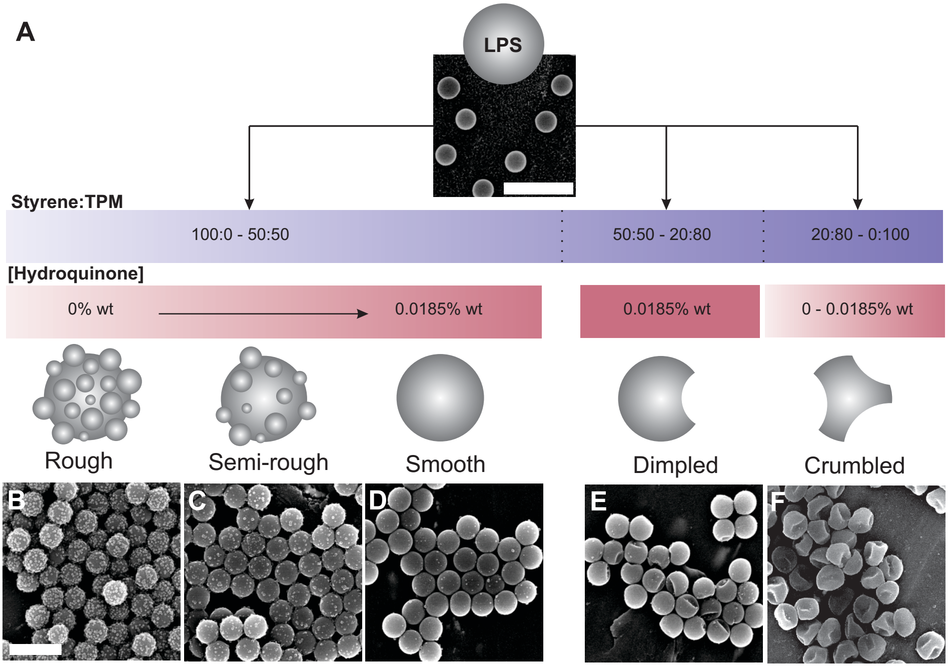


FIGURE 2.1: Synthetic approach to fabricate spherical colloids with tunable surface roughness and shape. The surface morphology is tuned by variation of the HQ concentration and styrene:TPM v/v ratio used for swelling linear polystyrene (LPS) particles. Scalebar is 3 μm. A) Spherical colloids are formed by swelling LPS particles with styrene:TPM v/v ratios between 100:0 and 50:50. By varying the HQ concentrations at these compositions, the surface morphology changes gradually from rough to smooth. Dimpled colloids are obtained after swelling with styrene:TPM v/v ratios of 50:50 to 20:80 at 0.0185% wt HQ. Crumpled colloids were observed at [TPM] $\geq$ 80% v/v. B-F) SEM micrographs of colloids with a rough (B), semi-rough (C) and smooth (D) surface morphology formed by swelling LPS particles with a 90:10 styrene:TPM v/v ratio with no, 0.0029 and 0.0185% wt HQ, respectively. Single-dimpled colloids (E) and crumpled colloids (F) were obtained by swelling with 50% v/v TPM (E, 0.0185% wt HQ) and 100% v/v TPM (F, no HQ), respectively.

Indeed, in the absence of HQ we readily obtained rough spherical colloidal particles for a wide range of styrene:TPM v/v ratios from 100:0 to 50:50, see Figure 2.1A and 2.1B. However, when we introduced increasing concentrations of HQ during swelling, the degree of surface roughness decreased, yielding a semi-rough (Figure 2.1C) and smooth (Figure 2.1D) surface morphology at 0.0029% wt and 0.0185% wt HQ, respectively. Thus, the presence of the inhibitor suppresses the formation and adsorption of secondary particles during polymerization and thereby enables control over the surface roughness.

Surprisingly, when the TPM concentration ([TPM]) in the swelling solution was increased to $\geq$ 50% v/v, anisotropic particle shapes were formed. At intermediate styrene:TPM v/v ratios of 50:50 to 20:80 and 0.0185% wt HQ, we obtained smooth colloids with a single dimple (Figure 2.1E). At high TPM concentrations $\geq$ 80% v/v, crumpled colloids of various shapes were observed, of which one is shown in Figure 2.1F. The TPM concentration therefore influences the overall particle shape.

Thus, the swelling-based synthesis approach allows the fabrication of hybrid polystyrene-TPM colloids with tunable surface morphology by controlling the TPM and HQ concentrations. Figure 2.1 schematically summarizes the conditions that lead to the different morphologies, ranging from spheres with controllable roughness to dimpled and crumbled particles. In the following sections, we will quantify these morphologies in more detail for each of the three regimes and discuss the role of TPM and HQ.

2.3.2 Spherical colloids with tunable surface roughness

We explored the effect of the TPM concentration by systematically varying the ratio of styrene and TPM during the swelling step. For TPM concentrations below 50% v/v of the monomer mixture, we always obtained spherical colloids (Figure 2.2A). In the absence of HQ, the surface of the spherical particles is rough through the adsorption of spherical particles with a diameter of 70-180 nm. Interestingly, these asperities become gradually more submersed into the particle surface with increasing TPM concentrations, see Figure 2.2B. While at styrene:TPM ratios of 100:0 to 90:10 the asperities are only slightly embedded in the particle, the asperities are submersed roughly halfway at volume ratios of 70:30 and 50:50.

