

Morphology-controlled functional colloids by heterocoagulation of zein and nanoparticles



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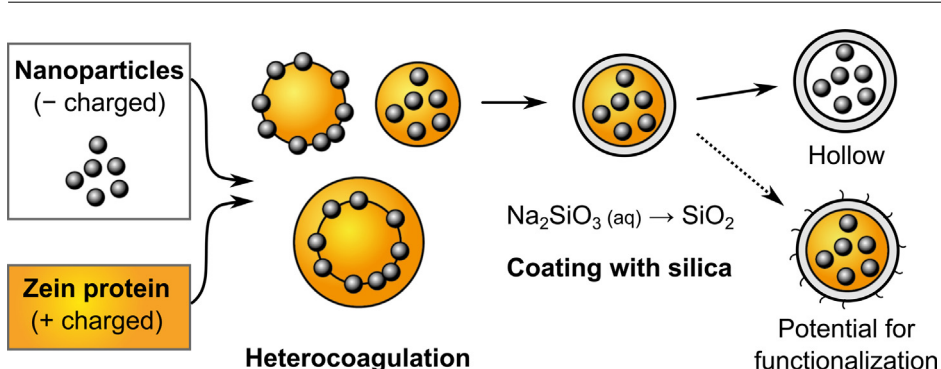
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HIGHLIGHTS

- We present a general synthesis method for composite colloids of varying morphologies.
- Positively charged zein is combined with different negatively charged nanoparticles.
- A layer of silica is deposited on the zein particles to increase applicability.
- Hollow silica shells containing nanoparticles can be formed.

GRAPHICAL ABSTRACT



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ABSTRACT

A general and reproducible heterocoagulation method is presented to prepare sub-micron sized zein protein particles, loaded with negatively charged nanoparticles. These composite carrier particles can be obtained in three different morphologies, and each morphology can be prepared using nanoparticles of various size, shape and composition. An important feature of the zein composites is their long-term stability in water even in conditions where free nanoparticles often aggregate within days. Additionally, we modify the composite particles by coating them with a thin layer of silica via condensation of sodium silicate, opening possibilities for highly specific, functionalized carrier particles. Finally, the formation of hollow silica shells containing negatively charged nanoparticles is demonstrated, using the zein composites as a template.

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1. Introduction

Nanoparticles provide many interesting new properties over their bulk material counterparts, because of their small size and high surface-to-volume ratio. The preparation of composite nanoparticles out of multiple materials can present further, important modifications of the nanoparticle properties, such as decreased reactivity [1], increased stability [2], combined properties within

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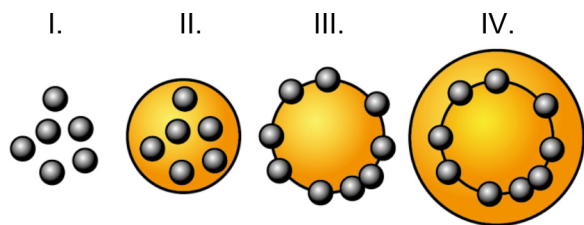


Fig. 1. Schematic representation of the four particle morphologies: (I) bare nanoparticles (NP), (II) zein with embedded nanoparticles (NP-Z), (III) zein with surface coverage of nanoparticles (Z-NP), and (IV) zein with an internal shell of nanoparticles (Z-NP-Z).

one system (such as optic and magnetic) [3] or highly specific and targeted interactions, useful in medical imaging [4] or drug delivery [5]. However, synthesis methods for such particles are usually laborious and require expensive starting materials or equipment. In addition, synthesis methods often lack general applicability, as they are designed for one specific material or morphology [6–8].

To alleviate some of these problems, we report in this paper a general and reproducible method to prepare sub-micron sized, core-shell particles that can contain a broad variety of nanoparticles, using the protein zein as a template material. Our method involves the heterocoagulation of positively charged zein together with, in principle, any negatively charged nanoparticle, into one composite colloid, without the use of any other additives.

