4

Polymer – surfactant interactions and their influence on zinc oxide nanoparticles morphology

Marta Fiedot[1], Olga Rac[1], Patrycja Suchorska - Woźniak[1*], Iwona Karbownik[2], Helena Teterycz[1]

[1]Wroclaw University of Technology, Faculty of Microsystem Electronics and Photonics, ul. Janiszewskiego 11/17, 50-370 Wroclaw, Poland
[2]Technical University of Lodz, Faculty of Material Technologies and Textile Design, ul. Zeromskiego 116, 90-543 Lodz, Poland

Outline:

Introduction

Currently zinc oxide is a semiconductor extensively analyzed due to specific traits, i.e. width bandgap about 3.37 eV [1], exciton binding energy of 60 meV at room temperature and UV absorption band [2]. It is chemical stable, non-toxic and has very good antibacterial and antifungal properties. It can be synthesised in a variety forms such as tubes, rods [3], whiskers [4], beads, plates, flowers [5] and olives [6]. Its advantages are widely used in many fields such as electronics, optoelectronics, photonics and medicine [7], in the construction of various types of electrical and optical equipment [8], chemical sensors [9], varistors [10] and solar cells [11]. Moreover antibacterial and antifungal textiles are obtained due to zinc oxide application [12].

There are many different methods of preparing the nano- and microstructures of zinc oxide inter alia: homogeneous precipitation from a solution [13] or by sol-gel method [14]. Size and shape of the resulting nanostructures primarily depends on the type and amount of stabilising agent which also affects the stability of the resulting colloid. The most commonly used stabilisers are surfactants or polymers. Many researchers uses those types of stabilisers to prepare of ZnO nanoparticles. However, for synthesis stabilisation both types has never been used simultaneously [15-16].

This chapter presents a simple new method for the synthesis of nanoparticles of zinc oxide by precipitation in the reaction hydroxide Zn^{2+} ions in the solution containing the cationic polymer and nonionic surfactant. The effect of the individual components of the reaction mixture arising from the morphology of the crystalline structure, in particular the polymer-surfactant interactions and their effect on the morphology of nanostructures was described for the first time. The polymer-surfactant-colloid interactions were carefully analyzed with regard to chemical reactions, electrostatic interactions and typical parameters for polymer-surfactant systems, such as CMC (critical micelle concentration) and CAC (critical aggregation concentration). This paper presents results of the analysis are pioneering in this field and may to assist in the further research on this type of nanosystems.

Materials and characterization methods

The following substrates were used for the nanoparticle synthesis: zinc nitrate hexahydrate $Zn(NO_3)\cdot 6H_2O$, sodium hydroxide NaOH, nonionic surfactant Triton® X-100 $C_{14}H_{22}(C_2H_4O)_{10}$ by POCH (Poland), polyethylenimine $(C_2H_5N)_n$ by Sigma-Aldrich (Germany) and polyvinylpyrrolidone (PVP) by Sigma-Aldrich (Germany). All initial substrates were analytical grade purity and used without preliminary purification.

During the synthesis of zinc oxide nanoparticles the following aqueous solutions were mixed at appropriate proportions:

- zinc nitrate at the concentration of 0.15 M,
- nonionic surfactant Triton® X-100 at the concentration of 0.08 M,
- polyethylenimine (PEI) at the concentration of 40 g/dm^3,

and then the aqueous solution of the sodium hydroxide at the concentration of 1.5 M was added.

A typical reaction mixture contained 5 mL of $Zn(NO_3)_2$, 4.5 mL of PEI, 15 mL of Triton® X-100 and 0.5 mL of NaOH, therefore the levels of individual reagents were as follows: 0.03 M; 0.18 M; 0.048 M; 0.03 M. A solution with this composition was named as the stock solution.

To determine the effects of individual components of a reaction mixture on dimensions and morphology of zinc oxide nanoparticles obtained the stock solution composition was modified and the following parameters were changed:

- the ratio of the surfactant amount to the polymer amount,
- polymer type,

Two polymers were used in these studies:

- high-molecular weight polyethylenimine,
- polyvinylpyrrolidone (PVP) with the mean molecular mass of 3.5 kDa.

The distribution of the ZnO particle sizes was determined with dynamic light scattering (DLS). Studies were performed with Nicomp 380ZLS (Particle Sizing Systems, USA). The frequency of photon counting by an autocorrelator was set at approx. 200 kHz, and the measurement time was 16 min. Calculations of the hydrodynamic diameter were based on the Stokes-Einstein equation assuming the measurement temperature of 298 K and continuous phase (water) viscosity of 0.891 mPa·s. The absorption (A) of solutions with zinc oxide nanoparticles was measured with the Ocean Optics QE65000 spectrophotometer. The absorption spectrum was measured for the wavelength of 200 to 1000 nm. The crystallographic structure of zinc oxide structures was determined using an X-ray diffractometer of Philips Materials Research Diffractometr (MRD) using CuK_α radiation. A scan type typical of powder materials, namely $\Theta/2\Theta$, was used.
Studies of the microstructure of zinc oxide nanoparticles were performed with the transmission electron microscope (TEM) EM900 (Zeiss, Germany) with the magnification of 81000×. Samples were prepared by applying a drop of an aqueous nanoparticle dispersion on copper meshes of 200 mesh, covered with a carbon layer and coated with the Formvar resin, then dried for 45 minutes.

Results and discussion

Synthesis

There are two general methods for obtaining metal oxide nanoparticles: physical (top down) and chemical (bottom up). Physical methods include gradual disintegration of bulky materials using different methods. Chemical methods involve the formation of nanostructures as a result of precipitation reactions between ion precursors and different hydroxides. Nuclei of crystallisation formed in the first stage of a precipitation reaction merge into larger systems called crystallites (Fig .4.1).

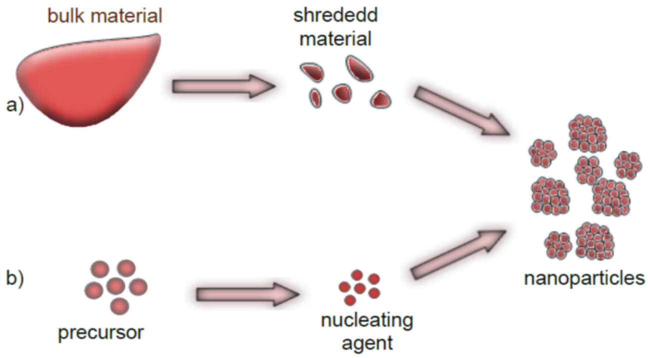

FIGURE 4.1
Methods of nanomaterials synthesis: a) physical; b) chemical

Theoretically, both methods can be used to obtain highly refined materials; however, physical methods cannot be used to obtain nanoparticles of identical shapes, and their distribution is not homogenous. Frequently, materials obtained using these methods also contain large particles, and as a result their activity is reduced. An additional disadvantage of physical methods used to obtain nanomaterials is associated with their low repeatability. Parameters of chemical processes can be controlled with much greater precision. When nanomaterials are synthesised using chemical methods, nanoparticles with desired sizes and morphology, and with a low degree of dimension dispersion can be obtained.
During the synthesis of metal oxide nanoparticles using chemical methods in solutions substrates include precursors of metal ions and a precipitating factor. Therefore, as early as when the first nanoparticles have been formed in a solution, they agglomerate. A system aims to achieve minimum thermodynamic energy. To avoid nanoparticle agglomeration stabilising agents are used and they provide a high level of dispersion of a colloid being formed. Stabilising agents may include different polymers or surfactants. In this method of synthesis stabilising agents include both polymer and a surfactant. Molecules of these compounds, when selected appropriately with regard to a type of a precursor used, may play two roles. They may form complexes with precursor ions and then nanoparticles are formed in the volume of a stabiliser macromolecule. On the other hand, stabilisers may become adsorbed on surfaces of nanoparticles that are formed, and as a result the speed of their Brownian motion is reduced, and there is a barrier making it impossible for nanoparticles to aggregate (Fig. 4.2) [17].

