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Nanoparticles on Polyelectrolytes at Low Concentration: Controlling Concentration and Size

B. V. Parakhonskiy,[†,‡] M. F. Bedard,[§] T. V. Bukreeva,[‡] G. B. Sukhorukov,[§] H. Möhwald,[†] and A. G. Skirtach*[,†]

Max-Planck Institute for Colloids and Interfaces, Golm/Potsdam, D-14424 Germany, Institute of Crystallography, Russian Academy of Sciences, Moscow 119333 Russia, and Department of Materials, Queen Mary University of London, Mile End Road, E1 4NS, London, U.K.

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Previously reported results on nanoparticle distribution control on polyelectrolyte multilayers at high concentrations are presented here for the case of low concentration (Skirtach, A. G.; Dejugnat, C.; Braun, D.; Susha, A. S.; Rogach, A. L.; Sukhorukov, G. B. *J. Phys. Chem. C* **2007**, *111*, 555). In sharp contrast to the earlier presented method, nonaggregated distributions of nanoparticles are obtained here by admixing them directly with polyelectrolyte multilayers; preaggregation of nanoparticles is used for aggregated distributions. Furthermore, control over the distribution of nanoparticles at low concentration is extended here for the case of the synthesis of silver nanoparticles or their reduction in a solution by the so-called "silver mirror" or Tollens reaction directly on polyelectrolyte multilayer capsules. In this case, temperature and time are found to control the size and the concentration of nanoparticles. Controlling size and distribution of nanoparticles on polyelectrolyte multilayer capsules is relevant for intracellular delivery and release.

1. Introduction

The synergy of nanotechnology and other sciences offers perspectives for development in various areas including biotechnology.[1,2] For example, self-assembly and defined distribution of nanoparticles (NPs) can be used in various applications on substrates and chips with DNA and proteins as well as with viruses, enzymes, dendrimers, and polymers.[3−9] Metal NPs can be also embedded in the walls of polymeric capsules[10] which are built by the so-called layer-by-layer technique.[11−14] Microcapsules can be made degradable,[15] UV-responsive,[16,17] and photo-oxidative;[18] they can also be used in conducting reactions[19,20] in confined volumes.[21] Functionalizing microcapsules with near-IR sensitive NPs induce absorption in the so-called biologically friendly near-IR window[22−28] for intracellular[29] and drug[30] delivery. In this regard, we have recently demonstrated microcapsule-mediated intracellular delivery of small peptides.[31] It was shown that upon a near-IR laser trigger, the peptides were released from microcapsules. Then, peptides formed a complex with MHC Class I proteins inside the cells, which enabled their subsequent transport to the cell surface, exhibiting a surface presentation;[31] these data are of importance in immunology. Release from liposomes[32−34] and investigation of the properties of lipid membranes[35,36] are other areas for which research on NP distribution is relevant. A desired distribution of NPs can also lead to a time-controlled[37] or direction-specific release from capsules,[38] a technique envisioned to be an analogue of gene-gun technology, or sequential release.[37]

Successful delivery of chemicals by microcapsules can be performed only by microcapsules able to withstand external pressure. Here, microcapsules with NPs were found to substantially improve Young's modulus.[39] In particular, mechanical properties of microcapsules with nonaggregated NPs were found to be substantially improved.[39] Thus, in addition to intracellular delivery, control over the distribution of NPs and their self-assembly leads to materials with improved mechanical properties.

Polymeric films also stand to benefit from control over the distribution of NPs. For example, functionalization of the surface of biocompatible and exponentially[40−43] grown films with aggregates of NPs enables near-IR light activation of such films.[44] Furthermore, magnetic NPs provide extensive functionalities for microcapsules, enabling manipulation and positioning control.[45,46] Besides, such applications as corrosion protection,[47,48] and NP embedding into films[49] for high density information processing, benefit from NP and nanocontainer distribution. Therefore, controlling the NP distribution is significant for both polymeric microcapsules and films.