To suppress the formation of these asperities and therefore the degree of roughness, HQ was added during swelling. In the presence of 0.0029% wt HQ polymerization of the monomer in the aqueous medium is partly suppressed, resulting in semi-rough particles (Figure 2.2A, middle column). Here, the number of asperities adsorbed on the surface of the swollen seed particles is drastically reduced compared to the rough particles formed in the absence of HQ. At 0.0185% wt HQ a smooth surface morphology was obtained, indicating that secondary nucleation is completely suppressed (Figure 2.2A right column). The particles shown in Figure 2.2A are representative of the respective batch of colloids obtained under these conditions. SEM images of a larger field of view of these batches can be found in Figure 2.3.

We quantified this observation of decreasing degree of roughness with increasing HQ concentration by measuring the average number of nanoparticles per surface area of the seed particles (Figure 2.2C). An average of 31 adsorbed asperities per

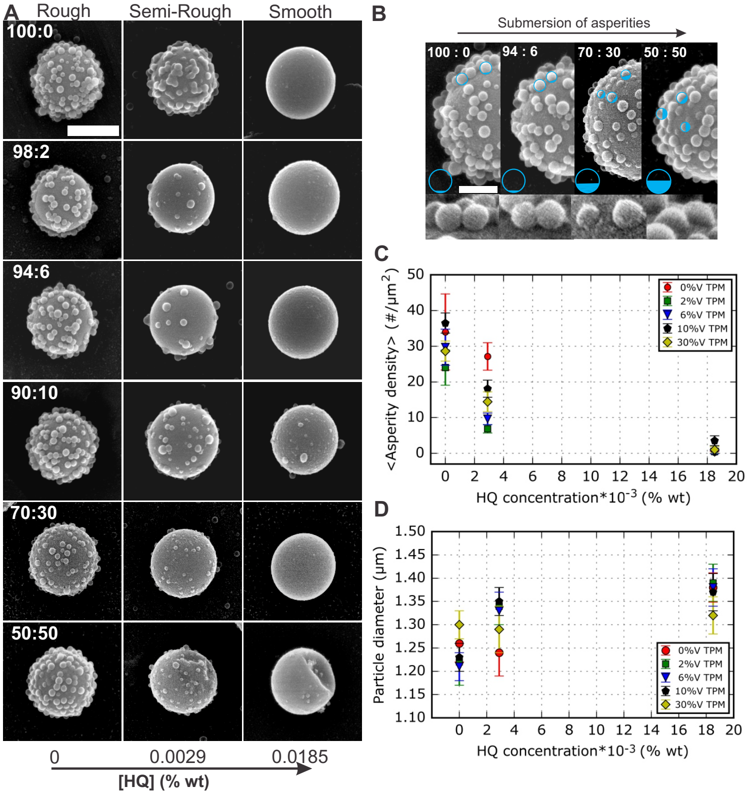


FIGURE 2.2: [HQ] and [TPM] dependent surface morphology at [TPM] $\leq$ 50% v/v. A) SEM micrographs of spheres obtained by swelling LPS colloids with styrene:TPM v/v ratios of 100:0, 98:2, 94:6, 90:10, 70:30 and 50:50. The particles were swollen in the absence of HQ (left column), in the presence of 0.0029% wt HQ (middle column) and with 0.0185% wt HQ (right column), resulting in rough, semi-rough and smooth particle surface morphologies, respectively. Scalebar is 1 μm. B) The submersion of asperities in the particle surface increases with the TPM concentration. The styrene:TPM v/v ratio is indicated on the upper left of the images. Scalebar is 500 nm. In the lower row, enlarged images of two submersed asperities of the respective samples are displayed. C) The average number of asperities per surface area decreases with the HQ concentration. D) The particle size increases slightly with the HQ concentration indicating that more monomer is absorbed by the seed particles.

μm^2 is measured for the rough particles, which decreases to 15 asperities per μm^2 for the semi-rough, and 1 for the smooth particles. The number of asperities per surface area also increases slightly with [TPM].
The part of monomer that is used for the formation of the asperities in the rough

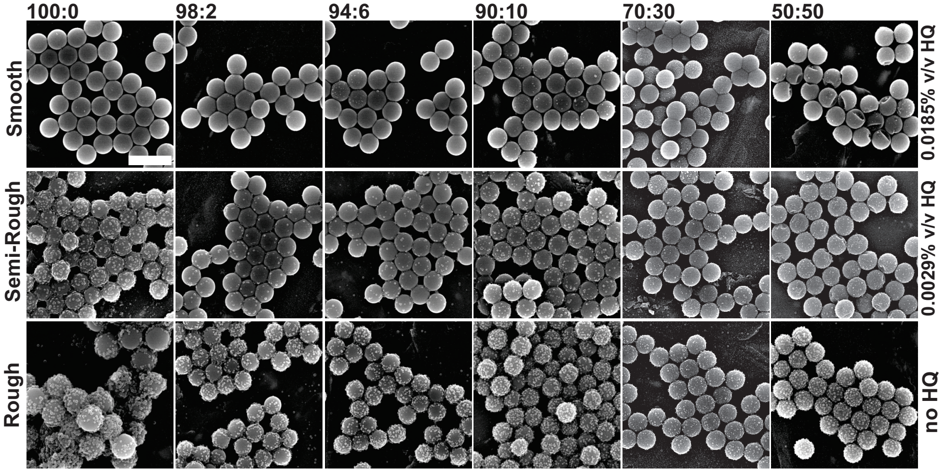


FIGURE 2.3: Spherical colloids with tunable surface roughness obtained by swelling linear polystyrene spheres with styrene:TPM ratios of 100:0 to 50:50. SEM micrographs of colloids synthesized at [TPM] $\leq$ 50% v/v corresponding to the batches of the single particles shown in Figure 2.2A. Scalebar is 3 μm.