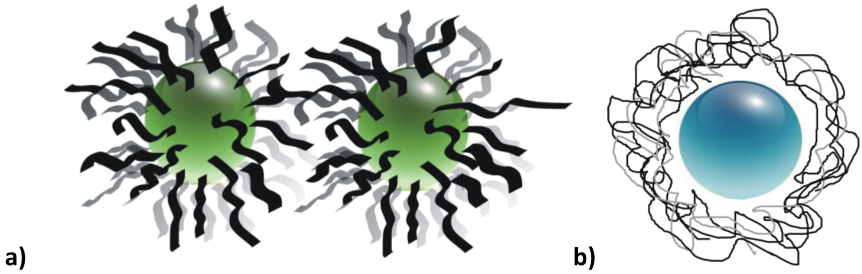

FIGURE 4.2
Steric stabilization of the metal oxides nanoparticles using a) surfactant; b) polymer

The process of zinc oxide nanoparticle production using chemical methods is multi-stage and complex. At the first stage a precursor and hydroxide are subject to electrolytic dissociation. Later, metal ions react with hydroxide ions, and as a result, molecules of zinc hydroxide are formed, and subsequently they are transformed into zinc oxide. ZnO molecules that have been formed collide with each other forming larger systems that transform into stable crystallites when their critical size has been exceeded. Crystallites grow further until substrates have been depleted (Fig. 4.3).

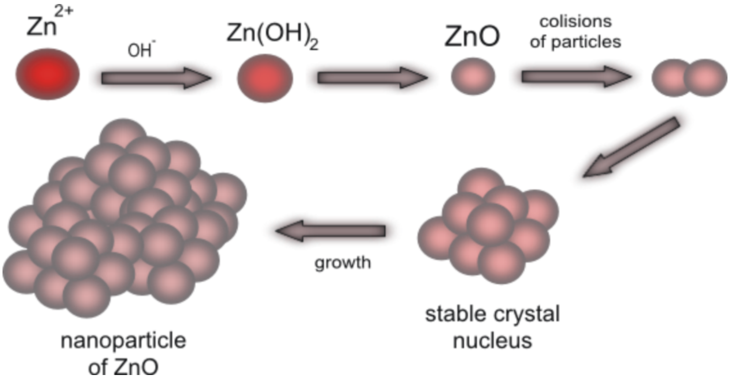

FIGURE 4.3
Schematic growth of ZnO nanostructures

As a standard, the synthesis of zinc oxide nanoparticles was conducted in the aqueous solution of a zinc ion precursor $Zn(NO_3)_2{\cdot}H_2O$, polyethylenimine and non-ionic surfactant Triton® X-100. The reaction mixture was mixed with a magnetic mixer at the 500 rpm and small amounts of the sodium hydroxide solution were added. The reaction was conducted at room temperature. As a result of a precipitation reaction zinc hydroxide nanoparticles were formed as the first ones (1), and subsequently they were transformed into zinc oxide molecules (2).

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \tag{1}$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \tag{2}$$

Spectroscopic studies of obtained colloidal solutions of zinc oxide indicated that at the wavelength of 360 nm there is a typical absorption peak (Fig. 4.4).

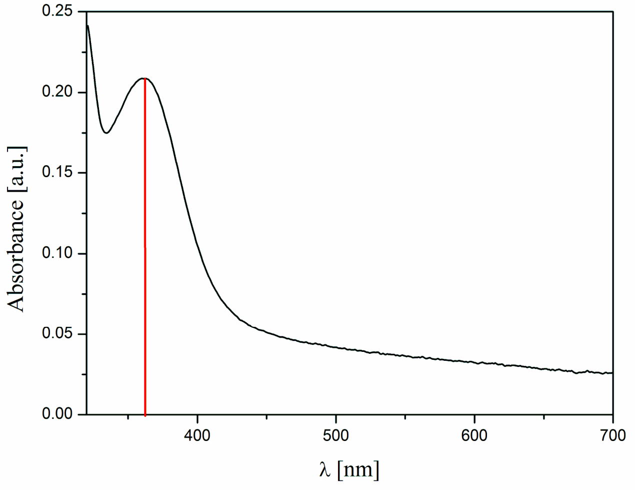

FIGURE 4.4
The absorption spectrum of stock solution after the precipitation

The position of a typical peak does not comply with literature data for zinc oxide molecules. Based on these literature reports aqueous solutions containing zinc oxide molecules absorb electromagnetic radiation in the range of approx. 368 nm [18]. The shift of the absorption maximum towards short waves is associated with a quantum size effect that involves increasing the width of the energy gap while the molecule dimensions decrease towards single nanometres (Fig. 4.5) [19].

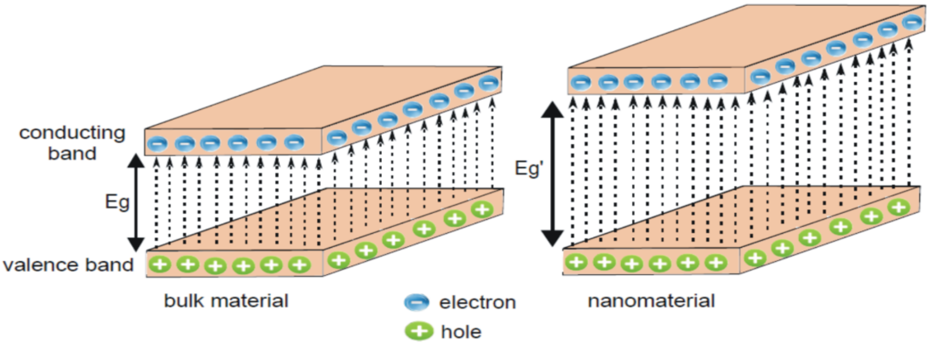

FIGURE 4.5
Schematic relationship between bandgap energy and size of particles

Based on the spectrum obtained the optical width of the energy gap was determined. To determine this value, first of all, it is necessary to determine whether the energy gap of a study material is straight or oblique. From the literature it is known that zinc oxide has a straight energy gap. In the case of such semiconductors in order to determine the width of the energy gap this graph can be used $(-\log T)^2=f(E)$. Using measurement data $A=F(\lambda)$, and commonly known relationships that $E=hc/\lambda$ and $T=A^{-1}$ the relationship of transmission as a function of electromagnetic radiation energy was determined (Fig. 4.6).

