Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
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Supporting Information

SI-1

List of chemicals

Chemical	Purity level	Supplier
$NaBH_4$ (granulate)	99.99 %	Sigma Aldrich
$HAuCl_4 \cdot 3\ H_2O$	99.9 %	Sigma Aldrich
$KAuCl_4$	99.995 %	Sigma Aldrich
NH_4AuCl_4	p.a.	Heraeus Feinchemikalien
$AgNO_3$	99.995 %	Alfa Aesar
$Ag(COOCH_3)$	99.99 %	Sigma Aldrich
$Cu(NO_3)_2 \cdot xH_2O$	99.999 %	Alfa Aesar
$Cu(COOCH_3)_2$	99.999 %	Sigma Aldrich
$Cu(ClO_4)_2 \cdot 6\ H_2O$	99.999 %	Alfa Aesar
$CuSO_4 \cdot 5\ H_2O$	99.999 %	Alfa Aesar
Na_2PdCl_4	99.99 %	Sigma Aldrich
$Pd(NO_3)_2 \cdot 2\ H_2O$	p.a.	Sigma Aldrich
$RhCl_3 \cdot x\ H_2O$	99.98 %	Sigma Aldrich
$H_2PtCl_6 \cdot x\ H_2O$	99.999 %	Alfa Aesar
NH_4Cl	99.998 %	Sigma Aldrich
KCl	p.a.	Carl Roth
NaOH (32%)	p.a.	Carl Roth
HCl (37%)	p.a.	Carl Roth

General synthetic procedure

All investigated syntheses comprise the fast reduction of an aqueous metal precursor solution with $NaBH_4$. The concentration of the precursors was 0.5 mM. The concentration of the reducing agent was 3 mM. The $NaBH_4$ solution was prepared freshly for each single experiment by dissolving 113.5 mg in 1 L of ultrapure water. Note that $NaBH_4$ is a hygroscopic solid. We recommend to use granulate rather than powder and to store the substance in inert atmosphere in small portions to avoid frequent opening of a large container. The precursor solutions and $NaBH_4$ were always mixed 1:1 either by using two identical Eppendorf pipettes or a Y-Teflon-mixer.

Setups

Characteristic features of the growth mechanisms of the herein investigated syntheses occur on two different time scales (100 ms - 5 s / 15 s – 2 h). To get a full picture of the growth processes, different setups need to be used to access both time ranges for small angle X-ray scattering (SAXS) experiments and UV-vis measurements.

SAXS 100 ms – 5 s, Continuous Flow Setup (CFS)

The basic principle of a CFS is to transfer the time to a length scale.[1] The reactants are pumped through a Y-mixer with a constant flow rate. This marks the starting point of the reaction t_0. The solution is then pumped through tubings to a point at which a measurement is carried out. The tubings (diameter, length) and the flow rate determine the time between mixing and measurement, thus reaction time t_1 is investigated. The setup has two major advantages. Very small reaction times t_1 become available limited only by the dead time of the system and data acquisition over a necessary period of time can be performed since the measurement time can be adjusted by increasing the volume of reactants.

A CFS was used to carry out SAXS measurements using a lab instrument (SAXSess, Anton Paar, Graz, Austria) equipped with a quartz capillary flow-through cell. The metal precursor solutions and $NaBH_4$ were mixed 1:1 using a self-manufactured Y-mixer made of Teflon. A constant flow rate was achieved by using a self-manufactured syringe pump. The resulting colloidal solution was pumped through Teflon tubings to a second Y-mixer were an aqueous solution of polyvinylpyrrolidon (PVP, M.W. 40 000, 100 mg/L) was mixed 1:1 to the liquid stream. PVP was shown to quench the growth of colloidal particles for a certain time and avoid agglomeration of particles at the walls of a quartz capillary.[2] Therefore, it can be used to avoid contamination of the measuring container during the course of the SAXS measurement. (A discussion of the influence of PVP addition during the experiment can be found in the following subsection.) The colloidal solution was allowed to mix with PVP for 150 ms. The tubings between the two Y-mixers were varied to access different reaction times between 100 ms and 5 s. Hence, every single data point was obtained in a separate experiment. The syringe pump was designed in a way that disposable 60 mL syringes (one for each liquid: metal precursor, $NaBH_4$, PVP) could be inserted. For each precursor solution, a new syringe was used to

avoid contaminations. The setup was cleaned after each experiment using either aqua regia (Au precursors) or HNO_3 (Ag, Cu, Pd precursors).

SAXS investigations using a CFS are extremely elaborate. Therefore, a selection of precursors was chosen for these investigations.

UV-vis 300 ms – 5 s, Stopped Flow Setup (SFS)

A Stopped Flow Setup[3] (SFS) was used to monitor reactions on a millisecond scale with spectroscopic methods. In general, reactants are mixed using a pump system with a static mixer. Behind the mixing device a flow through cell is used to monitor the reaction. As long as the reactants are pumped through the static mixer a certain minimal reaction time t_0 is observed in the flow through cell. When the pump is stopped the reaction continuous in the cell and reaction times > t_0 can be monitored.

