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Hybrid Microgels Containing Gold Nanoparticles

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Abstract: In present paper we report on a preparation of hybrid microgels filled with gold nano-particles (AuNPs). Temperature-sensitive VCL/AAEM microgels have been used as containers for deposition of Au by *in situ* formation of gold nano-particles. Synthesis of AuNPs has been performed by two methods: a) reduction of chloroauric acid with sodium borhydride and b) reduction of chloroauric acid by sodium citrate under ultrasonic agitation. In both cases AuNPs were deposited directly into microgels leading to formation of composite particles which exhibit temperature-sensitive properties, tunable gold contents and high colloidal stability. The influence of Au load on microgel size, morphology, swelling-deswelling behaviour and stability is discussed.

Introduction

Gold nanoparticles (AuNPs) are the most stable metal nanoparticles and have attracted much attention due to their assembly of multiple types, size related electronic, magnetic and optical properties (quantum size effect), and their applications to catalysis and biology.

Among the conventional methods of synthesis of AuNPs by reduction of gold(III) derivatives, the most popular are citrate reduction of $HAuCl_4$ in water [1]. The Brust-Schiffrin method for AuNPs synthesis [2] offered a facile synthesis of thermally stable particles of reduced polydispersity and controlled size (ranging in diameter between 1,5 and 5,2 nm). This technique uses thiol ligands that strongly bind gold and such AuNPs can be isolated and redissolved in common organic solvents without irreversible aggregation. Other sulphur-containing ligands such as xanthates, disulfides, di- and trithiols and resorcinarene tetrathiols have been used to stabilize AuNPs [3-6].

There exist a number of physical methods like photochemistry, sonochemistry, radiolysis and thermolysis which can improve the quality of AuNPs. UV irradiation has been used to prepare AuNPs in synergy with micelles [7] or seeds [8]. The presence of ultrasonic field allowed the control of the rate of $AuCl^-$ reduction in an aqueous solution containing small amounts of 2-propanol and final particle size by controlling the temperature as well as, intensity of ultrasound [9,10]. Sonochemistry

was also used for the synthesis of AuNPs within the pores of silica [11-13] and for the synthesis of Au/Pd bimetallic particles [14].

There exist a variety of ways to synthesize nanoparticle-polymer composites. In this case composite particles are prepared by in situ synthesis of AuNPs in the polymer matrix [15] or by polymerization of matrix around the particles [16]. The most important role of the stabilizing polymer is to protect the nanoparticles from coagulation and functionalize the surface of AuNPs by different reactive groups. AuNPs have been prepared in presence of poly(midoamine) dendrimers leading to stable hybrid particles and the average sizes of gold decreased with increasing concentration of dendrimers as well as their generations [17]. The assembly of aqueous gold nanoparticles on the surface of polyurethane spheres led to formation of gold “shells” through interactions of the nitrogen atoms in the polymer with AuNPs [18]. Polymeric microgels have often also been used as containers for deposition of different materials such as magnetite [19], semiconductor [20, 21] or metals [22]. Poly(NIPAAm-AA) microgels have been filled with gold nanorods [23]. The variation of the longitudinal surface plasmon of the nanorods with their aspect ratio tuned absorption of the hybrid microgels into the near-IR spectral range.

In the present paper preparation of hybrid microgels containing of polymeric matrix filled with AuNPs has been reported. The interest in microgels as polymeric templates has grown rapidly over the last 20 years because of their easy preparation and their potential uses in many industrial applications. Microgels are currently being investigated for their use as drug delivery systems, in chromatographic separation technology, as catalyst media, etc [24-26]. The aim of the present work was to explore the preparation of AuNPs nanoparticles in presence of polymeric microgels by different methods and obtain hybrid particles which combine thermo-sensitivity of microgels and typical physico-chemical properties of nano-sized gold. The microgel particles prepared by copolymerization of acetoacetoxyethyl methacrylate (AAEM) and *N*-vinylcaprolactam (VCL) in dispersion polymerization process have been selected for deposition of AuNPs. The VCL/AAEM microgels possess several interesting properties such as thermosensitivity, biocompatibility, excellent colloidal stability etc [27]. Additionally, *β*-diketone groups originating from AAEM provide effective formation of hydrogen bonds supporting the interactions with nanoparticles of metal oxides [19] and metal sulfides [28]. This results in more efficient incorporation of inorganic particles into microgels. The hybrid particles containing AuNPs integrated into microgel network can be interesting candidates for application as catalyst in aqueous systems. In this case one can expect that catalytic activity of AuNPs will be controlled to some extent by the microgel matrix. The thermo-reversible swelling-deswelling of microgel can provide control over the distance between gold nanoparticles in the polymer network. Additionally, the diffusion of the reactants and their adsorption on the catalyst surface can be better controlled.

Results and discussion

Synthesis of composite microgels

The course of VCL/AAEM/AuNPs hybrid particle formation during ultrasonic treatment was followed by UV-spectroscopy. Fig. 1a shows UV-spectra of microgel dispersions recorded at different reaction times. The absorption peak corresponding to the surface plasmon resonance effect originating from the quantum size of gold nanoparticles appears initially at ca. 600 nm. Fig. 1a shows that the intensity of the plasmon absorption band of AuNPs increases continuously as reaction proceeds

followed by the shift of absorbance maximum from 600 nm to 550 nm. The increase of the peak intensity is due to the increased amount of newly formed gold nanoparticles of lower dimensions or the formation of a mixture of very small crystalline AuNPs together with enlarged AuNPs [29]. Detailed microscopy investigations presented in next section confirm that in present system AuNPs of different dimensions have been incorporated into the microgel particles. Contrary, the shift of absorption maximum to larger wavelength would support the enlargement of AuNPs with reaction course [30].

