

Synthesis and Agglomeration of Silver Nanoparticles Stabilized with 5-R-Tetrazoles

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In this work we present a simple method to obtain silver sols stabilized by tetrazole derivatives. The well established metal precursor silver nitrate and the reductant sodium borohydride have been combined with 5-R-tetrazoles (R = CH₃, NH₂) acting as stabilizing ligands. Depending on the utilized tetrazole, different agglomeration kinetics could be observed. Long term stability and agglomeration processes have been *in situ* investigated by the use of UV/Vis- and Raman-spectroscopy.

1. Introduction

Metallic nanoparticles have attracted considerable interest both by fundamental researchers as well as by industry [1–5]. Until today a huge variety of different types of compounds has been investigated for their use as capping agents for nanoparticles. However, tetrazole derivatives constitute a peculiar class of heterocyclic organic compounds that until now has not been commonly used for that purpose. They represent a promising new group of ligands in nanochemistry which unites many desired properties, such as high coordination ability and a broad range of available derivatives [6–8]. Moreover thermally induced decomposition of tetrazoles leads to a high percentage of gaseous products which might be an interesting feature for future applications in coatings, since the removal of capping agents provides a tremendous potential to improve charge transfer, sensing and catalytic properties of the nanoparticles and their assemblies [9]. The tetrazole unit itself is a bioisostere to the carboxylate group and thus an interesting compound for pharmaceutical research [10].

In the following we present for the first time a synthetic procedure to fabricate silver nanoparticles stabilized by 5-amino-tetrazole (ATZ) and 5-methyl-tetrazole (MTZ), respectively. Therefore the new stabilizing agents were combined with the metal precursor silver nitrate and the reductant sodium borohydrate, both well established in

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Fig. 1. Structural formulas of the tetrazole derivatives used.

silver nanoparticle syntheses [11]. It was found that the synthesized particles tend to agglomerate slowly, which allows controllable *in situ* monitoring of the changes in the optical properties utilizing UV/Vis- and Raman-spectroscopy. The analysis of the data obtained was additionally supported by TEM measurements. The degree of agglomeration determines the plasmonic behavior of the nanoparticles, as well as changes in the SERS-spectra of the tetrazole stabilizers.

2. Experimental

5-Amino-tetrazole (95%) and 5-methyl-tetrazole (95%) were supplied by Aldrich. Silver nitrate (99.9+%) was supplied by Sigma-Aldrich and sodium borohydride (99%) was supplied by Riedel-de-Haen. All chemicals were used without further purification and Milli-Q water was used throughout.

A silver nitrate solution (0.2 % w/v), containing between 3 and 12 μmol of silver nitrate was added to a boiling solution of 0.05–1 mmol of a certain tetrazole derivative in 30 ml of water. Immediately afterwards, 2 ml of the reducing solution, containing 3 mg of borohydride, were quickly injected.

Depending on the desired state of aggregation, the reaction needs to be quenched, via quick cooling, directly after the injection of the borohydride or within a few minutes. Big aggregates were removed by use of 5 μm pore size PTFE syringe filters.

The characterization instrumentation used was a Varian Cary 50 for UV/Vis measurements, a Philips CM-120 (Philips, Netherlands) with 120 kV acceleration voltage and a Tecnai T20 from FEI with 200 kV acceleration voltage to obtain TEM-images. Raman spectra were obtained on a Renishaw RM-2000 Raman microscope using a 532 nm Laser (Gem532 from Laser Quantum) as the excitation source.

3. Results discussion

The two ligands used show slightly different stabilizing properties. However, in general the kind of the resulting nanoparticles is mainly determined by the reaction time. Independent of the stabilizer the particle size distributions are rather poor. The range of the diameters of the silver particles is between 2 and 16 nm.

