Microfluidic generation of metal nanoparticles by borohydride reduction

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Abstract

In this work a microfluidic system for the production of very small gold nanoparticles (GNP) by reduction with borohydride will be presented, as well as their direct surface modification with thiol ligands. Furthermore, the microsystem was tested for the generation of other metal nanoparticles, as for example, silver, copper and complex particles. The size distributions were determined using scanning electron microscopy and an analytical centrifugation method. Additionally, *in situ* UV–vis spectroscopy was applied for online monitoring and kinetic measurements. Reactor fouling in the course of the syntheses was monitored with a microscope camera, and methods like silanization and pH-adjustment were explored to minimize the fouling. The direct reduction of chloroauric acid with borohydride yielded reproducibly gold nanoparticles in the size range between 4 and 7 nm without recognizable fouling of the reactor. Between 200 and 4000 μl/min, the flow rate does not affect the size distribution of the obtained gold nanoparticle dispersions. An increasing dilution of the reactants leads to a decrease in the mean diameter of the particles. The influence of the concentration ratio $(BH_4^-)/Au$ and the effect of the pH were also investigated, but no significant trend was observed. Surface modification of these particles was achieved in the microsystem and monitored via UV–vis measurement and size distribution determination.
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1. Introduction

Microreactors are of interest for synthesis procedures due to the possibility of precise control of reaction and mixing conditions. The small distances for diffusive exchange of heat and matter are one of the key advantages of micro-reaction technology. Thus, micro-flow-through processes were introduced even for heterogenous processes despite all difficulties related to the high surface-to-volume ratios in micro-channels.

It was shown, that the formation of emulsions can easily be achieved by use of multilamination mixers or split-and-recombine mixers [1]. The generation of dielectric nanoparticles by precipitation succeeded in a micro-flow-through process [2]. Metal nanoparticles [3,4] as well as semiconductor nanoparticles [5,6] and polymer nanobeads [7] can be generated in microreactor arrangements. In addition, nanoparticle/molecule adducts can be produced and handled in micro-fluid devices [8–10].

The process parameters for the formation of nanoparticles are particular important for the control of particle size, particle shape, aggregation and composition in case of more complex particles. The rate of nucleation and the rate of particle growth depend in different ways on the local concentrations of educts. In particular, the conditions of local transport and mixing by interdiffusion depend strongly on the flow rate and the local geometric conditions. It was shown, that the particle size distribution of gold nanoparticles can be improved by a micro-flow-through process in comparison to a conventional synthesis [11]. Moreover, micro-flow-through synthesis was also successfully applied for the synthesis of metal nanorods [12,13].

The local concentration and the concentration change in time are of particular importance for the preparation of complex metal nanoparticles. The order of mixing and the flow-rate-controlled mixing rate change the product composition significantly in case of Au/Ag nanoparticles. The strong influence of mixing conditions is reflected by drastical changes in the optical spectra of colloidal product solutions [14]. These effects can be explained by the different behaviour of metal ions in relation to nucleation and particle growth.

In addition to the fluidic conditions and the local concentration, the reduction potential of reducing agent and the mechanisms of charge transfer between reducing agent and metal ions are of large importance for the quality of products in micro-flow-through nanoparticle synthesis. Therefore, the application of $NaBH_4$ as a reducing agent with very high reduction

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power for the generation of nanoparticles in micro-flow-through synthesis is reported, here. Boranates were applied for nanoparticle synthesis in conventional reactors earlier and were found to be well suited for the formation of special surface-modified nanoparticles [15,16]. Here, the application of this reducing agent in relation to the conditions in micro-flow-through processes is studied and compared with the behaviour in case of reducing agents with lower reduction power.

2. Mechanistic background of formation of metal nanoparticles

The formation of metal nanoparticles from metal ions or coordination compounds by a redox reaction with a reducing agent in solution is a rather complex process. Coordination chemistry of metal ions, ligand exchange and intermediate formation of multicenter complex compounds as well as electrochemical processes play a role beside the direct transfer of electrons between the participating ions and the reducing agent. The different electrochemical and coordination properties of different metal ions and the different mechanisms of oxidation of reducing agents have to be taken into account for the understanding of the influence of flow-through conditions on nanoparticle formation.

