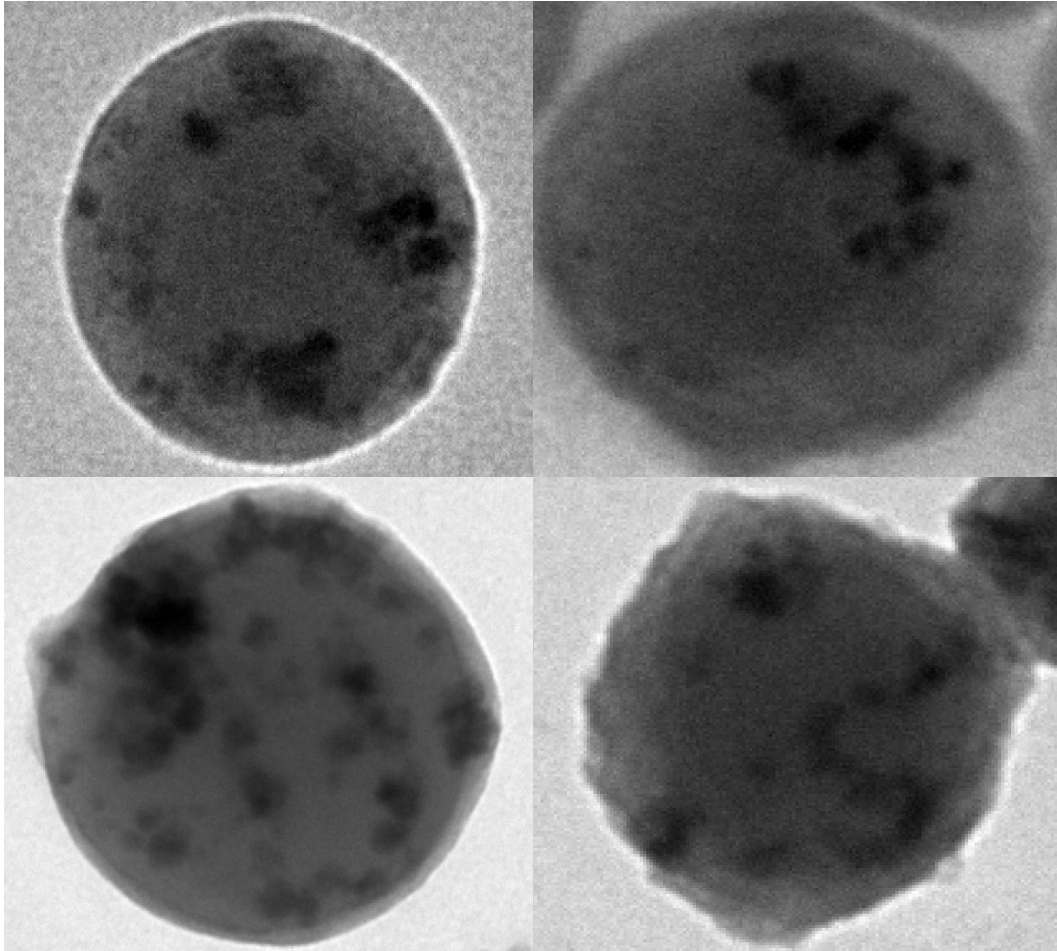


Masterthesis

Investigating silica coating of spontaneously formed Pickering emulsions and zein-based composite particles



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Abstract

The goal of this thesis was to make magnetic composite particles with a layer of functionalized silica for magnetic separation. Two different composite particles were investigated for this. One is a special Pickering emulsion that forms spontaneously and consists of TPM (3-(trimethoxysilyl)propyl methacrylate) and magnetite nanoparticles. The other one is zein-based. Zein is a protein that can form composite particles with magnetite nanoparticles by a simple co-precipitation. Both systems are interesting because of their simple formation and the ability to contain different nanoparticles. While both systems are interesting they are relatively new and during this thesis more research was done to acquire a better understanding of their properties.

These composite particles were coated with silica using several different methods based on the Stöber method and on the precipitation of sodium silicate. The coating of these particles with silica was to increase the stability of the composite particles and to enable the diverse possibilities of functionalizing (with for example a catalyst) the particles.

During the silica coating it was found that optimization was required for the methods used. After doing a number of experiments it was found using TEM that both systems could indeed be coated with silica. More experiments showed that the methods were reproducible, that by changing several conditions that the silica shell could change in size and shape, and that it is possible to make hollow silica spheres filled with nanoparticles.

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1 Introduction

1.1 Magnetic separation

Magnetic separation uses a magnetic force to separate magnetic material. This force depends on the magnetic properties of the magnetic material and on the gradient of the magnetic field.

The magnetic force on the magnetic material is strong with a high gradient [1].

A special magnetic separator is being developed with a separation column made from a random close packing of ferromagnetic rods. The setup for this separator is based on the design of permeation and filtration experiments from Thies-Weesie *et al.* [2]. An external magnetic field is created by electromagnets that are placed on the sides of the column. The field makes the close packed rods magnetic and therefore a local magnetic field with a high gradient is created. Magnetic particles that are pumped through the column experience a strong magnetic force towards the rods because of the high gradient. Small particles will stick onto the rods if the magnetic force overcomes the Brownian motion and opposite forces like hydrodynamic drag, until the particles are released by removing the external magnetic field.

The concept of using a ferromagnetic material to create high local field gradients inside a separation setup is not new and is already done, for example in mineral recovery and purification [3,4], removal of lubricant contamination [5], removal of catalysts [6] and the removal of phosphate from waste water with the help of magnetite particles [7]. This technique, commonly referred to as high gradient magnetic separation, is shown to be efficient in removing small particles by making use of the strong magnetic force that comes with a high local gradient.

Selective separation can be done by functionalizing magnetic spheres with specific groups that can bind to specific objects, for example biomolecules [1]. The spheres that are used for this are typically a few micrometers in size and have coatings around them that enable the functional groups to be attached onto the spheres. The amount of objects that can be captured depends on the amount of functional groups. More specific surface area, and therefore the amount of functional groups, can be gained by using smaller particles and therefore the capacity can increase while keeping the amount of magnetic material the same.

1.2 Spontaneously formed Pickering emulsion

One candidate for the small magnetic spheres to be used in the setup is a spontaneously formed composite particle. Forming composite particles with emulsions is not a strange idea since emulsions are already used in many applications. They are in food products, cosmetics and they are used in the synthesis of other products [8]. Oil-in-water emulsions are also interesting systems for scientific research. In normal conditions oil and water want as little interface as possible but they can be made stable by adding surfactants to the mixture. This decreases the surface tension between the two phases and adds steric repulsion to prevent coalescence [9]. Because of this, micro emulsions are stable and the de-emulsification occurs only because of exchange between surfactant molecules of different emulsion droplets. The emulsions have an opportunity for coalescence when their surfactants change position [9].

In the early twentieth century it was discovered first by Ramsden [10] and then by Pickering [8,9] that emulsions can also be stabilized by particles with sizes between a few nanometers to a few micrometers. These emulsions are called Pickering emulsions, named after S.U. Pickering. But even these Pickering emulsions still require mechanical work in order to form. In 2007 Sacanna *et al.* [11] discovered that there are exceptions to this. A mixture of 3-(trimethoxysilyl)propyl methacrylate (TPM) and a dispersion of tetramethylammonium hydroxide (TMAH) stabilized magnetite nanoparticles spontaneously formed a Pickering emulsion. This also worked with several other nanoparticles including cobalt ferrite and silica nanoparticles.

Evidence of thermodynamic stability was given by an experiment in which two different sized emulsions were mixed. After a few days the two size distributions became one size distribution with

an average size between the two previous averages. Because the bigger sized emulsions decreased in size, this could not have happened due to Ostwald ripening. These emulsions can be polymerized for analysis with TEM by using a radical initiator.

The fact that these emulsions do not require energy to form droplets around 100 nm in size at room temperature and that they can be filled with magnetic particle make them promising candidates for the magnetic separation.

1.3 Zein composite particles

Next to the TPM-magnetite emulsions, Zein composite particles have also been looked at. Zein is a storage protein from corn [12] and can be extracted relative easy. Compared to TPM, Zein is relative cheap(10-40 dollar/kg), it is less toxic and is biodegradable. Zein is already being used in chewing gum, fibers, biodegradable plastics, fat substitutes, hair fixative and paper surfaces, for example glossy magazine covers [12]. Zein is hydrophobic but can be dissolved in 50-90% ethanol, dependent on temperature and concentration. If it is then quickly added to a larger volume of water it can form colloidal particles [13,14] that have about the same size of TPM-magnetite emulsions. If prepared in the right way they can have magnetite particles inside or at the surface. Therefore also zein composite particles are small particles that can form without too much energy input and can be filled with magnetic particles making them promising candidates for the magnetic separation.

1.4 The Stöber method

For the magnetic separation of specific objects these composite particles still need to be functionalized. This can be enabled by coating them with a thin silica layer [15].

Trying to coat the polymerized emulsion particles was done with an adapted version of the Stöber method [16]. The normal Stöber method uses the sol-gel process of TEOS in a mix of an alcoholic solution with, water and a base to produce silica colloids. This method has since been studied and different people have used adaptations of it to produce silica colloids [17,18] or to coat other particles with silica[18,19].

1.5 Coating using sodium silicate

Another method to coat particles with silica was also investigated. This was a method that used sodium silicate. Sodium silicate is relative cheap and easy to make, except for the alkaline properties it is not harmful and already being used in all kinds of applications[20], for example the detergent industry, pulp and paper industry, adhesives, soil grouting, water treatment, oil reclamation, mineral ore flotation and inorganic binders like welding rods. The coating of particles with the use of sodium silicate has been done in previous work on boehmite needles [21] and magnetite particles [22]. The main method is to bring down the sodium content with ion exchange resin which exchanges Na^+ ions with H^+ ions. By lowering the pH even further by adding more resin or an acid, the solubility of silica goes down and silica is precipitated onto the particles.

2 Theory

2.1 Magnetic iron oxides

Magnetization occurs due to unpaired electrons in an orbital. Iron has a strong magnetic moment due to having 4 unpaired electrons in the 3d orbital. Different iron oxides have different magnetic properties. They can be paramagnetic in which the magnetic moments are randomly aligned and the net moment is zero unless an external magnetic field is applied the magnetic moment of the iron oxide aligns with the field. They can also be ferromagnetic or antiferromagnetic in which the magnetic moments are not randomly aligned and the net moment is not zero. If an external field is added to ferromagnetic material, the magnetization is aligned unless the field is not strong enough and hysteresis occurs as can be seen in figure 2.1.1. Hysteresis is the irreversibility of the magnetization when the field is turned off and even if it is slightly in the opposite direction. It is caused by different magnetic domains within the material or due to effects like the magnetic anisotropy of the crystalline lattice. If the particles are small enough that there is only one magnetic domain then it can rapidly respond to the external field, which corresponds to superparamagnetic behavior [1].

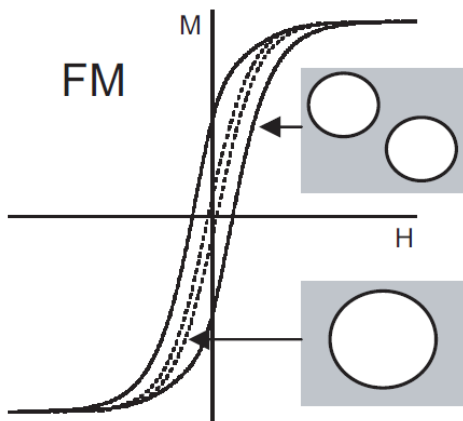


Figure 2.1.1: Hysteresis loop from the $M(H)$ curves of two different sized ferromagnetic particles. Taken from [1]

2.2 Pickering emulsions

Water molecules at an oil-water interface are energy unfavorable compared to those in the bulk due to having fewer water molecules next to them that they can interact with. This causes a surface tension. The most stable systems are therefore the ones with the least surface area. This also applies to interfaces between two non-mixing liquids like oil and water. Oil-in-water and water-in-oil emulsions are normally not stable because of this. There are ways to make them stable and Pickering emulsions use colloidal particles for that. After Ramsden's observation [10] and Pickering's discovery [9] of the Pickering emulsions a high amount of research has been done on these emulsions [8]. One of discoveries made was that the wetting properties of the colloids are an important factor. Hydrophilic colloids stabilize oil-in-water emulsions the most. These colloids stay at the interface and lower the interface area and therefore the interface energy.

Another important factor is the size of the colloidal particles. If the colloids are larger than the emulsion they cannot make them more stable. If two emulsions are stabilized with, chemically the same particles but with different sizes, then the emulsion with smaller particles is the one most stable. It has been shown that the colloids do not decrease the surface tension but that it stabilizes the emulsion by replacing the interfacial area and because of surface rheology effects. It costs

energy when colloids have to leave the surface when two emulsion droplets fuse together and therefore make a barrier, which other emulsions first need to overcome to come together [8].

2.3 Spontaneously formed Pickering emulsions

After the discovery of the spontaneously formed emulsion more research has been done on them. [11, 23, 24, 25]. It has been shown that the emulsion formed spontaneously because of three conditions that decrease the surface energy [23, 24]. The colloids help to decrease interfacial energy like colloids do in every Pickering emulsion as described in 2.2. The TMAH used to stabilize the magnetite nanoparticles, decreases the interfacial tension because of its amphiphilic nature and catalyzes the hydrolysis of TPM molecules at the interface. During the hydrolysis, the methoxy groups are replaced with hydroxide groups. The TPM molecules at the surface therefore have charged groups and like with surfactants, are surface-active molecules which decrease the interfacial tension. The interfacial tension was measured below 10 mN/m which is low enough for emulsion to be formed. Figure 2.3.1 gives a schematically representation of these conditions.

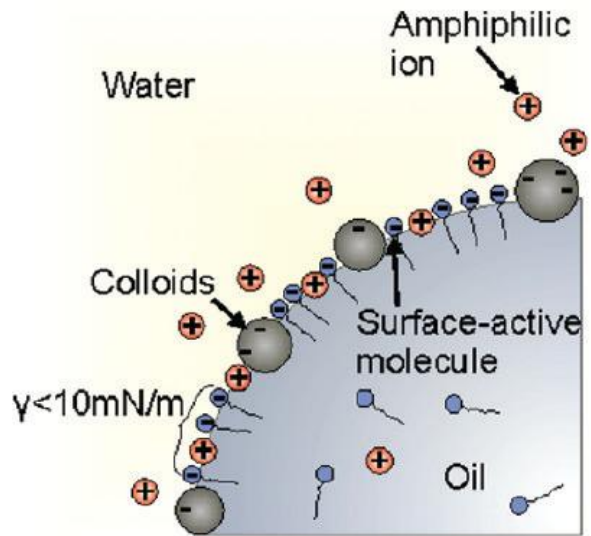


Figure 2.3.1 Image taken from [23] giving an overview of the different components helping to form a emulsion spontaneously

According the study done by Kegel and Groenewold [24] the stabilizing mechanism is: " the entropic contributions connected to ionic dissociation on the colloid surfaces."

The colloids prefer the oil phase of the emulsions. The preference of the colloids to stick to the oil phase keeps the colloids in the emulsion while the positive charge around the emulsion pulls the colloids to the interface. These two opposite forces keep the colloids at the surface while both the colloids and interface are negatively charged. Because of the negative charge at the interface, the emulsion droplets are charge stabilized.

Experiments have shown that the magnetite nanoparticles move slowly into the oil phase. The main reason for this is the condensation of the hydrolyzed TPM on the colloidal surface. The condensation makes the colloids more hydrophobic. Slow condensation of the hydrolyzed TPM is also the main reason behind growth of the average size of the TPM emulsion droplets. The interfacial potential becomes lower and the colloids move into the oil phase. The barrier for particles to merge together thus becomes smaller over time. The growth of the average size of TPM-cobalt ferrite emulsion droplets is shown in 2.3.2 which is taken from [25].

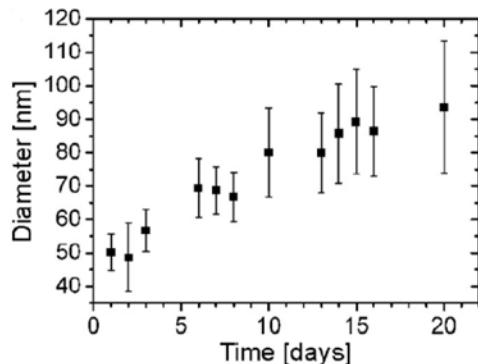


Figure 2.3.2: growth over time of TPM-cobalt ferrite particles

Time is not the only factor that changes the average size of emulsion droplets. Experiments were done [11,26] that show that the size of the emulsions is also depended on the ratio TPM:colloids.

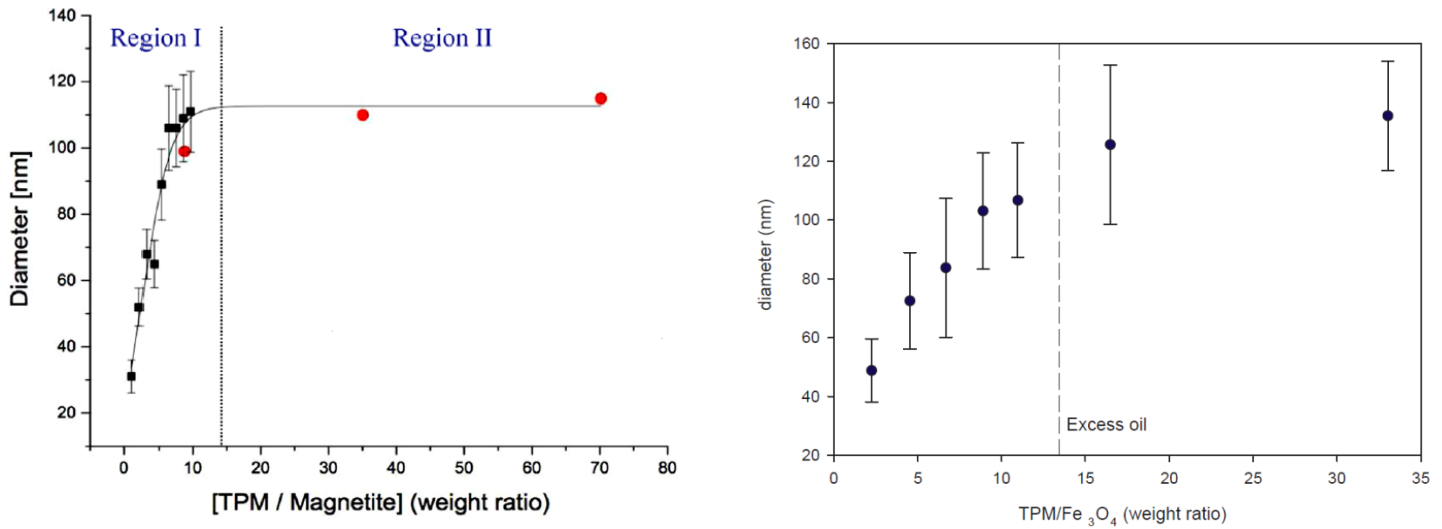


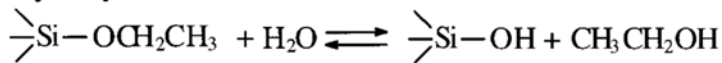
Figure 2.3.3: Two graphs taken from earlier work [11,26] showing increase average size with increase TPM/colloids ratio

2.4 The Sol-Gel reactions

The Stöber method uses a Sol-Gel process with a mixture of an alcohol, some water, a base and TEOS to produce silica colloids [16,17]. The method exists of the hydrolysis of tetraethyl orthosilicate (TEOS) and the condensation of hydrolyzed silica into silica colloids [27]. During hydrolysis the -OR group from the TEOS exchanges with an -OH group. Hydrolysis can be both acid and base catalyzed and almost does not happen under neutral conditions.

The condensation reaction can happen two ways. Either an alcohol or a water molecule can be formed. During the base catalyzed condensation gelation does not happen but instead particles are formed with negatively charged surfaces. Therefore during this thesis only the base catalyzed reaction is used. In figure 2.4.1 the reactions are shown

Hydrolysis:



Condensation:

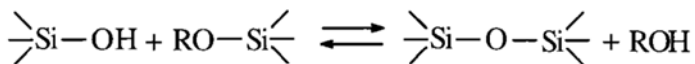


Figure 2.4.1: The hydrolysis and condensation of TEOS under alkaline conditions [19]

The Stöber method has been shown to be able to coat colloidal particles using the alkaline catalyzed sol-gel reactions before. [18,19]

2.5 Zein

From all proteins in corn around 50% is zein. Zein has a high amount of non-polar amino acids which causes it to be non-soluble in water unless modified with for example a base. Zein dissolves at room temperature in 50-90% ethanol and in other solvents like ketones, esters, or glycol [12].

Colloidal particles can be made with zein, which have a positive charge that stabilizes the particles. The isoelectric point of zein colloids is around pH 6 [14].

Zein based colloidal composite particles have been made recently with a relative simple method [13]. Negatively charged nanoparticles can be added to the positively charged zein colloids either before or after the zein particles are formed. If it is added before, the zein co-precipitates around the nanoparticles. If the nanoparticles are added after, the particles adsorb on the surface of the zein particles. This method has been shown to work with magnetite, cobalt ferrite and gold nanoparticles, iron pyrophosphate and hematite spindles. Different configurations can be made like can be seen in figure 2.5.1. All these configurations had a positive zeta potential and sizes between 100-250 nm [13]. Thus the co-precipitation of zein and nanoparticles is a general method to create positively charged composite particles.

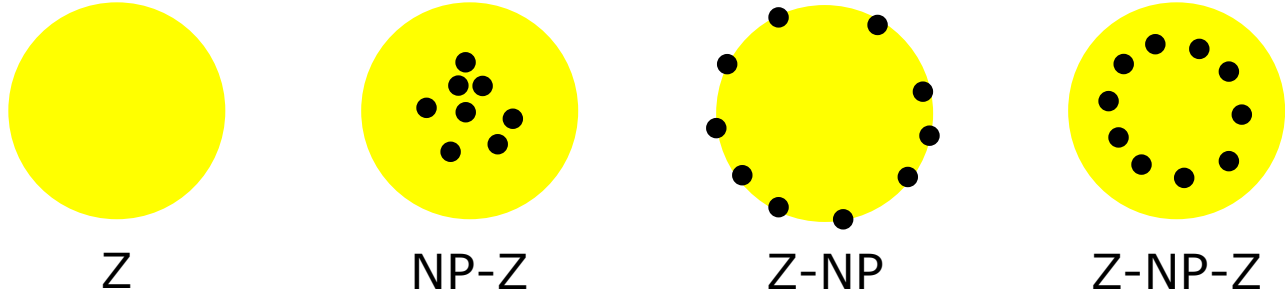


Figure 1.5.1 different configurations of zein and zein composite particles with magnetite.

2.6 Sodium silicate

The solubility of silica is pH dependent as can be seen in figure 2.6.1. At low and neutral pH, the silica on the surface of particles consists of SiOH_x but at high pH this becomes SiO^- [28]. If enough NaOH is added in water, the silica reacts with it into Na_2SiO_3 . As can be seen in figure 2.6.1, the solubility is a couple of orders of magnitude higher at pH 11 than at neutral pH. This means that high amounts of silica can be dissolved at high pH and then by decreasing the pH, most of the silica precipitates. Sodium silicate is part of the family of soluble silicate glasses where the general formula is $(\text{M}_2\text{O})_x \cdot (\text{SiO}_2)_y$ where the ratio $x:y$ can differ and indicate the grade of the product. With sodium silicate the M is Na. The structure of sodium silicate depends on the pH, concentration and on the ratio $\text{SiO}_2:\text{Na}_2\text{O}$. It can grow long polymer chains of silicate, it can form particles from a few nm to colloidal particles or it can form films and gels [29].