Previously, NP adsorption and synthesis were reported by several groups for capsules and films. For example, the influence of water evaporation and film structure on surface plasmon properties of the films was investigated.[50] Films functionalized with NPs were shown to possess sensor properties.[51−53] Metallic NPs are especially promising because of their field enhancement leading to strong optical absorption, excitation, and scattering.[54] Gold NPs were directly synthesized inside cationic polyelectrolyte brushes[51] and polyelectrolyte multilayer films.[7,55,56] The method for preparing gold NP films with high loading density based on the seed-mediated growth of gold NPs on polyelectrolyte multilayers was reported.[57] Also, gold nanorods (NRs) were synthesized on polyelectrolyte multilayer microcapsules.[58] Hybrid microcapsules have been constructed using polymers and NPs as alternative layers.[59] Also, silver NPs were synthesized and their stabilization was studied.[60] Silver NPs were successfully synthesized inside polyelectrolyte films,[61,62] and a $NaBH_4$ solution is typically used for reduction of silver ions.

In our previous work, we presented a rather simple method for controlling the distribution of NPs using direct adsorption of NPs or their adsorption with polymers.[1] In the former case,

* To whom correspondence should be addressed. E-mail: skirtach@mpikg.mpg.de, tel: +49-(0)-331-567-9235, fax: +49-(0)-331-567-9202.
† Max-Planck Institute for Colloids and Interfaces.
‡ Russian Academy of Sciences.
§ Queen Mary University of London.

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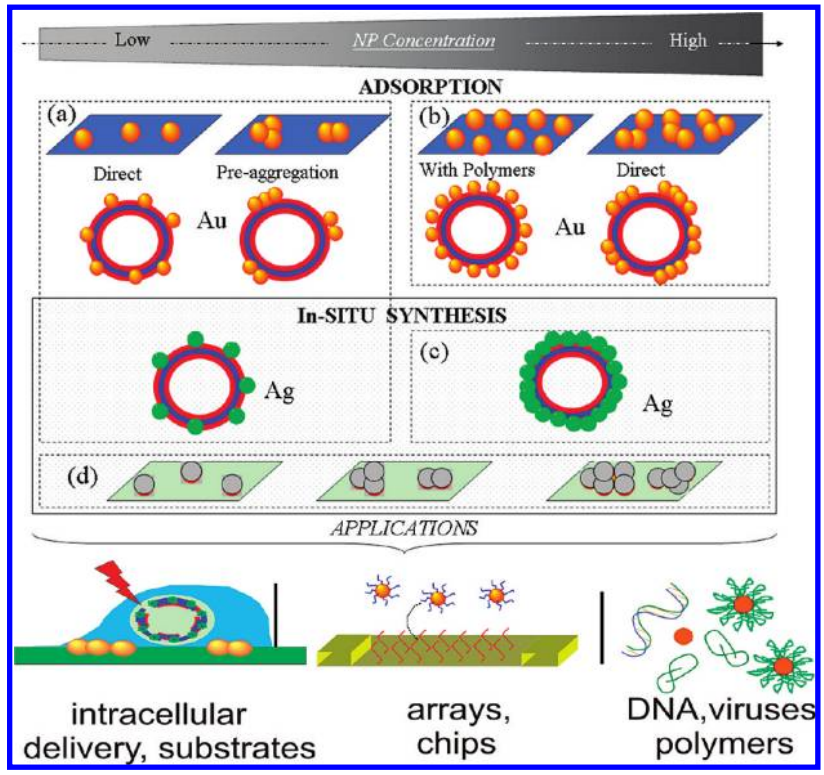

Figure 1. Adsorption and synthesis of metal NPs onto polyelectrolyte multilayer capsules and flat surfaces: (a) results reported here; (b) results reported at a high concentration of NP;[1] (c) results for silver-mirror reaction at a high concentration reported earlier;[63] (d) results of gold or silver NP direct reduction on flat surfaces reported previously.[57,61] Various applications are shown at the bottom of this schematic.[3]

aggregated, while in the latter case, nonaggregated, distributions were obtained; in both cases, a high NP concentration was considered.[1] However, at a low concentration of NPs, the situation is different, and we examine it in this work. On the one hand, direct adsorption led to formation of aggregates of NPs in the case of a high concentration limit;[1] on the other hand, it led to nonaggregated NPs in the case of a low concentration limit.

