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Au/Ag/Au double shell nanoparticles with narrow size distribution obtained by continuous micro segmented flow synthesis

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ABSTRACT

In this paper we present a two-step micro continuous flow-through method for synthesizing colloidal dispersions of noble metal core/shell and multishell nanoparticles in aqueous solutions in the presence of cetyltrimethylammonium bromide (CTAB). The synthesis is based on the reduction of the metal salts $HAuCl_4$ and $AgNO_3$ at the surface of seed particles by ascorbic acid. In the micro fluidic system, constant residence times and an effective mixing were achieved by applying the segmented flow principle. The colloidal solutions were analyzed by differential centrifugal sedimentation, UV–vis spectrophotometry, and scanning electron microscopy. The size distribution of the Au/Ag core/shell and multishell nanoparticles synthesized by the micro flow-through technique was very narrow. In case of Au/Ag core/shell nanoparticles, an average diameter of 20 nm with a distribution half width of 3.8 nm, and for Au/Ag/Au multishell nanoparticles an average diameter of 46 nm with a distribution half width of 7.4 nm were obtained. The optical spectra of the particle solutions exhibited drastic changes with the deposition of each additional metal shell. Due to the intense changes in their optical properties, the prepared particles are of interest for future sensing applications as well as for labelling in bioanalytics or as nonlinear optical devices. Furthermore, it is shown that micro reactors are well suited to control the synthesis of complexly structured Au/Ag multishell nanoparticles with a high homogeneity and an extremely narrow size distribution. Especially by applying a micro segmented flow, an improvement of the product quality is achieved because of a high internal segment mixing efficiency and a suppression of residence time distribution.

1. Introduction

Nanoparticles of noble metals are of great scientific and practical interest due to their stability and their unique optical properties [1–4]. The plasmonic response is marked by a characteristic narrow absorption band [5,6]. It depends on a number of parameters: its shape and the chemical surface state [3,7]. These particles are of great interest for nanoelectronic devices and for optical labelling [8]. It is easily possible to modify the particle surfaces by ligands and to include molecular recognition functions in order to use the nanoparticles for specific molecular binding [5,8,9]. The small size of nanoparticles allows for sufficient mobility by *Brownian* motion and specificity in molecular interactions. Therefore, functionalized noble metal nanoparticles can be applied as markers for microscopic investigations in cell biology as well as for detecting molecular interaction and for labelling biochips [10–13].

Binary metal nanoparticles of silver and gold can be used in particular for addressing different optical channels in the visible spectrum. While pure silver particles show an intensive plasmonic absorption at about 390–450 nm, spherical gold nanoparticles with diameter in middle nanometer range display characteristic plasmon absorption between 520 and 530 nm resulting in a typical red color of the colloidal solutions. Larger and non-spherical gold nanoparticles have absorption bands at much higher wavelengths, leading to a blue color of the particle dispersions. The wavelength of the plasmonic absorption peak can be tuned if silver and gold are integrated in binary metal nanoparticles. The shift of the plasmonic band is affected by the ratio between silver and gold, the shape and the size of the binary particles, and the distribution of the two metals inside the particle. Thus, a different plasmon absorption is obtained if both of the metals are forming core/shell particles with gold core and silver shell, silver core and gold shell or an alloy [2,14–16]. In fields of nanoparticle application such as Ag nanoparticles as catalysts or surface enhanced Raman spectroscopy, the surface conditions of the metal particles are of major importance. In case of thickness-controlled synthesis of core–shell structured Au/Ag or Ag/Au nanoparticles, the surface condition of the outer

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metal can be tuned as a function of the inner metal surface, provided that the outer shell is thin enough [14–19].

Many different protocols exist for the synthesis of pure gold and silver nanoparticles by chemical reduction of metal ions or complexes. The homogeneity of the obtained particles depends on the homogeneity of the nucleation and particle growth. Both of these processes are determined by the temperature, the solvent, and the local concentration of the reactants. In most of the reported procedures, the reaction is usually initiated by mixing the reactant solutions. This strongly affects the first phase of the reaction which is the nucleation process. The application of micro reactors leads to a considerable enhancement of the particle homogeneity due to fast mixing [20–27]. This effect was observed not only for the preparation of gold and silver nanoparticles but also for oxidic, semiconducting or salt-like materials [27–29].

A particularly strong effect of mixing conditions was found in micro continuous flow synthesis of binary Au/Ag nanoparticles by the application of a two-step static micro-mixer [30]. The optical absorption of the colloidal product solution shifted strongly in a comparatively small flow rate interval, this obviously reflects critical interdependence between nucleation of gold cores, particle growth by gold and silver deposition and aggregation of small nanoparticles to form larger ones.

