

Short note

Norrish type I photochemistry as a powerful tool in the isolation of thiol protected Au₂₅SR₁₈ clusters

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ABSTRACT

Metal clusters are a class of materials that exhibit highly tunable optical and electronic properties. The library of atomically precise clusters is rapidly growing, and the unique optical properties make clusters attractive materials for catalysis, photocatalysis [1,2], and photonics applications [3]. Thiol protected gold clusters, like Au₂₅SR₁₈, are among the most highly studied [4–7]. Synthesis and isolating of atomically precise clusters are typically challenging, with only small changes in the choice of ligands and/or the rate of addition of reducing agents often resulting in drastically different clusters [5,8]. Herein we report on a photochemical route for producing atomically precise gold clusters. The synthesis of Au₂₅SR₁₈ via a photochemical initiator, allows for timed delivery and in operando modulation of the concentration of reducing species, providing unprecedented control over the most challenging aspects of metal cluster synthesis.

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1. Introduction

Metal clusters are small particles with exact numbers of both metal atoms and stabilizing ligands. Due to their extremely small size (less than ~144 metal atoms) [9], clusters are typically characterized by mass spectrometry, which is how many stable clusters in solution were originally identified [10]. Larger, metal nanoparticles have stolen the spotlight of metal particle research for decades, which are characterized by periodic packing structures, plasmon absorbances, extremely short (femtosecond) excited state lifetimes, and do not display molecule like properties like appreciable amounts of photo-luminescence, or discrete HOMO-LUMO optical transitions [11–14]. Metal clusters, by contrast, adopt unique structures, and display optical/electronic properties that are dictated by discrete molecular orbitals [15–17]. For example, Au₂₅SR₁₈ is one of the most commonly studied gold clusters that exhibits a complex absorbance spectrum with multiple discrete electronic absorbance features spanning the visible and UV spectrum, as well as appreciable near infrared emission [18,19].

A recent interest in atomically precise metal clusters, has been partially spiked by their growing use as catalysts and photocatalysts, especially due to the versatility that can be achieved in material properties. The molecule-like properties of clusters can be

readily tuned through modification of either the metal component (size of the core or choice of metal) or with the choice of stabilizing ligand [20–23]. Minor changes in chemical composition have been shown to lead to drastically different optical and electronic properties [11,24–26]. The tunability of cluster properties provides a great deal of opportunity in discovering new and optimal functionality, especially in the area of photocatalysis [27–29].

One of the major hurdles to metal cluster research is the synthetic difficulty of isolating atomically precise clusters. A typical synthesis involves the addition of a reducing agent like NaBH₄ to a solution containing metal salts (i.e. HAuCl₄) and an exact concentration of stabilizing ligand (i.e. thiol ligands). The choice of ligand, concentration of ligand, and most importantly the choice and rate of addition of reducing agent, can have a dramatic effect on the species of clusters that is isolated [1,30,31]. For example, Au₂₅SR₁₈, Au₂₄SR₁₈ and Au₂₀SR₁₈ can each be isolated from the same precursor solution, with the only difference being the rate of addition of the reducing agent (NaBH₄) and the rate of stirring of the solution [11,32]. Additionally, the shelf life of aqueous NaBH₄ is strongly dependent on solution pH and how freshly prepared it is, leading to unwanted variability in reaction conditions, which can easily lead to low yields of the desired product.

Photochemical methods for nanoparticle synthesis have been extensively studied, especially in the original work of Henglein. In earlier work, clusters have been identified as short lived intermediates, but the isolated products were nanoparticles, with

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thousands of metal atoms/particle, and that display properties like plasmon absorbance [3]. The isolation of atomically precise clusters, with long-term stability under normal atmospheric conditions, was not considered. The isolation of stable clusters, however, requires careful selection of stabilizing ligands. The most common ligands for stabilizing nanoparticles (i.e. citrate ions) are not effective at stabilizing clusters. In fact, the surface of thiol-protected gold clusters requires a strong Au-thiolate structure, that aids in dictating the exact atomic composition of the isolated product.

In the present work, we illustrate the advantages of using a photochemical initiator (Omnirad 2959), as a source of alpha-hydroxy radicals, which have been previously shown to be strong reducing agents [33–35]. The concentration of the reducing agent is easily tuned by controlling the excitation of the initiator molecule. Not only is it synthetically facile to initiate and control the reaction by turning on the UV light source, the reaction can be easily stopped at a desired point by turning off the light as well. This is a particular advantage over thermal routes that rely on the addition of a reducing agent, which can easily lead to over-reduction and the accumulation of unwanted products. The procedure is illustrated in Scheme 1. Most importantly, by control of the excitation light (UVA vs UVB) and reagent concentrations, we are able to exact control over the final products of the reaction. In this case, Au₂₅SR₁₈ or gold nanoparticles (AuNP) can be obtained with minor variation in reaction conditions.

