Facile Syntheses of Monodisperse Ultrasmall Au Clusters

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Received: August 13, 2006; In Final Form: September 18, 2006

During our effort to synthesize the tetrahedral Au_{20} cluster, we found a facile synthetic route to prepare monodisperse suspensions of ultrasmall Au clusters Au_N ($N < 12$) using diphosphine ligands. In our monophasic and single-pot synthesis, a Au precursor $ClAu(I)PPh_3$ (Ph = phenyl) and a bidentate phosphine ligand $P(Ph)_2(CH_2)_MP(Ph)_2$ are dissolved in an organic solvent. Au(I) is reduced slowly by a borane-*tert*-butylamine complex to form Au clusters coordinated by the diphosphine ligand. The Au clusters are characterized by both high-resolution mass spectrometry and UV−vis absorption spectroscopy. We found that the mean cluster size obtained depends on the chain length M of the ligand. In particular, a single monodispersed Au_{11} cluster is obtained with the $P(Ph)_2(CH_2)_3P(Ph)_2$ ligand, whereas $P(Ph)_2(CH_2)_MP(Ph)_2$ ligands with $M = 5$ and 6 yield Au_{10} and Au_8 clusters. The simplicity of our synthetic method makes it suitable for large-scale production of nearly monodisperse ultrasmall Au clusters. It is suggested that diphosphines provide a set of flexible ligands to allow size-controlled synthesis of Au nanoparticles.

Introduction

A long-standing objective of cluster science is to identify and synthesize highly stable clusters and to exploit their unique chemical and physical properties, either as novel functional units or as building blocks for cluster-assembled materials. Gold nanoparticles have attracted considerable attention recently due to their unique catalytic, optical, and electronic properties, as well as their potentials in biological applications.[1−9] We have previously found that a 20-atom cluster of gold possesses a highly stable tetrahedral structure with all twenty atoms on the cluster surfaces, which may exhibit interesting catalytic properties.[10] The Au_{20} cluster has also been found to possess a large energy gap of 1.77 eV and may have interesting optical properties in the visible range. However, to explore the anticipated novel chemical and optical properties of Au_{20}, an effective synthetic method has to be developed to produce bulk quantities of this cluster with perhaps ligand protection. We have previously shown that the tetrahedral Au_{20} can form in solution protected by eight PPh_3 ligands.[11] However, only a mixed sample was obtained and the yield of the tetrahedral Au_{20} species was too low to allow us to obtain a purified sample. In a continuing effort to synthesize the tetrahedral Au_{20}, we have devised a new synthetic strategy by exploring different ligands and nucleation conditions while monitoring the reaction process using high resolution electrospray mass spectrometry. During this work, we observed that monodispersed and highly stable Au clusters can be formed when diphosphine ligands are used.

A number of small Au_N clusters ($N \leq 13$) with phosphine and halogen ligands have been synthesized and well studied.[12] However, in many cases the synthesis yielded polydisperse samples. For example, synthesis of the well-known Au_{11} cluster requires several purification cycles.[13−15] Larger Au nanoparticles are usually synthesized with thiol ligands with broad size distributions.[16−21] Some previous reports have suggested that size-selectivity can be improved by using bidentate phosphine ligands.[22−24] In an effort to find a synthetic route for the tetrahedral Au_{20} cluster, we have tested in the current study a series of diphosphine ligands of the general formula $P(Ph)_2$-$(CH_2)_MP(Ph)_2$, where the two P atoms are separated by an alkyl chain with a number M of CH_2 spacers. Although we have not found the conditions to produce the desired Au_{20}, we have found that the diphosphine ligands with $M \geq 3$ exhibit a high degree of size selectivity, giving rise to a simple method to synthesize monodispersed Au_N clusters with $N \leq 11$. The synthetic methodology described here has several advantages compared to more commonly employed techniques. It is monophasic and employs only commercially available precursors. Thus, it should be possible to scale it up to produce large quantities of ultrasmall and monodispersed Au clusters.

