



Functionalization of zinc ferrite nanoparticles: Influence of modification procedure on colloidal stability

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Abstract

The present work describes the synthesis of zinc ferrite nanoparticles by a chemical coprecipitation method and its surface modification with poly(diallyldimethylammonium chloride) (PDDA), tetramethylammonium hydroxide (TMAOH) and poly(ethylene glycol) (PEG). The effect of coating on the colloidal stability of obtained systems as well as the effect of modification procedure on the final characteristics of particles were studied. The unmodified and modified nanoparticles were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and Raman spectroscopy. The particle size distribution and stability of these systems were investigated by dynamic light scattering (DLS) and zeta potential measurements. The results have shown the profound effect of the used modification procedure on colloidal stability of the investigated particles.

Keywords: zinc ferrite, modification, surfactants, PEG, PDDA, TMAOH

I. Introduction

Nanoparticles in solutions present typical colloidal systems, consisting of a continuous phase, which is a dispersed medium (solvent) and a dispersed phase (nanoparticle) [1]. The stability of colloidal solutions is often difficult to achieve. Due to small size of nanoparticles (below 100 nm), these systems are highly reactive, but unstable and they undergo agglomeration. Consequently they form large clusters, resulting in increased particle size. This could be very unfavorable, especially in the case of magnetic nanoparticles, where besides usual Van der Waals forces, large clusters experience strong magnetic dipole-dipole interactions. One of the ways to prevent agglomeration is modification of the surface of nanoparticles with appropriate surfactant agents [2–4]. A large number of materials can be used for this purpose. They include both inorganic materials (silica or gold) and polymers such as chitosan, glucose, dextran, poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA) etc. Various surfactants, such as sodium oleate, dodecylamine, dopamine, silane agents etc. are also used for modification of surface. By covering the

surface of nanoparticles with appropriate surfactants, particles can be prevented from sticking to each other by two basic modes. The first one is the formation of an electric double layer at the particle surface that creates electrostatic repulsion between the particles, and the second one is coating of particles in order to prevent particles touching each other through steric repulsion [5]. The surface modification of the particles can be physical (by physisorption) or chemical (through covalent bonding) and can be done in situ or as a post modification procedure [6,7]. The in situ method involves the addition of surface modifying agents to the reaction system already during or even prior to nanoparticles formation to avoid aggregation, and to have better control over particle size and shape. Post modification method implies the modification of previously synthesized nanoparticles.

For better understanding how modification procedure can influence the performance of nanoparticles, we have synthesized zinc ferrite nanoparticles as a model system and functionalized them with different agents. For surface modification of zinc ferrite nanoparticles, several surfactants were used such as: poly(ethylene glycol) (PEG), poly(diallyldimethylammonium chloride) (PDDA) and tetramethylammonium hydroxide

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(TMAOH). Poly(ethylene glycol) is the most used polymer for modification of nanoparticles. This polymer is well soluble in a number of organic polar and apolar solvents, as well as in water. PEG is amphiphilic uncharged polymer which prevents aggregation of particles by steric stabilization [8,9]. PDDA is a water soluble cationic polyelectrolyte which keeps the nanoparticles from aggregating in solutions either by steric or electrosteric interactions [10]. TMAOH is a surfactant whose cationic species are adsorbed at the surface OH groups thus creating an electrostatic repulsion between particles [11].

The present work describes the synthesis of zinc ferrite nanoparticles by a chemical coprecipitation method and modification with PEG, PDDA and TMAOH in order to study the effect of modification procedure on the final characteristics of particles and their colloidal stability.

II. Experimental

2.1. Synthesis of unmodified zinc ferrite nanoparticles

The preparation scheme of zinc ferrite nanoparticles is shown in Fig. 1. Unmodified zinc ferrite nanoparticles were synthesized by coprecipitation method following the four steps:

1. Stoichiometric amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck KGaA, Germany) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck KGaA, Germany) were dissolved in distilled water, forming 0.2 M solutions and mixed together.
2. Sodium hydroxide was used as a precipitating alkali until pH value reached 12. The reaction was carried out at 80 °C for 60 min under continuous stirring.
3. The precipitates were separated from the slurry by centrifuging and washing a number of times with distilled water until the pH reached 7.
4. The obtained nanoparticles were dried at 120 °C/24 h and finally dry milled in a mortar. The obtained zinc ferrite nanoparticles were denoted as ZF.

