PLASMONIC DESIGN BY MICROFLUIDICS: SIZE-TUNED GOLD CUBES AND SILVER PRISMS OBTAINED BY SEGMENTED FLOW SYNTHESIS

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ABSTRACT

In this paper we present the segmented flow-through synthesis of triangular silver nanoprisms and single crystalline gold nanocubes with precisely adjustable particle sizes. Ag nanoprisms with edge length between 35 and 180 nm could be synthesized within micro fluid segments by adjusting the educts concentration ratios due to a simple variation of reactant flow rates. This addressability of the particle size enables a tuning of the in-plane plasmon mode resulting in resonance wavelength shifts between the visible and the near infrared region [1]. From the same method, homogeneous Au nanocubes with edge length between 90 and 250 nm were obtained.

KEYWORDS: single crystalline Au nanoparticles, shape anisotropic Ag nanoparticles, segmented flow synthesis

INTRODUCTION

By utilization of the micro segmented flow-through method, several types of micro and nanoparticles (NP) [2,3], as well as salt-like materials [4], and quantum dots [5] could have been synthesized successfully with high ensemble homogeneity and reproducibility of the particles geometry. A certain monodispersity is particularly important in case of noble metal nanoparticles because their optical properties are very sensitive towards changes in the particle shape or size. The presented works confirm that the micro segmented flow through method is especially suited for fast redox reactions, such as the reduction of metal salts by strong reducing agents. At high total flow rates a highly effective segment internal convection takes place [6], which provides mixing rates in the dimension of nucleation rates. Thus, the nucleation intervals are kept short and a homogeneous particle growth is promoted. An interaction with appropriate ligands leads to a shape-anisotropic growth.

COMBINATORIAL CONCENTRATION VARIATION PRINCIPLE

For the synthesis of triangular Ag nanoprisms an automated combinatorial variation of the educts concentration ratios was applied. In Fig. 1, the computer controlled runs of the four individual reactant solution flow rates are shown. The actual reactant flow rates of each individual combinatorial step can be taken directly from the diagram in Fig. 1. In total, 7500 segments were generated, which corresponds to about 200 segments per combinatorial step. One combinatorial step represents a separate experiment. Thus, as it can be seen from the figure, 36 experiments were carried out. Twenty five experiments led to the synthesis of Ag nanoprisms. Furthermore, 11 reference experiments were conducted in which at least one crucial reactant flow rate was set to zero. The total amount of consumed chemicals is comparatively low: 831 µL of the seed particle containing mixture and 554 µL of silver nitrate solution were used.

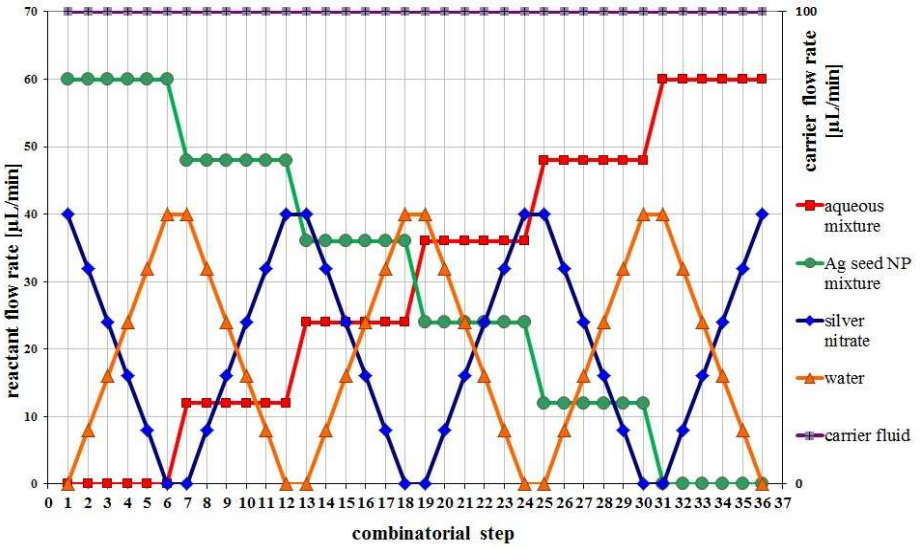

Figure 1: automated reactant flow rate run for a combinatorial concentration variation

EXPERIMENTAL

The micro fluidic system comprises a set of injectors for micro fluid segment generation. A fast mixing was ensured in all synthesis experiments. PC-controlled syringe pumps (Cetoni, nemesis system, Germany) have been used for the

actuation of the carrier solution (Perfluoro(methyldecaline)) and the reactant solutions. Micro flow-through photometric sensors and a fiber-based micro flow-through spectrometry have been applied for in-situ spectral monitoring. A schematic illustration of the experimental setup is given in Fig. 2. The processed NP have been additionally characterized by differential centrifugal sedimentation spectroscopy (DCS), dynamic light scattering (DLS), UV-Vis spectrophotometry, Zetapotential measurements, and scanning electron microscopy (SEM).

