Thioether-Polymer Coating for Colloidal Stabilization of Silver Nanoparticles

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Enhancing the colloidal stability of silver nanoparticles (AgNPs) is crucial to maintain their unique properties allowing broad application of these NPs. Stabilization of AgNPs is usually achieved by surface modification with thiol containing polymers showing limitations owing to the nucleophilic and oxidative character, whereas chemical inert thioethers have so far received little attention. Herein, AgNPs coated with mono- and multivalent thiol- and thioether polymers are prepared to systematically investigate the adsorption kinetics onto the silver surface as well as the colloidal stability after exposure to different conditions relevant for biomedical application, such as freeze-drying and treatment under physiological conditions. Although the thioether polymers show a slower immobilization onto AgNPs, the same or mostly even better stabilization is exhibited than for the thiol analogs. In addition, the polymer surface coverage and the polymeric arrangement of these polymers on AgNPs are calculated, as they supposedly influence the stability.

1. Introduction

Due to their interesting chemical, physical, and biological properties, colloidal silver nanoparticles (AgNPs) attracted enormous attention in nanotechnology and biomedicine, showing a wide range of applications, such as biosensor materials, drug delivery systems, dental restorative materials, antimicrobial agents, for wound healing, or in cosmetics.1] Ensuring the broad applicability of AgNPs, the stabilization efficacy plays a crucial role, as aggregation leads to a loss of their unique properties. Thus, it is relevant for enhancing the stability of such particles by attaching capping agents with high affinity to the surface, which consequently generate a barrier to aggregation. AgNPs are normally stabilized by charges or tenside double layer,2,3] and further stabilization and biocompatibility of the particles are usually achieved through ligand-exchange reactions especially with poly(vinyl pyrrolidone) (PVP)4,5] or thiolfunctional molecules, often with alkyl thiols6,7] or the commonly used thiol-terminated poly(ethylene glycol)8,9] (MeO-PEG-SH). Furthermore, it is recognized that surface modification, for example, with cysteine and other low molecular weight thiols affected the cytotoxicity of silver ions to organism.10,11] To date, a lot of reports intensively investigate the interaction of thiols with silver gaining fundamental insights into the adsorption mechanism.12–15 As thiols are oxidation sensitive, and the presence of the highly nucleophilic thiols in molecules restricts the possibility to introduce other functional groups,16] we have, thus, examined whether thioether may be used as alternative to thiols for stabilizing silver colloids. In case of thioethers, the synthesis of silver-thioether complexes17,18] or the attachment on flat silver surfaces19] is described in the literature, but to the best of our knowledge, there is nearly no study considering thioether-containing polymers as possible coating systems for AgNPs. Pletsch et al.20] for example, reported an in situ method using linear high-molecular poly(propylene sulfide) (PPS) for conjugation on AgNPs resulting in stabilization of such particles. Unlike in the case of the noble metal silver, in the last few years, there are a large number of investigations on thioether coatings on gold NPs (AuNPs)21,22] as an alternative to the well-studied thiols23,24] Recently, our working group presented a thorough contribution on immobilizing mono- and multivalent thiol- and thioether-polymers on AuNPs, yielding high colloidal stability for thioether modification especially for coating with the multivalent system.25]

Herein, we raise a question whether functionalization of AgNP with thioether is comparable or even enhances the stabilization efficacy compared with thiols and, particularly, whether the multivalency leads to stable AgNP conjugates even though a weaker sulfur–silver bond is proved compared with the sulfur binding on Au.26] For this, we systematically compare monovalent MeO-PEG-SH and MeO-PEG-SPentyl with multifunctional analogs, linear side-chain functionalized polyglycidol (PG) with multiple thiol (P(G-co-SH)), or ethylthioether (P(G-co-SE)) as a coating system for AgNPs. The modified AgNPs were characterized and exposed to conditions provoking aggregation of the NPs,
such as centrifugation, treatment at 80 °C, freeze-drying, and incubation in buffer and medium. In the literature, there are few contributions to the stability of capped AgNPs in different biological relevant media. However, most studies assessed only the influence of proteins on citrate-stabilized particles\cite{27,28} or additionally compared the colloidal stability of citrate AgNPs with PVP-coated or PEGylated particles,\cite{29–31} resulting in better stabilities. To date, there have been reports for thiol-terminated PEG attached to AgNPs, but yet no working group was focusing on thioether-polymer adsorption or multivalent systems, respectively.