Using MTZ as stabilizer, it is possible to adjust the degree of agglomeration of the particles in the final silver sol by quenching of the reaction at different points in time after injection of the borohydride solution. Direct quenching (only several seconds after the injection) results in a yellow solution with single silver particles, which

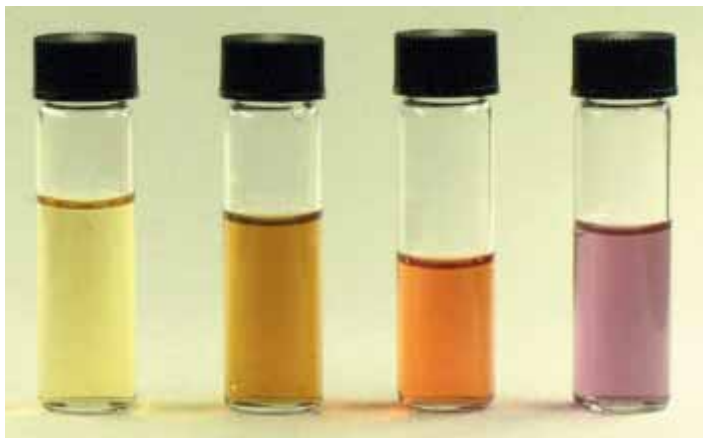


Fig. 2. MTZ-stabilized silver sols at different agglomeration states (quenched after 0 min, yellow; 1 min, orange; 2 min, red and 5 min, purple solution).

is stable for weeks. Whereas longer intervals between the injection and the cooling give successively orange, red and purple solutions, containing dimers, trimers and larger agglomerates, respectively. The resulting solutions are stable for days (see Fig. 2).

For the silver sols stabilized with ATZ a slightly different process needs to be applied. The reaction has to be quenched directly after the injection of the borohydride solution. Otherwise the agglomeration process will proceed until the complete destabilization of the colloid. The directly quenched colloid is stable for approximately one week. In order to start the agglomeration process slowly, the quenched solution was concentrated by vacuum evaporation at 30 mbar and 50 °C until a slight darkening of the yellow color of the solution appeared. From that point the aggregation started and proceeded over a time of one to two days.

The different agglomeration stages of both ligands have been investigated using UV/Vis- and Raman-spectroscopy. On the basis of the corresponding UV/Vis-spectra (see Fig. 3) of the MTZ-stabilized silver colloids shown in Fig. 2, the different agglomeration states are clearly comprehensible. For the yellow solution a single peak at about 395 nm originating in the surface plasmon resonance of single silver particles could be observed. With increasing agglomeration state this peak is first shifted to the higher energy region which leads to the assumption that the agglomeration starts with the bigger particles. Additionally there is a broadening of that peak and for the red and violet solutions another peak at lower energies, which is due to interparticle coupling, has been observed. For the silver sol, stabilized with ATZ, the contour plot in Fig. 4 shows the changes in the UV/Vis-spectra over time due to the agglomeration process. The dominating plasmon band at 390 nm in the absorption spectrum as well as the TEM-investigations revealed that at this stage mainly single silver nanoparticles are present. Thereupon more and more dimers and trimers are formed which are responsible for the increasing and red-shifting peak between 450 and 550 nm. Finally both peaks decrease and bigger network-like structures are formed. The slight blue shift of the plasmon band at 390 nm in the final solution leads to the assumption that the networks are mainly

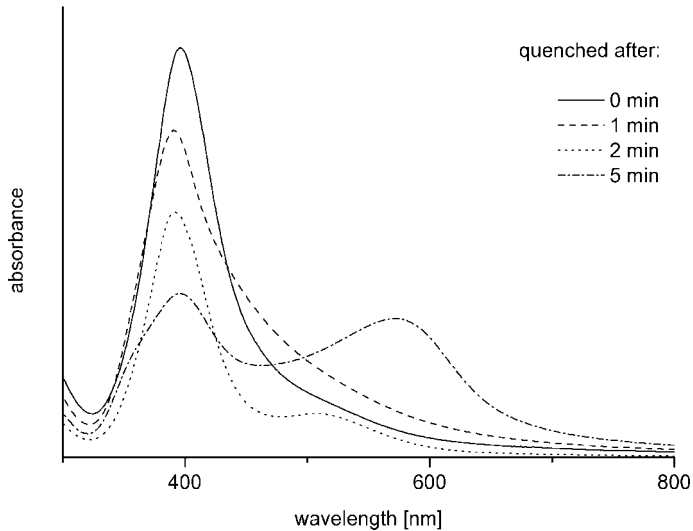


Fig. 3. UV/Vis-spectra of MTZ-stabilized silver sols at different agglomeration states (0 min, yellow; 1 min, orange; 2 min, red and 5 min, purple solution). Spectra are normalized at maximum absorbance to different absorbance values for better distinguishability and are therefore in arbitrary scale.

