New insights of the nucleation and growth process of gold nanoparticles via in situ coupling of SAXS and XANES

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Abstract. Although metallic nanoparticles play an important role in the area of nanotechnology, a coherent mechanistic explanation for the evolution of the particles during their chemical synthesis has not yet been provided in many cases. To gain a profound understanding of the growth mechanism of colloidal nanoparticles, new approaches using Small Angle X-Ray Scattering (SAXS) combined with X-ray absorption near-edge structure (XANES) are presented. This combination allows for insights into two prominent syntheses routes of gold nanoparticles (GNP): The “slow” reaction using sodium citrate (30-90 min) as a reducing agent and the “fast” reaction employing NaBH\textsubscript{4} (within few seconds). In the first case data derived with the coupled XANES and SAXS suggests a four-step particle formation mechanism. For the second system a time resolution in the order of 100-200 ms was achieved by coupling a common laboratory SAXS instrument with a microstructured mixer, which allows data acquisition in a continuous-flow mode. The results indicate a coalescence driven growth process. Based on the capabilities to deduce the size, number and polydispersity of the particles, the results of both methods enable the development of mechanistic schemes explaining the different phases of particle formation and growth, thus providing a basis for improved control over the synthesis processes.

1. Introduction

Gold nanoparticles (GNP) have attracted much attention due to their unique properties and promising applications covering the areas of biotechnology [1], catalysis [2] and optoelectronics [3]. Despite their widespread use, in many cases, a deeper understanding of the underlying formation processes is missing. Hence the size and shape control of nanoparticles often remained somehow “alchemical”. Therefore, a great deal of attention has been focused on understanding the process of nanoparticle formation [4-7]. When such phenomena are fundamentally understood, it becomes possible to tune the size and shape of nanoparticles and consequently improve their performance. This could potentially lead to the development of novel “tuned” materials. However, the realization of such designed nanoparticles is still difficult, since critical stages throughout the formation process are still not sufficiently understood.

In this context time resolved \textit{in situ} experimentation represents the most promising approach by which the key steps of nanoparticle formation can be revealed. Currently, many studies applying various analytical techniques to study this processes have been reported in literature [8-14]. However, these studies mostly focus on data obtained using imaging techniques and optical spectroscopy, which often
presents an incomplete picture of the particle synthesis. New insights, necessary for the interpretation of the underlying processes can be obtained by using SAXS, which offers an integral information about size, shape and polydispersity of particles in solution [15]. Additional secondary information derived i.e. from spectroscopic techniques then enables comprehensive studies. Employing such techniques simultaneously and in-situ ensures that data obtained with different analytical tools can be directly related to another. In consequence, corresponding time-resolved measurement provide access to process kinetics and the identification of possible intermediates.

The typical time resolution achieved in SAXS experiment amounts to several seconds using synchrotron radiation, and several minutes with a common X-ray tube. Studies of fast synthesis procedures often require a time resolution in the second or millisecond range, which is typically realized as a “stopped flow experiment” [14]. Unfortunately, for such stopped-flow experiments the use of synchrotron radiation, and in many cases a specially equipped beamlines, is essential [16].

In this contribution we present novel approaches of SAXS for detailed studies of slow and fast nucleation and growth processes of gold nanoparticles in solution phase. The studies provide a profound understanding of the mechanism of particle formation, which is essential for tuning their size and morphology and thus their properties. The possibilities of obtaining complementary information using SAXS in combination with XANES (small angle x-ray-scattering/x-ray near edge structure) are discussed, and illustrated for case studies. Whereas synchrotron SAXS experiments can be performed within several seconds, the time needed for a XANES measurement with sufficient quality was about 2-3 minutes and determined the time resolution of the presented SAXS/XANES coupling [17-18]. This technique was used to investigate the most prominent GNP synthesis - the reduction of HAuCl₄ with sodium citrate [19]. For the fast reduction of HAuCl₄ with NaBH₄ we demonstrate how a continuous-flow setup is able to achieve a sufficient time-resolution (200 ms) with a common laboratory SAXS instrument.