2. Results and Discussion

2.1. Ag Surface Modification with Thiol and Thioether Polymers

Figure 1a displays a simplified schematization of thiol- and thioether modification of AgNPs obtained by ligand exchange reaction with the mono- and multivalent sulfur-containing polymers used in this study. Before characterization of the polymer-capped AgNPs, first, the NP size and shape were analyzed using scanning electron microscopy (SEM) imaging (Figure S1a, Supporting Information), showing, in accordance with the manufacturer’s specification, that the particles are almost spherical and NP size deviation with less than 13% is realized, resulting in diameters with a deviation of 21.3 ± 2.7 nm. In addition, the citrate-stabilized AgNPs were characterized via dynamic light scattering (DLS) as well as UV–Vis absorbance and Fourier-transform IR (FT-IR) spectroscopy. Figure S1b–d, Supporting Information, shows a characteristic surface plasmon resonance (SPR) peak at 400 nm, a curve progression with a polydispersity index (PDI) of 0.229, and a mean hydrodynamic diameter (Z-average) of \(d = 26.2 \pm 0.5\) nm as well as the presence of the C=O-stretch vibration at 1579 and 1393 cm\(^{-1}\) assigned to the carboxylate moiety in the IR spectra, indicating that citrate is used as a capping agent. The latter could also be confirmed by the negatively charged surface determined by zeta measurements (Figure 1b). Due to the only negligible electrostatic interactions of the citrate molecules on the NP surface, the AgNPs can easily be modified with sulfur-containing compounds via ligand exchange under the formation of a quasi-covalent silver–sulfur bond.\cite{32} Such organosulfur molecules possess high affinity to the silver surface and have been used to stabilize the particles. It is known that the polymer-capped particles (steric stabilization) are more stable than citric acid-modified particles, which were charge stabilized.\cite{31} In this study, thiol- and thioether PEG and PG having a similar chemical structure and a comparable molecular weight were used for NP functionalization and sterical

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**Figure 1.** Polymeric modification of AgNPs. a) Simplified schematization of thiol- and thioether polymer-modified AgNPs used in this study. b) Values of SPR, \(d\), PDI, and \(\zeta\) of citrate- and polymer-stabilized AgNPs, determined by UV–Vis, DLS, and Zeta potential measurements. c) Normalized UV–Vis absorption and d) DLS spectra of 20 nm citrate AgNPs (grey) compared with particles functionalized with MeO-PEG-SH (green), MeO-PEG-SPentyl (light green), P(G50-co-SH6) (purple), and P(G50-co-SEt6) (light purple).

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**Table 1.**

| Sample               | SPR [nm] | \(d\) [nm] | PDI | \(\zeta\) [mV] |
|----------------------|----------|------------|-----|---------------|
| Citrate              | 400      | 26.2 ± 0.5 | 0.229 | -36.5 ± 2.5   |
| MeO-PEG-SH           | 407      | 48.8 ± 1.1 | 0.111 | -16.8 ± 1.4   |
| MeO-PEG-SPentyl      | 403      | 42.8 ± 0.9 | 0.201 | -21.1 ± 2.7   |
| P(G50-co-SH6)        | 406      | 33.5 ± 0.8 | 0.213 | -19.8 ± 1.3   |
| P(G50-co-SEt6)       | 403      | 36.2 ± 0.8 | 0.218 | -25.4 ± 2.6   |
stabilization. The functional groups were introduced by thiol–ene click reaction.\cite{25,33} Furthermore, the successful attachment of the polymers to the NP surface was confirmed via various spectroscopic data (UV–Vis, DLS, zeta potential, and FT-IR spectroscopy). The red shift in the SPR band of the polymer-capped NPs compared with the citrate-stabilized AgNPs (Figure 1c) is caused by a change in the dielectric constant at the surface of the particles.\cite{34} The detection of larger hydrodynamic diameter in the DLS spectra (Figure 1d) indicated the binding of these polymers on the NP surface, whereby the PG coating exhibited a lower hydrodynamic diameter than the functionalization with PEG (Figure 1b). The thinner coating layer for PGs in contrast to PEG suggested that according to the literature, the polymers display different conformations on the AgNP surface (Figure 1a). While, in case of PEG, there can only be an interaction via end group, which lead to a mushroom or brush-like configuration, PG can be possibly multiple bonded to the particle surface showing trains and loops.\cite{1,35} Zeta potential measurements of AgNPs before and after polymer coating displayed in Figure 1b show an increase from around −37 mV for citrate AgNPs to values between −26 and −17 mV for polymer functionalized NPs verifying the successful attachment with neutral capping agents. In addition, the comparison of the FT–IR data of polymer-coated AgNPs, pure polymers, and citrate-stabilized AgNPs in Figure S2, Supporting Information, suggests a complete ligand exchange.

