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

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.

Key words Noble metal colloid - block-copolymers - anisometry

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 hybride 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 color 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.

**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 $M_w = 18750$, 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 HAuCl₄ (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 Cu-Kα 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°. 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 cm⁻¹–400 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.

**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.