Time dependent intensity of the AuNPs peak is plotted vs. reaction time in Fig. 1b. Considering the shape of obtained curve it is possible to assume that there is a fast nucleation stage during first 10 min followed by the decrease in the AuNPs reaction rate formation and finally reaction is finished after 30 min. The rate of AuNPs generation in present system can be easily tuned by the controlling the ultrasound power and initial concentration of cloroauric acid in the reaction mixture.

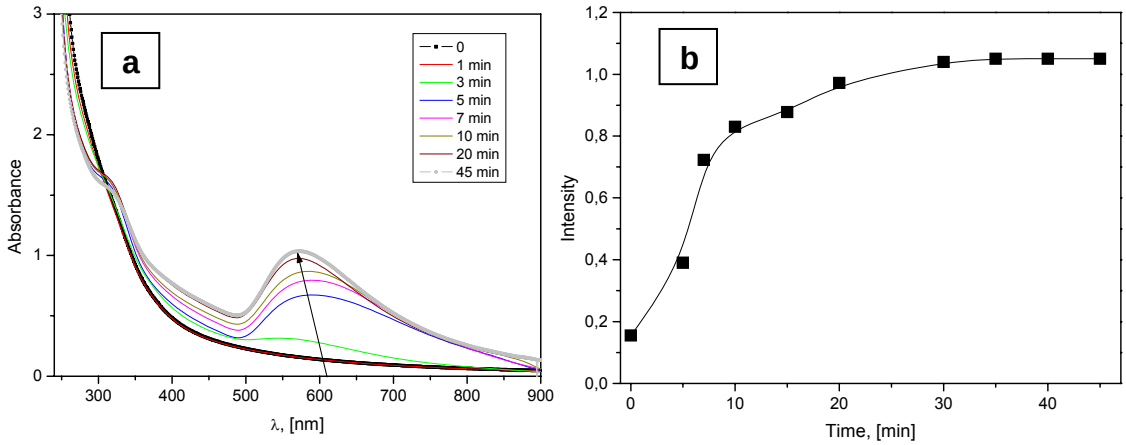

Fig. 1. UV spectra of hybrid microgels (a) and peak intensity (b) as a function of reaction time.

The variation of chloroauric acid concentration in the reaction system (if both the microgel concentration and ultrasonic power were unaltered) led to formation of hybrid microgels with different AuNPs contents (see Tables 1 and 2 for more details). Obtained particles have tendency to form transparent compact films after water evaporation. Such films formed on quartz plates have been investigated by UV-vis spectroscopy. Fig. 2 shows spectra of hybrid films formed from microgels containing different AuNPs amounts.

A steady increase of the plasmon absorption band is observed upon increase of AuNPs content in composite layer (Fig. 2). This effect is not followed by the red shift of the band because of the sufficient separation between AuNPs provided by microgel network and prevention of interparticle plasmon coupling. Similar effect was observed in case of hybrid layers consisting of AuNPs stabilized by poly(acrylic acid) [31].

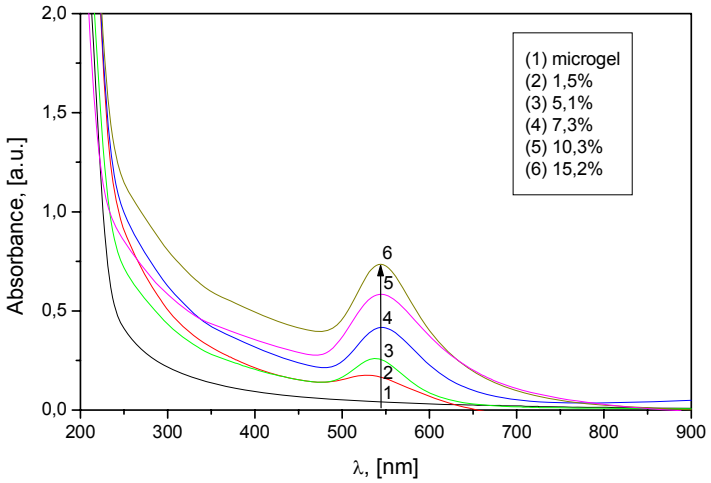

Fig. 2. UV-VIS spectra of VCL/AAEM/AuNPs particles with different Au contents.

Characterization of hybrid particles

- Particle morphology

SEM images presented in Fig. 3 indicate that there is indeed some morphology change of microgel particles due to the incorporation of AuNPs. VCL/AAEM microgels without AuNPs (Fig. 3e) appear as spherical objects and some deformation is caused by film-forming ability of VCL/AAEM copolymer at room temperature. This also led to partial flattering of the microgel particles after deposition on solid substrate. SEM images of hybrid microgels indicate two interesting effects. Firstly, particles shrink after deposition of AuNPs (compare images (a) and (c) with image (e). This correlates with our DLS measurements discussed in the next section. Secondly, in case of chemical reduction method of AuNPs preparation one can clearly see that high gold amounts in the system led to formation of particle aggregates. This effect is probably caused by spontaneous deposition of AuNPs not only inside, but also on the surface of microgel particles providing destabilization of colloidal system. This observation is in agreement with bad colloidal stability of dispersions prepared by chemical reduction method. On the contrary, hybrid particles prepared by ultrasonic treatment indicate no aggregate formation and it seems that in this case AuNPs have been mostly deposited in the interior of microgels. One can clearly see the deformation of microgel particles with gradual increase of gold content.