In the used SFS the reactants (metal precursor and $NaBH_4$) were mixed using Teflon tubings, a self-manufactured static Y-mixer and a peristaltic pump (Watson-Marlow, 323Du/314D). UV-vis spectra were recorded in a quartz flow through cell (Hellma Analytics) using an USB2000 spectrometer (Ocean Optics) including an ILX511B CCD detector (Sony) and a DT-MINI-2-GS deuterium/tungsten halogen lamp (Ocean Optics) connected via fiber optics. The lowest accessible reaction time at a certain flow rate is determined by the length of the Teflon tube between the static mixer and the flow through cell (here 300 ms). When the pump was stopped the NP growth continued in the flow through cell and UV-Vis spectra of the further reaction were acquired for reaction times of 300 ms – 5 s. After each run the setup was cleaned with nitric acid (Ag, Cu, Pd precursors) or aqua regia (Au, Pt, Rh precursors).

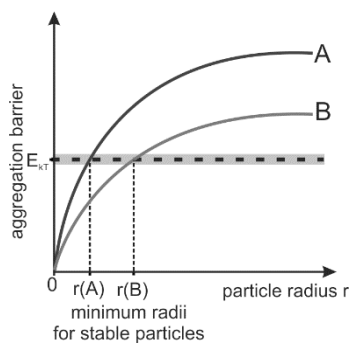
The spectra of the precursor solutions were recorded using the SFS by mixing the respective precursor solution with MilliQ water instead of $NaBH_4$.

SAXS and UV-vis 15 s – 2 h

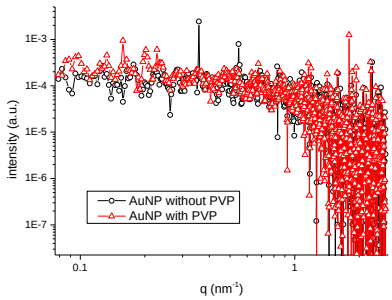
Precursor solution and $NaBH_4$ were mixed 1:1 in fresh disposable glass vials using two identical 10 mL Eppendorf pipettes. The stirring speed was 300 rpm for all syntheses. At different reaction times, 500 µL colloidal solution were extracted and mixed rapidly with 100 µL aqueous solution of polyvinylpyrrolidon (PVP, M.W. 40 000, 500 mg/L) to quench the particle growth. The resulting solution was inserted immediately into a SAXS flow through cell of a lab instrument (SAXSess, Anton Paar, Graz, Austria) or into a UV-vis cuvette (spectrometer: Evolution 220, Thermo Fischer Scientific), respectively. UV-vis and SAXS experiments were conducted separately. The stirring bars were used element specifically and cleaned with aqua regia (Au precursors) or HNO_3 (Ag, Cu, Pd precursors) and rinsed in large amounts of ultrapure water before use. Since Pt and Rh contaminations are difficult to remove, stir bars were used only once.

Addition of PVP during the CFS experiment

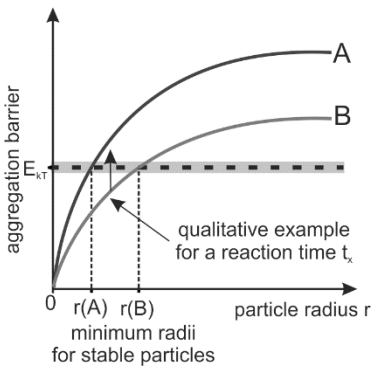
Polymers can adsorb on the surfaces of metal particles creating a steric barrier which in general increases the aggregation barrier and therefore the colloidal stability. Although the growth concept to describe particle growth introduced in the main paper is based on the ideas of the DLVO theory (which solely describes electrostatic stabilization of colloids), the growth concept can illustrate the effect of polymer addition by adding an “extra value” to the aggregation barrier thus shifting the stability curve qualitatively from B to A:



Thus, for most systems adding a polymer such as PVP to a colloidal solution which contains particles with a minimal stable radius r(B) does not change the particle size since the particle size is already clearly above the minimal stable size required for stability curve A. This idea is easy to validate. SAXS measurements before and after addition of PVP to a stable colloidal solution lead to identical scattering curves. For example, the scattering curves of a colloidal gold nanoparticle solution with a mean radius of 1.6 nm (10 % polydispersity) and the same colloidal solution with PVP (M.W. 40 000, final concentration: 50 mg/L) are almost identical:



In the CFS experiment, the particles were allowed to grow in the Teflon tubings for a certain reaction time. For very short reaction times, the particles cannot reach the minimum stable size. Consequently, the effect of PVP addition using the growth concept is illustrated by:



At reaction time t_x, a certain "unstable" size is reached. Addition of PVP adds steric stabilization and increases the colloidal stability. As a result, the growth is "quenched" for most reaction times and the PVP addition allows a SAXS measurement (150 ms were required for the herein setup). For extremely short reaction times such as 100 ms the extra steric stabilization might not be sufficient to prevent particle growth during the following 150 ms. However, this does not change the crucial information which is derived from the CFS experiment: The relative volume fraction is ~100 % for all data points, thus, the reduction is completed very fast and growth during the first seconds of the synthesis is only due to aggregation/coalescence.

