DOI: 10.1002/masy.200750820

Composite Particles: Design of Hybrid Materials on the Nano-Scale

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Summary: In the last decade there has been a steady increased interest in the techniques providing design of nano-structured materials. It has been demonstrated that colloidal polymeric particles can be successfully used for the deposition of different functional nano-materials. Due to their numerous attractive properties polymeric particles have been used as templates for the synthesis, storage and transportation of nanostructured materials. This contribution demonstrates the synthetic ways for the preparation of hybrid particles by effective control over the size, morphology and distribution of the non-miscible phases. Developed methods allow design of the composite particles on the nanometer scale and opens new possibilities for the preparation of the materials with advanced properties. The synthesis, characterization and applications of hybrid particles are discussed in detail.

Keywords: hybrid particles; latex particles; microgels; nanoparticles

Introduction

The high efficiency of chemical reactions as well as their coupling in time and space is realized in the nature by using well-defined reaction environments on the broad size scale varying from nanometer-sized objects (enzymes) to micrometer-sized assemblies (cells). The attempts to create such nano- or microreactors by fully synthetic pathways or the combination of natural and synthetic approaches resulted in a large amount of reports available in the literature.[1] The wide range of nano- and microreactors that have been constructed include molecular structures like micelles[2–3] and vesicles,[4–5] macromolecular structures like polymersomes[6–7] and block copolymer micelles,[8–9] polymer capsules[10–11]) and biomacromolecular structures[12–13] like protein cages,[14–15] viruses[16–17] etc. It has been realized that polymeric particles can be also effectively used for the preparation of the composite materials on sub-micrometer scale. This can be achieved by the introduction of different materials such as conjugated polymers, proteins, semiconductors, metals or metal oxides, bio-minerals in form of nanoparticles into the porous microgel structure or onto the surface of compact latex particles. In this way one can expect the formation of multi-functional colloids where typical features of polymeric particles (defined size and morphology, large surface area etc.) can be combined with the properties of incorporated functional materials such as conductivity, magnetic response, catalytic activity etc. This approach can open principally new possibilities for application of colloidal particles in different technological systems.

Different functional materials can be incorporated into the microgel or latex particle structure by following approaches. Firstly, the pre-formed nanoparticles can be integrated into the polymeric beads by encapsulation during microgel or latex particle synthesis (for example in inverse heterophase polymerization process). In

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this case filler material with pre-selected properties (size, morphology etc.) is mechanically ''locked'' within the polymeric network. Secondly, nanoparticles can be generated inside of the swollen microgel or at the surface of latex particles acting as templates by means of polymerization processes, reduction/oxidation or precipitation reactions. In this case one can expect that the structure of the polymeric template will influence the properties of formed nanoparticles as well as their fixation and distribution in the microgel interior or at the latex surface. Thirdly, one can prepare composite particles using so called ''breathing in'' method e.g. soaking pre-designed nanoparticles into the microgel network during swelling process or adsorbing them on the latex surface. The first two approaches are the most promising since they provide better control over the filler content and its distribution inside of the microgels or at the latex particle surface.

Experimental Part

Materials

Styrene (ST) (from Fluka), *N*-vinylcaprolactam (VCL) (from Aldrich) and acetoacetoxyethyl methacrylate (97%) (AAEM) (from Aldrich) were purified by conventional methods and then vacuum distilled under nitrogen. ω-hydroxy poly(ethylene glycol)methacrylate (PEGMA, Aldrich) with average $M_w =$ 526 g/mol was used as supplied. Zinc acetate ($Zn(Ac)_2$), thioacetamide (TAA) were received from Aldrich and used as commercially available. Initiators, 2,2′-azobis(2- methylpropyonamidine) dihydrochloride (AMPA) and sodium peroxodisulfate (97%) (SPDS) were obtained from Aldrich and used as received. Cross-linker *N,N′*-methylenebisacrylamide (BIS) from Aldrich was used without further purification. Distilled water was employed as polymerization medium.

Synthesis of PS/AAEM Core Particles

A double-wall glass reactor equipped with stirrer and reflux condenser was purged with nitrogen. Water (170 g) and appropriate amounts of ST (19,5 g) and AAEM (0,5 g, 2,5% to ST) were added into the reactor and stirred at room temperature. After 10 min the temperature was increased up to 70 °C and a water solution of the initiator SPDS (0,3 g in 10 g water) was added to start the polymerization process. Latex with a approximately 10% solid content were achieved.

