Small-Angle X-ray Scattering (SAXS). SAXS measurements were performed at the µSpot beamline at BESSY II (Berlin, Germany). 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.

The SAXS data were processed and converted into diagrams of scattered intensities versus scattering vector q employing the computer program FIT2D. The scattering vector q is defined in terms of the scattering angle θ and the wavelength λ of the radiation: thus $q = 4\pi / \lambda \sin(\theta / 2)$. For free jet experiments to investigate the gold nanoparticle formation process the photon energy was set to 12keV which corresponds to a λ of 0.103nm.

The data obtained were corrected for background scattering. Curves were fitted using SANS Analysis 3_v3.00 implemented in the software suite IGOR. The experimental scattering curves were fitted with a model which describes the scattered intensity of hard spheres possessing a Schultz-Zimm size-distribution. This approach was chosen since for high polydispersities a asymmetrical size distribution is often a reasonable assumption, and since electron microscope image confirm the presence of spherical particles.

When evaluating SAXS curves it is common to use model curves to fit the experimental scattering curves. A detailed review is given by Pedersen (J. S. Pedersen, Advances in Colloid and Interface Science, 1997, 70, 171-210.). In our case the experimental scattering curves were fitted with a model which describes the scattered intensity of hard spheres having a Schultz-Zimm distribution. This approach is choosen since for high polydispersities a asymmetrical size distribution is reasonable and since any electron microscope image show spherical particles.

The Schultz-Zimm distribution is given by

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

where R_{Avg} is the mean radius, $x = r / R_{Avg}$, z is related to the polydispersity ($p = \sigma / R_{Avg}$) by $z = 1/p^2 - 1$ m where 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. Thus the scattering intensity of monodisperse hard spheres with volume V is given by

$$I(q,r) = scale \cdot P(qr) = scale \cdot \left[\frac{3V(\Delta\rho)(\sin(qr) - qr\cos(qr))}{(qr)^3} \right]^2 \tag{2}$$

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. Hence the scattering intensity is given by

$$I(q) = scale \cdot \int_0^\infty f(r)P(r)dr \tag{3}$$

An analytical solution of that integral can be found in Kotlarchyk et al.(M. Kotlarchyk, R. B. Stephens and J. S. Huang, Journal of Physical Chemistry, 1988, 92, 1533-1538).

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

$$I(q=0) = N\langle V^2 \rangle (\Delta\rho)^2 \tag{4}$$

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[0], thus I(q = 0) is only accessible via the extrapolation of I(q) for $q \rightarrow 0$.

Figure S1 Representative SEM image of the formed final gold nanoparticles prepared by citrate synthesis in a free-liquid-jet experiment at 75°C (colloid was dried on a silicon wafer coated with mesoporous titania for SEM imaging; bright spots indicate gold nanoparticles, grey and dark grey areas result from the substrates)

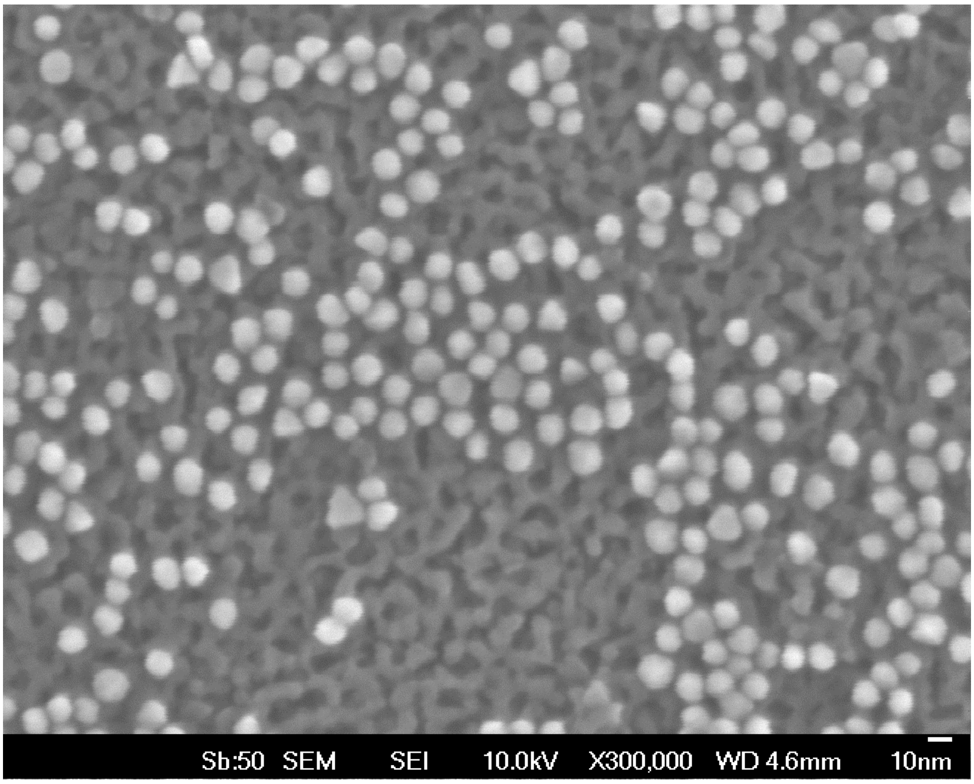

Figure S2 Representative experimental scattering curves and corresponding mathematical fit for SAXS analysis in a free-liquid-jet experiment of GNP synthesis at 75°C shown for different reaction times ranging from 6 to 100 minutes. Dots denote experimental data, lines show the mathematical fit. The respective time is indicated in each diagram.