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Rapid Size-Focusing of Gold Nanoclusters with an Oxidant

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Abstract

Rapid size-focusing of gold nanoclusters can be achieved by the addition of $K_3[Fe(CN)_6]$. The conditions for this have been optimized, and the possible role that it plays proposed.

Keywords: Gold; nanocluster; size-focusing; oxidant

Introduction

The advent of metal nanoparticles as an important class of nanomaterials with a wide range of applications was followed by that of atomically precise metal nanoclusters.¹ They differ from gold nanoparticles in possessing definite formulae,² and stability arising from their geometric,³ and electronic properties.⁴ There are many new and exciting opportunities in both fundamental studies and applications,⁵ and beginning with the work of Brust, et. al.,⁶ interest in thiolate-protected Au nanoclusters has grown considerably.⁷ The development of synthetic methods has allowed study into their fundamental properties;⁸ their sizes tunable through the reaction conditions, such as, the gold to thiol ratio, nature of the ligand, temperature, solvent, and the reduction conditions. For example, $Au_{19}(SC_2H_4Ph)_{13}$ was obtained instead of $Au_{25}(SC_2H_4Ph)_{18}$ by replacing $NaBH_4$ with *t*-butylamine-borane complex as the reducing agent.⁹ More recent nanocluster syntheses have employed ligand-exchange methods, for example, in the displacement of phosphine ligands in phosphine-protected gold clusters by thiols;¹⁰ $Au_{36}(SPh)_{24}$ was first synthesized via ligand exchange under etching,¹¹ and various Au_{38} clusters using different thiols have been synthesized since.¹² A similar thiol-for-thiol exchange has also been introduced;¹³ core-size conversion of bulk $Au_n(SR)_m$ crude mixtures into a series of nanoclusters has been demonstrated, which involves the synthesis of a crude $Au_n(SR)_m$ mixture and subsequent thermochemical treatment with excess thiols.¹⁴ This size-focused synthesis has also been demonstrated for protein-protected nanoclusters,¹⁵ and a number of $Au_{36}(SR)_{24}$ clusters.¹⁶ Nevertheless, achieving monodispersity is time consuming, often involving multistep synthesis, or post-synthetic separation.¹⁷

Thiolate-stabilised gold nanoclusters comprise a core of Au(0) atoms with a Au(I)-thiolate layer on the surface. It may thus be expected that besides the nature of the ligand, the ratio of Au(0) to Au(I) may also influence the size of the nanocluster formed. Indeed,

observations that the formation of Au₂₅(SG)₁₈ (where SG = glutathionato) under aerobic and anaerobic conditions differ suggest this; the presence of air accelerates the rate of formation.¹⁸ There is also a recent report on size interconversion of phosphine-stabilised Au nanoclusters via oxidation and reduction.¹⁹ We have recently reported the ligand exchange reaction of {Au₁₃[Sb(*p*-tolyl)₃]₈Cl₄}Cl with excess glutathione to form Au₂₅(SG)₁₈ and found that an oxidant enhanced the reaction rate.²⁰ Since various nanoclusters could be formed starting with Au_n(SG)_m as the gold precursor, albeit with rather long reaction times and high temperatures,¹⁴ we thought that an oxidant may also accelerate this reaction. The results of our investigation are presented here.

Results and Discussion

A variety of oxidants with differing oxidation potential has been examined for their effect on the formation of Au₃₆(S-*p*-tolyl)₂₄, **1** (table 1). The results show that K₃[Fe(CN)]₆ is superior to FeCl₃ and I₂; in the case of AgNO₃ and CuSO₄, some other nanoclusters are formed. Varying the amount of K₃[Fe(CN)]₆ under the same reaction conditions show that 7.5 μmol of the oxidant is sufficient to complete the reaction, and excess of the oxidant is detrimental to the yield (Figure 1A); the optimal reaction time with that amount of oxidant is about 5 h (Figure 1B). These reaction conditions (45 °C, 5 h) are significant better than the reported ones (80 °C, 22 h), and the yield estimated from peak integration of the UV spectra show that it has almost doubled.

Table 1: Effect of the addition of different oxidants for size-focusing to **1**.

S/No	Oxidant (10 ⁻⁵ M)	Redox potential vs SHE (v)	UV peak area ^b
1	AgNO ₃ (1.7 mg)	0.8	- ^a
2	FeCl ₃ (1.6 mg)	0.77	3.5
3	I ₂ (1.3 mg)	0.5	2.9
4	K ₃ [Fe(CN)] ₆ (3.3 mg)	0.36	4.0
5	CuSO ₄ (1.6 mg)	0.15	-
6	-	-	2.1

*All experiments were with Au_n(SG)_m (100 mg), thiol (600 mg), water (3 ml), toluene (2 ml) and ethanol (0.15 ml), 45 °C, 5h. ^a Different species formed. ^b Integration over 520-650 nm.