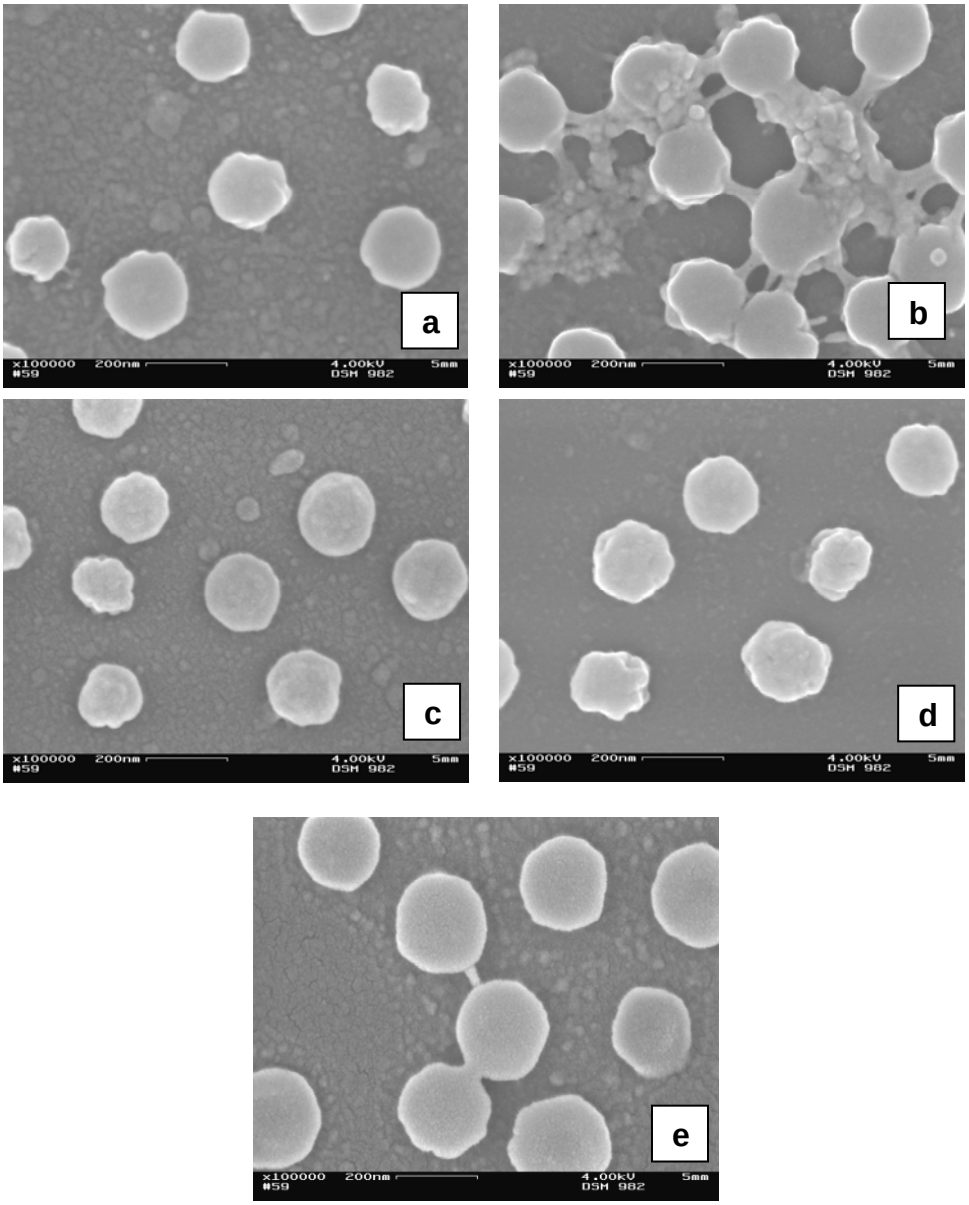

Fig. 3. SEM images of hybrid microgels: chemical reduction: a) 5 %, b) 10 %; ultrasonic treatment: c) 5,1 %, d) 15,2 %; e) no AuNPs.

Conventional SEM images give necessary information regarding particle morphology. But such images are unable to illustrate the compositional difference at the surface layer of the sample. To overcome this drawback morphology studies by SEM have been combined with back-scattered electron technique. Back scattered electrons are produced by elastic interactions of beam electrons with nuclei of atoms in the specimen. The fraction of beam electrons backscattered in this way varies strongly with the atomic number 'Z' of the scattering atoms. It is well known that gold particles have high backscattered electron co-efficient and therefore for hybrid particles an electron microscope has the capability to produce images in which the contrast is controlled by differences in atomic number across the specimen. The images obtained by SEM measurements combined with back scattered electron technique are shown in Fig. 4.

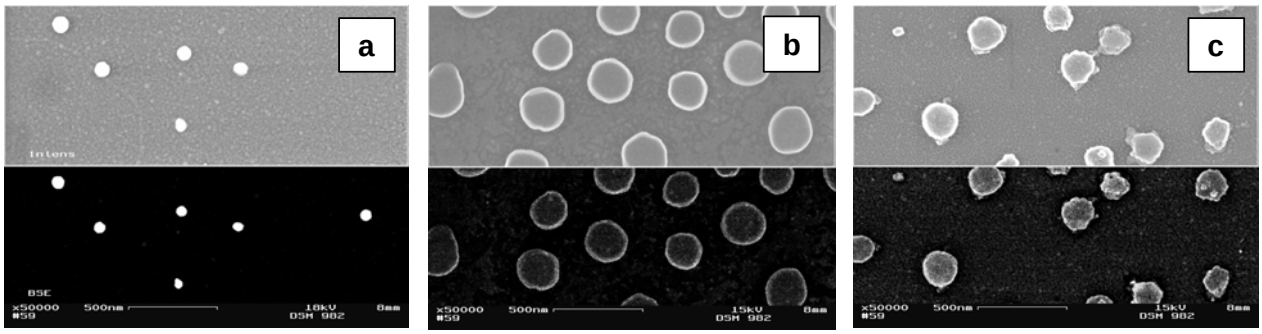

Fig. 4. a) AuNPs; b) microgel; c) microgel with 15,2 % AuNPs (ultrasonic method).

In the Fig. 4, each image has two parts, the upper brighter portion represents the conventionl SEM image of the sample and the lower darker portion represents the back-scattering SEM image. Presence of gold can be seen by the bright points in the lower images in Fig. 4 (a) and (c) for pure gold nanoparticles and hybrid microgels containing 15,2 % Au respectively. A careful examination of the image for hybrid particle shows that the Au particles are present in the surface layer of the hybrid particles.

