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Dynamics study of green AuNP formation and their basis for Au-Pt core-shell nanostructure synthesis

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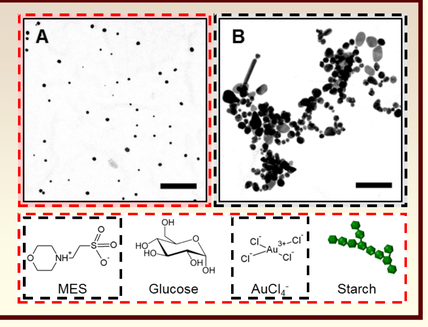
The SAMENS method (saccharide-based approach to metallic nanostructure synthesis) is a synthesis platform for metallic nanostructures. The method has been developed since 2008 and can produce nanostructures of various sizes, shapes and compositions. Recently, a new methodology for studying the details of nanoparticle formation has been developed employing readily available electrochemical and optical techniques. The aim is to understand which parameters control the growth and shape and at which stages of the synthesis. The gold nanoparticles (AuNPs) studied are further used as seeds for size controlled AuNPs and Au-Pt core-shell NPs with an atomically thin Pt shell.

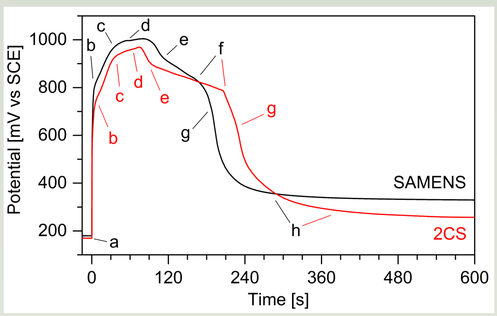
THE GOLD NANOPARTICLE SYNTHESES

Two different syntheses were studied. The standard **SAMENS** recipe (A, green) and a simplified two-component synthesis "**2CS**" (B, blue). (A) resulted in homogenous spherical AuNPs while (B) provided a mixture of shapes and sizes. TEM scale bars are 100 nm.