Zein is a major storage protein from corn (*Zea mays*). It is used in a variety of foodstuffs, pharmaceuticals and other applications such as binders, adhesives and fabrics [9,10]. Because of its hydrophobic nature and biocompatibility, its use as a potential drug or nutrient delivery mechanism has received increased attention recently [11]. Our method of incorporating nanoparticles expands the number of possible applications of zein-based particles. For instance, incorporation of magnetic or optically active materials may result in particles relevant for medical imaging or (targeted) drug delivery.

The application of zein particles is hindered in several ways, related to its poor colloidal stability in aqueous media [12], with an iso-electric point around pH 6. Patel et al. [12] show that the particle stability could be increased by coating the zein particles with sodium caseinate. We provide an alternative method to increase the stability of zein composite particles by coating them with a thin layer of silica via the condensation of sodium silicate. This layer additionally expands the versatility of zein composites, as it provides a starting point for a variety of surface functionalization through the use of silane coupling agents [13]. In addition, we also show that the protein can be removed after the growth of a silica layer, leaving hollow silica shells containing nanoparticles.

In this work we investigate the incorporation of six different types of nanoparticles into the zein protein matrix: iron (III) pyrophosphate (FePP_i), magnetite (mag), cobalt ferrite (CoFe), gold (Au), silver (Ag) and hematite spindles (hem). Three different composite morphologies are prepared, schematically shown in Fig. 1: zein with embedded nanoparticles (NP-Z), zein with nanoparticles on its surface (Z-NP) and Z-NP particles with an added layer of zein (Z-NP-Z). Silica coating is applied to bare zein particles and composite systems of NP-Z containing magnetite and silver.

2. Methods

2.1. Materials

The following chemicals were obtained from their respective suppliers: zein protein, ammonia solution (28–30% in water), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (98%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (ACS Reagent Grade, 97%), NaBH_4 (reagent grade, $\geq 98.5\%$), $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ (crystalline), HAuCl_4

(puriss. p.a.) and sodium silicate solution (reagent grade) from Sigma–Aldrich Chemie B.V., ethanol (100%) from Interchema, tetramethyl ammonium hydroxide solution (TMAH, 25% in water), NaH_2PO_4 (purum p.a., $\geq 99.0\%$ (T)), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (purum, ≥ 98.0 (KT)) and Dowex 50Wx8-200 ion exchange resin from Fluka Analytical (Sigma–Aldrich Chemie B.V.), $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (ACS reagent grade), trisodium citrate dehydrate (crystalline), NaOH (pellets, pure), HCl (fuming, 37%) and HNO_3 (GR p.a., 65%) from Merck, urea (ACS, 99%) and AgNO_3 (ACS, 99.9%) from Brunschwig Chemie B.V and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99+%, p.a.) from Acros Organics.

Chemicals were used as received. In all experiments, deionized water was used from a Millipore Synergy purification system.

2.2. Nanoparticle preparation

2.2.1. Iron pyrophosphate (FePP_i)

Iron pyrophosphate nanoparticles were prepared by coprecipitation following the method described by Rossi et al. [15]. In a typical preparation, 50 mL of an aqueous solution of 0.86 mol FeCl_3 is added drop-wise to 100 mL of an aqueous solution of $\text{Na}_4\text{P}_2\text{O}_7$, over a period of 15 min. A turbid white suspension forms in the final minutes of the addition (at pH 4). Nanoparticles were prepared shortly before further processing with zein, as colloidal iron pyrophosphate aggregates over time in water [16].

