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## Synthesis and characterization of non-spherical gold colloids in block-copolymer micelles

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**Abstract** Gold colloids of well-defined shape, size and polydispersity are synthesized by heterogeneous reduction of gold salts in amphiphilic block-copolymer micelles. The resulting hybrid systems consisting of the noble metal colloid and the stabilizing shell of block-copolymers are characterized by electron microscopy and small-angle x-ray scattering. Opposite to classical noble metal colloids, the block-copolymer stabilized systems exhibit an extraordinary high colloidal stability which makes analysis and sample handling very simple.

It turned out that non-spherical metal colloids are formed in the early stages of the reduction process where the amount of gold exceeds the reduction agent. At later stages, the colloids break up to globular subunits again.

The reaction period of colloidal anisotropy is reflected in a violet color of the reaction solution, which is caused by a typical structured, double-resonance plasmon band.

Small- and wide-angle x-ray scattering reveal a quantitative measure for the size, shape, anisotropy and local order in each step of the reduction process. It is suggested that the primary aubergine-shaped particles consist of globular primary particles which are glued together via non reacted gold salt. This observation gives rise to some interesting possibilities of the supramolecular handling of colloids.

**Key words** Noble metal colloid – block-copolymers – anisotropy

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### Introduction

In a previous paper, we have presented the controlled synthesis of well stabilized noble metal colloids in the micelles of amphiphilic block-copolymers. The binding process as well as the colloidal structure parameters were characterized by IR- and UV-spectroscopy, dynamic light scattering and small-angle x-ray scattering [1]. During these examinations and a following paper related to a broader variation of the block-copolymer structure and metal salts [2], it turned out that there are three reaction limits of colloid production which deeply influence the structure of the hybrid material:

- The use of a soluble reducing agent and slow nucleation results in one colloidal particle per micelle.
- The use of a soluble reducing agent with fast nucleation results in many colloidal particles per block-copolymer micelle.
- Reduction with a macroscopically heterogeneous reaction agent (two macroscopic phases) results in micelle growth and a colloid size which depends on time. The colloid size is only indirectly controlled by the original micelle. In this case and for the formation of gold-colloids, a colour change usually translated to a decreasing particle size with increasing reaction time was observed.

The present paper is addressed to clarifying the processes on which the color changes in the macroheterogeneous reduction of gold salts loaded in block-copolymer micelles are based on. For this purpose, the reduction process is stopped after distinct periods, and the particle evolution is controlled with dynamic light scattering, small-angle x-ray scattering, UV-spectroscopy and electron microscopy.

It will turn out that this type of process handling enables the controlled synthesis of non-spherical noble metal colloids for different applications.

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## Experimental section

### Colloid synthesis

The synthesis of PS-P4VP-block-copolymers via anionic polymerization and their characterization was performed as described in previous publications [1, 3]. For the present examinations, we restricted ourself to one block-copolymer sample which was rated in earlier examinations to be a very effective stabilizer, PS 3, 2. The overall molecular weight of this sample is  $M_w = 18\,750$ , the polydispersity index is  $M_w/M_n = 1.14$ , and the relative 4-vinylpyridine content is 22%. The described effects occur most clearly when small block-copolymers and relative low metal loads are used.

Metalation of the micelles was performed by simple mixing of the block-copolymer solutions in toluene with substoichiometric (1:9 with respect to the 4-vinylpyridine units) amounts of  $\text{HAuCl}_4$  (Aldrich Co.). The gold salt containing micellar solutions were reduced with  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , thus forming a two-phase system (toluene and hydrazine hydrate do not mix). The formation of gold colloids was observed by an instantaneous color change towards a violet solution, which changed in the later stages to a claret solution again.

To keep a good control of the reduction periods, the macroheterogeneous mixtures were just gently stirred; small samples were taken with a syringe after stopping the stirring at distinct times and fast deposition of the hydrazine droplets at the bottom of the reaction flask. After separation from the phase of the reducing agent, the block-copolymer stabilized metal colloids are stable and do not change their colloidal or spectroscopic properties, the block-copolymer/colloid-hybrids can easily be precipitated, isolated and redissolved in all solvents for polystyrene; these handling procedures also do not change the colloidal and spectroscopic properties. Therefore, all stages of the reduction are regarded to represent stable systems.

### Small- and wide-angle x-ray scattering

The set-up and procedure of small-angle-x-ray scattering (SAXS) as well as the data treatment was already described in previous publication [1, 4]. The measurements were performed on solid films of the metal colloid containing block-copolymers which were obtained by simple evaporation of appropriate amounts of toluene solutions onto thin cellophane supports. In addition, some experiments with dilute solutions using Mark-tubes were also performed, thus resulting in essentially the same results.