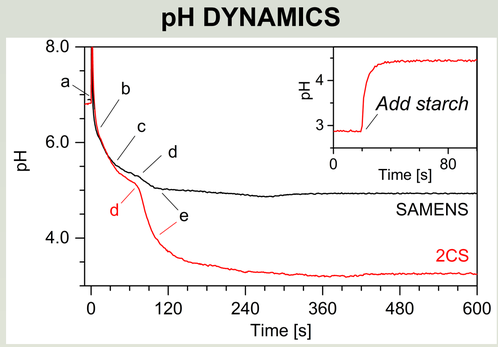


DYNAMICS OF GOLD NANOPARTICLE FORMATION

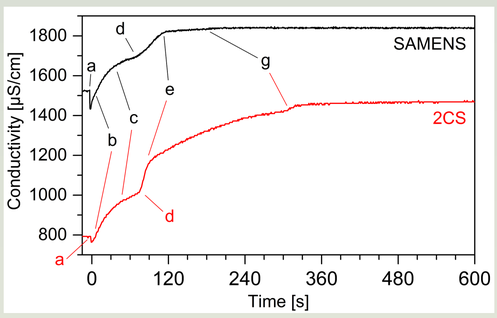
POTENTIAL DYNAMICS



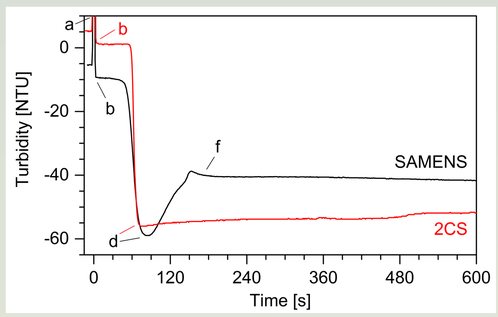
pH DYNAMICS



CONDUCTIVITY DYNAMICS

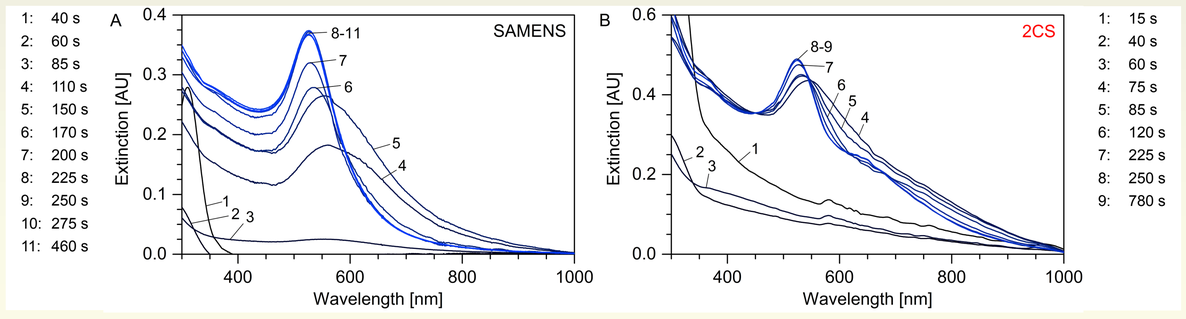


TURBIDITY DYNAMICS



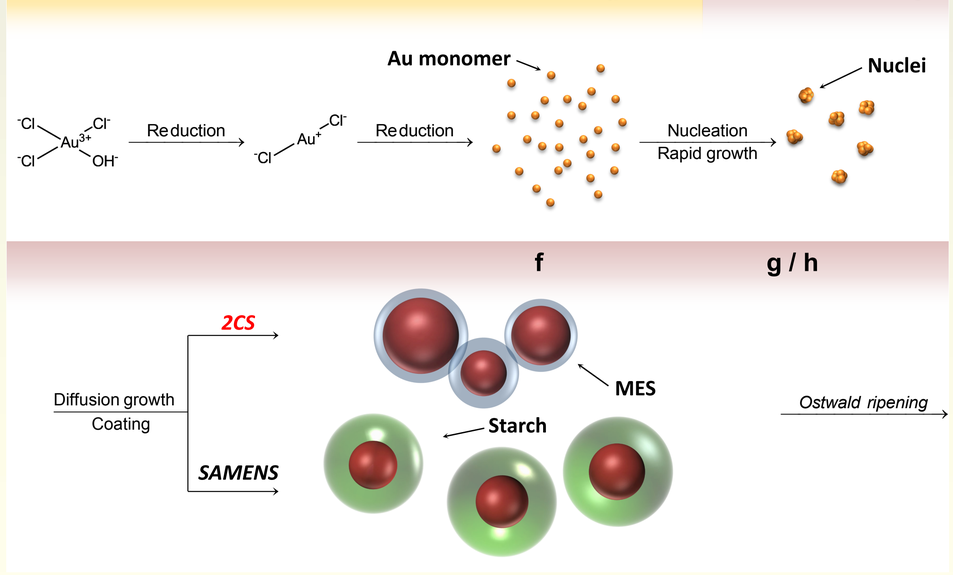
The formation of AuNPs by the two different syntheses was followed by a range of time-resolved in situ techniques leading to a proposed mechanism of AuNP formation. The first phase, **(a) to (b)**, is equilibration of the sensors to the addition of $HAuCl_4$ at (a). **(b) to (c)** is partial reduction of $[AuCl_4]^-$ to $[AuCl_2]^-$ leading to a drop in pH, increased conductivity as protons and chloride are released into solution and a rise in electrochemical potential. The second 1-electron reduction step, **(c) to (d)**, gives a smaller pH change but no significant increase in conductivity. Both reduction steps are distinguishable in the rising potential peaking around the end of reduction. The potential starts to drop as nucleation begins, **(d) to (e)**. Chloride coordinated to $[AuCl_2]^-$ is believed still to be associated with the monomer and only released as nucleation starts which explains the "delay" of increased conductivity from the reduction to the nucleation phase. This drastically changes the turbidity as the solution turns black and the pH dynamics starts to divert between the two syntheses. The lack of starch coating in **2CS** results in the buffer adsorbing on the freshly produced gold surface and a large drop in pH. Starch added to the **2CS** AuNP solution quickly substitutes the buffer as coating and pH rises (inset in pH dynamics). After (e), features are observed at **(f) and (g)**. These are believed to relate to a slow growth phase, reorganization of coating layers, and Ostwald ripening.

UV-VIS DYNAMICS



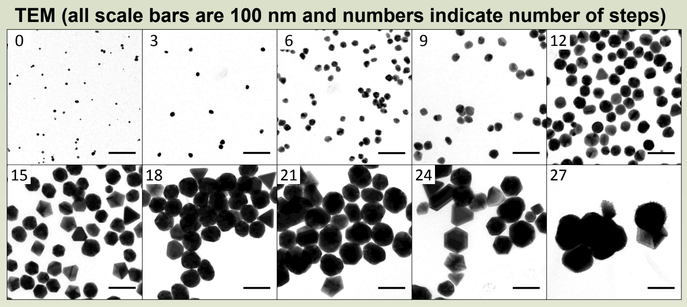
UV-vis spectra were recorded during syntheses, with lower time-resolution than the other in situ methods, but supports the observations above. First the absorbance from $[AuCl_4]^-$ disappears completely before any plasmon resonance appears, indicating an intermediate between $[AuCl_4]^-$ and NPs. As monodisperse and well-defined NPs are formed in **SAMENS**, the plasmon band grows and narrows. For **2CS**, a shoulder appears shortly after NPs are formed due to flocculation of poorly stabilized **2CS** AuNPs.