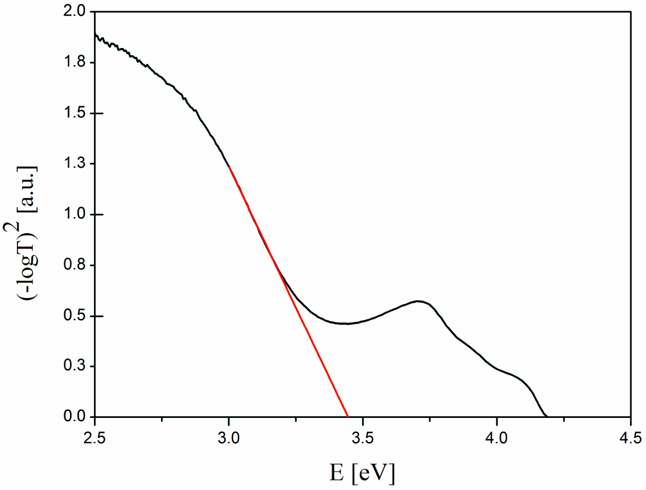

FIGURE 4.6
The relationship of transmission as a function of electromagnetic radiation energy

When the rectilinear section of the graph was extrapolated to the transmission value of zero the energy of the optical energy gap was determined and its value is 3.44 eV. From the literature data it can be concluded that the value of this parameter for volumetric zinc oxide is 3.37 eV. Consequently, the experimental value of optical energy of the energy gap that was obtained indicates that there is a size effect in nanoparticles obtained [19]. The width of the energy gap of the study material associated with the *r* dimension of the studied particles can be expressed with the Brus equation (3) [20].

$$E_{nano} = E_{g(bulk)} + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1{,}8e^2}{4\pi\varepsilon\varepsilon_0 r} \tag{3}$$

where: $E_{g(nano)}$ – width of the energy gap of the nanometric material [eV], $E_{g(bulk)}$ – width of the energy gap of the micrometric material [eV], h – Planck constant, R – particle radius, m_h^* - hole effective mass, m_h^* - electron effective mass, e – electron charge, ε – ZnO dielectric constant, ε_0 – dielectric permittivity of free space.

If the following have been assumed: $E_{g(nano)} = 3.44$ [eV], $E_{g(bulk)} = 3.37$ [eV], $h = 4.125*10^{-15}$ [eVs], $m_e^* = 2.19*10^{-31}$, $m_h^* = 5.37*10^{-31}$, $e = 1.602*10^{-19}$ [C], $\varepsilon = 8.66$, $\varepsilon_0 = 8.85*10^{-12}$, the mean size of nanoparticles calculated based on the equation (3) is 2.3 nm. Based on the calculations performed it can be concluded that the radius of zinc oxide particles obtained is 2.3 nm, namely their diameter is 4.6 nm. Moreover, the position of a typical peak for the electromagnetic wavelength of 360 nm complies with the literature data [21]. The presence of this peak at this wavelength indicates that there are hexagonal ZnO nanoparticles (with the diameter of several nm) in the solution and their diameter is equal to their height. The results of studies obtained by article authors confirm this statement.

In order to evaluate the crystal structure of zinc oxide formed in the stock solution the colloidal solution that was obtained was subject to lyophilisation. The lyophilisation product was obtained as a result of heating at 100°C for 6 hours. The X-ray analysis has indicated (Fig. 4. 7) that the material has the structure of wurtzite which is typical of zinc oxide (Fig. 4.8).

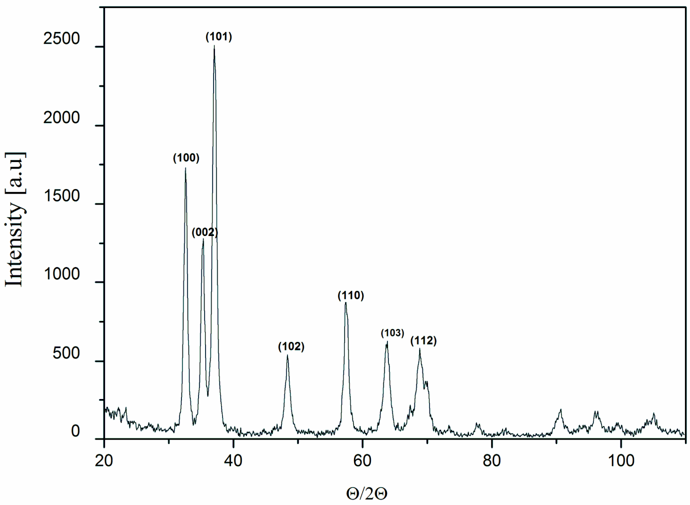

FIGURE 4.7
XRD pattern of prepared ZnO nanoparticles

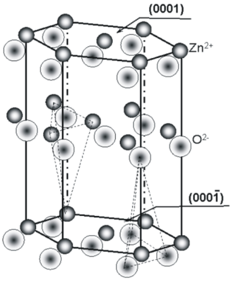

FIGURE 4.8
The wurtzite structure of ZnO

The average crystallite size ($L_{(002)}$) determined by Scherrer equation (4):

$$L_{(002)} = \frac{K \cdot \lambda}{B \cdot \cos\Theta} \tag{4}$$

where: K – Scherrer constant (0.7-1.7), θ – glancing angle a given interference band [rad]; λ – length of an X-ray radiation beam [A], B – integral width (FWHM) of the peak (002) [rad].

As a result of an analysis of a diffraction peak corresponding to the plane (002) B parameters and 2θ value were calculated, and then the mean size of ZnO crystallites was determined. If the following data have been assumed: K = 0.89; λ = 1.542 [Å]; B = 0.013 [rad]; 2θ=0.617 [rad], the mean size of crystallites calculated based on the equation (4) is 1.18 nm.

Consequently, as it can be concluded from the X-ray analysis nanoparticles are not monocrystals, but they are conglomerates of crystallites with the mean dimension of approx. 1.2 nm. However, the study results comply with the results of studies based on an optical analysis.

Effect of surfactant and polymer on zinc oxide morphology

When the effects of the surfactant levels on the dimensions and morphology of ZnO nanoparticles were determined Triton® X-100 was used, and it is a nonionic surfactant with a molecular formula of $C_{14}H_{22}O(C_2H_4O)_n$ (n = 9-10) (Fig. 4.9). This compound has a hydrophobic section, namely an aliphatic chain, and a hydrophilic section that includes a chain of ethylene oxide. As a result of such as structure, Triton® X-100 is a surface active agent, and therefore it tends to be adsorbed on the interface of colloidal systems resulting in stabilisation of their dispersions.