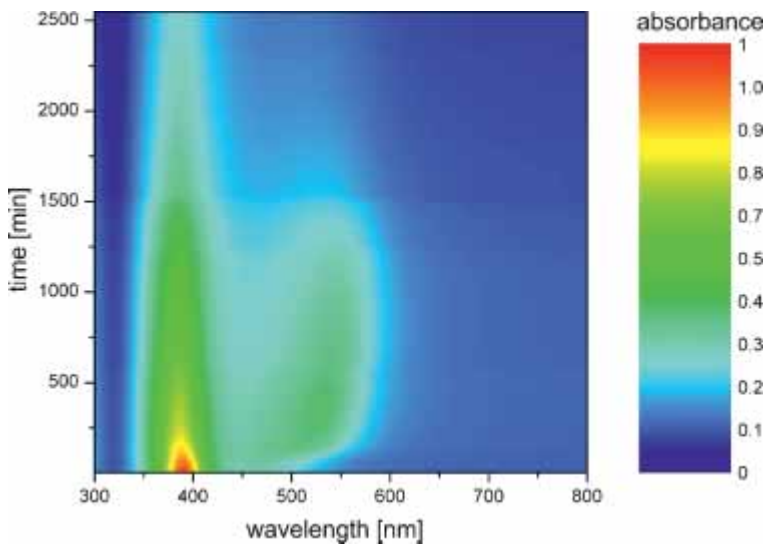


Fig. 4. Contour plot of evolving UV/Vis-spectra of ATZ-stabilized silver sol, beginning from the start of the destabilization process at 0 min.

formed by the bigger particles and the slight yellowish color of the final colloid is due to small silver nanoparticles. Figure 5 shows UV/Vis-spectra and related TEM-images of different stages during the agglomeration.