SAXS Evaluation

The scattering curves of the colloidal solution were analyzed assuming spherical shape, a homogeneous electron density, and a Schulz-Zimm size distribution. The Schulz-Zimm distribution was shown to be a suitable approximation for gold and silver nanoparticles synthesized with $NaBH_4$[1,2] and is given by:

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

where $\mathrm{R_{avg}}$ is the mean radius, $\mathrm{x = r/R_{avg}}$, z is related to the polydispersity p ($p = \sigma/\mathrm{R_{avg}}$) by $z = 1/p^2 - 1$, and σ^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 P(q). Thus, the scattering intensity of N monodisperse spheres with homogeneous electron density with volume V_{part} is given by:

$$I(q) = N \cdot I_{part}(q) = N \cdot V_{part}^2 P(q)$$
$$= N \cdot V_{part}^2 \cdot \left[\Delta\rho \frac{3(sin(qR) - qRcos(qR))}{qR}\right]^2.$$

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. It is common to use the Schulz-Zimm distribution for polydisperse particles. Hence, the scattering intensity is given by:

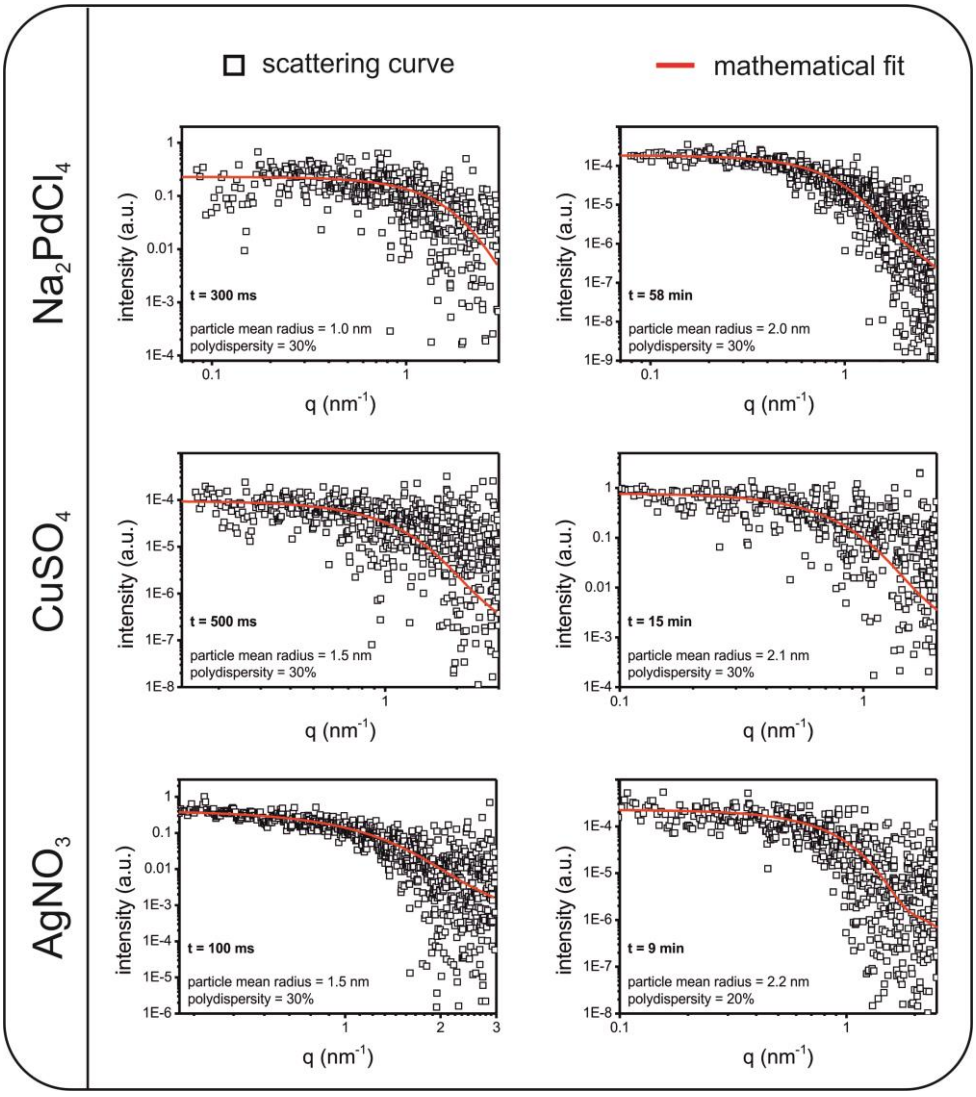
$$I(q) = N \int_0^{\infty} f(r)\, V_{part}^2 P(q) dr.$$