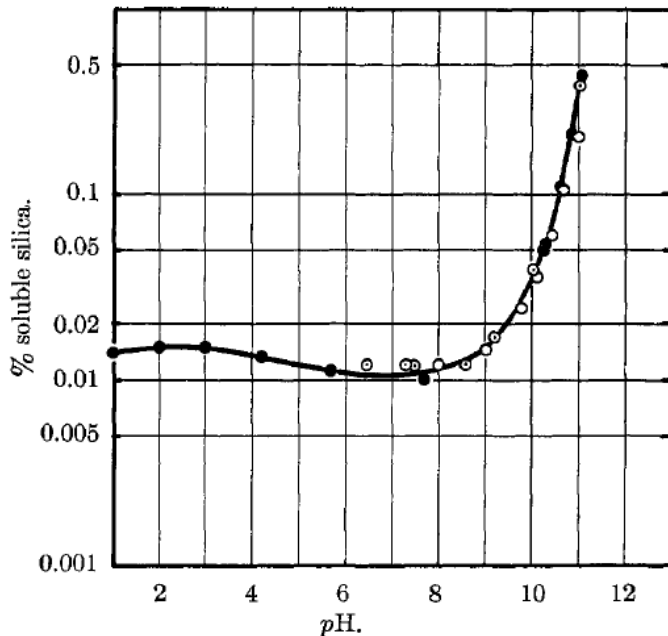


Figure 2.6.1 Graph taken from [28] showing the solubility of silica at different pH at 25 °C. The black dots are the measurements of silica where pH is adjusted by adding HCl or NaOH and the white dots with small dots inside are measurements where sodium was removed from sodium silicate with ion exchange resin.

2.7 Transmission electron microscopy

While normal microscopy can be used in research on objects that are in the order of visible light or larger, electron microscopy can be used to investigate objects which are as small as a few angstrom. This is because of the smaller wavelength of electrons in the microscope. An electron source shoots electrons which are then focused to the sample by different electrostatic and electromagnetic lenses. The electron waves that leave the sample are then used for imaging. The electron source, the number of and difference in lenses and the imaging method all depend on the TEM used [30].

2.8 DLS/Zeta-potential measurements

When photons reach particles that are small compared to the wavelength they scatter. When a monochromatic light beam (like a laser) passes through a colloidal dispersion, the time-dependent fluctuations in the scattered intensity can be observed. The fluctuations are caused by the colloids moving constantly in the dispersion due to Brownian motion. Analyzing the time dependence of the intensity fluctuations, gives the diffusion coefficient. The diffusion coefficient can be used to calculate the hydrodynamic radius of the particles using the Stokes Einstein equation. By adding an alternating electric field, the particles will diffuse accordingly to their zeta-potential which then can be measured as well [31].

3 Experiments

Chemicals used

- AgNO₃ (silver nitrate) CAS: 7761-88-8 Engelhard-CLAL/drijfhout BV
- AIBN (2,2'-azobis-(2-methylpropionitrile) CAS: 78-67-1 Sigma-Aldrich
- Ammonia (28-30%) CAS:1336-21-6 Sigma-Aldrich
- Ethanol 100% CAS: 64-17-5 Interchema
- FeCl₂ • 4H₂O (Iron(II) chloride tetrahydrate) CAS: 13478-10-9 Sigma-Aldrich
- FeCl₃ • 6H₂O (Iron (III) chloride hexahydrate) CAS: 10025-77-1 Sigma-Aldrich
- Hydrochloric acid (37%). CAS: 7647-01-0
- Ion exchange resin (DOWX 50WX8 hydrogen form) CAS: 69011-20-7 Sigma-Aldrich
- KPS: potassium persulfate. CAS: 7727-21-1. Acros Organics
- MPTMS (3-mercaptopropyl)trimethoxysilane CAS 4420-74-0 FLuka
- NaBH₄ (sodium borohydride) CAS: 16940-66-2 Sigma-Aldrich
- PVP (polyvinylpyrrolidone) CAS: 9003-39-8. Sigma-Aldrich
- Sodium silicate ((NaOH)_x(Na₂SiO₃)_y•zH₂O) CAS: 6834-92-0. (NaOH %:13.7, Si %: 12.8) Sigma-Aldrich
- TEOS (tetraethyl orthosilicate) CAS: 78-10-4 Sigma-Aldrich
- TMAH N(CH₃)₄OH (25%), (tetramethylammonium hydroxide solution) CAS 75-59-2 Fluka
- TPM 3-(trimethoxysilyl)propyl methacrylate. CAS: 2530-85-0 Aldrich chemistry
- Trisodium Citrate(Na₃C₆H₅O₇) CAS: 68-04-2 Merck
- V50 (2,2'-azobis(2-methylpropionamidine) dihydrochloride) CAS: 2997-92-4
- V65 (2,2'-azobis (2,4-dimethylvaleronitrile) CAS : 4419-11-8 Acros Organics
- Water filtrated with Millipore purification system
- Zein (storage protein from corn) CAS: 9010-66-6 Sigma-Aldrich

All chemicals were used as received. PVP with a molecular mass of 40kg/mol was used unless stated otherwise.

Sample names

- Mt: magnetite nanoparticles
- TM: TPM emulsion with magnetite nanoparticles
- TMS: TPM emulsion with magnetite nanoparticles coated with silica using the Stöber method
- TMW: TPM emulsion with magnetite nanoparticles coated with silica using sodium silicate
- Ag: silver nanoparticles
- Z: colloidal zein
- ZM: colloidal zein with magnetite nanoparticles
- ZA: colloidal zein with silver nanoparticles
- ZW: colloidal zein coated with silica using sodium silicate
- ZMW: colloidal zein with magnetite nanoparticles coated with silica using sodium silicate
- ZAW: colloidal zein with silver nanoparticles coated with silica using sodium silicate
- ZWS: colloidal zein coated with silica using sodium silicate, functionalized with MPTMS
- ZMWS: colloidal zein with magnetite nanoparticles coated with silica using sodium silicate, functionalized with MPTMS

All samples have a number behind the name according to the chronological order in which they were made.

3.1 Magnetite nanoparticles Synthesis

Magnetite nanoparticles have been used for the magnetic composite particles. All magnetite samples were prepared using an adaption of the Massart method [32]. 0.02 mol $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ was dissolved in 10 mL 2 M HCl and 0.04 mol of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ was dissolved in 40 mL water. These two solutions were mixed and put in an ultrasonic bath for 20 seconds to reduce the amount of aggregates. This solution was then quickly added to 500 mL 0.7 M ammonia while vigorously stirring. Magnetite was formed instantly through co-precipitation. After half an hour of stirring the formed magnetite was captured by holding a permanent magnet under the flask. After removing the supernatant, an excess ($\sim 18.9 \text{ g } 25\%$) of TMAH was added to stabilize the magnetite particles. The magnetite particles were captured again and redispersed in water after stirring overnight. 1 mL of the magnetite dispersion was dried and weighed so that the concentration could be determined. The dispersion was then diluted to a lower concentration. For Mt1 this was 2.6 g/L, for Mt2 3.6 g/L and for Mt3 2.7g/L.

3.2 Spontaneously formed Pickering emulsion

The formation of the emulsions during this thesis was done following the method of Stefano Sacanna [11].

3.2.1 General emulsion formation

The TPM-magnetite emulsions were prepared by adding TPM to a magnetite dispersion. The emulsions form spontaneously which can be seen as the sample becomes turbid. The formation of an emulsion takes about a day, which required that all samples were left standing at least one full day. For a more homogeneous formation of emulsion, the dispersion was once or twice shaken. This is needed because the formation happens mostly on the bottom due to the higher density of TPM than water. For further use most emulsions were polymerized. A radical initiator (most samples used 0.4 mM KPS) was added after which the samples were heated to 70-80 °C overnight in an oil bath while stirring. The polymerized emulsions were then washed by centrifugation at 2000 RPM for 2-3 hours, redispersing in ethanol to dissolve all remaining TPM and centrifugation again. After the last centrifugation the polymerized particles were redispersed in about the same volume ethanol as used for the emulsification.

3.2.2 Different initiators

To investigate whether the initiator influences the polymerization step, three other initiators (other than KPS) were tried. Three emulsions were made. Each emulsion was made by adding 0.2 mL TPM to 4 mL Mt1 and 6 mL water. 2 mL of each formed emulsion was put in 3 mL vials in which the polymerization took place. To the first emulsion 3.44 mg V50 was added, to the second 6.95 mg AIBN, and to the third 4.02 mg V65. The three emulsions were polymerized using the general method described in 3.1.1. In the sample with V50, aggregates were formed right away which indicates that V50 makes the emulsions unstable. In the other two samples, turbid light brown dispersions were seen. After the polymerization, the samples were washed by centrifugation.

3.2.3 Influence of time on emulsions

A series of emulsions was made to investigate the influence of time on the emulsions. Three emulsions were made by adding 0.1 mL TPM to 4 mL Mt1 and 6 mL water. The emulsions were left standing for 9, 6 and 1 days respectively. 2 mL from each was polymerized. 10 g PVP was dissolved in 100 mL water. 15 mL of this was added to each polymerized sample. The samples were stirred for a day to let the PVP adsorb to the polymerized particles which were then washed by centrifugation.

3.2.4 Influence of dilution

To investigate the influence of the amount of emulsion droplets per volume three emulsions were made. While keeping the TPM:magnetite ratio constant at 10, the amounts of TPM were different for each sample namely 0.625%, 1% and 2.5%. After one day, 2 mL from each sample was polymerized. After the polymerization, 15 mL of the PVP (10 g in 100 mL water) solution was added to each sample. These were then stirred for a day. The three samples were centrifuged at 2000 RPM for 3 hours and redispersed in ethanol.

After that another two samples were made with different amounts TPM and magnetite using the same method. This time the amounts of TPM were 0.1% and 0.3%.

3.2.5 Influence of pH

To see how a high pH influences the formation of the emulsion, 50 μ L TPM was added to a dispersion of 1 mL Mt1 in 12 mL water with 0.5 mL 1% TMAH. Also a control emulsion was made by adding 50 μ L TPM to 1 mL Mt1 and 12.5 mL water. 2 mL of both was then polymerized and washed.

To see if a low pH influences the emulsion 1 mL 0.5 M HCl was added to 10 mL of just formed emulsion. After one day 2 mL of this dispersion was polymerized and washed.

3.2.6 Different ratios TPM-magnetite

A series was made with different ratios TPM/magnetite. While keeping the amount of TPM constant at 0.25%, the amount of magnetite used for each emulsion was different to reach ratios of: 1, 2.5, 5 and 10. After one day, 2 mL of each emulsion was polymerized and after the polymerization 0.5 g PVP was dissolved in 20 mL ethanol. 3 mL of this was added to each sample. The polymerized samples were then washed by centrifugation.

3.3 The Stöber method

The first method to form silica around the polymerized particles was by using an adaption of the Stöber method [16]. This method uses the sol-gel process of TEOS in a mix of ethanol, water and ammonia to produce silica colloids. With an adaption this can also be used to use it in seeded-growth to coat the polymerized particles.

3.3.1 First Stöber method used

PVP was added to 3.3 mL TM1, the first emulsion made in an excessive amount (\sim 0,07 g/ mL) and stirred for a day. The sample was washed with centrifugation at 2000 RPM for an hour and redispersed in ethanol. The TM1 was put with 250 mL ethanol in a 1L 2-neck round bottom flask together with 5 mL of 1 w% TMAH and 33 mL water. By using a peristaltic pump a solution of 5 mL TEOS in 15 mL ethanol was added slowly (45 minutes) while stirring with a mechanical stirrer and during sonication in an ultrasonic bath.

After the TEOS solution was added, an excessive amount (10 g in 50 mL ethanol) PVP was added to stop the reaction. The sample was stirred overnight and then washed by centrifugation at 2500 RPM for 2-3 hours and redispersing in ethanol.

3.3.2 Upscaling the Stöber conditions

Different things were tried to reduce the secondary nucleation of silica, produce a more evenly covered coating with a well-defined shape and tune the shell thickness. The first thing tried was upscaling. This was done by doubling the amounts. 0.9 g PVP was dissolved in 25 mL water and added to 83.5 mL TM2. After a day stirring, it was washed by centrifuging twice at 2000 RPM for 3 hours and redispersing in ethanol. The PVP-coated TM2, 400 mL ethanol, 10 mL of 1w% TMAH, 66 mL water were put in the 1L-2neck round bottom flask and while stirring and during sonication, a

solution of 10 mL TEOS with 10 mL ethanol was slowly (2 hours) added. 17g PVP dissolved in 100 mL ethanol was then added. The sample was washed by centrifugation after stirring overnight. Because no coating was seen on the TEM pictures of TMS2 (see results) the reaction was done again on the same sample. TMS2 in 350 mL ethanol, 10 mL of 1 w% TMAH and 66 mL water was put in the 1l 2-neck round bottom flask and while sonication and stirring, a solution of 5 mL TEOS and 15 mL ethanol was slowly (45 minutes) added. It was stirred overnight after which it was washed by centrifugation at 2500 RPM for 3 hours.

3.3.3 Influence of the amount of TMAH

The influence of the TMAH concentration on the formation of silica was investigated. Three samples were created using the same conditions as in 3.3.2. TM3 was used and the TMAH used was 10 mL of 0.5%, 0.75% and 2% respectively.

Then another three TMS samples were made with different amounts of TMAH. These were created using the same conditions as in 3.3.1. TM4 was used and the TMAH used was 5 mL of 1%, 0.5% and 2% respectively.

3.3.4 Increasing the reaction time

With three new TMS samples it was tested whether increasing the amount of time in which the TEOS solution is added to the polymerized emulsion particles would increase the shell thickness and decrease the amount of secondary nucleation. The series was made by using for each sample 180 mL ethanol with 40 mL TM9, 33 mL water and 5 mL 1w% TMAH and adding 5 mL TEOS in 15 mL ethanol in 40, 60 and 100 minutes respectively for each sample.

3.3.5 Increasing reaction time at half the concentration

Two more samples were made with increasing reaction time and also using half the amount of sample and half the concentration of TEOS. They were made by using for each sample 200 mL ethanol with 40 mL TM20, 33 mL water and 5 mL 1w% TMAH and adding 2.5 mL TEOS in 15 mL ethanol in 6 and 3 hours respectively.

3.3.6 Second coating

It was investigated what would happen if a second coating reaction took place on a TMS sample. For this half of TMS13 (which was one of the samples made in 3.3.5) was taken using the same conditions as TMS13 was made with (200 mL ethanol, 33 mL water, 5 mL 1w% TMAH and adding 2.5 mL TEOS in 15 mL ethanol in 6 hours).

3.3.7 Difference between PVP-10 and PVP-40

It was investigated whether it matters if the PVP used is the PVP with a molecular mass of 10 kg/mol or the PVP with a molecular mass of 40 kg/mol in the Stöber synthesis on the emulsions.

Two samples were made by using for each sample 200 mL ethanol with one third of TM30, 33 mL water, 5 mL 1w% TMAH and adding 1 mL TEOS in 18 mL ethanol in 40 minutes. TMS16 was made using PVP-40 and TMS17 using PVP-10.

3.3.8 Difference between PVP-10 and PVP-40 and second PVP addition

Two more samples were made to investigate the difference between PVP-10 and PVP-40 in the coating. The two samples were made by using for each sample 180 mL ethanol with half TM36, 33 mL water, 5 mL 1w% TMAH and adding 1 mL TEOS in 18 mL ethanol in 80 minutes. TMS18 was made using PVP-40 and TMS19 using PVP-10. After all TEOS was added and before the second PVP addition, half of TMS18 was transferred to another bottle in which no extra PVP was added. This was

done to investigate whether the addition of PVP after the TEOS is causing at least part of the secondary nucleation.

3.4 Zein experiments

Colloidal zein particles can be made by dissolving zein in 80% ethanol and quickly pouring the dissolved zein in water. The zein particles in this thesis were typically made in a zein:ethanol:water ratio of 1g:80 mL:160 mL.

Magnetic zein particles were made by adding magnetite nanoparticles using the method of van Leeuwen [13] to make loaded zein-based composite particles. Zein particles with magnetite inside (MZ) were made by adding the magnetite first to the water and then the zein solution. Zein particles with magnetite on the surface (ZM) were made by adding the zein solution first and then the magnetite. Zein-magnetite-zein particles (ZMZ) were made by adding another portion of dissolved zein on the zein particles with magnetite on the surface. All adding was done while magnetically stirring.

3.4.1 Testing amount of magnetite

It was tested how much magnetite could be used during the formation of magnetic zein particles. Four samples were made using the typical ratio and the method for ZMZ particles. The amount of magnetite used per gram zein was respectively 0.26 g Mt1 for ZM1, 0.52 g Mt1 for ZM2, 1.04 g Mt1 for ZM3, 1.04 g of the non-diluted Mt1 for ZM4, 26 mg Mt1 for ZM5 and 78 mg Mt1 for ZM6. (See Appendix A for the exact quantities.)

The samples were put on a permanent magnet overnight after which the supernatant was removed and the sediment was redispersed in water.

3.4.2 Zein samples for zeta-potential measurements

Four new Zein samples were made for measuring the zeta-potential of the different zein samples. 0.65 g Zein was dissolved in 40 mL 80% ethanol. 10 mL water was added in four bottles. In the first bottle 4 mL of the zein solution was poured (ZM7), In the second one 1 mL Mt1 was first added and then 4 mL of the zein solution was poured (ZM8), In the third bottle 4 mL Zein was first poured and then 1 mL Mt1 (ZM9) and in the fourth bottle 3 mL zein was first poured, then 1 mL Mt1 and then another 3 mL zein was added. (ZM10). These samples had to be remade after the zeta-potential measurements showed negative charges which was because the dispersions had neutral pH for an unknown reason, instead of a pH around 4 which is the standard pH for these particles.

3.4.3 Problem with dialysis

A new ZM sample was made by dissolving 0.53 g Zein in 40 mL 80% ethanol which was then poured in 80 mL water while stirring. To this 16 mL Mt 2 was added after which it was left standing overnight on a magnet.

With a pipet the supernatant of ZM11 was removed and the remaining ZM11 was redispersed in 100 mL water. ZM11 was dialyzed against water. This was to remove most ethanol for sodium silicate experiments. However a day later, ZM11 was flocculated.

It was tested whether this could be redispersed by adding parts to different solutions. A solution with ethanol, an acid solution and an alkaline solution was tried. In the alkaline solution, a dispersion could be seen in the sample. TEM pictures were taken. However after a few hours the zein was dissolved.

3.5 Sodium silicate experiments

Sodium silicate is being used in all kinds of applications. Sodium silicate is used in this thesis to coat particles with a layer of silica. The coating of particles with the use of sodium silicate has been done in previous work on boehmite needles [21]. The main method is to bring down the pH of an alkaline solution with sodium silicate. The solubility of silicate then goes down and silica is precipitated on the particles.

3.5.1 First sodium silicate experiments

2 mL sodium silicate was diluted to 1.3% by adding 8 mL water. The pH was lowered by adding ion exchange resin. It was tested in which order the sample, the water and the sodium silicate should be added to coat the polymerized emulsion particles.

TMW1: 1 mL of the diluted sodium silicate was added to 1 mL TM20 and then 15 mL water was added.

TMW2: 0.4 mL of the sodium silicate was added to 1 mL TM20 in 4 mL water.

TMW3: 0.4 mL of the sodium silicate was added to 4 mL water and then 1 mL TM20 was added.

In all three samples a white suspension formed. This could have been because of the ethanol in the TM20.

3.5.2 More controlled coating

4 mL of stock sodium silicate was diluted to 1.3% by adding 36 mL water. The pH was lowered by adding ion exchange resin which then was removed by filtration. A fifth of TM20 was centrifuged at 2000 RPM for 3 hours and redispersed in 100 mL water. 1 mL 1w% TMAH was added so that the pH of this solution was close to 10.5. The dispersion was then put in a 250 mL 3-neck round bottom flask which was in an ultra-sonic bath. While the polymerized emulsion particles were sonicated and stirred with a mechanical stirrer, the sodium silicate solution was slowly (40 min) added using a peristaltic pump.

The pH was checked periodically by taking small portions which were measured with a pH meter. The pH was kept in the range of 8.5-10.5 by adding more ion exchange resin. The product was filtrated and dialyzed against water.

Another sample was made using the same method but with a much lower concentration of sodium silicate and starting with a low pH. 0.2 mL sodium silicate was added to 20 mL water. 50 mL of 0.5 M HCl and a third of TM30 in 60 mL water were added to a 250 mL 3-neck round bottom flask. The pH was measured around 4. Slowly the sodium silicate was added and after half of the sodium silicate was added resin and extra HCl solution was added to bring pH down again. After all of the sodium silicate solution was added the pH was 8.25. After a few hours of stirring, the sample was filtrated and dialyzed against water.

3.5.3 Trying to coat zein samples

Two new zein samples were made. Both were made by dissolving 0.5 g Zein in 40 mL 80% ethanol, pouring it in 80 mL water while stirring and adding 12 mL Mt2 after five minutes. ZM13 was put on a permanent magnet so that all particles sediment on the bottom. The supernatant was removed and the sediment was redispersed in water. This was then repeated. ZM14 was transferred into dialysis tubes and dialyzed. After a week it was removed from the tubes. The sample did flocculate like ZM11 but it also redispersed like ZM11 at high pH.

The same method as described in 3.5.2 for TMW4 was used on both zein samples. The pH however had to be lower during the whole addition of sodium silicate due to dissolving of zein at high pH. 40 mL of 1.3% sodium silicate was slowly added while keeping pH low by adding ion exchange resin and HCl. The dispersions were filtrated overnight and then dialyzed against water.

3.5.4 Using zein colloidal particles with magnetite inside

Because of the formation of aggregates in the dialysis tubes of zein samples with magnetite on the surface it was chosen to use zein samples with the magnetite inside which did not flocculate. Two new zein samples were made (ZM16 and ZM17) by dissolving 0.5 g zein in 40 mL 80% ethanol. 12 mL Mt2 was first added to 80 mL water and then the dissolved zein was added. ZM16 was washed like ZM13 with the use of a magnet and ZM17 was washed like ZM14 by using dialysis. 40 mL of 0.13% sodium silicate was slowly added while keeping pH low by adding ion exchange resin and HCl. The dispersions were filtrated overnight and then dialyzed against water.

3.5.5 Using a different method

Based on a method used to coat magnetite particles [22] a different approach was taken. 4 mL of sodium silicate was added to 36 mL water. Ion exchange resin was then added to this. ZM18 was made and washed using the same method as ZM17 by dissolving 0.5 g zein in 40 mL 80% ethanol. 12 mL Mt3 was added to 80 mL water and then the dissolved zein was quickly added. Most of the ethanol was removed from ZM18 with dialysis against water. 15 mL of ZM18 was added to 35 mL water in a 100 mL 3-neck-round bottom flask. While stirring 10 mL of the sodium silicate solution was quickly added. Slowly, the pH was brought to 7-8 by adding 2.5 mL 0.5 M HCl. This was stirred for 3 hours and left standing overnight. It was then centrifuged at 1000 RPM for 3 hours and redispersed in water.