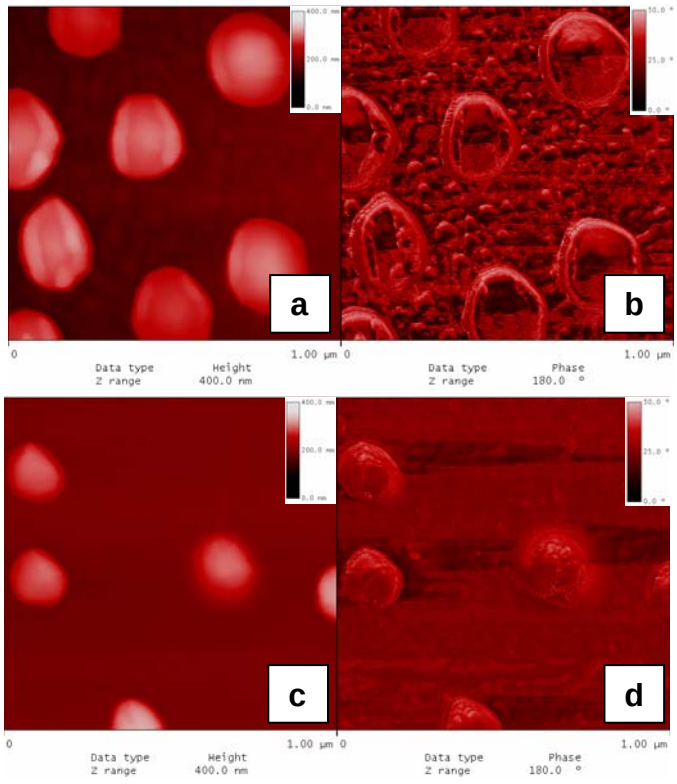

Fig. 5. AFM images of microgel (a, b) and hybrid microgel with 15,2 % AuNPs (c, d) (left – topography image, window size 1µm, height 0 – 400 nm; right – phase image, window size 1µm, angle 0 – 50°).

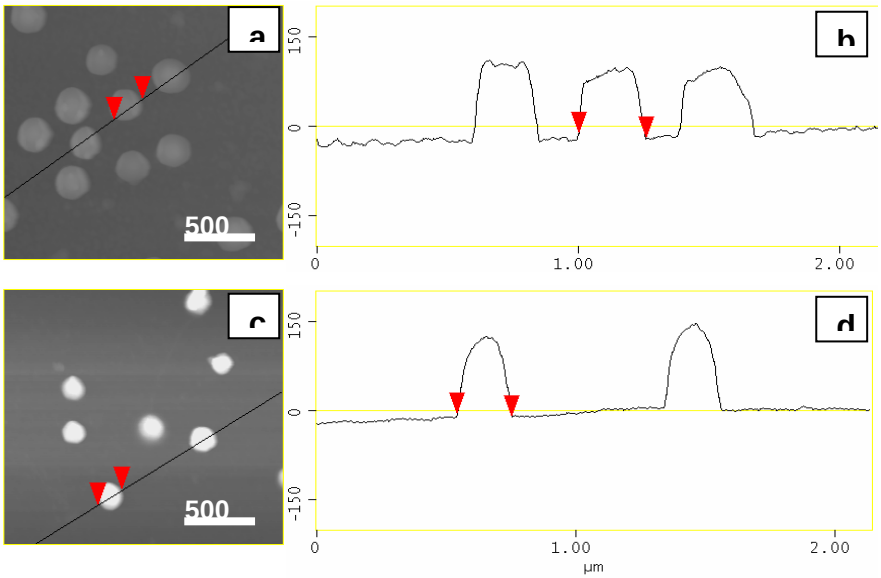

Fig. 6. AFM images of microgel (a) and hybrid microgel with 15,2 % AuNPs (c) with corresponding height profiles (b, d) obtained from line-scans showed as black lines in images a and c (window size for images (a) and (c) is 2 µm).

AFM images of microgel particles are presented in Figure 5. Comparing the height images in Fig 5a and Fig. 5c one can see that particle size of microgels is reduced considerably after incorporation of AuNPs by ultrasonic method. Phase image shown in Fig. 5b indicates that microgels are highly deformed during drying process; while in contrary hybrid particles remain spherical as it is presented in Fig. 5d. Particle flattering after deposition on solid substrate was also detected by height profiles obtained from line-scans (Figure 6a, b).

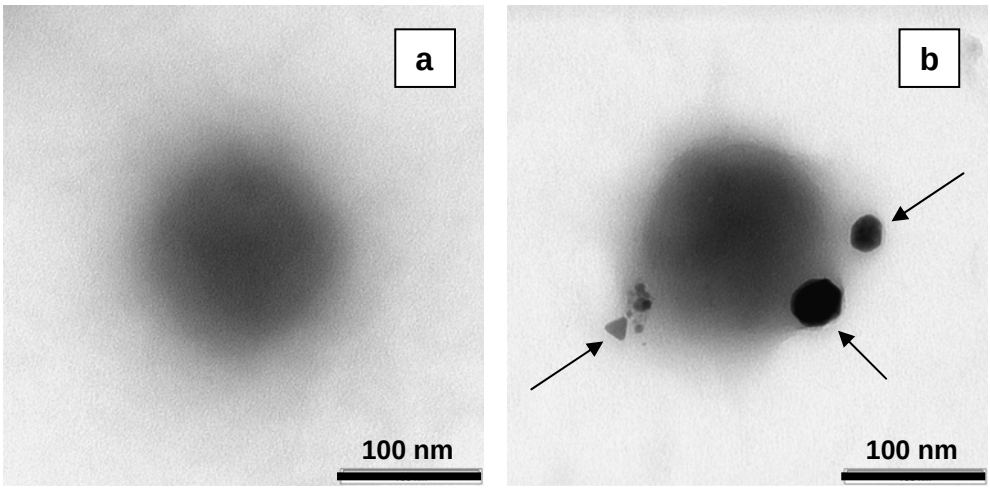

Fig. 7. TEM images of microgel particles (a) and hybrid microgels with 15,2 % AuNPs (b).