Experimental Section

In a typical synthesis, $Au(PPh_3)Cl$ was dissolved in deaerated $CHCl_3$ to reach a final concentration of 10^{-3} mol L^{-1} (M). The solution was stirred under Ar, and a reducing agent (a borane-*tert*-butylamine complex) was added in a concentration of 5×10^{-3} M.[25] To attain size-selectivity, 10^{-3} M of a diphosphine ligand, $P(Ph)_2(CH_2)_MP(Ph)_2$ (abbreviated as L^M in the following) was added prior to the reducing agent. The products were

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J. Phys. Chem. B, Vol. 110, No. 43, 2006 **21417**
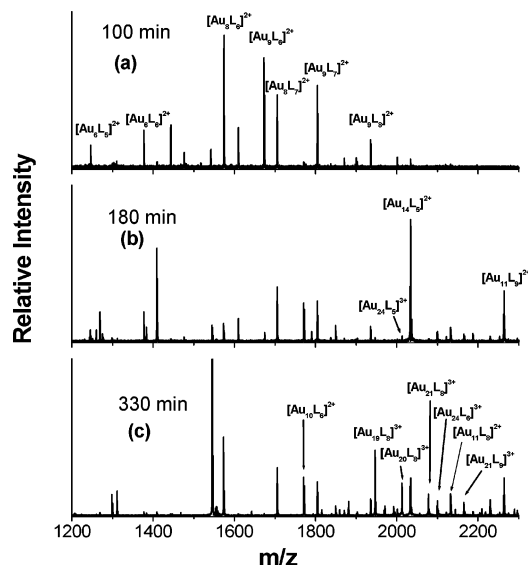
Figure 1. High-resolution mass spectrometry characterization of Au−PPh$_3$ complexes (Au−L), taken at the indicated times after addition of the reducing agent. Unlabeled peaks correspond to singly charged fragments, originating from Au dimers and trimers.

characterized with UV−vis absorption spectroscopy and high-resolution Fourier transform ion cyclotron resonance (FTICR) mass spectrometry, which was accurately calibrated and equipped with an electrospray ionization (ESI) source. The solution sample was introduced into the ESI ion source through direct infusion using a syringe pump. The mass analysis was carried out in the positive ion mode. Mass scans were optimized for different mass-to-charge (m/z) ranges from 1000 up to more than 10 000. The mass resolution was $M/\Delta M \sim 10^5$ and the mass accuracy was 0.8 ppm.

Results and Discussion

At room temperature, reduction of the Au(I) precursor was quite slow. The solution started to change color after about 30−45 min, and the reaction was completed in 4−8 h. Due to the slow reduction rate, the nucleation process could be monitored in real time. We took aliquots of the solution at regular time intervals and determined the content with ESI−FTICR mass spectrometry. Figure 1 shows the cluster growth processes in the presence of triphenyl-phosphine, which is not strongly size-selective. For short reaction times (Figure 1a), only peaks corresponding to small Au$_N$ clusters were detected, $N < 10$. The clusters were coordinated by various numbers of triph-enylphosphine ligands, in agreement with previous reports on the synthesis of small Au clusters.[12] For longer reaction times, the Au cluster sizes increased, as shown in Figure 1b and 1c. Note that under the current reaction conditions, a polydispersed sample was obtained and the desired Au$_{20}$ cluster was not particularly prominent.