3.5.6 Starting with low pH and sonication

15 mL of ZM18 was added to 35 mL water in a 100 mL 3-neck-round bottom flask. While stirring 2.5 mL 0.5 M HCl was first added and then 10 mL of the same sodium silicate solution as in 3.5.5 was added. The pH was higher than 7 so another 0.6 mL HCl was added. The dispersion was then sonicated for 15 minutes in an ultrasonic bath after which it was stirred for another 3 hours and left standing overnight. Half of the sample was put on a magnet. After a day the supernatant was removed and the sediment was redispersed in water. The other half of the sample was centrifuged at 1000 RPM for 3 hours and redispersed in water.

3.5.7 Trying to reproduce ZMW6

In order to show that the method used in 3.5.6 to make ZMW6 was reproducible, a new stock sodium silicate solution was made. 8 mL 13% sodium silicate was added to 72 mL water. To this Ion exchange was added. While trying to reproduce ZMW6, 15 mL of 0.5 M HCl was needed to bring pH all the way down to 7. However, aggregates were formed. A new zein sample was made because it could be that ZM18 was the one causing the flocculation. This was done with the method described in 3.5.5. The silica coating was done again on the new zein sample but the resulting sample also became unstable.

What also could have been happening was that due to the high amount of NaCl that was formed during the addition of HCl, the charge repulsion became too small.

More ion exchange resin was added to the sodium silicate solution so that less HCl was needed and the coating was then tried again. Again flocculation occurred because too much HCl was needed (10 mL 0.5 M). More resin was added after which the pH of the sodium silicate solution was so low that the solution turned yellow, since silica was precipitating.

A new stock solution was made by adding 8 mL sodium silicate to 72 mL water and slowly adding ion exchange resin. The solution was tested by adding 1 mL of it to 5 mL water and slowly adding HCl until the pH was around 7. If too much HCl was needed more resin was added to the solution until a maximum (which was chosen to be 0.5 mL 0.5 M HCl) was reached. After three times adding resin and testing the solution, this was reached.

Then 2.5 mL 0.5 M HCl was added to 15 mL of ZM19 and 35 mL water. While stirring 10 mL of the sodium silicate solution was added. To bring the pH down to around 7, 2.7 mL 0.5 M HCl was added. The sample was sonicated for 10min in an ultrasonic bath and stirred for 2 more hours. Right after that the sample was centrifuged at 1500 RPM for 2 hours and redispersed in water.

3.5.8 Using the same method on polymerized emulsion

The method described in 3.5.6 for ZMW6 was tried on the polymerized magnetic emulsion particles. 4 mL of sodium silicate was added to 36 mL water. Ion exchange resin was added until only 0.5 mL 0.5 M HCl was needed to bring 1 mL of the solution back to pH 7. 40 mL of TM35 was put in the 100 mL 3-neck round bottom flask. 1 mL 0.5 M HCl was then added and while stirring 10 mL of the sodium silicate solution was added. 7.5 mL 0.5 M HCl was slowly (5 minutes) added while checking the pH to achieve a pH between 7 and 8. It was then sonicated for 15 minutes and stirred for another 2 hours. The sample was then centrifuged at 1500 RPM for 2.5 hours and redispersed in ethanol.

This was tried again with 30 mL TM35 which was first sonicated for 5 minutes. 2 mL of 0.5 M HCl was added to this and while stirring 10 mL of the sodium silicate solution was added. Slowly more HCl was added until pH was between 7 and 8. 8 mL was needed for this. The sample was sonicated for 10 minutes and then stirred for another 3 hours.

3.5.9 Upscaling the coating of zein particles

The method described in 3.5.6 was tested if it also works using higher amounts. 10 mL 0.5 M HCl, 70 mL ZM20 and 180 mL water were stirred and sonicated in a 1L 2-neck round bottom flask. During stirring and sonication, 50 mL of the sodium silicate solution made in 3.5.7, was added. Slowly more HCl was added until pH was around 7. An extra 15 mL 0.5 M HCl was needed for this. The sample was sonicated for 15 minutes and then stirred for 21 hours. It was washed by centrifuging at 1500 RPM for 3 hours and redispersing in water.

3.5.10 Second coating

A new stock sodium silicate solution was made by adding 8 mL 13% sodium silicate to 72 mL water. Using the same test as described in 3.5.7 with ZMW7, just enough resin was added that only around 0.3 mL 0.5 M HCl was needed to reduce the pH of 1 mL sodium silicate solution to 7. 20 mL of ZMW9 which was made in 3.5.9, was added to 10 mL water in a 100 mL 3-neck round bottom flask. While stirring 3 mL 0.5 M HCl was added after which 10 mL sodium silicate was quickly added. Then another 1.5 mL HCl was added to bring the pH down to 7. The dispersion was sonicated for 10 minutes and then stirred overnight. It was centrifuged at 1500 RPM for 3 hours and redispersed in water.

3.5.11 Zein samples for empty silica particles

Using the same method described in 3.5.6, two more samples were made. Using 15 mL ZM20 and 10 mL sodium silicate solutions which were tested using the method described in 3.5.7. ZMW11 used 2.5 mL 0.5 M HCl and ZMW12 used 2 mL 0.5 M HCl.

3.5.12 Coating emulsion droplets

TM37 was made by adding 0.5 mL TPM to 20 mL Mt3 in 60 mL water and letting it left standing overnight. 10 mL TM37 was put in the flask with 25 mL water. 10 mL of the sodium silicate was added and then 3 mL 0.5 M HCl was added to bring the pH back to neutral. It was then sonicated for 10 minutes and left stirring overnight, after which it was washed with centrifugation. 2 mL of this sample was polymerized and again washed with centrifugation.

3.5.13 Coating zein particles without magnetite

Z1 was made and washed with the same method described in 3.5.5, only without adding magnetite. Dissolved zein was poured in water and dialyzing against water. A new sodium silicate solution was made and just enough resin was added by testing it like described in 3.5.7. Using the same method as described in 3.5.6 with ZMW6, two samples were made. This was done by using 15 mL of Z1, 10 mL of the sodium silicate solution and respectively 4.2 mL 0.5 M HCl for ZW1 and 3 mL 0.5 M HCl for ZW2. The dispersions were then sonicated for 15 minutes in an ultrasonic bath after which they were stirred overnight. They were then centrifuged at 1500 RPM for 3 hours.

3.5.14: Making and coating zein-silver composite particles

ZA1 was prepared using the typical way to make MZ particles as described in 3.5.5 but with silver nanoparticles instead of magnetite. The silver nanoparticles used for this experiment were made by dissolving 0.32g trisodium citrate and 0.0665g silver nitrate in 100 mL water and in a different bottle dissolving 0.0119g NaBH₄ in 100 mL water. The two solutions were slowly mixed while magnetically stirring.

ZA1 was then dialyzed in water for a week to remove most ethanol.

15 mL of ZA1 was added to 35 mL in a 100 mL 3-neck-round bottom flask. While stirring 2.5 mL 0.5 M HCl was first added and then 10 mL of the sodium silicate solution made for ZW2. After that 0.5 mL HCl was added to bring the pH back to around 7. The dispersion was then sonicated for 15 minutes and stirred overnight. It was centrifuged at 1500 RPM for 3 hours and redispersed in water.

3.5.15 More silica coated zein-silver particles

Using the same method as described in 3.5.14 for ZAW1, two more samples were made. New sodium silicate solutions were made for each by adding 4 mL stock sodium silicate to 36 mL water. Using the same method as with ZMW7 ion exchange resin was added until respectively 0.2 and 0.5 mL 0.5 M HCl was needed to bring down the pH to 7.

Using 15 mL of ZA1, 35 mL water, 10 mL of sodium silicate and respectively 2 mL and 5 mL 0.5 M HCl ZAW2 and ZAW3 were made after which they were sonicated for 15 minutes and stirred overnight. They were washed by centrifugation at 1500 RPM for 4 hours and redispersing in water.

3.5.16 Hollow silica particles

Hollow silica particles were made by adding either 80% ethanol to ZMW particles or the ZMW particles to 80% ethanol. This was first tried and when the results were promising, centrifuge was used to remove the zein. To counter aggregation, the influence of PVP was investigated. Also several silica coated zein particles were tried. They were washed with centrifugation at 1500 RPM for 3 hours. See Appendix A for more details.

3.6 Functionalize

It was tried to functionalize the ZMW samples. There are multiple ways to functionalize a silica surface [15] but during this thesis it was chosen to do the functionalizing using MPTMS. MPTMS is a molecule with a thiol group and 3 methyl groups with in the center a silicon atom. MPTMS can undergo hydrolysis in which the methyl groups switch with hydroxide groups that can react with a silica surface creating bonds between the silica and the thiol groups. These thiol groups can adsorb gold nanoparticles with which it can be shown that the functionalizing was successful

3.6.1: First attempt functionalizing

10 mL of ZMW6 was centrifuged at 1500 RPM for 3 hours and redispersed in 30 mL ethanol. A solution was made of 10 mL ethanol, 5 mL ammonia and 0.5 mL MPTMS. This solution and ZMW6

were put in a 3-neck 100 mL round bottom flask. While stirring it was heated to the boiling point until half of the solution was gone. It was then cooled and left stirring overnight.

3.6.2 Using a different method and trying with different pH

Three samples were made using a different method. 3 solutions were made with different pH. 15 mL water was added to three bottles. In the first solution the pH was dropped to 4.5 by adding HCl, in the second solution the pH was kept the same and in the third solution the pH was raised to 9.5 by adding NaOH. Three centrifuge tubes were filled with 15 mL ZMW9. After centrifuging at 1500 RPM for 3 hours, each of the sediments was redispersed with one of the three solutions. To each dispersion 0.25 mL MPTMS was added after which they were shaken on a shaking machine overnight. They were then washed by centrifuging two times at 1500 RPM for 3 hours and redispersing in water. To each, 1 mL dispersion of gold nanoparticles was added. These gold particles were made and given by van Leeuwen [13]. The dispersions were shaken overnight. The dispersions were washed again with centrifuging three times at 1500 RPM for 3 hours and redispersing in water.

3.6.3 Using more MPTMS and gold nanoparticles

5 mL of ZMW9 was centrifuged at 1500 RPM for 3 hours and redispersed in 18 mL water which had enough HCl to obtain a pH of 3.6. To this 0.1 mL MPTMS was added and this was magnetically stirred overnight. This was then centrifuged at 1500 RPM for 3 hours and redispersed in water three times. 4 mL of the gold nanoparticles dispersion used with the previous ZMWS samples was added and this was left standing for a day. It was centrifuged two more times after that.

3.6.4 Functionalizing zein colloidal particles

ZW2 was centrifuged at 1500 RPM for 3 hours and redispersed in acidic water (pH was 4.5 by adding HCl). 0.5 mL MPTMS was added and the dispersion was shaken over 2 days. This was centrifuged at 1500 RPM for 3 hours and redispersed in water two times.

The gold nanoparticles used also in 3.6.2 and 3.6.3, was added to the dispersion and after two days it was centrifuged one more time.

3.7 Analysis

Almost all samples were analyzed by transmission electron microscopy. Samples were diluted if necessary and a small droplet of the sample was gently put on a copper TEM grid coated with formvar and dried under a heating lamp. The non-coated emulsions and zein particles were dried at room temperature due to melting at higher temperatures.

The TEM grids were analyzed by taking transmission electron micrographs with a Philips TECNAI10.

Dynamic light scattering and zeta-potential measurements were done by using a Malvern Instruments Zetasizer Nano series machine.

For the sample ZMW9, the isoelectric point was measured by adding either a diluted solution of HCl or NaOH to decrease/increase the pH and then measuring the zeta-potential.

Rough pH measurements were done with pH indicator paper from Macherey-Nagel. More precise pH-measurements were done with a pH210 Hanna instruments microprocessor pH meter.

4 Results/discussion

4.1 Magnetic nanoparticles

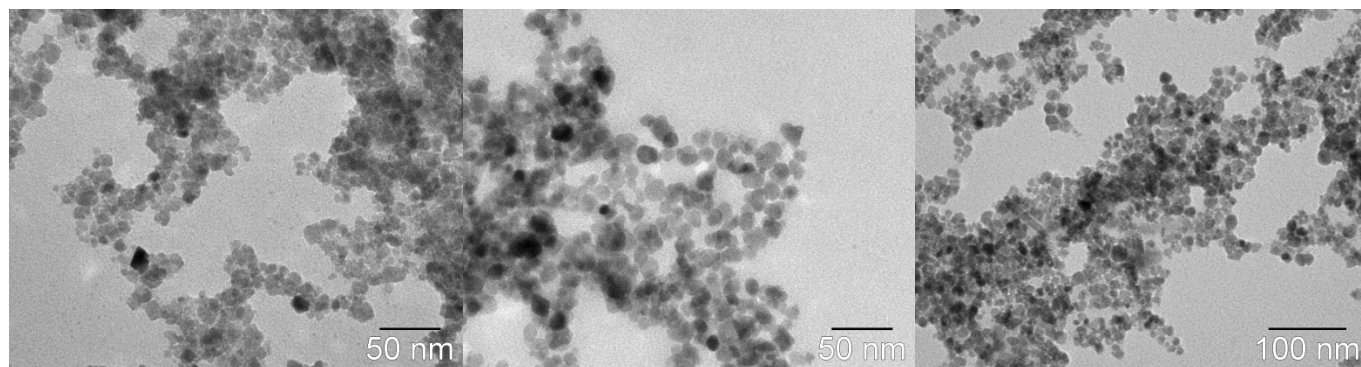


Figure 4.1.1: Magnetic nanoparticles

Figure 4.1.1 shows that in all three magnetite syntheses, stable magnetic nanoparticles were successfully made with the method described in 3.1 as expected. The particles had a diameter of 10-12 nm with a polydispersity around 20%. The dispersion began as black magnetite but over time the dispersion became more brownish due to oxidation to maghemite which has somewhat the same magnetic properties as magnetite.

4.2 Emulsions

4.2.1 General emulsion

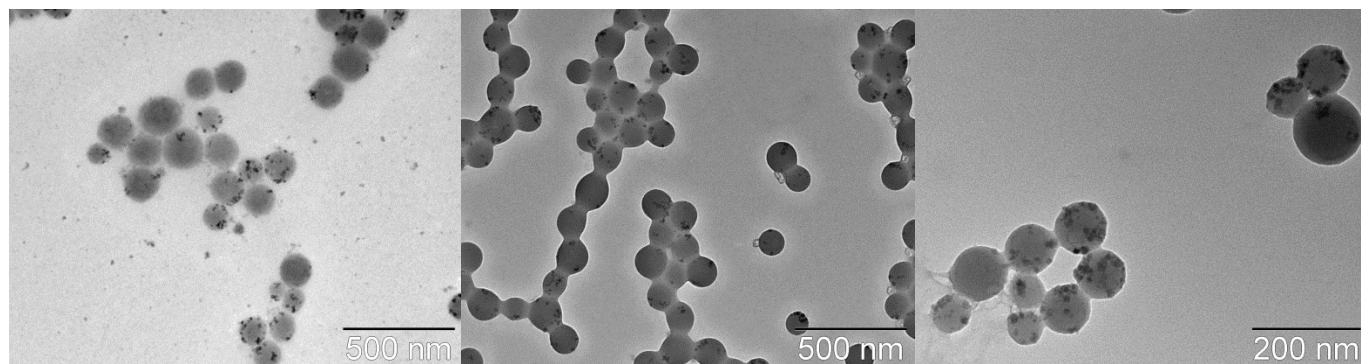


Figure 4.2.1: A small selection of typical TEM images of polymerized emulsions

TPM and magnetite in water formed spontaneous magnetic emulsions with diameters around 100-140 nm. This could be seen as the dispersion went from a clear black liquid to a turbid grey-brownish liquid. These emulsions were successfully polymerized as can be seen in figure 4.2.1. It can be seen that the spherical structure remained after being dried on the TEM grids. The black dots in the TEM images are the magnetite nanoparticles.

In the samples there are some particles present that are significantly larger than the average sized particle. This can be seen in almost all samples while the theory predicts that the emulsion droplets should have one average size in equilibrium. This observation has not been reported before. Like discussed in 2.3, there are factors, which have been investigated in previous studies, that can increase the average size but this does not apply to single particles in a sample. Measurements from both DLS and TEM show uneven size distributions where the median is larger than the mode. This observation and the large particles in the TEM images were unexpected. A possible explanation is that the emulsion droplets are able to fuse with each other into larger particles. It is then likely that

there is an equilibrium between the amount of fused particles and non-fused particles because these fused particles are larger than the size which the theory predicts as the most energy favorable size. On one side there will be droplets fusing and on the other side particles that shrink back into the size of a non-fused droplets.

This hypothesis is made likely by looking at the histograms of the volumes of the polymerized emulsion samples. In these histograms peaks can be seen around n (1,2,3 etc.) times the volume of non-fused particles. In figure 4.2.2 this is made clear as the different particles were tried to be separately measured on TEM images. However the polymerized emulsion samples have a high polydispersity and it is likely that fused particles will shrink again which makes it harder to distinguish the difference between fused and non-fused particles

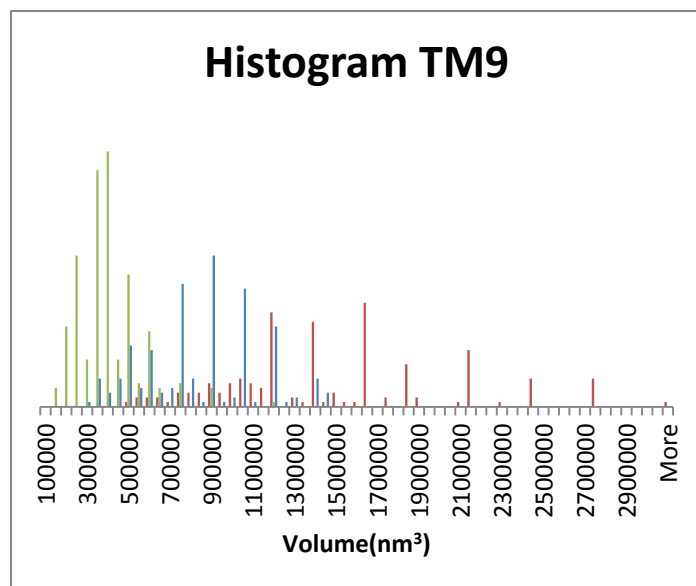


Figure 4.2.2: The histograms of the same particles but in which it was tried to separate non-fused particles, double volume particles and larger particles.

4.2.2 Different initiators

Polymerized emulsions were successfully made with the oil soluble initiators AIBN and V65 as can be seen in figure 4.2.3. The sample with V50 became unstable right after adding the initiator. The sample which was polymerized using AIBN contained larger particles than what was expected but aside from larger particles, no significant difference could be seen between each sample.

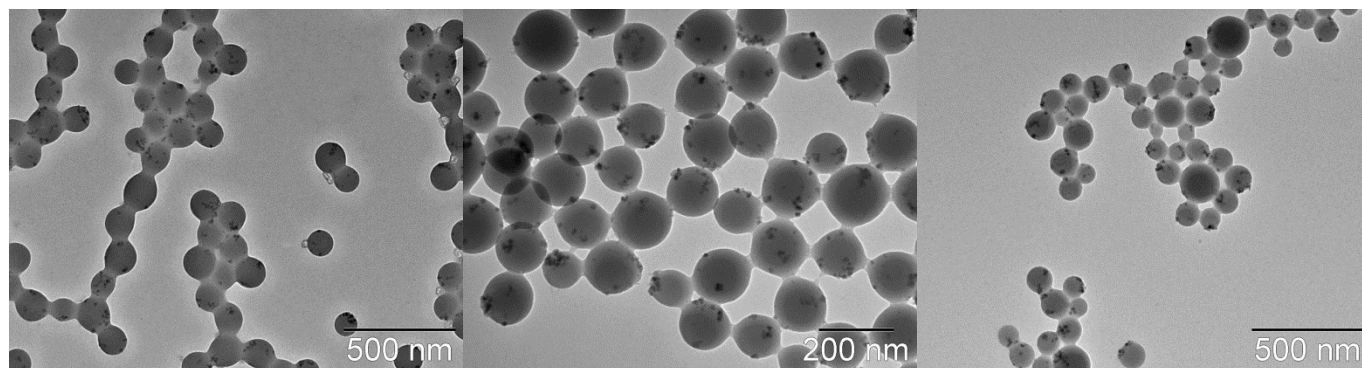


Figure 4.2.3: Emulsions made with different initiators. Left: KPS, middle: AIBN and right: V65

4.2.3 Time effect on emulsion

Table 4.2.1: Results time effect on the emulsions

Sample	Time (Days)	Average diameter (nm)	Polydispersity	% non-fused particles	Radius non-fused particles(nm)
TM12	1	103	15%	81%	50
TM11	6	115	16.7%	69%	53
TM10	9	120	18%	52%	53

The three samples made with difference emulsification times were successfully formed and polymerized as can be seen in the TEM images (see appendix B). Table 4.2.1 shows that the older emulsions have a larger average size and it looks like the older droplets fused more into each other than the younger ones. The larger average size in older samples is in agreement with earlier work like discussed in 2.3. The reason for the larger size is the condensation of the hydrolyzed TPM molecules. The condensation reaction reduces the amount of available hydroxyl groups on the surface. The particles become more hydrophobic which aside from making the energy tension higher, also makes the magnetite nanoparticles to slowly go into the TPM and leave the surface [25].

4.2.4 Influence of t dilution

Four samples of the series emulsions that were made to investigate the influence of the dilution factor were successfully formed and polymerized as can be seen on the TEM images (see appendix B). They also show that the most diluted sample wasn't formed or polymerized. The samples with more diluted systems have smaller average sizes as can be seen in table 4.2.2. This is likely due to the fact that the emulsions droplets have fewer collisions and therefore have a lower chance to fuse together and therefore shift the equilibrium to the side of non-fused particles. This can also be seen in table 4.2.2 since the percentage of non-fused particle is higher for the more diluted systems.

Table: 4.2.2: Results influence of the dilution factor

Sample	Concentration TPM	Average diameter (nm)	Polydispersity	% non-fused particles	Radius non-fused particles(nm)
TM17	0.31%	91	12%	84.5%	45
TM14	0.625%	116.5	16%	60%	54
TM12	1%	103	15%	81%	50
TM13	2.5%	140	19%	3.5%	58

4.2.5 Influence of pH

The pH of the control sample was 9.6 and the pH of the sample with extra TMAH was 10.6. After 3 hours of adding the TPM to both samples, the sample with extra TMAH was already turbid while the control sample was still clear. The TEM images (see Appendix B) show that in control sample emulsions were successfully formed and polymerized while in the sample with extra TMAH no polymerized particles could be seen.