spheres should in the presence of HQ be absorbed by the seed particles instead. As a consequence, the total absorbed monomer volume should increase, resulting in colloids of a larger size. To confirm this hypothesis, we measured the size of the rough, semi-rough and smooth particles using SEM micrographs. Here, the diameter of the colloids was measured by fitting a circle to the circumference of the colloids without taking the protruding part of the asperities into account. Figure 2.2D displays the average particle diameter as a function of the HQ concentration. On average, particles of 1.24 $\pm$ 0.04 μm in diameter are formed without HQ, which increases to 1.31 $\pm$ 0.04 μm in the presence of 0.0029% wt HQ and 1.37 $\pm$ 0.04 μm with 0.0185% wt HQ. While the particle diameter averaged over all TPM:styrene ratios clearly increases, for a given ratio this trend only becomes convincing for high HQ concentrations: all particle diameters increases significantly compared to the case when no hydroquinone was present except the sample containing 30% v/v TPM. These observations support our hypothesis that more monomer is adsorbed by the seed particles in the presence of HQ. Swelling linear polystyrene colloids with [TPM] $\leq$ 50% v/v results in particles with not only a different degree of surface roughness, but also different surface properties. Figure 2.2B already showed that submersion of the asperities increases with the TPM concentration. Besides the submersion of the asperities, we observed that the colloidal stability of these rough particles also depends on the [TPM]. When colloids were swollen solely with styrene, we frequently observed aggregates of

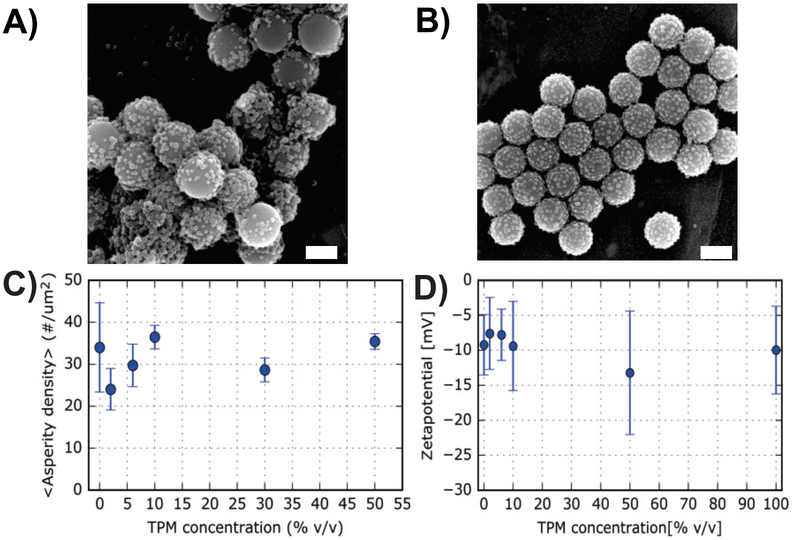


FIGURE 2.4: Surface roughness uniformity and stabilization for colloids swollen with [TPM] $\leq$ 50% v/v. Scalebar is 1 μm. A-B) SEM micrographs of LPS colloids swollen in the absence of HQ. A) Rough colloids obtained by swelling with 100% v/v styrene. The asperities on these colloids are non-uniformly distributed on the surface. (B) Rough stable colloids were formed by swelling with a styrene:TPM v/v ratio of 50:50. The particle surface is uniformly covered with asperities. C) The spread in the distribution of asperities on the surface of the particles decreases with the TPM concentration. D) Zetapotential values of polystyrene-TPM hybrid colloids, obtained by swelling with styrene:TPM ratios of 100:0 to 0:100. The zetapotential is not sufficient to contribute electrostatically to the stabilization of the colloids.

rough colloids in the SEM images, see Figure 2.4A. Furthermore, it can be seen that the asperities are non-uniformly distributed on the particle surface and that the nanoparticles seem to glue the colloids together. In contrast, when 2-50% v/v TPM was introduced in the swelling solution, stable rough particles with a uniform distribution of asperities were formed (Figure 2.4B and 2.4C).

A statistical analysis confirms that the roughness is non-uniformly distributed on the surface of colloids swollen with solely styrene: the number of asperities per surface area shows a large spread (Figure 2.4C). Already by introducing 2% v/v TPM during swelling the standard deviation of the asperity density decreases drastically, resulting in a more uniformly covered surface. The spread becomes even smaller for colloids swollen with 6-50% v/v TPM. This shows that the roughness uniformity is increased by the addition of TPM to the swelling solution. Since the zetapotential of the colloids was measured to be on the order of -10 mV and independent of the [TPM], which is not sufficient to induce electrostatic stabilization, we can rule out that TPM led to an additional stabilization by charge (see Figure 2.4D). Therefore, we assume that the increased stabilization of the colloids originates mainly from the adsorbed PVA molecules on the particle surface. The adsorption of this polymer to the surface is dependent on the affinity of the PVA molecules to the particle material. Apparently, the PVA molecules have a higher affinity for TPM compared to polystyrene leading to an increase in stability in the presence of TPM. We also note that aggregation of the polystyrene colloids is not observed in the presence of HQ, pointing towards either an additional stabilization by HQ or that the secondary nucleated particles are causing this aggregation.