Furthermore, to extend the capabilities of NP distribution control and simplify the deposition of NPs onto polyelectrolyte multilayers, we present here the results of controlled synthesis of silver NPs directly on polyelectrolyte multilayers under a low concentration limit. To the best of our knowledge, no controlled silver NP growth on polyelectrolyte multilayer capsules has been demonstrated to date. This work extends previously reported results for the so-called "silver mirror" (or Tollens) reaction in which silver NPs are reduced directly on the surface of polyelectrolyte microcapsules with complete coverage.[63] Here we demonstrate that the reaction can be stopped at a desirable time interval, thus creating a shell with a low concentration of NPs. In addition, it is demonstrated that the size of the NPs can be controlled by the temperature of the reaction. Figure 1 presents an overview of previous work on NP distribution control on microcapsules and flat polyelectrolyte multilayers. Figure 1a shows the area under consideration presented in this work (the low concentration limit, both adsorption and synthesis of NP). Figure 1b demonstrates the area reported in preceding work.[1] Figure 1c demonstrates a sketch of the "the silver mirror" reaction,[63] while Figure 1d presents a sketch of the synthesis of gold[57] and silver NPs[61,62] on polyelectrolyte multilayers.

2. Experimental Section

Materials. Poly(sodium 4-styrenesulfonate) (PSS, 70 kDa), poly(allylamine hydrochloride) (PAH, 70 kDa), poly(diallyldimethylammonium chloride) (PDADMAC, 250−350 kDa), polyethyleneimine (PEI), acetaldehyde, $AgNO_3$, and 20 nm colloidal gold (the concentration of NPs may vary depending on the batch) were purchased from Sigma-Aldrich (Germany). Colloidal templates SiO_2 (4.8 μm) and polystyrene (PS) (4.4 μm) were obtained from Microparticles GmbH, Germany. Inorganic acids, bases, salts, and tetrahydrofuran (THF) were obtained from Roth (Germany). Water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system which had a resistivity higher than 18.2 MΩ cm^{-1}.

Layer-by-Layer Assembly of Hollow Polyelectrolyte Microcapsules with NPs. Hollow microcapsules containing gold NPs (1 mL of solution with colloidal gold; concentration 4×10^{11} NP/mL) in their walls were built onto sacrificial SiO_2 (0.25 mL of 50 mg/mL solution with SiO_2 colloids) particles by the layer-by-layer (LbL) protocol sequentially adsorbing PDADMAC (in solution: 2 mg/mL, 0.5 M NaCl) and PSS (in solution: 2 mg/mL, 0.5 M NaCl), starting with PDADMAC.[18,24] The silica templates were dissolved in hydrofluoric acid (0.3 M), and the sample was washed with water until the pH of the solution reached 5. Gold NPs were added on the fifth layer, and a neutral pH was maintained during the assembly.

For preparation of microcapsules with nonaggregated NPs, gold NPs were added to SiO_2 templates after the fifth PDADMAC-terminated layer. Aggregates of gold NPs were obtained by adding an aliquot of gold NP solution to an equal volume of saline solution (0.1 M NaCl). The gold solution was gently mixed for 60 s before being used to resuspend silica templates with the last PDADMAC layer. The final shell construction sequence was $(PDADMAC/Au/PSS)_4$. Typical incubation time for adsorption of polymers and NPs was 12 min.

Polyelectrolyte multilayer shells for in situ synthesis of silver NPs were prepared by the LbL approach on PS particles using PAH (2 mg/mL, 0.5 M NaCl) and PSS (2 mg/mL, 0.5 M NaCl).