Synthesis of VCL/AAEM Microgels

Appropriate amounts of AAEM (0,16 g), VCL (1,98 g) and cross-linker (3 mol-%) were added in 145 ml deionized water. Double-wall glass reactor equipped with stirrer and reflux condenser was purged with nitrogen. The solution of the monomers was placed into the reactor and stirred for 1 h at 70 °C under purging with nitrogen. After that a 5 ml water solution of initiator (5 g/l) was added under continuous stirring. Reaction was carried out for 8 hours. Microgel dispersion was purified by dialysis with Millipore Dialysis System (cellulose membrane, MWCO 100.000).

Synthesis of Composite Particles

Diluted dispersions of the latex particles (PS/AAEM) or microgel particles (VCL/AAEM) were placed into a glass vessel and $Zn(Ac)_2$ and TAA solutions were added ($Zn(Ac)_2$:TTA molar ratio was 1:1). The reaction mixture was ultrasonically agitated by a titanium tip which was directly immersed into the solution (Branson Sonifier, power output 90 W, pulsed operation regime 20%). After 6 hours the formed composite particles were removed from the reaction vessel and cleaned by precipitation to remove all by-products. The pH of purified dispersions was around 5,8.

Analytical Methods

Particle Size Analysis

A commercial laser light scattering (LLS) spectrometer (ALV/DLS/SLS-5000) equipped with an ALV-5000/EPP multiple digital time correlator and laser goniometer system ALV/CGS-8F S/N 025 was used with a helium-neon laser (Uniphase 1145P, output power of 22 mW and wavelength of 632.8 nm) as the light source.

Scanning Electron Microscopy (SEM)

SEM images were taken with Gemini microscope (Zeiss, Germany). Samples were prepared in the following manner. Dispersions were diluted with deionized water, dropped onto aluminium support and dried at room temperature. Samples were coated with a thin Pd layer to increase the contrast and quality of the images. Pictures were taken at a voltage of 4 kV.

Transmission Electron Microscopy (TEM)

TEM images were obtained with Zeiss Omega 912 at a voltage of 10 kV. Diluted microgel dispersions were placed onto Au nets and dried at room temperature.

UV Measurements

Thin transparent films have been prepared on quartz plates and investigated with PerkinElmer UV/VIS spectrometer Lambda 45.

Thermo Gravimetrical Analysis (TGA)

To determine the ZnS content in the composite particles TGA 7 Perkin Elmer instrument (Pyris-Software Version 3.51) was used. Before measurement the samples were dried in vacuum for approx. 48 hours. The samples were analyzed in closed aluminium cups in a temperature range from 25 to 600 °C (heating rate 5 K/min in nitrogen atmosphere).

Results and Discussion

Herein we demonstrate several synthetic approaches for the preparation of composite particles containing metal sulphides. Zinc sulphide (ZnS) is widely used in numerous technical systems such as paints,[18] solar cells,[19] IR-windows[20] etc. The formation of ZnS colloids with a defined size can be achieved by precipitation and aggregation methods.[21,22] The preparation of composite particles containing metal sulphides in nanocrystalline form can provide new application possibilities for this important sub-division of semiconductors.

General Synthetic Route

The general synthetic route is schematically shown in Figure 1. The initial step is the preparation of the polymeric template (in present case porous microgel or dense latex particle). The most important requirements to the polymeric template are: colloidal stability, reactive surface and narrow size distribution. During the second step the starting materials in the form of soluble salts are introduced into the colloidal system and the preparation of nanocrystals begins by the addition of the reducing agent, precipitation agent or the application

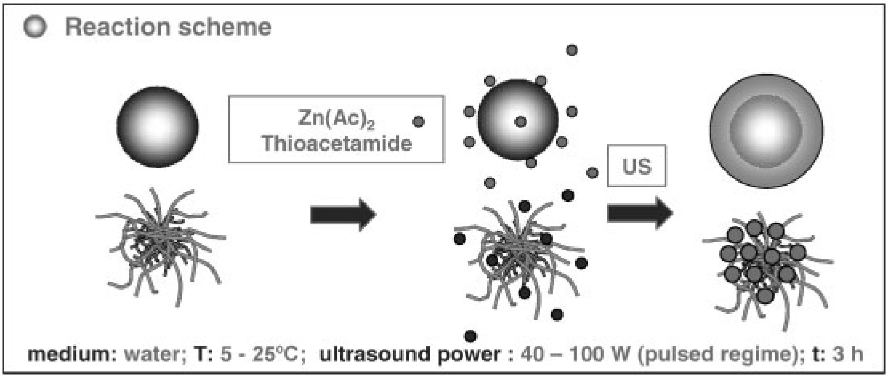

Figure 1.
The simplified synthetic route for the preparation of hybrid particles.

of a microwave, e-beam, laser irradiation or ultrasound as in the case with metal sulphides.