The nucleation proceeds under completely different conditions as the particles growth. Nucleation occurs in a locally homogenous solution. It is determined by the coupling between ligand exchange in the direct environment of the metal ions and the charge transfer (Fig. 1a). Therefore, the direct interaction between coordinating ligands, reducing agent and metal ions is decisive for the formation of metal cores. That is why the nucleation is very strongly controlled by the specific chemical properties of the involved species. In particular by the conditions for the formation of chemical species with two or more metal atoms in near neighborhood, which are able to interact directly after reduction in order to form a metallic bond. Nucleation must be understood as a coordination chemistry process leading from single coordination compounds via double or multicenter complexes to coordination compounds of metal multiatom centers. Therefore, the following generalized reaction equation is proposed:

$$a[ML_n]^+ + R \rightarrow [M_aL_m]^{a-1} + R^+ + (na-m)L \qquad (1)$$
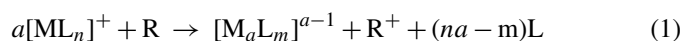
M: metal; R: reducing agent; L: ligand; a, m, n: stoichiometric coefficients.

In contrast to nucleation, the growth of nanoparticles can be understood as composed of two separate electrochemical processes, which are coupled only by the electrochemical potential of the growing metal nanoparticles (Fig. 1b). The electrochemical reactions can be described as cathodic and anodic partial processes in analogy to the mixed potential formation in electrochemical open-circuit processes well known from open-circuit metal deposition, from corrosion and from technical etching processes of metal films. The transition of metal ions to metal atoms at the surface of the nanoparticles represents the cathodic partial process:

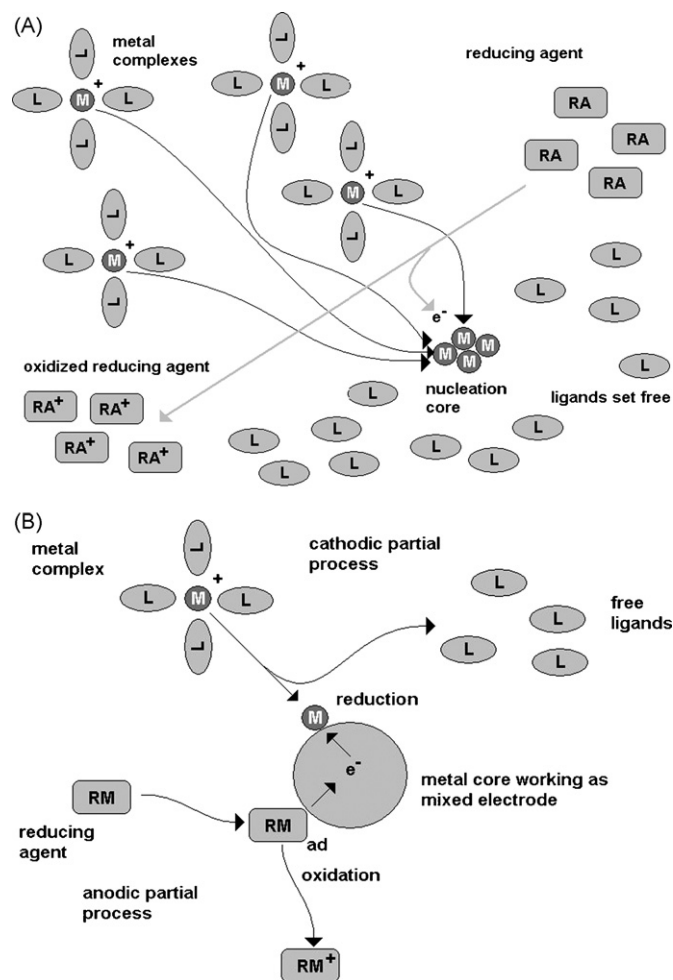$$[ML_n]^+ + e^- \rightarrow M + nL \qquad (2)$$

Fig. 1. Nanoparticle formation (schematically): (A) nucleation and (B) electrochemical processes in particle growth (ad = adsorbed).