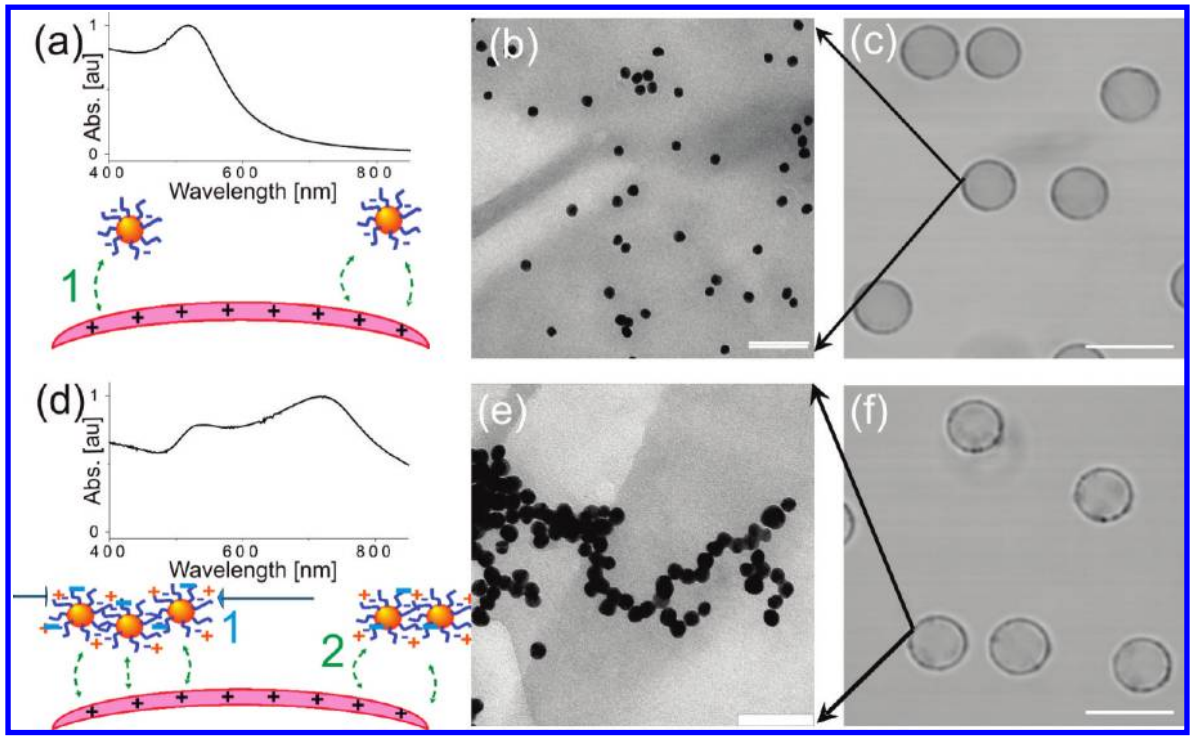

Figure 2. Distribution control of presynthesized gold NPs by adsorption onto polyelectrolyte multilayer capsules in the low concentration limit. (a) Absorption spectrum and the scheme of interaction for nonaggregated NPs (nonaggregates are obtained upon direct adsorption by admixing (1 in the scheme)); (b) TEM image of nonaggregated NPs on a microcapsule; (c) CLSM image of microcapsules. (d) Absorption spectrum and the scheme of interaction for aggregated NPs (aggregates are obtained by aggregating NPs first (1 in the scheme) and then adsorption (2 in the scheme); (e) TEM image of aggregated NPs on a microcapsule; (f) CLSM image of microcapsules ($F_s \sim 0.05$). The scale bars in b and e correspond to 100 nm; those in c and f correspond to 6 μm.

Acetaldehyde (20 μL) was added to a 1.5% suspension (2 mL) of the PS particles coated with six bilayers $(PAH/PSS)_6$ ($\sim 10^8$ capsules) according to previously reported methods.[63] A tube with the prepared mixture was placed in an ultrasonic bath (ultrasound frequency, 35 kHz), the freshly prepared 5% $[Ag(NH_3)_2]OH$ solution (150 μL) was added dropwise, and stirring of the reaction mixture was continued. $[Ag(NH_3)_2]OH$ was prepared via addition of a 0.5 M NH_4OH solution to a 0.5 M $AgNO_3$ solution with stirring until dissolution of the AgOH precipitate. The reaction is very sensitive to experimental conditions. It leads to reduction of silver ions on polyelectrolyte multilayer templates with metallic particles in the outer shell. In the next step, the polystyrene templates were dissolved in tetrahydrofuran, producing microcapsules with metallic NPs on the walls.

Characterization and Calculations of the Size Distribution. TEM was done using a Zeiss Omega EM 912 at an operating voltage of 120 kV. Confocal laser scanning microscopy (CLSM, Leica) was used to visualize the microshells in solution. Images were recorded by means of a 40×/1.4−0.7 oil immersion objective. A Cary 50 conc. (Varian, Germany) UV−vis spectrophotometer was used for absorption spectra measurements. AFM measurements were performed in air at room temperature using a Nanoscope III Multimode AFM (Digital Instruments, Maynard, Massachusetts) operating in tapping mode.

TEM images were used for analyzing the size distribution of NPs; for the selected areas, capsule shells with no creases were chosen. The size distribution is calculated treating NPs as spheres. An average value of 10 measurements for each sample was taken; the standard deviation is under 5%.