Line scan shows that the surface of pure microgel is flat and relatively soft while the surface of the hybrid microgel is somewhat spherical and hard. This information leads to the conclusion that the observed topographical difference is due the influence of hard AuNPs inclusions in the microgel network.

Morphology studies by TEM represent the distribution of gold nanoparticles in the microgel network. The small dark dots (marked by arrows) in Fig. 7b represent gold nanoparticles while the grey large sphere represents the microgel. TEM images of hybrid microgel indicate that AuNPs are located mostly in the outer region of the microgel and not homogeneously distributed within microgel network. It seems that AuNPs does not penetrate deeply into the microgel particles.

The possible reason for such effect is the heterogeneity of VCL/AAEM microgel particles consisting of loosely crosslinked VCL-rich shell and more compact AAEM-rich core which hinders the penetration of AuNPs to the particle interior. Morphology studies indicated that AuNPs are not of uniform size and at some locations small aggregates can be seen. This effect was more pronounced in case of hybrid particles prepared by chemical reduction method. Fig. 7b demonstrates that even by the ultrasonic method of preparation it was not possible to avoid some tendency of aggregation. It can be also assumed that some aggregates are formed during drying process prior to TEM measurements because microgel particles shrink due to water evaporation. The number of AuNPs per microgel particle was difficult to determine but the average value oscillates between 10 and 30. It has been observed that in present system the AuNPs amount introduced in microgel particles varies considerably for different hybrid particles.

-Particle size and colloidal stability

Incorporation of gold nano-particles into microgels has a strong influence on particle size of obtained hybrid colloids. Fig. 8 shows hydrodynamic radii of hybrid microgels prepared with different gold contents determined by dynamic light scattering.

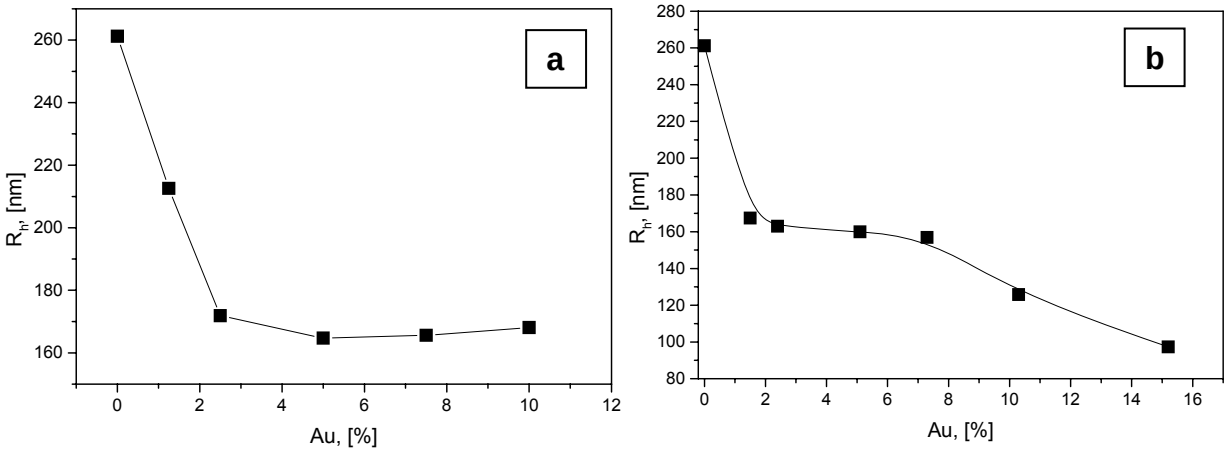

Fig. 8. Hydrodynamic radii of hybrid microgels containing different gold amounts (measurements performed at 10 °C; (a) - chemical; (b) - ultrasound).

It is obvious that incorporation of small amount of AuNPs into microgels leads to decrease of the particle radius from 260 nm to 170 nm. This shrinkage of microgels after incorporation of AuNPs can be explained by effective interactions of AuNPs with polymeric network. The origin of such interactions can be explained in following way.

The pH values of investigated dispersions were close to 6 and, as it will be shown later AuNPs particles are negatively charged in this pH range. In contrast, VCL/AAEM microgel particles possess weak positive charge from initiator fragments incorporated into polymer chains during polymerization process. This leads to the conclusion that the interaction of AuNPs particles with polymeric network possess electrostatic character, which influences probably also swelling degree of microgel in aqueous phase. Increase of AuNPs content can induce shrinkage of the microgel to some critical value which limited by the chain mobility of the swollen microgel shell. Stronger decrease of hybrid microgel size in case of ultrasonically-made hybrid particles (Fig. 8b) can be explained by more effective incorporation of AuNPs into the porous microgel structure under the action of ultrasound. Additionally, it can been observed that during ultrasonically mediated reaction much smaller AuNPs can be formed in the microgel network as compared to samples of similar gold load but prepared by borohydride reduction process. Following these considerations reduction of AuNPs size at similar metal load will lead to increase of the surface area of AuNPs and therefore more intensive interaction with microgel network can be expected.

Based on the above it can be assumed that incorporation of inorganic material into porous polymeric particles will increase particle density and influence colloidal stability of hybrid particles. The stability of hybrid microgels was investigated by sedimentation method developed by Lerche et al. [32].

