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Thiolate-Protected Au_{20} Clusters with a Large Energy Gap of 2.1 eV

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The size-dependent physical and chemical properties of noble metal nanoparticles, in particular gold, have stimulated tremendous research interest in recent decades.[1] Crystalline gold nanoparticles (i.e., nanocrystals, typically >2 nm) exhibit one or multiple localized surface plasmons depending on their size and shape;[1d] such plasmon excitation modes do not exist in bulk gold and are unique to nanocrystals. The structure of gold nanocrystals, however, still resembles bulk gold, i.e., face-centered cubic (fcc). On the other hand, when the gold nanoparticles fall in the extremely small size regime (e.g., <2 nm), drastic changes occur in terms of the atomic packing structure[2−9] as well as their optical properties.[9−11] Recently, we have determined the crystal structure of a thiolate-capped 25-atom Au nanocluster[9a,b] (also determined independently by Murray et al.[8]). The Au_{25} cluster features an icosahedral Au_{13} kernel encapsulated by an exterior gold shell comprised of the remaining 12 gold atoms, and the entire particle is stabilized with 18 thiolate ligands. The pursuit of size-controlled synthesis of gold nanoclusters and the study of the evolution of their structural and optical properties from small clusters to nanocrystals forms a central task. We are motivated to develop new synthetic approaches to create well-defined Au_n nanoclusters with a specific number of gold atoms in the size range (n) from a dozen to a hundred or so, since gold nanoclusters in this size range show particularly interesting optical properties[9] that are fundamentally different from those of larger counterparts—gold nanocrystals.

In this work, we report the synthesis of a gold thiolate cluster composed of 20 gold atoms and 16 thiolate ligands (*vide infra*), abbreviated as $Au_{20}(SR)_{16}$, where $R = CH_2CH_2Ph$. These clusters exhibit a stepwise, multiple-band optical absorption spectrum with a large HOMO−LUMO gap, $E_g \approx 2.15$ eV. These clusters are also extraordinarily robust against excess thiol etching.

In a typical experiment, gold salt ($HAuCl_4 \cdot 3H_2O$, 0.4 mmol) was phase-transformed from an aqueous solution into toluene in the presence of tetraoctylammoniun bromide (TOAB) (see Supporting Information for details). Briefly, the solution was cooled to 0 °C, and the magnetic stirring speed was reduced to ~50 rpm. Phenylethylthiol (abbreviated as HS-R hereafter) was added to the cold $Au^{(III)}$ solution, and the solution was kept still. After the formation of the $[Au^{(I)}SR]_x$ aggregates, $NaBH_4$ (~1 equiv of gold) solution was slowly added over a 30 min period to reduce the $[Au^{(I)}SR]_x$ aggregates, during which time the reaction mixture was under constant *slow* stirring; these conditions (~1 equiv of $NaBH_4$ and *slow* reduction of $[Au^{(I)}SR]_x$) were found to be critical in order to effect $Au_{20}(SR)_{16}$ growth. After overnight, ethanol was added to the reaction products to precipitate gold nanoclusters. Very pure Au_{20} nanoclusters were obtained by extraction of the nearly dried solids with a mixed CH_2Cl_2/CH_3CN (1:4, v/v) solvent. The purity of as-collected gold clusters was analyzed by size exclusion chromatography (SEC). A representative chromatogram of the clusters is shown in Figure 1. Only one peak, eluting at ~16.05 min, was observed. Its symmetric shape indicates the as-prepared gold clusters should be pure, which is further evidenced by the close resemblance of the UV−vis spectra corresponding to the peak position and its left and right sides (Figure 1 inset).

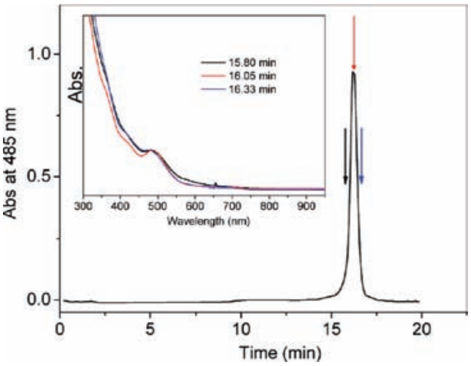

Figure 1. Size exclusion chromatogram of $Au_{20}(SC_2Ph)_{16}$ clusters monitored at 485 nm (eluent, CH_2Cl_2, 0.5 mL/min). (Inset) Online-recorded UV−vis spectra corresponding to the 16.05 min peak (red) and its left/right sides (black, 15.80 min; blue, 16.33 min).

To determine the exact composition of the gold clusters, we have performed various characterizations. Elemental analysis shows that the Au cluster contains 24.42% C, 2.31% H, 7.80% S, and 0.00% N. Thus, the converted atomic ratio of C/H/S is 8:9:1, in good agreement with the phenylethylthiolate formula (C_8H_9S). Since no nitrogen was found, the cluster should contain no tetraoctylammonium (TOA^+, the phase transfer agent). Note that in Au_{25} thiolate clusters, TOA^+ was found to coexist with the cluster to compensate the −1 charge of the Au_{25} cluster.[9a] The charge neutrality of the cluster prepared in this work is further confirmed by XPS measurements and ^1H NMR analysis (see Supporting Information); both analyses did not identify any other organic components except phenylethylthiolate. These results taken together reveal that the Au cluster should be charge neutral and should only contain gold (65.47 wt %) and thiolate ligand (34.53 wt %, elemental analysis). The ratio of gold to total organic content is also consistent with thermogravimetric analysis (observed loss, 34 wt %). Therefore, the Au-to-ligand number ratio is determined to be 1.3/1.