WAXS measurements were performed with a Nonius PDS120 Powder diffractometer in transmission geometry. The unique features of the diffractometer are a FR590 generator as the source of  $\text{Cu-K}_\alpha$  radiation, monochromatization of the primary beam with a curved Ge crystal of the scattered radiation with a CPS120 position-sensitive detector. The resolution of this detector is below  $0.018^\circ$ . For our purpose the measured scattering intensity as a function of the scattering vector was sufficient without further data correction.

### Spectroscopic techniques and electron microscopy

UV-measurements were performed with a UV-Ikon 931 instrument (Kontron), working in a spectral range between 190 nm–900 nm. IR-spectra were recorded in KBr-pellets with a Nicolet Impact 400 FT-IR spectrometer working in a range between  $4000\text{ cm}^{-1}$ – $400\text{ cm}^{-1}$ .

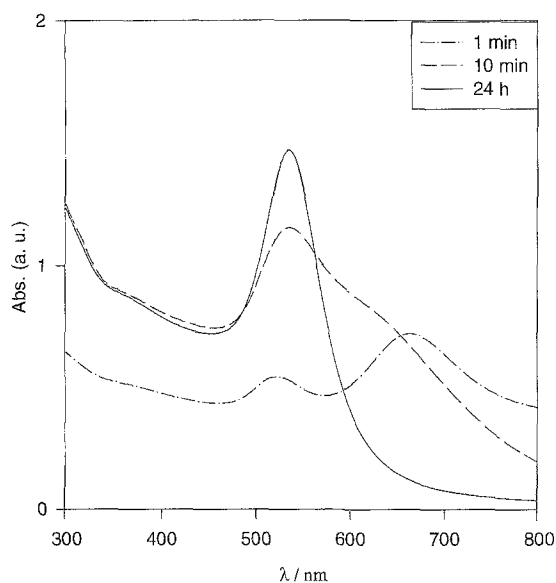
Samples for electron microscopy were prepared by suspension preparation. The dilute micellar or colloidal solutions were sprayed on a 400 mesh, carbon film-coated copper grid, and the solvent was evaporated. Electron microscopy was performed with a Zeiss 940 omega electron microscope operating at 100 kV. Variation of the preparation condition in a rather broad range always resulted in the same type of colloidal morphologies. Therefore, we assume that the EM-pictures in the dried state depict the situation of the gold-colloids being present in solution.

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## Results and discussion

A good selection of proper reduction periods to receive maximal differences of the colloidal morphology can be simply performed on the base of the developing plasmon band of the gold colloids.

Figure 1 shows the UV-Vis spectra of the block-copolymer stabilized gold-colloids in toluene after 1 min, 10 min, and 24 h.



**Fig. 1** UV-spectra of Au-PS-3,2 (1:9), reduced with hydrazine at different stages of the reduction process. After 1 min, a typical double-resonance plasmon resonance is observed. With further increase in reduction time, the resonance narrows and shifts towards smaller wavelengths

In the beginning of the reaction, quite immediately after addition of the reductant, the spectrum is characterized by a split plasmon resonance and a violet color. It is worth recapitulating that the gold colloids with violet color of the present series are far from any instability: once they separated from the hydrazine, they can be stored for months without any change of the spectral or colloidal properties.

After 10 min of reduction, the noble metal colloids are characterized by a broad, single plasmon resonance, having a tail towards longer wavelengths. This band continuously narrows with further progress of reaction and is slightly shifted towards shorter wavelengths. The 24 h measurement shown in Fig. 1 is typical for the fully reacted particles. Parts of these spectra mainly describing the last stages of the reaction were already described in our earlier publication [1]. It must also be underlined that the observed phenomena seem to be rather general: similar spectra and a related time dependence were already described for other synthetic approaches to well defined and stable gold colloids [5, 6]. In the later paper, the occurrence of the second, long wavelength absorption was explained with the existence of “large, fluffy aggregates” [6] which enable electronic coupling of the plasmon resonances between different particles. This follows a classical interpretation, where the whole set of experiments has to be described as a deaggregation and decreasing particle size with advancing time, i.e., the regular scenario with an

inverted time vector. Since neither deaggregation nor shrinking is usually expected for colloids, additional experimental evidence for this very unconventional behavior is desirable.