2.3.3 Buckling mechanism for colloids swollen with mainly TPM

Surprising results were obtained when the linear colloids were swollen with [TPM] $\geq$ 50% v/v. At these compositions, the seed particles remained spherical in shape during swelling (Figure 2.5A), but buckling occurred during polymerization leading to an anisotropy in the particle shape (Figure 2.5B). Buckling has been observed previously for hollow shell-like structures and core-shell particles.[6,50,58,71] Experiments and simulations have shown that for shell-buckling to occur the volume in the shell needs to decrease.[49,69] This can be achieved by removal of the core, or by decreasing the core volume due to changes in density or pressure. Another important parameter for shell-buckling is the ratio between the thickness of the shell h compared to the radius of the particle R.[12,72] Thinner shells from siloxanes and silica, where h/R is in the order of 0.3 and lower, are more elastic and therefore more prone to buckling due to the lack of mechanical strength.[70] For the final shape obtained after buckling the elastic properties of the shell are determinative, where elastic shells buckle into multi-dimpled colloids and less elastic shells buckle into a single dimple.[52] Besides the dimpled particles, shells can also completely collapse at high compression rates and large volume changes, resulting in crumpled particles.[51]

We believe that by swelling linear seeds with both styrene and TPM, we synthesized particles with a core-shell structure. We expect that while the styrene monomer is mostly absorbed by the linear seeds, TPM is more prone to be located at the surface of the particles since TPM is more hydrophilic compared to styrene.[73] While the styrene is a good solvent for the linear polymer in the core, TPM is known to form oligomer networks through a hydrolysis-condensation reaction, potentially creating a rigid shell at the surface, even before polymerization.[6] Upon polymerization, the volume of the swollen core will decrease with respect to the hardened shell due to the higher density of polystyrene (1.04 g/cm^3) and polymerized TPM (1.31 g/cm^3) compared to liquid styrene (0.90 g/cm^3) and

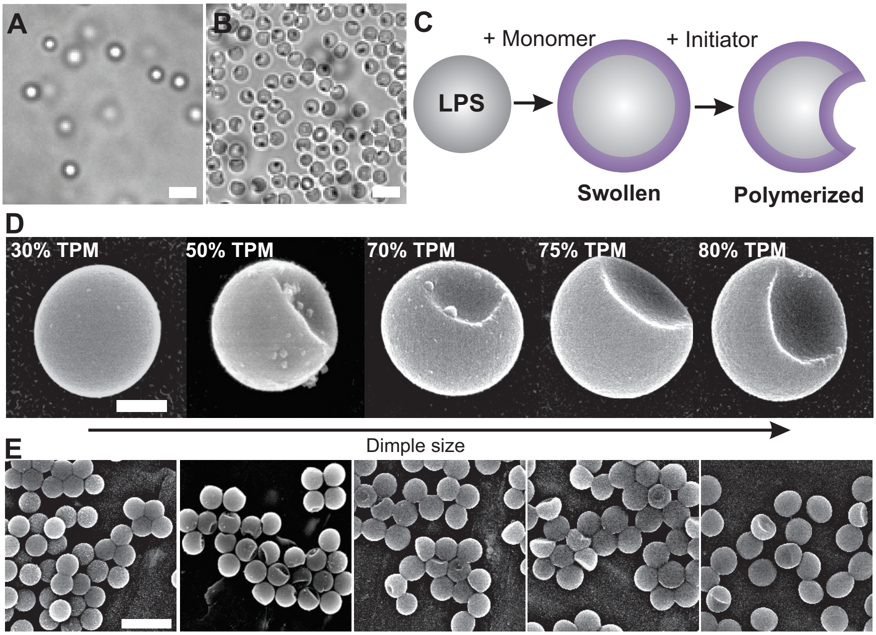


FIGURE 2.5: Dimpled colloids with tunable dimple size at [TPM] of 50-80% v/v. A) Bright field microscopy image of large spherical colloids obtained after swelling with a styrene:TPM v/v ratio of 20:80 for 23 h. B) Bright field microscopy image of dimpled colloids formed after polymerizing colloids swollen 50% v/v TPM. Scale bar in (A) and (B) is 2 μm. C) Illustration of the buckling process. First, a TPM shell is deposited on the particle during swelling. During polymerization, this shell buckles resulting in the formation of a dimple. D) Series of SEM micrographs of dimpled colloids obtained at TPM concentrations of 30-80% v/v in the presence of 0.0185% wt HQ. The dimple size increases with the TPM concentration. At [TPM] $\geq$ 75% v/v, besides dimpled, crumpled colloids were formed as well. Scale bar is 500 nm. E) SEM images of colloids in the batches corresponding to the single dimpled particles shown (D). Scalebar is 3 μm.