The diphosphine ligands [P(Ph)$_2$(CH$_2$)$_M$P(Ph)$_2$] with $M \leq 2$ also yielded polydispersed samples. However, diphosphines containing longer aliphatic chains showed remarkable size selectivity. Figure 2 displays mass spectra obtained for samples stabilized by diphosphines with $M = 3$ to 6. The spectra exhibited only a few peaks which did not vary over time. Most remarkably, Figure 2a shows the spectrum obtained with P(Ph)$_2$-(CH$_2$)$_3$P(Ph)$_2$ (L^3 ligand). Only one intense peak, corresponding to [Au$_{11}$(L^3)$_5$]$^{3+}$, was observed in the mass spectrum. The inset of Figure 2a displays the isotopic pattern of the observed peak for [Au$_{11}$(L^3)$_5$]$^{3+}$, compared with the simulated isotopic pattern.
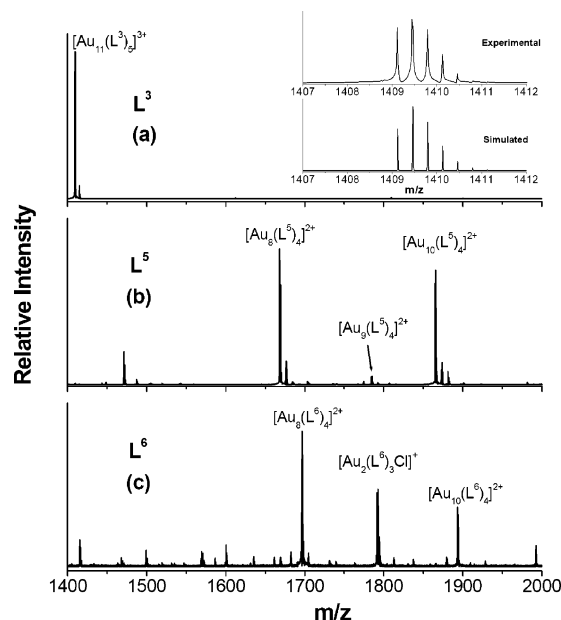
Figure 2. High-resolution mass spectrometry characterization of Au clusters stabilized with the indicated diphosphine ligand (L^M). The inset in (a) shows the isotopic pattern of the [Au$_{11}$(L^3)$_5$]$^{3+}$ mass peak, and the simulated isotopic pattern using the natural isotopic abundances of Au, P, C, and H.
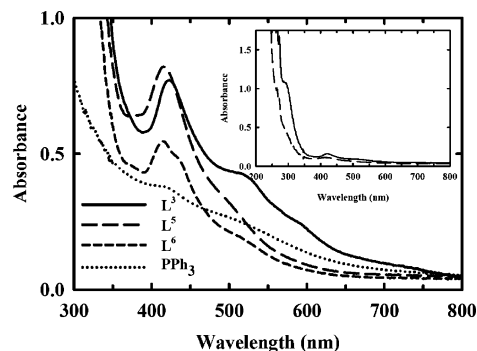
Figure 3. Optical absorption of Au clusters stabilized with the indicated ligands. The inset shows the absorption over a wider range of wavelengths for L^3- (solid line) and L^5- (dashed line) stabilized samples, after dilution (12 times) in CHCl$_3$.

The excellent agreement between the simulated isotopic pattern and the experimentally observed peaks confirmed unequivocally the mass assignment for [Au$_{11}$(L^3)$_5$]$^{3+}$. It is worth noting that no Cl was observed in the ligand shell because the five bidentate L^3 ligands occupied all the ten surface sites of the Au$_{11}$$^{3+}$ cluster core.[13−15] The ligand L^4 yielded a rather polydisperse mixture of clusters ranging from Au$_8$ to Au$_{11}$. Surprisingly, when the spacer length was increased to L^5, the number of species present in the suspension decreased. The spectrum of Figure 2b shows an intense peak due to Au$_8$, accompanied by an almost equally intense peak due to Au$_{10}$ and a very weak Au$_9$ peak. Except for some weak peaks corresponding to singly charged Au dimers and trimers, no other clusters were detected. For the longest diphosphine spacer used in these experiments (L^6), we also only observed Au$_8$ and Au$_{10}$, with the intensity of the Au$_{10}$ peak being decreased somewhat relative to Au$_8$ (Figure 2c).