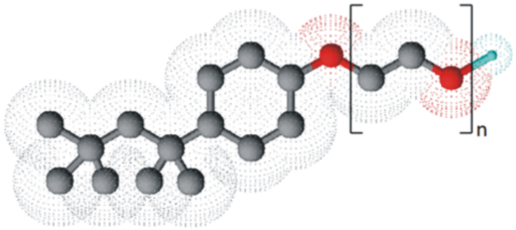

FIGURE 4.9
Molecular structure of Triton® X-100. Colors: gray-carbon, red-oxygen, cyan-hydrogen, n= 9-10

As a stabilizing polimer was used polyethylenimine (PEI). This cationic polymer has imine groups (Fig. 4.10) responsible for its excellent solubility in water in accordance with the following reaction (5).

$$R_3N + H_2O \leftrightarrow R_3NH^+ + OH^- \tag{5}$$

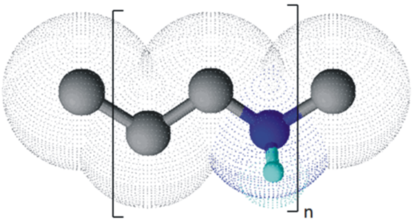

FIGURE 4.10
Molecular structure of PEI. Colors: gray-carbon, blue-nitrogen, cyan-hydrogen

As a result of a simultaneous use of two stabilising agents the system may be responsible for changes of parameters of the system that is being formed. The system that will be formed will have completely different parameters than the one synthesised in the presence of only one stabilising agent. In case of a simultaneous use of a cationic polymer and a surfactant when the amount of only one stabilising agent has been changed it can be observed that changes of surface tension are significantly different from the ones observed when the surfactant alone is used. It can be concluded from this relationship the addition of a polymer affects the shift of the critical micelle concentration (CMC) and as a result, a new typical inflexion on a graph is formed, and it is named critical aggregation concentration (CAC), and the polymer saturation point (PSP) is also formed [22] (Fig. 4.11).

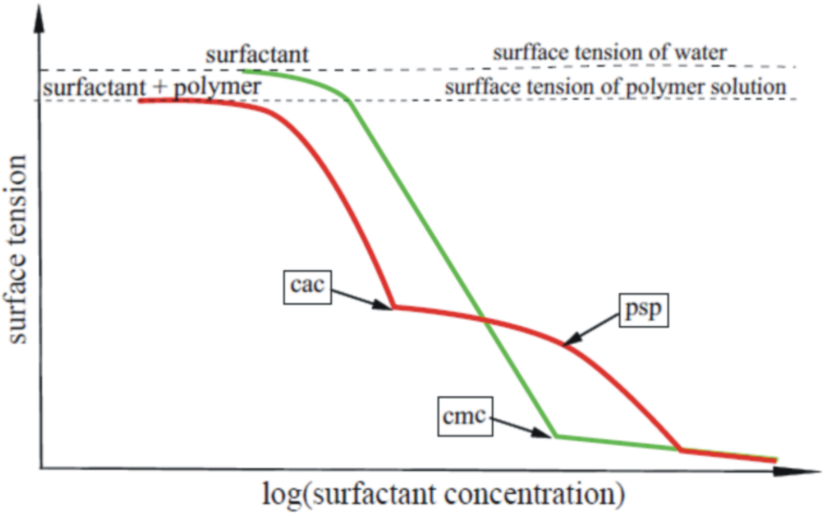

FIGURE 4.11
The relations between surface tension and amount of surfactant: green curve-only surfactant is present, red curve – surfactant and polymer

In order to describe physical changes that are present in the system it can be concluded that at the surfactant levels below CAC surfactant particles combine with polymer macroparticles as a result of electrostatic interactions, and micelles are not formed. When the CAC has been exceeded surfactant particles start to form micelles that are still attached to a polymer chain . When the surfactant amount still increases a polymer becomes saturated and cannot be bound to any more surfactant particles. Consequently, free micelles become to be visible in the system (Fig. 4.12) [22].

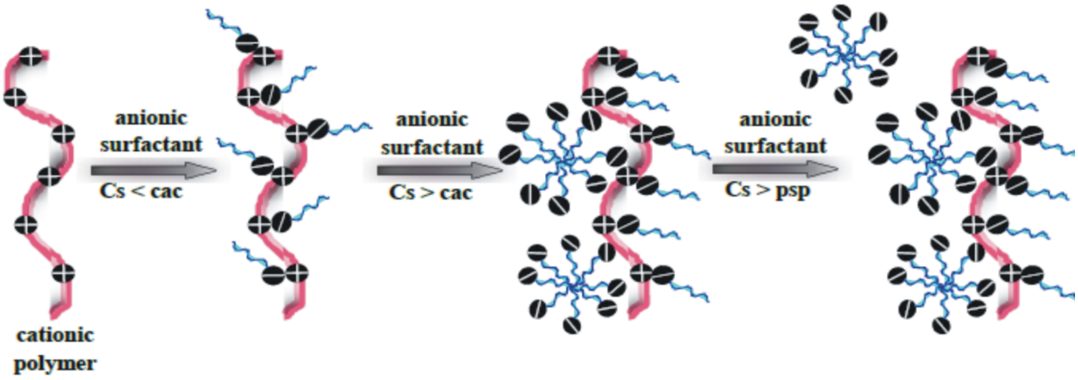

FIGURE 4.12
Diagram of changes which are present in a polymer-surfactant system when the surfactant amount is increased

The literature does not contain any information regarding the interactions between a cationic polymer and a nonionic surfactant. The authors of this paper suspect that the behaviour of a polymer-surfactant system in this situation is adequate to interactions observed in the case of two particles that are positively charged. In this case complexes are formed not as a result of electrostatic interactions, but of hydrogen bonds or van der Waals forces. When PEI and Triton® X-100 are used hydrogen bonds seem to be the most important. They can be observed between a hydrogen atom of the imine group of the polymer, and an oxygen atom within a surfactant molecule with an excessive negative charge which is a result of high electronegativity of this element.

The organisation of polymer-surfactant systems becomes significantly more complex when nanoparticles are additionally present in the system. In such a case a colloidal system is formed and there are new phenomena associated with the presence of interfaces at the nanoparticles-water border, and as a result one can observe interactions between system components that are completely different from the ones presented above. Such systems have not yet been described in the literature; however, there is information regarding the behaviour of polymer-surfactant systems in emulsions, that from a physical viewpoint, are similar to colloids. The main differences is the state of aggregation of the dispersed phase that can be of low significance with regard to phenomena under the analysis. The interface plays the most important role in this case, as it is a place where stabilising agents, namely a polymer and a surfactant become adsorbed.

Some publications report that different organisation variants in such systems can be observed, depending on the amount of a surfactant that has been used [23], and the order the components were added [24].

In the case of a constant polymer amount and gradually increasing surfactant levels several typical stages can be observed. When there is no surfactant in the system a polymer is adsorbed on the interface, and its excessive amount in the solution is formed in balls (Fig. 4.13a). When a surfactant is gradually added the system behaves similarly to a polymer-surfactant mixture. At first, single surfactant particles combine with polymer chains that are adsorbed on the interface ($C_s<CAC$) (Fig. 4.13b). When the surfactant levels exceed CAC micelles adsorbed on a polymer chain start to be formed (Fig. 4.13c).