For this process the standard potential of the metal, the character of ligands, respectively the stability of coordination compound and the electrode potential are of importance. The pH is only in relation to the effect of protons to the ligands state of interest. The concentration of reducing agent is only of importance in relation to the covering of nanoparticle surface by the reducing agent or in case that the reducing agent acts as ligand.

The oxidation of reducing agent can occur nearly independently from the metal reduction at the surface of the same metal nanoparticle. The spontaneously formed open-circuit electrode potential of the growing metal nanoparticle is the only obligatory link between cathodic and anodic partial process. Following formulation characterizes the anodic partial process, in general:

$$R \rightarrow R^+ + e^- \qquad (3)$$

In many oxidation processes, in particular in case of oxoanions and of many organic reducing agents protons are involved in the reaction, and, therefore, the pH is of large importance. In case of using metal compounds as reducing agents, the present types and concentrations of ligands will be of importance for the anodic partial process, too.

Following to this, the electrochemical potential represents the central parameter for the open-circuit electrochemical conditions for metal nanoparticle growth. This potential is determined by the character and intensity of all involved electrode processes. The standard electrochemical potential of the reducing agent oxidation is of particular importance, therefore. Borohydrides are under use as reducing agents of high reduction power in chemical synthesis since many years. Their high reduction power is due to a very low electrochemical potential. They are suited for the preparation of metal nanoparticles. But, their properties as ligands and the sensitivity against pH is quite different to other well introduced reducing agents like citric acid, ascorbic acid or others. Thus, it was expected, that the formation of nanoparticles by sodium borohydrate reduction in a micro-flow-through arrangement will differ considerably from the known metal nanoparticle synthesis in microsystems by use of organic reductions agents.

3. Experimental

3.1. Synthetical method

The applied syntheses are derivations of a conventional method for the synthesis of small GNP, as earlier described [15].

3.2. Experimental arrangements and devices

Static chip micro-mixers based on Si/glass technology were used for the preparation of nanoparticles. The mixers contain eight split and recombine units. The fluid channels are designed through three planes resulting in an efficient lamination of the inlet streams of liquids as described earlier [17].

An arrangement with two or three mixing steps was necessary in order to study the influence of concentrations, concentration ratios during the micro-flow-through synthesis. A modular arrangement with residential loops was applied instead of an integrated multistep mixer in order to allow longer time for interdiffusion during the passage of residential loops.

The principle arrangement is shown in Fig. 2. The fluid inlets are differently addressed for the three classes of experiments reported here: for the synthesis of GNPs, the tetrachloroaurate solution and the buffer solution (potassium carbonate) were mixed at first, then water could be added in the second mixing step in order to vary the absolute concentration of metal complex and carbonate. After the second residence loop, the reducing agent was mixed with the other educts (Fig. 2a).

