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Thiol-protected gold (Au:SR) clusters have been attracted enormous interest in recent years due to their versatile synthetic strategies, unique properties and several application possibilities, especially in nanoscale devices [1]. The electrochemical measurements of size controlled Au:SR clusters is an ideal probe to understand the core-size dependent evolution of the electronic structures. Indeed, electrochemistry has been proven to be one of the useful techniques to elucidate the electronic properties of these materials [2]. The electrochemical determination of single-electron charging events is possible due to their tiny capacitive nature (sub-aF), termed as quantized double layer charging. In contrast, when size approaches to certain threshold value, evolution of size dependent HOMO-LUMO gap (HLG) becomes evident as a result of quantum size effect. In this presentation, we will present our recent progress on the synthesis and electrochemical measurement of $\text{Au}_{38}(\text{SC}_{12})_{24}$ and $\text{Au}_{55}(\text{SC}_{12})_{32}$ clusters to clearly demonstrate metal-to-nonmetal transition behavior and the variation of HLG with size of Au:SR clusters.

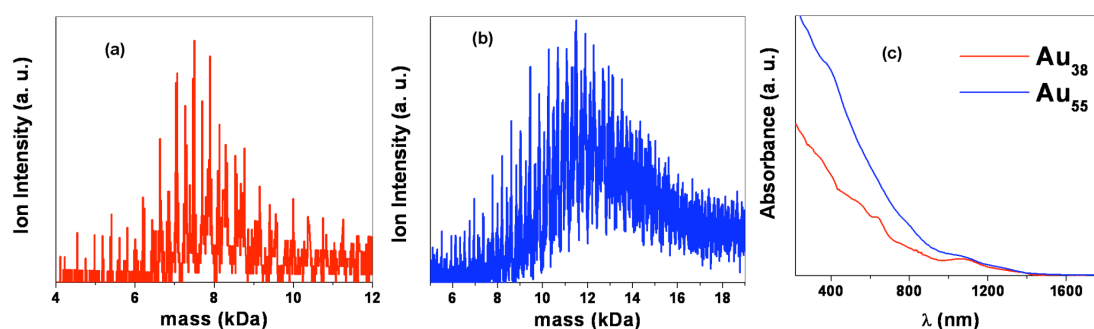


Figure 1 Positive ion LDI mass spectra of (a) $\text{Au}_{38}(\text{SC}_{12})_{24}$ and (b) $\text{Au}_{55}(\text{SC}_{12})_{32}$ clusters. (c) Superimposed UV-Vis spectra of chromatographically separated $\text{Au}_{38}(\text{SC}_{12})_{24}$ (red) and $\text{Au}_{55}(\text{SC}_{12})_{32}$ (blue) clusters.

We first prepared alkanethiolated gold clusters ($\text{Au}:\text{SC}_n$; $n = 12$) by thiolation of the preformed Au clusters, which were weakly stabilized by poly(N-vinyl-2-pyrrolidone). Then, the $\text{Au}:\text{SC}_n$ clusters thus prepared were fractionated into several components using recycling size exclusion chromatographic method [3]. Mass spectrometric analysis revealed that two of the components were composed of clusters with a core mass of 8 and 11 kDa (Figure 1a and 1b). These clusters were assigned to $\text{Au}_{38}(\text{SC}_{12})_{24}$ and $\text{Au}_{55}(\text{SC}_{12})_{32}$ after various characterizations, respectively. The superimposed optical spectra are shown in Figure 1c, where several discrete electronic transitions are clearly visible. Further, these discrete electronic states have been identified using electrochemical studies. Our preliminary electrochemical results (Figure 2) reveal a significant molecular nature of

both (a) $\text{Au}_{38}(\text{SC}_{12})_{24}$ and (b) $\text{Au}_{55}(\text{SC}_{12})_{32}$ as reflected by the presence of 0.9 and 0.7 eV HLG respectively. The results for $\text{Au}_{38}(\text{SC}_{12})_{24}$ are essentially the same as those reported for 8 kDa clusters in ref. [2]. Formal potential spacing at various charge states and HLG variation of (a) $\text{Au}_{38}(\text{SC}_{12})_{24}$ and (b) $\text{Au}_{55}(\text{SC}_{12})_{32}$ clusters in dichloromethane are summarized in Table 1.