Hybrid Microgels

The basic microgel system used in the present study was prepared by copolymerization of acetoacetoxyethyl methacrylate (AAEM) and N-vinylcaprolactam (VCL) in a dispersion polymerization process.[23] The VCL/AAEM microgels possess several interesting properties such as thermosensitivity, biocompatibility, excellent colloidal stability etc. Additionally, β-diketone groups originating from AAEM provide effective formation of hydrogen bonds supporting the interactions with inorganic nanoparticles offering more efficient incorporation of inorganic particles into microgels. The variation of the zinc acetate concentration in the reaction mixture allows an effective control over the deposited ZnS amount in the polymeric particles. TEM investigations allowed obtaining elemental mapping images (EMI) for hybrid particles prepared with different ZnS contents. Results are presented in Figure 2a–c for microgels containing 3,26%, 13,62% and 18,84% ZnS. In this case the light areas are polymeric particles and areas enriched with Zn appear as black dots. Figure 2d–f presents inverse images of similar samples where only Zn areas are visible as light dots. One can see that the increase of the Zn-signal in EMI images increase with increasing ZnS content in the hybrid microgels. At low ZnS content (Figure 2a) one can find large areas where Zn-signal is very strong. This effect is present due to the migration of ZnS inclusions during drying and partial film-formation process which leads to some local phase separation. Particles with higher ZnS contents show less tendency to film-formation therefore such effects are not present.

It has been found that controlled drying of concentrated microgel dispersions leads to the formation of thick, optically transparent films with an excellent quality. Figure 3a–c shows photographs of such films prepared on a glass surface by drying at room temperature.

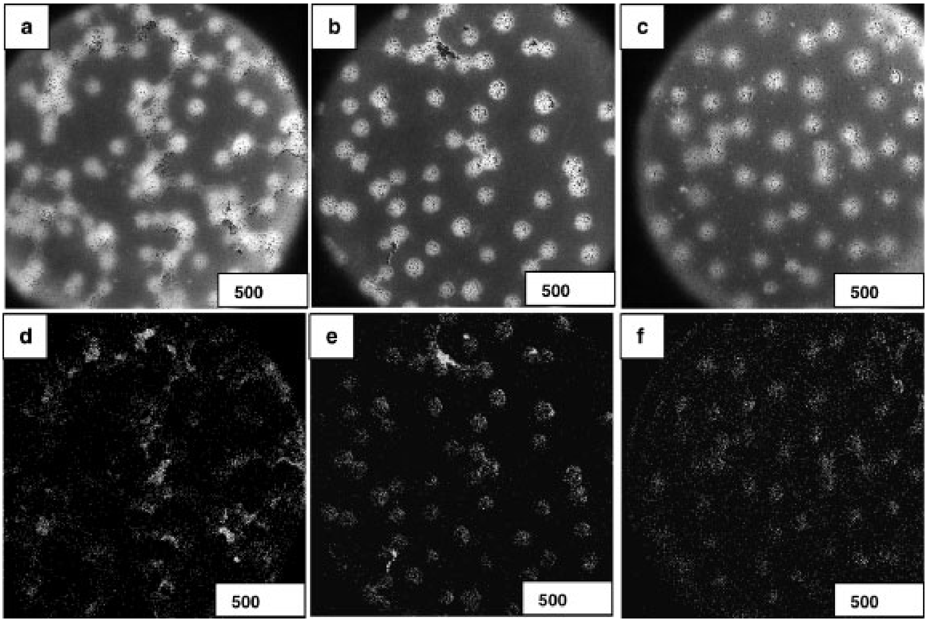

Figure 2.
Elemental mapping images of microgels containing 3,26% (a, d), 13,62% (b, e) and 18,84% (c, f) ZnS.