The first mixer was used for the introduction of desired metal concentrations in the experiments of silver nanoparticle preparation (Fig. 2b). In this case, the reducing agent was added by the second micro-mixer. In this way, the absolute concentrations as well as the concentration ratio of metal salt and sodium borohydrate can be choosen arbitarely. The third mixer can be used for the application of ligands for the modification of the molecular shell around the primerly formed metal core.
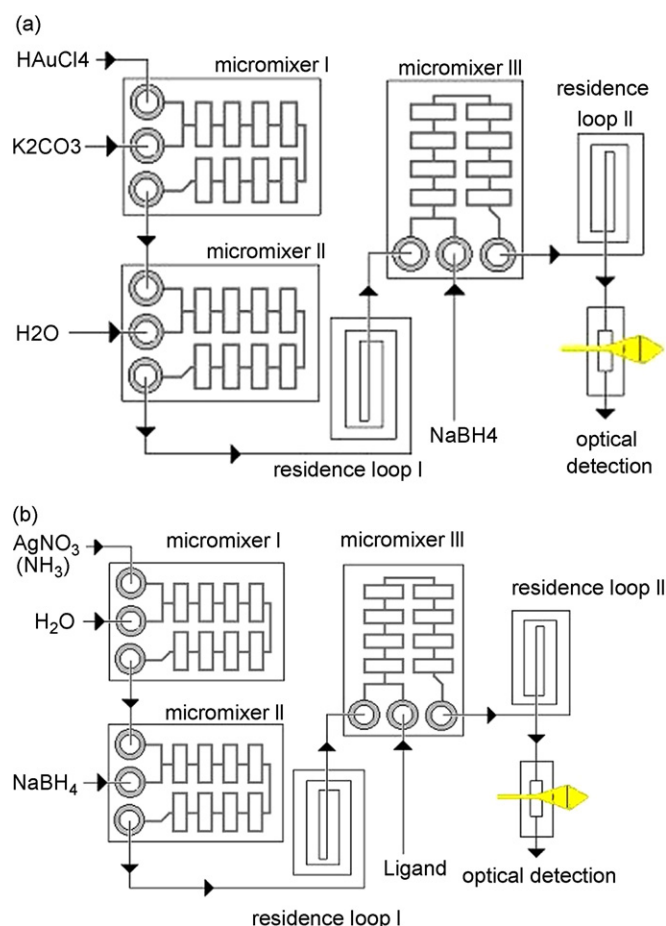

Fig. 2. Modular microreactor arrangement for flow-through process: (a) synthesis of gold nanoparticles and (b) synthesis of surface-modified silver nanoparticles.

3.3. Nanoparticle characterization

The obtained colloidal solutions were characterized by UV/VIS spectralphotometry (Specord 200, Analytik Jena AG) and by differential centrifugation sedimentation DCS (CPS Instruments Inc., USA). For SEM imaging, droplets of colloidal solution were placed on chips of polished monocrystalline silicon. After a short drying, the chips were rinsed with deionized water and dried again. In this way, nanoparticles became adsorbed at the electrically conductive substrate (it cannot be excluded that some particle aggregation is due to the adsorption process).

3.4. Chemicals

All used chemicals were p.A. graded and used as obtained from the corresponding suppliers: tetrachloroacid (Roth, Germany); mercaptoundecanoic acid, mercaptoundecanol (Sigma–Aldrich); sodiumborohydride, silver nitrate (Merck, Germany).

4. Results and discussion

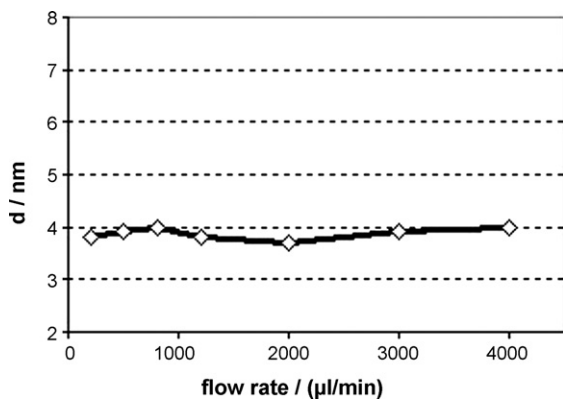The micro-flow-through synthesis allows the formation of stable colloidal solutions of gold nanoparticles (GNPs) with-

Fig. 3. Flow rate dependence of GNP formation by micro-flow-through reduction with borohydride.

Fig. 5. Reduction of particle size distribution with flow rate in the flow-through synthesis of SNPs by use of borohydride at room temperature.

out cooling, despite the high reactivity of the borohydride. GNP solutions were obtained at flow rates between 200 µl/min and 4 ml/min at room temperature using an experimental arrangement as shown in Fig. 2a. The well reproducible synthesis of GNPs is (probably) due to the high mixing efficiency and the low interdiffusion time in the static micro-mixers. It was found, that the mean size was nearly the same over the comparable high flow rate range (Fig. 3). There was also no significant influence of flow rate on size distribution. The obtained particles possess a mean diameter of a little less than 4 nm in all experiments. This observation suggests rate-independent nucleation conditions in the experiments.