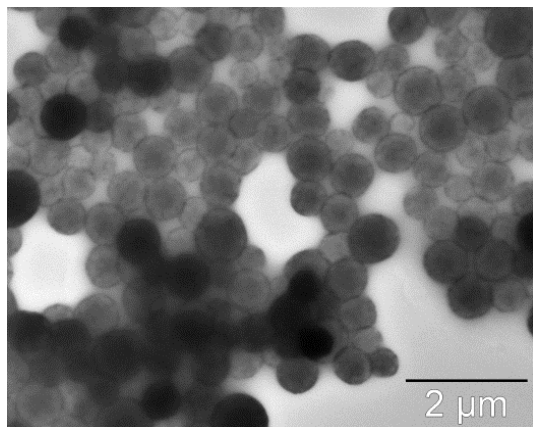


Figure 4.2.4 TEM image of emulsion with HCl

Right after adding 1 mL 0.5 M HCl to the just formed emulsion the dispersion changed. The TEM images (see figure 4.2.4) of the emulsion with HCl after polymerization and washing, show that the emulsion droplets swelled up to much larger spheres with an average diameter of 660 nm and polydispersity of 15.6%. At the interface of the particles a dark layer can be seen in the TEM images. Also all the magnetite was gone. This is because iron oxides dissolve at low pH. This shows that the magnetite is either indeed at the interface or that the HCl can diffuse through the hydrophobic TPM. It also shows that the hydrolyzed TPM molecules are enough to keep the colloidal particles stable. The stability is indicated by the low polydispersity and spherical shape of the particles.

4.2.6 Different ratios

The four samples that were made with different TPM-magnetite ratios were successfully formed and polymerized which is shown on the TEM images (see appendix B). The results are shown in table 4.2.3. The expected results would have been that a lower ratio would give smaller particles liked discussed in 2.3. Only TM27 (the sample with ratio 2.5) and TM29 (the sample with ratio 10) followed this trend. TM26 the sample with ratio 1, did not because while the emulsion was indeed formed, the TEM images showed that it contained also a lot of free magnetite and malformed emulsion particles. The average size of TM28 (the sample with ratio 5) was larger than that of TM29 and while this goes against the trend which is discussed in 2.3 the size of TM28 is still inside the error bars of figure 2.3.2. The amount of fused particles was low for TM27 and TM29 which was also expected since the amount TPM was 0.25% which is even lower than with the most successful diluted sample made in the series which was made for investigating the influence of the diluting factor.

Table 4.2.3: Results influence of the ratio TPM-magnetite

Sample	Ratio TPM/magnetite	Average diameter (nm)	Polydispersity	% non-fused particles	Radius non-fused particles(nm)
TM26	1	86.8	24%	48%	37
TM27	2.5	53	26%	91%	27
TM28	5	88.9	22%	52.5%	38.5
TM29	10	82.3	16%	79%	39.6

4.2.7 DLS/zeta potential measurements

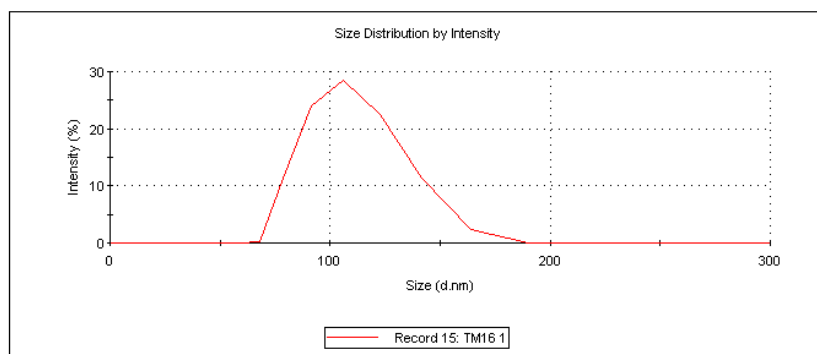


Figure 4.2.5 DLS emulsion droplets

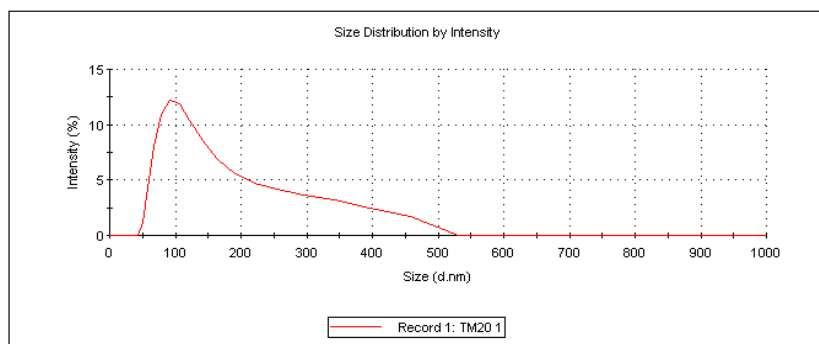


Figure 4.2.6 DLS TM20

Figure 4.2.5 and figure 4.2.6 show the DLS results from an emulsion sample without polymerization (TM16) and one after polymerization (TM20). They show that in both samples there most likely fused particles. Especially the sample with polymerized particles shows a high amount of particles that are larger than expected. Also the zeta-potential of the sample with polymerized emulsion particles was measured around at -27 mV.

4.3 Adapted Stöber method

4.3.1 The first TMS samples

The TEM image of the first TMS sample (see figure 4.3.1) shows that the first attempt to coat the polymerized magnetic emulsions with silica was less successful than expected. Silica indeed formed but during this reaction a high amount of secondary nucleation happened and more silica formed around that. While the polymerized emulsion particles are coated with silica, this silica was not spherical because more silica nucleated on the coating which deformed the spheres. Likely this was because too little polymerized emulsion was used and too much TEOS was used.

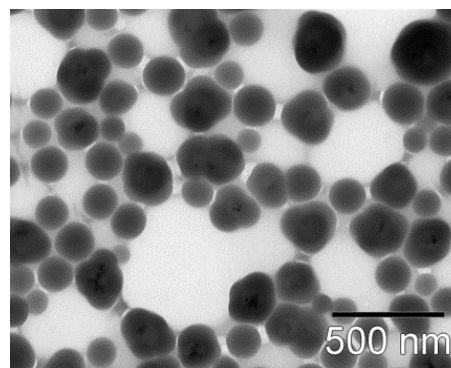


Figure 4.3.1: The first silica coated sample

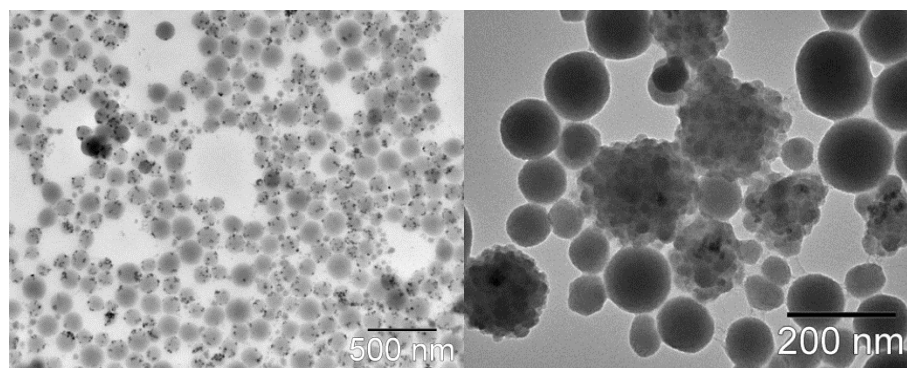


Figure 4.3.2: TEM images of the second sample (left) and the third sample (right) that was tried to be coated with silica

The next reaction was even less successful. This was the experiment where all amounts were upscaled. The TEM picture of this sample (see figure 4.3.2) showed that no visible amount of silica was formed. No significant change from normal polymerized emulsion particles could be seen. It can be concluded that something went wrong during the reaction. The most likely reason for the failing of the experiment is that the concentration of TMAH was too low.

The third attempt was more successful because silica could be seen in the TEM images as can be seen in figure 4.3.2. Two kinds of silica were formed. Larger silica spheres and smaller spheres attached to each other in groups. Black dots can be seen in those groups which would indicate magnetite nanoparticles are present in them which would mean that the cores of these groups are polymerized emulsion particles.

4.3.2 Different concentrations TMAH

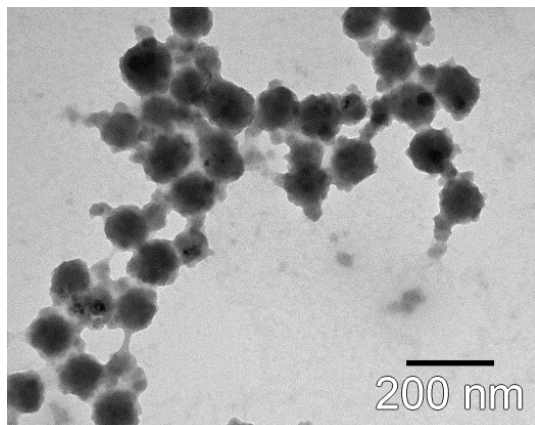


Figure 4.3.3: What is likely non-polymerized TPM around silica spheres

TEM images of the first series of samples in which the influence of TMAH was investigated (see appendix B) show that these samples failed. In the first two of the series only dried dissolved emulsion can be seen and in the third sample, there are particles visible but these are most likely silica spheres with non-polymerized emulsion around them as can be seen in figure 4.3.3. These samples failed because the emulsion which was used for these samples wasn't successfully polymerized. However they do show something important. The amount of TMAH is important because with a too low concentration of TMAH, no visible silica can be seen on TEM images indicating that no silica is formed. This has most likely to do that the pH of the dispersion needs to be high enough to catalyze the TEOS reaction to form silica.

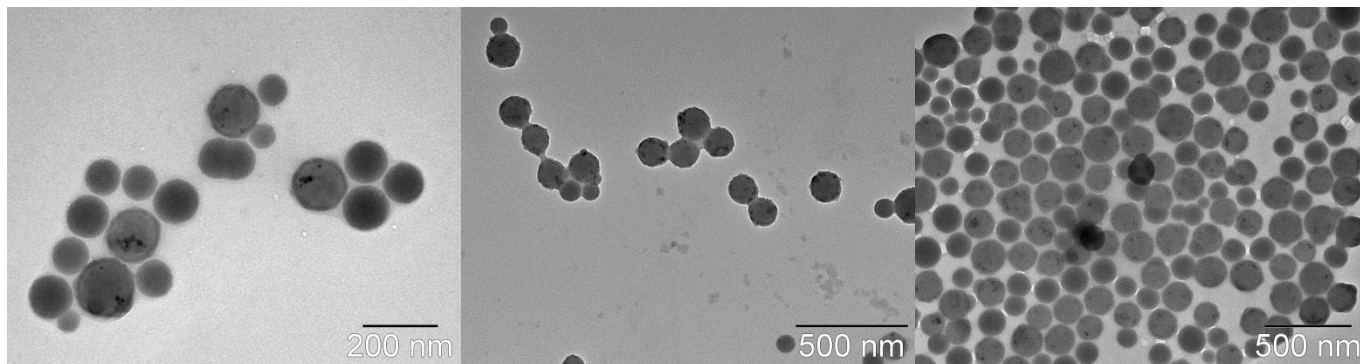


Figure 1.3.4: A small selection of samples with silica coated polymerized emulsion particles

Figure 4.3.4 shows the TEM images of the second series of samples in which the influence of TMAH was investigated. They show that the coating of emulsions with silica were successful. The coatings have a more defined shape than with the first samples but there is still a high amount of silica spheres from secondary nucleation. In figure 4.3.5 the result of the second series are shown. The shell thickness was calculated by assuming that it is the radius of the silica coated emulsions minus the radius of the polymerized emulsions particles before the coating. From the results a trend can be concluded that the shell thickness is proportional to the concentration of TMAH used.

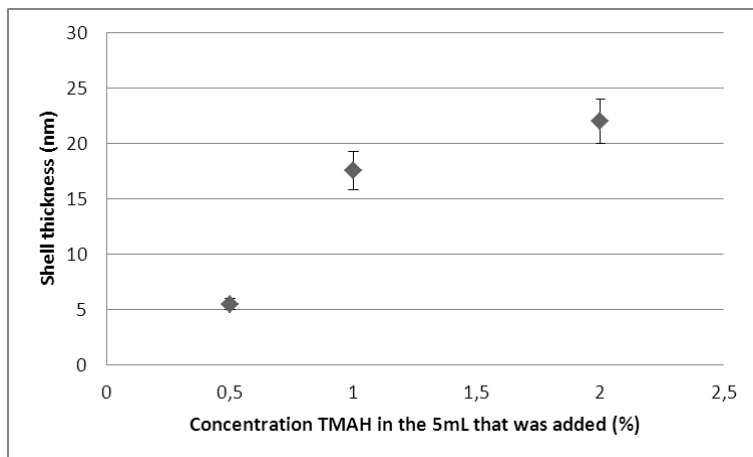


Figure 4.3.5: graph of the results from the second series that were made to investigate the influence of the TMAH concentration

4.3.3 Increasing reaction time

TEM images of the samples TMS10-TMS13 and TMS15 (see appendix B), which were made with different amounts of time in which the TEOS was added, show no significant differences between them or with the samples from the second series that were made to investigate the influence of the TMAH concentration. All emulsions were coated with a thin layer of silica with shell thickness between 13.5 nm and 28.5 nm but as can be seen in figure 4.3.6 no real trend can be seen in these results. All samples had more silica spheres from secondary nucleation than silica coated polymerized emulsion particles.

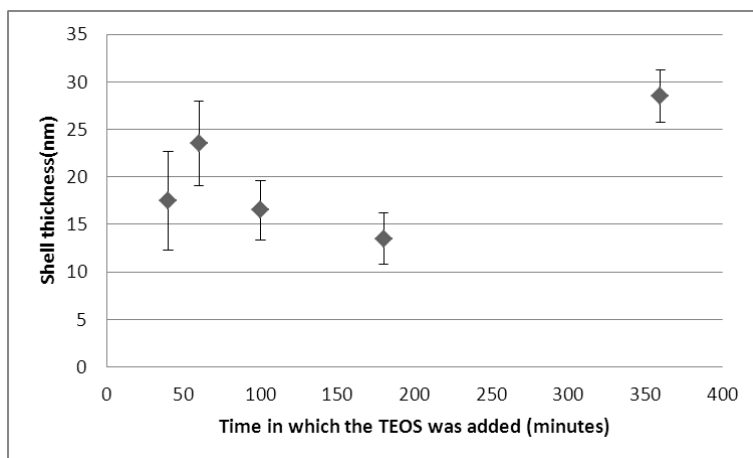


Figure 4.3.6 graph of the results from the series of samples that were made to investigate the influence of the time in which the TEOS was added.

4.3.4 Second coating

The TEM images of TMS14 (see figure 4.3.7) show that the second coating was successfully. The shell thickness grew from 28.5 nm to 73.5 nm. The large increase in shell thickness is remarkable because it is much more than one would expect. While only half of what remained of TMS13 after centrifuge steps (with no visible remaining particles in the supernatants) was used, the lower amount of particles was compensated by the silica particles that were formed due to secondary nucleation. The high amount of increase in shell thickness shows that the silica nucleates on silica covered with PVP is more favorable than on the polymerized TPM covered with PVP. Not much can be said about the amount of secondary nucleation that formed during the second coating except that it is likely less than during the first coating because more silica went to the shells of the polymerized emulsion particles than during the first coating.

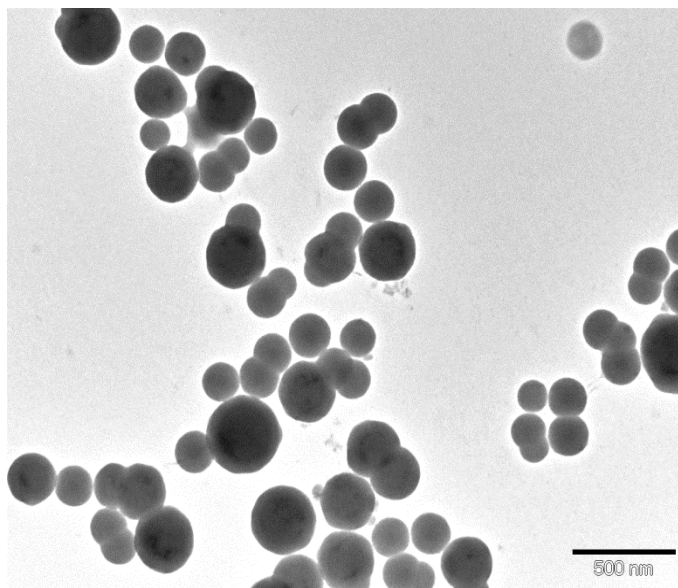


Figure 4.3.7: TEM image of the second coated sample

4.3.5 Difference between PVP-10 and PVP-40

TMS16 and TMS17 were the first two samples made to investigate if there is a difference in the results if PVP-10 is used instead of PVP-40. The TEM images of these two show that the coatings did not work. These experiments were done again and were then more successful.

The TEM images of TMS18 and TMS19 (see appendix B) show that both samples contained silica coated emulsion particles and silica spheres from secondary nucleation. No significant difference could be seen between both samples. The silica coated emulsion particles had in both samples an average diameter of 150 nm.

TEM images of the part of TMS18 in which no extra PVP was added show only silica spheres and no polymerized emulsion particles. This shows that it is likely a necessary step in the method and that secondary nucleation happened even without it.

4.3.6 DLS

Table 4.3.2 DLS results from different emulsions coated with silica

Sample	average radius(nm)	Difference (shell thickness)
TM9	97.3	-
TMS12	111.4	14.1
TM20	58	-
TMS13	108.1	10.8
TMS14	127.7	30.4
TMS15	108.4	11.1

TMS samples were measured with DLS to validate the results from the TEM images. The results can be seen in table 4.3.2. While the DLS measurements do not distinguish the silica spheres from silica coated polymerized emulsion particles they do show that the trends are the same. There is an increase in radius compared to the polymerized emulsion particles but the difference between TMS12, TMS13 and TMS15 is small and only the second coating (TMS14) has a larger shell. Also with these samples it can be seen there is an uneven distributions with more particles on the right side of the mode. This could be because of the fusing of particles as discussed in 4.2 however it can also be caused by the silica spheres from secondary nucleation.

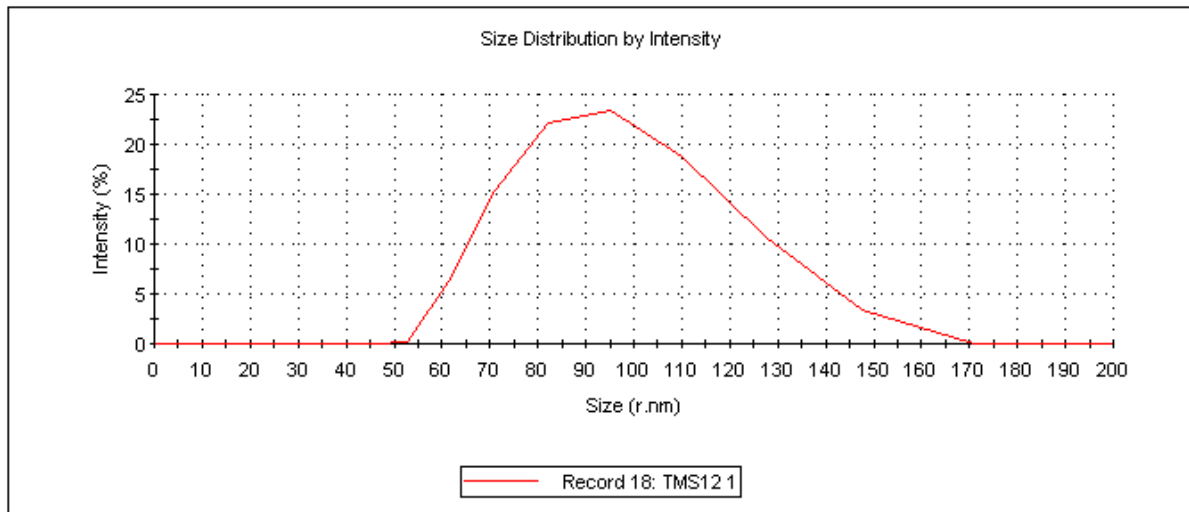


Figure 4.3.6 DLS TMS12

4.4 Zein

4.4.1 Different amounts of magnetite nanoparticles

The dispersion of colloidal zein particles looked light yellowish and turbid while the dispersions of the colloidal composite particles with magnetite were more dark brownish. The TEM pictures of the zein samples showed that zein melts easily while drying even at room temperature and that all particles have a high polydispersity.

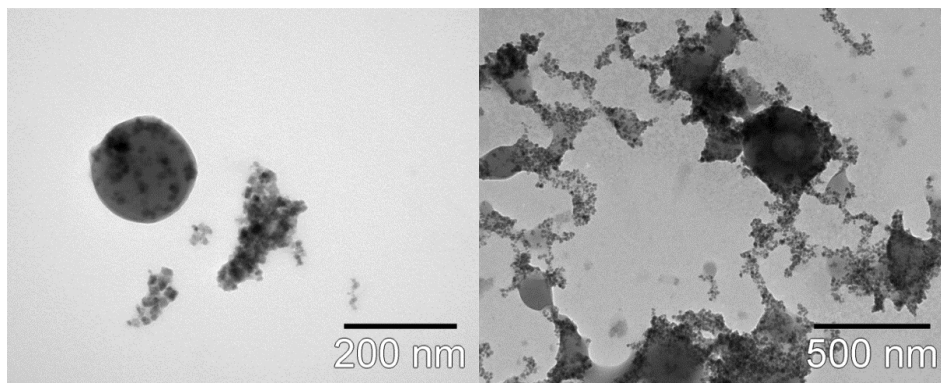


Figure 4.4.1: TEM pictures of zein-magnetite sample in which too much magnetite is used

The TEM images of ZM1 and ZM2 can be seen in figure 4.4.1. These samples were made to see how much magnetite could fit in the zein colloidal particles. The images show that the amount of magnetite which was used for these two samples was too high. Few spherical particles could be seen in ZM1 and none in ZM2. Loose magnetite particles were present next to the zein which also indicated that too many magnetite particles were used.

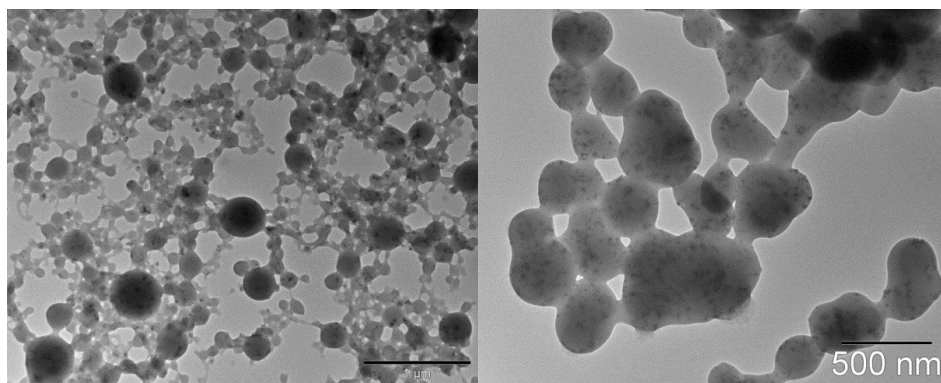


Figure 4.4.2 TEM pictures of zein-magnetite samples in which no loose magnetite can be seen

Figure 4.4.2 shows the TEM images of the zein samples ZM5 and ZM6. ZM5 is the sample with 26mg magnetite per gram zein. Its TEM images show zein particles with magnetite nanoparticles inside and melted zein between spherical zein particles. The TEM images ZM6, the zein sample with 78mg magnetite per gram zein, show blobs of zein with magnetite in them. While loose zein particles could be seen, most of the objects in the TEM images of ZM6 were bigger blobs of fused particles without any defined shape. Most likely the blob forming was because the positive charge on the surface of the zein particles became too low due to the too many negative magnetite nanoparticles inside. This would indicate that the right amount magnetite was more towards that of ZM5 which was around 26mg/g zein.