An analytical solution of the integral can be found in Kotlarchyk et al.[4] In order to analyze the nucleation and growth mechanism of nanoparticles, the number of particles is important. This information 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. $I = (\Delta\rho)^2 V^2$. Thus the scattered intensity $I(q=0)$ of polydisperse particles can be written as

$$I(q=0) = N\langle V^2\rangle\, (\Delta\rho)^2$$

where N is the number of particles and $\langle V^2\rangle$ the mean value of V^2. Due to the overlapping of the scattering intensity with the primary beam, $I(q=0)$ cannot be measured directly but is accessible *via* the extrapolation of $I(q)$ for $q \to 0$

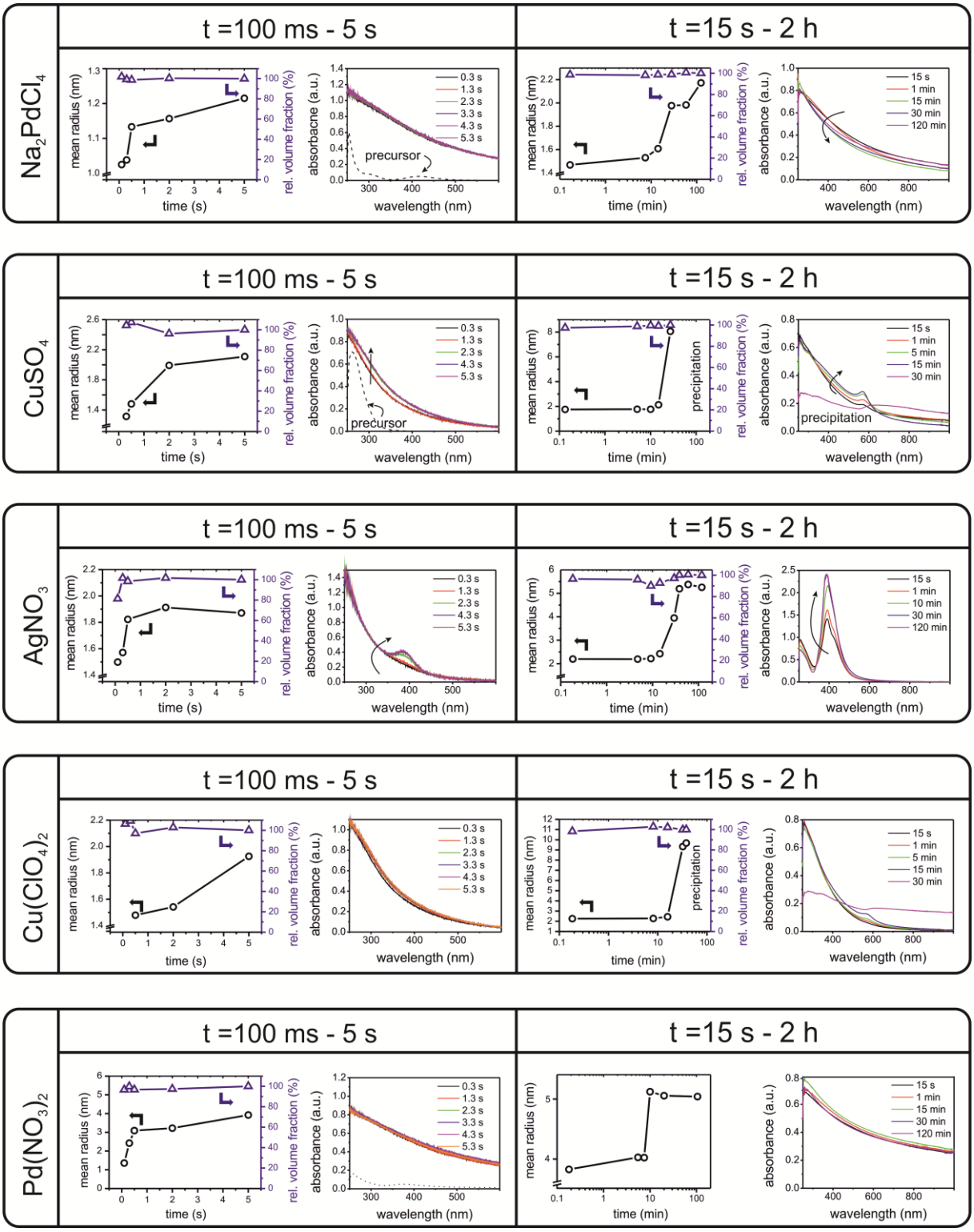
Selected scattering curves and corresponding fits