The influence of absolute concentration of tetrachloroaurate and borohydride on the nucleation was studied by experiments with a variation of the ratio of both educts and an additional water input. The volume part of water in relation to the flow of tetrachloroaurate and borohydride solution was varied between 0 and 225%. The diluted solutions also yield GNPs in form of a stable colloidal solution in a well reproducible manner. However, we found a clear tendency to smaller mean particle diameters with decreasing Au and BH_4 concentration (Fig. 4), the effect seems to be stronger at small flow rate ratios.

This observation can only be interpreted by an increasing nucleation number in case of decreasing concentration. This effect could be due to a fast growth of formed metal cores at

higher concentration leading to a fast drastical lowering of tetrachloroaurate content under the nucleation threshold. At lower concentrations, the growth is less quick, which means that the nucleation threshold is later achieved. In result, more and smaller cores could be formed at lower concentrations.

A well reproducible formation of stable colloidal solutions was also found in micro-flow-through synthesis experiments of silver nanoparticles (SNPs) with borohydride at room temperature. In contrast, to the GNP synthesis, the mean diameters of the formed SNPs were much larger and amounted to about 15 nm in experiments with the experimental arrangement of Fig. 2b and in a flow rate range of educt solutions between 200 and 8000 µl/min. The higher diameter of SNPs can only be explained by a higher ratio of growth rate to nucleation rate in the formation of silver nanoparticles. It is well known from many other experiments, that the nucleation of silver is kinetically hindered in relation to the growth in comparison to gold, which also shows a higher nucleation tendency in case of other reducing agents.

Whereas the mean particles size of SNPs is nearly uneffected by the flow rate in the investigated flow rate range, the size distribution width is lowered with increasing flow rate in contrast to the GNP formation (Fig. 5). This finding hints to the importance of mixing rate for the duration of nucleation. A higher value for the size distribution width speaks for a longer duration
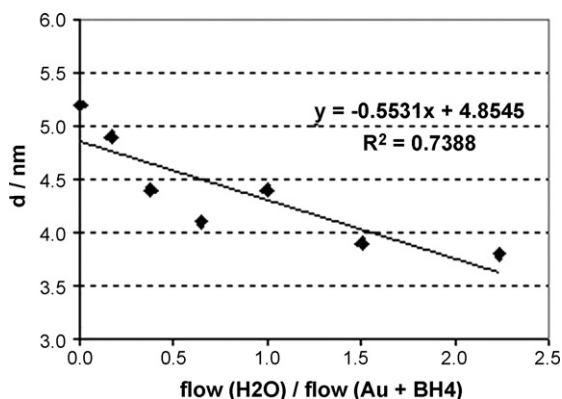

Fig. 4. Influence of dilution on GNP formation under conditions of constant flow rate-ratios of tetrachloroaurate, carbonate and sodium borohydride.
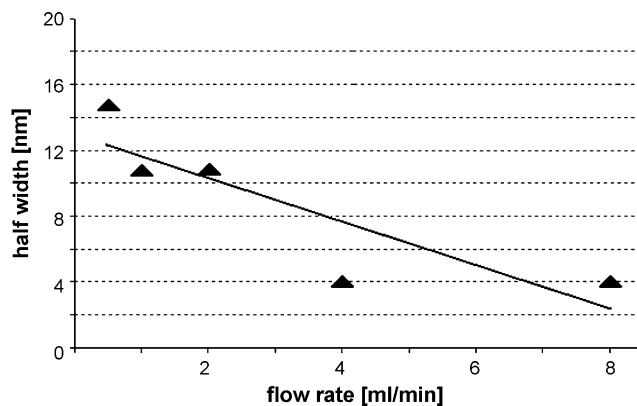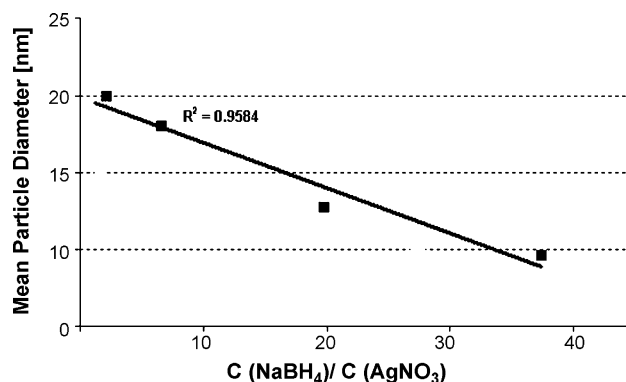

