Convenient Preparation of Stable, Narrow-Dispersity, Gold Nanocrystals by Ligand Exchange Reactions

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Received August 18, 1997

An important advance in metal cluster chemistry came when Brust et al.[1] reported the solution-phase synthesis of alkanethiol-stabilized gold nanocrystals. This discovery sparked great interest in the potential uses of these metal nanocrystals: multifunctional catalysts, chemosensors, nanoelectronic circuit elements, and soluble analogs of self-assembled monolayers. The physical properties of these nanocrystals can be tuned by variations in both the nature of the ligand shell, and the size of the metal core. Large metal clusters possess the requisite properties for use as building blocks for nanoelectronic devices such as single electron transistors and electron turnstiles.[2] Such devices rely on the phenomenon of Coulomb blockade, observable at room temperature only if the individual metal cores are smaller than 2 nm in diameter.[3] Ideally, these clusters would also be monodisperse and indefinitely stable in both solution and the solid state. Currently, there exist few convenient large-scale preparations for stable clusters of this size range with a narrow dispersity. Here, we describe a general synthesis of narrow dispersity, stable gold nanocrystals (d_{core} < 2 nm) via ligand exchange reactions.

The preparative method popularized by Brust et al.[1] employs a two-phase system involving reduction of $HAuCl_4$ (aq) which is transferred to a passivant-containing organic layer. The passivant prevents coalescence of clusters into bulk metal.[3a−5] Crude control over the mean cluster size can be effected by adjusting the ratio of gold salt to alkanethiol.[6] Unfortunately, little control is possible over the size distribution. Fractional crystallization can narrow the dispersity but it is a very time-intensive method.[1b]

A preparation of small phosphine-stabilized gold clusters described by Schmid et al. in 1981[7] involves the reduction of $AuCl[PPh_3]$ with diborane to yield a gold cluster typically formulated as $Au_{55}(PPh_3)_{12}Cl_6$. One unique feature of this preparation is the relatively narrow size envelope of the product.[8] The

inherent instability of these phosphine-stabilized clusters in dilute solution and at elevated temperatures limits their utility.[9]

Our approach to small, stable gold clusters blends the narrow size distribution (1.4 ± 0.4 nm)[8] of $Au_{55}(PPh_3)_{12}Cl_6$ with the established stability of thiol-passivated gold clusters.[10] Here, we show that phosphine-stabilized gold clusters undergo controlled ligand-exchange with alkyl- and arylthiols to give the corresponding thiol-stabilized cluster. Substitution in this manner is applicable to a wide variety of ligands and, importantly, gives retention of cluster size. With this method, the size, functionality, and physical properties of the ligand shell surrounding the gold nanocrystals can be tuned.[11]

Stirring $Au_{55}(PPh_3)_{12}Cl_6$[12] in the presence of excess thiol in dry CH_2Cl_2 leads to complete exchange of the phosphine ligands by thiols. A variety of thiols can be engaged in the substitution including 1-propanethiol (PTh, a short-chain alkanethiol), 1-octadecanethiol (ODT, a long-chain flexible alkanethiol), and 4-mercaptobiphenyl (MBP, a rigid aromatic thiol). Required exchange times depend upon the thiol selected and range from 30 min to overnight. Workup involves removal of the solvent, followed by trituration or precipitation. No recrystallization is performed.

Physical characteristics of the clusters show a marked dependence on the ligand shell. This dependence is illustrated by the solubility properties of the prepared clusters. Although $Au_{55}(PPh_3)_{12}Cl_6$ shows good solubility in CH_2Cl_2, $CHCl_3$, and pyridine, the thiol-stabilized clusters display enhanced solubility in less polar solvents such as benzene. The ODT-stabilized cluster shows unusually slow dissolution kinetics compared to the other clusters investigated, due probably to interdigitation of the ligands on adjacent clusters.[10,13]

Chemical composition is obtained from X-ray photoelectron spectroscopy (XPS). Quantification of XPS spectra gives a gold to sulfur ratio varying from 2.3:1.0 (PTh-passivated) to 2.7:1.0 (MBP-passivated) and shows a complete absence of phosphorus or chlorine. As with $Au_{55}(PPh_3)_{12}Cl_6$, a broad doublet is observed for the Au 4f level.[5,14] The binding energy of the Au 4f 7/2 level is 84.0−84.2 eV (for the three different ligands reported) versus that of adventitious carbon, 284.8 eV. This indicates absence of Au(I)[5,15] and is similar to binding energies obtained for clusters such as $Au_{55}(PPh_3)_{12}Cl_6$.[5,14,16] The binding energy of the S 2p 3/2 peak ranges from 162.4 to 162.6 eV for the series of clusters. These values are shifted to lower energy than those found for free thiols (163.3−163.9 eV)[17,18] and are close to the values reported for thiolates bound to gold (162.0−

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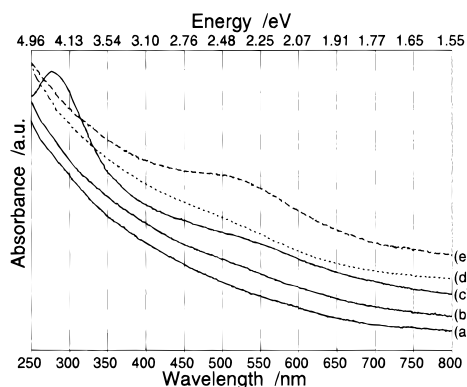(8) Rapoport, D. H.; Vogel, W.; Cölfen, H.; Schlögl, R. *J. Phys. Chem. B* **1997,** *101,* 4175.