2.2. Colloidal Stabilization Efficacy

Before evaluating the colloidal stability of the thiol- and thioether polymer-coated AgNPs, an adsorption kinetics study was recorded by performing a time-dependent polymeric incubation using different time points ranging from 5 min to 12 h. As displayed in Figure 2a–d, the multivalent P(G50-co-SEt6) needs longer complete particle passivation than the thiol analog as well.
as the monovalent polymers, which is in accordance with the literature for monolayer formation of thiol versus thioether on flat metal surfaces. However, the longer passivation time must not be necessarily related to a weaker thioether–silver bond and as already verified for AuNPs, Barngrover and Aikens found a residue group dependency of the binding energy in silver–sulfur clusters, however, observing no significant differences using chemical and structural similar groups such as hydrogen and methyl groups.

While an incubation time of at least 2 h was required for P(G50-co-SEt6), 5 min incubation was enough reaching steric stabilization for MeO-PEG-SPentyl functionalized particles, indicating that the initial adsorption is dependent on the ligand structure. In case of the side-chain functionalized PG, a slower ordering respective reorganization process occurs probably due to steric hindrance. The faster thioether passivation of the monovalent system might possibly be further provided by additional stability due to van der Waals interactions of the extended PEG brushes.

Besides the study on binding kinetics, the colloidal stabilization efficacy of the different polymer coatings was evaluated. Therefore, the particles were exposed to conditions provoking aggregation, such as centrifugation, high temperatures, freeze-drying, treatment in phosphate buffered saline (PBS), and Delbecco’s modified Eagle medium (DMEM) as well as incubation in 5 mM phosphate buffer (PB) with different pH values (4.0, 5.4, 7.4, and 9.4). As AgNPs have a strong SPR band in the UV–Vis spectrum, the stability of coated particles can generally be determined by changes in the curve progression or absorbance intensities.

Thus, the colloidal stabilization in percent was analyzed by measuring the absorption before and after each treatment. In addition, this allows providing a statement on the stability in percent (see Figure 2e), for what the absorbance value at a wavelength of 410 nm, obtained by measurements before (mean 100%) and after, was situated in relation. For this purpose, it was relevant to verify no absorption of the used polymers at the considered wavelength of 410 nm (Figure S4, Supporting Information).

First, the impact on the colloidal stability after five centrifugation and resuspension cycles was investigated. While there was no notable influence on the stabilization for thioether-polymer coatings, thiol functionalization leads to a polymer-dependent decrease, even though the polymer coverage was much higher than for thioether, as listed in Table S2, Supporting Information. The better colloidal stability values indicate a stronger thioether–silver interaction under centrifugation conditions in comparison with the thiol linkage. Attachment with multivalent P(G50-co-SH6) ensured good stabilities around 70%, whereas modification with thiol-terminated PEG exhibited a significant particle loss of 51%. In case of thiol functionalized polymers, the amount of thiol moieties influences the stabilization efficacy, as a higher number of anchor groups ensured better colloidal stability.

In addition, heating up the particle solution to 80 °C for 12 h resulted in good colloidal stabilities for thiol- and thioether-polymer functionalized AgNPs (81–89%) with exception of P(G50-co-SH6). In accordance with the centrifugation studies, there was no correlation between the coverage density and the particle stability. Here, the type of the anchor group influences the stabilization efficacy, indicating a weaker thiol-silver correlation upon high temperatures than the thioether linkage. Due to additional stability of the PEG brushes by van der Waals interactions, the single anchor unit shows less impact on colloidal stability.

Furthermore, the stabilization after a lyophilization process, which is an important method improving the long-term stability of NPs relevant for clinical applications, was studied. Therefore, the colloidal solutions of the modified particles were deep-frozen followed by removing the ice under reduced pressure. Afterward, the dried samples were resuspended in milli-Q H2O before analyzing the absorbance value at 410 nm. Figure 2e shows that the stabilization effect is highly dependent on the polymer coating. A thioether functionalization possesses the best colloidal stability of 89% for P(G50-co-SEt6) and 87% for MeO-PEG-SPentyl, and also, the monovalent thiol polymer reached the good stabilization values of 71%. In contrast, the AgNPs modified with P(G50-co-SH6) resulted in aggregation possibly due to oxidative crosslinking of the multiple thiol moieties. The oxidative effect was less crucial for MeO-PEG-SH due to single end group functionalization, achieving less poor colloidal stabilization.