Fig. 6. Influence of $AgNO_3/NaBH_4$ ratio on the size and size distribution of silver nanoparticles formed in micro-flow-through process.

of the nucleation phase, a lower value for a shorter duration of the nucleation phase. Hence, it can be concluded, that the nucleation occurs only in a short time interval, but under very well mixed conditions in case of high flow rates (4 and 8 ml/min). It can further be concluded, that the realization of fast mixing by a micro-flow-through process under high flow rates allows a drastical narrowing improvement of size distribution of silver nanoparticles.

The size of SNPs can be tuned by the ratio of flow rates of borohydride and silver salt solution. The SNP size decreases with increasing ratio of the both educts (Fig. 6). This behaviour is obviously due to the increasing nucleation rate in case of increasing borohydride concentration. Thus, the density of silver

cores increases with increasing excess of borohydride in relation to silver cations.

The addition of specific ligands in the last mixing step leads to a shift of spectral properties of the formed colloidal solutions. The effect of ligands on the shape of the gold plasmon and the
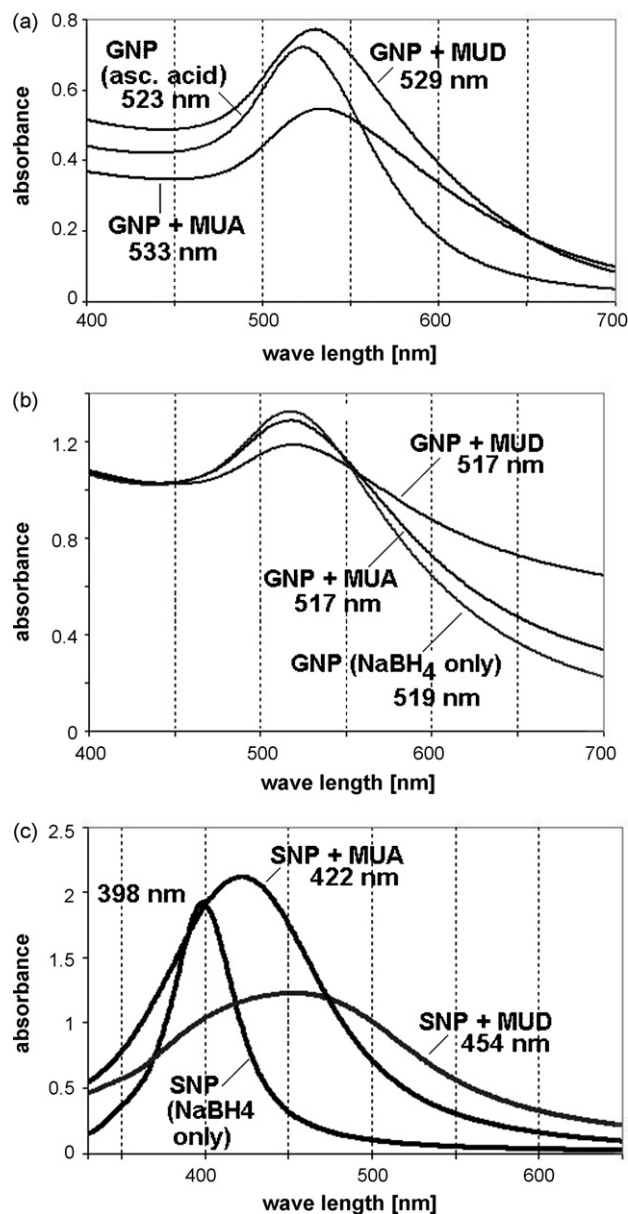