3. Results and Discussion

NPs of noble metals convert electromagnetic into thermal energy. The mechanism for laser−NP interaction is thermal,[64,65] and the total temperature rise depends on incident intensity, size of NP, and the surface density of NP or surface filling factor, or the so-called surface filling factor F_s.[22] In the latter work the temperature rise was measured experimentally.[22] In practice the localized temperature rise can be used for release of attached materials directly from the NPs.[66,67] Also, metal NPs were shown to locally melt the polymer matrix, inducing release of encapsulated materials from microcapsules.[22] Changing the size[68] and shape[18,69] as well as the distribution[28] or interaction[24,70] of NPs leads to near-IR absorption. Infrared absorption can be also induced by dyes,[71−73] but the overall importance of infrared-sensitive microcapsules is assigned to the fact that this range falls into the biologically "friendly" window.[74] Infrared-sensitive microcapsules were found to react violently with laser excitation, exhibiting strong deformation and explosion.[73] Such a system with a high concentration of NPs is suitable for photothermal methods of cancer treatment.[64] Recent studies on living cells for controllable release have shown, however, that it is desirable to induce release nondestructively.[26] Thus, the concentration of NPs on polyelectrolyte multilayer capsules is one of the factors which determines the amount of generated heat.[1] As a result, the low NP concentration limit considered is important for reduction of the total amount of heat generated within the shell of the polyelectrolyte multilayer for creating only local, nanometer-sized "hot spots."

Commercially available citrate-stabilized gold NPs were chosen for distribution control experiments in the low concentration limit. In striking difference to the case of adsorption of NPs in the high concentration limit[1] where direct admixing led to aggregates, in the low concentration limit reported here direct admixing of NPs and microcapsules leads to their nonaggregated and uniform distribution, Figure 2a−c. This result can be interpreted as follows: colloidal NPs are typically stabilized in the solution. Since citrate-stabilized gold NPs are negatively

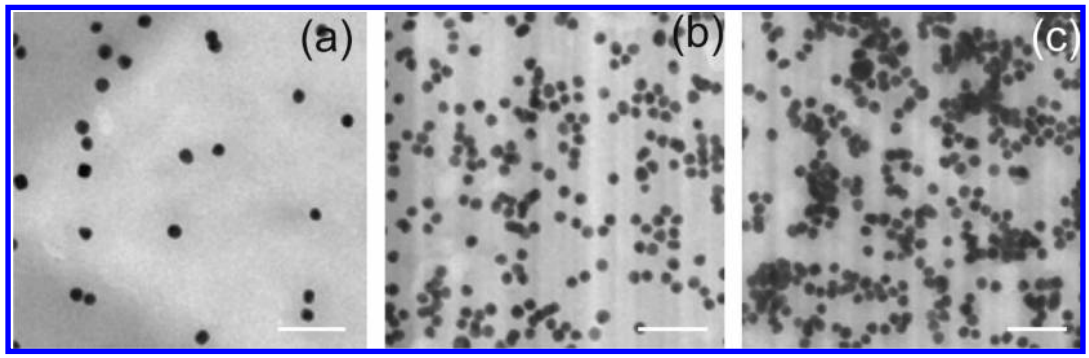

Figure 3. TEM images of gold NPs obtained by direct adsorption on polyelectrolyte multilayer capsules at various values of surface filling factor, F_s: (a) 0.04; (b) 0.15; (c) 0.3. The scale bars in all images correspond to 100 nm.

charged, they are adsorbed onto a positively charged polymeric layer (PDADMAC), Figure 2a. This electrostatic interaction leads to complete adsorption of NPs (1 in the scheme of interaction, Figure 2a) from the supernatant solution, and, upon full adsorption of NPs, the initially pink supernatant turns colorless, while templates gain a light pink color. In the low concentration limit there are simply not enough NPs to produce a dense coverage of the surface of the polyelectrolyte multilayer capsules (schematics in Figure 2a). Nonaggregated distribution of NPs in the shell of a polyelectrolyte multilayer capsule can be seen in the TEM image, Figure 2b. Microcapsules with nonaggregated NPs can be seen in Figure 2c.

