# Synthesis of Stable and Surface Functionalized Nanoparticles in an Amphiphilic Block Copolymer Melt

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## ABSTRACT

We report on an ultrafast and simple one pot synthesis of noble metal nanoparticles and semiconducting metaloxide nanoparticles with aminoblockcopolymer O,O'-Bis (2-aminopropyl) polypropylene glycol- block- polyethylene glycol- block- polypropylene glycols. No additional organic or anorganic solvents are used during synthesis. For demonstrating the universal application of the amino block copolymer for multiple nanoparticle formation we present exemplary syntheses and their characterizations for the following precursor metal compounds: $HAuCl_4$, $AgNO_3$ and $Zn(Ac)_2$.

***Keywords***: synthesis, noble metal nanoparticles, semiconducting nanoparticles, block copolymer melt

## 1 INTRODUCTION

Since nanoparticles are of high industrial and even on the laboratory scale interest multiple efforts were undertaken to get quick and simple syntheses of nanoparticulate materials. For the use in diverse applications like electronics, optics, and catalysts polymer assisted syntheses of e.g. gold nanoparticles were systematically investigated. Sakai et al. were using a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) block copolymer as a reducing agent for a gold precursor [1] whereas Iwamoto et al. used polyethyleneoxide diamine terminated polymers (PEO-$NH_2$) to illustrate gold nanoparticle formation [2]. Our work is presenting a fast and simple route to form noble metal nanoparticles according to [3] and even semiconducting oxides like ZnO. Au and Ag nanoparticles are formed using the precursors $HAuCl_4$, $AgNO_3$ and $CuCl_2$. $CuCl_2$ reacts to Cu nanoparticles which are oxidized under ambient conditions (not shown here). $Zn(Ac)_2$ is found to react to semiconducting oxide nanoparticles that build up hierarchical superstructures. Our investigations were done by TEM, SEM and spectroscopy techniques like UV/ vis or FTIR. Furthermore we performed X-ray diffraction (XRD) to verify the crystallographic properties of the nanoparticles. Solid sols like nanoparticulate waxes can be formed after syntheses.

## 2 EXPERIMENTAL SECTION

All chemicals were purchased from Sigma Aldrich and were used without further purification. O,O'- Bis (2-aminopropyl) polypropyleneglycol- block- polyethylene-glycol- block- polypropyleneglycols (Jeffamine ED-2001) with a specific molecular weight of 1900 g/mol was used for syntheses. Milli-Q-water from a Millipore system (> 18 MΩ) was used for dissolving the product. The polymer is heated up and stirred in a conventionally one neck flask. Proper monodisperse and uniform particles were achieved by an initial molar ratio of 25 to 1 for the polymer to precursor ratio. To remove the excess polymer post synthesis the solid sol was dissolved in water and 3 times centrifuged with 14000 rpm for 10 minutes. The supernatant was decanted and the particles were suspended in the desired solvent. Reaction times do not exceed 5 min (5 min for noble metals and 1 min for ZnO).

## 3 RESULTS AND DISCUSSION

We observed that the polymer melt (fp. 113°C) acts as a reducing agent for precursor noble metal salts and moreover, takes part in the reaction as solvent, as stabilizing and dispersing agent and base, respectively. Figure 1 a) depicts the chemical formula of the polymer: an amphphilic block copolymer exhibiting amino group terminations and functional ether bridges.

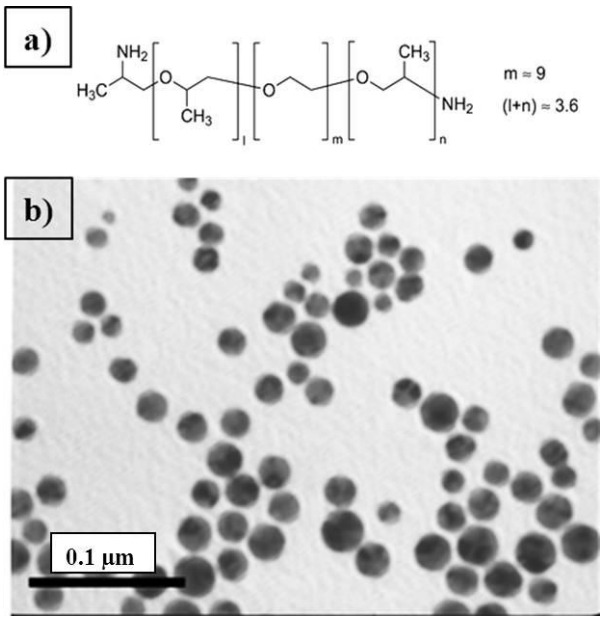


Figure 1: a) Chemical formula of the Polymer.b) TEM image of spherical gold nanoparticles.

A representative TEM image of gold nanoparticles after 5 minutes reaction time is shown in figure 1b. Figure 2 documents the time dependent absorption behavior of a gold colloid. The typical gold band with a maximum of 525 nm originates from the surface plasmons of the free electron gas of the gold clusters, the surface plasmon resonance (SPR). Since the absorption band is very sensitive to agglomeration or ripening of the particles resulting in a blue shift we conclude long term stability from these spectra. There is no shift concerning the single bands. Even after 10 months the colloid is well stabilized by the adsorbed polymer at the particles´ surface and shows no aggregation.