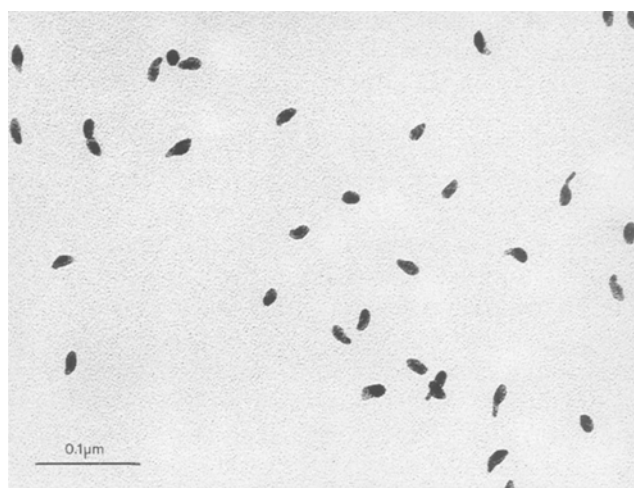
For this purpose, high-resolution transmission electron microscopy was performed with the same samples where the UV-spectra had been recorded. The corresponding electron micrographs are presented in Figs. 2a–c.

To our surprise, it turned out that the gold colloids formed after 1 min reduction period are not spherical: all of them have about the same shape which is clearly anisometric and sometimes slightly bent. Since the particles are practically monodisperse, we can exclude the effects of any uncontrolled aggregation process. Due to the typical shape and the violet color of their solutions, we call this type of colloidal architecture “aubergine”-morphology.

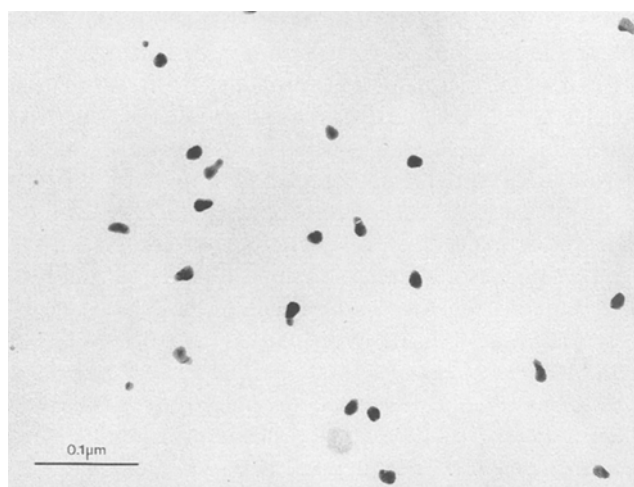
From electron microscopy solely, we can also speculate about the origin of this rather funny shape. A more careful look at the micrograph reveals that each aubergine consists of two, sometimes three primary, close-to-spherical particles which seem to have aggregated and glued together. The longish shape might be a memory that this colloid nucleation and aggregation took place on the two-dimensional surface of the heterophase reducing agent, the hydrazine droplets. Since all particles have about the same size and shape, this aggregation does not occur at random, but is obviously heavily controlled by the block-copolymers being bound in the hydrophobic half-room near the colloids.

After 10 min, the aubergine-morphology starts vanishing as indicated by the changed plasmon resonance, and the steady progress of reduction leads to the reappearance of spherical particles. Finally, after 24 h reduction period, all particles are about spherical, with a tendency to show the typical polyhedral morphology of single colloidal crystals. These particles are significantly smaller than the aubergines, and only slightly larger than the aubergine constituting particles. A statistical evaluation of the electron micrographs results that the aubergine aggregates exhibit an average size of about  $24 \times 10$  nm including nuclei with an estimated diameter of roughly 8 nm, where the 24 h colloids show a sphere diameter of 12 nm.

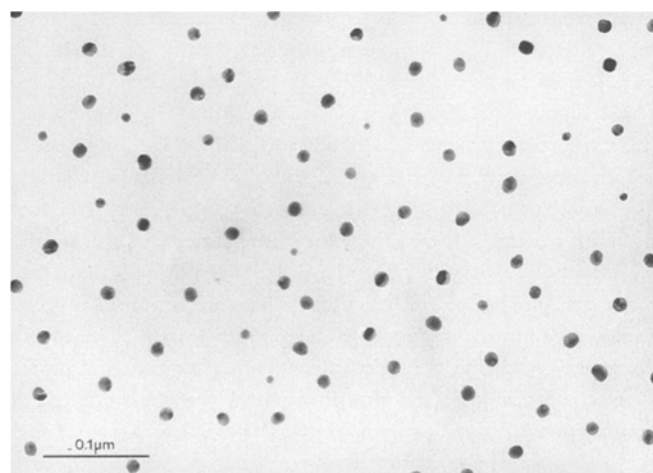
Obviously, consumption of the surplus salt leads to a deaggregation of the particles: the salt acts as the glue. Further progress in reaction only results in a ripening of the gold-colloids: they become slightly larger and more monodisperse. The first change of the UV-spectra from the split to the single plasmon band is therefore due to deaggregation from the aubergines to spherical particles; similar spectra were also described in the work of Kreibig and Vollmer [7]. The further blue shift of the plasmon band is however not described by continued deaggregation, since something like a remainder of aggregates is not seen in