Figure 1: The formation of **1** (a) with various amounts of $K_3[Fe(CN)_6]$ added, and (b) with 7.5 μ mol of $K_3[Fe(CN)_6]$ as a function of reaction time.

In a typical reaction, the initial phase transfer can be observed within 1 h when the black gold nanoclusters transfer from the aqueous to the organic phase. After this phase transfer, the formation of **1** starts and increases exponentially up to 5 h of the total reaction time. SEM-EDX analysis of the product shows that no iron is present (Table S1). The MALDI-MS spectrum shows a peak clustered around m/z ~9670 which corresponds to a fragment of **1** with the loss of three thiolate ligands (Figure S5); this lability of aromatic thiolate ligands has been observed previously.¹⁴ The absorption spectrum shows prominent peaks at 374 and 570 nm, matching the literature values and confirming its monodispersity.¹⁴

Figure 2: UV-Vis-NIR absorption spectra illustrate the signature absorbance peaks at 375 and 570 nm for **1**.

Similar treatment of $\text{Au}_n(\text{SG})_m$ with 4-*t*-butyl benzenethiol under the above optimized conditions (7.5 μmol of $\text{K}_3[\text{Fe}(\text{CN})]_6$, 45 $^\circ\text{C}$, 5 h) gives the corresponding nanocluster $\text{Au}_{36}(\text{SR})_{24}$ ($\text{R} = 4\text{-}t\text{-butylphenyl}$), **2**. In contrast, the reaction with 2-phenylethanethiol (PET) to form $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$, **3** is comparatively slow and requires a slightly higher temperature (60 $^\circ\text{C}$). This is, nevertheless, a significant improvement (Table S2), in comparison with the literature method (5 h at 60 $^\circ\text{C}$ vs 70 h at 80 $^\circ\text{C}$).¹⁴ The faster kinetics observed for **1** and **2** may be ascribable to the higher acidity of the aromatic thiols. The monodispersity of the products were also confirmed by their absorption spectra (see SI).

The role of the oxidant in the rate accelerations is unclear, although we believe that it probably promotes size interconversion, like those which we and others have observed, by modifying the $\text{Au}(\text{I}):\text{Au}(\text{0})$ ratio through oxidation.^{19,20} The polydispersed $\text{Au}_n(\text{SG})_m$ is a mixture of Au clusters ranging from Au_{38} to Au_{75} , and a small amount of Au_{102} . In a typical thermochemical treatment, these glutathione-capped clusters are transferred from the aqueous to the toluene phase with retention of their core sizes. It is believed that during the $-\text{SG}$ to $-\text{SR}$ ligand exchange process, smaller, unstable clusters (core size < 25) are formed which decompose into an $\text{Au}(\text{I})\text{-SR}$ polymer.²¹ The size-focusing is thus the result of removal of nanoclusters with less stable core sizes, the thermodynamically most stable core size being dictated by the nature of the stabilizing ligand. A possible role of the added oxidant is to allow for more rapid oxidation of smaller clusters to the $\text{Au}(\text{I})\text{-SR}$ polymer, as well as for downsizing of larger nanoclusters. That $\text{K}_3[\text{Fe}(\text{CN})]_6$ seems to work best may be related to the mechanism of inner-sphere electron-transfer which we have proposed earlier.²⁰

Experimental procedure

General methods

Reagents were used as obtained from commercial sources. UV-VIS-NIR spectra were recorded on a Shimadzu UV-1800 double-beam spectrometer. MALDI-TOF-MS spectra were recorded on a JEOL JMS-S3000 SpiralTOF, at an accelerating potential of 20 kV, laser frequency of 250 Hz, in the positive spiral mode, using trans-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix. DCM was used to dissolve the cluster and matrix, which were mixed in a mass ratio of 1:1000. SEM-EDX spectra were recorded on a JEOL 7600F operating at 20 kV in LEI mode using powder sample coated on conducting carbon tape. $\text{Au}_n(\text{SG})_m$ was prepared following the literature method.¹⁴

Conversion of Au_n(SG)_m to **1** in the presence of K₃[Fe(CN)₆].

Solid 4-methylbenzenethiol (600 mg, 4.83 mmol) was added to an aqueous solution of Au_n(SG)_m (100 mg) in water (3 ml), followed by toluene (2 ml), ethanol (0.15 ml) and an aqueous solution of K₃[Fe(CN)₆] (3.3 mg, 0.01 mmol) in water (0.1 ml). The reaction mixture which was then heated at 45 °C for 5 h. After cooling to room temperature, the organic layer was separated and the solvent removed to give a black solid. This was washed with methanol (6×5 ml) and then extracted with toluene (3×5 ml).

The nanoclusters **2** and **3** were prepared similarly using Au_n(SG)_m (100 mg) with 2-phenylethanethiol (1 ml, 7.46 mmol) and 4-*t*-butylbenzenethiol (1 ml, 5.8 mmol), respectively.

Supporting Information

Absorption spectra of **1-3**, EDX and MS characterization of **1**, optimization studies.

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