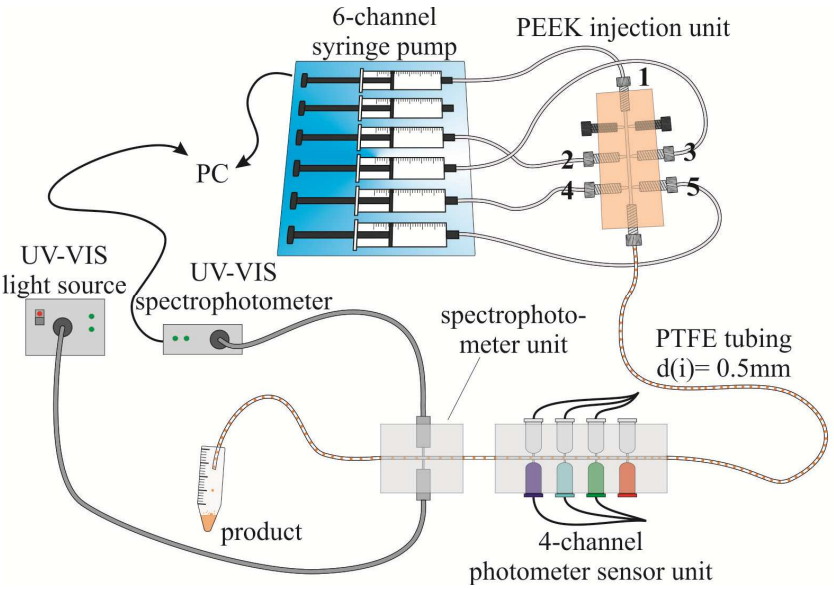

Figure 2: general experimental setup for the processing of noble metal nanoparticles

The syntheses of silver nanoprisms and single crystalline gold nanocubes are seed mediated synthesis strategies. Homogeneous seed NP are essential for an uniform particle growth. The synthesis of Ag seed particles in micro fluid segments is reported in [3]. For the nanoprism growth step under conditions of combinatorial reactant concentration variation in micro fluid segment sequences, a premix of 500 µL silver seed particles, 5 mL water and 75µL of 50 mM ascorbic acid was dosed into the reactor channel at inlet 2 and the same mixture but with water instead of the respective volume of Ag seed particles was added at the opposite inlet. The organic carrier is presented at inlet 1 and thus fluid segments are generated, which contain a well-defined dilution of colloidal silver seed particles. At inlet 4 and 5 silver nitrate (1 mM) and accordingly water are dosed into the preformed segments. Homogeneous crystallization seeds for the generation of gold nanocubes were obtained by a fast reduction of 0.25 mM tetrachloroauric acid in the presence of 100 mM cetyltrimethylammonium chloride (CTAC) with 10 mM sodium borohydride. Again, the organic carrier is presented first. The premix of CTAC and $HAuCl_4$ and - at the opposite nozzle - $NaBH_4$ are dosed into the channel. A total flow rate of 200 µL/min was found sufficient for the seed particle generation. In the first subsequent batch growth step, 25 µL of seed particle solution were added to a premixture of 10 mL 100 mM CTAC, 0.5mL 5 mM $HAuCl_4$, 10 µL 10mM NaBr, and 72 µL 50 mM Ascorbic Acid. From this batch reaction Au NP with an average diameter of 10 nm were resulting. To obtain Au nanocubes with an edge length of 100 nm, 25 µL of the freshly prepared 10 nm Au NP are dosed in a second batch step into the same premixture as described above.

RESULTS AND DISCUSSION

During the combinatorial synthesis of Ag nanoprisms, the optical extinction spectra of the colloidal solution within each micro fluid segment were measured in situ. An average spectrum based on the data generated in one combinatorial step was calculated and regarded as representative for the respective step. The micro fluidic conditions of chosen steps were afterwards continuously operated for producing sufficient sample volumes for further offline analysis (DCS, SEM). In Fig. 3a, the in-situ UV-Vis spectra of 5 different nanoprism ensembles are shown. In this diagram, combinatorial steps with constant (maximum) addition of $AgNO_3$, but successively in steps of 20% decreasing Ag seed NP density are compared. The corresponding DCS size distribution spectra are shown in Fig. 3b. Since sedimentation spectroscopy only provides the Stokes equivalent sedimentation diameters, the actual edge lengths were derived from SEM analyses. In Fig. 3 c – d, the SEM images of three samples, significantly different in size, are given. From Fig. 3 can be seen clearly, that under conditions of constant addition of metal salt but decreasing seed NP concentration, the average particle size is shifted towards higher values. During the whole combinatorial run, the spectral position of the main plasmon resonance mode was shifted from 550 to 950 nm, which corresponds to a variation of the nanoprism edge lengths between 35 and 180 nm.