TPM (1.05 g/cm^3) present in the swollen state.[74,75] Since the polymerized particles were roughly 1.4 μm in diameter, which is an increase of 490 nm compared to the linear seed particles, we can estimate the decrease in volume upon polymerization to be at least 10%. This volume decrease may exert a sufficient elastic stress on the shell that can result in shell-buckling (Figure 2.5C).[12]

Indeed, for [TPM] below 50% v/v buckling was not observed (Figure 2.2A), suggesting that the [TPM] was too low to form a shell of sufficient thickness. At 50% v/v TPM, buckled colloids were only formed in the presence of HQ (Figure 2.2A). This can be understood from the observation that the monomer volume

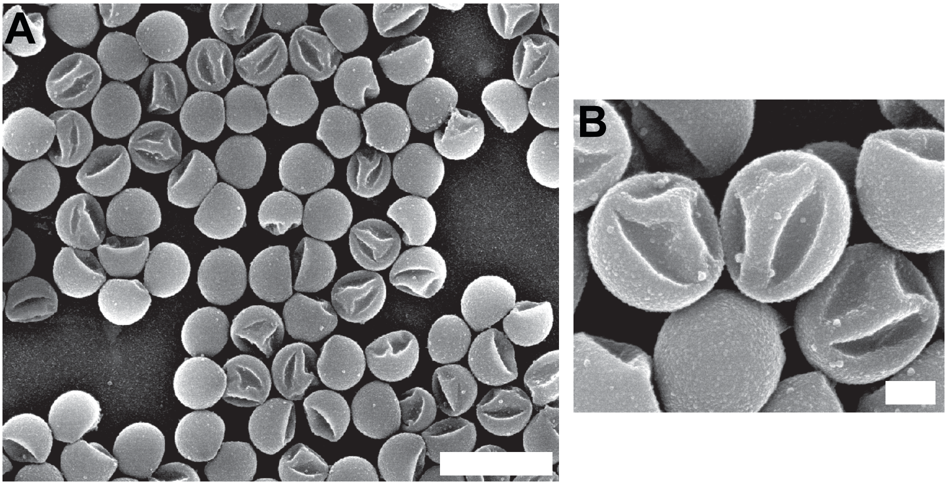


FIGURE 2.6: 'Smiley-faced' colloids. A) SEM micrograph of uniform colloids with three small dimples on one side of the sphere, obtained by swelling linear polystyrene colloids with 80% v/v TPM. Scalebar is 3 μm. B) SEM micrograph with a high magnification of three 'smiley-faced' colloids. Scalebar is 500 nm. Note: The image has won the image award of the Leiden Institute of Physics (Leiden University) in 2016.

absorbed by the seeds increases with the [HQ] (Figure 2.2D), resulting in an increase in shell thickness. At [TPM] of 50 - 80% v/v single dimpled colloids were obtained where the dimple size increased with the TPM concentration, see Figure 2.5D and 2.5E. The increase in dimple size implies a larger volume decrease upon polymerization[12,51], caused by the gradually bigger density difference between the polymerized and the swollen colloid. At [TPM] $\geq$ 75% v/v some crumpled colloids were observed as well and in a rare case, smiley-shaped colloids were obtained, where three small dimples were formed on one side of the sphere instead of one large dimple, see Figure 2.6. At even higher TPM concentrations the volume decrease during polymerization was sufficiently large to always result in the formation of crumbled colloids. These observations indicate that swelling with a mixture of styrene and TPM leads to the formation of a core-shell structure in the particles. At sufficient shell-thicknesses, the shell can buckle or crumple during polymerization if the core volume decreases strongly by the density increase.

2.3.4 Crumpled colloids of various shapes

At high TPM concentrations $\geq$ 80% v/v, we found anisotropic, crumpled shapes after polymerization. In the absence of HQ, deformed colloids with a rough surface morphology were obtained at 80% v/v TPM (Figure 2.7A). This adsorption