4.4.2 Zeta potential measurements

Table 4.4.1 Zeta potentials of different zein samples at pH 4 and 7

sample	Zeta potential pH 4 (mV)	Zeta potential pH 7 (mV)
TM7: Zein	50.11	-26.25
TM8: Magnetite-zein	35.95	-44.3
TM9: Zein-magnetite	43.85	-36.35
TM10: Zein-magnetite-zein	33.4	-20,55

Table 4.4.1 gives the results from zeta potential measurements. The zeta-potentials were negative at a pH of 7 and positive at a pH of 4. The pH of zein particles normally is around 4 and zein has a isoelectric point around 6.2 [13]. These results are in agreement with earlier work as can be seen in figure 4.4.3

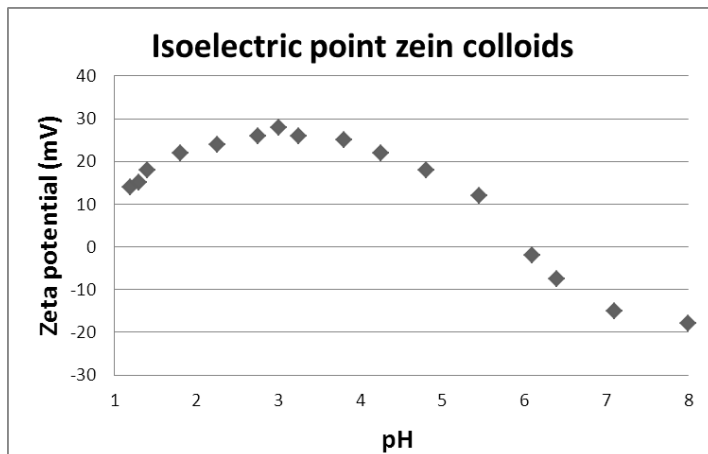


Figure 4.4.3: Zeta potential of zein at different pH taken from [13]

4.4.3 Zein samples with silver nanoparticles

Silver nanoparticles were successfully synthesized as can be seen in figure 4.4.4. The average size was 24 nm with a polydispersity of 32% and a zeta-potential of -38 mV. Zein-composite particles with these silver nanoparticles were also successfully formed even though the silver nanoparticles were larger than the magnetite nanoparticles

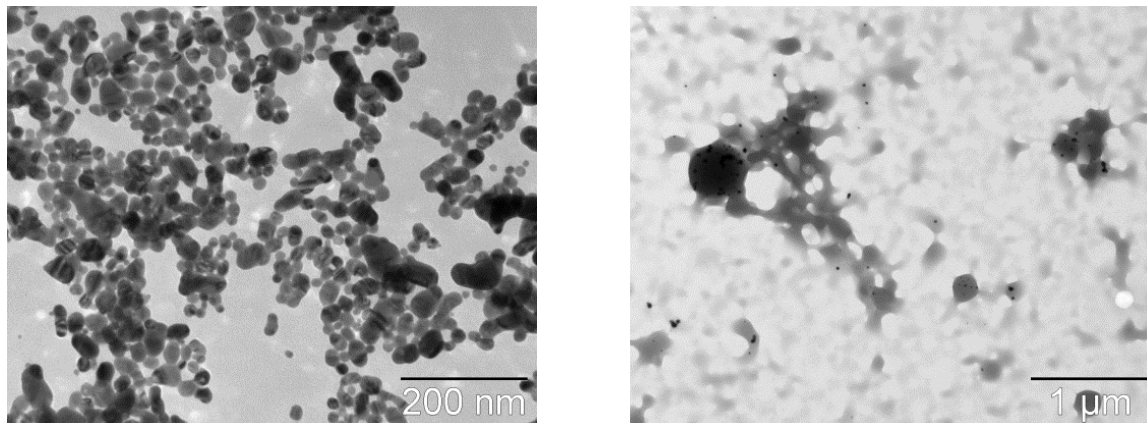


Figure 4.4.4 TEM images of silver nanoparticles (left) and zein composite particles with silver nanoparticles (right)

4.5 Sodium Silicate experiments

4.5.1 First results

TEM images of the first results from sodium silicate experiments (see figure 4.5.1 and appendix B) show that a gel like silica structure was formed. For TMW4 this is most likely because too much sodium silicate was used and dialysis did not remove the excess. For ZMW1 and ZMW2, zein samples that were also trapped in a silica structure on the TEM images, this could also be because the pH was decreased too much. Sodium silicate forms a silica gel if the pH is brought below 6-7 [28].

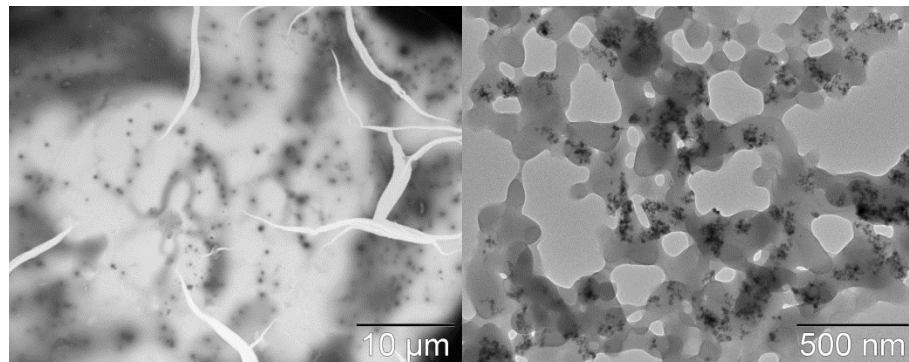


Figure 4.5.1 TMW4 a sample with too much sodium silicate, ZMW4 a sample with too little sodium silicate

With TMW5, ZMW3 and ZMW4, the samples that used less sodium silicate, no visible silica remained which could be seen on the TEM images (see 4.5.1 and appendix B). TMW5 only showed polymerized emulsion particles and ZMW3 and ZMW4 zein particles on the TEM images. What most likely happened was that a too diluted sodium silicate solution was used. These results indicate that using an exact concentration of sodium silicate is crucial.

4.5.2 Optimizing a different method

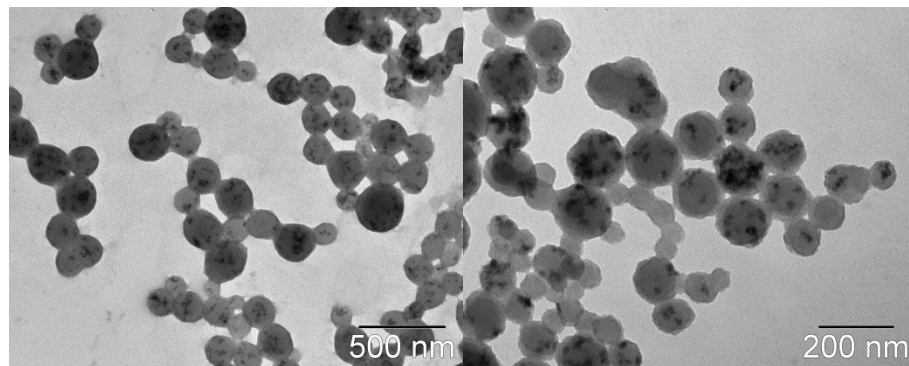


Figure 4.5.2 TEM images of ZMW5 (left) and ZMW6 (right), the samples made with the 2nd method

The TEM images of ZMW5 (see figure 4.5.2 left) which was the first sample made with the 2nd method to use sodium silicate, showed spheres containing zein and magnetite particles. While it is not that clear to see, it is likely those zein particles are covered with silica because the particles keep their spherical shape while other zein particles melt into more undefined shapes while drying. The successful silica coating on the zein particles is made more clear on the TEM images of ZMW6 (see figure 4.5.2 right) which was the sample made after experiments were done to optimize the method. A thin layer of silica can be seen as light grey round the darker zein and even particles that are most likely silica spheres since no black dots (magnetite particles) are inside.

ZMW7 was the sample made after ZMW6 to show that the method is reproducible but had difficulties with the ion exchange resin as described in 3.5.7. The TEM images from this sample (see Appendix B) show two kinds of particles: Zein-magnetite particles coated with silica like ZMW6 and large spherical particles with magnetite nanoparticles in them and an average diameter of 406 nm as can be seen in figure 4.5.3. Loose silica can be seen around the larger particles however it is still unknown exactly how they were made

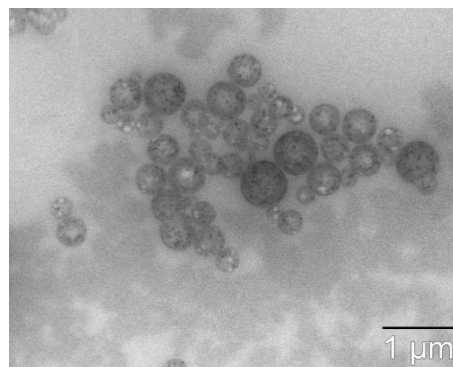


Figure 4.5.3 ZMW7 unknown particles

4.5.3 Trying to coat emulsion particles

TEM images of TMW6 and TMW7, polymerized emulsion particles that were tried to be coated using the same method as the one that made successful silica coated zein particles (see appendix B), show malformed particles with some silica around them. This was unexpected because the polymerized emulsion particles (TM35) used for these two samples was just fine as seen in its TEM images (see appendix B). The silica which is present shows that the right concentration is used but that it didn't coat the polymerized emulsion particles which would indicate that this method does not work on the polymerized emulsion particles.

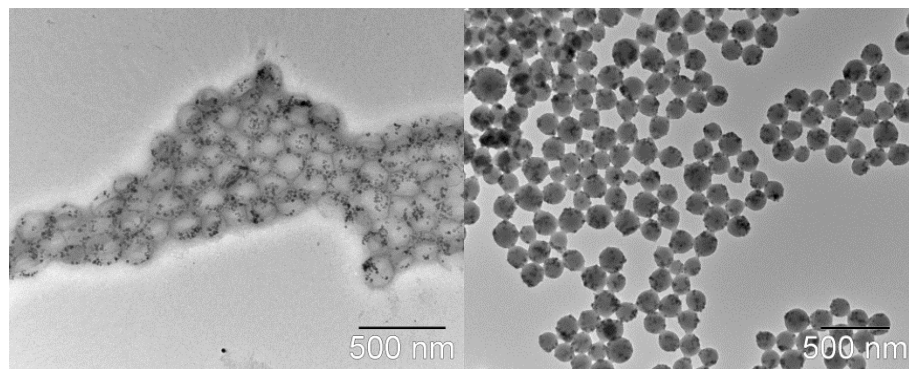


Figure 4.5.4 TEM images of the silica coated emulsion droplets, before and after polymerization

The TEM images (see figure 4.5.4) from before polymerization of TMW9, the non-polymerized emulsion that was tried to be coated with silica, show unexpected results. The expectation from this sample was that it contained particles that looked like the silica coated zein particles. That this would not happen was also possible since the emulsion particles are negatively charged instead of positive and adding HCl before the sodium silicate led to the results of TM37 with acid (large empty spheres). The result that was found however was even more unexpected. The droplets are crushed together while the interfaces between the particles remained. A silica layer around the group of clustered particles can be seen which would explain why it is even possible to see particles on the TEM grid while normally only polymerized emulsions particles can remain some of their structure while drying. While small silica shells could be the reason why the interface is visible on the TEM image but they are too small to be seen on the images. Why the emulsion droplets are crushed together is still unknown because the silica layer around the group indicates that it happens before the centrifugation.

The TEM images of this sample after polymerization show successful loose polymerized emulsion particles without any silica. Most likely the silica was dissolved during the polymerization because silica is solvable in water especially at high temperatures.

4.5.4 Upscaling and second coating

The TEM images (see figure 4.5.5) of ZMW9, the zein sample that was coated with silica using five times the amounts of all components, show that zein-magnetite particles were successfully coated with silica. A high amount of these particles aggregated against each other with the silica. While the dispersion was still stable and the aggregation mostly only happened on the scale of a few microns. The TEM images of ZMW10, the zein sample that was coated twice, show that a lot of silica was formed between the silica coated particles. The particles increased in size from an average diameter of 158 nm (ZMW9) with a polydispersity of 38% to a diameter of 209 nm with a polydispersity 41%.

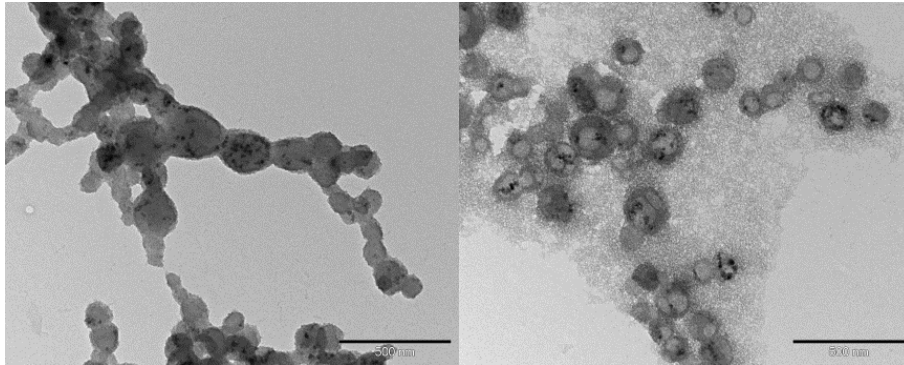


Figure 4.5.5: The silica coated zein samples made with upscaling (ZMW9 left) and with second coating (ZMW10 right)

Figure 4.5.6 shows the zeta potential of ZMW9 at different pH (silica coated zein composite particles) and compares it with normal silica colloids from reference [33]. This shows that the zein particles are indeed covered with silica. Comparing this to figure 4.4.3 which shows the zeta potential at different pH of zein particles, the first thing to notice is that no positive charge remains at low pH after the silica coating. Also the zeta potential becomes more negative. DLS shows that the sample contains a high amount of clusters. The sample is too polydisperse to acquire a good measurement and the sizes it gives are much larger than the normal sizes of the particles which are around 100-200 nm

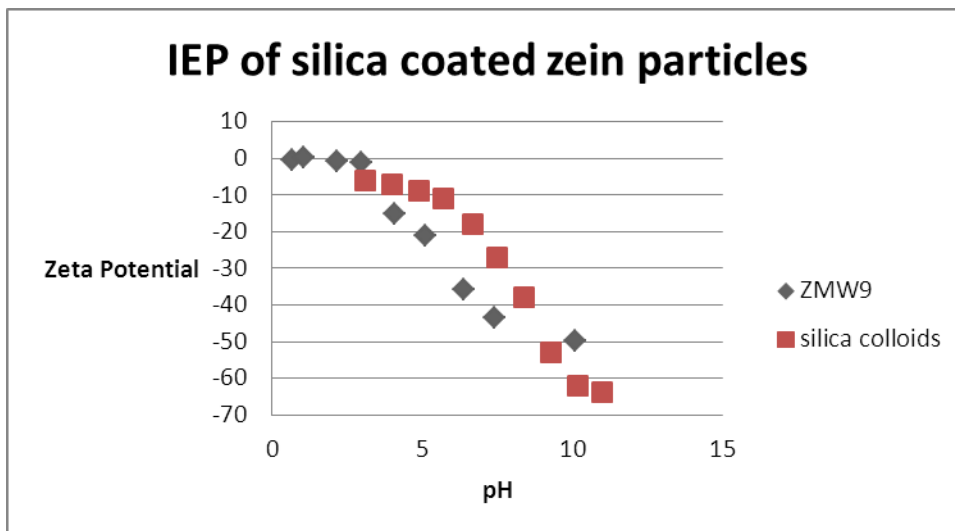


Figure 4.5.6: Zeta potential at different pH of silica coated zein composite particles (ZMW9) and silica colloids taken from [33]

4.5.5 More silica coated zein composite particles

The TEM images of ZMW11 and ZMW12 (see appendix B) show two more samples in which zein-magnetite were coated with silica. This shows that this method used to coat zein composite particles with silica is reproducible.

This method also works on zein particles without any nanoparticles as can be seen on the TEM images of ZW1 and ZW2 in figure 4.5.7. Again the silica in the TEM image has a light grey color due to being highly porous, and the silica is coated around the darker zein.

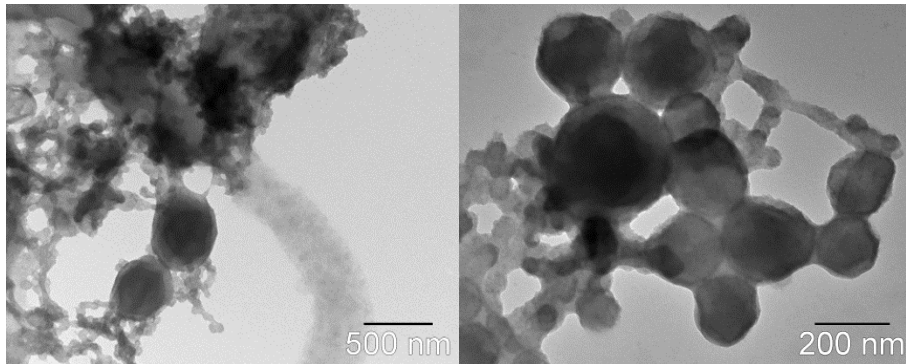


Figure 4.5.7 silica coated zein particles

Figure 4.5.8 shows the TEM images of the three silica coated zein-silver composite particles which show that ZA1 is successfully coated with silica thrice. ZAW1 and ZAW3 however contained particles where it seems like the zein was gone from the silica coated particles and hollow silica particles with silver nanoparticles remained. This can be seen in figure 4.5.8 in the right and left image as the silica is darker on the outside layer than in the center because the zein is gone.

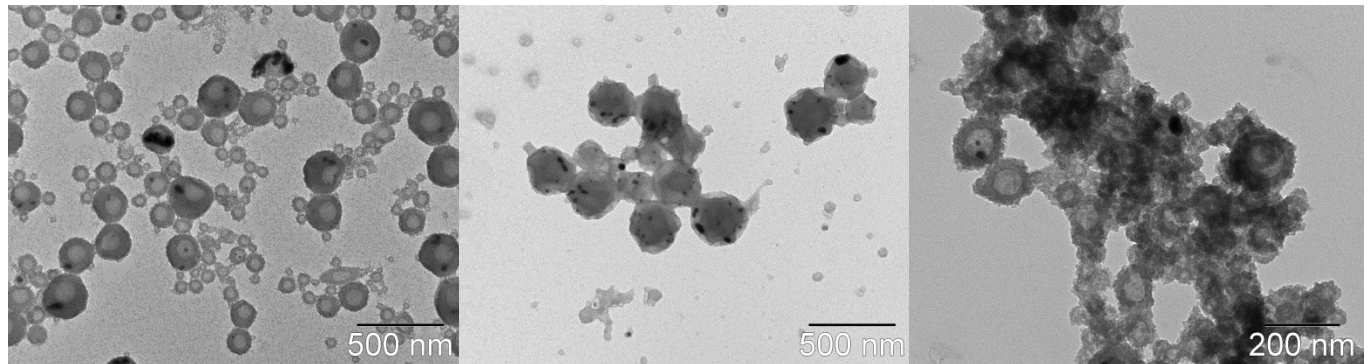


Figure 4.5.8 TEM images of silica coated zein-silver composite particles

4.5.6 Hollow silica spheres

The first attempt to remove the zein from the silica coated zein particles looked like it could have worked because the TEM images of that sample, ZMW5E (see appendix B) show particles which most likely are silica particles that contain no more zein. This can be seen by the lighter grey in the middle of the particles than on the outside where the shell is. However the sample contains a lot of material that most likely is the dried zein.

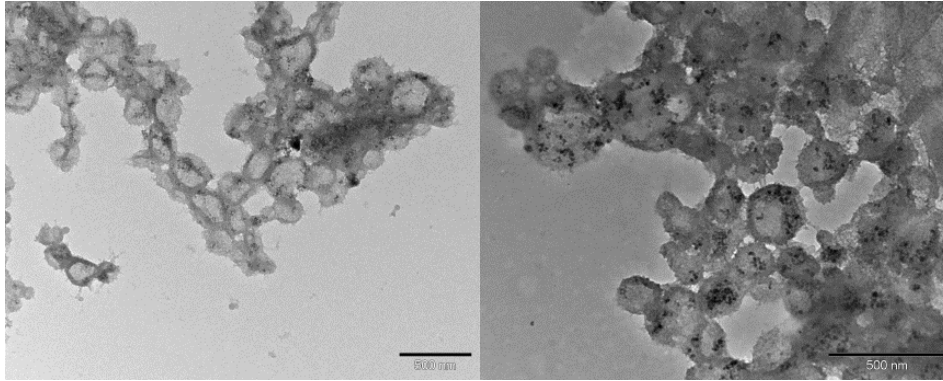


Figure 4.5.9 TEM images of hollow silica spheres with magnetite still in them with (right) and without (left) PVP

In figure 4.5.9 the TEM images of ZMW9E, a sample with hollow silica sphere, it is more clearly shown than with ZMW5E that hollow particles remained because the dissolved zein was washed away. Trying to reproduce the hollow particles showed that not every time when silica coated zein particles were added to 80% ethanol empty silica spheres were produced. The TEM images of ZMW11E (see appendix B) showed silica without a defined shape and ZMW12E showed areas with zein and areas with silica without zein but a high amount of this silica was collapsed. To enhance stability it was tried to add PVP before removing the zein but TEM images of these particles (see figure 4.5.9 and appendix B) show that this did not help and it even made some of the zein stick to the silica.

Silica coated zein-silica composite particles that were tried to make hollow also show that a lot of particles collapsed. Still, hollow particles with silver nanoparticles could be found on the TEM images (see appendix B)

4.6 Functionalized silica coated particles

The TEM images of the first sample that was tried to be functionalized, ZMWS1 show that the structure of the silica did not remain. The structure was destroyed by the use of ethanol and high temperature.

The TEM images of the samples that were functionalized in an acid solution (ZMWS2) and the one in a neutral solution (ZMWS3) show no significant difference to ZMW9, the silica coated zein-magnetite composite sample used for these samples. It could be that gold particles are attached to the silica if the samples were indeed functionalized but the difference between magnetite and gold nanoparticles is hard to see on the TEM image, all black dots could also be magnetite particles which are known to be in the sample.

The TEM images of the sample that was functionalized in an alkaline solution (ZMWS4) shows aggregates. This might have happened because the high pH can make the silica soluble again. When the sample centrifuged the particles were pushed against each other and when the supernatant was removed, the particles were tried to be redispersed in water which made the pH drop, causing the particles stay stuck to each other.

Figure 4.6.1 shows the TEM images of ZWS1, which is the sample in where silica coated zein particles were functionalized and then gold nanoparticles were added. Gold nanoparticles can be seen that are stuck to the silica which most likely is now functionalized with thiol groups that bonded to the gold nanoparticles.

