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Surfactant-free coating of thiols on gold nanoparticles using sonochemistry: A study of competing processes

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ABSTRACT

A method for the surfactant-free coating of gold nanoparticles with thiols using sonochemistry is presented. The gold nanoparticles were prepared by a modified Zsigmondy method, affording good control over the particle-size distribution, and the thiol coating was performed by the sonication of a biphasic system consisting of a nanoparticle suspension in water and thiols in toluene. The effects of two important reaction parameters on the particle morphology, *viz.* sonication time and thiol concentration, were investigated in detail using transmission electron microscopy. The effect of the thiol chain length was also studied. We show that the morphology of the coated particles is determined through a competition between two opposing effects: particle fusion, due to the sonication conditions, and digestive ripening, due to the action of the thiols. Additionally, we illustrate the utility of our technique for various applications, including surface-enhanced Raman scattering from bound molecules, and further functionalization using a thiol-exchange reaction. Our technique paves the way for an efficient synthesis of thiol-coated AuNPs of different shapes and sizes, suitable for a range of diverse applications.

1. Introduction

Gold nanoparticles (AuNPs) have been used for a variety of purposes for a very long time, from making medieval colored glass windows [1] to, more recently, treating cancer [2,3]. Due to their great chemical affinity for thiols and other organic molecules [4], AuNPs have also found application as substrates for enhancing spectroscopic (e.g. Raman-scattering) signals from molecules bound to them, by the action of localised surface plasmons [5–7]. Many of the current applications of AuNPs are dependent on their morphology [8,9], and therefore there is much interest in producing monodisperse particle distributions with controllable shapes and sizes [10,11].

A popular means of tuning the size of AuNPs for a given application is Zsigmondy's seed-mediated growth method [12], in which the size distribution is controlled via a two-stage preparation. In the first step, a solution of seed particles is produced, that are then grown to larger sizes in a second step, by controlling the reaction conditions such that particle growth is favored over the nucleation of new particles.

For many applications, such as in the field of sensing [13] and biomedical diagnostics [14], it is desirable to functionalise the AuNPs by coating them with organic molecules, which is typically achieved using thiol chemistry. However, in the Zsigmondy preparation, the AuNPs are prepared in an aqueous medium, whereas the thiol must typically be introduced in an organic solvent, necessitating the use of additional reagents (e.g. surfactants [15] or concentrated mineral acids [16]) to facilitate transfer between the phases. This adds complexity to the preparation, and, since extra purification steps are required to remove the surfactant after coating, can be time consuming.

As an alternative to surfactants, AuNPs have been functionalised with long-chain thiols at a water/hexane interface [17]. The efficiency of this process could be enhanced by using sonochemistry to increase the interface area, e.g. by sonicating a biphasic system of immiscible liquids [18]. Indeed, due to its ability to produce an environment with localized high temperatures and pressures, sonication is a powerful tool for the synthesis of NPs [19].

Abbreviations: AuNPs, gold nanoparticles; ODT, 1-octadecanethiol; HT, 1-hexanethiol; DLS, dynamic light scattering; TEM, transmission electron microscopy; OD, optical density; SERS, surface-enhanced Raman scattering.

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Sonication techniques have been used for the direct synthesis of AuNPs, and the effects of ultrasound frequency [20] and sonication time [21] on pre-synthesized AuNPs have been investigated. In terms of functionalization, AuNPs have been coated with short-chain thiols in ionic liquids using a sonication method [22], and the sonication of a biphasic system of aqueous AuNPs and thiols in toluene has been reported to form vesicles, in which the AuNPs are coated with thiols [23].

Although the findings in Ref. [23] show much synthetic potential, a detailed study of the size distribution and morphology of functionalized AuNPs prepared by this method has yet to be carried out. It has been shown that sonication of pre-synthesized AuNPs leads to particle fusion, both in the presence and absence of surfactants, forming dumbbell-shaped particles at short sonication times, and worm-like (elongated) structures at longer sonication times [21]. The presence of thiols, on the other hand, is known to lead to "digestive ripening" [24,25], a process in which the NPs are etched by the thiols, leading to the excision of small fragments and yielding a monodisperse particle distribution. Sonication and the action of thiols hence act in opposition to each other, influencing the morphology of the coated AuNPs and, as such, sonication time and thiol concentration are both important reaction parameters.

In this work, we present a simple sonochemical technique to prepare thiol-coated AuNPs, with the NPs prepared using the seed-mediated growth method. We use transmission electron microscopy (TEM) to investigate in detail the influence of sonication and digestive ripening on particle morphology, studying the effects of sonication time, thiol concentration, and thiol chain length. Finally, we illustrate potential applications of AuNPs prepared using our method, by demonstrating enhancement of Raman-scattering signals from bound thiols, and a simple thiol-exchange reaction for further functionalization.