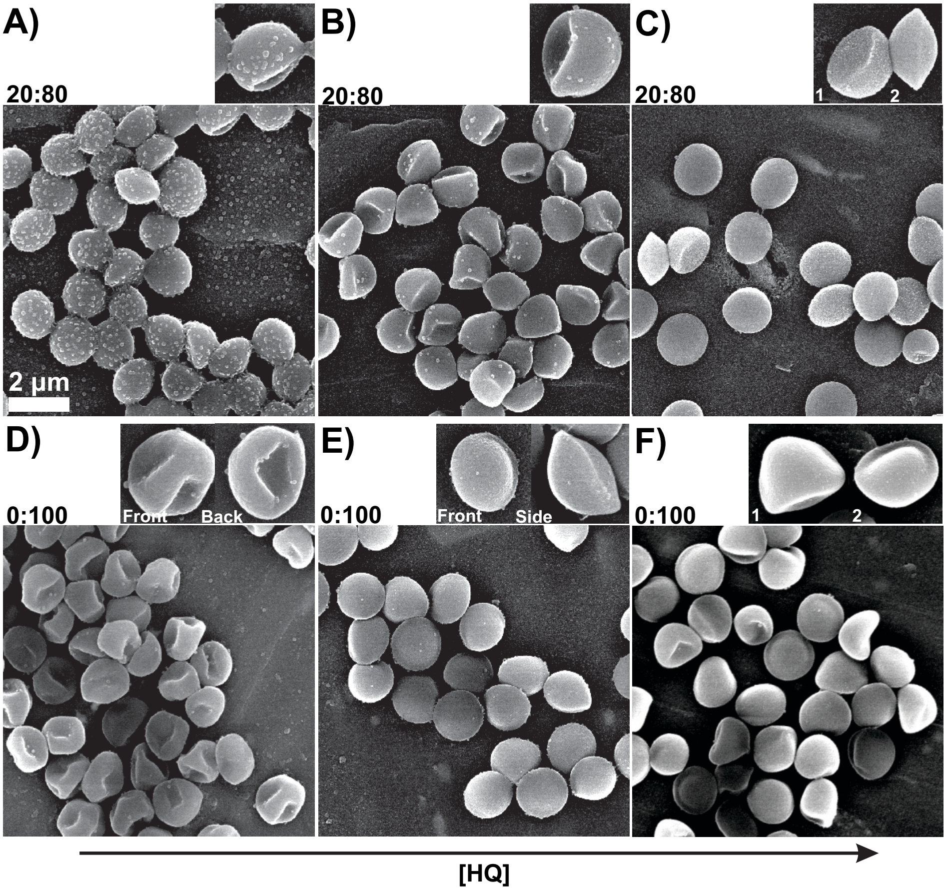


FIGURE 2.7: Crumpled colloids of various shapes at [TPM] $\geq$ 50%. SEM micrographs of crumpled colloids formed by swelling LPS colloids with a styrene:TPM v/v ratio of 20:80 or 0:100 at different HQ concentration. The enlarged images of the particle above the larger field of view is the predominant shape observed in the corresponding sample. A-C) Particles formed by swelling with 20:80 v/v styrene:TPM. A) Non-spherical deformed colloids obtained in the absence of HQ. Some asperities are adsorbed on the surface. B) Highly asymmetric shapes with several dents acquired in the presence of 0.0029% wt HQ. C) UFO-shaped and dimpled colloids are formed at 0.0185% wt HQ. D-F) Particles formed by swelling with 100% v/v TPM. D) Non-spherical colloids with three distinct dents without asperities at the surface formed in the absence of HQ. E) UFO-shaped particles with a rim in the middle, obtained at 0.0029% wt HQ. At even higher [HQ], 0.0185% wt, colloids crumpled asymmetrically (F).

of secondary particles on the surface is almost completely inhibited in the presence of HQ, resulting in particles of different shapes. An asymmetrical shape with two or more non-spherical dents was formed at 0.0029% wt HQ (Figure 2.7B) and as discussed in the previous section, dimpled and UFO-shaped colloids are found at 0.0185% wt HQ (Figure 2.7C). Dented colloids were also formed by swelling solely with TPM in the absence of HQ, see Figure 2.7D. Here, uniform shapes with two or more dents, similar to the shapes obtained at 80% v/v TPM and 0.0029% wt HQ, were observed. In the presence of HQ a rim is formed resulting in UFO-shaped colloids (Figure 2.7E and 2.7F). This rim formation was observed previously in simulations, where the UFO-shaped colloids were referred to as symmetrically crumpled particles.[12] Remarkably, when solely TPM is used for swelling, no nanoparticles adsorbed on the particle surface (Figure 2.7E-F), in line with the observation that the asperities become gradually more submersed in the particles with increasing TPM concentration (Figure 2.2B). Therefore, one would expect the same colloidal shape at all HQ concentrations. However, while in all three cases (no, 0.0029% and 0.0185% wt HQ) crumpled colloids were obtained, the crumpled shapes differ. We speculate that HQ not only suppresses the formation of secondary nuclei in solution, but also affects the formation of the TPM oligomer network and thus the elastic properties of the shell. Since shell-buckling is highly dependent on the elastic properties of the shell, different shapes were formed.[52,72] The final shape of the buckled colloids is therefore dependent on both the HQ and the TPM concentration.

2.3.5 Silica coated colloids with rough, smooth, dimpled and crumpled surface morphology

The hybrid polystyrene-TPM colloids obtained with our method are sterically stabilized by PVA. To obtain electrostatically stabilized rough, smooth and dimpled colloids we coated the particles with silica. Silica colloids are known to exhibit hard-sphere behavior which is crucial for studying for example the role of frictional forces in shear thickening suspensions.[43,45] Besides, suspensions of rough silica colloids can be used to tune wetting properties to achieve superhydrophobicity.[56,57] By coating the polystyrene-TPM hybrids with silica, colloids with the surface properties of silica are formed, but with the core properties of polystyrene-TPM. Depending on the application these coated particles can be favoured over solid silica particles because of their relatively low density and the possibility to remove the core.[69]

To improve the adhesion of silica on the colloids, we partly replaced the PVA molecules by poly(vinyl pyrrolidone) (PVP). We achieved the formation of a silica layer by the addition of tetraethyl orthosilicate (TEOS) under basic media conditions.[61] Silica colloids with a rough and smooth surface morphology were obtained using polystyrene-TPM colloids formed by swelling with a styrene:TPM