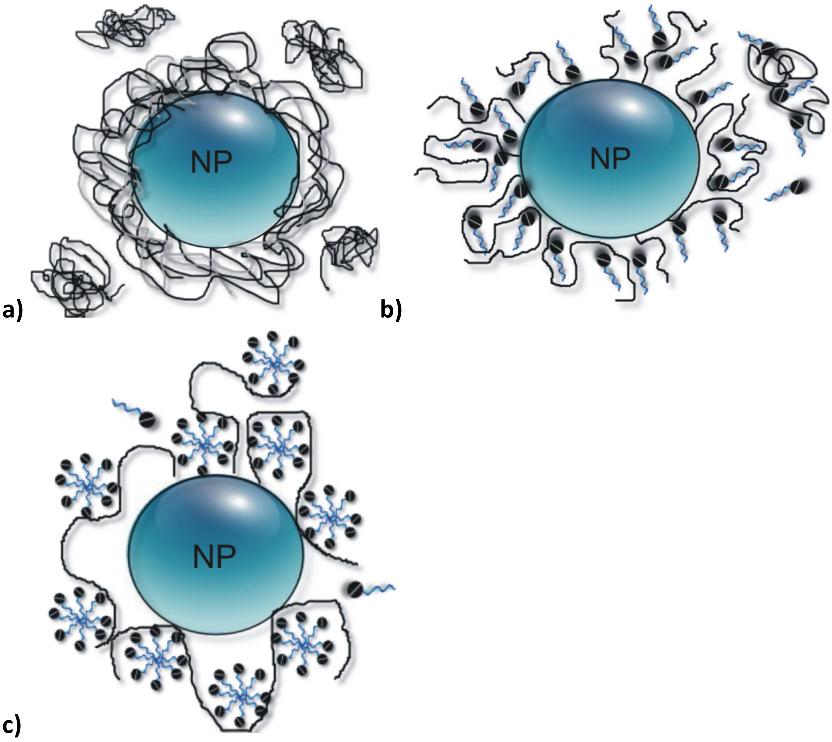

FIGURE 4.13
Diagram of interactions in the colloidal solution of nanoparticles (NP) when solution contains: a) only polymer, b) polymer and low surfactant levels, c) polymer and high surfactant levels

As the studies on emulsions [23-24] have demonstrated the fact what component (stabilising agent) was added as the first one is extremely significant for the system morphology. If the colloidal solution with nanoparticles is first supplemented with high surfactant levels then with a polymer, surfactant particles become adsorbed on the interface and micelles in the solution will be formed later. These micelles will be surrounded by polymer particles (Fig. 4.14a). When the colloidal solution of nanoparticles contains low surfactant levels, and then it will be additionally added to the system with a polymer, the particle structure in the solution will be the same as in the previous case (Fig. 4.14a). This situation will change drastically if a polymer is the first one to be added to the colloidal solution, followed by a surfactant. In this case at the initial stage the polymer becomes adsorbed on the nanoparticle surface. The surfactant that is added will also change conformation of particles of the polymer that has been adsorbed. Under its presence micelles that are also surrounded by a polymer chain will attach with one end of the polymer chain to the compact polymer capsule that is adsorbed on the nanoparticle surface (Fig. 4.14b).

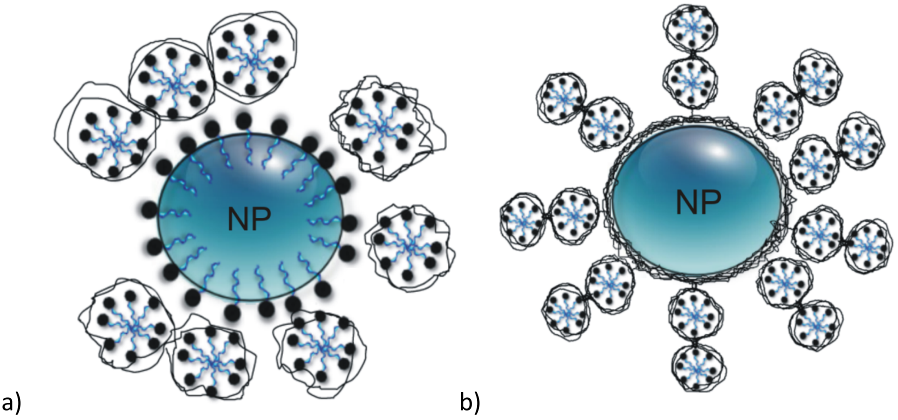

FIGURE 4.14
Diagram of interactions in the colloidal solution of nanoparticles when the following were added to the solution: a) first, excess surfactant levels, followed by a polymer; b) a polymer, followed by a polymer combined with a surfactant

To confirm the correctness of the theory above with regard to colloidal systems a series of synthesis processes of ZnO nanoparticles was performed, with changes of the ratio of the surfactant amount to the polymer amount in the stock solution in the range of 0.18% to 1200%. Zinc oxide colloidal solutions that were obtained were analysed in order to determine morphology and sizes of nanoparticles.
Studies regarding the average size of zinc oxide nanoparticles obtained using the DLS method indicated that the amount of the surfactant added slightly affected the size of nanoparticles obtained. When the amount of Triton® X-100 in the system increased suddenly, the average size of nanoparticles doubled (Tab. 4.1). These results confirm the statement that in the case of high surfactant levels micelles that are formed are built into a polymer chain (Fig. 4.14b) and as a result, the hydrodynamic radius of a nanoparticle that is measured with the DLS method increases.

TABLE 4.1
Size of ZnO nanoparticles depending on the quantity of the surfactant

Triton® X-100/PEI [%]	**Average size of ZnO nanoparticles [nm]**
0.18	5.5
12.00	5.6
26.67	5.6
44.44	5.7
1200	12.6

Analysis of ZnO nanoparticle morphology using TEM indicated that the surfactant amount also affected their shapes. A significant divergence between sizes of nanoparticles measured with DLS and TEM were also observed. This may be a result of differences in the behaviour of a colloid during preparation for tests. When measurements are performed with the DLS method a colloid suspension is diluted, and as a result, nanoparticle agglomeration is prevented. However, when samples are prepared for the TEM analysis, a diluent evaporates, and consequently, the levels of not only nanoparticles, but also stabilising agents increase, and it may be a factor responsible for agglomeration. This hypothesis is confirmed by TEM images that under great magnification demonstrate that these structures are made of an extremely large amount of nanoparticles (Fig. 4.15a). According to the authors these zinc oxide nanostructures are connected with ends of a polymer chain inside which there are micelles (Fig. 4.15b).

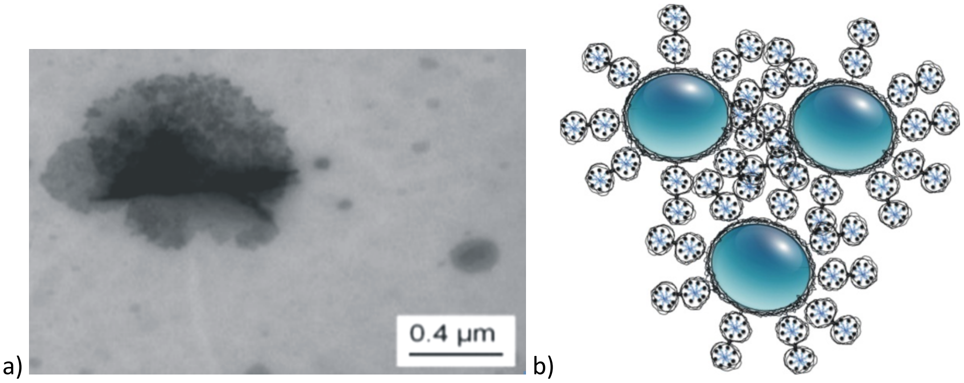

FIGURE 4.15
Zinc oxide nanoparticles: a) TEM images; b) scheme

TEM studies of zinc oxide nanoparticles also demonstrated that in a solution with low surfactant levels zinc oxide nanoparticles do not form agglomerates with irregular shapes (Fig. 4.16a). When zinc oxide was manufactured in the solution with slightly higher levels of Triton® X-100, regular circular agglomerates of ZnO were observed. It may indicate that the critical aggregation concentration (CAC) was exceeded and when samples were prepared for the TEM analysis micelle structures were formed (Fig. 4.16b). When the surfactant levels increased further TEM images presented circular structures as well, but their concentration was higher. It may be associated with the presence of free micelles as their presence prevents nanoparticles from combining into larger groups (Fig. 4.16c). When the surfactant levels increased again, the surface tension in the solution significantly reduced and therefore the tendency for agglomeration was lower in the system (Fig. 4.16d). When the highest levels of Triton X-100 were used the largest structures were observed, but they did not exhibit spherical symmetry. This time irregular agglomerates were formed, and they might have been a consequence of the fact that under such conditions a polymer was saturated (PSP was exceeded) and specific polymer-surfactant complexes were formed, as well as free micelles in a volumetric solution (Fig. 4.17e).