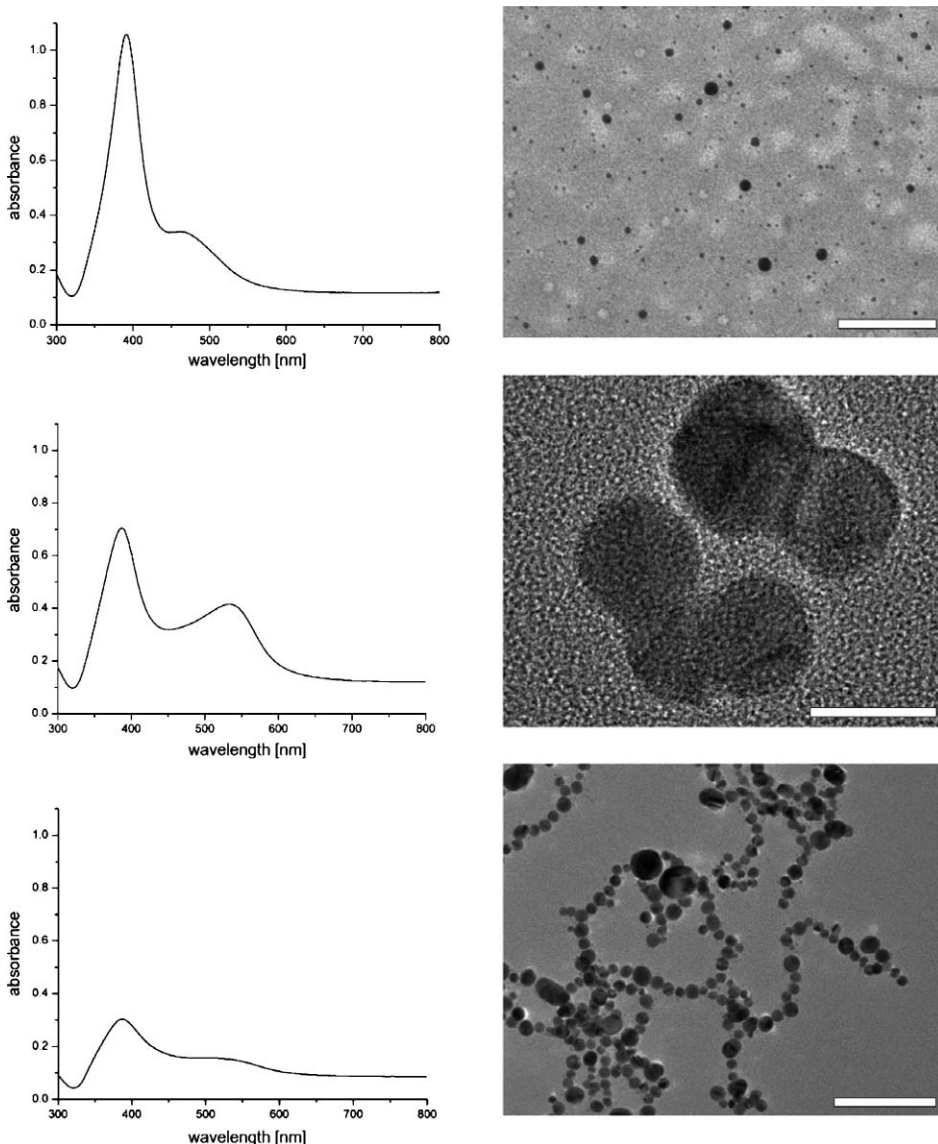


Fig. 5. UV/Vis-spectra and corresponding TEM-images of ATZ-stabilized silver sol; 3, 180 and 2700 min after the start of the destabilization process. Scale bars are 100, 15 and 100 nm, respectively.

In order to investigate the agglomeration process with the aid of Raman-spectroscopy we used the special features of surface enhanced Raman scattering (SERS) [12,13]. It is well known that the Raman scattering intensity of an observed molecule in close vicinity to a nano scaled rough metal surface can be enhanced by several orders of magnitude. The enhancement is extraordinarily high if the analyte is located inside

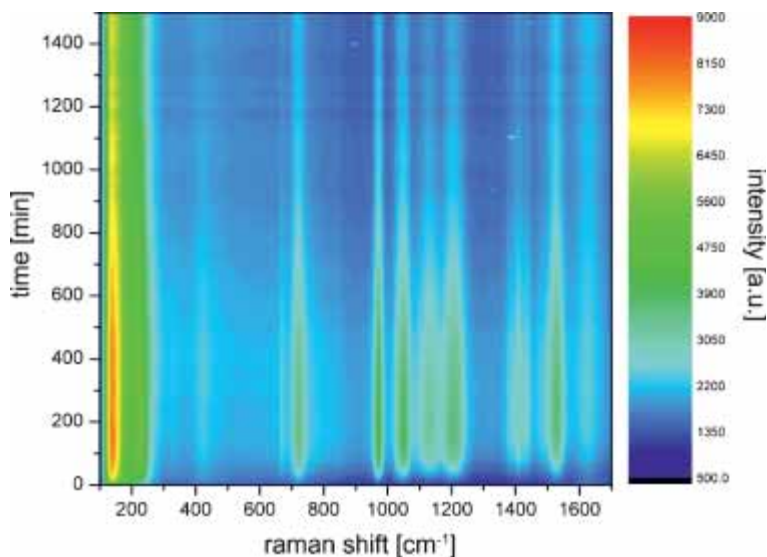


Fig. 6. Contour plot of evolving Raman-spectra of ATZ-stabilized silver sol, beginning from the start of the destabilization process at 0 min.

of a small gap between two metal nanostructures. This is due to an extreme amplification of the electromagnetic field inside these geometries, which are therefore also called “hot-spots” [14,15].