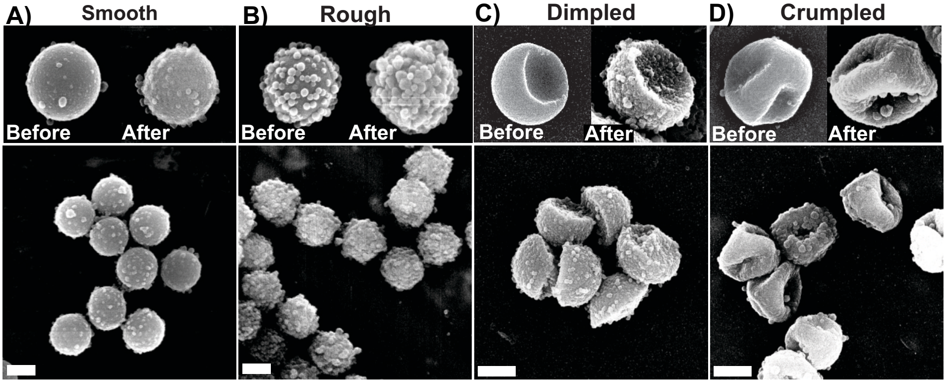
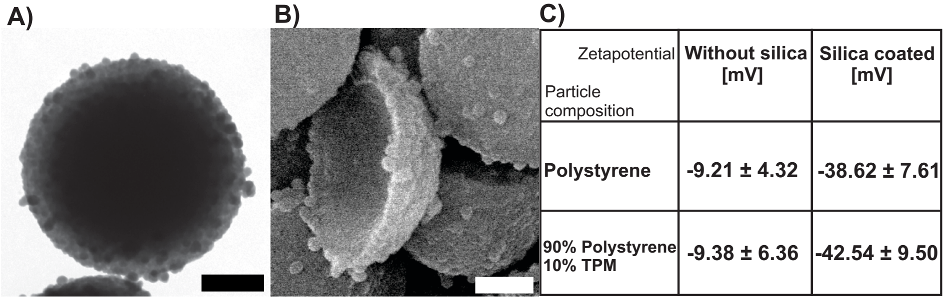


FIGURE 2.8: SEM micrographs of silica coated polystyrene-TPM hybrid colloids of various morphologies. In all cases the morphology of the colloids was preserved during silica coating. The surface roughness increased slightly. Scalebar is 1 μm. The enlarged images of the particles above the larger field of view show single particles before and after silica coating. A) Colloids with a smooth surface morphology, obtained by swelling with a 90:10 styrene:TPM v/v ratio in the presence of 0.0185% wt HQ, coated with silica. B) Colloids with a rough surface morphology formed by swelling with 90:10 v/v styrene:TPM and coated with silica. C) Single-dimpled colloids obtained by swelling with 80% v/v TPM in the presence of 0.0185% wt HQ, coated with silica. D) Crumpled colloids made by swelling solely with TPM and coated with silica.

ratio of 90:10 in the absence and presence of 0.0185% wt HQ, respectively. After coating, the initial surface morphology was mostly preserved, as can be seen in Figure 2.8A and 2.8B. From SEM images before and after coating it can be concluded that the surface of the initially smooth hybrid particles remained relatively smooth (Figure 2.8A), while for the polystyrene-TPM colloids with asperities the surface roughness increased during the silica coating. Multiple washing steps showed that the silica nanoparticles were permanently attached to the colloids. Besides the rough and smooth particles, we also achieved a silica coating on the dimpled colloids (prepared by swelling with 80% v/v TPM in the presence of 0.0185% wt HQ) and crumpled colloids (prepared by swelling with 100% v/v TPM without HQ). Again, in both cases the shape of the coated colloids was similar to the original particles. In Figure 2.8C and 2.8D the silica coated dimpled and crumpled colloids are shown, respectively. From the analysis of TEM and SEM images we could determine the shell thickness to be on the order of 100 nm, see Figure 2.9. The shell consisted of small silica nanoparticles connected by a matrix of silica (Figure 2.9A and 2.9B). The zetapotential of the silica-coated colloids was measured to be on the order of -40 mV, whereas -10 mV was measured for the hybrid seed particles (see Figure 2.9C and 2.4D). This indicates that whereas the initial colloids were solely sterically stabilized by the PVA coating, the silica



Zetapotential Particle composition	Without silica [mV]	Silica coated [mV]
Polystyrene	**-9.21 ± 4.32**	**-38.62 ± 7.61**
90% Polystyrene 10% TPM	**-9.38 ± 6.36**	**-42.54 ± 9.50**

FIGURE 2.9: Properties of the silica coated colloids. A) TEM image of hybrid colloids swollen with 80% v/v TPM coated with silica. A clear distinction between the black inner organic core and the grey silica shell is observed. The shell thickness is in the order of 100 nm. B) SEM image of a broken silica shell of a 20:80 silica coated colloid. The surface morphology inside the shell is smooth indicating that the silica nanoparticles are connected by a silica matrix. C) Zetapotential measurements of polystyrene and polystyrene-TPM colloids before and after silica coating. The silica layer drastically decreases the zetapotential of the colloids providing electrostatic stabilization.

coated colloids are primarily electrostatically stabilized. These silica-coated electrostatically stabilized colloids are specifically interesting to study shear thickening behavior, superhydrophobicity and viscoelastic properties.[43,45,55,65,67]