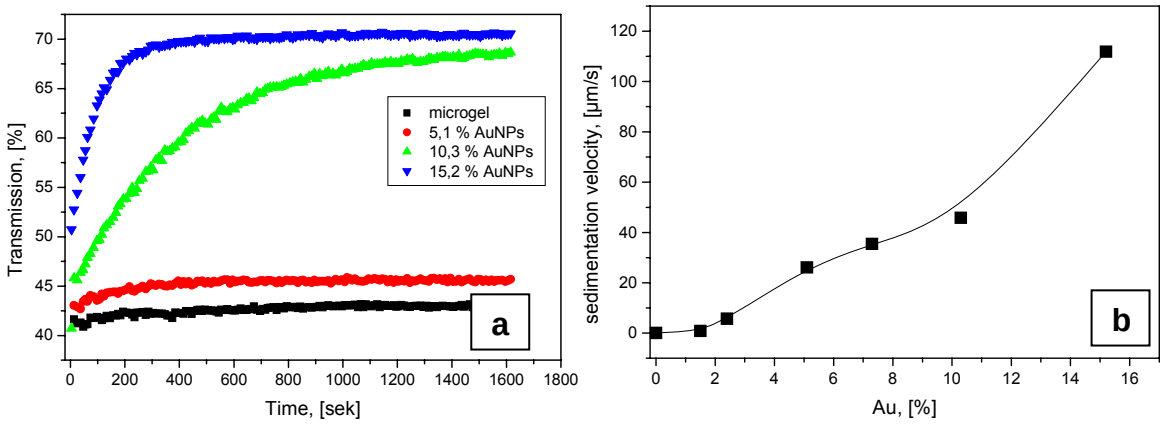

Fig. 9. Transmission-time (a) and calculated sedimentation velocity data (b) for hybrid microgels with different gold contents prepared by US method.

In analytical centrifuge an integrated optoelectronic sensor system allows spatial and temporal changes of light transmission during the rotation. Throughout the measurement, transmission profiles are recorded and sedimentation process can be depicted as a time course of the relative position of the boundary between supernatant and sediment (resolution better than 100 µm) or of the transmission averaged over the entire or a chosen part of the sample length. On the basis of obtained data the sedimentation constants, the packing density, etc., can be derived.

The experimental results from sedimentation centrifuge are summarized in Fig. 9. Fig. 9a indicates that light transmission increases with time indicating that particles precipitate due to the action of centrifugal force. The increase of inorganic filler content induces faster particle sedimentation at similar experimental conditions. From experimental data presented in Fig. 9a sedimentation velocity was calculated for different samples (Fig. 9b). It is obvious that sedimentation velocity increases in

linear order with increase of AuNPs content due to increase of particle density. Similar results have been obtained for hybrid microgels prepared by chemical reduction method. This leads to the conclusion that incorporation of inorganic material has a strong influence on particle stability and probably at some critical AuNPs value microgel template will not be able to provide effective stabilization for hybrid particles. Such effect was indeed observed for hybrid particles prepared at highest AuNPs contents (see Table 1 and 2).

- Electrophoretic mobility measurements

Another important property of hybrid polymeric particles is their electrophoretic mobility which can provide information about particle charge at different pH values. In the present system inorganic material was incorporated into polymeric particles and this modification can influence the behaviour of hybrid particles in electric field. Electrophoretic measurements for different samples were performed at different pH values and experimental results are summarized in Fig. 10. From Fig. 10a it is obvious that for AuNPs, electrophoretic mobility increases rapidly with pH increase passing through isoelectrical point at pH=3. For microgel particles without AuNPs weak electrophoretic mobility has been determined in all pH range. In this case the electrophoretic mobility is slightly higher at pH 3-5 due to the protonization of the functional groups originating from cationic azo-initiator incorporated into polymer structure during polymerization process [20, 21].

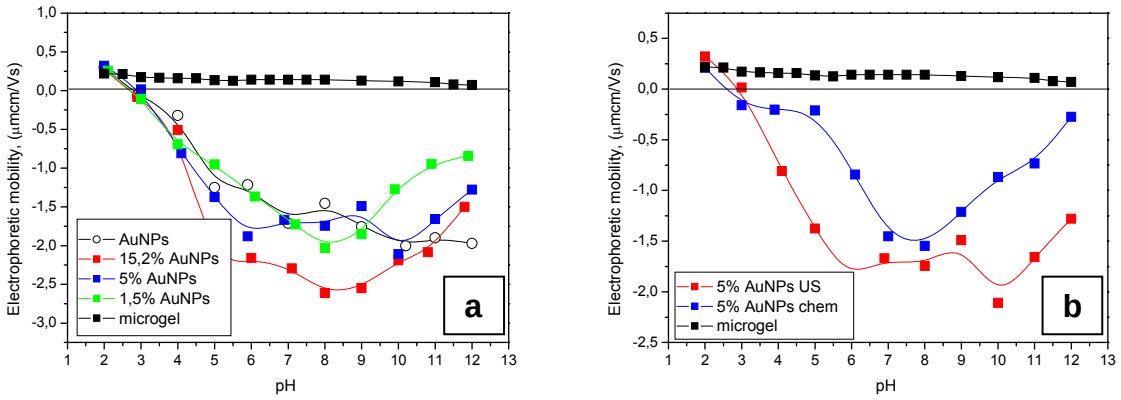

Fig. 10. Electrophoretic mobility measurements for AuNPs, microgel template and hybrid particles as a function of pH (measurements performed at 22°C).

Fig. 10a indicates that hybrid microgels exhibit similar behaviour to AuNPs and isoelectrical point for hybrid particles was detected at pH=3. In acidic region (pH range 4 – 6) there is a clear trend indicating increase of electrophoretic mobility with increase of AuNPs content in microgel, however this tendency is not observed at neutral and basic pH. The electrophoretic mobility data of hybrid particles are significantly higher if compared with microgel without AuNPs indicating that incorporation of gold changes the particle behaviour in electric field. The electrophoretic mobility data showed in Fig. 10b demonstrate comparison of two samples prepared by chemical reduction and ultrasonic method. One can see that similar results have been obtained in both cases; however for hybrid particles prepared by chemical reduction method weaker electrophoretic mobility values have

been measured in both acidic and basic region. This can be explained by absence of sodium citrate molecules on the surface of particles prepared by reduction with sodium borohydride which can be protonized at pH>5.