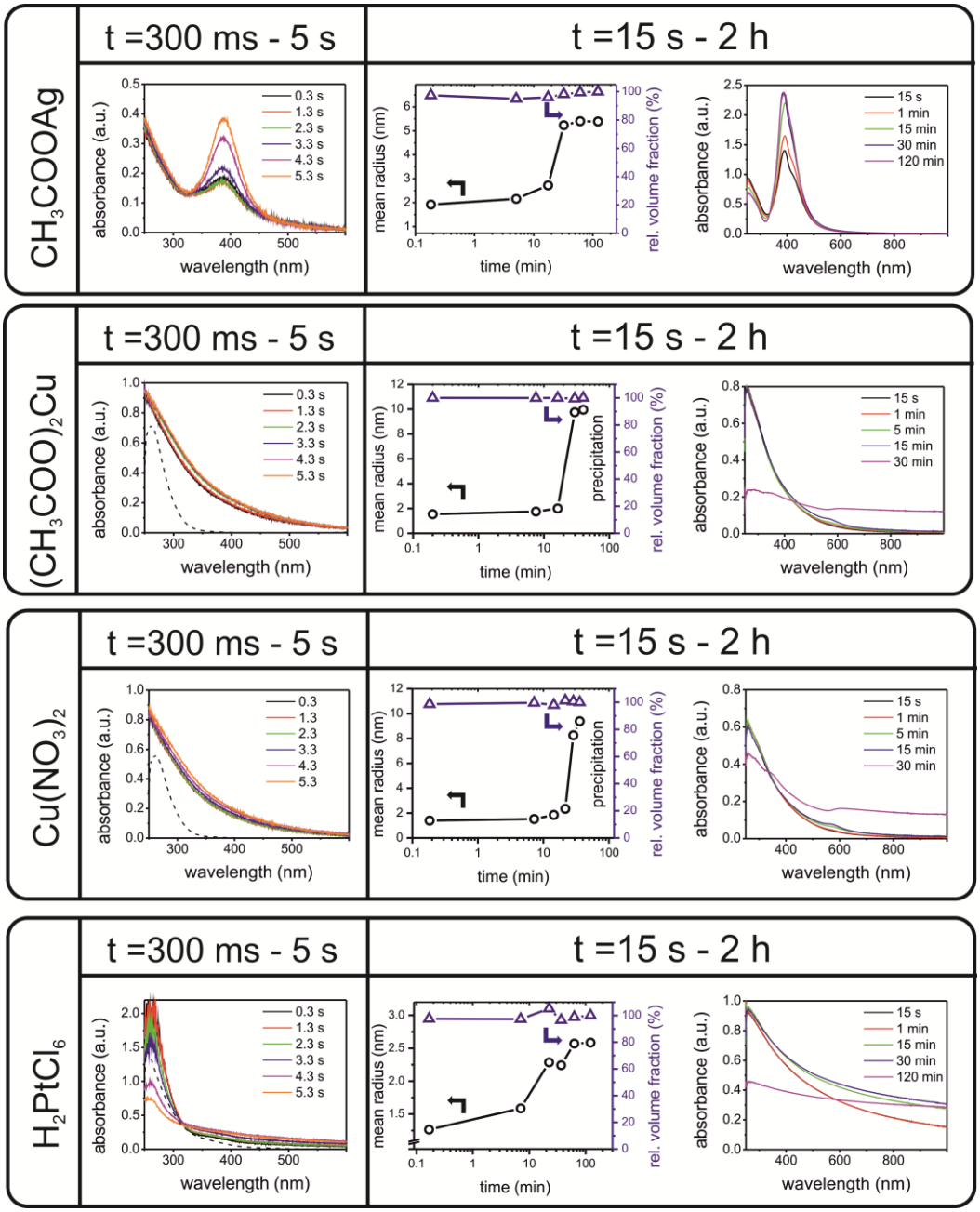


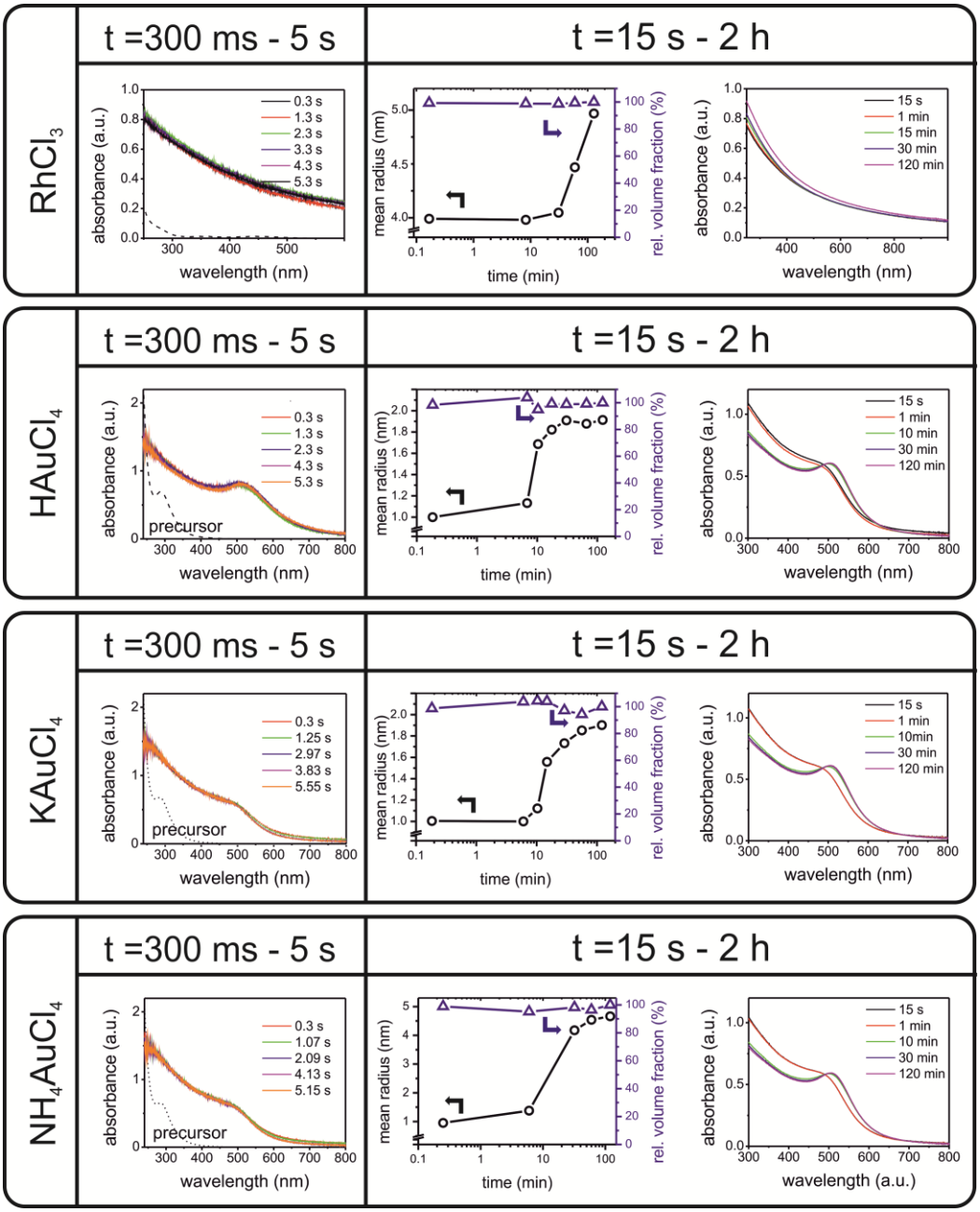
SI-2

The figures below display the results of the SAXS and UV-vis investigations for the different metal precursors. Polydispersities are 30 % with exception of AuNPs (10 %), AuNPs from NH_4AuCl_4 15 s - 2 h (30 %), AgNPs 15 s-2 h (20 %). For the metal precursors which show an absorbance, the spectra are displayed with dotted lines.

The SAXS data reveal that growth due to coalescence (for a molar ratio metal precursor/$NaBH_4$ = 1:6 → two separated steps of coalescence) is a general principle for all nanoparticle syntheses which comprise the fast reduction of a metal precursor with sodium borohydride. The relative volume fraction normalized to the last data point remains almost constant through particle growth. The relative volume fraction is already ~100 % for t = 100 ms which confirms the rapid and complete reduction of the metal precursors. The fast formation of nanoparticles becomes also evident from time-resolved UV-vis spectroscopy. For t = 300 ms, the solutions show either a distinct plasmon band (AgNPs, AuNPs) or a broad absorbance which is clearly different from the spectra of the according metal