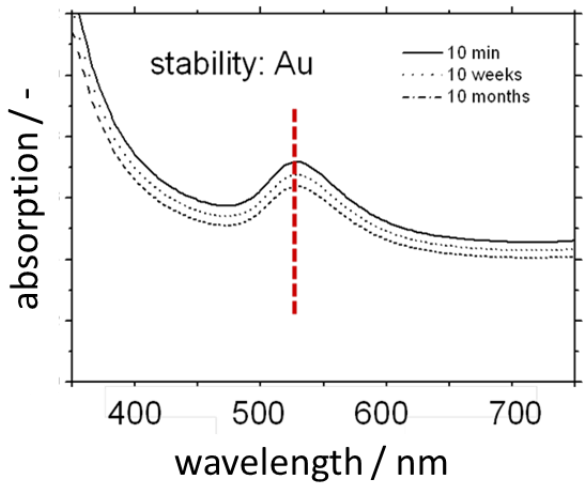


Figure 2: long term stability regarding the absorption characteristics of a gold colloid

On every sample XRD was performed to verify the crystallographic properties of the nanoparticles. In figure 3 we present a XRD spectra from Bragg Brentano geometry confirming the presence of elementary fcc silver (JCPDS 4-0783) for example. Within the range of 20° – 50° = 2θ the dominant (111) and (200) of fcc silver is detected.

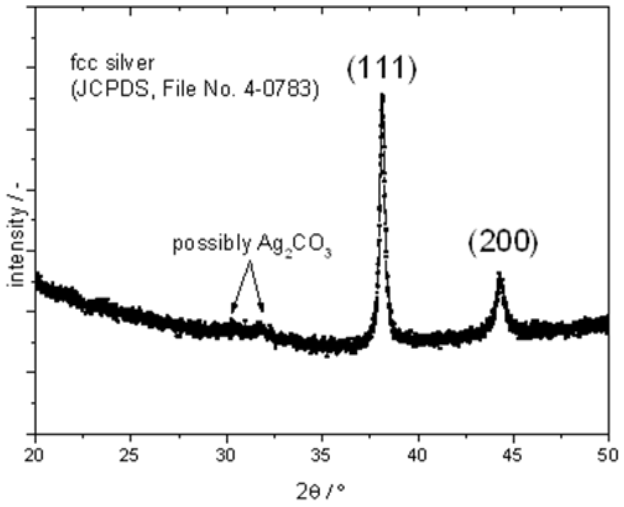


Figure 3: XRD pattern of a silver colloid sample exhibiting the fcc structure of elementary silver nanoparticles.

The particle size distribution of a silver particle suspension is shown in figure 4 a). The spherical silver particles are 25 nm in diameter on the average. No particles with diameter above 18 nm were seen in the particle-size-.distribution (PSD) of our particle suspension. The TEM insertion b) is just illustrating the identical sample.

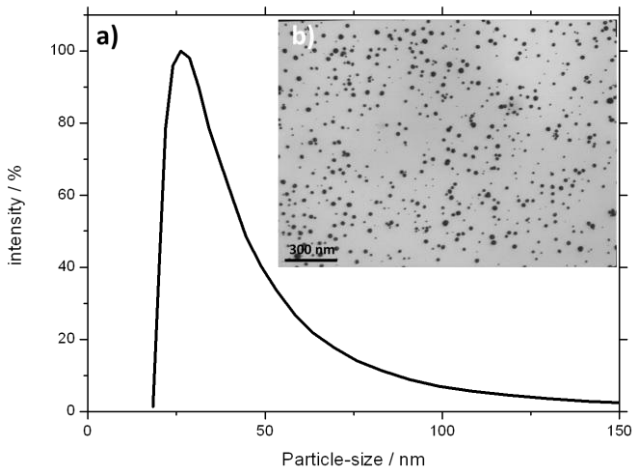


Figure 4: particle-size-.distribution of a silver colloid in a) and corresponding TEM image in b).

The ZnO particle formation (see figure 5) seems to be indeed much more complicated and is ongoing work. So we will comment on the specific synthesis route in a different paper that is upcoming soon.

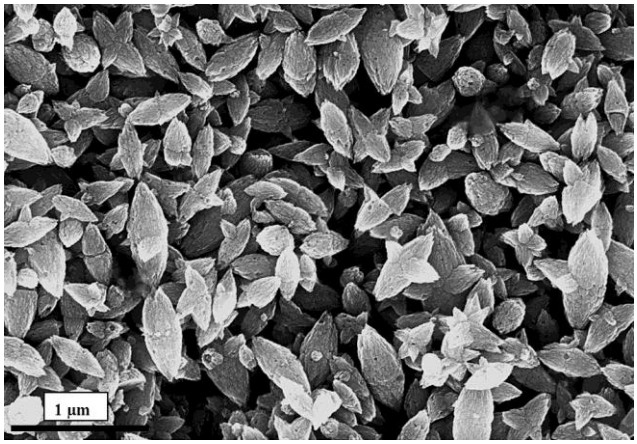


Figure 5: SEM image of an ultrafast ZnO synthesis. The particles are clearly nanostructured and offer diverse x-fold (x=1-~8) symmetries with cone-shaped subunits: The extreme short reaction time of only 1 minute suggests that single assemblies are formed by oriented aggregation (OA) far from equilibrium processes.

Since the polymer has got an amphiphilic nature synthesized particles are easily dispersible in both polar and apolar solvents. Even after multiple washing the particles offer an amino-terminated surface which is clearly visible by FTIR-spectroscopy (not presented here). The polymer functional groups on the particle surface are able to stabilize the particles as well as provide anchoring points for further potential functionalization.

## 4 CONCLUSIONS

Microscopy images and spectroscopy scans prove the successful and powerful formation and synthesis of uniform metal colloids with narrow PSD by reducing of different metal salts like $HAuCl_4$, $AgNO_3$ and $CuCl_2$ with an amino group terminated block copolymer. This method even leads to semiconducting particles like hierarchical ZnO micro- and nanostructures that are build up by OA. The advantages of this presented synthesis are obvious: it is a simple, fast and many-sided method. The particle dispersions show long term stability and do not agglomerate since the amino block copolymer also acts as a stabilizer.

## REFERENCES

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