Supporting information

Electrochemical insight into the Brust-Schiffrin synthesis of Au nanoparticles

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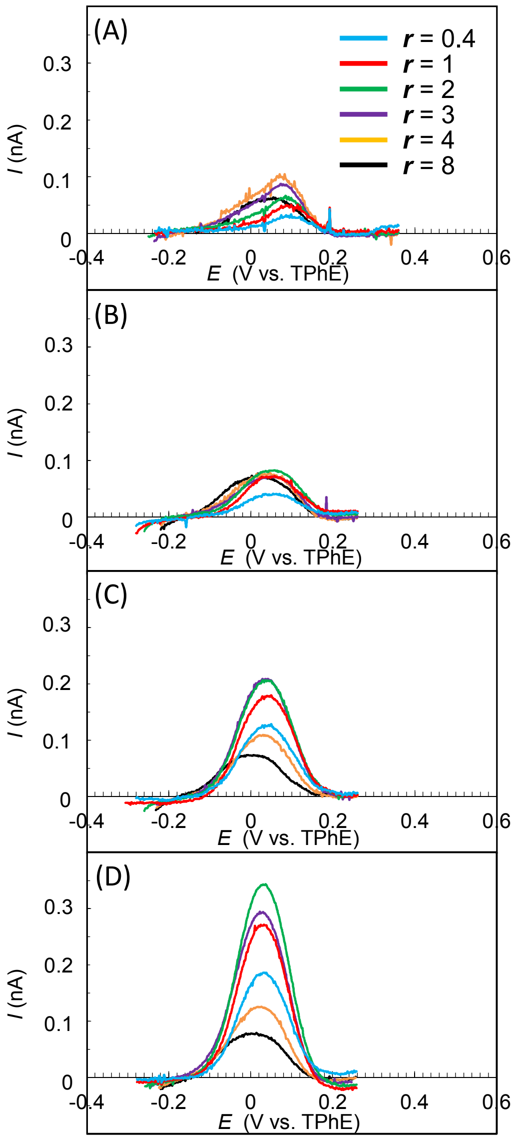

Figure S1

Calculation of the $[AuCl_2]^-$ concentration corresponding to the 2nd current wave observed in Figure 4. Voltammograms at the micro-interface between 10 mM HCl in water and 0.5 mM $TOA^+[AuCl_4]^-$ + 0, 0.2, 0.5, 1, 1.5, 2, and 4 mM RSH (corresponds to $\boldsymbol{r}$ = 0, 0.4, 1, 2, 3, 4 and 8) + 1 mM TOA^+TFPB^-. Voltammograms were measured right after preparation, and 1, 2, and 5 days later. The scan rate was 5 mV s^{-1}. Voltammetric curves obtained in Fig. 4 were subtracted using standard curves of $[AuCl_4]^-$ and Cl^- in Fig. 2. These peak currents correspond to the $[AuCl_2]^-$ concentration.

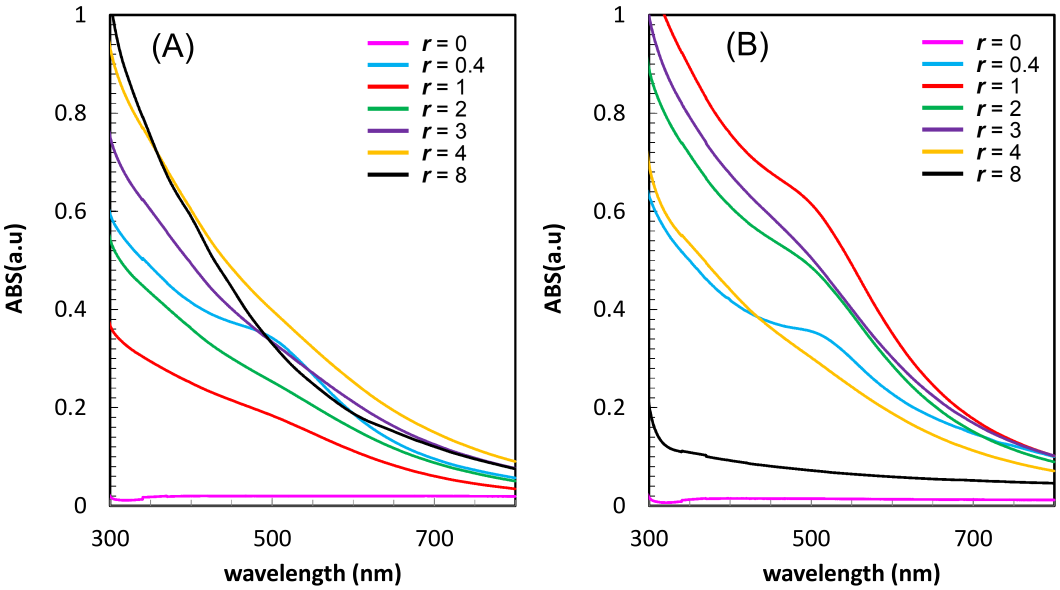

Figure S2

UV-Vis absorption spectra in DCE phase after reduction by BH$_4^-$. Series (a) are samples prepared by BH$_4^-$ addition right after mixing of [AuCl$_4$]$^-$ and RSH (***r*** = 0.4 – 8). Series (b) are samples prepared by BH$_4^-$ addition 5 days after mixing of [AuCl$_4$]$^-$ and RSH (***r*** = 0.4 – 8).

