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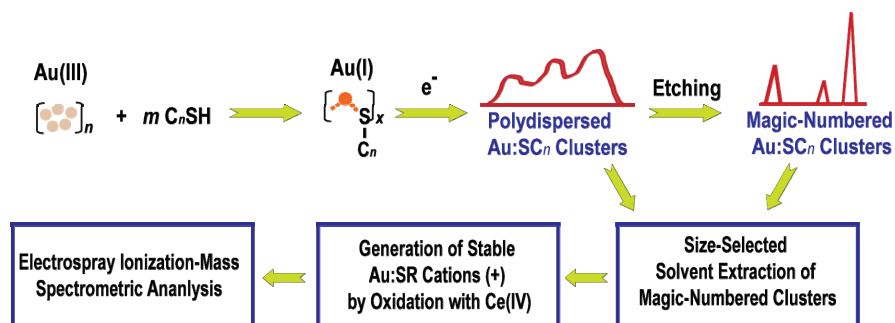
Electrospray Ionization-Mass Spectrometric Study of Alkanethiol-Protected Gold Clusters

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Thiolate-protected gold (Au:SR) clusters have attracted enormous interest in recent years due to their several application possibilities, especially as building blocks in nanoscale devices [1]. As a consequence, immense efforts have been devoted for the precision synthesis and establishment of the structure-property co-relationship of size-selected Au:SR clusters [2,3]. For example, chemical compositions of alkanethiolate-protected gold (Au:SC_n) clusters have been conventionally studied by laser-desorption ionization mass spectrometry (LDI-MS), which have revealed that several specific core mass clusters (8, 14, 22 and 29 kDa) show extraordinarily high stability [2]. These magic-numbered Au:SC_n clusters were isolated using several analytical approach and were found to exhibit fascinating optical, electronic and electrochemical properties [1-3]. Among several isolated magic-numbered clusters, 8 and 29 kDa core mass clusters have been extensively investigated due to their ease of synthesis, purity and stability [1-3]. However, confirmative determination of the analytical composition for these magic-numbered clusters remains illusive as LDI-MS approach inevitably induces extensive fragmentation [2,3]. On the other hand, electrospray-ionization mass spectrometry (ESI-MS) (nondestructive and softer than LDI-MS) could not be directly applied so far to these as-synthesized hydrophobic clusters as they do not have any charging site. To overcome this difficulty, we adopt a strategy to analyze hydrophobic Au:SC_n clusters by ESI-MS after subsequent generation of stable clusters cations by oxidation with Ce(IV) (Scheme 1). Recently, we have successfully applied this approach to precise characterization and determination of the charge state of as-synthesized hydrophobic Au₂₅(SC_n)₁₈ clusters [4]. In this presentation, we will show our recent progresses to determine the chemical composition of 8 and 29 kDa Au:SC_n clusters using this newly-developed ESI-MS approach.



Scheme 1 Schematic representation of synthesis and ESI-MS analysis approach of hydrophobic magic-numbered Au:SC_n clusters.

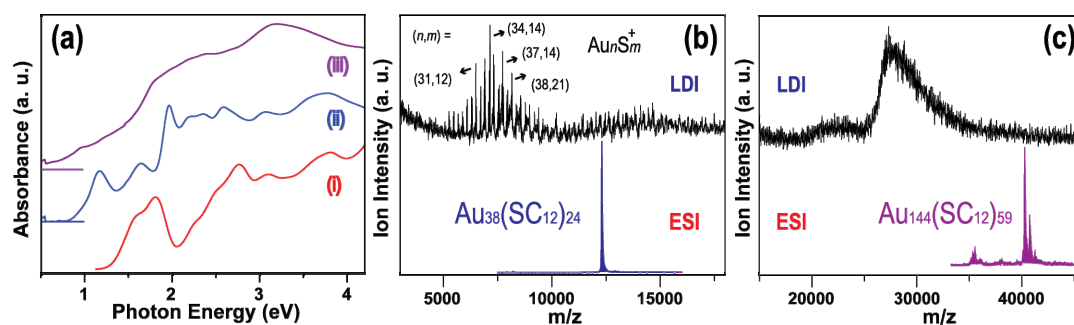


Figure 1 (a) Superimposed optical absorption spectra of isolated (i) $\text{Au}_{25}(\text{SC}_{12})_{18}$, (ii) 8 kDa and (iii) 29 kDa $\text{Au}:\text{SC}_{12}$ clusters. Superimposed LDI and ESI-mass spectra of (b) 8 and (c) 29 kDa $\text{Au}:\text{SC}_{12}$ clusters. The 8 kDa clusters have been confirmed to have $\text{Au}_{38}(\text{SC}_{12})_{24}$ composition, while we tentatively assigned 29 kDa clusters to $\text{Au}_{144}(\text{SC}_{12})_{59}$.

Alkanethiolate-protected gold clusters were prepared by modified Brust synthesis and subsequently etched in neat thiol at 80°C to populate stable magic-numbered clusters (Scheme 1) [2]. Stable magic-numbered gold clusters thus prepared were extracted into several fractions using solvent-nonsolvent interactions at different stages of preparation (Scheme 1). These isolated clusters are characterized by optical absorption spectroscopy, LDI and ESI-MS. For example, the superimposed optical spectra of isolated dodecanethiolate-protected (i) Au_{25} , (ii) 8 kDa and (iii) 29 kDa clusters are shown in Figure 1 (a), where unique absorption features as a function of cluster compositions are evident. Figures 1 (b) and (c) show the superimposed LDI and ESI-mass spectra of 8 and 29 kDa $\text{Au}:\text{SC}_{12}$ clusters respectively, which clearly demonstrates that our ESI-MS approach is nondestructive and effective to determine the chemical composition of these clusters. Analysis of several other alkanethiolate-protected clusters led us to confirm the composition of 8 kDa core mass fraction as $\text{Au}_{38}(\text{SC}_n)_{24}$. Further, our initial ESI-MS results for 29 kDa clusters indicate that $\text{Au}_{144}(\text{SC}_n)_{59}$ may be the most plausible composition. Our research work now is in progress to further confirm this composition by use of several alkanethiols with different chain lengths.

The structural determination of $\text{Au}:\text{SR}$ clusters is of urgent need to understand the origin of their magic stability as well as for their application possibilities. Recent theoretical and experimental studies indicated “core-in-cage” structural motif might be responsible for the unprecedented stability of $\text{Au}_{25}(\text{SR})_{18}$ and $\text{Au}_{38}(\text{SR})_{24}$ clusters [5,6]. In light of the “core-in-cage” structural model discussed above, we believe that the magic stability of $\text{Au}_{144}(\text{SC}_n)_{59}$ species is also may be associated with such kind of structural motif. In summary, we note that our mass spectrometric approach is nondestructive and highly effective in determining the chemical compositions of hydrophobic $\text{Au}:\text{SC}_n$ clusters.

References

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