Obtaining aggregates of NPs on polyelectrolyte multilayer capsules needs to be pursued differently here. Specifically, aggregates need to be obtained before their adsorption onto microcapsules, Figure 2d. In the case of citrate-stabilized gold NPs the aggregation can be induced by salt (1 in schematics in Figure 2d), thus screening the charge on the colloidal NPs. The ability to halt the growth of aggregates of NPs is desirable because this offers a way of tuning these absorption properties. Aggregation of Au NPs in the solution is visible by the eye since a drastic color change from ruby to blue/gray is the hallmark of this process. Citrate molecules are added as a coordinating agent during the preparation of NPs, and they prevent the latter from aggregating with each other through electrostatic stabilization. Aggregation of the NPs in solution occurs when the stabilizing charges of the citrate molecules are screened by salt ions, reducing the long-range electrostatic repulsions and allowing short-range attractive forces (van der Waals forces) to dominate.[75] After a solution of NaCl (0.1 M) was mixed with a solution of citrate-stabilized Au NPs (20 nm) for 60 s (1:1), the latter became unstable and the solution rapidly changed color as aggregation proceeded. The corresponding absorption spectrum displays a new (compared to typical surface plasmon of gold NPs, Figure 2a) broad absorption region between 700 and 900 nm with a maximum centered at 740 nm, Figure 2d. Besides the appearance of a large absorption peak in the near-infrared region, the addition of NaCl to the gold particle solution leads to a minor bathochromic shift of its surface plasmon resonance (SPR) band from 521 to 526 nm. Subsequent adsorption of these aggregates (2 in scheme Figure 2d) produces aggregates on polyelectrolyte multilayer capsules, Figure 2e. Microcapsules with aggregates (small black dots) can be seen in Figure 2f; these aggregates are the only difference in otherwise similar microcapsules, Figure 2c and 2f because the concentration of NPs is low, $F_s \sim 0.05$.

To link our previous results obtained for high concentration of NPs and current results at low concentration, we have adsorbed gold NPs onto polyelectrolyte multilayers at various concentrations, Figure 3. NPs were deposited on the surface of capsules by direct adsorption, and no preaggregation was made in this case. It can be seen from Figure 3a that a nonaggregated distribution is obtained at the lowest concentration, $F_s \sim 0.04$. As the concentration of NPs increases, the distance between NPs decreases, Figure 3b. A further increase in concentration of NPs leads to formation of some aggregates, Figure 3c. For $F_s \sim 0.3$, formation of aggregates was observed. The average distance between nanoparticles can be expressed as follows:[22]

$$\langle d \rangle = r_0 \times \frac{2}{\sqrt{F_S}} \quad (1)$$

It can be seen from eq 1 that at $F_s = 0.3$ the average distance between NPs $\langle d \rangle \approx 3.65 r_0 \approx 1.8D$, where D is the diameter of a NP. As this distance decreases with increasing surface density, F_s, NPs get closer thus forming aggregates. It can be noted that data presented in Table 1[1] represent adsorption of NPs in the presence of polymers; in that case (a) not all NPs are adsorbed and (b) NPs are prevented from interaction by polymers. It can be noted that similar behavior of NPs on flat surfaces was also observed, Supporting Information. Supporting Information also provides data on aggregation of gold/gold sulfide[1] NPs.

In addition to the direct adsorption of metal NPs onto the polyelectrolyte multilayer shell, a complementary technique has been developed. In this technique, ions are directly reduced on the shell from a solution forming metal NPs. LbL films can be tuned due to multifunctionality in film composition, chemical structure, or the number of functional groups.[76] Porosity of films can be used to limit the size, regulate, or even prevent the growth of NPs. For example, both ionized and nonionized groups of weak polyelectrolytes can influence binding of metal ions in films.[61,62,77,78] Also, the size and the content of the NPs in the film can be tuned by adjusting the ionic strength in the polyelectrolyte solutions used for the assembly:[79] It was shown that there always exists an excess of charged groups and counterions at the surface of polyelectrolyte multilayers.[80,81] Therefore, we used these charged groups for in situ synthesis of NPs on the surface of polyelectrolytes.

To date, silver[63] and gold ion reduction[58] has been reported, in both cases forming metallic NPs in the shell of the microcapsules. The "silver mirror" reaction is a quick and simple way to produce silver NPs with narrow size distribution in solution.[82] So far, only a complete coverage of silver NPs on microcapsules has been reported[63,73] Here, we extend the method of the "silver mirror" reaction and present results of NP synthesis at low concentration. In this study we demonstrate that the reaction can be stopped at a desirable time interval, thus creating