2.2. Modification of zinc ferrite nanoparticles

For modification of zinc ferrite nanoparticles, several surfactants were used such as: PDDA (Sigma Aldrich), TMAOH (Sigma Aldrich) and PEG 600 (Fluka Chemika). In order to investigate the influence of the modification procedure on final powder morphology, two groups of powders were prepared, using two procedures.

Procedure 1: in the first group, surfactants were

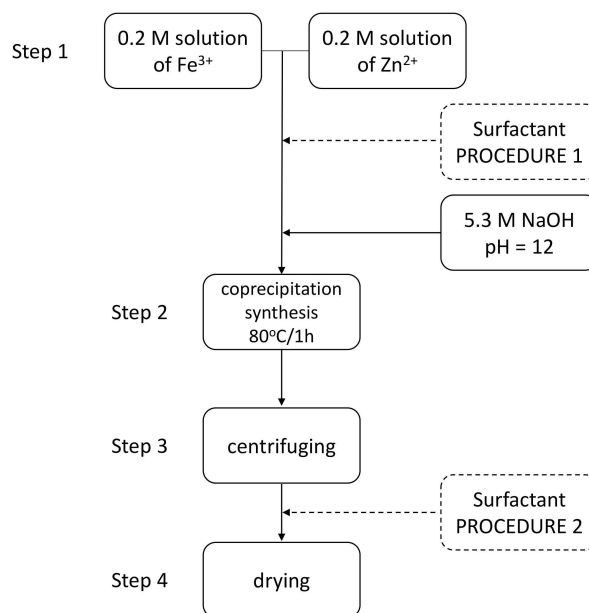


Figure 1. Flowchart representing the preparation of unmodified and modified zinc ferrite nanoparticles by coprecipitation method

added during the synthesis, after the step 1 in the procedure for preparation of unmodified zinc ferrite nanoparticles. The concentration of surfactant/ferrite was 5 mmol/g. The following steps 2, 3 and 4 were the same as described above.

Procedure 2: in the second group, surfactants were added after the synthesis (after the step 3). Namely, washed zinc ferrite nanoparticles were dispersed in distilled water in the concentration of 6 g/L. The solutions were treated with surfactants (concentration 5 mmol/g) and ultrasonically agitated for 60 min, in order to stabilize the solution of zinc ferrite nanoparticles. Finally, the powders were obtained following the steps 3 and 4. Sample notations were listed in Table 1.

2.3. Characterization of nanoparticles

The crystal structure of the powders was investigated by X-ray diffraction (XRD) using a Rigaku MiniFlex 600 diffractometer ($\text{CuK}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$). X-ray diffraction patterns were recorded in the range 10–80° with a scan rate of 0.03°/s. Particle size distribution was measured by dynamic light scattering (DLS) and the zeta potential of particles was determined by phase analysis light scattering and mixed mode measurement using a Zetasizer Nano ZS with MPT-2 Autotitrator Malvern Instruments, Malvern, United Kingdom. Size and morphology of particles were examined using trans-

Table 1. Sample notations of modified zinc ferrite nanoparticles and conditions of surfactant addition

Surfactant	During synthesis, procedure 1 ($T = 80 \text{ }^\circ\text{C}$, $\text{pH} = 12$)	After synthesis, procedure 2 (Room temperature, $\text{pH} = 7$)
PDDA	ZF-PDDA 1	ZF-PDDA 2
PEG	ZF-PEG 1	ZF-PEG 2
TMAOH	ZF-TMAOH 1	ZF-TMAOH 2