precursors. After ~30 min, the spectra show changes due to the second growth steps. The plasmon band is increasing and shifting (e.g. for AgNPs), the broad absorbance changes (e.g. for PdNPs) or a large scattering background is observed which can be attributed to the formation of large aggregates and particle precipitation (e.g. CuNPs).


Na2PdCl4
t =100 ms - 5 s
t =15 s - 2 h
mean radius (nm)
rel. volume fraction (%)
time (s)
time (min)
absorbacne (a.u.)
absorbance (a.u.)
wavelength (nm)
precursor
precipitation
0.3 s
1.3 s
2.3 s
3.3 s
4.3 s
5.3 s
15 s
1 min
5 min
10 min
15 min
30 min
120 min
CuSO4
AgNO3
Cu(ClO4)2
Pd(NO3)2


CH3COOAg
t =300 ms - 5 s
t =15 s - 2 h
absorbance (a.u.)
wavelength (nm)
0.3 s
1.3 s
2.3 s
3.3 s
4.3 s
5.3 s
mean radius (nm)
rel. volume fraction (%)
time (min)
15 s
1 min
15 min
30 min
120 min
(CH3COO)2Cu
precipitation
5 min
Cu(NO3)2
H2PtCl6


RhCl3
t =300 ms - 5 s
t =15 s - 2 h
absorbance (a.u.)
wavelength (nm)
0.3 s
1.3 s
2.3 s
3.3 s
4.3 s
5.3 s
mean radius (nm)
rel. volume fraction (%)
time (min)
15 s
1 min
15 min
30 min
120 min
HAuCl4
precursor
10 min
KAuCl4
0.3 s
1.25 s
2.97 s
3.83 s
5.55 s
10min
NH4AuCl4
0.3 s
1.07 s
2.09 s
4.13 s
5.15 s
wavelength (a.u.)