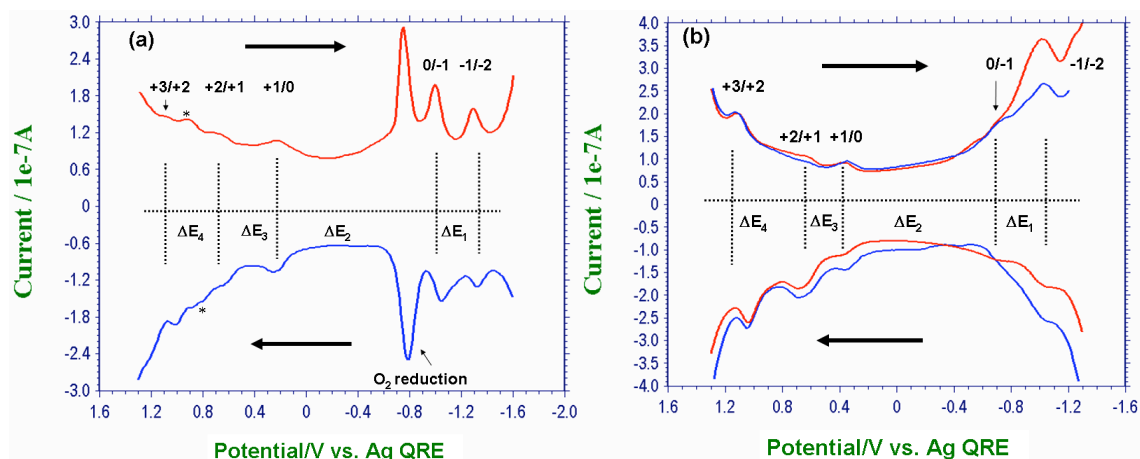


Figure 2 Differential pulse voltammetric (DPV) plots of (a) 0.5 mM $\text{Au}_{38}(\text{SC}_{12})_{24}$ and (b) 0.15 mM $\text{Au}_{55}(\text{SC}_{12})_{32}$ clusters in dichloromethane using 0.1 M tetrabutylammonium hexafluorophosphate on a Pt (1.6 mm diameter) working electrode at -40°C and at room temperature, respectively, under Ar atmosphere.

Table 1 Variation of formal potential spacing and HLG of $\text{Au}_{38}(\text{SC}_{12})_{24}$ and $\text{Au}_{55}(\text{SC}_{12})_{32}$ clusters

Clusters	ΔE_1^1 (V)	ΔE_2^1 (V)	ΔE_3^1 (V)	ΔE_4^1 (V)	HOMO-LUMO Gap ² (eV)
(a) $\text{Au}_{38}(\text{SC}_{12})_{24}$	0.29	1.25	0.41	0.42	0.9
(b) $\text{Au}_{55}(\text{SC}_{12})_{32}$	0.35	1.04	0.31	0.42	0.7

¹ ΔE (peak spacing as indicated in Figure 2), which is estimated from the averaged peak positions values of cathodic and anodic going scans to minimize iR_{UNC} distortion. ²HOMO-LUMO Gap = $[\Delta E_2 - (\Delta E_1 + \Delta E_3)]/2$

In summary, we have demonstrated the isolation and electrochemical properties of $\text{Au}_{38}(\text{SC}_{12})_{24}$ and $\text{Au}_{55}(\text{SC}_{12})_{32}$ clusters for the first time to understand the electronic property variations as a function of core size. Systematic electrochemical measurements are underway for these clusters, which will provide a strategy for tuning the electronic properties of gold clusters through precise control of thiolate ligation as well as core size.

References

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