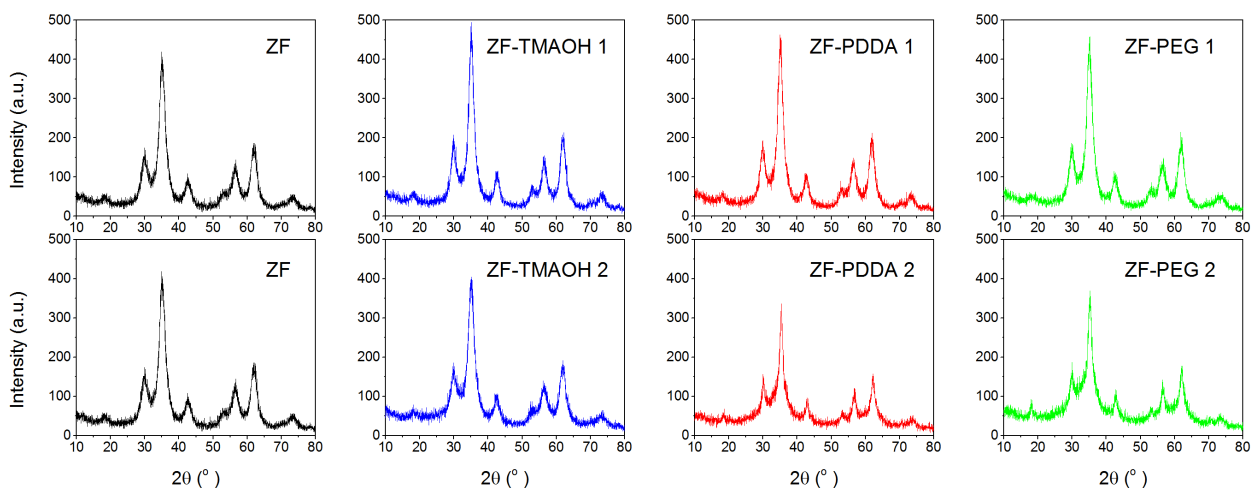


Figure 2. XRD patterns of zinc ferrite nanoparticles unmodified and modified during and after synthesis

mission electron microscopes: JEOL JEM 1400 Plus, operating at 120 kV (for modified zinc ferrite) and a Philips CM20 operating at 200 kV (for unmodified zinc ferrite). Raman spectroscopy of the powders were performed at room temperature using a Thermo Fisher Scientific DXR™ Raman Microscope. The device is equipped with DPSS (Diode Pumped Solid State) laser using $\lambda = 780$ nm excitation. A CCD camera has been used as detector. The spectral range 200–1000 cm^{-1} was examined using a 900 lines/mm grating paired with 10 microscope objective.

III. Results and Discussion

The X-ray patterns of unmodified zinc ferrite nanoparticles, ZF and zinc ferrite nanoparticles modified during and after synthesis are shown in Fig. 2. All samples have the characteristic reflections of the cubic spinel phase with broad peaks indicating the small crystallite size. The average crystallite size of the samples, calculated by Scherrer's formula from 311 peak of the spinel phase is around 5 nm. The intensities of the peaks in the samples modified during synthesis (procedure 1) are somewhat higher compared to the samples modified after synthesis (procedure 2) implying the higher crystallinity, Fig. 2. When surfactant is added to the sample during synthesis, it promotes a better dispersion of the partially amorphous nanoparticles and enhances the degree of spatial arrangement of the matter, thus increasing the crystallinity. This effect was proposed by other authors [11,12]. Moreover, in procedure 1, surfactants together with metal ions undergo coprecipitation reaction at 80 °C. In this way, the procedure 1, driven by the temperature, pH, hydrophilicity (PEG) and the charge (cationic groups in TMAOH and PDDA adsorbed onto negatively charged zinc ferrite surfaces), could lead to the steric effect around the particles that promote a better arrangement during growing and crystallinity.

Further examination of crystallinity and phase com-

position was done by Raman spectroscopy at room temperature, Fig. 3. There are five Raman active modes ($A_{1g} + E_g + 3T_{2g}$) in cubic spinel structure. The modes above 600 cm^{-1} mostly correspond to the motion of oxygen in the tetrahedral MO_4 groups and it can be considered as A_{1g} symmetry. The other low frequency modes represent the characteristics of the octahedral sites (FeO_6). In the region of 200–1000 cm^{-1} , all samples presented in Fig. 3, have similar broad Raman peaks centered at around 330, 480, and 660 cm^{-1} , which are associated with E_g , $T_{2g}(2)$ and A_{1g} modes of standard spinel structure ZnFe_2O_4 [13–15]. The E_g band is due to symmetric bending of Fe–O bonds with peak around 250–360 cm^{-1} , and $T_{2g}(2)$ band is from the asymmetric stretch of Fe–O bonds with peak around 450–520 cm^{-1} [16]. The broadening of peaks due to the small particle size was observed. It can be seen from the Raman spectra that used surfactants do not change the structure of the obtained spinel nanoparticles. However, when we compare the used modification procedure, the intensities of the peaks are higher in samples modified during synthesis than in the case of the samples modified after synthesis. It can be concluded that addition of surfactants during the synthesis (procedure 1) results in higher crystallinity of the obtained samples which is in good agreement with the presented XRD results.