A

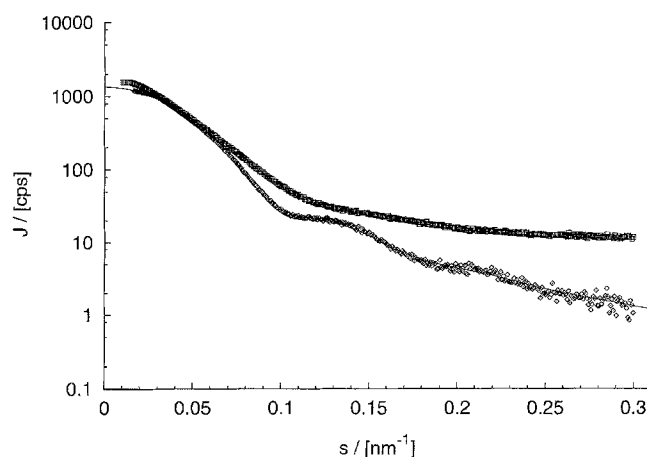


B



C

**Figs. 2A–C** Micrographs of transmission electron microscopy after different reduction times: **A** 1 min; **B** 10 min; **C** 24 min



**Fig. 3** SAXS diffractograms of Au-PS-3,2 (1:9) after 1 min (■) and 24 h (○) reduction with hydrazine. The straight line represent a fit with the form factors of a sphere

electron microscopy, therefore, we conclude that the wavelength change at the end of reduction has to be due to a change in the dielectric environment of each particle.

Although these pictures give a good indication for the shape and size of the formed particles, quantitative statements on the base of electron microscopy required careful exclusion of all types of artifacts and a statistically significant data base. For those reasons, it is more precise to add x-ray analysis for the quantitative description of such samples where the properties of some  $10^{12}$  particles are averaged without any selection. The small-angle diffractograms of the aubergine-like colloids and the spherical colloids being present at the end of the reaction are compared in Fig. 3.

The scattering from the particles produced in the late stages of reaction are perfectly described with the form factor of a sphere with a sharp, well defined interface and a homogeneous density. The fit of the experimental curve with this structure model (straight line) works almost perfectly and results in an averaged diameter of  $d = 12.5$  nm and a Gaussian width of the size distribution of 13%.

The scattering of the aubergine-like particles is remarkably different and can be described by the form factor of prolate ellipsoids. Since polydispersity and axial ratio have a similar influence on the scattering curve of such particles, a quantitative fit of these data only reproduces the input information of electron microscopy.

From linewidth analysis of the wide-angle x-ray peaks of the gold nanocrystals by the Scherrer method [8], we are able to estimate the size of the primary crystals in the aubergine morphology as well as those of the ripened noble metal colloids after 24 h reduction period. Primary crystal sizes of 8 nm in the aubergine colloids and 10 nm

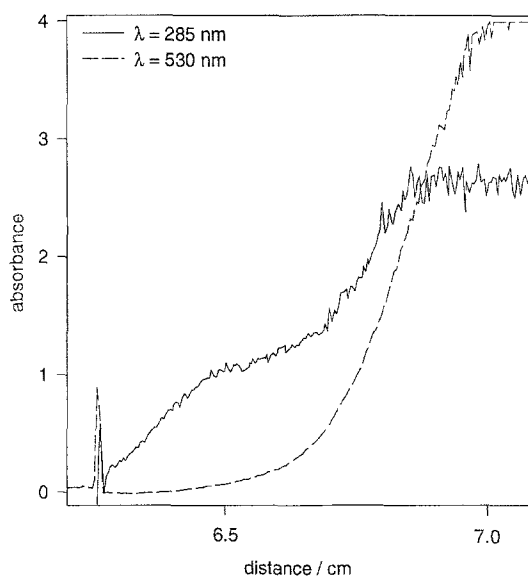
in the spherical particles are obtained, respectively, which agree well with the data as obtained from electron microscopy.