2. Experimental section

2.1. Small angle X-ray scattering (SAXS)
Small angle X-ray scattering is a common method to determine the shape and size of particles in colloidal solutions. The measured scattering signal originates from the contrast between the (growing) nanoparticles and the solvent. The scattering vector q is defined in terms of the scattering angle θ and the wavelength λ of the radiation: thus $q = \frac{4\pi}{\lambda} \sin(\theta/2)$. A detailed overview on SAXS data evaluation procedure using model fit functions is given by Pedersen [20]. The curve fitting was carried out using SANS Analysis 3_v3.00 implemented in the software suite IGOR [21]. For the nanoparticle synthesis discussed in the following the experimental scattering curves could be fitted with a model which describes the scattered intensity of hard spheres having a Schultz-Zimm distribution. The Schultz-Zimm distribution is given by

$$f(r) = (z + 1)^{z+1} x^2 \exp[-(z+1)x] \frac{R_{Avg}^2}{\Gamma(z+1)}$$

where $R_{Avg}$ is the mean radius, $x = r / R_{Avg}$, $z$ is related to the polydispersity ($p = \sigma / R_{Avg}$) by $z = 1 / \sigma^2 - 1$ m where $\sigma^2$ is the variance of the distribution.

The scattering intensity of non aggregated particles can be assumed to be proportional to the form factor of a single particle. Thus the scattering intensity of monodisperse hard spheres with volume V is given by
\[ I(q, r) = \text{scale} \cdot P(qr) = \text{scale} \left[ \frac{3V(\Delta \rho)(\sin(qr) - qr \cos(qr))}{(qr)^3} \right]^2 \]  

(2)

where \( P(qr) \) is the form factor of a single hard sphere and \( \Delta \rho \) the scattering length density.

In case of polydisperse spherical particles one has to sum the scattering intensities over all particle sizes weighted by their frequency or to integrate using a size distribution function, respectively. It is common to use the Schulz-Zimm distribution for polydisperse particles [22]. Hence the scattering intensity is given by

\[ I(q) = \text{scale} \int_0^\infty f(r) \cdot P(qr) dr \]  

(3)

An analytical solution of that integral can be found in Kotlarchyk et al. [23].

In order to analyze the growth mechanism of nanoparticles the number of particles is an important part of information. This can be obtained by using the general relation of \( I(q = 0) \) for a single particle which is independent of its shape and size, i.e. \( I_s = (\Delta \rho)^2 V^2 \). Thus the scattered intensity \( I(q = 0) \) of polydisperse particles can be written as

\[ I(q = 0) = N \langle V^2 \rangle (\Delta \rho)^2 \]  

(4)

where \( N \) is the number of particles and \( \langle V^2 \rangle \) the mean value of \( V^2 \). \( I(q = 0) \) can not be measured directly due to the overlapping of the scattering intensity with the primary beam, and as such, \( I(q = 0) \) is accessible via the extrapolation of \( I(q) \) for \( q \to 0 \). Additionally the number of particles can be obtained.

2.2. X-ray absorption near edge spectroscopy (XANES).

XANES measurements were performed at the µSpot beamline of BESSY II [24] . The beam was monochromatized using the double-crystal monochromator (DCM) installed at the beamline. A torroidal mirror in front of the DCM suppresses the harmonics and focuses the beam. This constellation provides a precise energy adjustment with an energy resolution of about \( \Delta E/E = 2 \times 10^{-4} \), i.e. 2.4 eV at the energy of the Au L III edge (11.919 keV). The excitation energy was varied from 11889 eV to 11933 eV in steps of 1.2 eV, resulting in 20 recorded XANES-channels. The fluorescence radiation of the sample was detected at an angle of approximately 90° with respect to the X-ray beam. The X-ray fluorescence of the Au L III line was detected with a silicon drift detector (KETEK, model AXAS) at a working distance of 30 mm. The measurement time per XANES scan was determined by the progress of the observed reaction and the needed statistics (relative error less than 1%). All measured XANES spectra were normalized to 0 at the lowest and 1 at the highest used excitation energy. XANES was applied to a gold foil and to a HAuCl₄ solution as reference for the final and initial oxidation state. The oxidation state of Au during the process of nanoparticle synthesis was modelled as superposition of the start (Au(III)) and the final state (Au(0)).

2.3. Micro-structured mixer

A micro-structured static caterpillar mixer CPMM R600 SO (IMM, Mainz, Germany) was used at a total liquid flow rate of 50 mL min⁻¹ to continuously join and mix equal volumes of the two respective reactant solutions according to the split-and-recombine mixing principle. The principle of the mixing device is described elsewhere [25].

2.4. Preparation method

2.4.1. Citrate reduction
The GNP were synthesized at 75°C according to the procedure described by Turkevich et al. [19] in which the chemical reduction of the gold precursor HAuCl₄ occurs by dissolved trisodium citrate. The aqueous solutions containing 0.25 mmol/L and 2.5 mmol/L of gold precursor and citrate, respectively.