To investigate the influence of ions and proteins on the colloidal stability, the different polymer coated AgNPs were incubated for 12 h in PBS and DMEM, the most common medium for cell culture. After centrifugation, the particles were resuspended in PBS and DMEM, respectively. As shown in Figure 2e, AgNPs modified with MeO-PEG-SH reached highest stability values (83%) after treatment in the standard working concentration of 1× PBS, associating with the high number of polymers per particle (see Table S2, Supporting Information). On the contrary, the polymer coverage has no influence on colloidal stabilization for the other polymer coatings. Instead, both thioether functionalization displayed good stabilities around 70%, whereas the multivalent thiol polymer showed the worst colloidal stabilization of 30%. In case of PG coating, the type of anchor groups was decisive regarding the stability of the particles. Here, a lower thiol-silver bonding strength resulted in aggregation enabling adsorption of ions from the salt solution on the particle surface.

Besides the previously discussed stability studies, suspension in DMEM, a complex mixture of proteins, sugars, and amino acids, demonstrates no polymer dependency in view of the stabilization in percentage terms. Here, all coatings resulted in good colloidal stabilities (72–78%) with a slightly improved stabilization for thiol-functionalized AgNPs, which is accompanied with a larger number of polymers on the particle surface.

Finally, the influence of different pH values on the stabilization effect of coated AgNPs was checked. Therefore, the functionalized particles were suspended in 5 mM PB with the pH values between 4.0 and 9.4, which covers a significant range of ion strength. Figure S5, Supporting Information, shows that only for modification with MeO-PEG-SPentyl, there are major differences in SPR peaks, decreasing in the order 7.4 > 9.4 > 5.4 > 4.0. Thiol-PEG functionalized particles had similar absorbance values for pH 4.0 and 5.4 and an equal peak disappearance for higher pH levels. In contrast to this, the multivalent PG coating was more stable in neutral and alkaline buffer than in acidic environment, whereby this effect is less pronounced for AgNPs modified with P(G50-co-SH6).
3. Conclusion

In summary, different physicochemical techniques verified the successful thiol and thioether surface functionalization of AgNPs, whereas the number of polymer molecules loaded onto the particles as well as the conformation of PEG on the AgNPs surface was quantified via micro-TGA. As previously reported for AuNPs, thioether binding onto AgNPs is slower than the adsorption of analog thiols. However, the presented study on the colloidal stabilization after centrifugation, high temperature treatment, and lyophilization suggested a thermodynamically stronger attachment for thioethers. Also, the aim of receiving stability in biological fluids could be reached after coating the AgNPs with these functional polyethers except for particles capped with P(G50-co-SH4) suspended in PBS. In all studies using thioether as a binding agent, there are nearly similar results for PEGylated and PG-coated particles indicating no substantially stable silver–ligand interactions for multidentals. The excellent stabilization efficacy of thioether-coated AgNPs in water as well as the good colloidal stability in biological environment and, especially, the ability of introducing different chemical or biological functionalities to the backbone of the thioether PEG make these NP systems of great interest in biomedical applications.

4. Experimental Section

Materials: AgNPs (20 nm) (TJC0126, nanoComposix Inc, San Diego, CA, USA) and poly(ethylene glycol) methyl ether thiol (MeO-PEG-SH) (Sigma Aldrich, St. Louis, MO, USA) were used as received. MeO-PEG-SEt6, P(G50-co-SH4), and P(G50-co-SEt6) were synthesized according to the literature.[23] For preparing PB (0.1 m, pH 7.5), 16 mL of a 0.2 M sodium dihydrogen phosphate solution (NaH2PO4) and 100 mL of deionized water (H2O), PBS (1× PBS, pH 7.4) was prepared by dilution of sodium chloride (NaCl) (8.00 g, 137 mmol), potassium chloride (KCl) (200 mg, 2.68 mmol), sodium phosphate dibasic decahydrate (Na2HPO4·12H2O) (2.80 g, 7.82 mmol), and potassium dihydrogen phosphate (KH2PO4) (200 mg, 1.47 mmol) in 1 L of deionized water. All salts used for PBS preparation were purchased from Merck GmbH, Darmstadt, Germany. DMEM (Thermo Fisher Scientific, Waltham, MA, USA) was supplemented with 10% fetal calf serum and 1% Pen-Strep.

Polymer Functionalization of Citrate AgNPs: For polymeric modification, 100 μL of the respective polymer solution (310 μM) was added to 1 mL of the purchased 20 nm citrate-stabilized AgNPs and incubated overnight. According to inductively coupled plasma-mass spectroscopy (ICP-MS) measurements, the Ag mass concentration of the purchased particle solution was 19.4 mg L−1. During the incubation process, the colloidal solutions were shaken with 200 U min−1 at room temperature (RT) and covered with aluminum foil. The incubation was stopped by centrifugation (20 000 g, 25 min, 4°C) (Mega Star 1.6R, Thermo Fisher Scientific, Waltham, MA, USA), the supernatant was removed, and the residue was redispersed in 1 mL of milli-Q H2O. The purification step by centrifugation was performed twice.