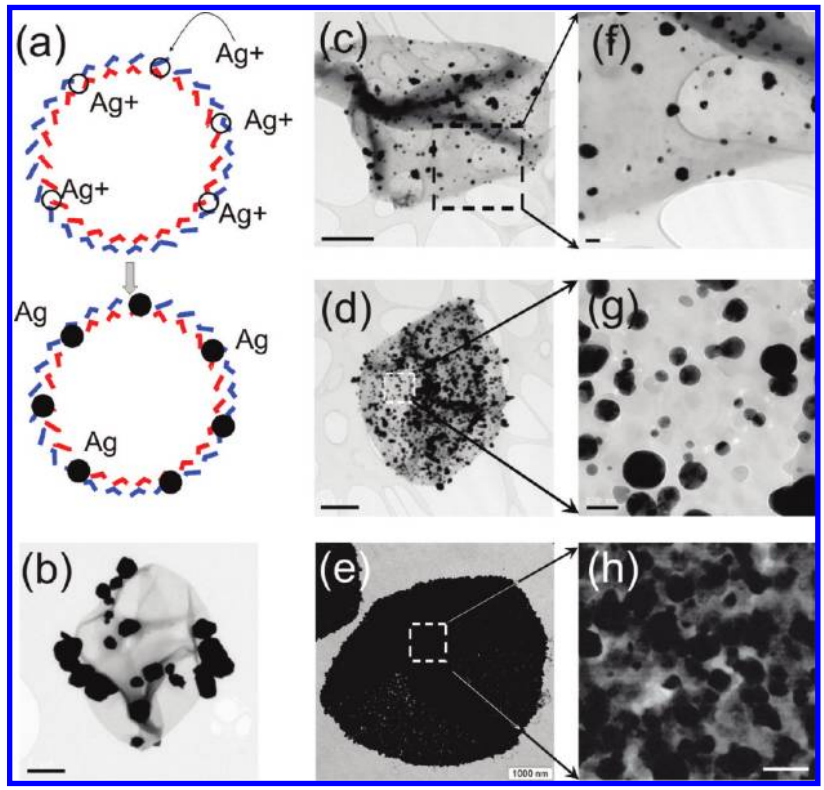

Figure 4. (a) Schematic of the reduction of silver ions forming metallic silver NPs in situ directly on polyelectrolyte multilayer capsules at low concentration. TEM images of microcapsules with metal silver NPs obtained at (b) elevated temperature: 50 °C, reaction time 5 min and (c−e) all at room temperature varying the reaction time: (c) 5 min, $F_s = 0.05$; (d) 10 min, $F_s = 0.3$; (e) 60 min, $F_s = 0.8$. (f−h) Zoomed-in areas of respective TEM images. The scale bars in b−e correspond to 1 μm, and those in f−h to 100 nm.

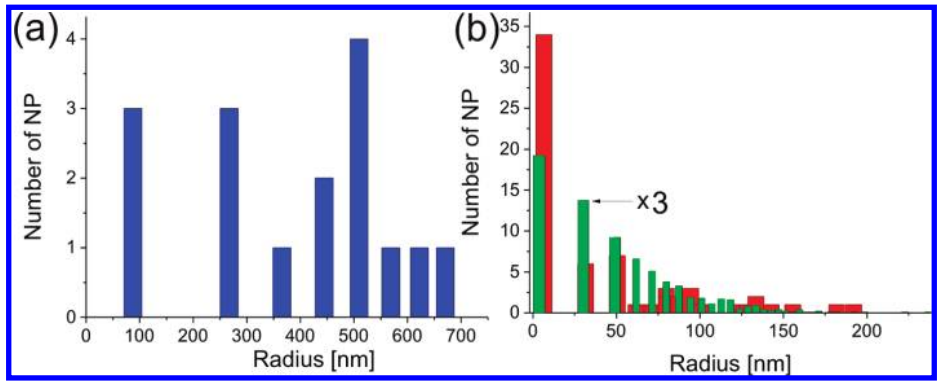

Figure 5. Statistical analysis of size distributions of silver NPs (derived from TEM analysis) synthesized directly on polyelectrolyte microcapsules using the silver mirror reaction and obtained at (a) elevated temperature: 50 °C, reaction time 5 min, and (b) room temperature varying the reaction time: 5 and 10 min, green and red bars, respectively. Data represented by green bars were multiplied by a factor of 3. At 60 min, NPs cannot be separated; therefore, this case is not presented in b.

a shell with a low surface filling factor. In addition, we demonstrate in this study that the size of the NPs can be controlled by adjusting the temperature of the reaction.