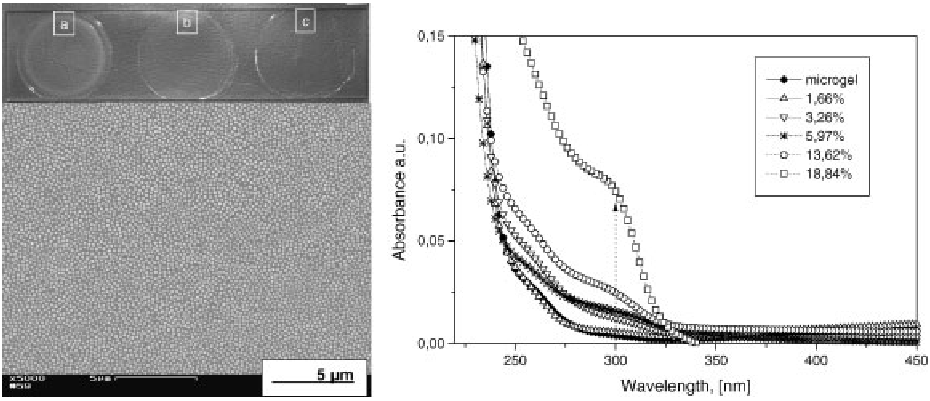

Figure 3.
Photographs of films prepared from hybrid microgels with different ZnS contents: 1,66% (a); 5,97% (b); 18,84% (c) (bottom image – SEM micrograph of sample c) (left); UV-VIS spectra of composite films (right).

One can see that there is no influence of the ZnS content on the film quality and in all cases no visible phase separation can be detected. A closer look on the morphology of such coatings with microscope (Figure 3) clearly indicated an organized arrangement of hybrid particles into special arrays where white dots represent microgel cores with ZnS and flexible shells form the continuous phase. UV/VIS-measurements have been performed to characterize the optical properties of the optically transparent composite microgel films. As shown in Figure 3, the sample prepared at the smallest ZnS content showed an onset of absorption at approx. 350 nm. The increase of the ZnS content in the samples leads to the gradual shift of the onset absorption to higher wavelengths. It is known that the UV/VIS onset absorption of semiconductor particles is attributed to the band gap absorption and, as expected, it should be red-shifted if ZnS particles grow in size.

In similar way, microgels have been present in the reaction system during the synthesis of the conducting polymers,[24–26] noble metals,[27] metal sulphides[28] or magnetic oxides.[29] As shown in Figure 4, inorganic materials in form of nanoparticles are integrated into the microgel structure.

The microgel network provides stabilization of the nano-materials as well as control of size and morphology of the nano-crystals to some extent. The hybrid particles containing noble metal nanoparticles integrated into the microgel network have been used as catalyst in aqueous systems for chemical synthesis or water cleaning. In our recent studies we demonstrated that catalytic activity of metal nanoparticles can be controlled by the microgel matrix. The thermoreversible swelling-deswelling behavior of the microgel can provide control over the distance between the gold nanoparticles in the polymer network. Additionally, the diffusion of the reactants and their adsorption on the catalyst surface can be better controlled. The hybrid microgels filled with semiconductor nanoparticles (metal sulphides) can be used effectively as photocatalyst in aqueous or organic media. Microgel particles containing magnetic metal oxides have been used as enzyme carriers in the direct bleaching of textiles or waste-water treatment. The microgels with incorporated biominerals such as hydroxyapatite or calcium carbonate can be used for the dug delivery purpose or preparation of synthetic scaffolds for the bone repair.

Hybrid Core-Shell Particles

For the preparation of the hybrid core-shell structures PS/AAEM particles have been prepared by a surfactant-free copolymerization of styrene (ST) and acetoacetoxyethyl methacrylate (AAEM).[30] Due to the hydrophilic character of AAEM it can be predominantly located on the particle sur-