Before mixing the solutions 35 mL aqueous (Millipore) solution of gold precursor (7 mg HAuCl₄ x 3H₂O, Aldrich) and 35 mL aqueous solution of trisodium citrate (51.45 mg Na₃C₆H₅O₇ x 2 H₂O, Aldrich) were prepared and pre-heated to the reaction temperature (75°C). The synthesis was carried out under stirring in a flask immersed in a temperature-controlled water bath, adding the citrate solution to the gold solution.

2.4.2. NaBH₄ reduction.
The GNP synthesis by reduction of tetrachloroauric acid using sodium borohydride was adopted from a procedure published by Wagner et al. [26]. As for the citrate reducing the final gold concentration was 0.25 mmol/L. Briefly, 39.28 mg tetrachloroauric acid were dissolved in 200 mL water (Millipore) and 15.10 mg sodium borohydride were dissolved in 200 mL water. Solutions of NaBH₄ were prepared freshly for each experiment.

2.5. SAXS / XANES coupling using an ultrasonic levitator as a sample holder
The combined SAXS and XANES-analysis was carried out at the µSpot beamline at BESSY II (Berlin, Germany) using an ultrasonic levitator as a sample holder (further information see [27]). The focusing scheme of the beamline is designed to provide a divergence < 1 mrad (horizontally and vertically) and a beam diameter of 100 µm at a photon flux of 5 × 10^9 s⁻¹ at a ring current of 100 mA.

Data from both measurements were recorded continuously and in parallel, since the small changes of the wavelength required for the XANES measurement can be neglected in the evaluation of the SAXS data. The two dimensional SAXS data were converted into one dimensional diagrams of scattered intensities versus scattering vector \( q \) using the computer program FIT2D [28]. For each experimental data point a fresh sample was extracted from the reacting batch solution and injected in the ultrasonic levitator. The small sample droplet was exposed for ca. 130 s to the incoming x-ray beam.

2.6. Continuous flow setup (CFS) for ms-time resolution using a conventional X-ray tube
In Figure 1b the CFS using a micro mixer, peristaltic pump and a conventional SAXS instrument (SAXSess, Anton Paar, Graz, Austria) is illustrated. The instrument uses focusing multilayer optics in combination with a slit collimation to provide an intense monochromatic primary beam with low
background. The interconnection of the micro mixer to the SAXS instrument was established via a delay coil (Teflon tubing). The solutions were transported via a peristaltic pump (Ismatec Laboratoriumstechnik GmbH, Wertheim-Mondfeld, Germany) at a flow rate of 50 mL min$^{-1}$ through a flow capillary (quartz, inner diameter of 1 mm and wall thickness of 10 µm) embedded in the SAXS instrument. The delay time between the micro-mixer and the SAXS instrument represents the variable reaction time and was adjusted by varying the length and diameter of the teflon tubing between the two devices which enables the SAXS analysis at different stages of the reaction. The range of the corresponding addressable reaction times ranges from 100 ms (19 cm tube length at 1 mm diameter) to about 136 s (10 m tube length at 3.8 mm diameter). For colloid samples with reaction times exceeding 140 s, liquid samples were collected at the mixer outlet and aged while stirring in a beaker. For the SAXS analysis of such samples the aged batch solution was directly injected into the flow cell.

Tubing, flow capillary and glassware were cleaned consecutively with aqua regia, water and isopropanol prior to each experiment. The successful cleaning of the SAXS capillary was confirmed via recording a scattering curve of ultrapure deionized water.