Fig. 7. Optical absorption characteristics of nanoparticles without and with specific ligand shells: (a) GNPs prepared by reduction with ascorbic acid; (b) GNPs prepared by reduction with sodium borohydride; (c) SNPs prepared by reduction with ascorbic acid; MUD: mercaptoundecanol, MUA: mercaptoundecanoic acid.
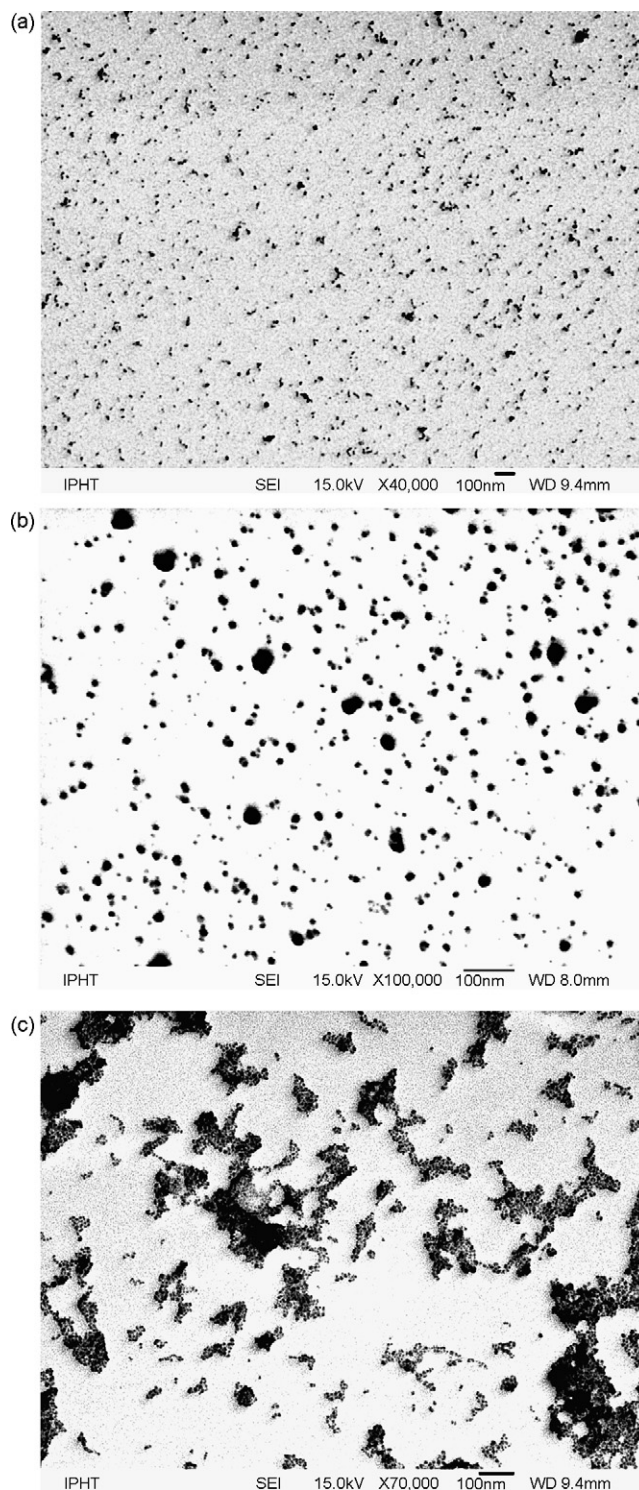

Fig. 8. Examples of prepared nanoparticles (SEM images). (a) Gold nanoparticles (borohydride reduction, without ligands); (b) silver nanoparticles (borohydride reduction, without ligands); (c) gold nanoparticles (borohydride reduction, with thiolated ligands), scale bar 0.1 μm.

silver absorption band speaks for the integration of these ligands in the molecular shell of the metal nanoparticles (Fig. 7). The influence of thiolated ligands on gold nanoparticles seems to be a little stronger in case of an ascorbic acid reduction (Fig. 7a) than in case of a borohydride reduction process (Fig. 7b). The effect of ligands on the spectral properties is still more important in case of SNPs than in the case of GNPs. The addition of MUD or MUA leads to a remarkable bathochromic shift of the silver plasmon absorption band (Fig. 7c).