2. Experimental

For the synthesis of Au₂₅(SR)₁₈ clusters, a 9.5 mM aqueous solution of glutathione was first reacted with aqueous HAuCl₄ (3.8 mM), in the presence of Omnirad 2959. The initial yellow solution (aqueous HAuCl₄) became clear, due to the initial reaction of HAuCl₄ with thiols to form a thiol coordinated intermediate Au(I) species (see reaction (i)) [19,36]. It is important to note that the presence of Omnirad 2959 at this stage has no effect on the reaction. This solution was subsequently irradiated with UVA (360 nm) light, in order to excite Omnirad 2959, initiating reaction (ii) below. The triplet excited state of Omnirad 2959 reacts to produce alpha-hydroxy radicals with a quantum yield of radical formation of 0.29 [37]. The alpha-hydroxy radicals subsequently reduce Au(I) to Au(0), as illustrated in reaction (iii).

3. Result and discussion

The UVA initiated reaction was monitored in time and Fig. 2a shows the evolution of growth of Au₂₅SR₁₈ clusters over

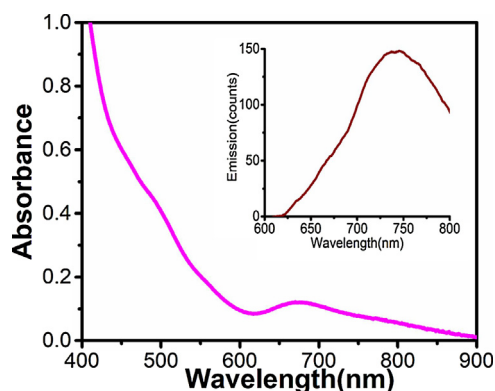


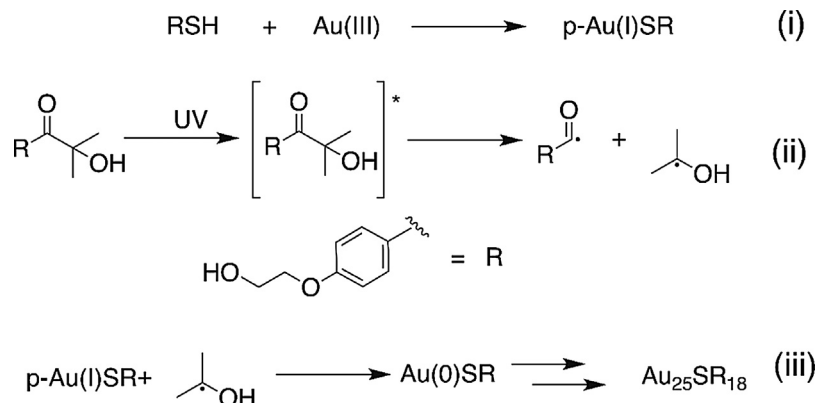
Fig. 1. Absorbance spectrum of a solution containing 3.8 mM HAuCl₄, 9.5 mM glutathione and 9.5 mM Omnirad 2959, after 120 min of UVA irradiation, inset shows the emission spectrum of Au₂₅SR₁₈, as formed.

approximately 120 min. Absorbance and Emission of Au₂₅GS₁₈ after 120 min of UVA irradiation, are shown in Fig. 1. The absorbance features at ~500 nm and from ~650–750 nm are characteristic of Au₂₅SR₁₈ clusters [11,38–40]. The shorter wavelength features have been attributed to ligand-to-metal charge transfer electronic transitions, and the features around 700 nm are associated with metal–metal electronic transitions of the core of these clusters [29,32,40]. Mass spectrometry experiments that confirm the presence of Au₂₅SR₁₈ are presented in the Supporting information. This evidence, along with UV–vis absorbance and NIR emission, provide strong support of Au₂₅SR₁₈ as the major component of our synthesis. Similar to thermally synthesized Au₂₅GS₁₈ clusters, these materials are indefinitely stable (see Supporting information, Fig. S7).

For similar reactions that have been reported, where carbon monoxide is used as a reducing agent, pH has been used to control the final cluster size/morphology. To investigate the role of pH on final product herein, NaOH(aq) was used to adjust solution pH, and the effect on the final product is reported in Fig. S2. Similarly, the effect of gold concentration on the reaction was also investigated, (see Fig. S3).

While relatively high concentrations of gold precursor lead to the formation of Au₂₅SR₁₈ clusters (Fig. 2a), with low concentrations of gold salts, the reaction produces nanoparticles, as evidenced by the characteristic plasmon absorption maximum at 530 nm for AuNP (Fig. 2b) [35]. A similar result was obtained when using UVB irradiation, where again AuNP were observed (Fig. 2c).

The effect of UVB irradiation intensity was further investigated and can be found in the Supporting information (Fig. S4).



Scheme 1. Formation of Au₂₅SR₁₈ using Omnirad 2959 as a photochemical initiator.

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