2.3.6 Hollow silica shells

Finally, we demonstrate that hollow silica shells of various morphologies can be obtained by removal of the organic core by thermal decomposition at 450°C for 5 hours. After this treatment smooth polystyrene:TPM (90:10) spheres without silica were almost completely decomposed, see Figure 2.10A. The remnants is likely silica stemming from the TPM. For the same spheres coated with silica, hollow shells remained (Figure 2.10B). A hollow shell was obtained, indicating that the organic core was completely removed. Surprisingly, although some of the morphologies seem mechanically unstable, the majority of the shells stayed intact independent of particle shape (Figure 2.10B-E). The number of broken shells observed with electron microscopy seemed to decrease when more TPM was present during swelling. Since TPM is an alkoxysilane, we expect some of the silica after decomposition to originate from the TPM. It is thus likely, that the thickness and therefore stability of these shell-structures is enhanced by silica stemming from the TPM. Shell breakage is less frequently observed for colloids with the organic core still present. We therefore believe that this is caused by shrinking of the porous silica shell into a more dense state due to drying at high temperature or by illumination of the electron beam.[76] These effects possibly also explain

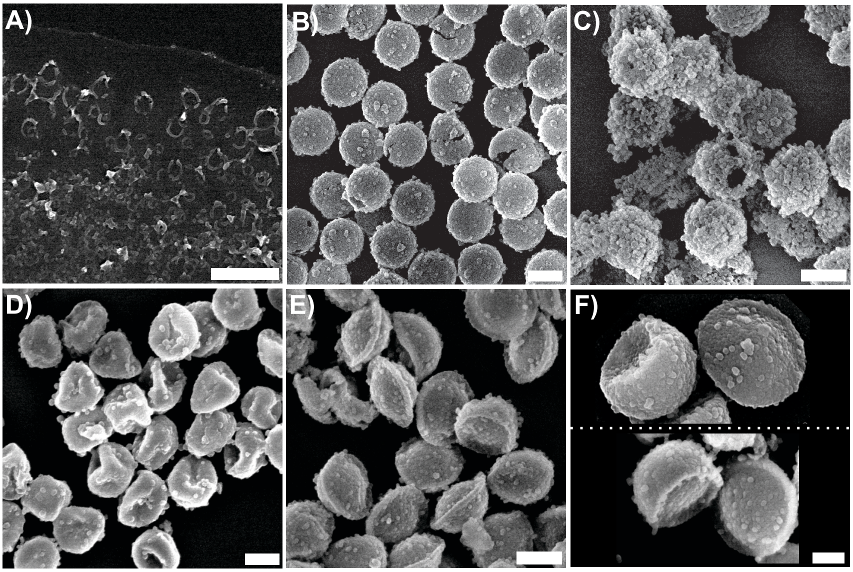


FIGURE 2.10: Silica shells after thermal decomposition of the organic compounds by heating at 450°C for 5 hours. SEM micrographs of remnants from smooth polystyrene:TPM (90:10) spheres without silica (A) and silica coated (B). Scalebar in (A) is 3 μm, in (B)-(E) 1 μm. Of silica coated rough, crumpled and dimpled particles the silica shell also remained and the shape stayed intact, see (C), (D) and (E), respectively. Although most shells stay intact some broken shells are observed as well. F) A dimpled and UFO-shaped silica colloid before (top) and after core removal (bottom). Scalebar is 500 nm.

the small differences in shape observed between the dimpled and UFO-shaped colloids (obtained by swelling with 80% v/v TPM) before and after core removal, see Figure 2.10F. Here, it can be seen that the characteristic of the shapes, such as the rim, are more pronounced after core removal. These silica shells of various morphologies can be exploited for their mechanical and cargo carrier properties.

2.4 Conclusions

We presented a robust and reliable synthesis method to obtain hybrid spherical, dimpled or crumpled colloids consisting of polystyrene, polystyrene-TPM or polystyrene-TPM-silica with tunable surface roughness. By swelling linear polystyrene colloids with a mixture of styrene and TPM not exceeding 50% v/v TPM, particles with a smooth, semi-rough and rough surface morphology could be synthesized by variation of the concentration of HQ. The asperity density on the particle surface decreases with increasing HQ concentration, since HQ inhibits the formation of secondary particles during polymerization. The size of the particles increases with the HQ concentration as well, indicating that a larger monomer volume was absorbed.

At TPM concentrations $\geq$ 50% v/v in the swelling solution buckling occurred upon polymerization of the swollen particles. We hypothesize that during swelling the TPM forms a shell on the surface of the swollen seed particle. Upon polymerization this shell buckles due to the high stress exerted on the shell by the volume decrease of the core, resulting in buckled colloids. At increasing TPM concentration the shell thickness increases, while the volume decreases further upon polymerization and therefore the degree of buckling increases. The final shape of the colloids depends on the thickness and elasticity of the shell and the change in volume upon polymerization.

At intermediate TPM concentrations of 50-80% v/v, single-dimpled colloids were formed with tunable dimple size. At even higher TPM concentrations, 80-100% v/v, we obtained crumpled colloids of various shapes, including three-dented and UFO-shaped colloids. We also showed that these hybrid colloids could be coated with a silica layer resulting in silica-coated polystyrene-TPM colloids with a rough, smooth, dimpled or crumpled surface morphology. By decomposition of the organic core hollow silica colloids were obtained as well. Since our approach is based on a standard dispersion polymerization method, large quantities of monodisperse colloids of various morphologies can be acquired. Our results show that by simply tuning two experimental parameters, the TPM and the HQ concentration during swelling, a wide variety of colloids with tunable surface roughness, dimple size and shape can be synthesized in a controlled fashion. These colloids are suitable for self-assembly[2,3,11] and to study the influence of surface morphology on physical properties of colloidal dispersions such as their viscoelastic behavior, wettability or stability.[43,45,55,65,67]