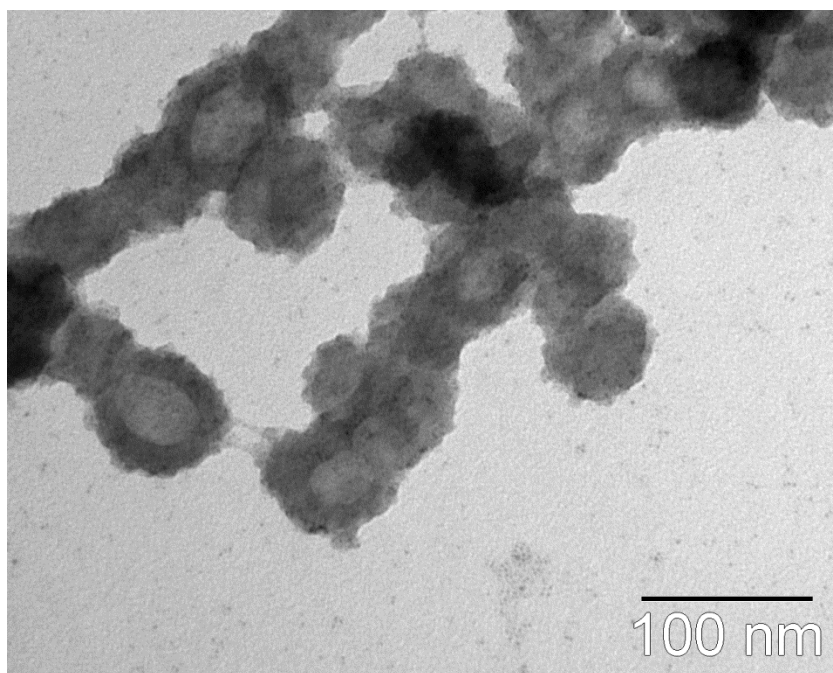


Figure 4.6.1 Functionalized silica-zein particles made visible with gold nanoparticles

5. Conclusion

The first goal, to make both composite particles without high energy inputs was done successfully. With the TPM emulsions this goal was reached within the first few tries after which experiments could be done that showed that the size of the TPM emulsion droplets can be changed by changing conditions like: how diluted the system was, the age of the emulsion and the ratio of TPM:magnetite.

With the zein particles it was first needed to obtain the right amount of magnetite needed to form zein particles without deformations. After using 26 mg magnetite nanoparticles per gram zein measurements showed spherical composite particles with a positive zeta potential. Next to magnetite particles the formation of zein composite particles was also done using silver nanoparticles.

The second goal, which was to coat the composite particles, was also successfully done. Using an adaption of the Stöber method the polymerized emulsion particles were coated with a thin layer of silica. Experiments showed that if enough TMAH is used, some of the silica forms around the polymerized emulsion particles. The remaining silica forms silica particles through secondary nucleation.

The coating of zein composite particles was done by adding a sodium silicate solution. This solution had to be first treated with just enough ion exchange to remove sodium ions. While experiments were first needed to be done in order to obtain the right method, the method obtained was a general method that was able to coat reproducibly the different zein particles with a layer of silica.

By dissolving the zein from the silica coated composite zein particles, hollow silica spheres with nanoparticles inside could be made.

The third goal, which was to functionalize the composite particles after coating them with a silica layer, was also successful. By using MPTMS in an acid solution, the particles were indeed functionalized which was made visible by gold nanoparticles that bonded with the thiol groups.

6. Outlook

While the results are promising, optimization of methods that are in this thesis could make them even better. For example, the alkaline conditions during the Stöber method, the dialysis steps preparing the zein samples, and the whole sodium silicate addition step are left to be optimized.

To prove the fusing of particles, an experiment can be done in which two TPM emulsion with different nanoparticles are mixed. If the two emulsion fuse, the nanoparticles should also travel into the same fused droplet and after a while all droplets should have both nanoparticles.

The functionalizing which has been done on the silica coated zein particles could also be tried on the silica coated polymerized emulsion particles.

While the silica coated zein-based composite particles were successfully made with magnetite and silver nanoparticles it can also be tried to make them for drug delivery by replacing the nanoparticles with drugs/antibiotics. It would be even more interesting to see if the zein particles can then be filled with drugs and also magnetic particles to do specific drug delivery. Since the particles should be non-toxic and relatively simple to make it could have a promising future as a drug delivery system.

It will be interesting to see if these particles can be used in magnetic separation for which they were made for. In theory these particles can be used in almost endless ways depending on the functional group and then be separated with magnetic separation to be reused.

One of the reasons to choose for these particles instead of the commercial micrometer sized particles for binding biomolecules was to increase the specific surface area which increases the amount of functional groups that can bind to these particles.

An example for an application is using the particles with a catalyst. In a paper by Zhang *et al.* [6] iron particles are used to catalyze the Fischer-Tropsch reaction and then they are separated with magnetic separation. The particles made in this thesis have much potential to replace these iron particles. By binding a catalyst to the composite particles that is smaller and can lower the energy barrier further than the iron particles, the reaction could be even more energy efficient.

Another example is in the paper of Zhao *et al.* [7]. Magnetite particles are bonded to phosphate in waste water with the help of a coagulant to make it possible to separate phosphate from waste water. The particles made in this thesis have potential in replacing the coagulant because of increase in surface area and therefore increase in capacity of amount of phosphate that can be removed.

Acknowledgments

The first persons I want to acknowledge are the supervisors, Roel Baars and Albert P. Philipse for their supervision, meaningful discussions and suggestions. I want to thank Roel for the numerous TEM sessions as well. During the TEM sessions which were almost every 2-3 weeks I received enough feedback which helped to keep track on what I was doing.

Also want to thank a lot of people at the FCC group, because I did a lot of experimental work where sometimes Roel could not help but then I received help from other people. Especially Lisette Pompe helped in the beginning with experimental work, like explaining how the adapted Stöber method was done. Also want to thank Mikal for his work on the zein composite particles which helped me find another interesting system after the silica coating of the emulsions did not improve anymore. I also would like to thank him for the gold nanoparticles used and the meaningful discussion.

Finally I also want to thank all the people and especially all the master students that were at FCC during the time I was there for a great time.

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Appendix A

Sample Tables

Magnetite	concentration	date made	average diameter (nm)
Mt1	0.26 w%	28-9-2012	10.15
Mt2	0.36 w%	19-4-2013	12.12
Mt3	0.27 w%	22-7-2013	12.24

silver np's	average Size(nm)	p.d.
Ag1	24,39	32.35%

Emulsion	amount magnetite	amount TPM (mL)	solvent	initiator	emulsification time (days)
TM1	1.2 mL Mt0	0.06	1.74 mL water	0.3 mL 4.4mM KPS	1
TM2	20 mL Mt1	1.00	56 mL water	7.5 mL 4.4mM KPS	1
TM3	60 mL Mt1	3.00	-	6.3 mL 4.4mM KPS	1
TM4	20 mL Mt1	1.00	111 mL water	15 mL 4.4mM KPS	1
TM5	4 mL Mt1	0.20	6 mL water	0.00344g V50	1
TM6	4 mL Mt1	0.20	6 mL water	0.00695g AIBN	1
TM8	4 mL Mt1	0.20	6 mL water	0.00402g V65	1
TM9	40 mL Mt1	1.00	59 mL water	10 mL 4.4mM KPS	1
TM10	4 mL Mt1	0.10	6 mL water	0.4 mL 4.4mM KPS	9
TM11	4 mL Mt1	0.10	6 mL water	0.4 mL 4.4mM KPS	6
TM12	4 mL Mt1	0.10	6 mL water	0.4 mL 4.4mM KPS	1
TM13	4 mL Mt1	0.10	-	0.4 mL 4.4mM KPS	1
TM14	4 mL Mt1	0.10	12 mL water	0.4 mL 4.4mM KPS	1
TM16	4 mL Mt1	0.10	6 mL water	-	1
TM17	2 mL Mt1	0.05	14 mL water	0.25 mL 4.4mM KPS	2
TM18	2 mL Mt1	0.05	48 mL water	0.2 mL 4.4mM KPS	2
TM20	20 mL Mt1	0.50	140 mL water	15 mL 4.4mM KPS	1
TM22	1 mL Mt1	0.05	12.5 mL water	0.2 mL 4.4mM KPS	5
TM23	1 mL Mt1	0.05	12 mL water and 0.5 mL 1% TMAH	0.2 mL 4.4mM KPS	5
TM26	4 mL Mt1	0.01	-	0.25 mL 4.4mM KPS	1
TM27	8 mL Mt1	0.05	12 mL water	0.25 mL 4.4mM KPS	1
TM28	4 mL Mt1	0.05	16 mL water	0.25 mL 4.4mM KPS	1
TM29	2 mL Mt1	0.05	18 mL water	0.25 mL 4.4mM KPS	1
TM30	20 mL Mt2	0.30	100 mL water	4 mL 4.4mM KPS	1
TM35	10 mL Mt3	0.25	40 mL water	5 mL 4.4mM KPS	1
TM36	20 mL Mt3	0.50	80 mL water	10 mL 4.4mM KPS	1
TM37	20 mL Mt3	0.50	60 mL water	-	1

emulsion coated with silica by Stöber method	Sample used	first PVP addition	water (mL)	TMAH	total ethanol used (mL)	TEOS amount in 20 mL ethanol solution (mL)	Amount of time TEOS solution is added	Second PVP (in ethanol)
TMS1	3.3 mL TM1	0.18g in 5 mL water	33	5 mL of 1w%	250	5	45min	10g in 50 mL
TMS2	83.5 mL TM2	0.88g in 25 mL water	66	10 mL of 1w%	400	10	2hours	17g in 100 mL
TMS3	all TMS2	10g in 80 mL ethanol	66	10 mL of 1w%	350	5	45min	20g in 100 mL
TMS4	20 mL TM3	7.7g in 100 mL water	66	10 mL of 0.5w%	400	10	1hour	18g in 100 mL
TMS5	20 mL TM3	7.1g in 100 mL water	66	10 mL of 0.75w%	400	10	1hour	16g in 100 mL
TMS6	20 mL TM3	8.1g in 100 mL water	66	10 mL of 2w%	400	10	45min	18.9g in 100 mL
TMS7	40 mL TM4	4.43 g in 50 mL water	33	5 mL of 1w%	180	5	45min	9.67g in 50 mL
TMS8	40 mL TM4	3,48g in 50 mL water	33	5 mL of 0,5w%	180	5	45min	9.81g in 50 mL
TMS9	40 mL TM4	3.78 g in 51 mL water	33	5 mL of 2w%	180	5	45min	10.67g in 50 mL
TMS10	40 mL TM9	4.5 g in 50 mL water	33	5 mL of 1w%	180	5	40min	10.01g in 50 mL
TMS11	40 mL TM9	3.9g in 50 mL water	33	5 mL of 1w%	180	5	60min	10.50g in 50 mL
TMS12	40 mL TM9	4.5g in 50 mL water	33	5 mL of 1w%	180	5	100min	9.95g in 50 mL
TMS13	40 mL TM20	-	33	5 mL of 1w%	200	2.5	6hours	5.6g in 40 mL
TMS14	half of TMS13	-	33	5 mL of 1w%	200	2.5	6hours	2.6g in 20 mL
TMS15	40 mL TM20	-	33	5 mL of 1w%	200	2,5	3hours	4.9g in 40 mL
TMS16	60 mL TM30	3,5g	33	5 mL of 1w%	200	1	40min	5,7g in 40 mL
TMS17	60 mL TM30	2,5g PVP-10	33	5 mL of 1w%	200	1	40min	5,8g PVP-10 in 40 mL
TMS18	50 mL TM36	3.07g	33	5 mL of 1w%	180	2,5	80min	2,28g in 40 mL
TMS19	50 mL TM36	2.89g PVP-10	33	5 mL of 1w%	180	2,5	80min	2.21g PVP-10 in 40 mL

emulsion with sodium silicate	sample used	water and acid	sodium silicate
TMW1	1 mL TM20	15 mL water	1 mL of 1.3%
TMW2	1 mL TM20	4 mL water	0,4 mL of 1.3%
TMW3	1 mL TM20	4 mL with 0,6-0,8g resin	0,4 mL of 1.3%

TMW4	20 mL TM20	~120 mL water	40 mL of 1.3%
TMW5	60 mL TM30	~50 mL 0.5 M HCl	20 mL of 0.13 %
TMW6	40 mL TM35	10 mL 0.5 M HCl	10 mL of 1,3%
TMW7	30 mL TM35	10 mL 0.5 M HCl	10 mL of 1,3%
TMW8	4 mL TM35	0.45 mL 0.5 M HCl	1 mL of 1.3%
TMW9	10 mL TM37(non-polymerized)	35 mL water and 3 mL 0.5 M HCl	10 mL of 1.3%

zein samples	structure	Zein	magnetite	water(mL)
ZM1	ZMZ	2x 0,05g in 4 mL 80% ethanol	10 mL Mt1	8
ZM2	ZMZ	2x 0,05g in 4 mL 80% ethanol	20 mL Mt1	8
ZM3	ZMZ	2x 0,025g in 2 mL 80% ethanol	20 mL Mt1	8
ZM4	ZMZ	2x 0,025g in 2 mL 80% ethanol	1,3 mL 4 w%	8
ZM5	ZMZ	2x 4 mL of 0.1 g in 8 mL 80% ethanol	1 mL Mt1	8
ZM6	ZMZ	2x 4 mL of 0.1g in 8 mL 80% ethanol	3 mL Mt1	8
ZM7	Z	1x 4 mL of 0,65g in 40 mL 80% ethanol	-	10
ZM8	MZ	1x 4 mL of 0,65g in 40 mL 80% ethanol	1 mL Mt1	10
ZM9	ZM	1x 4 mL of 0,65g in 40 mL 80% ethanol	1 mL Mt1	10
ZM10	ZMZ	2x 4 mL of 0,65g in 40 mL 80% ethanol	1 mL Mt1	10
ZM11	ZM	40 mL of 0,56g in 80% ethanol	12 mL Mt2	80
ZM13	ZM	40 mL of 0,49g in 80% ethanol	8 mL Mt2	80
ZM14	ZM	40 mL of 0,51g in 80% ethanol	12 mL Mt2	80
ZM16	MZ	1x 40 mL of 0,50g in 80% ethanol	12 mL Mt2	80
ZM17	MZ	1x 40 mL of 0,49g in 80% ethanol	12 mL Mt2	80
ZM18	MZ	1x 40 mL of 0,46g in 80% ethanol	12 mL Mt3	80
ZM19	MZ	1x 40 mL of 0.48g in 80% ethanol	12 mL Mt3	80
ZM20	MZ	1x 80 mL of 0.98g in 80% ethanol	20 mL Mt3	160
Z1	Z	1x 20 mL of 0.24g in 80% ethanol	-	40
ZA1	MZ	1x 40 mL of 0.5g in 80% ethanol	10 mL of Ag1	80

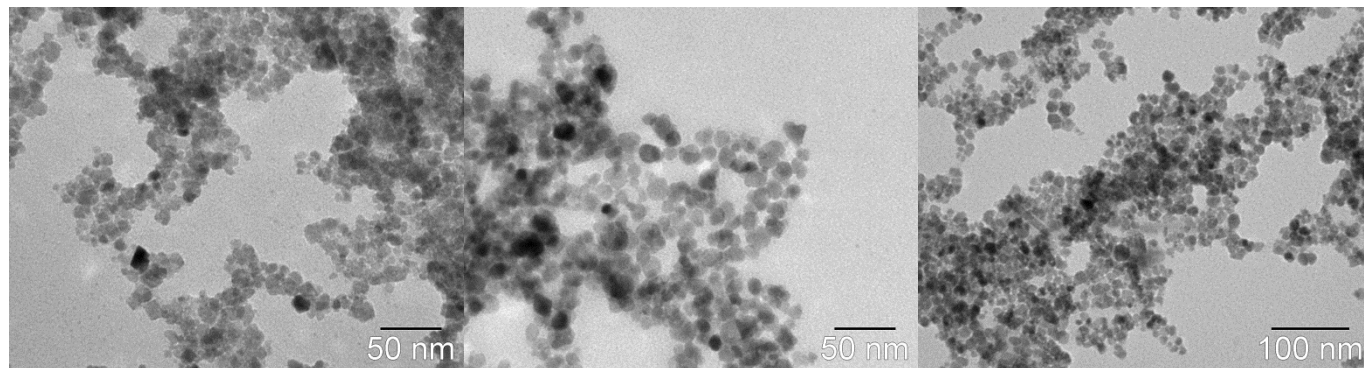
zein with sodium silicate	zein	sodium silicate	water and acid
ZMW1	ZM14	40 mL of 1.3%	Resin, few mL 2M HCl, water
ZMW2	ZM13	40 mL of 1.3%	Resin, few mL 2M HCl, water
ZMW3	ZM17	40 mL of 0.13%	Resin, few mL 2M HCl, water
ZMW4	ZM16	40 mL of 0.13%	little bit resin, 150 mL 0,25mM HCl
ZMW5	15 mL ZM18	10 mL of 1.3%	2.5 mL 0.5 M HCl, 40 mL water.

ZMW6	15 mLZM18	10 mL of 1.3%	3.1 mL 0.5 M HCl, 40 mL water.
ZMW7	15 mLZM19	10 mL of 1.3%	5 mL of 0.5 M HCl 35 mL water
ZMW8	15 mLZM20	10 mL of 1.3%	7,5 mL of 0.5 M HCl, 35 mL water
ZMW9	70 mL ZM20	10 mL of 1.3%	25 mL 0.5 M HCl, 170 mL water
ZW1	15 mL Z1	10 mL of 1.3%	25 mL water and 4.2 mL 0.5 M HCl
ZMW10	20 mL of ZMW9	10 mL of 1.3%	10 mL water and 4.5 mL 0.5 M HCl
ZW2	15 mL Z1	10 mL of 1.3%	10 mL water and 3 mL 0.5 M HCl
ZMW11	15 mL ZM20	10 mL of 1.3%	35 mL water and 2.5 mL 0.5 M HCl
ZAW1	15 mL ZA1	10 mL of 1.3%	35 mL water and 3 mL 0.5 M HCl
ZMW12	15 mL ZM20	10 mL of 1.3%	35 mL water and 2 mL 0.5 M HCl
ZAW2	20 mL ZA1	10 mL of 1.3%	35 mL water and 2 mL 0.5 M HCl
ZAW3	20 mL ZA1	10 mL of 1.3%	35 mL water and 5 mL 0.5 M HCl

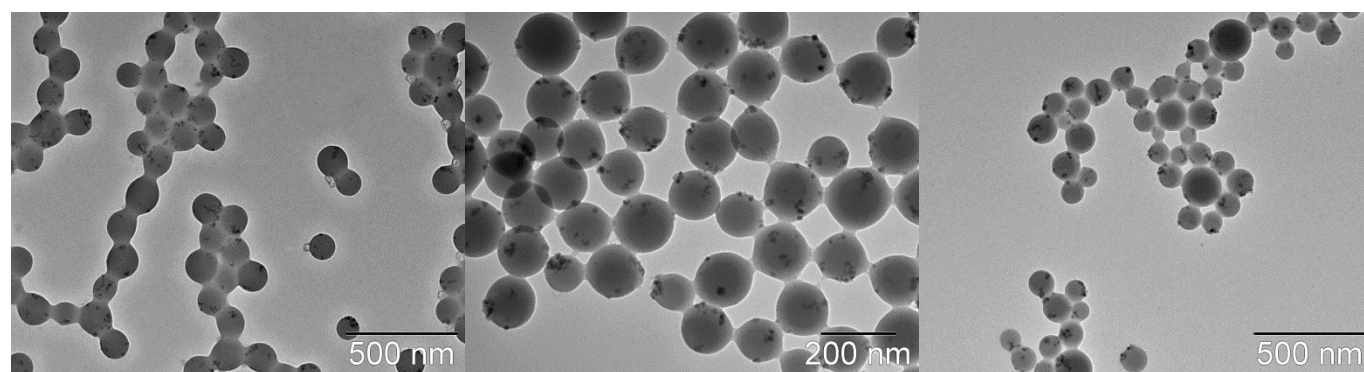
functionalized sample	sample used	MPTMS (mL)	solvent
ZMWS1	ZMW6	0.5	40 mL ethanol 5 mL ammonia
ZMWS2	ZMW9	0.25	18 mL water + HCl pH=4.5
ZMWS3	ZMW9	0.25	18 mL water
ZMWS4	ZMW9	0.25	18 mL water + NaOH pH=8.5
ZMWS5	ZMW9	0.1	18 mL water +HCl pH = 3.8
ZWS1	ZW2	0.5	18 mL water + HCl pH = 3.6

empty zein-silica particles	sample used	how
ZMW6E	ZMW6	Adding 8 mL ethanol to 2 mL sample
ZMW9E	ZMW9	Adding 8 mL ethanol to 2 mL sample
ZMW9PE	ZMW9	Adding PVP, redispersing 3 mL in ethanol
ZMW11E	ZMW11	redispersing half in ethanol
ZMW12E	ZMW12	Adding 20 mL ethanol to 5 mL sample
ZMW12PE	ZMW12	Adding PVP, redispersing in ethanol
ZAW2E	ZAW2	Adding 20 mL ethanol to 5 mL sample
ZAW3E	ZAW3	Adding 20 mL ethanol to 5 mL sample