The micro fluidic technique of the particle synthesis in fluid segments is of particular interest for time controlled processes. The techniques use the slug-like transport of small droplets (segments) of the reaction mixture – which are embedded in a non-miscible and inert carrier liquid – inside capillaries, micro tubes or micro fluidic chips. The micro segmented flow leads to a very narrow residence time distribution [31–33]. Under conditions of a high wetting of the internal wall of the micro channels or the tubes by the carrier liquid coinciding with a low wetting of the wall by the reaction mixture, the deposition of the particles at the walls or a wall-initiated nucleation can be reduced drastically. These advantages make the micro segmented flow well suited for the synthesis of nanoparticles [34]. The nucleation can be initiated homogeneously by a fast mixing due to an intensive segment-internal convection in case of high flow rates. This can be used for the generation of homogeneous nanoparticles as well as for the synthesis of core/shell nanoparticles [27,35–37].

Thus, the high homogeneity of the mixing conditions creates a lot of interest in the segmented flow technique as well as in the generation of complexly structured materials. It can also be applied for multi-step processes with fast mixing and well-controlled residence times between the single mixing steps. Here, we report the first time about the continuous synthesis of complexly structured binary metal nanoparticles in a micro fluidic set-up using the micro segmented flow technique.

2. Experimental

The preparation of nanoparticles was carried out both in batch and in micro continuous flow-through syntheses. First, the reported batch protocols [14] were miniaturized to microliter scales and the products were characterized. The successful protocols were then adapted for micro segmented flow synthesis. All chemicals were used as received. Tetrachloroauric(III) acid trihydrate (Carl Roth GmbH, Karlsruhe, Germany) with a purity of 99.5%, silver nitrate (Merck KGaA, Darmstadt, Germany, purity: 99%), ascorbic acid (Merck KGaA, Darmstadt, Germany, purity: 99.7%), sodium citrate (Merck KGaA, Darmstadt, Germany, purity: 99%), and sodium hydroxide (Merck KGaA, Darmstadt, Germany, purity: 99%) were used to prepare gold/silver multishell nanoparticles. Cetyltrimethylammonium bromide (Merck KGaA, Darmstadt, Germany, purity: 99%) was used to stabilize the nanoparticles.

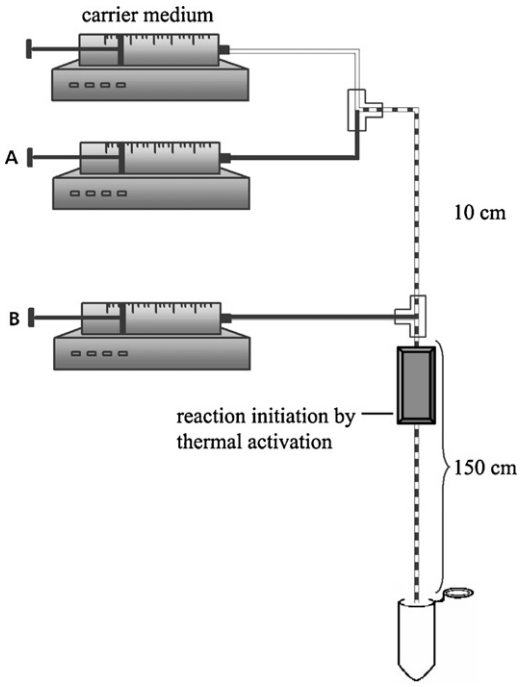

Fig. 1. General set-up for micro segmented flow synthesis of bimetallic multishell nanoparticles.

Tetradecane (Acros Organics, Geel, Belgium) with a purity of 99% was used as carrier medium. All solutions were prepared in distilled and particle filtered water (filter system: Aqua purification G 7795, Miele) with a specific electric resistivity of 18.2 MOhm cm. The experiments were carried out under clean room conditions to prevent cross contamination.

2.1. Batch experiments

The gold seeds were prepared by heating a mixture of 500 μl 0.5 mM $HAuCl_4$ and 500 μl 1.7 mM sodium citrate solution to boiling for about 20 min in a capped glass bottle. The solution was heated till it acquired a stable reddish-pink color. In the second 1.5 ml Eppendorf® cup 1 ml of 50 mM CTAB, 50 μl 0.1 M ascorbic acid and 25 μl of 10 mM of $AgNO_3$ were added. An aliquot of 25 μl gold seeds was added to this cup, and shaken vigorously with dropwise addition of 10 μl of 1 M NaOH (in 4–5 steps). In this way, the seeds were coated with first silver shell. In order to get these particles covered with the second shell of gold, a volume of 500 μl of the above sample was taken, and 25 μl of 0.1 M ascorbic acid and 2 μl 0.1 M $HAuCl_4$ were added then under vigorous shaking.

2.2. Micro fluidic arrangement and experimental

The protocols of batch experiments were adapted for the conditions of a micro continuous-flow system. Therefore, a strategy was developed that allowed a grouping of the reactants from the batch protocols for application in the syringes and keeping the system complexity and number of syringes and syringe pumps at a minimum. In order to realize the segmented flow reaction, the reactant concentrations and volumes were recalculated, proportionate to the volume of a single segment. The general experimental set-up for the micro fluidic synthesis is shown in Fig. 1. Three syringes were mounted on individual syringe pumps. The segmented flow is generated when two continuous flows of immiscible liquids are united in a micro channel. The carrier medium and the reactant solutions were consolidated in a PTFE reactor channel using PTFE