**Seeded Gold Nanorod Growth Proceeds via Formation of an Autocatalytic Surface.**

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Introduction.

The applications of gold nanorods reach over a broad range in biology, plasmonics and sensing. Recent progress in understanding of the growth mechanism at different stages, including the symmetry breaking step, renewed the interest in wet-chemical nanoparticle growth processes. Despite several studies of the crystallisation dynamics of ascorbic acid-catalysed nanorod syntheses, the growth kinetics of gold nanorods in a hydroquinone-based synthesis are not well-understood. A more detailed insight into the growth of nanocrystals can be provided by in-situ observations. Time-dependent optical properties of growing gold nanorods can be analysed using absorption spectroscopy, whereas in-situ investigations of structural evolution are more challenging, making the use of strong X-ray scattering sources such as the synchrotron necessary. This provides sufficient time resolution to detect single steps of nanoparticle growth to study the growth kinetics.

Methods.

We discovered a way to form highly monodisperse gold nanorods via seeded-growth mechanism from spherical seeds using hydroquinone as mild reducing agent. The solution containing the growing nanoparticles was filled in an air-tight Hamilton© syringe, connected over tubing to a 1 mm quartz capillary and placed in a 3D-printed holder in the X-ray beam (shown in Figure). The solution was pumped through the capillary at a rate of 100 μL/h to ensure no beam damage during the growth phase of gold nanorods. These experiments were carried out for various combinations of HAuCl4 and HQ concentrations and the total measuring time adjusted until no change in the measured curved could be seen, varying from one to seven hours. Additionally, varying factors like pH, temperature and silver nitrate concentration and (over)growth with anisotropic seeds were investigated to result in an overall rate law.

Results and Discussion.

We studied the growth process of hydroquinone-based seeded-growth of gold nanorods in-situ. The synthesis in aqueous CTAB solution showed a novel double-sigmoidal growth, which can be linked to the reaction speed of single gold crystal facets. We find this optimised synthesis route as highly reproducible, resulting in monodisperse gold nanorods without significant side products. From the spectral and scattering data, we can explain for the first time the growth mechanism of the hydroquinone-based synthesis from cuboctahedral seeds to an ellipsoidal state to the final spherical capped cylinder. Furthermore, the influence of changing the gold acid and hydroquinone precursor concentrations in the initial solution was investigated, giving further insights into the nanoparticle growth mechanism. The high quality of the synthesis and X-ray scattering experiments made it possible to actually determine the size of the CTAB layer around the growing nanorod during the synthesis.

**References**

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