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Figure 1. UV−vis spectra (CH₂Cl₂ solution) of Au clusters stabilized with the following ligands: (a) ODT, (b) PTh, (c) MBP. The spectra are normalized arbitrarily at 375 nm and offset vertically. For comparison, we show (dashed lines) (d) starting material $Au_{55}(PPh_3)_{12}$-Cl_6 and (e) a sample of larger ODT-stabilized cluster, synthesized according to the literature.[1]

162.4 eV).[17,19] The possibility that unattached thiols may be present in the sample is unambiguously ruled out by ^{1}H and ^{13}C NMR.

Thermal gravimetric analysis confirms the Au:S ratio obtained from XPS. On heating to 600 °C, ODT-stabilized clusters display a 40% mass loss, corresponding to 26 ODT ligands on an assumed 55-atom gold cluster. This ratio alludes to the retention of a small cluster size. A sample of the larger hexadecanethiol-stabilized gold cluster has been shown to give a 33.5% mass loss, corresponding to ∼95−126 ligands per cluster (diameter = 2.4 nm).[10]

Optical spectra of gold colloids and clusters exhibit a size-dependent surface plasmon resonance band at ∼520 nm (e.g., trace (e) in Figure 1). In the absorption spectra of our ligand-exchanged clusters (Figure 1, solid traces), we find the interband transition typically observed for small clusters including $Au_{55}(PPh_3)_{12}Cl_6$.[20−22] Little or no plasmon resonance is observed, consistent with a cluster size of ∼1.7 nm or less.[20b,d] For the ODT-passivated cluster, no plasmon resonance is observed.

Quantitative size information can be obtained using transmission electron microscopy (TEM). The core size obtained from TEM images of the ODT-stabilized cluster (Figure 2) is found to be 1.7 ± 0.5 nm and is in good agreement with that obtained from atomic force microscope images.[23]

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(22) In the MBP-stabilized cluster, an absorption also appears at 276 nm. This peak is attributed to the $\pi-\pi^*$ transition of the MBP ligands. For the free ligand, this absorption is found at 271 nm in CH₃CN solution.

(23) Tapping mode AFM images obtained by us indicate cluster heights of 1.7 ± 0.6 nm for the ODT-stabilized clusters. It is to be expected that AFM would be relatively insensitive to the ligand shell.
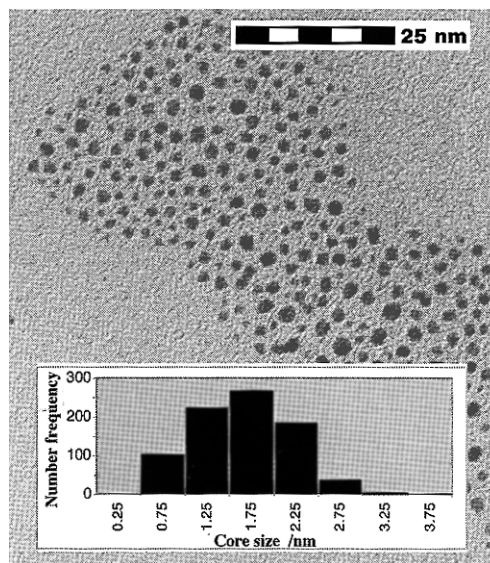
Figure 2. TEM of ODT-stabilized cluster (aerosol-deposited from CH₂-Cl₂ solution onto a carbon-coated copper grid).

Our thiol-stabilized clusters display remarkable stability relative to $Au_{55}(PPh_3)_{12}Cl_6$, which undergoes decomposition in solution at room temperature to give bulk gold and AuCl-[PPh₃].[7,9] We did not observe any decomposition for the thiol-stabilized clusters, despite the fact that some samples were deliberately stored in solution for weeks. In other tests, we heated the MBP- and ODT-stabilized clusters (in the absence of free thiol) to 75 °C for periods of more than 9 h in dilute 1,2-dichloroethane solution with no resultant degradation.[24] Under identical conditions, $Au_{55}(PPh_3)_{12}Cl_6$ is observed to decompose to Au(0) and AuCl[PPh₃] within 2 h.

In conclusion, we have demonstrated the facile process of ligand-exchange on $Au_{55}(PPh_3)_{12}Cl_6$ to yield thiol-stabilized ∼1.7 nm diameter gold clusters. The clusters produced have narrow size distributions and excellent thermal and air stability. Due to the mild conditions during the exchange process, any number of potential ligands may be employed. The generality of this method allows tuning of the physical properties of the clusters and of the electronic properties of the intercluster tunneling barrier. Proper choice of the ligand shell can potentially allow self-assembly of the clusters into arrays or provide reactive sites for attachment of the clusters to contacts or templates. The physical and chemical properties of these clusters render them excellent candidates for the fabrication of tunable single-electron-transfer devices.

Supporting Information Available: Preparative method for ligand-exchanged clusters, along with corresponding selected ^{13}C NMR, XPS and TGA data (5 pages). See any current masthead page for ordering and Internet access instructions.

JA972900U

(24) Cluster degradation was monitored by UV−vis spectroscopy. No change in the optical spectrum was observed.