In order to examine the effect of modification procedure on the size and surface morphology of zinc ferrite nanoparticles, particle size distribution and zeta potential measurements were conducted. Unmodified zinc ferrite has a broad distribution of hydrodynamic radius of particles with an average value around 100 nm, Fig. 4. This size value is considerably higher than in the case of XRD measurements, which suggests the high degree of agglomeration of the particles. Agglomeration is well expected in systems with a large surface to volume ratio with high surface energy, like in the case of fine nanoparticles presented in this paper. However, the addition of surfactants have a positive effect on deag-

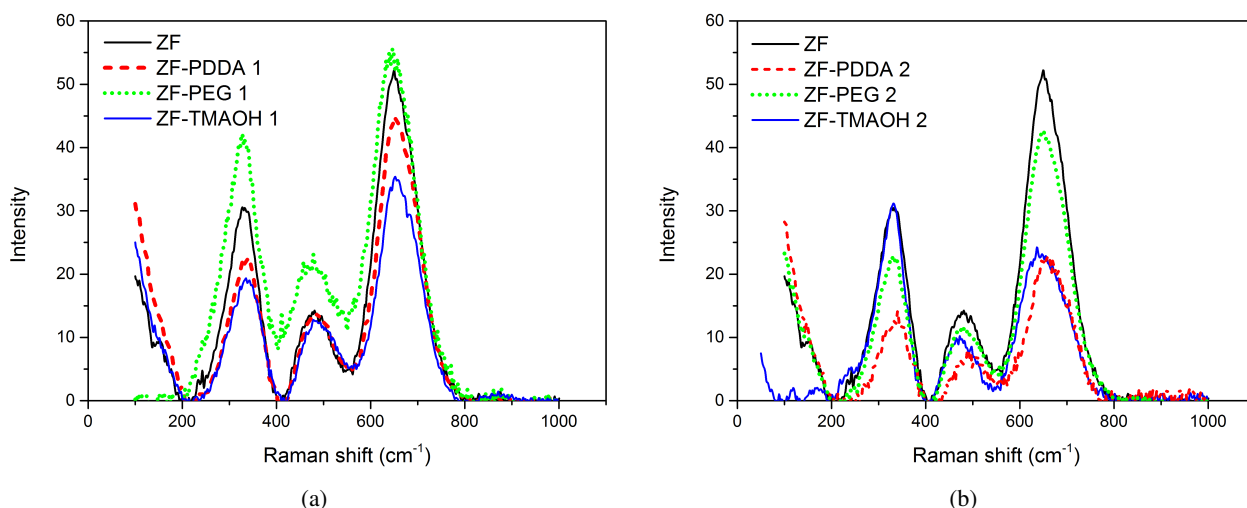


Figure 3. Raman spectra of the zinc ferrite nanoparticles modified during synthesis (a) and after synthesis (b)

glomeration, shifting the particle size distribution towards smaller values. Comparing the diagrams shown in Fig. 4, an obvious influence of the type of used surfactant as well as the type of used procedure on the hydrodynamic radius of particles could be noted. In both procedures, the smallest average particle size was measured for the samples modified with TMAOH. In addition, the smaller particle size of the samples modified after synthesis, Fig. 4b, compared to the samples modified during synthesis, Fig. 4a, could be a result of more efficient deagglomeration of the particles since ultrasonic agitation is used in procedure 2. The ultrasonic agitation provides larger surface available for surfactant adsorption, resulting in smaller nanoclusters of primary particles [17]. According to DLS measurements, the smallest hydrodynamic radius has a sample modified with TMAOH and ultrasonically treated, where $d \sim 25$ nm (sample ZF-TMAOH 2), Fig. 4b.