During the agglomeration process, single particles first loosely bound together, which gives the geometry needed for strong Raman enhancements [16]. Later the particles start to coalesce and the gaps between adjacent nanoparticles are vanishing again. These aggregates increase further in size and finally will precipitate so they will not contribute to the measurement anymore. Hence, by *in situ* measurements one should see an increasing Raman scattering intensity, which is passing a maximum and finally will decrease. That is exactly what has been observed for the agglomeration process of the silver sol stabilized with ATZ as shown in the contour plot in Fig. 6. Starting from a Raman scattering intensity of the ATZ in initial reaction mixture (at 0 min), that is just slightly stronger than that measured in absence of the silver nanoparticles, a significant increase followed by a slow decrease of the Raman intensity are observed upon nanoparticle formation and aggregation. The same results could be found for the silver sols stabilized with MTZ. Comparing the Raman spectra of the MTZ for all different agglomeration stages reveals an increase in Raman scattering intensity from the yellow to the orange and red solutions and a diminishment for the purple solution (see Fig. 8).

Figures 7 and 8 show detailed SERS-spectra of ATZ and MTZ stabilized silver sols, respectively. The strong band at 130 cm^{-1} and the broad band at 1630 cm^{-1} are caused by water. Between 600 and 1500 cm^{-1} both samples show various bands that are mainly originating from different ring vibrational modes. At 230 cm^{-1} the Ag–N stretching-vibration appears, which proves that the tetrazoles are bond to the nanoparticle surface. The spectrum of the ATZ stabilized sol additionally exhibits a band at 1540 cm^{-1} , which

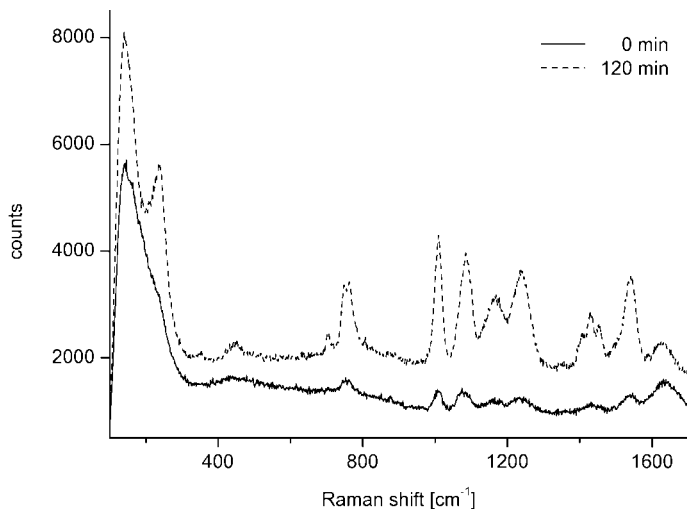


Fig. 7. Raman-spectra of ATZ-stabilized silver sol; 0 and 200 min after the start of the destabilization process.

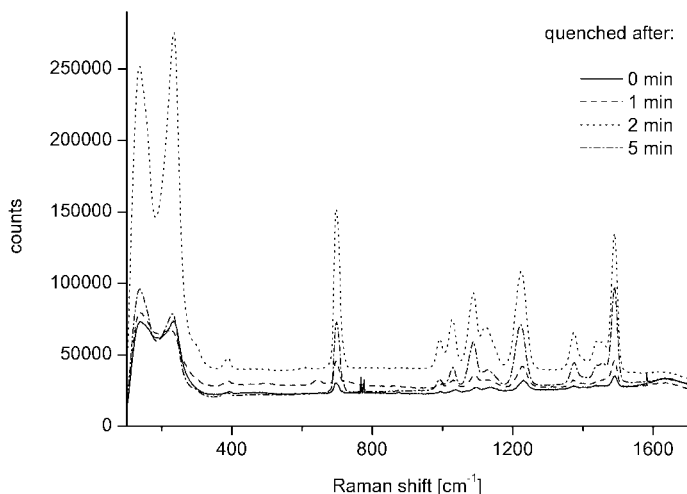


Fig. 8. Raman-spectra of MTZ-stabilized silver sols at different agglomeration states (0 min, yellow; 1 min, orange; 2 min, red and 5 min, purple solution).

could be assigned to the NH₂ scissoring vibration and the lack of the NH mode at 1286 cm⁻¹ leads to the assumption that the nitrogen atom at position “1” in the ring of the ATZ is deprotonated and hence the tetrazole is negatively charged [17].