- Influence of the temperature on particle size

Another important feature of polymeric microgels used as templates in the present study is their thermo-sensitive character. In our previous studies [27] we demonstrated that VCL/AAEM microgel particles possess core-shell structure due to fast consumption of more reactive methacrylic monomer (AAEM). The PVCL-rich microgel shell exhibits lower critical solution temperature (LCST) in aqueous solution and this transition temperature was detected at ~28 °C in comparison to reported 32 °C for pure PVCL. AAEM-rich particle core is more hydrophobic and is less temperature sensitive as compared to the VCL-rich shell. VCL/AAEM microgel particles exhibit fully reversible “soft - hard sphere “transition induced by collapse of highly swollen VCL-rich shell during heating. To investigate the influence of AuNPs inclusions on thermo-sensitivity of obtained particles DLS measurements have been performed at different temperatures. Fig. 11 shows experimental results of hydrodynamic radii for several hybrid particles determined at different temperatures.

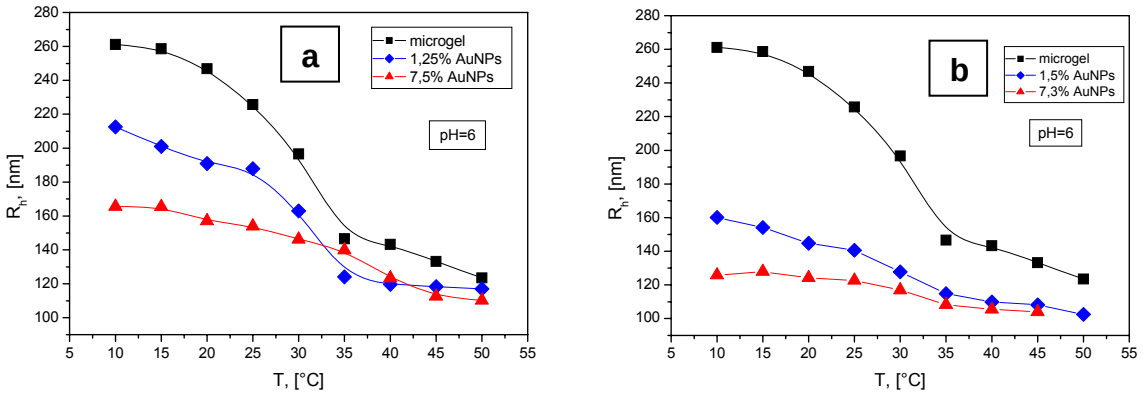

Fig. 11. Hydrodynamic radii vs. temperature for hybrid microgels with different gold contents: a) chemical; b) ultrasonic.

It is obvious from Fig. 11 that incorporation of AuNPs into microgel particles changes considerably the behaviour of hydrodynamic radius at different temperatures. Incorporation of very small AuNPs amount leads to much smaller particle shrinkage at high temperatures. As AuNPs amount in microgels increases the temperature-sensitivity is nearly lost. This effect is present for microgels prepared by chemical reduction and by ultrasonic treatment. This observation is in agreement with our conclusion about possible electrostatic interaction between AuNPs and microgel template which leads to reduced mobility of polymer chains and vanishing of thermo-reversible volume phase transition behaviour of hybrid particles.

Conclusions

In the present paper we report on preparation of hybrid microgels which consist of polymeric matrix and AuNPs as filler material. Incorporation of AuNPs into microgel structure was performed by two different ways, namely chemical reduction of

chloroaurate with sodium borohydride and ultrasonically mediated reduction of chloroaurate in presence of sodium citrate. In this way hybrid microgels with variable AuNPs contents have been prepared. Comparing the two preparation methods it can be concluded that ultrasonically mediated synthesis provided more effective incorporation of AuNPs into microgels leading to better colloidal stability of hybrid particles. It has been found that the hybrid particles possess both thermo-sensitive properties of VCL/AAEM matrix and typical physico-chemical properties of bulk AuNPs. Obtained hybrid microgels are quite stable in aqueous solution, but increase of AuNPs content increases the sedimentation velocity of particles due to the increased particle density. Microscopy investigations indicate that AuNPs are located mostly in the surface layer of the microgel particles and are not homogeneously distributed within polymer matrix.

Experimental part

Materials

Acetoacetoxyethyl methacrylate (AAEM) was obtained from Aldrich and purified by conventional methods and then distilled under vacuum. *N*-vinylcaprolactam (VCL) was obtained from Aldrich and purified by distillation. Initiator, 2,2'-azobis(2-methylpropyonamidine) dihydrochloride (AMPA) was obtained from Aldrich and used as received. Cross-linker *N,N'*-methylenebisacrylamide (BIS) from Aldrich was used without further purification. Chloroauric acid ($HAuCl_4$) and reducing agents sodium borohydride ($NaBH_4$) and trisodium citrate ($NaC_6O_7H_5$) were received from Aldrich and used as commercially available. Distilled water was employed as polymerization medium for microgels.