These findings are further verified with the TEM analysis as presented in Fig. 5. The size of unmodified

zinc ferrite primary particles is in accordance with XRD results, but particles are strongly agglomerated, Fig. 5a. However, Figs. 5b and 5c clearly indicate that the degree of agglomeration is reduced when particles are modified with TMAOH which resulted in a lower value of the hydrodynamic diameter (Figs. 4a,b). Moreover, the presence of the isolated, non-agglomerated particles in ZF-TMAOH 1 sample (Fig. 5b) could be noticed. This can be explained by adsorption of the $[(CH_3)_4N]^+$ cations onto the surface of the zinc ferrite nanoparticles that gives rise to repulsive stabilization and prevents the agglomeration of particles. A loose connection between particles in ZF-TMAOH 2 sample, Fig. 5c, indicates that ultrasound agitation as well as the type of ions on the nanoparticle surface have profound effect on the formation of soft agglomerates. The particles in such agglomerates can be reconnected and regrouped especially when they are dispersed in aqueous media as in DLS measurements, which very well supports the result in Fig. 4b.

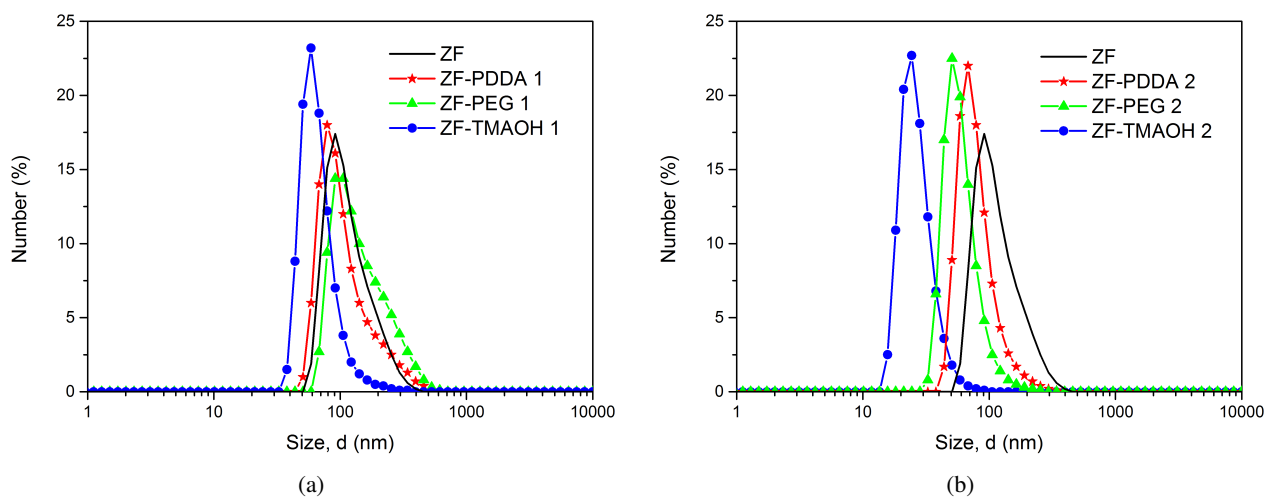
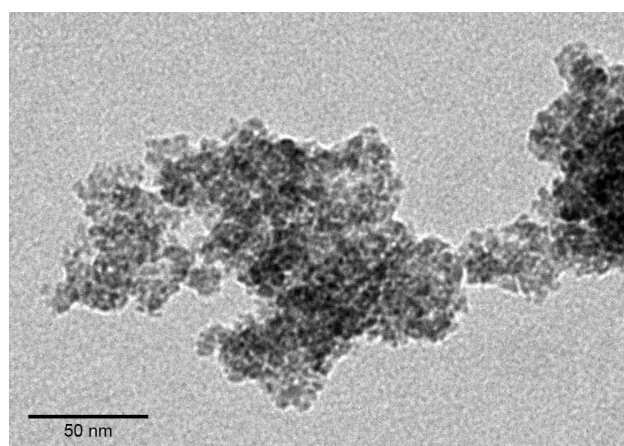
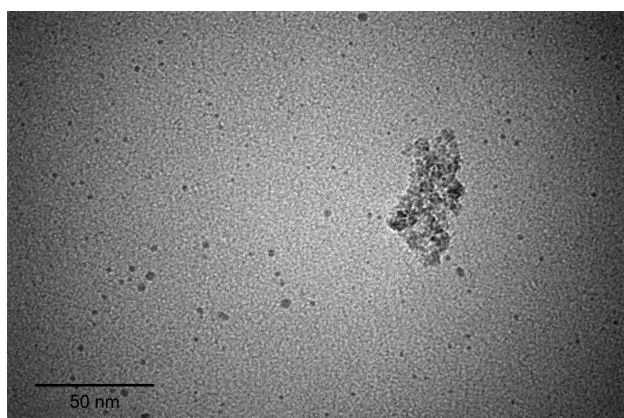