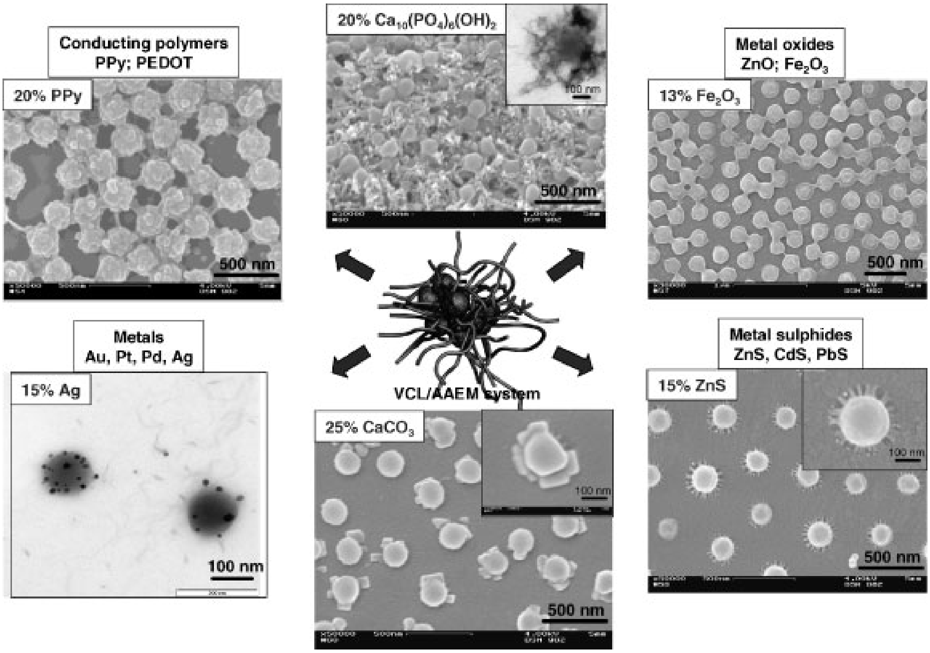

Figure 4.
Hybrid microgels prepared by filling VCL/AAEM microgel particles with different materials.

face after the copolymerization process with styrene and stabilizes the obtained colloidal system. In this system it is easy to control the particle size by changing the amount of AAEM in the reaction mixture.

The growth of the ZnS shell on the polymeric particle surface has been monitored by microscopy measurements. SEM images presented in Figure 5 confirm clearly the homogeneous distribution of

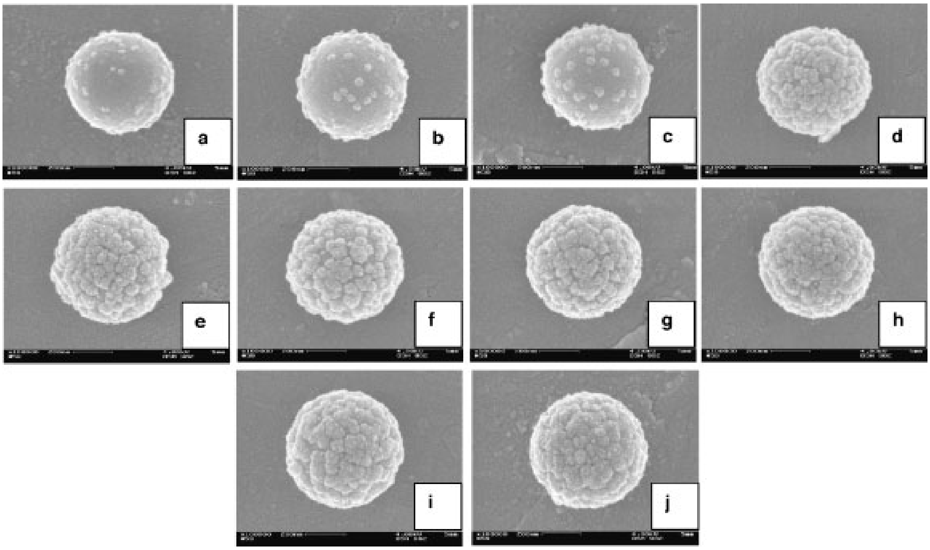

Figure 5.
SEM images of PS/AAEM/ZnS particles at different reaction times (min): a – 5; b – 10; c – 15; d – 20; e – 60; f – 120; g – 180; h – 240; i – 300; j – 360.