2.2.2. Magnetite (Mag)

Superparamagnetic magnetite (Fe_3O_4) nanoparticles stabilized by tetramethylammonium hydroxide (TMAH) were prepared by the Massart coprecipitation method [17]. A typical preparation involves mixing 0.02 mol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ dissolved in 10 mL 2 M hydrochloric acid with 0.04 mol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in 40 mL water. After brief ultrasonication, the mixture is added to 500 mL 0.7 M ammonia while stirring vigorously, where a black precipitate forms immediately. The mixture is stirred for another 10 min, after which the magnetite is collected by a hand magnet and the supernatant is discarded. The particles are redispersed in 50 mL 1 M TMAH solution and stirred overnight. To remove excess TMAH, the particles are collected again and redispersed in water, yielding a typical stock solution of 2.7 g/L.

2.2.3. Cobalt ferrite (CoFe)

Nanoparticles of cobalt ferrite (CoFe_2O_4) were prepared following the coprecipitation method described by Claesson [18], following earlier work by Tourinho [19]. In a typical preparation 0.01 mol CoCl_2 is dissolved in 5 mL 2.4 M hydrochloric acid and 0.02 mol FeCl_3 is dissolved in 40 mL water. The solutions are heated to 50 °C, mixed and then immediately added to 200 mL of boiling 1 M NaOH solution while stirring vigorously. After 30 min of stirring at 100 °C, the black mixture is cooled to room temperature. The particles are washed four times with 100 mL water and then redispersed in 30 mL 2 M HNO_3 . To this dispersion 30 mL 0.35 M $\text{Fe}(\text{NO}_3)_3$ is added and it is heated to 100 °C, at which it remains for 45 min. After cooling to room temperature, the particles are sedimented on a magnet, redispersed in 50 mL 1 M TMAH and stirred overnight. To remove excess TMAH, the particles are collected again and redispersed in 50 mL water.

2.2.4. Hematite (Hem)

Spindles of hematite ($\alpha\text{-Fe}_2\text{O}_3$) were prepared by the method described by Ocaña [20,21]. The preparation consists of dissolving 0.1 mol $\text{Fe}(\text{ClO}_4)_3$, 0.1 mol urea and 0.004 mol NaH_2PO_4 in 200 mL and ageing the mixture for 24 h at 100 °C. The mixture is purified by centrifugation and the particles are redispersed first in water, then in 1 M TMAH and finally in again in water.

2.2.5. Gold (Au)

Citrate coated gold nanoparticles were synthesized as described by Pérez-Juste [22]. Typically, 0.3 mL freshly prepared, ice cold 0.01 M NaBH₄ solution is added to 20 mL of an aqueous mixture of 1.25×10^{-4} M HAuCl₄ and 2.5×10^{-4} M trisodium citrate, while stirring vigorously. The reaction is completed by storing the dispersion at 40 °C for 15 min.

2.2.6. Silver (Ag)

Silver nanoparticles were prepared through an aqueous reduction process with citrate at reflux temperature [23]. In a typical synthesis, 52 mL 0.769 M AgNO₃ solution in water is heated to reflux temperature, after which 4 mL 1.0 weight percent trisodium citrate solution is added. The reaction is completed by refluxing for 1 h, during which a grey/yellow dispersion is formed.

2.3. Preparation of zein-based composites

Zein particles were prepared by an anti-solvent method, making use of the insolubility of zein in water [12,24]. A stock solution of zein is typically made by dissolving 1.0 g zein in 40 mL 80%. The solution is then poured slowly into 120 mL of pure water while stirring, resulting in a yellow turbid dispersion of colloidal zein particles. The size of the particles can be controlled by the concentration of ethanol [25]. Composite zein particles incorporating negatively charged nanoparticles were prepared with different morphologies.

For the general formation of NP-Z particles (Fig. 1b), the nanoparticle dispersions were diluted to a final volume of 120 mL, containing the following weight percentages of nanoparticles: magnetite and cobalt ferrite 0.3 wt% (at pH 8 and pH 7 respectively), hematite 0.03 wt% (at pH 7). To these dispersions, 40 mL zein solution (1.0 g zein in 80% ethanol) was added, while stirring. The dispersions were stirred for another 5 min after complete addition.