The differences in the size of nanoparticles and their aggregation behaviour is well confirmed by the SEM images. The size of particles at silicon surfaces is in good agreement with the data of DCS. The electron micrograph shows small particles with a narrow size distribution (Fig. 8a) in case of GNPs (without additional ligands), larger particles in case of SNsPs (Fig. 8b) and a significant enhanced tendency for aggregation in case of thiolated ligand addition (Fig. 8c).

5. Conclusions

Gold and silver nanoparticles can be prepared by reduction of metal salt solutions with borohydride in micro-flow-through systems at room temperature. At higher flow rates, stable colloidal solutions of both metals are obtained. A modular arrangement of three static chip micro-mixers is well suited for the miniaturized synthesis.

The size and size distribution of metal nanoparticles depends on the process parameters. Thus, size and size distribution were controlled in a continuous micro-reaction process more easily than in a batch reactor. The size of gold nanoparticles can be tuned by the educt concentration in a certain range. Silver nanoparticles of particular narrow size distribution were obtained at high ratios of borohydride to metal salt.

References

[1] T. Herweck, S. Hardt, V. Hessel, H. Löwe, C. Hofmann, F. Weise, T. Dietrich, A. Freitag, Visualization of flow patterns and chemical synthesis in transparent micromixers, in: Proceedings of the IMRET 5, Strasbourg, France, 2001, pp. 215–229.
[2] R. Schenk, M. Donnet, V. Hessel, Ch. Hofmann, N. Jongen, H. Löwe, Proceedings of the IMRET 5, Strasbourg, France, 2001, p. 489.
[3] X.Z. Lin, A.D. Terepka, H. Yang, Nano Lett. 4 (2004) 2227–2232.
[4] J. Wagner, T. Kirner, G. Mayer, J. Albert, J.M. Köhler, Chem. Eng. J. 101 (2004) 251.
[5] H. Nakamura, Y. Yamaguchi, M. Miyazaki, M. Uehara, H. Maeda, P. Mulvaney, Chem. Lett. (2002) 1072–1073.
[6] E.M. Chan, R.A. Mathies, A.P. Alivisatos, Nano Lett. 3 (2003) 199–201.
[7] J.M. Köhler, J. Wagner, J. Albert, J. Mater. Chem. 15 (2005) 1924.
[8] M. Mertig, L.C. Ciacchi, R. Seidel, R. Pompe, A. DeVita, Nano Lett. 2 (2002) 841.
[9] C. Niemeyer, Curr. Opin. Chem. Biol. 4 (2000) 60.
[10] W. Fritzsche, Rev. Mol. Biotechnol. 82 (2001) 37–46.
[11] J. Wagner, J.M. Köhler, Nano Lett. 5 (2005) 685.
[12] H.C. Soennichsen, III. Ilmenauer Workshop "Chemische und Biologische Mikrolabortechnik", Elgersburg, 2006.
[13] C. Sönnichsen, A.P. Alivisatos, Biophys. J. 88 (2005) 364A–365A.
[14] J.M. Köhler, U. Hübner, J. Wagner, M. Held, AICHE Spring National Meeting/5th World Congress on Particle Technology, Orlando, USA, 2006, paper 98c.
[15] G.T. Hermanson, Bioconjugate Techniques, Academic Press, San Diego, USA, 1996, p. 597.
[16] H.F. Zhang, I. Hussain, M. Brust, Adv. Mater. 16 (2004) 27.
[17] T. Kirner, J. Albert, M. Günther, G. Mayer, K. Reinhäckel, J.M. Köhler, Chem. Eng. J. 101 (2004) 65–74.