We obtained optical absorption spectra (Figure 3), which confirmed the findings of the mass spectrometry experiments. The UV−vis absorption spectra of L^3- and L^5-stabilized samples are shown in the inset of Figure 3. The absorption of the L^3-stabilized sample exhibits two maxima around 300 and 415 nm, in overall agreement with previously reported spectra of

undecagold (Au_{11}) clusters.[12–14] Samples stabilized with the L^5 and L^6 ligands exhibit weak shoulders in the ultraviolet, but they have clearly distinguishable absorption maxima in the 400–450 nm region, as shown in more detail in the main body of Figure 3. The absorption maximum at 415 nm, which is characteristic of the undecagold Au_{11} (L^3 ligand), shifted to 411 nm in the L^5-stabilized samples. Absorption in the 410–412 nm range is characteristic of Au_8,[12] and is consistent with the large Au_8 peak observed in the mass spectrum (Figure 2b). In L^6-stabilized samples, which contained a larger fraction of Au_8, the peak at 411 nm was accompanied by a shoulder at about 430 nm. Samples stabilized with the monophosphine ligand exhibited a broad, featureless spectrum, in agreement with the polydispersity observed in the mass spectra (Figure 1). The 415 nm absorption in the Au_{11} complex has been suggested to be due to $5d \rightarrow 6s$ interband transitions in the $Au_{11}{}^{3+}$ core.[26] The slight blue-shifts of this feature in the Au_{10} and Au_8 complexes are consistent with this suggestion.

The size selectivity of the long-chain diphosphines is remarkable, considering the fact that both Au clusters and diphosphines with an alkyl chain spacer are quite flexible objects.[12,27] For the L^3 ligand, the size selectivity can be partly understood from previous results. It is known that the L^3 ligand can replace the ligands of preformed Au_{11} clusters with monophosphine and chloro ligands to yield $[Au_{11}(L^3)_5]^{3+}$,[28] suggesting that the diphosphine ligands have strong interactions with the Au_{11} core, probably due to steric effect induced by the L^3 ligands. $[Au_{11}(L^3)_5]^{3+}$ appears to be an extremely stable compound, since the geometry of the Au_{11} core is not significantly altered by the ligand exchange, nor are other cluster sizes generated in the ligand exchange process. The stability of the $Au_{11}{}^{3+}$ core is well known due to the shell closing with 8 valence electrons, as revealed by previous molecular orbital calculations.[29] The stability of the $Au_8{}^{2+}$ and $Au_{10}{}^{2+}$ cores is also understandable because they have been synthesized before with monophosphine and chloro ligands and well characterized.[12] However, the size selectivity of the diphosphine ligands toward a particular Au cluster core observed in the current study is not well understood at present. Our results, together with the recent observation of an unusual optical activity of Au_{11} capped with 2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl (BINAP),[24] indicate that the interaction between Au clusters and bidentate phosphines is complex and intriguing. Additional work, including computational and crystallographic studies, is required to clarify these issues and to pave the way to selectively synthesize other Au clusters with higher nuclearity by using bidentate phosphine ligands.

Conclusions

In conclusion, we report that monodisperse Au_{11} clusters and bimodal distributions of Au_8 and Au_{10} can be produced by reducing a Au(I) precursor in the presence of bidentate phosphine ligands. Our synthesis is easy and simple because it is monophasic and all precursors are commercially available. Thus, our technique could be used for large-scale synthesis of monodisperse small Au clusters. Our study reveals that the cluster size can be varied by simply varying the length of the spacer separating the P atoms in the ligand and that certain diphosphine ligands can be extremely size-selective. We also demonstrate that high-resolution ESI−FTICR mass spectrometry is a highly informative technique to monitor nucleation processes and probe the cluster growth. Further studies of the interactions between diphoshines and Au clusters may lead to considerable improvements of the size-selectivity of Au cluster syntheses and are promising to achieve our eventual goal of synthesizing the tetrahedral Au_{20}.

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