Z-NP composites (Fig. 1c) were prepared by pouring 40 mL zein solution (0.5 g zein in 80% ethanol) into 80 mL water while stirring. After complete addition, 40 mL of nanoparticle dispersion was added to the dispersion, resulting in the same final weight percentage of nanoparticles as in the NP-Z system. To prepare Z-NP-Z composites (Fig. 1d), another 40 mL zein solution is added immediately after the preparation of Z-NP particles. The dispersion is then stirred for another 10 min.

The formation of iron pyrophosphate composites requires special care due to the instability of colloidal iron pyrophosphate [16,24]. For FePP_i-Z composites 40 mL zein solution (1.0 g in 80% ethanol) is poured slowly into a volume of 130 mL FePP_i dispersion (as prepared above). The dispersion turns more turbid and slightly yellow. Some formed aggregates are removed by filtration before further analysis. Z-FePP_i composites are prepared by slowly pouring 40 mL zein solution (0.5 g in 80% ethanol) into 120 mL water. To the resulting turbid yellow dispersion, 0.21 mmol Na₄P₂O₇ in 5 mL water is added, immediately followed by 0.29 mmol FeCl₃ in 5 mL water. The dispersion slowly turns more turbid. Finally, Z-FePP_i-Z composites are prepared as was done for other nanoparticles.

Composite particles with silver and gold were prepared using the same methods as for other nanoparticles, but in 10 times smaller volumes and with concentrations of 0.003 wt% (at pH 5) and 0.008 wt% (at pH 5) gold and silver respectively. Due to the large size of the nanoparticles in comparison with the zein particles, silver and hematite composites were only prepared as NP and NP-Z morphologies. All resulting dispersions have a pH of 4, regardless of the pH of the initial nanoparticle dispersion.

The composites filled with magnetic material were purified by sedimenting the dispersions next to a magnet, decanting the supernatant and redispersing the dark brown sediment in water.

2.4. Modification of zein particles with silica

Silica-zein core-shell colloids were prepared from bare zein particles and NP-Z particles, containing magnetite and silver nanoparticles. A silica layer is grown through condensation of sodium silicate, based on the method described by Philipse et al. [26], following earlier work by Iler [27]. First, the ethanol present in the zein samples was removed by rotary evaporation under reduced pressure until approximately half of the original volume was left, as ethanol may induce gelation of the sodium silicate solution. Shortly before use, a stock solution of aqueous sodium silicate is diluted with water to 1.28% Si content. The diluted silicate solution is passed through a column with acidic ion exchange resin (Dowex 50 Wx8) to reduce the sodium content and to lower the pH to a value of 11 [26]. An aliquot of 10 mL of NP-Z dispersion, prepared as above, is diluted to 50 mL with water and 10 mL of treated sodium silicate solution is quickly added while stirring. The pH of the dispersion is lowered by addition of 0.1 M hydrochloric acid, until a value of pH 8. The mixture is stirred for 1 h and afterwards the excess sodium silicate is removed by dialysis against water over a period of 2 days, refreshing the water daily. Afterwards, particles are collected by magnetic sedimentation or centrifugation, the supernatant is discarded and the particles are redispersed in water.

2.4.1. Hollow silica shells

Hollow shells can be formed by transferring silica coated particles into 80% ethanol. After stirring for 1 h, the dissolved zein is washed away by centrifugation at 1500 rpm for 3 h. Afterwards the hollow silica colloids are redispersed in water.

2.5. Characterization

Transmission electron microscopy (TEM) images were obtained using a Philips Tecnai 10 or Tecnai 12, operating typically at 100 kV or 120 kV, respectively. Samples were diluted and dried in air on copper grids coated with formvar. Dynamic light scattering (DLS) and electrophoretic mobility measurements for the determination of the zeta potential (ZP) were performed with a Malvern Instruments Zetasizer Nano in backscatter mode at 25 °C with 5 min of equilibration time. Samples were filtered and diluted appropriately before analysis. The DLS measurements were performed in ten runs of 15 measurements per run, electrophoretic measurements used 10 runs of 50 measurements.