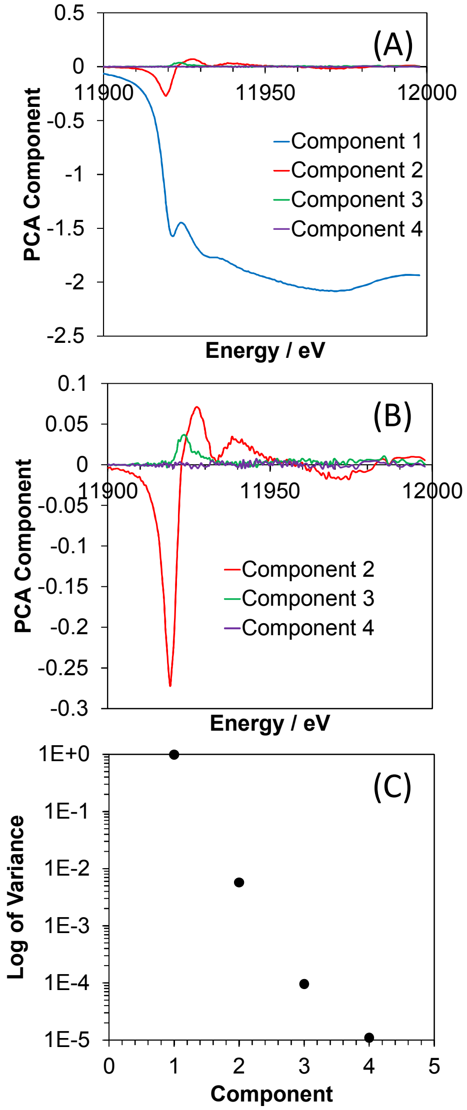

Figure S3

Principal component analysis (PCA) was performed on the XANES data set in order to examine the number of distinct component species. This is a statistical method which requires no prior knowledge of the sample and therefore provides a useful comparison to the linear combination fitting. Plot (a) component 1 is the average spectral line shape from the data set. Plot (b) shows the same samples with component 1 removed to show the other contributions more clearly. As can be seen components 2 and 3 have some structure whereas component 4 only comprises of background noise. Plot (c) shows the log of variance with each component. In this plot a change in the gradient between points indicates a new component. Therefore plots (b) and (c) indicate the presence of 3 distinct species in the samples. In order to verify this each sample (***r*** = 0.5, 1, 2 and 5) was reconstructed from the components and it was found that the plot could be recreated using 3 components.

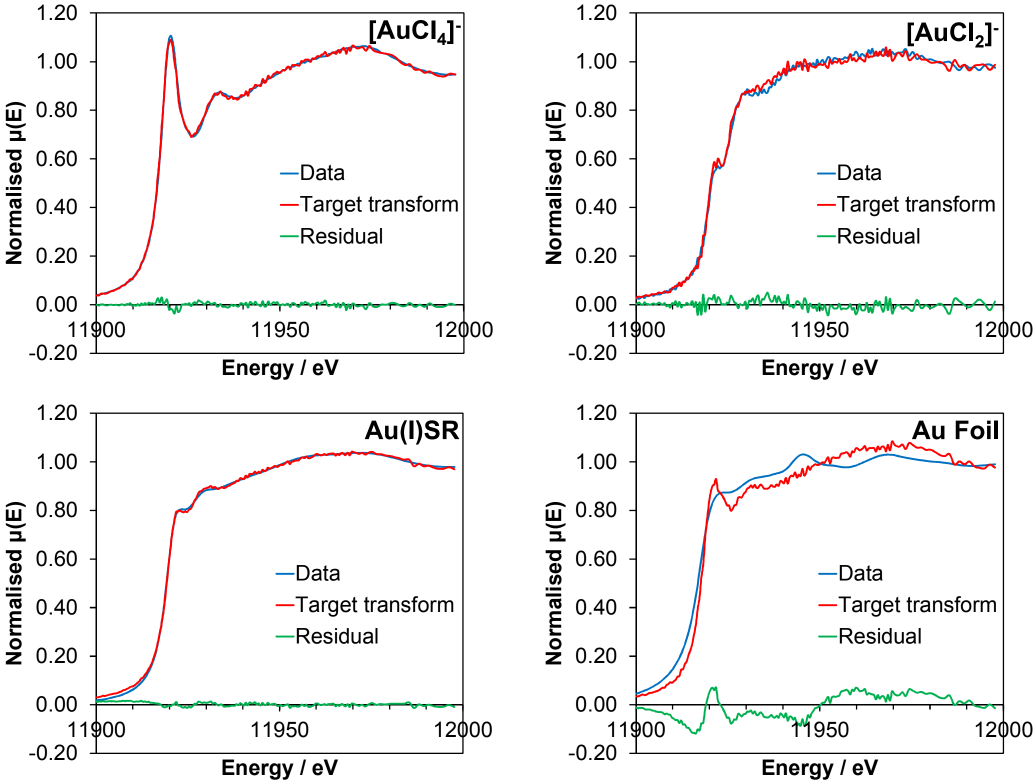

Figure S4

PCA analysis is also a useful way of verifying the use of the correct standards for linear combination analysis. This technique is the inverse of linear combination fitting as the components produced from the data set are used to replicate the spectral shape of the standards. As can be seen above the spectra collected for $[AuCl_4]^-$, $[AuCl_2]^-$ and [Au(I)SR] are all well described indicating that they are clearly present in the data set. For comparison it was found that Au Foil could not be described by the data indicating that there is no Au(0) formation due to reduction by thiol or disproportionation of Au(I) before the addition of $NaBH_4$. Gold foil has previously been shown to produce a similar spectrum to thiol protected nanoparticles of 3 nm.[Ref: D M Chevrier, A Chatt, T K Sham and P Zhang, A Comparative XAFS Study of Gold-thiolate Nanoparticles and Nanoclusters, XAFS15, doi:10.1088/1742-6596/430/1/012029] Smaller nanoparticles have proven harder to characterize due to the large influence of surface Au(I)-thiol relative to the metallic core producing a XANES spectrum similar to that of Au(I)SR shown above.