Infra-red Spectroscopy of Size Selected \( \text{Au}_{25}, \text{Au}_{38} \) and \( \text{Au}_{144} \) Ligand Protected Gold Clusters

Mostafa Farraga\(^a\), Martin Tschurla\(^a\), Amala Dass\(^b\), Ulrich Heiz\(^a\)

\(^a\) TECHNISCHE UNIVERSITÄT MÜNCHEN, LEHRSTUHL FÜR PHYSIKALISCHE CHEMIE, LICHTENBERGSTRAßE 4, 85748 GARCHING, GERMANY

\(^b\) DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, UNIVERSITY OF MISSISSIPPI, 352 COULTER HALL, UNIVERSITY, MISSISSIPPI 38677, USA.

1. Experimental Section:

**Chemicals.** Tetrachloroauric (III) acid (HAuCl\(_4\)·3H\(_2\)O, >99.99\% metal basis, Aldrich), sodium borohydride (NaBH\(_4\), ≥96\%, Aldrich), tetraoctylammonium bromide (TOAB, ≥98\%, Fluka), cesium acetate (CsOAc, 99.9\%, Aldrich), 2-phenylethanethiol (2-PET) and L-glutathione (\(\gamma\)-L-Glutamyl-L-cysteinyl-glycine, \(\gamma\)-Glu-Cys-Gly, L-GSH) reduced (98\%, Aldrich) were used for synthesizing the ligand protected nanoparticles. As solvents tetrahydrofuran (THF, HPLC grade, ≥99.9\%, Aldrich), toluene (HPLC grade, ≥99.9\%, Aldrich), methylene chloride (HPLC grade, ≥99.9\%, Aldrich), ethanol (HPLC grade, Aldrich), and methanol (HPLC grade, Aldrich) were taken. All chemicals were used as received. Deionized water was purified by a Millipore Milli-Q water system to obtain Milli-Q water (resistivity 18.2 MΩ x cm). All glassware was thoroughly cleaned with aqua regia (HCl:HNO\(_3\) = 3:1 v/v), rinsed with Milli-Q water, and then dried in an oven prior to use.
**Instrumentation.** All UV-vis spectra were recorded at ambient temperature from 190 to 1100 nm with a single-beam spectrophotometer (Analytik Jena, Specord 40). Infrared spectra of the 2-phenylethanethiol ligand and the three gold nanoclusters were measured with an FTIR spectrometer (Nicolet 380, resolution: < 0.9 cm\(^{-1}\), transmission mode). Each spectrum was obtained by accumulating 200 scans. The samples were prepared as dry, thin, optically translucent films by casting a drop of a toluene solution on a KBr disk. Mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer, after mixing the particle solution with DCTB matrix in 1:1000 mol ratio. To keep fragmentation as low as possible the laser power was reduced to a threshold value.\(^1\)

**Preparation of Au\(_{25}\)(SCH\(_2\)CH\(_2\)Ph)\(_{18}\)clusters (1).** We followed the synthetic route of Jin and co-workers as it produces reasonable amounts of pure Au\(_{25}\) clusters.\(^2\) In short, HAuCl\(_4\).3H\(_2\)O was reduced by NaBH\(_4\) in the presence of the ligand (PhCH\(_2\)CH\(_2\)SH) in THF at 0\(^\circ\)C and by continuous stirring. Monodisperse clusters were obtained by an aging process (i.e. a prolongation of the reaction time for another 114 h at room temperature) and the succeeding precipitation of the clusters.

**Preparation different charge states of Au\(_{25}\)(SCH\(_2\)CH\(_2\)Ph)\(_{18}\) clusters.** While the synthetic method described above already results in negatively charged Au\(_{25}\)(SCH\(_2\)CH\(_2\)Ph)\(_{18}\) cluster,\(^2\) these clusters are converted to neutral ones via oxidation by air or H\(_2\)O\(_2\) (~30% aqueous).\(^3\) To re-prepare the negatively charged Au\(_{25}\) cluster with different counterions, i.e. tetraoctylammonium (TOA\(^+\)) and Cs\(^+\), all reactants were dissolved in toluene and a 70% toluene/30% methanol mixture, respectively. By the reaction with the salts (i.e. tetraoctylammonium bromide and caesium acetate; molar ratio of gold cluster to salt: 1:100) the neutrally charged Au\(_{25}\) clusters were converted to their negatively charged form again after stirring at room temperature.\(^4\) While the conversion with TOA\(^+\) as counterion is achieved within some minutes, the reaction with caesium acetate is significantly slower (full conversion after 10 h). For both cases, the conversion was monitored by UV-vis spectroscopy (see Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics This journal is © The Owner Societies 2013
below). TOA\(^+\) and Cs\(^+\) were chosen as counterions since they are known to stabilize the anionic form of Au\(_{25}\) clusters, while smaller ions, such as Na\(^+\) do not protect the cluster from oxidation.\(^4\) Repeatedly, the UV-vis spectra of \([\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]\text{Cs}^+\) and \([\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]\text{TOA}^+\) clusters were recorded and no significant oxidation of the clusters was found over three months.