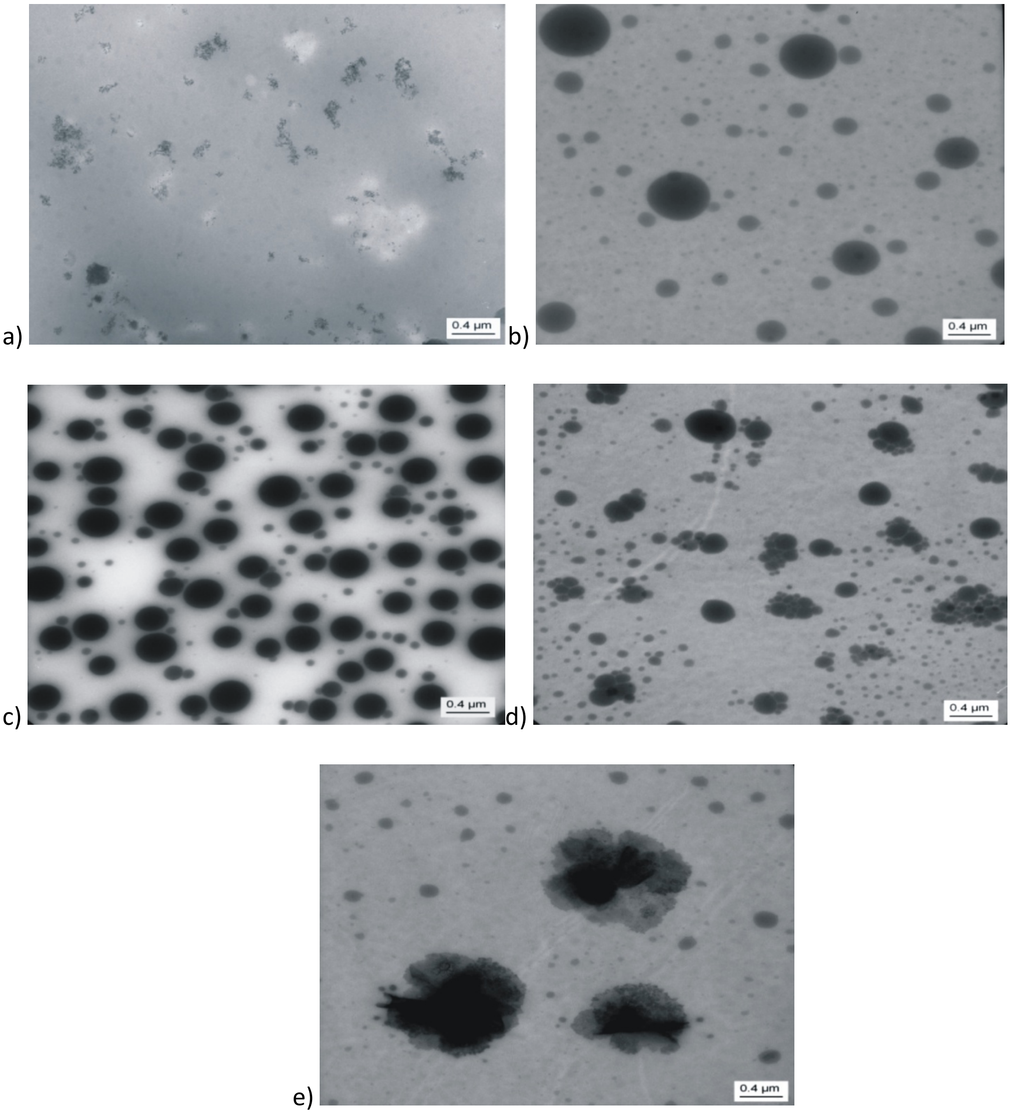

FIGURE 4.16
TEM images of zinc oxide nanoparticles synthesized in solution where ratio of Triton® X-100/PEI was a) 0.18%; b) 12.00 %; c) 26.67 %; d) 44.44 %; e) 1200 %

When comparing previous conformation patterns for polymer-surfactant-nanoparticle systems obtained for different surfactant amounts (Fig. 4.13) there is a clear analogy with TEM images obtained (Fig. 4.16). It is clearly visible that the system morphology changes when the surfactant is gradually added - from single zinc oxide nanoparticles that are surrounded only by a polymer to systems including single nanoparticles connected with each other with polymer and surfactant molecules.

Effect of the type of polymer on zinc oxide morphology

In addition, the effects of the type of a polymer used on dimensions and shapes of nanostructures that were formed were tested. In these studies high molecular weight polyethylenimine (PEI) and polyvinylpyrrolidone (PVP) with the mean molecular mass of 3.5 kDa were used (Fig. 4.17). During these studies the polymer levels in a reaction mixture were always 0.18 M.

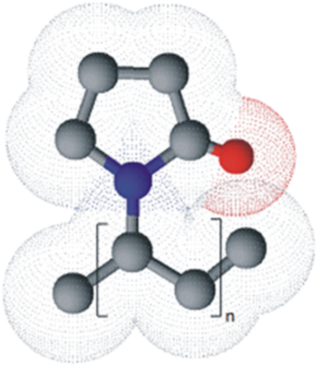

FIGURE 4.17
Molecular structure of PVP. Colors: gray-carbon, blue-nitrogen, red-oxygen

Studies indicated that the mean size of zinc oxide nanostructures that were formed significantly depends on a type of a polymer used. ZnO nanoparticles of significantly smaller dimensions were formed in a solution containing polyethylenimine than in a solution with polyvinylpyrrolidone (Tab. 4.2).

TABLE 4.2
The average size of ZnO nanoparticles obtained in presence of a different type of polymer

Type of polymer	Average molecular weight of polymer	Average particles size [nm]
PEI	high molecular	5.7
PVP	Mw = 3.5 kDa	150

Differences in sizes of nanoparticles measured with the DLS method may be associated with differences in the structure, namely the effects of polymers used as stabilising agents.The literature presents much information regarding stabilisation of metal oxide nanoparticles with polyvinylpyrrolidone. The first example may include the synthesis of cerium oxide nanoparticles in the presence of polyvinylpyrrolidone as a stabilising agent [25]. According to the authors of the publication a polymer applied may be bound to the nanoparticle surface with hydrogen bonds, and as a result, system agglomeration is not possible. Hydrogen bonds can be formed thanks to a stratal structure of nanoparticles, namely the core-shell type. It means that such a system contains an outer layer formed of metal hydroxide apart from the inner phase with its oxide.