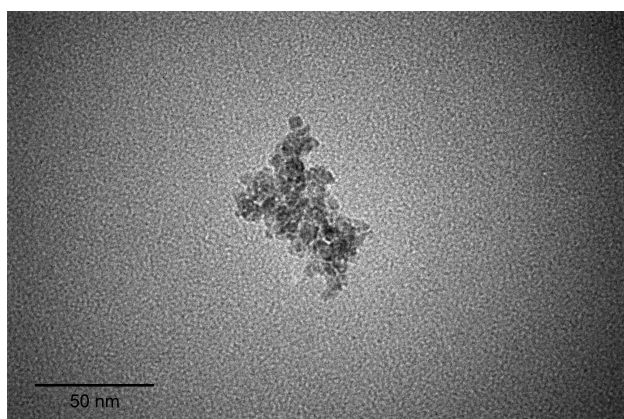
Figure 4. Particle size distribution of zinc ferrite nanoparticles modified during synthesis (a) and after synthesis (b)



(a)



(b)



(c)

Figure 5. TEM images of ZF (a), ZF-TMAOH 1 (b), ZF-TMAOH 2 (c)

The stability of nanoparticles dispersed in aqueous media was investigated by measuring the zeta potential and results are shown in Fig. 6. Since zeta potential is related to the surface charge on the nanoparticles, its value indicates the degree of electrostatic repulsion between the nanoparticles. If the zeta potential is higher than ± 30 mV, then it is generally accepted that the particles are electrostatically stable [8]. The isoelectric point (pI) is the point at a particular pH where particles carry no net electric charge on their surfaces.

The isoelectric point of the unmodified zinc ferrite nanoparticles synthesized in this work is around $pI \sim 4.6$. The observed shifts of pI for modified systems may be associated with successful coating of used surfactant onto the surface of particles. However, it can be noticed that pI of the modified nanoparticles is strongly influenced by the modification procedure. This is more obvious for TMAOH-modified particles where pI is shifting from 7.3 to 2.9 depending upon whether the addition step is performed during or after synthesis. The increase in pI of ZF-TMAOH 1 sample, with respect to ZF, Fig. 6a, indicates that $[(CH_3)_4N]^+$ cations were adsorbed onto the surface decreasing the negative charge of the zinc ferrite nanoparticles at alkaline pH, which is in accordance with literature data [11]. In comparison to unmodified zinc ferrite nanoparticles with $pI \sim 4.6$, the pI of ZF-TMAOH 2 sample is decreased to value of 2.9, while the overall zeta potential is more negative in the whole range of pH, Fig. 6b. This result suggests that changing of the ionic strength of the aqueous media (alkaline in procedure 1 to neutral in procedure 2) could change the electrical double layer around the particle which influences the colloidal stability. The smallest value of hydrodynamic diameter of ZF-TMAOH 2 nanoparticles indicates that electrostatic repulsive forces are acting between the particles that opposes the agglomeration of these nanoparticles and increases the dispersion and colloidal stability in water. The zeta potential of solution with ZF-TMAOH 2 nanoparticles at neutral pH was found to be -40 mV, suggesting their stability in aqueous medium. Moreover, the colloidal stability of ZF-TMAOH 2 sample is observed for all $pH > 4.5$, Fig. 6b, while addition of TMAOH during synthesis resulted in stable colloids only at high pH, Fig. 6a.

For the PDDA-modified particles the procedure 1 seems to be more effective, Fig. 6a. The large negative potential value (absolute value above 25 mV) at neutral pH for the solution with ZF-PDDA 1 nanoparticles, implies that the particles will have excellent stability in an aqueous medium due to repulsive, interparticle electrostatic force. These functionalized particles tend to show a negative potential as the pH value further increases. Thus the surface modification with PDDA was successful in this procedure. Solution with ZF-PDDA 2 particles at $pH > 5$ showed extensive aggregation and consequent precipitation, Fig. 6b.