SCHEME OF AuNP FORMATION



GOLD/PLATINUM SHELLS ON GOLD NANOPARTICLE CORES

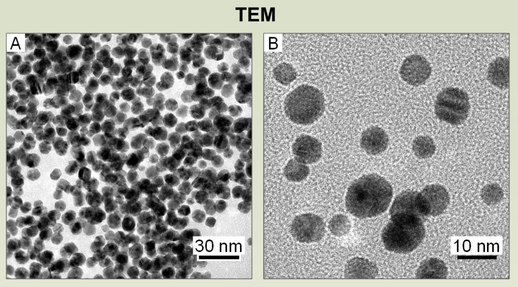
TEM (all scale bars are 100 nm and numbers indicate number of steps)



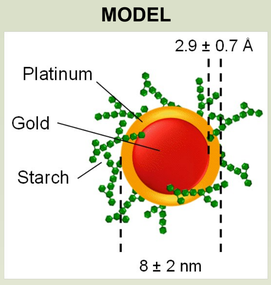
SIZE CONTROL

SAMENS AuNPs of varying size were prepared by a seeded growth approach modified from Bastús et al. (DOI: 10.1021/la201938u). It included sequential reduction of precursor and extraction of partitions every third step. The plasmon band grew and narrowed as the particle size increased with increasing number of synthesis steps up to step 12 after which broadening and redshift were seen. The core (TEM) and hydrodynamic size (NP tracking analysis) increases steadily until about 80 nm. Aggregation then occurs leading to new nucleation rather than growth after step 27.

TEM



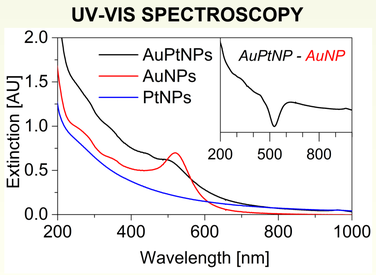
MODEL



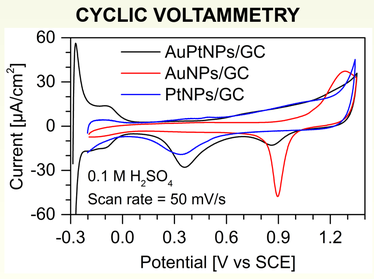
PLATINUM MONOLAYER SHELLS

Reduction of $[PtCl_6]^{2-}$ following AuNP formation led to the formation of a thin Pt shell around the AuNPs. The atomically thin Pt layer was not visible in TEM (above) but a clear electrochemical signal from surface Pt was seen in cyclic voltammetry. A small signal from uncovered gold was also present. Drastic changes appeared to the plasmon resonance that was quenched, indicating that significant changes to the surface had occurred.

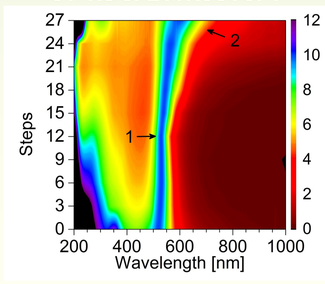
UV-VIS SPECTROSCOPY



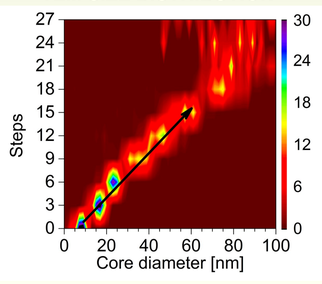
CYCLIC VOLTAMMETRY



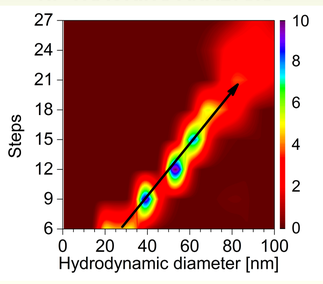
UV-VIS SPECTROSCOPY



TEM SIZE DISTRIBUTION



NP TRACKING ANALYSIS



CONCLUSIONS

A combination of electrochemical and optical in situ methods enabled us to follow the dynamic processes related to formation of AuNPs via different synthesis routes supported by TEM and UV-vis spectroscopy.

Better understanding of processes related to NP formation is important for design and preparation of new functional nanomaterials.

The AuNPs were used for size controlled synthesis of AuNPs in the range of 8-80 nm and core-shell NPs where the gold core is covered by an atomically thin platinum layer.

Acknowledgement: Support from the Danish Council for Technology and Production Sciences is acknowledged.

[1] C. Engelbrekt, P. S. Jensen, K. H. Sørensen, J. Ulstrup, J. Zhang, *J. Phys. Chem. C*, 2013, **117**, 11818-11828

[2] C. Engelbrekt, K. H. Sørensen, J. Zhang, A. C. Welinder, P. S. Jensen, J. Ulstrup, *J. Mater. Chem.*, 2009, **19**, 7839-7847