A last problem which should be addressed in the present context is that the metal colloids are far too large to result from the metal load of one micelle only, and the proposed heterogeneous reaction pathway offers a possibility to explain the difference. Since the specific interface area of the gold colloid which has to be stabilized decreases with colloid size ( $A_{sp} = 3/R$ ), the growth of the gold colloid above the original micelle core directly implies the existence of non-metal bound block-copolymer molecules or micelles at the end of the reaction. A proof for the existence of these empty micelles would give additional evidence for the proposed reaction scheme. First experimental indications for those free stabilizers were already seen in the electron microscopy experiments where background textures typical for thin block-copolymer films were observed.

The most elegant and simple proof of the coexistence of free or non-metal containing micelles is given by ultracentrifugation. Since the block-copolymer/colloid-hybrids not only exhibit a red color, but also a higher density, a simple sedimentation run where the optical absorption is simultaneously measured in the plasmon band as well as in the absorption of the block-copolymer enables separation and detection of metal as well as of non-metal containing micelles. The result of such an experiment is shown in Fig. 4.

The profile of the optical density at the wavelength of block-copolymer absorption indicates that the colloidal solution contains two different, but well defined species with different sedimentation coefficient. The mass of block-copolymer bound in these structures is about balanced, as taken from the absolute values of the step heights. On the other hand, we observe absorption at the wavelength of the plasmon band from the species with the higher sedimentation coefficient only. Consequently, we attribute the second step to the block-copolymer stabilized gold colloids whereas the first step proves the existence of free micelles.

Finally, it must be underlined that the nonspherical morphology completely explains the observed UV-spectra. Creighton and Eadon calculated the plasmon resonances for spheroidal colloids and found that the longitudinal resonance is shifted to longer wavelengths whereas the transversal resonance stays nearly unaffected [9]. Very recently, Esumi et al. described similar spectra from gold colloids made on rod-like micelles as templates [10]. Their characterization by electron microscopy however did not allow a clear differentiation between anisometry or aggregation as the source of the blue band in the spectra, since heterogeneous and complex aggregates



**Fig. 4** Optical density in the ultracentrifuge cuvette in a sedimentation run (10 000 rpm, 2 h sedimentation time) detected at two different wavelengths. The scan with  $\lambda = 520$  nm just reflects the position of the gold colloids whereas the  $\lambda = 280$  nm scan is sensitive towards the block-copolymers. Empty micelles coexist with micelles which contain gold colloids

were obtained in all cases. In contrast to that, block-copolymer stabilizers are so effective that they allow synthesis of single colloidal particles only.

## Conclusion and outlook

Analytical data of a number of techniques suggest that heterogeneous reduction of metal salts in block-copolymers occurs via an interface reaction where the block-copolymer micelles are strongly attracted by the surface of the hydrazine-droplets and get disintegrated in a first step. The primary nuclei of gold colloids in this interface region are not stable and bind with each other into particles with an "aubergine-morphology". This aggregation, although it results in unusual shapes, is a controlled process, since all particles have about the same size and shape. The aubergine-like gold colloids are also the first in this reaction which can be isolated and are characterized by a violet color of the solutions.

Further reduction changes these anisometric particles to spherical structures with a diameter of ca. 12 nm and a comparably low polydispersity index in the order of 13% Gaussian width. Related to the defined architecture, the UV-spectra of these model particles are characterized by a single narrow plasmon resonance.

From the linewidth analysis of WAXS, it was shown that the aubergines contain smaller gold crystallites of about 8 nm which are glued together, presumably with the non reacted gold salt. The final colloids consist of one crystallite each, as proven by the identity of particle and crystallite size. The consumption of the gluing salt and the related deaggregation explains the odd effect that the colloids become smaller with time.

In all stages the block-copolymer micelles get rearranged after metal colloid formation, and all isolated block-copolymer/colloid hybrids which are isolated are perfectly stable systems. The micelle rearrangements in the heterophase reaction however prevent a relation between the original micelle dimension and the size of the formed colloid which is, in general, slightly larger than the original micelle core. This growth also results in a surplus of free

block-copolymer molecules which are not required for colloid stabilization and can be detected at the end of reaction as coexisting empty micelles.

In the future, we want to gain a better control of the primary interface aggregation process by variation of the metal concentration as well as the stabilizing chemical groups of the block-polymers to adjust other particle morphologies, e.g., to create particles with a further increased anisometry. In addition, one might speculate about addition of other, not reactive salts which also act as a glue, but maintain their effect throughout the course of the reaction.

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