3. Results and discussion

We successfully prepared each of the composite morphologies as depicted in Fig. 1 with each type of nanoparticle, as can be seen in the TEM images of Fig. 2. Silver and hematite composites were only prepared as NP and NP-Z systems due to the large size of the nanoparticles. No nanoparticles were found outside the zein, except when gold nanoparticles were used (Z-Au and Z-Au-Z), as can be seen from electron microscopy images and from the pink colour of the supernatant after centrifugation of Z-Au (Fig. 3). The morphology of the particles in Fig. 2 sometimes seems distorted (c.f. Fig. 2g), which may be attributed to drying effects.

Unfilled zein particles were found in nearly all samples (not shown), but their occurrence was somewhat less in the Z-NP-Z systems. Furthermore, some differences were found between NP-Z and Z-NP morphologies regarding the filling of the zein: for unknown reasons the NP-Z systems usually seemed more concentrated (compare for example Fig. 2j and k).

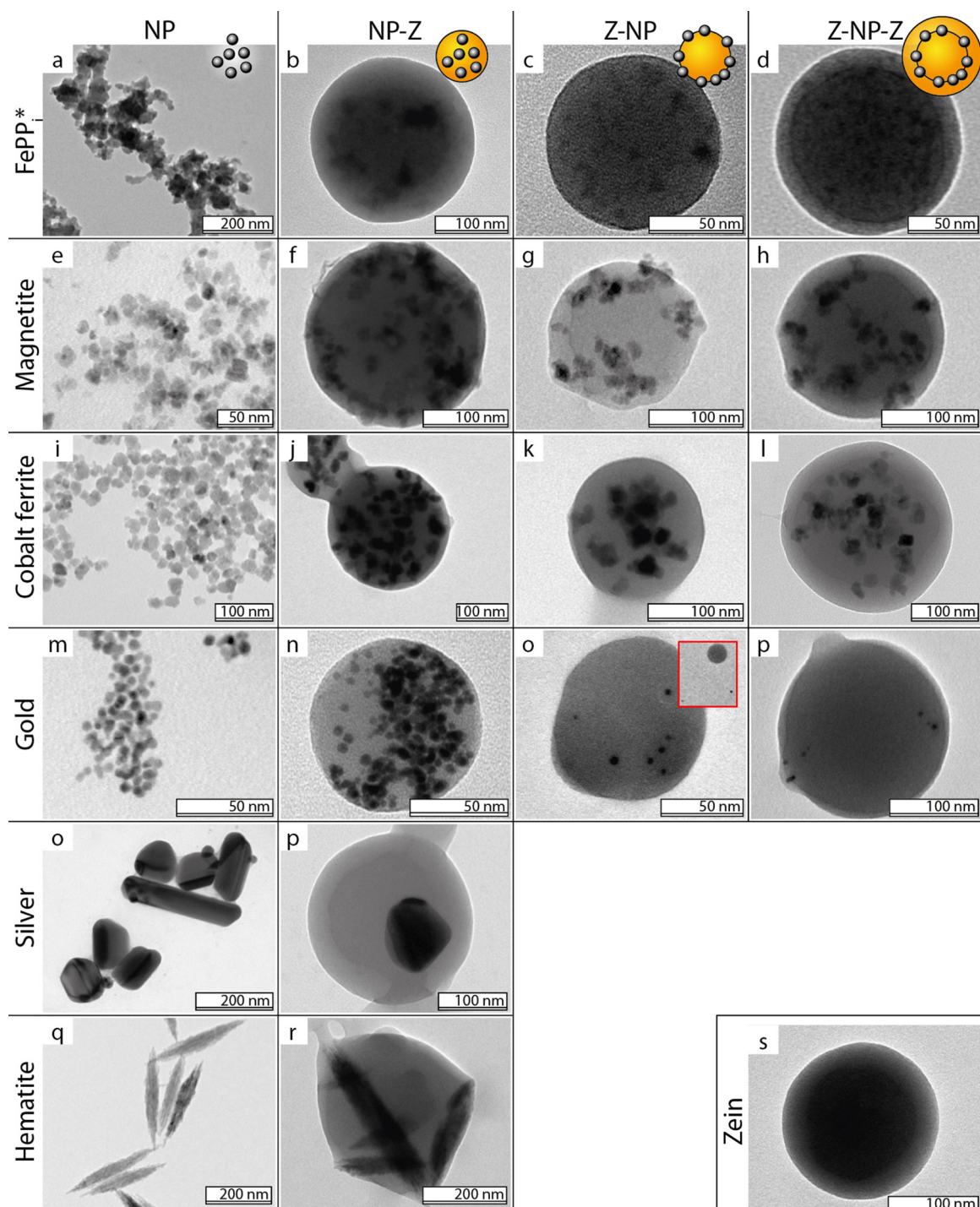


Fig. 2. An image matrix of transmission electron micrographs of all prepared morphologies and compositions. Columns represent the different morphologies, from left to right: bare nanoparticles, NP-Z, Z-NP and Z-NP-Z. The different nanoparticle systems are represented in the rows, from top to bottom: iron pyrophosphate, magnetite, cobalt ferrite, gold, silver and hematite. A bare zein particle is shown in the bottom right corner, where the dark inner ring is due to the contact with the polymer film of the sample grid.