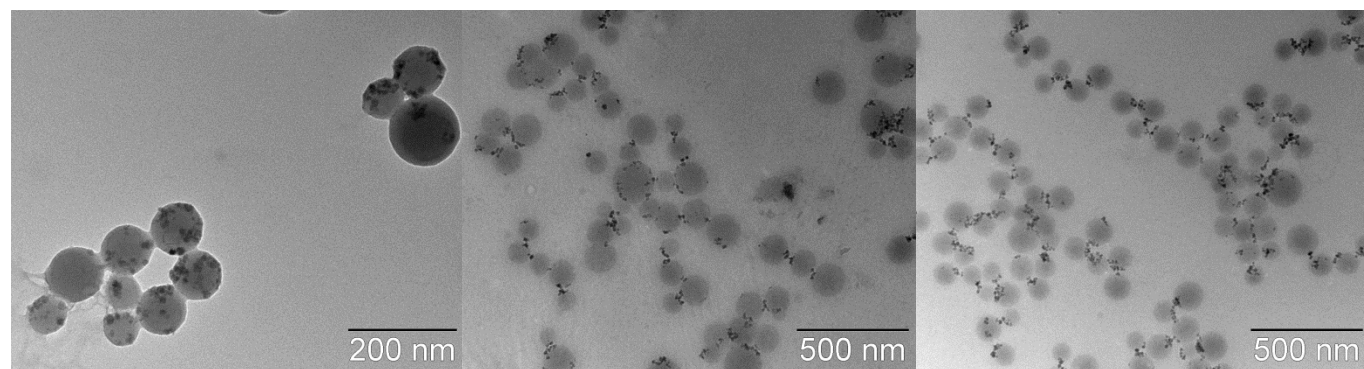
Appendix B: TEM images of all samples



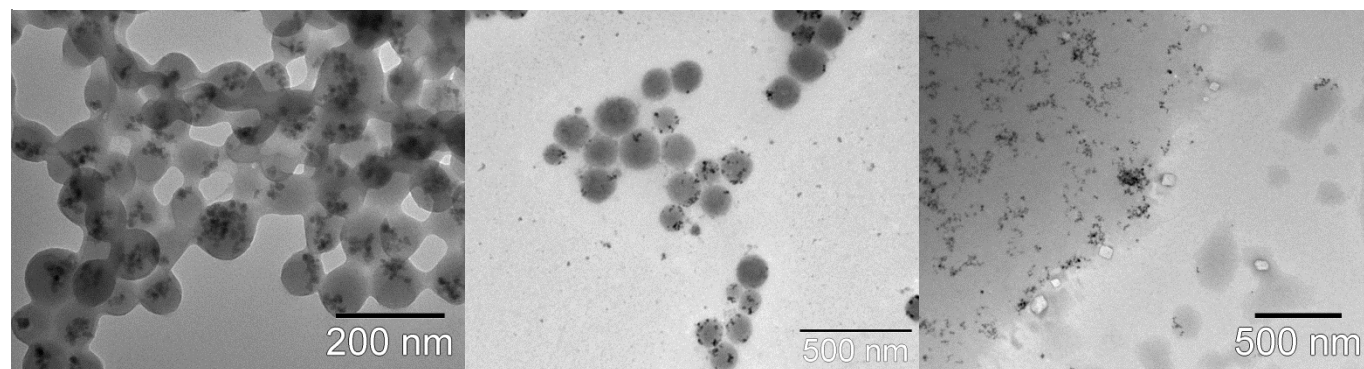
Mt1, Mt2, Mt3



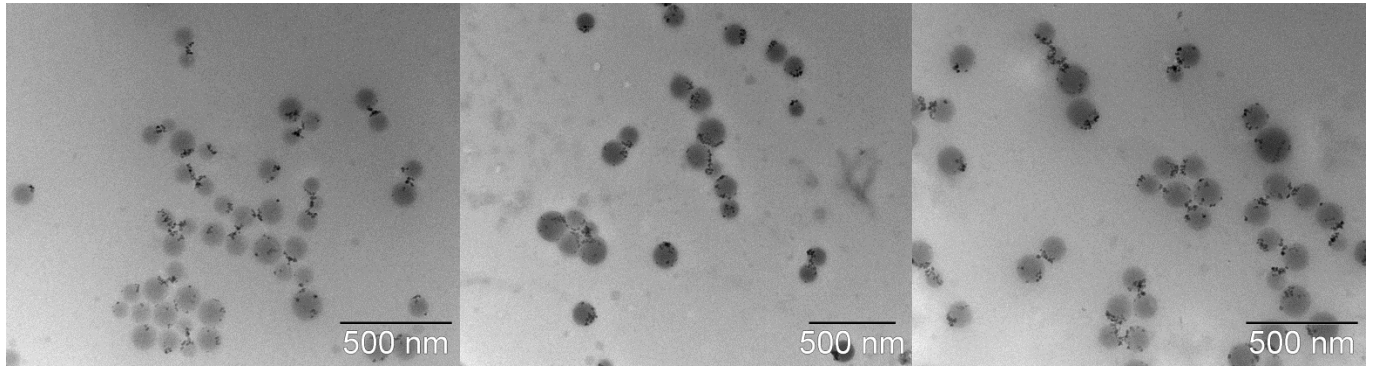
TM4, TM6, TM8



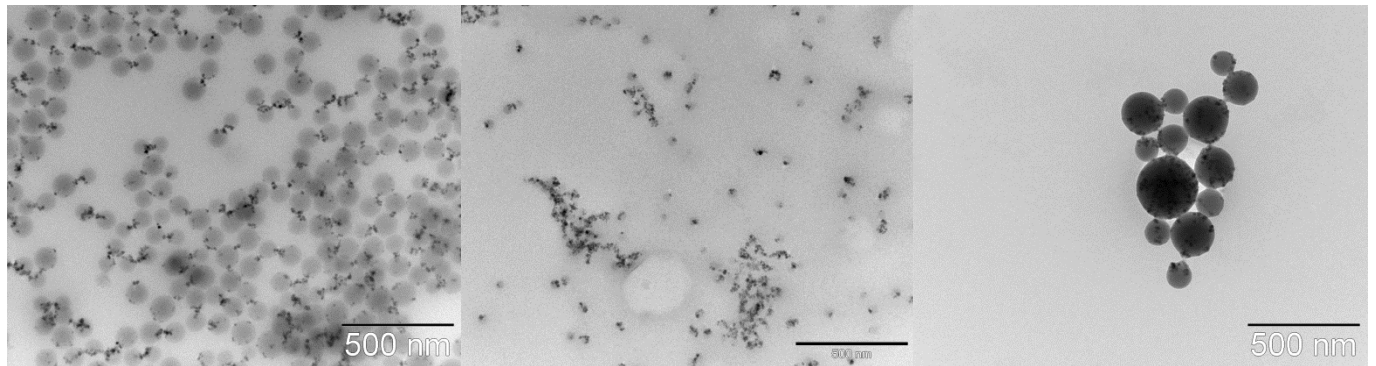
TM9, TM10, TM11



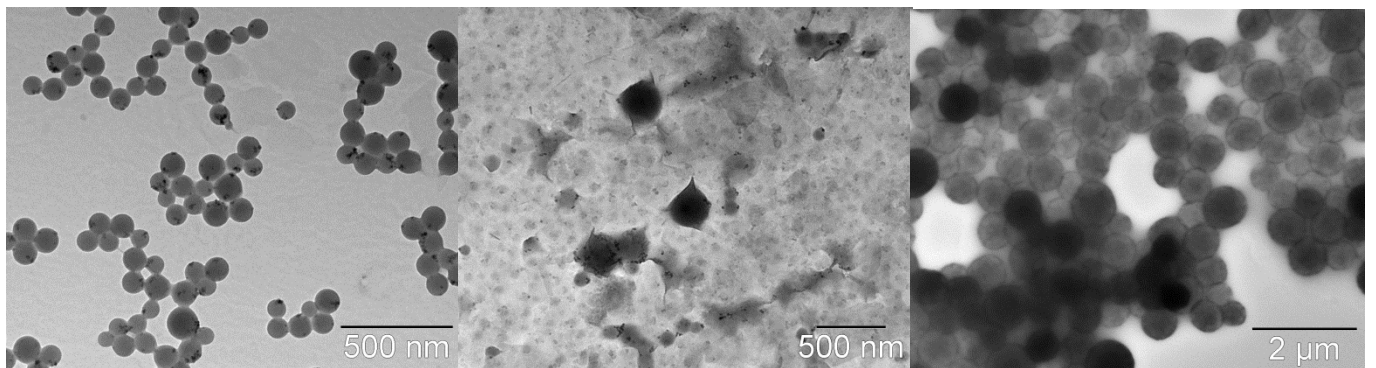
TM1, TM2, TM3



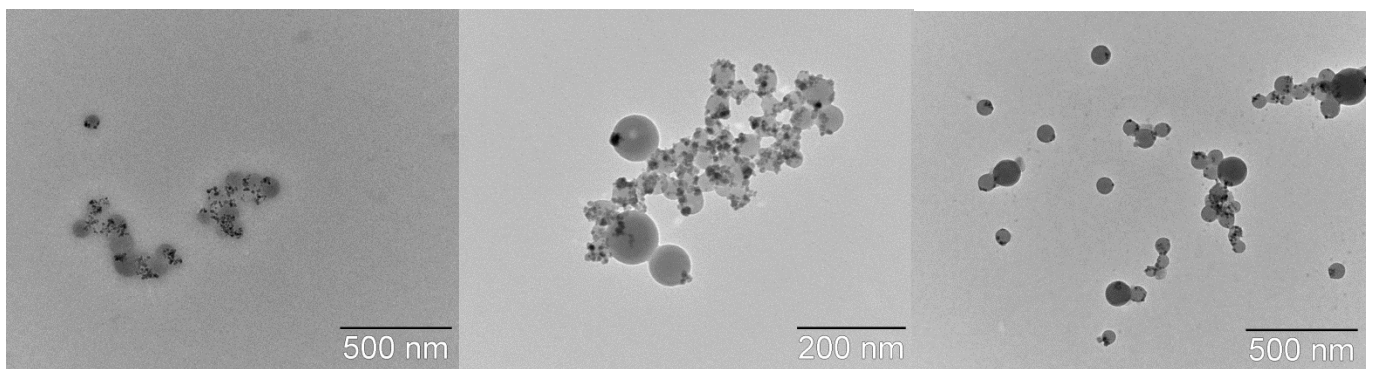
TM12, TM13, TM14



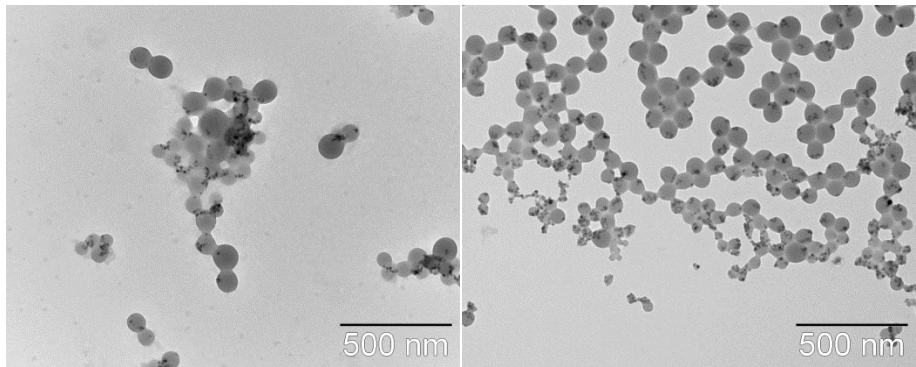
TM17, TM18, TM20



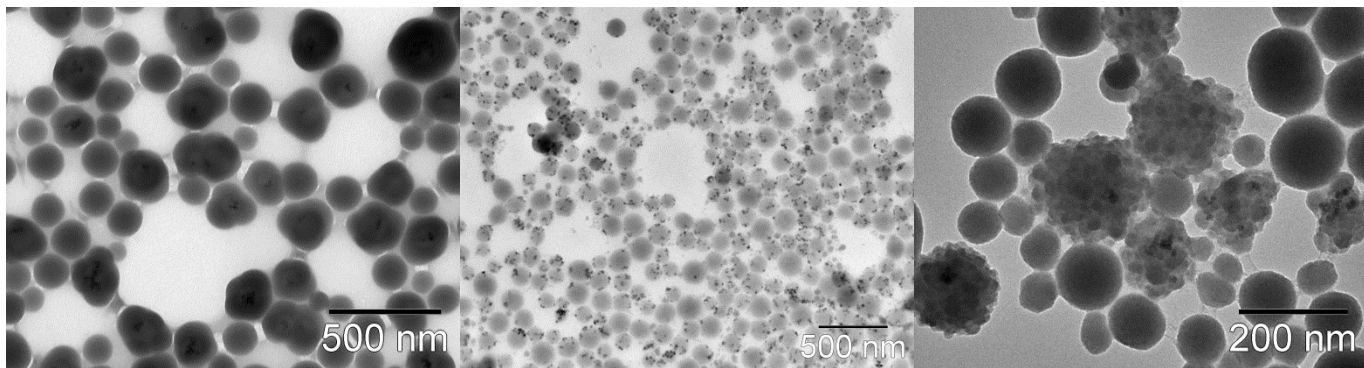
TM22, TM23, TM37 with acid



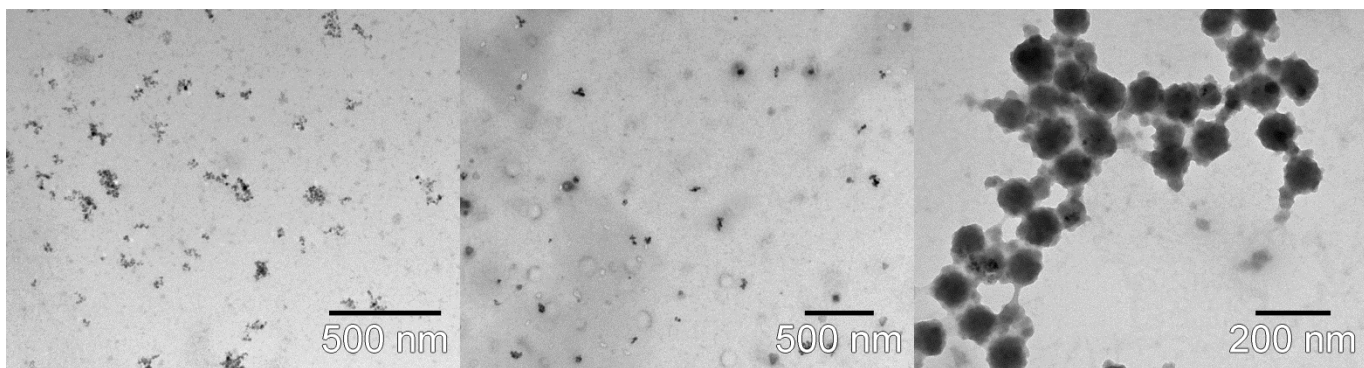
TM26, TM27, TM28



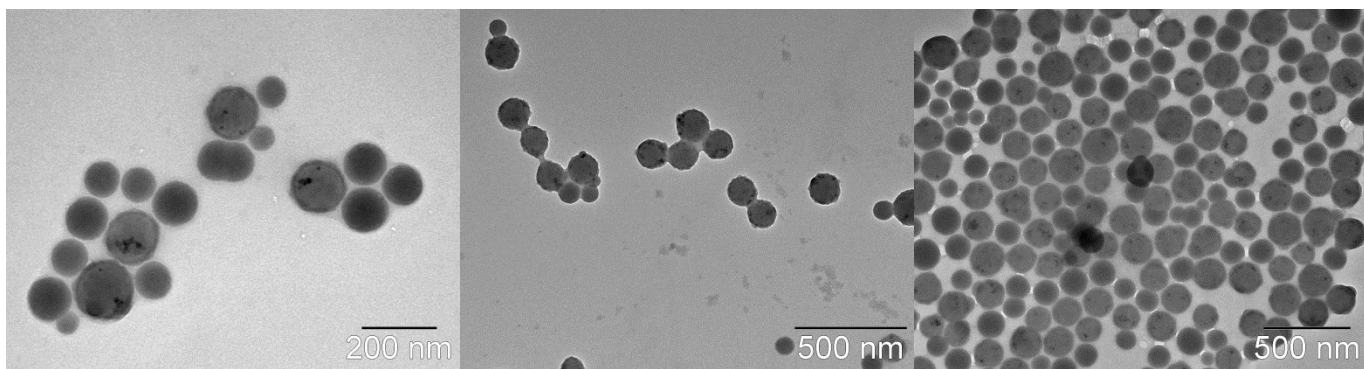
TM29 and TM35



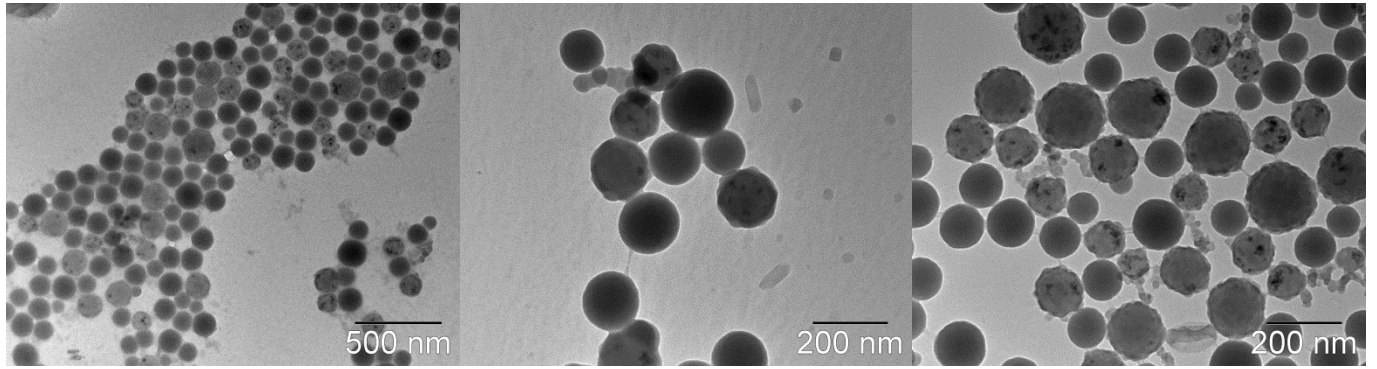
TMS1, TMS2, TMS3



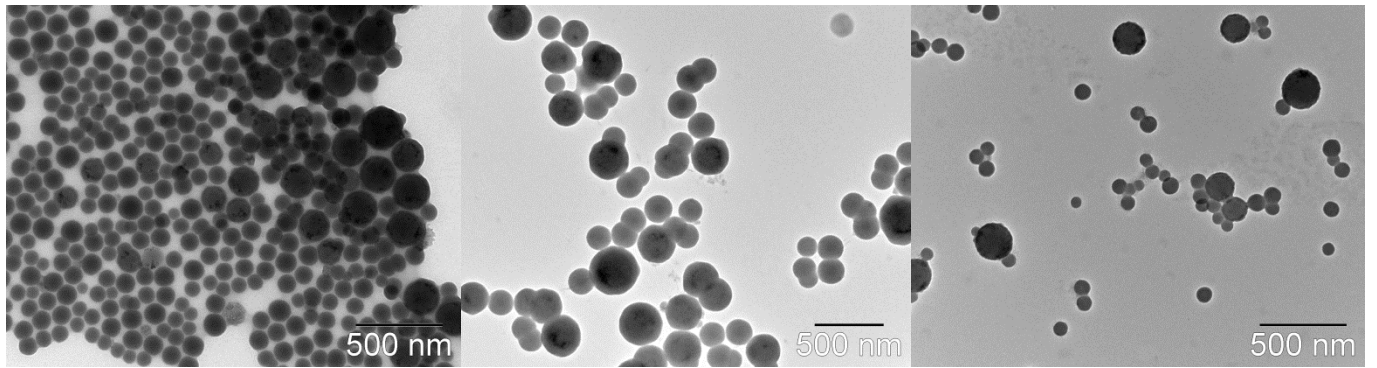
TMS4, TMS5, TMS6



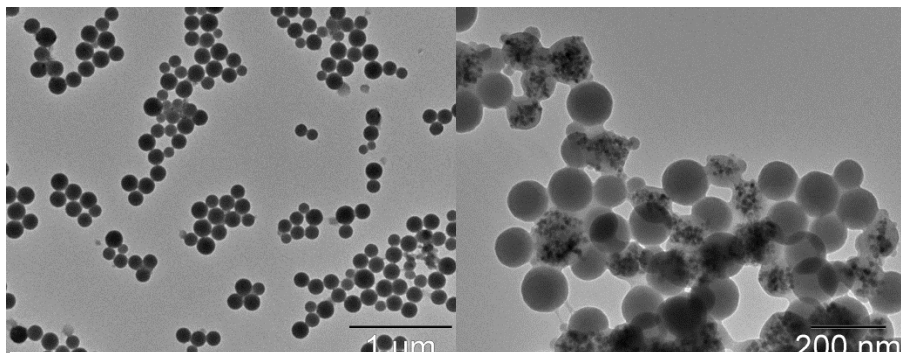
TMS7, TMS8 and TMS9



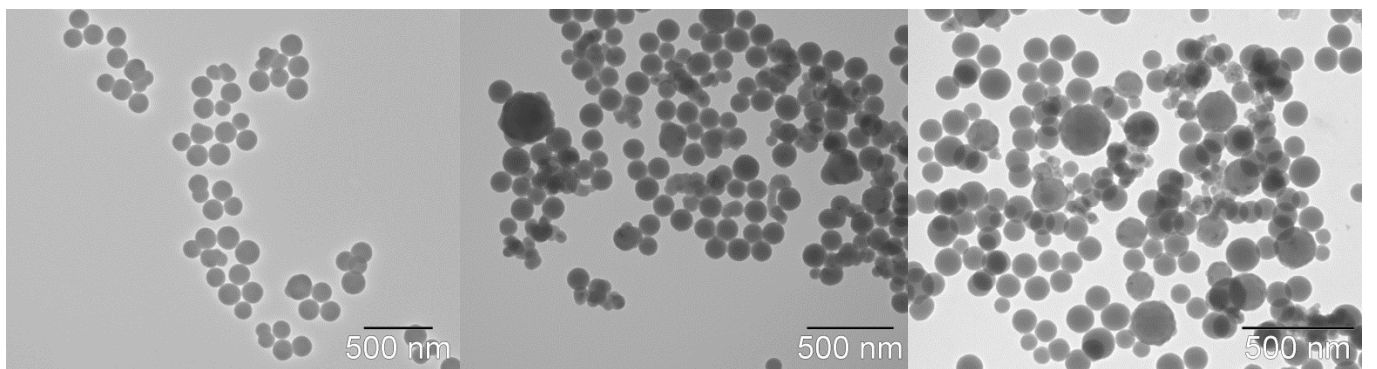
TMS10, TMS11, TMS12



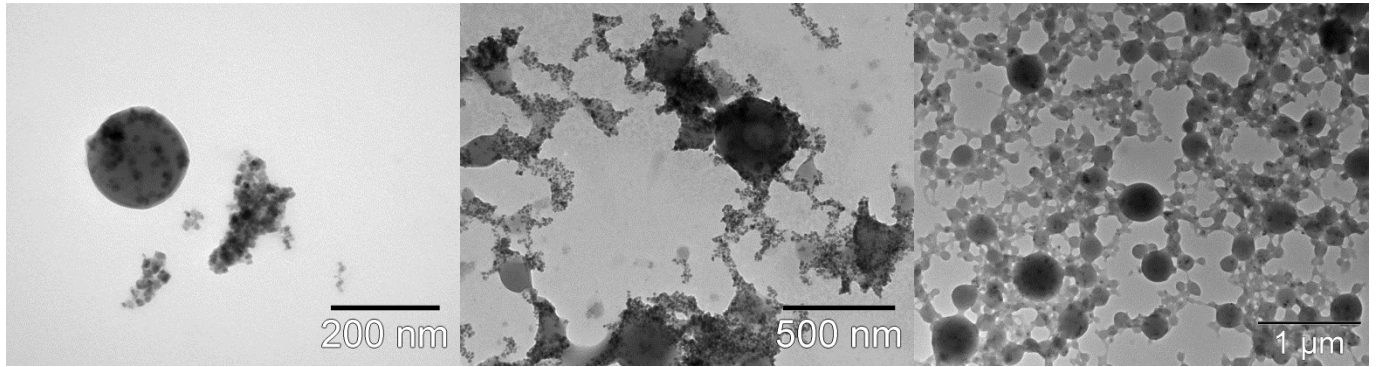
TMS13, TMS14, TMS15



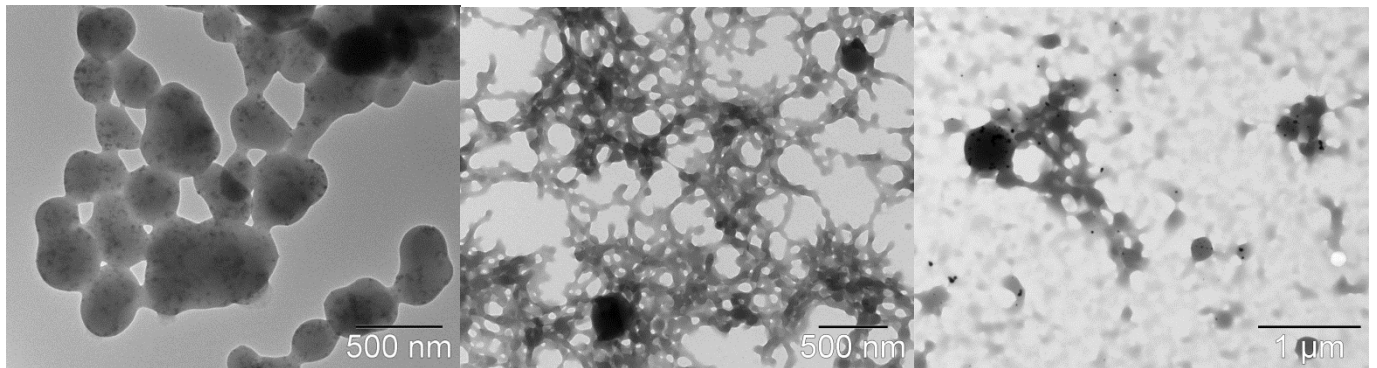