The "silver mirror reaction" is based on the chemical reduction of the metal upon oxidation with acetaldehyde, according to the following equations:[83]

$$AgNO_3 + NH_4OH = AgOH + NH_4NO_3 \quad (2)$$

$$AgOH + 2NH_4OH = [Ag(NH_3)_2]OH + 2H_2O \quad (3)$$

$$2[Ag(NH_3)_2]OH + CH_3CHO = 2Ag + CH_3COONH_4 + 3NH_3 + H_2O \quad (4)$$

There are several reaction parameters, for example temperature and the reaction time, which affect the size and concentration of NPs. Temperature controls the size of silver NPs. Indeed, silver NPs reduced at 50 °C, Figure 4b, are larger (micrometer range) than those synthesized at room temperature.[63] The increase in the size of the silver NPs can be assigned to the fact that particle growth prevails over their nucleation because of a decrease in the saturation of the solution at elevated temperatures. Larger NPs were more easily removed from the surface than the small ones.

It was also found in our studies that the duration of the reaction affects the concentration of NPs: the longer the reaction time the higher the concentration of NPs. This can be illustrated in Figure 4c−h. If the reaction is carried out for 5 min, a very low concentration of NPs is obtained, Figure 4c. It was observed that aggregation of NPs is insignificant, Figure 4f. In this case, the surface plasmon absorption of individual NPs prevails. Further, if the reaction is carried out for 10 min, a higher concentration of NPs is obtained, Figure 4d. It can be seen from

the enlarged zoomed-in area, Figure 4g, that the average distance between the NPs is decreased, Figure 4f. It can be noted from Figure 4 that as F_s reaches 0.3 some NPs are situated in proximity to other NPs, Figure 4d and 4g. This is similar to the case when NPs were adsorbed directly on microcapsules, Figure 3. Qualitatively, $F_s = 0.3$ can be used as an estimate of the limit of high concentration of NPs. Further prolongation of the reaction leads to increasing coverage of the surface of polyelectrolyte multilayer capsules by NPs. Specifically, after 60 min the capsules were fully covered by silver NPs, Figure 4e. Such a dense distribution of NPs leads to enhanced near-IR absorption of silver NPs for remote release applications.[73]

Further quantification of the influence of temperature and reaction time was conducted by analyzing the statistics of the size distribution, Figure 5. For analysis of NP concentration, we calculated the filling factor defined as the ratio of the sum of all cross-sections s_i of n metal NPs on the surface of a capsule to the surface area of the capsule S_c:[22]

$$F_s = \frac{\sum_i^n s_i}{S_c} \quad (5)$$

The distribution of the size of NPs is presented in Figure 5. It can be seen from Figure 5a that at 50 °C, silver particles of submicrometer size, from 100 to 700 nm ($F_s = 0.25$, 25% surface coverage), were formed. If this reaction proceeds at room temperature, then the amount of NPs increases from 5% ($F_s = 0.05$), for 5 min, to 30% ($F_s = 0.3$), for 10 min (the average size of NPs increased from 56 to 70 nm, Figure 5b). If the reaction was carried out for 60 min, the polyelectrolyte shell is almost entirely ($F_s = 0.8$) covered with a layer of silver NPs, Figure 4e and 4h; in this case, the calculation of the size distribution was not performed because individual NPs cannot be separated.

4. Conclusions

Adsorption of NPs on polyelectrolyte multilayer capsules in the low concentration limit is in sharp contrast to the case of high NP concentration.[1] In the latter case, direct admixing of NPs and polyelectrolyte-coated templates leads to aggregates of NPs, while in the low concentration limit studied here, direct admixing leads to a nonaggregated distribution of NPs. Aggregates of NPs can be obtained in this case by preaggregation in solution before their adsorption. Furthermore, we have also extended the control of the distribution of NPs to the case when silver NP synthesis occurs directly on polyelectrolyte multilayer capsules. The previously demonstrated method of producing microcapsules with completely covered silver NPs (by the so-called "silver mirror" or Tollens reaction) is extended in this work to produce microcapsules with partial NP coverage. Both time and temperature are found to affect NP formation: longer time leads to higher density of the NPs, while higher temperature leads to NPs of larger size. The methods of NP control reported here are relevant for a number of applications including release[27,84] and intracellular remote release[29,31] of encapsulated materials, remote control of bioreactions in confined volumes,[21] multicompartment[85] micro- and nano-[86] capsules,[87] biochips,[88] and mass spectrometery.[89,90]

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Supporting Information Available: AFM images of gold NP aggregates and nonaggregates on flat surfaces. Also, aggregation of gold sulfide/gold NPs, analyzed in detail in previous work,[1] by centrifugation is described. Absorption spectra and TEM and AFM images are provided. This information is available free of charge via the Internet at http://pubs.acs.org.

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