Synthesis of VCL/AAEM microgels

Detailed information about synthesis of VCL/AAEM microgels has been reported in earlier publication [27]. Appropriate amounts of AAEM (0,16 g), VCL (1,98 g) and cross-linker (3 mol-%) were added in 145 ml deionizer water. Double-wall glass reactor equipped with stirrer and reflux condenser was purged with nitrogen. Solution of the monomers was placed into reactor and stirred for 1 h at 70°C by purging with nitrogen. After that 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 microgels

Preparation of Au-containing composite microgels has been performed by two different methods. In the first method VCL/AAEM dispersion was diluted by 100 ml water and placed into glass vessel and chloroauric acid was added followed by sodium borohydride (aurate:reducing agent molar ratio was 1:18). In the second method VCL/AAEM dispersion was diluted by 50 ml water and placed into glass vessel and chloroauric acid was added followed by addition of trisodium citrate solution (aurate:reducing agent molar ratio was 1:1). Reaction mixture was ultrasonically agitated (output 100 W) by titanium tip immersed directly into the solution (Branson Sonifier). After 1 hour formed composite particles were removed from reaction vessel and cleaned by dialysis to remove all by-products.

A sequence of hybrid particles has been prepared by using VCL/AAEM microgel as a template and varying the AuNPs content deposited into polymeric network. Tables 1 and 2 summarize the amounts of ingredients used for preparation of hybrid particles as well as the finally measured gold content.

Tab. 1. Ingredients used for preparation of VCL/AAEM/Au particles by chemical reduction method.

Sample	Microgel*, [g]	$HAuCl_4$, [g]	$NaBH_4$, [g]	Au^M, [%]	Colloidal stability
1	2,1	0,00212	0,005	1,25	+
2	2,1	0,00424	0,01	2,5	+
3	2,1	0,00848	0,02	5	+
4	2,1	0,0126	0,03	7,5	+
5	2,1	0,0176	0,04	10	+/-
6	2,1	0,0212	0,05	14,2	-

(*- solid content 2; Au^M – AuNPs content in microgels measured by TGA)

Tab. 2. Ingredients used for preparation of VCL/AAEM/Au particles by ultrasonic method.

Sample	Microgel*, [g]	$HAuCl_4$, [g]	$NaC_6O_7H_5$, [g]	$HAuCl_4$: $NaC_6O_7H_5$	Au^M, [%]	Colloidal stability
1	2,1	0,00424	0,00359	9 :1	1,5	+
2	2,1	0,00848	0,00718	9:1	2,4	+
3	2,1	0,0126	0,01077	9:1	5,1	+
4	2,1	0,0176	0,01436	9 :1	7,3	+
5	2,1	0,0212	0,01795	9 :1	10,3	+
6	2,1	0,0272	0,02154	9 :1	15,2	+

(*- solid content 2%; Au^M – AuNPs content in microgels measured by TGA)

During VCL/AAEM/AuNPs particle synthesis by ultrasound the reaction mixture was cooled down to 5°C to avoid overheating and to keep VCL/AAEM particles in swollen state. This can ensure more effective incorporation of gold nano-particles into microgels due to better conditions for diffusion of reactants as well as formed AuNPs. Generally, with both methods stable dispersions have been obtained, however ultrasound method lead to preparation of hybrid particles with larger AuNPs content and much better colloidal stability.

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. In dynamic LLS, the intensity-time correlation function $g_2(q,t)$ in the self-beating mode was measured and can be expressed by the Siegert relation:

$$g_2(q,t) = A(1+\beta|g_1(q,t)|^2) \quad (1)$$

where t is the decay time, A is a measured baseline, β is the coherence factor, and $g_1(q,t)$ is the normalized first-order electric field time correlation function and $g_1(q,t)$ is related to the measured relaxation rate Γ:

$$g_1(q,t) = \int G(\Gamma)\exp(-\Gamma t)d\Gamma \quad (2)$$

A line-width distribution $G(\Gamma)$ can be obtained from the Laplace inversion of $g_1(t)$ (CONTIN procedure) [10]. For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D at $q\rightarrow 0$ and $c\rightarrow 0$ by:

$$D = \Gamma/q^2 \quad (3)$$

or a hydrodynamic radius R_h given by:

$$R_h = k_B T/(6\pi\eta D) \quad (4)$$

with q, k_B, T and η being scattering vector, the Boltzman constant, absolute temperature, and solvent viscosity respectively. All DLS experiments were carried out at angles θ = 30°-140°. The sample in a 10 mm test tube was immersed in a toluene bath and thermostated within an error of ± 0.1°C. Typically, five measurements were performed for determination of the hydrodynamic radius. Accuracy of measurements for hydrodynamic radius is ±3%.

-Stability measurements

Stability measurements were performed with separation analyser LUMiFuge 114 (L.U.M. GmbH, Germany). Measurements were made in glass tubes at acceleration velocity 3000 rpm. The slope of sedimentation curves was used to calculate the sedimentation velocity and to get information about stability of the samples.

-Scanning electron microscopy (SEM)

SEM images were taken with Gemini microscope (Zeiss, Germany). Samples were prepared in the following manner. Microgel dispersions were diluted with deionized water, dropped onto cleaned support and dried at room temperature or 45°C. Samples were coated with thin carbon layer to increase the contrast and quality of the images. Pictures were taken at voltage of 4 kV.

-Atomic Force Microscopy (AFM)

AFM images were obtained with Dimension 3100 Scanning Probe Microscope (SPM, Digital Instruments, Santa Barbara) operating in tapping mode with a drive

frequency 257 kHz. Samples were prepared by casting 4-5 drops of dispersion onto freshly cleaved quartz plates and they were allowed to dry.

-Transmision Electron Microscopy (TEM)

TEM images were obtained with Zeiss Omega 912 at voltage10 kV. Diluted microgel dispersions were placed onto Au nets and dried at room temperature.

-Thermo Gravimetrical Analysis (TGA)

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

-Elecrophoretic mobility measurements

Elecrophoretic mobility measurements have been performed with Zetasizer 2000, Malwern Instruments. pH value of diluted microgel samples was adjusted by addition of 0,01M NaOH or 0,001M HCl. Average value of at least 10 measurements was adopted as electrophoretic mobility at given pH value.

-UV-vis measurements

Colloidal dispersions of hybrid microgels were investigated with PerkinElmer UV-VIS spectrometer Lambda 45.

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