TMS16, TMS17



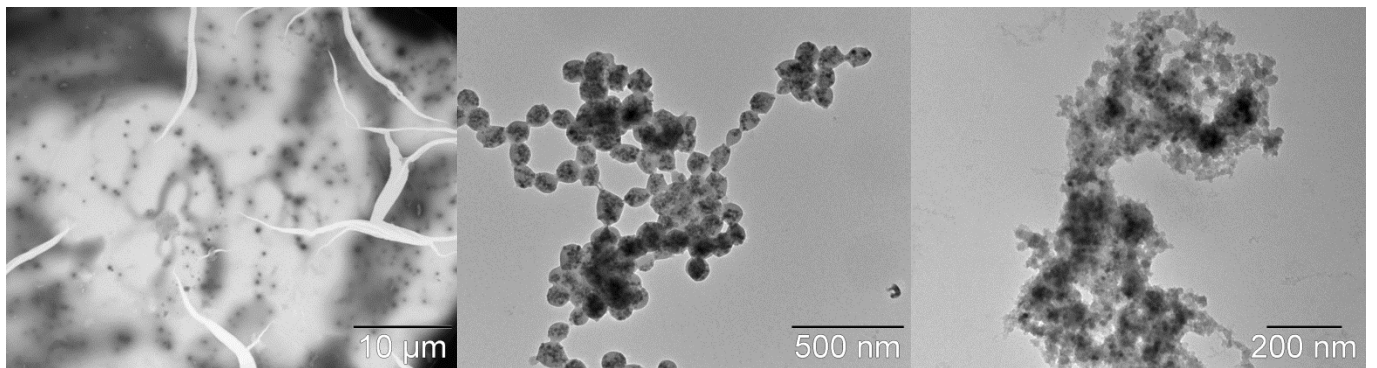
TMS18 without 2nd PVP, TMS18, TMS19



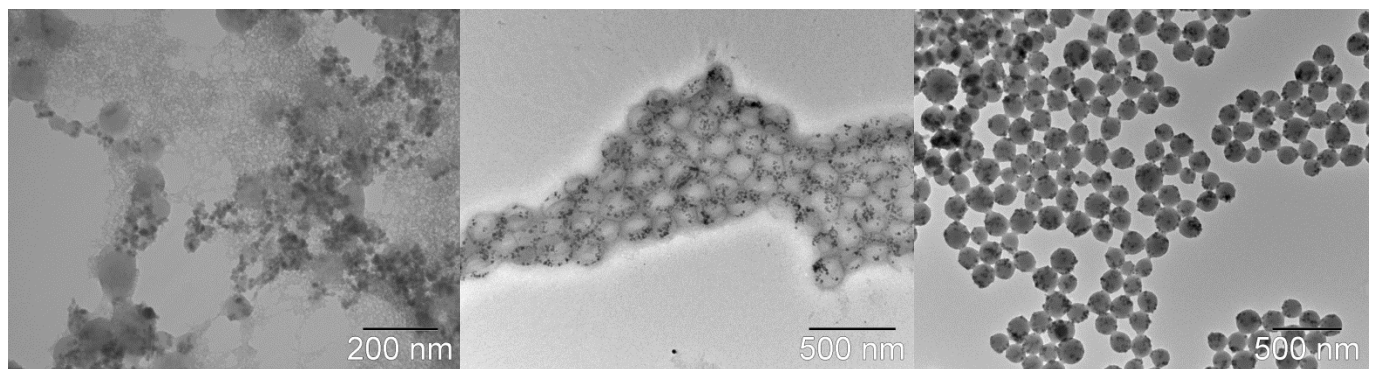
ZM1, ZM2, ZM5



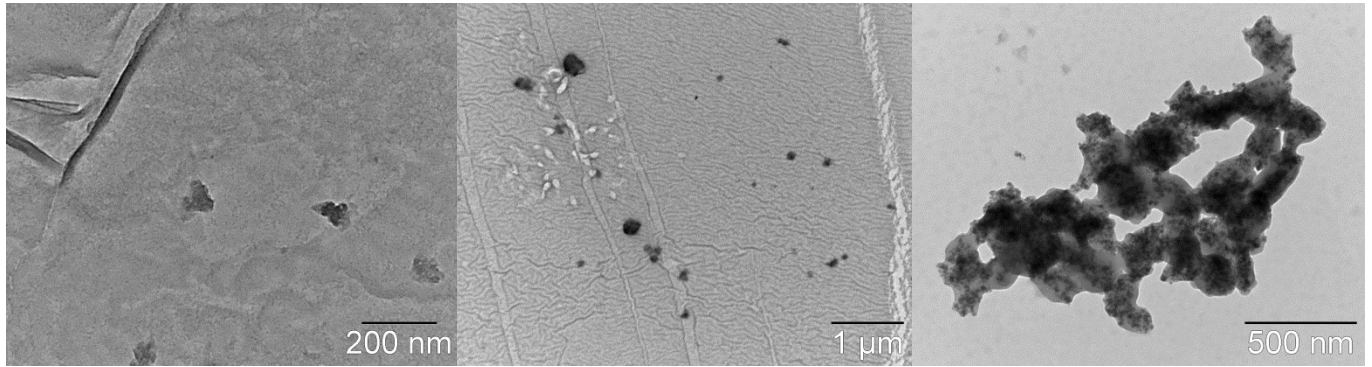
ZM6, Z1, ZA1



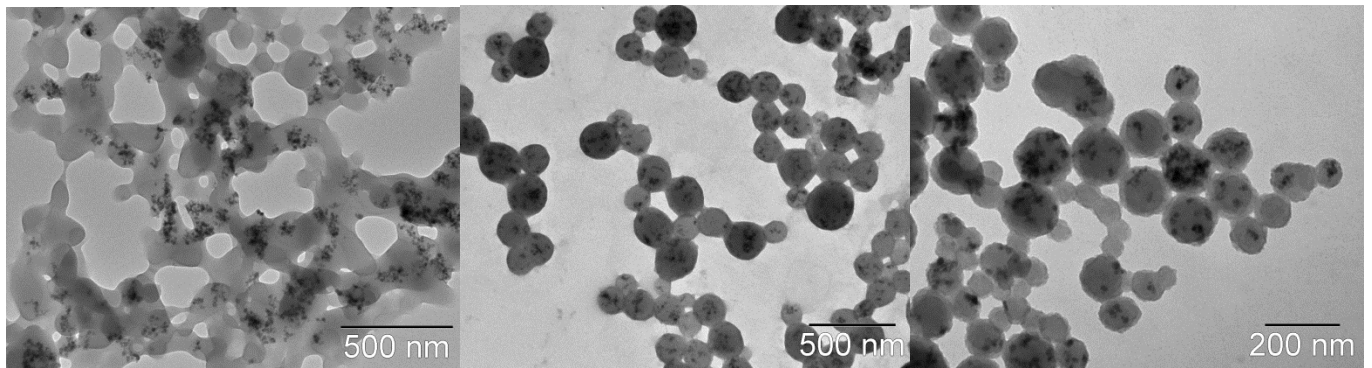
TMW4, TMW5, TMW6



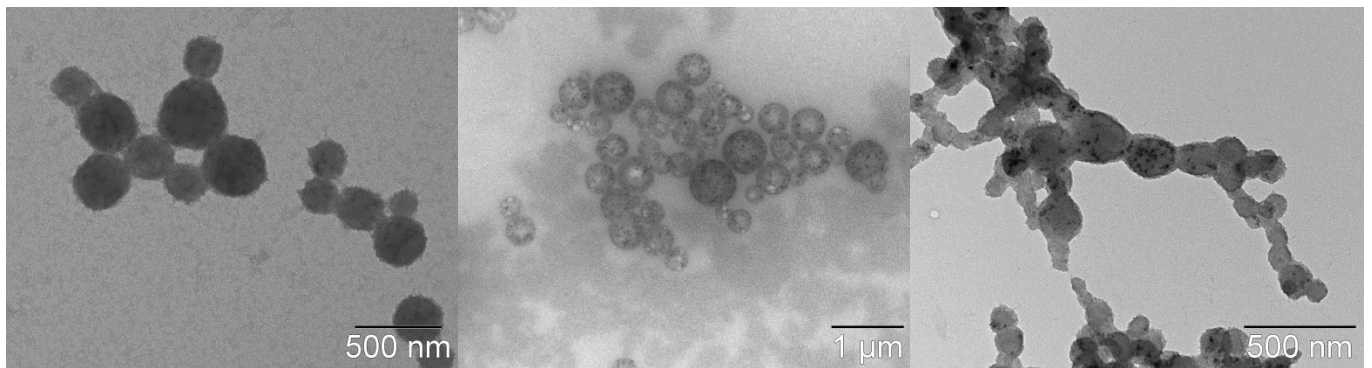
TMW7, TMW9 before polymerization, TMW9 after polymerization



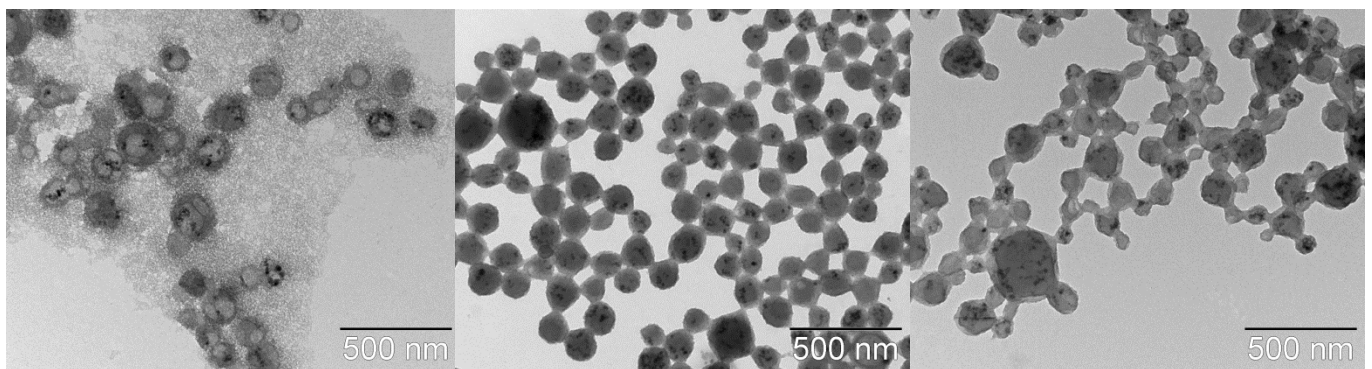
ZMW1, ZMW2, ZMW3



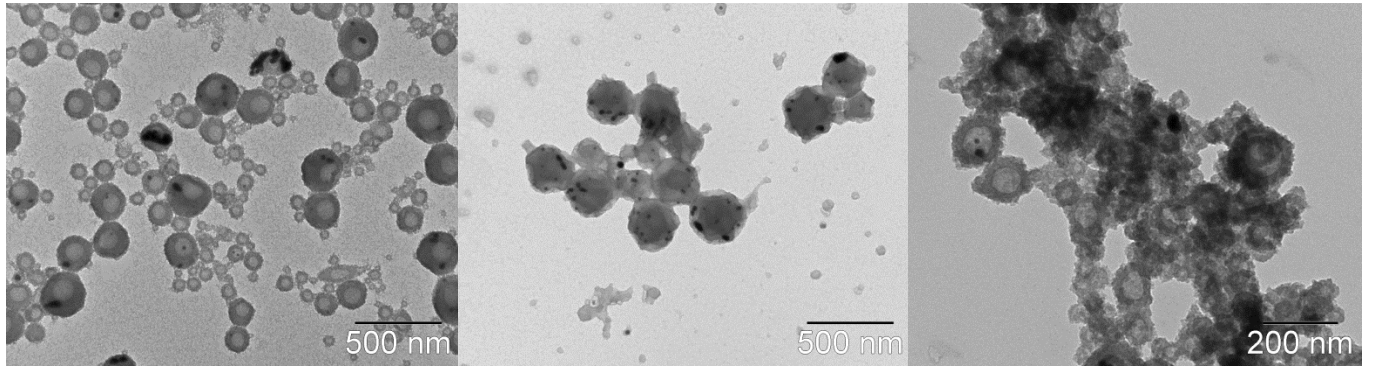
ZMW4, ZMW5, ZMW6



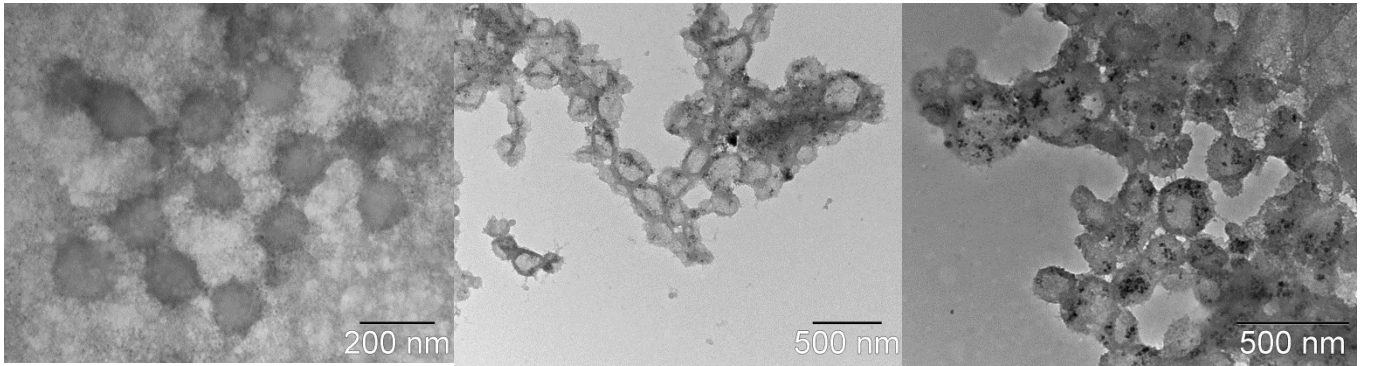
ZMW7 silica-coated zein particles, ZMW7 unknown particles, ZMW9



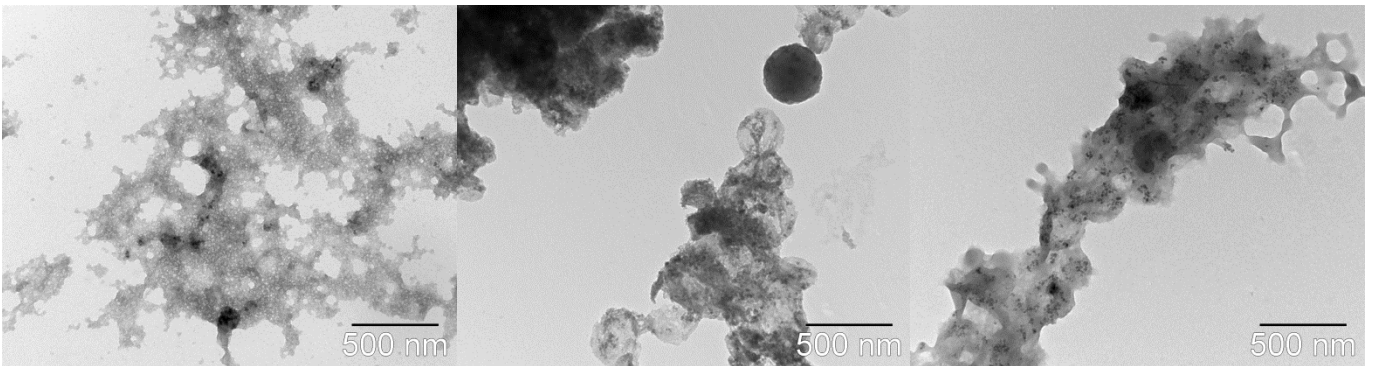
ZMW10, ZMW11, ZMW12



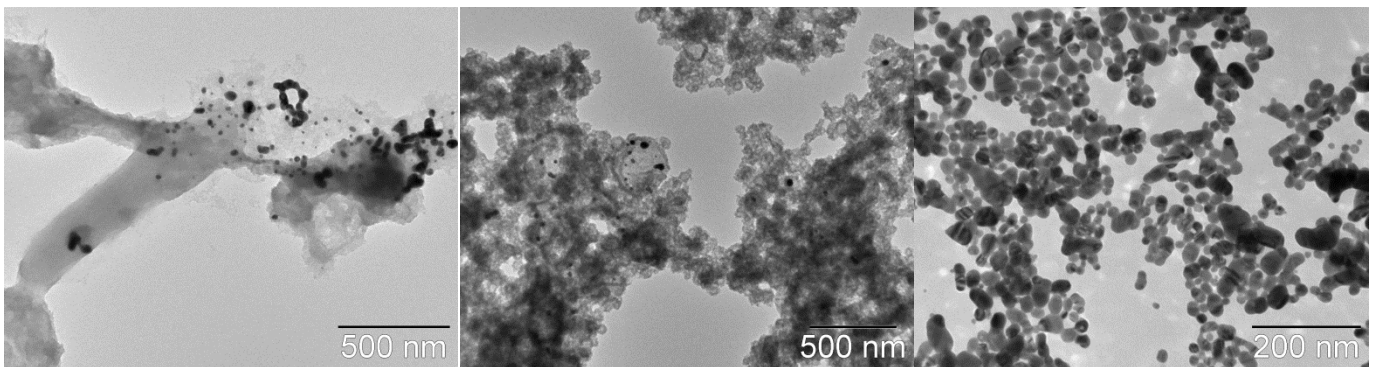
ZAW1, ZAW2, ZAW3



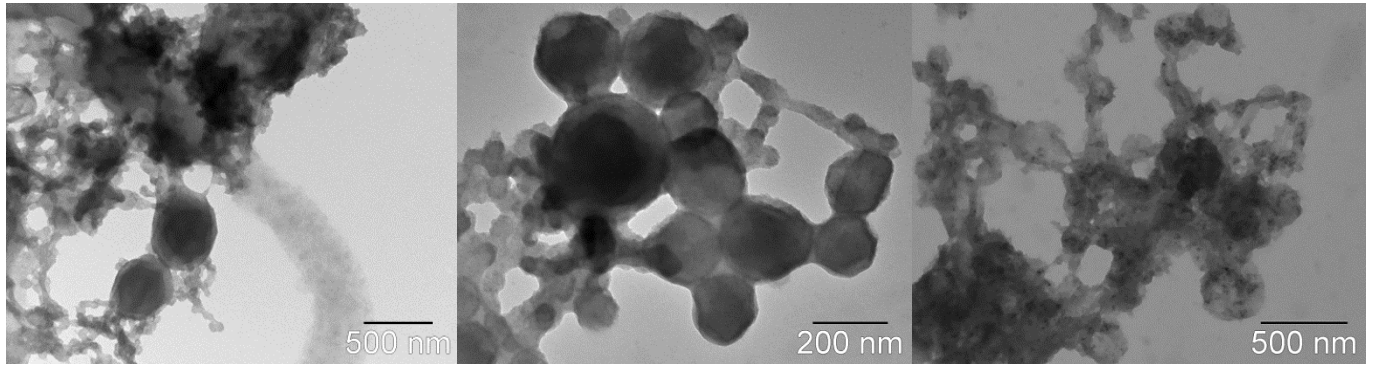
ZMW5E, ZMW9E, ZMW9PE



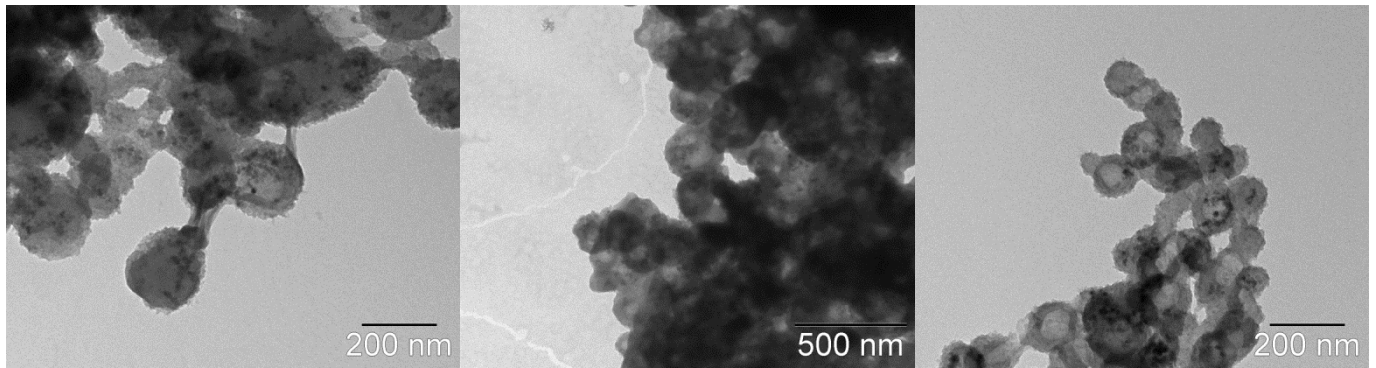
ZMW11E, ZMW12E, ZMW12PE



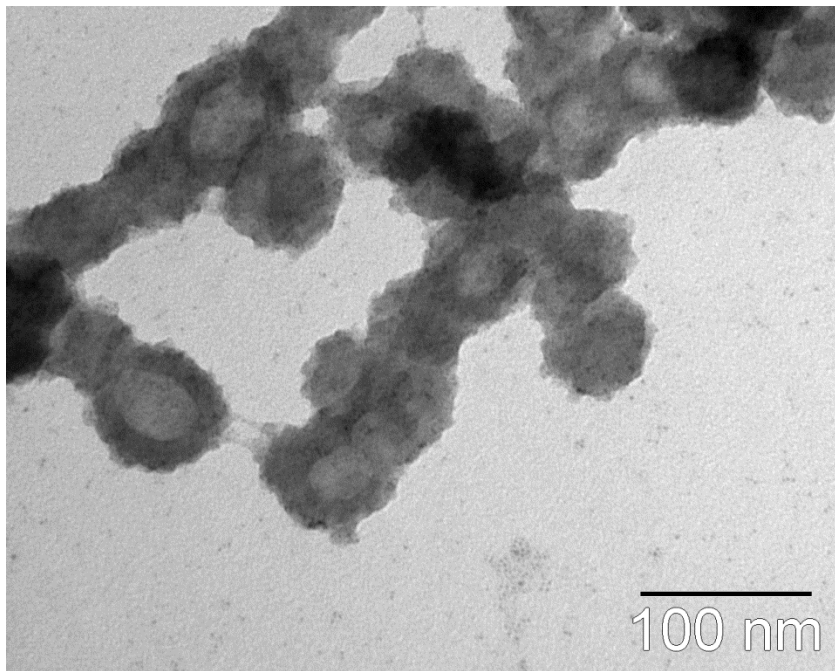
ZAW2E, ZAW3E, Ag1



ZW1, ZW2, ZMWS1



ZMWS2, ZMWS3, ZMWS4



ZWS1