3. Results and discussion

Figure 2 shows the evolution of the SAXS and XANES data recorded at different reaction times for (i) the method coupling applied to levitated sample droplets, and (ii) the continuous-flow setup. In case of the method coupling (i) the XANES spectra indicate an initially slow reduction process but a strong decrease in the Au(III) content after 50 minutes, which coincides with an increase in the intensity of the SAXS curves recorded in parallel. The corresponding data evaluation of SAXS and XANES (Figure 3a-c) allows the differentiation of three phases during the growth process. The first phase of the growth is characterized by coalescence processes, since the volume fraction of particles remains almost constant (about 15%) whereas the number of particles decreases significantly. As a result of this process the mean radius of the particles increases from 2 to 4 nm accompanied by a decrease of the polydispersity from 50% to approx. 20%. The observed coalescence-related increase in particle size corresponds to the XANES data, which indicate a slow reduction of the precursor (see Figure 3c). In a second phase between 25 and 50 min, the particles grow continuously to a mean radius of ca. 5 nm (Figure 3a). The number of particles remains almost constant and the polydispersity decreases to 14% (Figure 3a and b). This is characteristic for the so-called “focusing effect” or “growth by diffusion” model first described by Reiss et al. [29-30]. The final phase consists of a rapid consumption of the remaining Au(III) precursor (Figure 3c), which leads to an increase in the particle size and a further decrease of polydispersity to 10%. The final mean radius of the GNP is 7.6 nm. This last phase of an accelerated consumption of Au(III) at a GNP radius of about 5 nm can be attributed to a surface enhanced reduction. The deduced mechanism consisting of four steps is displayed in Figure 4a. After a fast nucleation (step 1), the resulting entities undergo coalescence processes (step 2) forming colloids with a mean radius of about 4 nm. This is followed by a diffusional growth to a mean radius of about 5 nm (step 3) and completed by an autocatalytic growth (step 4).
Figure 2 Data obtained from SAXS and XANES measurements under different experimental conditions. i) SAXS (a) and XANES (b) data as a function of time obtained during the reduction of $\text{AuCl}_4^-$ ions with sodium citrate. Red curves belong to the first phase of the experiment; green curves belong to the final phase of the experiment. The SAXS data indicate the formation of spherical nanoparticles with a narrow size distribution. The XANES data show, that the precursor material is reduced throughout the process. ii) SAXS (c) and XANES (d) data obtained during the reduction of $\text{AuCl}_4^-$ ions using sodium borohydride. The SAXS curves derived directly after the start of the experiment show the formation and growth of spherical particles. The XANES data illustrate that the reduction is completed after 2 s. Figures reproduced with permission from [17-18].

The rapid formation of GNP by reducing $\text{AuCl}_4^-$ with sodium borohydride was followed by SAXS using a continuous flow setup. The SAXS curves obtained directly after mixing the reactants indicate already the presence of particles. XANES measurements under similar conditions reveal the completed reduction of the precursor at this stage of the synthesis (Figure 2 c and d). Even after completed reduction, evaluation of the scattering curves show the growth of spherical nanoparticles starting from a mean radius of about 0.8 nm to 1.5 nm within 10 s, whereas the volume fraction as well as the polydispersity remain constant throughout the growth process. Subsequently, the particles grow within one hour up to a size of about 1.7 nm, showing up to 140 s no significant change in polydispersity(Figure 3d-f). (Note: An increase in polydispersity is experimentally observed after 140 s, which coincides with switching the observation method from in-situ SAXS in continuous flow to SAXS analysis on colloid samples aged under agitation in a separate beaker. The associated change is therefore probably due to the method of sample aging at times exceeding 140 s or the sample transfer, and not the original particle growth mechanism.) Since the volume fraction of particles remains constant throughout the time-scale of the experiment, and reduction of the gold precursor completes within the first 100 ms, the subsequent formation of particles is only due to coalescence processes. Hence, the growth process starts with rapid reduction followed by a nucleation process of gold clusters (step 1) which undergo coalescence processes until the final size is reached (step 2), which is defined by a yet unknown stabilization (see Figure 4 b). This stabilization is most probably of electrostatic origin.
Figure 3 Results of the evaluated SAXS and XANES data plotted vs. reaction time (for the continuous-flow setup in log scale) derived from scattering curves recorded during the synthesis of gold nanoparticles. 
a) Mean sphere radius and normalized number of particles plotted vs. reaction time derived from SAXS. 
b) Polydispersity of particles as a function of time and corresponding particle size distribution of the Schulz-Zimm distribution exemplarily shown for three reaction times (inset). 
c) Average formal oxidation state of gold derived from normalized XANES spectra plotted vs. reaction time; volume fraction of particles calculated from SAXS data. 
d) Evolution of radius (bullets) and polydispersity (triangles) of gold nanoparticles throughout the reaction process. The values were derived applying a solid sphere model with a Schultz-Zimm distribution whereas the polydispersity was constrained to values of 10% (aging in continuous flow) and 20% (further aging in a stirred beaker). 
e) The number of gold nanoparticles derived from the fit (normalized to the last measurement). Inset: Schultz-Zimm distribution of particle size at different reaction times. 
f) Volume fraction which represents the relative total volume of all gold nanoparticles calculated from the evaluated SAXS data. Figures reproduced with permission from [17-18].
4. Conclusions

The presented case studies for the synthesis of colloidal gold nanoparticles via different chemical routes shows that the developed methods for analyzing nanoparticles with SAXS in a time-resolved manner provide valuable information about the underlying growth mechanism. XANES analysis carried out in parallel provided the required complementary chemical information regarding the rates of precursor consumption. The presented experimental setups are suitable for both, rapid synthesis processes requiring a time resolution in the millisecond range, as well as reaction occurring within minutes to hours. In particular, application of the methods is not limited to the studied specific systems of gold nanoparticle, but applicable to a wide range of other colloid synthesis reactions.

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