Unfilled zein material was easily removed from the magnetically loaded zein particles by magnetic sedimentation and redispersal in water. The hematite composites proved insufficiently magnetic to be collected in this fashion. Separation by slow centrifugation was necessary for these particles and the non-magnetic particles; fast centrifugation usually led to the formation of aggregates that were no longer redispersable.

Zeta-potential analysis by electrophoretic mobility measurements show that for all composites, the nanoparticles were

negatively charged and the composites were positively charged (see Table 1). As expected, the NP-Z and Z-NP-Z morphologies with an outer surface of zein show the highest zeta potential. DLS analysis showed average diameters comparable with values found for TEM, always with a broad size distribution. The Z-NP-Z systems always have a larger diameter because of the added layer of zein, although the thickness of this layer is not constant.

All dispersions remain stable for several weeks, and can be redispersed by simple shaking, except the zein particles with exposed

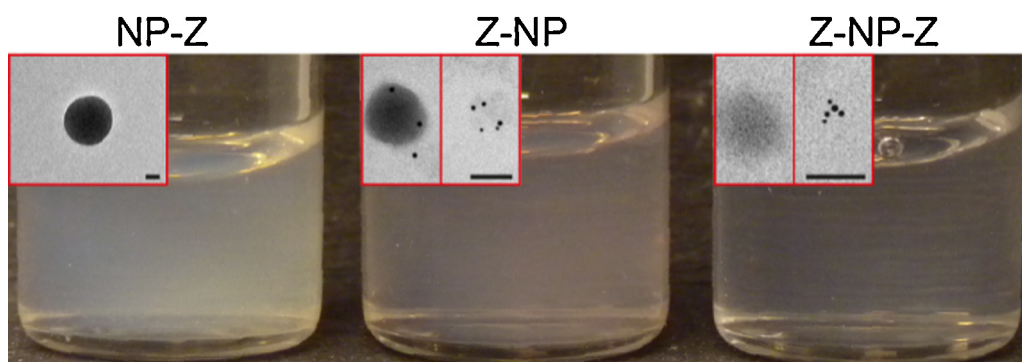


Fig. 3. Supernatants after preparation of the gold composite systems. The lower turbidity of the Z-NP-Z supernatant shows the presence of less unfilled zein. Electron micrographs (insets) show empty zein particles (NP-Z) and separate nanoparticles (Z-NP, Z-NP-Z). Scale bars are 50 nm.

Table 1

Results from electrophoretic mobility measurements and dynamic light scattering, providing the particle zeta-potential (Z-pot) and average particle diameter (*D*).