NP Characterization: To acquire SEM image of AgNPs, the particle solution was dropped onto a silicon wafer, which was fixed with conductive silver to the SEM stubs. After evaporation of the water, the sample was placed inside the device from Carl Zeiss microscopy (Göttingen, Germany) and measured with a secondary electron detector. The ImageJ software was used for particle analyzing and area calculations.

The hydrodynamic diameter and the zeta potential of the colloidal particles were determined via DLS measurement at 25 °C using a Zetasizer Nano ZSP from Malvern. The light source was a He–Ne laser with 633 nm wavelength and an intensity of 10 mW with a detection angle of 173°. For measuring, the colloidal NPs were dissolved in milli-Q water.

UV-Vis measurements were performed on a GenesyS 105 Bio spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA), using UV-transparent plastic cuvettes at RT. The device has a Xenon flash that covers a wavelength range from 190 to 1100 nm. Accordingly, milli-Q water was used as reference, and the particle solution was characterized without any dilution. Absorption measurements of the used thiol and thioether polymers were conducted with 310 μM polymer solutions. UV–Vis absorbance scans were taken in the range of 300–700 nm.

The Ag mass concentration was determined by ICP-MS (ThermoFisher Scientific, Waltham, USA). The purchased AgNP solution was diluted 1:100 with 0.69% nitric acid and measured against standard solutions of different dilutions (10, 1, 0.1, and 0.01 mg L−1).

FT-IR experiments were performed with a Nicolet iS10 FT-IR spectrometer with Smart iTX accessories from Thermo Fisher Scientific (Waltham, MA, USA) measuring in a spectral range from 650 to 4000 cm−1. The samples were measured with a diamond attenuated total reflectance unit. The spectra were analyzed using the software OMNIC 8.2 from Thermo Fisher Scientific, Waltham, MA, USA.

Micro-TGA measurements were performed by NETZSCH GmbH (Selb, Germany) using a micro-TG 209 F1 Libra. For evaporating water, the samples were pre-dried at 80°C in a compartment dryer. During the measurement, the samples were heated from 30 to 80°C with a heating rate of 10 K min−1 under nitrogen atmosphere and retained 15 min at 80°C, proving the complete removal of the water. Afterward, the samples were heated up to 900°C with the same heating rate of 10 K min−1. After reaching a temperature of 550°C, the atmosphere was switched from nitrogen to oxygen. The weight loss in the region of 230 to 320°C was considered for PG bound to the AgNP surface, whereas the attached PEG showed a weight loss between 320 and 430°C. These temperature regions were used for calculating the polymer to AgNP ratio.[41]

Binding Kinetics Study: For studying the binding kinetics of the thiol and thioether polymers to the AgNP surface, the citrate-stabilized particles were modified with the respective polymeric solutions as described earlier. After 5 min, 30 min, 2 h, 6 h, and 12 h, aliquots (220 μL) of the particle solution were taken out, and the incubation was stopped by centrifugation (20 000 g, 25 min, 4°C). The supernatant was removed, and the residue was redispersed in 800 μL of milli-Q H2O, followed by absorbance measurements.

Colloidal Stability Studies: The stabilization effect of the different polymer modifications was examined under conditions provoking aggregation of the particles. For each stabilization test, 1 mL of the citrate-stabilized particles were incubated with 100 μL of the respective 310 μM polymeric solution by shaking overnight, followed by centrifugation and removal of the supernatant. For the centrifugation, temperature, and lyophilization studies, these concentrated modified AgNPs were suspended in milli-Q H2O and exposed to four centrifugation and resuspension cycles, to 80°C for 12 h or were freeze-dried. In case of freeze-drying, the received pellets were once again dissolved in milli-Q H2O. Considering the colloidal stability studies in PBS, DMEM, and PBS with different pH values, the concentrated functionalized AgNPs were suspended in the corresponding buffer or medium for 12 h. After centrifugation, the supernatants were removed, and the residues were resuspended again in PBS, DMEM, and PBS, respectively. Investigating the colloidal stabilization efficacy for each mentioned procedure, the particle solutions before and after each treatment were measured via UV–Vis absorbance spectroscopy. To determine the stability in percent, the absorbance values at a wavelength of 410 nm obtained by UV–Vis before (mean 100%) and after were situated in relation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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