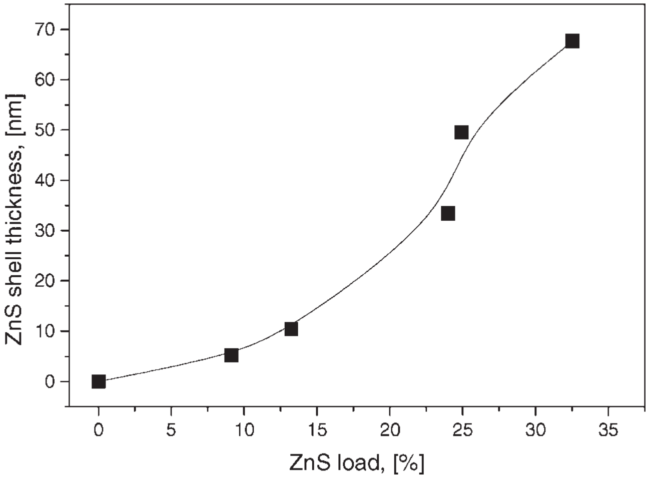

Figure 6.
Thickness of inorganic shell on the particle surface as a function of ZnS load.

the growing ZnS nanoclusters at different reaction times. After 20 min polymeric particles are nearly completely covered with ZnS. With increasing reaction time the ZnS shell becomes more compact and thicker leading to some increase of the hybrid particles size.

The average thickness of the ZnS shell obtained from SEM measurements as a function of ZnS load is shown in Figure 6. Results presented in Figure 6 indicate that the shell thickness increases continuously and it is well-controlled by amount of loaded ZnS.

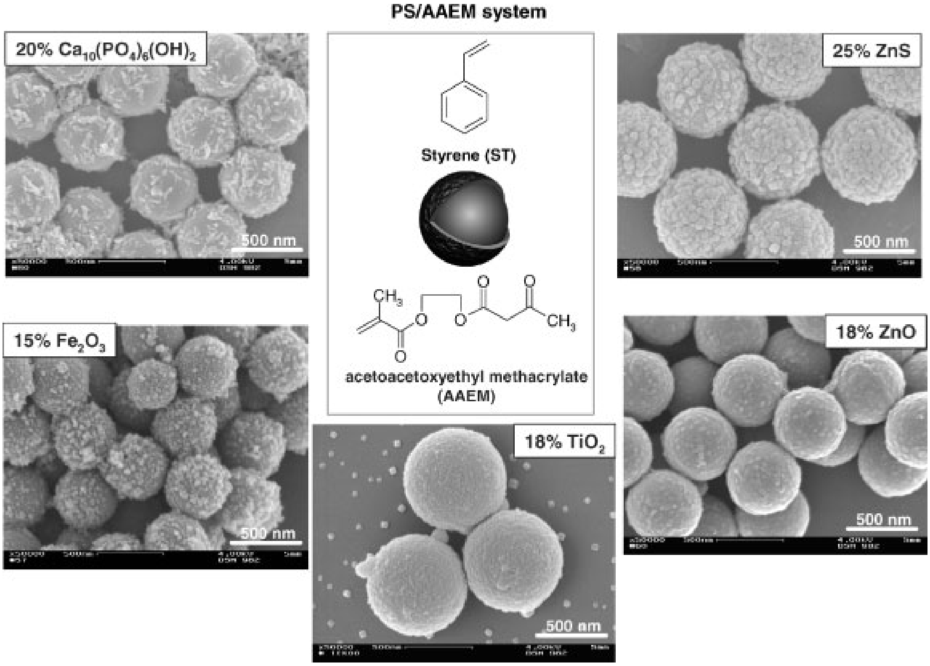

Figure 7.
Hybrid core-shell particles prepared by using PS/AAEM polymeric particles as cores.

The PS/AAEM particles have been successfully used for the deposition of different inorganic materials on their surface. Figure 7 demonstrates the SEM images of different hybrid particles.

The PS/AAEM system was effective for the deposition and growth of different nanoparticles such as magnetic oxides,[30,31] metal sulphides,[32] metal oxides and biominerals (hydroxyapatite). This effect was achieved due to the ability of the β-diketone groups of AAEM to complex metals and to build hydrogen bonds with different inorganic materials. In the case of different materials it was possible to control: a) the amount of the nanoparticles on the polymer surface; b) the morphology of the hybrid particles (raspberry or core-shell) and c) the colloidal properties of the hybrids.

Conclusions

The presented results demonstrate that the combination of polymeric colloids with inorganic nanoparticles provides an effective way for the preparation of nanostructured particles with interesting properties. The most important parameters are the morphology and chemical composition of the polymeric template which leads to the great extent concerning the growth, attachment and distribution of nanomaterials on the particle surface or in the particle interior. The effective control over the preparation method of the hybrid materials as well as their physico-chemical properties provide effective utilization of the hybrid particles for the design of multifunctional materials with advanced properties.

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