SI-3

For the reduction of $HAuCl_4$ with $NaBH_4$ one or two steps of coalescence are observed depending on the molar excess of the reducing agent. It was shown for $AgClO_4/NaBH_4$ that the duration of the metastable state correlates with the conversion of residual BH_4^- to $B(OH)_4^-$ in the colloidal solution.[5] Hence, the two coalescent steps merge with decreasing amount of residual BH_4^-. The same effect accounts to the $HAuCl_4/NaBH_4$ system. For a small excess of BH_4^-, only one step of coalescence is observed. The table below summarizes the observations made for different concentrations of $HAuCl_4$ and $NaBH_4$. The displayed concentrations refer to a 1:1 mixing of the reactants. Polydispersity is 10 %.

	[$NaBH_4$]=0.5 mM	[$NaBH_4$]=1 mM	[$NaBH_4$]=2 mM	[$NaBH_4$]=4 mM
[$HAuCl_4$]=0.125 mM	2nd coalescent step at 0:50 min Final mean radius: 1.8 nm	2nd coalescent step at 1:20 min Final mean radius: 2.2 nm	2nd coalescent step at 7:00 min Final mean radius: 2.0 nm	2nd coalescent step at 13:00 min Final mean radius: 2.0 nm
[$HAuCl_4$]=0.25 mM		Only one coalescent step Final mean radius: 2.1 nm	Only one coalescent step Final mean radius: 2.1 nm	2nd coalescent step at 14:45 min Final mean radius: 2.0 nm
[$HAuCl_4$]=0.5 mM			Only one coalescent step Final mean radius: 1.9 nm	2nd coalescent step at 6:10 min Final mean radius: 2.3 nm
[$HAuCl_4$]=1 mM				Only one coalescent step Final mean radius: 1.7 nm

SI-4

The total amount of gold was retained for all studies on the influence of parameters. A solution containing 0.5 mM $AuCl_4^-$ was mixed 1:1 with a 2 mM solution of fresh $NaBH_4$ (75.6 mg/1 L).

Influence of cationic species

Solutions of $HAuCl_4$, $KAuCl_4$ and NH_4AuCl_4 with a concentration of 0.5 mM were prepared. Mixtures of two or three precursors in different ratios were reduced with $NaBH_4$. The final size distribution was determined after 2 h using SAXS.

Influence of ionic strength

Stock solutions of $HAuCl_4$, $KAuCl_4$ and NH_4AuCl_4 (10 mM), respectively, were prepared and diluted with KCl or NH_4Cl solutions of different concentration to give a mixture of 0.5 mM gold precursor and salt with different total ionic strengths. The mixture was reduced with $NaBH_4$. The final size distribution was determined after 2 h using SAXS.

In addition, a highly concentrated KCl and NH_4Cl solution, respectively, was added to a AuNP solution obtained from $HAuCl_4$ (after 2 h reaction time) in different volumes to increase the ionic strength subsequently to the synthesis. The obtained solutions were stirred for 30 min. The final size distribution was determined using SAXS.

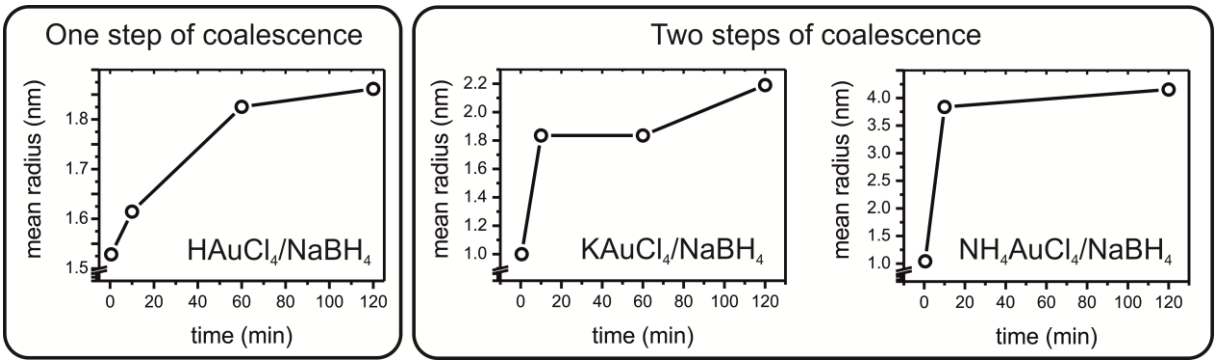
Influence of temperature

The synthesis of AuNP by reduction of $HAuCl_4$ was carried out at different reaction temperatures. The gold precursor was heated to 40, 60 and 80 °C, respectively. 1 mL of a 20 mM $NaBH_4$ solution (75.6 mg/100 mL) was added to 9 mL preheated ultrapure water. Both reactant solutions were mixed immediately in a glass vial tempered in an according water bath. The final size distribution was determined after 2 h using SAXS.