	NP		NP-Z		Z-NP		Z-NP-Z	
	Z-pot (mV)	<i>D</i> (nm)	Z-pot (mV)	<i>D</i> (nm)	Z-pot (mV)	<i>D</i> (nm)	Z-pot (mV)	<i>D</i> (nm)
Zein	50	112	–	–	–	–	–	–
FePPi	42	135	42	166	15	188	53	228
FeO (mag)	–52	57	33	248	34	163	49	239
CoFe	–54	38	39	189	34	149	46	261
Au	–17	15	53	133	45	150	50	187
Ag	–43	84	54	145	–	–	–	–
FeO (hem)	–49	158	55	152	–	–	–	–
SiO ₂ @Mag-Z	–	–	–36	158	–	–	–	–

nanoparticles (Z-NP). These form aggregates on similar timescales as dispersions of these nanoparticles [16].

The successful coating of zein with a thin layer of silica is illustrated in Fig. 4 for unfilled zein particles, and NP-Z composites containing magnetite or silver nanoparticles. In all cases additional silica particles are present due to secondary nucleation. These particles are usually much smaller and can be removed by repeated centrifugation, or magnetic sedimentation. Sometimes larger, network structures are present which we attribute to drying effects, since no macroscopic aggregation is present and DLS

measurements show size distributions that confirm that only single, non-aggregated particles are present in dispersion (see also Table 1).

While the visibility of the silica layer is sometimes low due to surface irregularities, a clear indication that the coating is successful is provided by the much improved stability of the particles on the TEM grids. Uncoated particles consistently show many ‘molten’ or fused particles, because of the drying on the TEM grids (see Fig. 4e).

The presence of silica is confirmed by determination of the isoelectric point of the particles (Fig. 5). The silica layer clearly shifts

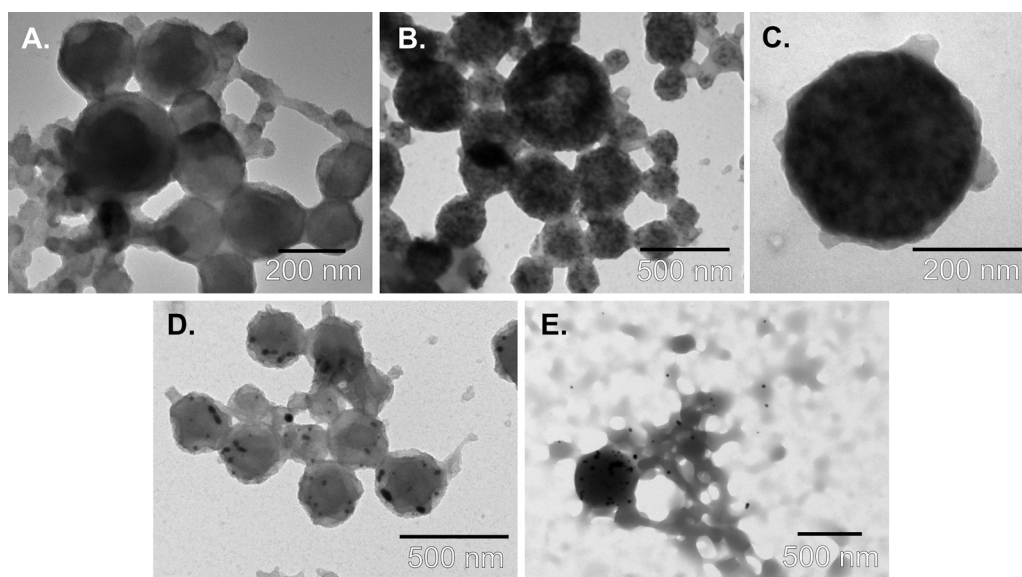


Fig. 4. Silica coating of (A) zein particles and (B) zein with embedded magnetite nanoparticles, (C) single coated particle with embedded magnetite, and (D) zein with embedded silver nanoparticles. In all cases some residual silica is present from secondary nucleation. A typical uncoated NP-Z system is shown (E) as a reference image for the usual melting of zein particles during electron microscopy measurements.