The mechanism of zinc oxide nanoparticle formation in the presence of a stabilising agent such as polyvinylpyrrolidone may be similar to the formation of zirconium oxide (IV) in the presence of this stabilising agent (Fig. 4.18).

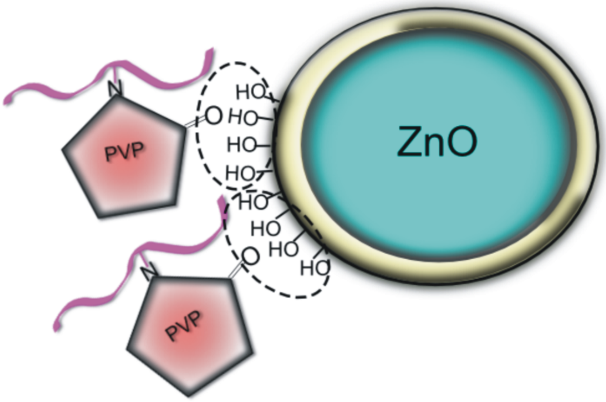

FIGURE 4.18
Schematic interactions between PVP and surface of ZnO nanoparticles

Polyvinylpyrrolidone, similarly to polyethylenimine, is a cationic polymer however, with a completely different structure. In the PVP structure there is a ring with a nitrogen atom and an oxygen atom connected with a double bond to the ring. Therefore, this polymer does not form branched structures such as the ones formed by PEI. In PVP molecules there is a reversible electron transfer between a nitrogen atom and an oxygen atom, and consequently, the macromolecule is both negatively and positively charged (Fig. 4.19) [26]. This phenomenon is not observed in the case of polyethylenimine that only has a positive charge.

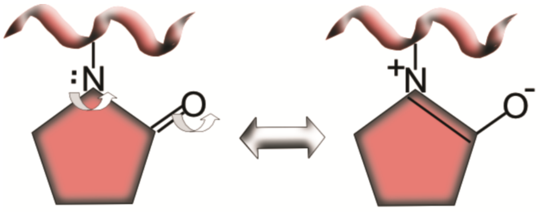

FIGURE 4.19
Charge transfer in the PVP ring

When this compound is used as a stabilising agent during the synthesis of zinc oxide it was observed that this polymer forms a very strong complex with metal ions as a result of a strong interaction between these ions and negatively charged oxygen atoms [27]. Formed complexes of zinc with PVP were permanent, and only when an appropriate amount of hydroxide was added to the solution the complex was split and metal oxide nanoparticles were formed. (Fig. 4.20). When complexes split zinc oxide particles and PVP macroparticles are formed, and the latter stabilise nanoparticles that are formed. For this reason the formation of significantly larger ZnO nanoparticles in the presence of polyvinylpyrrolidone than in the presence of polyethylenimine (Tab. 4.2) is a result of temporary lack of stabilisation of zinc oxide after its precipitation from the complex, because during ZnO precipitation a stabilising agent is not present as it is connected with remaining zinc ions in a complex.

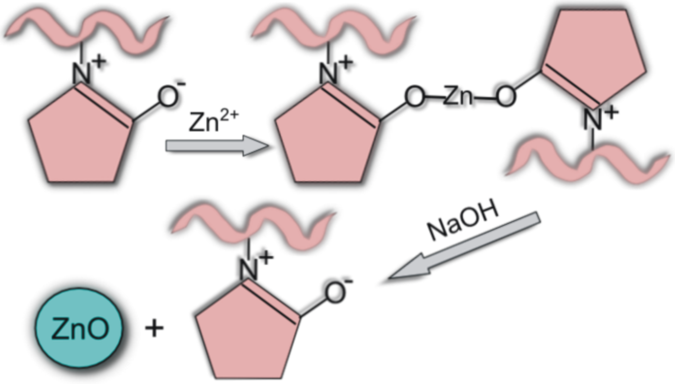

FIGURE 4.20
Diagram of the Zn-PVP complex split under the influence of sodium hydroxide

Microscopic observations performed with TEM clearly demonstrated that a type of a polymer stabilising agent significantly affects the shape and dimensions of nanoparticles that are formed. When PEI is used as a nanoparticle stabilising agent regular circular structures are observed (Fig. 4.16c). In the presence of PVP crystallites with a hexagonal structures were formed, and with dimensions that significantly exceeded the ones obtained when PEI was used (Fig. 4.21).

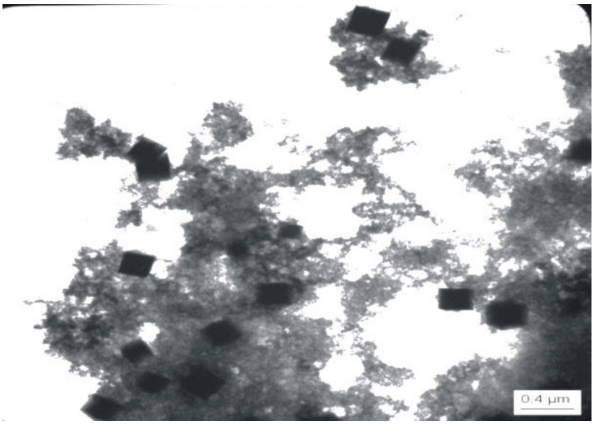

FIGURE 4.21
TEM images of zinc oxide nanoparticles formed in a solution stabilised with PVP with the mean molecular mass of 3.5 kDa

It can be suspected that low molecular mass polymers containing rings as substituents have a lower tendency for folding into structures similar to balls. As a result, a nanoparticle that is formed is surrounded by quasi-linear chains. As a result of this process of stabilisation hexagonal particles are formed because zinc oxide crystallises in the wurtzite structure. Additionally, structures that are formed stabilise surfactant particles (Fig. 4.22).

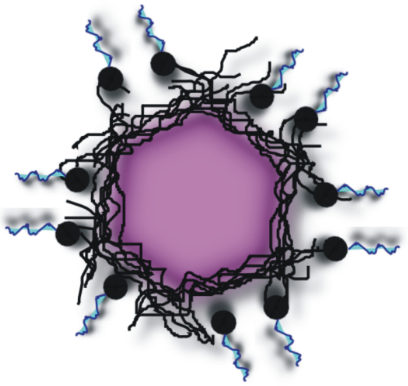

FIGURE 4.22
The possible way to create hexagonal ZnO particles

Conclusions

A simple method to synthesis zinc oxide nanoparticles in the presence of polymer and surfactant stabilising agents is described. This repetitive and cost-effective method can be used to synthesise zinc oxide nanostructures with the mean dimension of approx. 6 nm. Nanoparticles that are formed were not monocrystals, but they are conglomerates of crystallites with the mean dimension of approx. 1.2 nm. The optical energy gap of nanoparticles that are formed is 3.44 eV, which is higher than that of volumetric material.

The analysis of the effects of the amount of a nonionic surfactant to the amount of a cationic polymer clearly demonstrated that there are numerous interactions between these components. When the surfactant amount was increased with regard to the polymer amount changes typical of polymer-surfactant systems were observed. DLS and TEM studies showed that also for polymer-surfactant-colloid systems specific transfers such as CAC (critical aggregation concentration) and PSP (polymer saturation point) are observed. Results indicate that in order to describe phenomena occurring in three-component systems described in this section rules describing two-component systems such as polymer-surfactant systems can be successfully used.