By a similar strategy of adjusting the seed NP density and the metal salt concentration, Au nanocubes with edge length between 90 and 250 nm were synthesized. In Figure 4, two exemplary SEM images are shown.

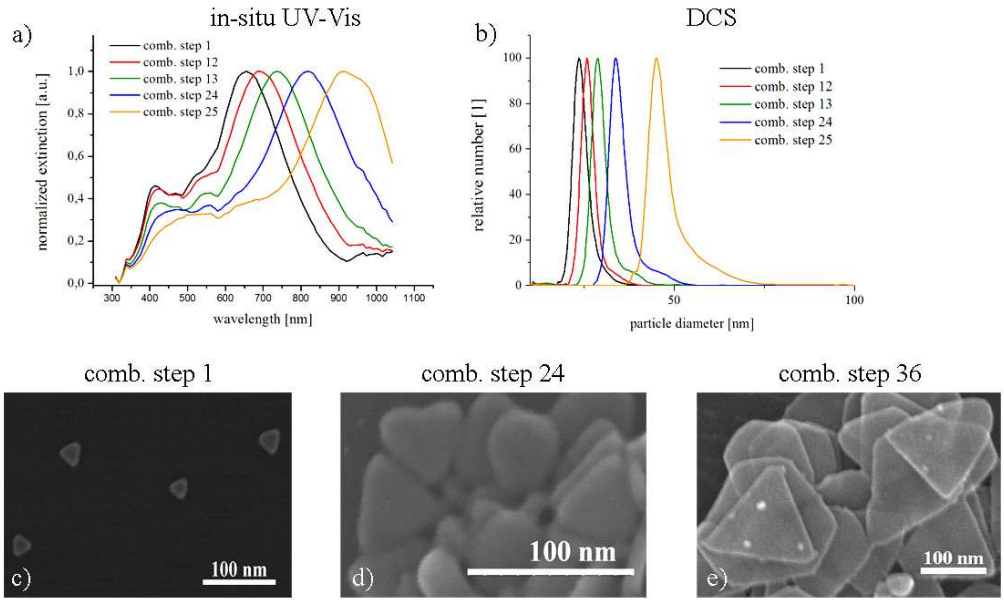

Figure 3: a) in-situ measured optical extinction spectra of silver nanoprisms with increasing edge length; b) corresponding DCS size distribution spectra, c-d) SEM images of exemplarly samples

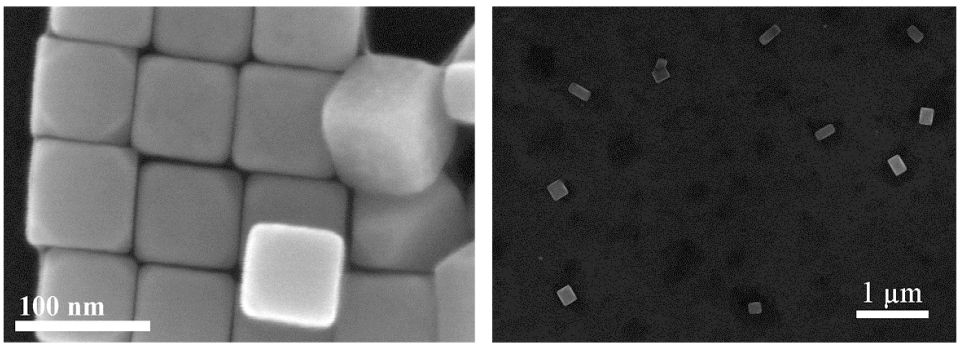

Figure 4: left: Au cubes with an edge length of 90 nm, right: Au cubes and rods with edge lengths of 250 nm

CONCLUSION

The presented experiments confirm that the principle of the micro segmented flow is well applicable for the synthesis of gold nanocubes and triangular silver nanoprisms. The application of micro fluid segments allows obtaining a high yield of the desired product particles as well as tuning the size of the particles and therefore their electronic and optical properties. By a defined adjustment of the chemical conditions within the fluid segments, homogeneous silver nanoprisms with precisely tunable edge lengths between 35 and 180 nm and corresponding main plasmon absorption wavelengths between 550 and 950 nm could be obtained. Furthermore, cube edge lengths between 90 and 250 nm were achieved in the micro segmented flow-through synthesis method.

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