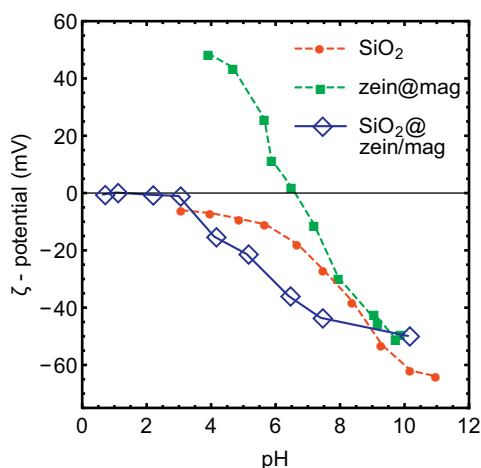


Fig. 5. A comparison of the zeta-potential of bare silica particles (red circles, taken from [28]), bare zein particles (green squares) and our silica coated composite particles (blue diamonds) at different pH. A clear shift in behaviour is visible for the coated zein in comparison with the bare zein, suggesting successful coating of the particles.

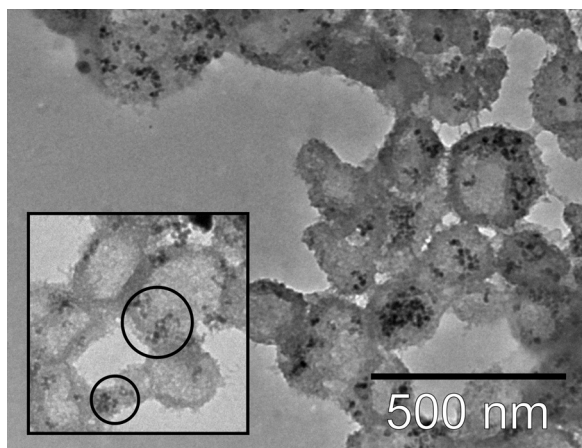


Fig. 6. Electron micrograph showing irregularly shaped and collapsed shells of silica coated zein particles where the zein has been dissolved. Magnetite particles that were coagulated together with the zein (highlighted inside the open circles) remain inside the hollow shell. Inset: close-up of several hollow silica shells.

the iso-electric point of the zein particles towards the values for pure silica colloids. Slightly higher values for the zeta potential are likely due to the presence of uncoated zein, or partially covered zein surfaces.

Fig. 6 shows the hollow silica shells formed by dissolving the zein after the growth of a silica shell. The porosity of the silica layer allows for zein to diffuse through, but the nanoparticles are too large and remain inside the hollow silica shell. The mechanical stability of the shells is insufficient to keep them spherical, as many shells are deformed and collapsed.

4. Conclusion

We have demonstrated the use of zein protein in a general heterocoagulation process to prepare composite colloidal particles in aqueous environment. We used negatively charged nanoparticles of iron(III)pyrophosphate, cobalt ferrite, silver, gold and two types of iron oxides to prepare colloidal dispersions of different morphology (NP-Z, Z-NP and Z-NP-Z), establishing the versatility and broad applicability of the method. The composites are stabilized

by a positive surface charge and are prepared without any further additives.

We further improved the potential of zein composites by coating them with a thin layer of silica through condensation of sodium silicate, enabling further surface modification, such as the grafting of thiol-groups to bind gold colloids [14]. The silica layer acts as a stabilizing agent, preventing irreversible aggregation of the zein particles, in a similar fashion to stabilization with sodium caseinate [12]. An additional interesting morphology created is hollow silica shells containing nanoparticles, by dissolving the zein from a core-shell particle after its formation. Further investigation may open up possibilities for zein-based ‘microreactors’ when catalytic nanoparticles are embedded [29].

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