In solutions stabilised with PEI when the surfactant levels are increased agglomeration can be observed as a result of the formation of micelles in a polymer chain.

It was observed that there may be significant differences between dimensions of nanoparticles measured with DLS and TEM methods. These differences are due to differences with regard to methods of preparing samples for tests. In the TEM method samples are dried and consequently, nanoparticle agglomerate during this process.

The stabilisation mechanism changed when the polyvinylpyrrolidone (PVP) with the mean molecular mass of 3.5 kDa was used as a stabilising agent. Due to a charge transfer observed in particles of this polymer this compound forms a stable complex with zinc ions. The presence of this complex and the presence of a ring in a PVP molecule affect the dimensions and shape of ZnO particles that are formed.

Acknowledgments

Scientific work financed from funds for science in the years 2013 – 2017 as a research project within the program under the name „Diamond Grant” No DI2012 008542 and the project was funded by the National Science Centre based on decision number DEC-2012/07/N/ST7/02304.

References

1. Xiaoming P, Yiwang C, Fan L, Weihua Z, Yuehui H. Preparation and optical properties of ZnO@PPEGMA nanoparticles. Applied Surface Science 2009; 255 (16) 7158-7163.
2. Hong R Y., Li J H, Chen L L, Liu D Q, Li H Z, Zheng Y, Ding J. Synthesis, surface modification and photocatalytic property of ZnO nanoparticles. Powder Technology 2009; 189 (3) 426-432.
3. Shih-Wei C, Jenn-Ming W. Nucleation mechanisms and their influences on characteristics of ZnO nanorod arrays prepared by a hydrothermal method. Acta Materialia 2011; 59 (2) 841-847.
4. Xiulan H, Yoshitake M, Tatsuki O, Kazumi K. Fabrication of ZnO nanowhiskers array film by forced-hydrolysis-initiated-nucleation technique using various templates. Thin Solid Films 2009; 518 (2) 621-624.
5. Wang W-W, Zhu Y-J. Shape-controlled synthesis of zinc oxide by microwave heating using an imidazolium salt. Inorganic Chemistry Communications 2004; 7 (9) 1003-1005.
6. Ju M, Li Q, Wang E. Facile template-free fabrication of olive-like ZnO nanoparticles and their photoluminescence properties.Materials Letters 2011; 65 (3) 507-509.
7. Hong R Y, Qian J Z, Cao J X. Synthesis, and characterization of PMMA grafted ZnO nanoparticles. Powder Technology 2006; 163 (3) 160-168.
8. Tan W K, Razak K A, Ibrahim K, Lockman Z. Formation of ZnO nanorod arrays on polytetraflouroethylene (PTFE) via a seeded growth low temperature hydrothermal reaction. Journal of Alloys and Compounds 2011; 509 (3) 820-826.
9. Wu R, Xie C, Xia H, Hu J, Wang A. The thermal physical formation of ZnO nanoparticles and their morphology. Journal of Crystal Growth 2000; 217 (3) 274-280.
10. Hembram K, Sivaprahasam D, Rao T N. Combustion synthesis of doped nanocrystalline ZnO powders for varistors applications. Journal of the European Ceramic Society 2011; 31 (10) 1905–1913.
11. Fortunato E, Barquinha P, Pimentel A, Goncalves A, Marques A, Pereira L, Martins R. Recent advances in ZnO transparent thin film transistors. Thin Solid Films 2005; 487(1-2) 205−211.
12. El Shafei A, Shaarawy S, Hebeish A. Application of reactive cyclodextrin poly butyl acrylate preformed polymers containing nano-ZnO to cotton fabrics and their impact on fabric performance. Carbohydrate Polymers 2010; 79 (4) 852-857.
13. Baruah S, Dutta J. pH-dependent growth of zinc oxide nanorods, Journal of Crystal Growth 2009; 311 (8) 2549-2554.
14. Xiao-bo L, Hong-lie S, Zhang H. Optical properties of nanosized ZnO films prepared by sol-gel process. Transactions of Nonferrous Metals Society of China 2007; 17 814-817.
15. Kim K S, Jeong H, Jeong M S, Jung G Y. Polymer-templated hydrothermal growth of vertically aligned single-crystal ZnO nanorods and morphological transformations using structural polarity. Advanced Functional Materials 2010; 20 (18) 3055–3063.

16. Ito S, Makari Y, Kitamura T, Wada Y, Yanagida S. Fabrication and characterization of mesoporous SnO2/ZnO-composite electrodes for efficient dye solar cells. Journal of Materials Chemistry 2004; 14 385-390.
17. Golas P L, Louie S, Lowry G V, Matyjaszewski K, Tilton R D. Comparative study of polymeric stabilizers for magnetite nanoparticles using ATRP. Langmuir 2010; 26 (22) 16890–16900.
18. Liu M, Nam C-Y, Black C T, Kamcev J, Zhang L. Enhancing water splitting activity and chemical stability of zinc oxide nanowire photoanodes with ultrathin titania shells. The Journal of Physical Chemistry C 2013; 117 (26) 13396–13402.
19. Wei B, Zheng K, Yuan Ji Y, Zhang Y, Zhang Z, Han X. Size-dependent bandgap modulation of zno nanowires by tensile strain. Nano Letters 2012; 12 (9) 4595–4599.
20. Brus L E. Electron–electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state. The Journal of Chemical Physics 1984; 80 4403.
21. Balachandra Kumar K, Raji P. Synthesis and characterization of nano zinc oxide by sol gel spin coating. Recent Research in Science and Technology 2011; 3 (3) 48-52.
22. Felippe A C, Bellettini I C, Eising R, Minatti E, Giacomelli F C. Supramolecular complexes formed by the association of poly (ethyleneimine) (PEI), sodium Cholate (NaC) and sodium dodecyl sulfate (SDS). Journal of the Brazilian Chemical Society 2011; 22 (8) 1539-1548.
23. Philip J, Gnanaprakash G, Jaykumar T, Kalyanasundaram P, Mondain-Monval O, Raj B. Interaction between emulsion droplets in the presence of polymer-surfactant complexes. Langmuir 2002; 18 (12) 4625–4631.
24. Philip J, Gnanaprakash G, Jayakumar T, Kalyanasundaram P, Raj B. Three distinct scenarios under polymer, surfactant, and colloidal interaction. Macromolecules 2003; 36 9230-9236.
25. Otsuka T, Chujo Y. Preparation and characterization of poly(vinylpyrrolidone)/zirconium oxide hybrids by using inorganic nanocrystals. Polymer Journal 2008; 40 1157–1163.
26. Zhu S, Chen X, Zuo F, Jiang M, Zhou Z, Hui D. Controllable synthesis of ZnO nanograss with different morphologies and enhanced performance in dye-sensitized solar cells. Journal of Solid State Chemistry 2013; 197 69–74.
27. Kavitha M K, John H, Gopinath P. Polyvinyl pyrrolidone assisted low temperature synthesis of ZnO nanocones and its linear and nonlinear optical studies. Materials Research Bulletin 2014; 49 (1) 132–137.