The pI shift could be observed also in PEG-modified zinc ferrite nanoparticles, regarding the modification procedure. ZF-PEG 1 sample, Fig. 6a, exhibited an isoelectric point of $pI \sim 7$ which is very well expected since PEG is an amphiphilic polymer without cationic or anionic end groups. This result indicates successful coating of PEG surfactant onto the negative surface of zinc ferrite nanoparticles. However, increasing the pH in the investigated range, changes the zeta potential from positive to negative. This could be explained by the uptake of ions in the PEG layer, since HCl or NaOH were used as titrants [5,8]. For ZF-PEG 2 particles, Fig. 6b, the iso-

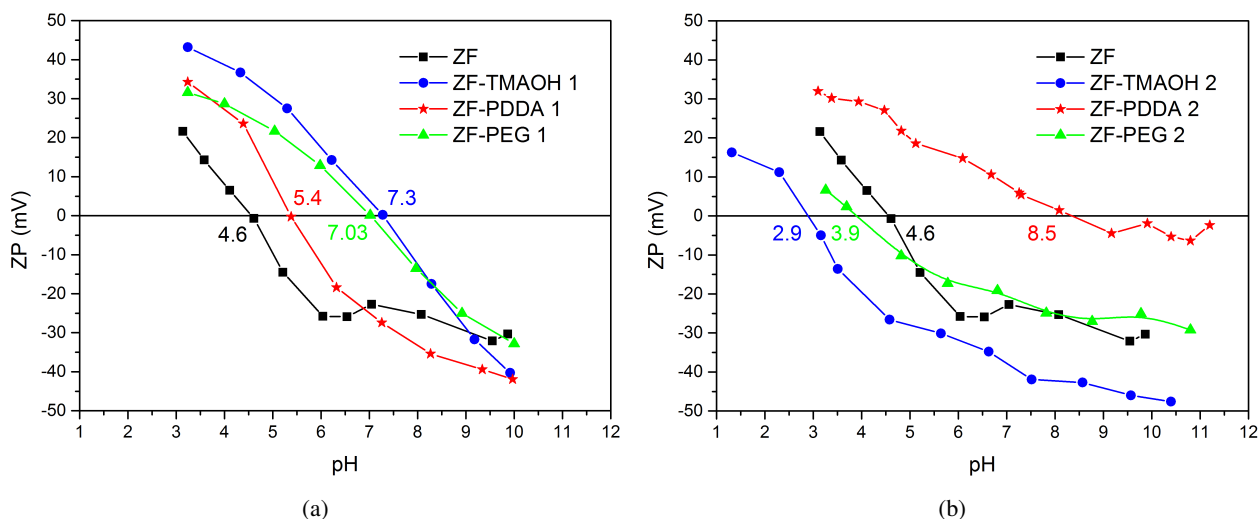


Figure 6. Zeta potential as a function of pH of zinc ferrite nanoparticles modified during synthesis (a) and after synthesis (b)

electric point is observed at $\text{pH} \sim 3.9$ while overall zeta potential is close to the unmodified zinc ferrite particles. Solution with ZF-PEG 2 particles precipitated suggesting an unsuccessful covering. Results of DLS measurements (Fig. 4b) imply on partially deagglomerated particles (the smaller particle size of ZF-PEG 2 in comparison to ZF sample), but this is probably governed by ultrasound agitation, as in the case of ZF-PDDA 2 sample.

The profound impact of the pH on the stability of TMAOH and PDDA coatings shows that electrostatic repulsion might be crucial for these types of dispersions [8,18,19].

IV. Conclusion

Single phase spinel zinc ferrite nanoparticles were successfully synthesized by coprecipitation method. These nanoparticles were modified with different surfactants in order to investigate the influence of type of used agent as well as the applied modification procedure on the final characteristics of nanoparticles. Surfactants do not change the structure of the obtained spinel nanoparticles. However, the surface properties of the particles are significantly changed by surfactants. The highest stability of particles in aqueous media is obtained with TMAOH. In addition, TMAOH proved to be the most efficient for deagglomeration of particles (ZF-TMAOH 2 sample). The results have shown that modification protocol (including type of surfactant and type of treatment) influences the final morphology of these particles and especially their size, agglomeration degree and charge of their surface.

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