To determine the exact Au atom/ligand numbers for the cluster, eletrospray ionization (ESI) mass spectrometry is indispensable. ESI-MS-TOF analysis (with CsOAc added to the gold cluster solution to enhance the cluster ionization) shows an intense peak at *m/z* 6267, which is assigned to the gold cluster:Cs^+ adduct (Figure 2). Slight fragmentation of the cluster and recombination of fragments occurs even under the ESI soft ionization conditions, evidenced by a series of small peaks with a 334 Da spacing (corresponding to Au-SR). The isotopic pattern analysis (Figure 2 inset) of the *m/z* 6267 peak indicates that the cluster ion bears one

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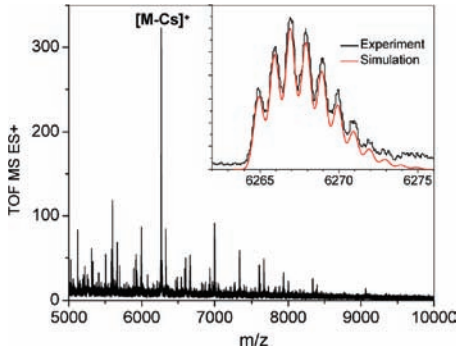

Figure 2. ESI-TOF mass spectrum of $Au_{20}(SC_2Ph)_{16}$ clusters. (Inset) The isotopic pattern of *m*/*z* 6267 (assigned as a cluster:Cs^+ adduct), together with a simulated pattern based on a formula of $[Au_{20}S_{16}C_{128}H_{144}]Cs^+$ and a resolving power of 8000.

charge (spacing of the isotopic peaks = 1); thus, the ion mass is 6267 Da. After subtracting one Cs^+ ion, the cluster mass is determined to be 6134 Da. With the Au-to-ligand ratio and exact cluster mass determined, it is straightforward to deduce the exact formula of the cluster, i.e., $Au_{20}(SCH_2CH_2Ph)_{16}$ (theoretical mass, 6134.0 Da for the most abundant species, and Au/S = 1.25). The perfect agreement between the experimental and simulated isotopic patterns, and the accurate measured mass, unequivocally confirmed the $Au_{20}(SR)_{16}$ formula.

The optical absorption spectrum of the as-prepared Au_{20} clusters (dissolved in toluene or CH_2Cl_2) shows a stepwise, multiple-band spectrum (Figure 3), which is a common feature of Au_n clusters[9−11] and is also reminiscent of the absorption behavior of semiconductor quantum dots. The most prominent absorption band is centered at ~485 nm (2.56 eV); additional spectral features include a broad band at ~420 nm (2.95 eV) and another band at ~350 nm (3.5 eV). These optical spectral features indicate a strong quantum confinement effect of electrons in the Au_{20} cluster. The optical energy gap was determined to be $E_g \approx 2.15$ eV (Figure 3 inset), much larger than that of Au_{25} ($E_g \approx 1.3$ eV).[9a]

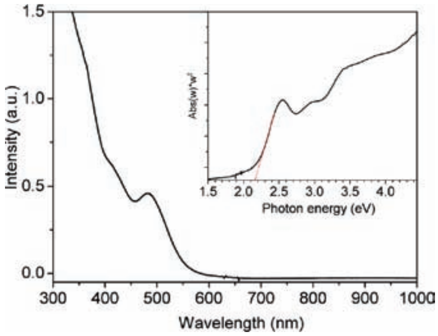

Figure 3. Optical absorption spectrum of $Au_{20}(SC_2Ph)_{16}$ clusters dissolved in toluene. (Inset) The spectrum on the energy scale (eV); the HOMO−LUMO gap is 2.15 eV (see red intercept).

The $Au_{20}(SCH_2CH_2Ph)_{16}$ clusters were also found to be particularly stable against excess thiol etching. This is in contrast to previous work on thiol etching on a series of glutathione-capped $Au_n(SG)_m$ clusters. Tsukuda and co-workers demonstrated that $Au_n(SG)_m$ clusters ($n < 25$) decompose in excess thiol.[11b] The extraordinary stability of $Au_{20}(SCH_2CH_2Ph)_{16}$ against etching may indicate some structural differences between this cluster and glutathione-capped ones. However, our attempts to crystallize $Au_{20}(SCH_2CH_2Ph)_{16}$ clusters have not been successful.

It is worth noting that previously Wang et al. reported that gas-phase bare Au_{20} clusters should possess a highly stable tetrahedral structure with all 20 atoms located on the surfaces.[12a] This unique structure is supported by experiment[12] and theory.[12−18] Phosphine-stabilized $Au_{20}(PPh_3)_8$ clusters were also observed in mass spectrometry analysis.[12b] The HOMO−LUMO gap of bare Au_{20} was determined to be 1.77 eV.[12a] In contrast, the large E_g of $Au_{20}(SR)_{16}$ and thiol etching stability remain to be answered.

In summary, this work reports the synthesis of thiolate-capped 20-gold-atom clusters; their formula was determined to be $Au_{20}(SCH_2CH_2Ph)_{16}$. The optical absorption spectrum of these clusters shows a multiple-band feature and a large HOMO−LUMO gap ($E_g \approx 2.15$ eV). The crystal structure of $Au_{20}(SCH_2CH_2Ph)_{16}$ remains to be unraveled in future work.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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