Since the tetrazoles are probably bound to the surface via the ring nitrogen atoms, the amine group in ATZ and the methyl group in MTZ are pointing away from the particle surfaces. This could be the reason for the different agglomeration behaviors of the

two sols because the amine groups can interact via hydrogen bonds whereas the methyl terminated nanoparticles cannot. Therefore the ATZ stabilized sols agglomerate faster.

4. Conclusions

It could be shown that tetrazole derivatives are possible stabilizing agents in the synthesis of silver nanoparticles. Evolution of physical properties related to different agglomeration stages have been investigated by UV/Vis- and Raman-spectroscopy as well as TEM measurements. Another appropriate method to further characterize the agglomeration behavior would be the dynamic light scattering and will definitely be part of forthcoming work. The new group of stabilizers introduced here offer great potential for further post processing work, like the thermal removal of the tetrazols. This might result in clean surfaces, which would be ideal for sensing and catalytic applications.

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Supporting Information

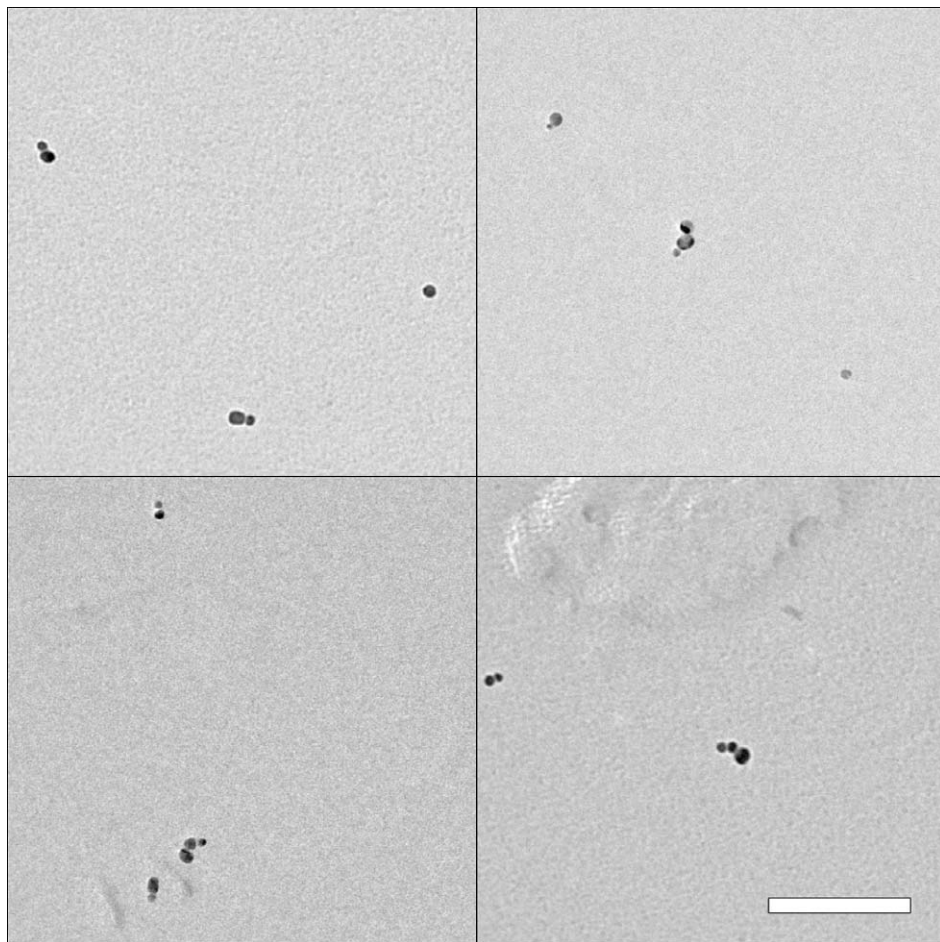


Fig. 9. Overview TEM-images of ATZ-stabilized silver sol 180 min after the start of the destabilization process. Due to very low particle concentrations on the TEM-grid, four typical regions are shown. The sample mainly consists of dimers and trimers. Scale bar is 200 nm.