In addition, a colloidal solution obtained at room temperature was heated to 80 °C directly and in steps (40, 60, 80 °C). Each heating step was given a time of 30 min before the size distribution was determined using SAXS.

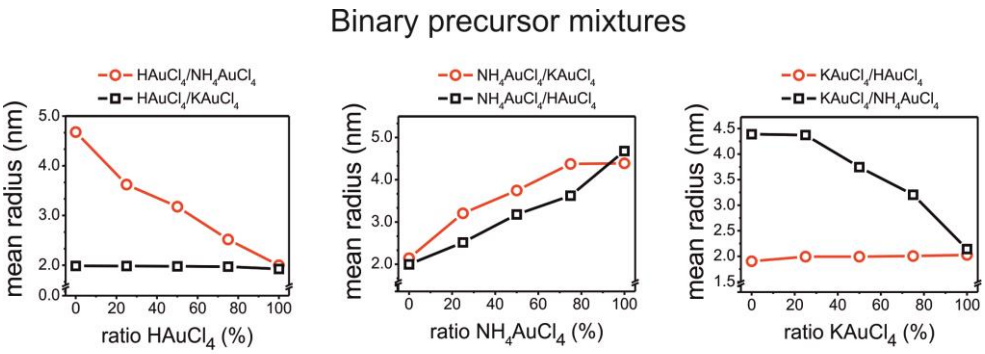
SI-5

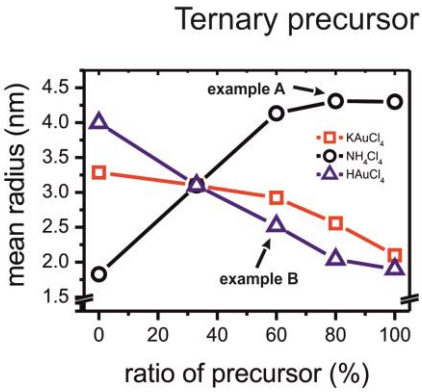
The figure below shows the results of time-resolved SAXS investigations on the growth of AuNPs obtained by reduction of $HAuCl_4$, $KAuCl_4$ and NH_4AuCl_4 with $NaBH_4$ (0.5 mM/2 mM) between 15 s and 2 h. (Therefore, the first coalescent step is not displayed!) The $HAuCl_4$ system shows a slow growth from 1.5 nm to 1.9 nm in mean radius while the other two systems show a second “jump-like” growth step.



SI-6

The figures below display the final mean radii of AuNPs obtained by reduction of different precursor mixtures. Polydispersity is 10 %.



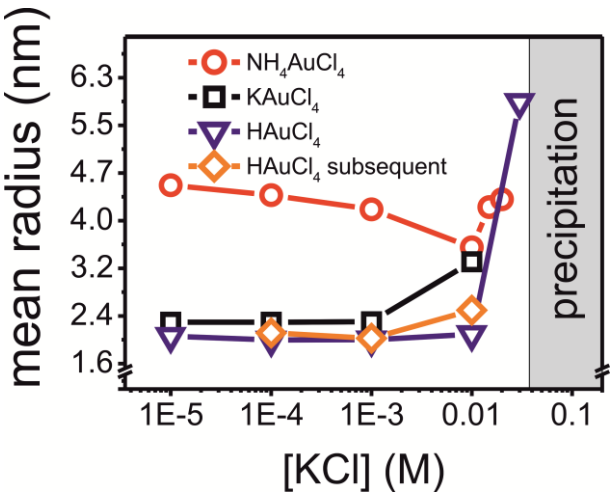


example A:
80% NH_4AuCl_4= 0.4 mM NH_4AuCl_4
10% $HAuCl_4$ = 0.05 mM $HAuCl_4$
10% $KAuCl_4$ = 0.05 mM $KAuCl_4$

example B:
60% $HAuCl_4$ = 0.3 mM $HAuCl_4$
20% NH_4AuCl_4 = 0.1 mM NH_4AuCl_4
20% $KAuCl_4$ = 0.1 mM $KAuCl_4$

SI-7

The figure below displays the final mean radii of AuNPs vs concentration of added KCl.



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[2] J. Polte, X. Tuaev, M. Wuithschick, A. Fischer, A. F. Thuenemann, K. Rademann, R. Kraehnert, F. Emmerling, *ACS Nano* **2012**, *6*, 5791–5802.

[3] B. Chance, *Rev. Sci. Instrum.* **1951**, *22*, 619.

[4] M. Kotlarchyk, S.-H. Chen, *J. Chem. Phys.* **1983**, *79*, 2461–2469.

[5] M. Wuithschick, B. Paul, R. Bienert, A. Sarfraz, U. Vainio, M. Sztucki, R. Kraehnert, P. Strasser, K. Rademann, F. Emmerling, et al., *Chem. Mater.* **2013**, *25*, 4679–4689.