**Preparation of Au\(_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}\) clusters (2).** The preparation of monodisperse Au\(_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}\) clusters was achieved by the exchange of glutathione ligands (GSH) with 2-phenylethylthiol as reported in literature.\(^5\) In short, glutathione-protected gold clusters were obtained via the reduction of HAuCl\(_4\)·3H\(_2\)O with NaBH\(_4\) in the presence of the ligand (GSH) at 0\(^\circ\)C and with vigorous stirring. After the reaction was finished, the clusters were collected as a precipitate and dissolved in water. The solution was then treated with an excess of PhC\(_2\)H\(_4\)SH in toluene and a small amount of ethanol, thus enabling ligand exchange. The diphase solution was heated to and maintained at 80\(\circ\)C under air, so that Au\(_{n}\)(SG)\(_m\) clusters were transferred from the water phase to the organic phase accompanied by the exchange of the protecting ligands. Monodispersity of the clusters was achieved by an etching process at 80\(\circ\)C, which lasted over 40 h. With this synthetic route a yield of Au\(_{38}\) nanoclusters of \(~25\%\) (Au atom basis) was reproducibly obtained.

**Preparation of Au\(_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}\) clusters (3).** Au\(_{144}\) clusters were prepared following the procedure of H. Qian et al.\(^6\) Briefly, in a two phase reaction of water and toluene HAuCl\(_4\)·3H\(_2\)O and TOAB (tetraoctylammonium bromide) were dissolved under vigorously stirring. After the phase transfer of Au(III) was achieved (indicated by a red color of the toluene phase and a colorless aqueous phase), the aqueous phase was discarded and PhCH\(_2\)CH\(_2\)SH was added to the cooled (0\(\circ\)C) toluene solution. Afterwards, reduction with NaBH\(_4\) was performed. The reaction was allowed to proceed for \(~24\) hours and the black toluene phase was then dried by rotary evaporation. Ethanol was used to separate the Au nanoparticles from TOAB and other side products.
Monodisperse Au$_{144}$ nanoparticles were obtained by etching the clusters at 80°C in the presence of excess PhCH$_2$CH$_2$SH for 24 hours under constant magnetic stirring and the succeeding controlled precipitation with methanol. With this method usually a yield of 20 to 30 % (Au atomic basis) is achieved.

Characterization. For the particles’ characterization two main methods were applied UV-vis spectroscopy and MALDI-TOF-MS. UV-vis spectroscopy is sensitive to the metal core and each cluster size studied in this work gives a typical spectrum$^{6-8}$, which is depend on change of the charge state, too. On the other hand, mass spectrometry enables an exact analysis of the size distribution of the clusters and the mass of the parent ion is obtained. Hence the chemical formula of the particle can be derived. The all these results are summarized in Figure S1, clearly confirming the monodispersity and purity of the samples. In addition, a more detailed description of the results is given in the sections below.
Figure S1. UV-vis spectra of size selected gold clusters as well as MALDI spectra of Au\textsubscript{25} (B), Au\textsubscript{38} (C), and Au\textsubscript{144} (D) clusters. The mass spectra as well as the UV-vis spectra clearly confirm the purity and monodispersity of the samples (for a more detailed discussion see the sections below).

1. **UV-vis spectroscopy** was used to determine the charge states of the Au\textsubscript{25} clusters. Neutrally charged Au\textsubscript{25}(SCH\textsubscript{2}CH\textsubscript{2}Ph\textsubscript{18})\textsuperscript{0} nanoclusters show a more pronounced peak at 400 nm (Figure S1A), while [Au\textsubscript{25}(SCH\textsubscript{2}CH\textsubscript{2}Ph\textsubscript{18})\textsuperscript{−}] clusters give a more distinct peak at 450 nm. Furthermore, a transition of less intensity at 400 nm and very small shoulder at around 780 nm (see Figure S1) can be observed for negatively charged clusters. Note, that the shoulder does not appear in the neutral form.\textsuperscript{3}

UV-vis spectroscopy was further used to characterize the individual samples, since this technique is sensitive to changes of the metal core. The spectrum of each cluster size is in good agreement with previous studies\textsuperscript{2,5,6} and is shown in Figure S2.

![Figure S2. UV-vis spectra of Au\textsubscript{25} clusters in (a) neutral form Au\textsubscript{25}(SCH\textsubscript{2}CH\textsubscript{2}Ph\textsubscript{18})\textsuperscript{0} and in the anionic form Au\textsubscript{25}(SCH\textsubscript{2}CH\textsubscript{2}Ph\textsubscript{18})\textsuperscript{−} with (b) TOA\textsuperscript{+} and (c) Cs\textsuperscript{+} as counterion.](image-url)
Nanoclusters of \([\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^0\) exhibit a more distinct peak at 400 nm (Figure S1A), while clusters of \([\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^-\) in the negative charge state show a more pronounced transition at 450 nm and one of less intensity at 400 nm. In addition, a very small shoulder at around 780 nm (Figure S1B and C) is found for negatively charged clusters, which does not appear in the neutral form.\(^3\)

2. MALDI-TOF spectra were used to assess the monodispersity of the clusters. All spectra are in good agreement with spectra published in literature\(^2,5,6\) and confirm the monodispersity of the samples. The mass spectra of all samples are displayed in Figure S1.

The spectrum of Au\(_{25}\) clusters (Figure S1B) is dominated by one peak at \(m/z = 7394\) Da, which is due to the parent ion of \(\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}\). Another smaller peak at \(m/z = 6052\) Da can be found. This peak is due to fragmentation of the \(\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}\) clusters, since its relative intensity strongly depends on the intensity of the desorbing/ionizing laser beam.

For Au\(_{38}\) clusters (Figure S1C) a dominant peak at \(m/z = 10780\) Da is found, which is assigned to the parent ion of \(\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}\). Additional peaks of very small intensity indicate some fragmentation in the MALDI process.

MALDI spectra of Au\(_{144}\) clusters (Figure S1D) give a broad peak at \(m/z = 35000\) amu that clearly confirms the existence of \(\text{Au}_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}\). A minor amount of impurities consisting of smaller clusters may be indicated by the feature below 20000 amu.

References