2. Experimental

2.1. Synthesis of Au nanoparticles

The following chemicals were purchased from Sigma Aldrich and used as received: gold(III) chloride hydrate ($HAuCl_4{\cdot}3H_2O$, 99.99% metal-based), sodium citrate tribasic dihydrate (99%), sodium borohydride ($NaBH_4$, 98+% powder), 4-aminothiolphenol, 1-hexanethiol and 1-octadecanethiol ($\geqslant$98%). Aqueous solutions required for the synthesis were prepared in milliQ water (18.2 MΩ), and thiol solutions were prepared in toluene. All glassware was washed with aqua regia (3:1 HCl:HNO_3) before use.

The seed solution required for Zsigmondy's method was prepared by a modified version of the original protocol. Aqueous trisodium citrate (1 ml, 1% w/v) was added to an aqueous solution of $HAuCl_4{\cdot}3H_2O$ (100 ml, 0.01% w/v) under vigorous stirring. After 1 min, $NaBH_4$ (1 ml, 0.075% (w/v) in 1% w/v trisodium citrate) was added, and the solution subsequently stirred for 5 min; this was then stored in an amber bottle at 4 °C.

The growth step of the preparation was then carried out as follows. Gold chloride (50 ml, 0.01% w/v) was heated under reflux for 45 min, with the temperature of the oil bath being maintained between 120 and 130 °C. When the solution started to boil, 30 μl of the seed solution was added. One minute later, trisodium citrate (0.2 ml, 1% w/v) was added dropwise, and the solution was boiled for a further 15 min before being allowed to cool gradually. As for the seed solution, the preparation was stored in an amber bottle.

2.2. Sonochemical functionalisation

1:1 v/v combinations of the prepared AuNPs (approx. 4.33×10^{-11} M, determined from the optical density at 542 nm, measured from UV–visible spectra (see below)) and 1-octadecanethiol (ODT) solutions of various concentrations were sonicated at 40 °C using a VWR Ultrasonic Cleaner HF (45 kHz, 60 W). To study the effects of ODT concentration and sonication time on the NPs, combinations of 3 different ODT concentrations (3 mM, 3 μM and 3 nM) and 4 sonication times (1, 5, 15 and 30 min) were tested. To investigate further the effect of thiol chain length on the reaction, sonication experiments were also carried out with 3 mM 1-hexanethiol (HT) and 3 mM ODT for 6 different sonication times (1, 5, 10, 15, 30 and 45 min).

2.3. Characterisation

UV–visible spectroscopy and dynamic light scattering (DLS; Malvern NanoZS-Zetasizer, which uses the Stokes–Einstein relationship to obtain particle-size distributions from particle-diffusion measurements) measurements were carried out on the prepared AuNP solution at 32 °C (see Figs. S1–S3, Supporting information). The functionalized AuNPs were black in color, and could not be dispersed in any of the media tested without causing aggregation; therefore, these could only be studied by electron microscopy.

Bright-field electron micrographs were obtained using an FEI Tecnai F20 FEG TEM operated at 200 kV. The NPs were drop-cast onto lacey carbon grids (Agar Scientific), and the images were analyzed using the ImageJ software (distributed by National Institute of Health, USA, developed by Wayne Rasband) to obtain information about particle size and morphology. To obtain particle-size distributions from the micrographs, the projected 2D surface area and principal axes of approximately 100 particles per sample were recorded, and the data were used to generate histograms, which were fitted to Gaussian functions. The data processing was implemented in Python 3 [26], using the Numpy [27] and Scipy [28] packages.

To prepare samples for Raman microscopy, microscope glass slides were rinsed with milliQ water, ethanol, and then hexane, and then dried under nitrogen and placed in the biphasic system before sonication. After sonication, the system was allowed to stand for 30 min before the slide was removed from the biphasic system, dried in air (in the dark), washed with milliQ water, and then dried under nitrogen. We found that the thiol-coated AuNPs climbed up the glass slides, leading to self-assembly. The slide was then exposed to an air plasma at 10^{-2} to 10^{-3} bar for 5 min, to remove physisorbed solvent molecules and impurities, which we found contributed to the background noise in the Raman spectra during initial experiments. The slides were examined using a Renishaw inVia Raman Microscope (633 nm laser wavelength), to confirm the presence of the thiols.

3. Results and discussion

3.1. Synthesis and characterization

Seeds prepared using $NaBH_4$ were purple in color and, when analysed by DLS, were found to have a bimodal size distribution, which peaked at diameters of 26 and 380 nm (Fig. S1, Supporting information). From the volume-particle distribution, the scattering of these larger particles with respect to the total volume of particles showed only a 0.3% contribution, suggesting that there were very few particles of this size.

The average diameter of the AuNPs prepared from the seeds in the second step was measured by DLS to be 88 nm (Fig. S2, Supporting information), showing the expected increase in size. However, a small shoulder to the curves at 26 nm suggests that there were seed particles remaining which did not undergo further growth. Comparison of the UV–visible spectra of the seeds with