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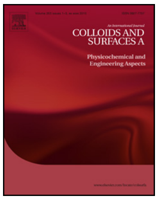

One-step synthesis of star-shaped gold nanoparticles

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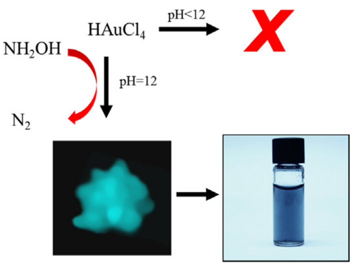
HIGHLIGHTS

- Gold nanostars were synthesized by a one-step reduction process.
- The effect of the pH on the reduction mechanism was investigated.
- Gold nanostars showed an intense absorption band in the red in agreement with theoretical simulation.
- Gold nanostars showed a higher Raman enhancement respect to spherical nanoparticles of the same dimension.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper we report on a simple synthesis procedure with which to fabricate stable gold nanostars (AuNS). Gold nanostars were synthesized by the reduction of a gold precursor in a basic environment using hydroxylamine as a reducing agent. Our investigation revealed that the pH of the solution is a crucial parameter in order to obtain stable gold nanostars suspension in water. At pH between 12 and 12.5 the nanostars formed a strong blue colored suspensions in water. The nanoparticles showed an intense absorption band in the red region of the visible spectrum. Numerical simulations attributed the strong absorption at around 610 nm to the plasmon resonance localized on the nanoparticles tips. Finally, star-shaped gold nanostructures showed a higher amplification of the Raman scattering of Rhodamine 6G molecules with respect to spherical nanoparticles of the same dimension.

1. Introduction

The production of metallic nanoparticles with controllable shapes has gained even more importance for different kinds of applications [1]. In the last years, a wide number of gold nanoparticles with unique shapes have been obtained through wet-chemistry approaches, as nanorods [2], nanotriangles [3] hollow nanocages [4] and branched nanoparticles [5]. The latter have been extensively studied over the last few years because of their interesting properties [6,7]. As distinct from spherical gold, star-shaped nanoparticles possess unique optical properties that make them desirable for emerging applications including biolabels [8], chemical sensing [9] and surface enhanced Raman scattering (SERS) [10]. The synthesis strategies to obtain star-shaped gold nanoparticles can be roughly divided in two categories: seed and non-seed methods. The first requires the preformation of a metallic seed that acts as a nucleation point for the formation of the metallic branches. In this process the ramifications growth is a consequence of the passivation of certain crystalline facets by surfactant or capping agents that inhibited the reduction of the gold precursor in a specific crystallographic orientation [11,12]. The seed-based strategies however have some drawbacks that may strongly influence the quality of the final nanoparticles. Moreover the use of various stabilizing agents and surfactants complicates the post-synthesis

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purification of the nanoparticles, an essential step to obtain optimal substrates for the aforementioned applications [13].

The non-seed strategies (called one-pot) involve the reduction of the gold precursor by reducing agents with the formation of star shaped gold nanoparticles. This strategy results in fewer complications with respect to the seed-growth approach and can be completed in a one single step. Some methods can be carried out also in the absence of surfactant, which simplifies the post synthesis purification and the problems related to the remove of the surfactant from the surface of the nanoparticles. One of the most significant drawbacks of these methods is the difficulty of controlling the dimensions of the resulting nanoparticles [14]. Moreover, the high sensitivity of the growth reaction to changes of the reaction parameters (reagents concentration, pH, temperature) has a strong effect on the reproducibility of the experiments.

In this paper we report an easy, one-pot, surfactantless method to synthesize branched gold nanoparticles by the reduction of a gold precursor. Gold nanostars were produced by direct reduction of the $HAuCl_4$ precursor in a strong basic water environment by hydroxylamine without the need of other external reagents. The reaction is very fast and required less than 1 s to be completed.

Thanks to absence of surfactants or stabilizing agents, the nanoparticles can be easily purified through centrifugation or dialysis and used directly for SERS applications or directly functionalized with anti-fouling polymers for biological purposes.

The nanoparticles showed a strong absorption peak in the red region of the visible spectrum with absorption maximum of 610 nm. Numerical simulations of the extinction properties of the nanoparticles revealed that the main contribution in the extinction spectrum is due to the plasmon resonance modes localized in the proximity of the nanoparticles tips. Finally, star-shaped gold nanostructures showed a higher amplification of the Raman scattering of Rhodamine 6G molecules relative to spherical nanoparticles of the same dimension.

2. Experimental

2.1. Reagents

All the reagents were purchased from Sigma–Aldrich otherwise as specified in the text. Spherical gold colloids (60 nm mean diameter) were purchased from Ted Pella, Inc.

2.2. Synthesis of AuNS

1 ml of hydroxylamine water solution (100 mM) at pH 12 adjusted with sodium hydroxide was stirred for 1 min. 100 μl of a 10 mM solution of $HAuCl_4$ in Milli-Q water was fast introduced into the vial under vigorous stirring. The color of the solution changed instantaneously from transparent to deep blue. The nanoparticles were purified by repeated centrifugation (three times) to remove the NaOH from the suspension. The AuNS were stored in water at room temperature.

2.3. Synthesis of AuNS and AuNP rhodamine conjugates

0.5 mg of AuNS were redispersed in 10 ml of 10^{-8} M Rhodamine 6G (Rh6G) solution and stirred for 2 h. The suspension was purified by centrifugation at 12,000 rpm for 10 min and the supernatant was replaced with Milli-Q water. For spherical gold nanoparticles, 1 ml of the gold colloid suspension (0.055 mg/ml, 42 pM) was centrifuged at 12,000 rpm for 10 min and the supernatant was replaced with Milli-Q water. The nanoparticles were redispersed in 10^{-8} M Rh6G solution in water by sonication and mixed for 2 h. The suspension was purified by centrifugation at 12,000 rpm for 10 min and the supernatant was replaced with Milli-Q water. Before each Raman measurement, the suspensions were sonicated for 5 min to ensure optimal dispersion of the nanoparticles.

2.4. Characterization

Scanning electron microscopy (SEM) images were acquired using a Zeiss Supra 40 FE SEM at different magnifications by an InLens detector at a 2–4 kV acceleration voltage. Transmission electron microscopy (TEM) analysis was carried out using a Philips CM12 operated at 120 kV and equipped with an energy dispersive X-ray spectrometer. The X-ray photoelectron (XPS) spectra were acquired by using a Scienta ESCA 200 analyzer (Gammadata, Sweden) equipped with a monochromatized Al Kα X-ray source. UV–vis absorption measurements have been performed using an UV–visible–near infrared spectrophotometer (Cary 5000) in dual beam mode. Particle size was determined at 25 °C by dynamic light scattering (DLS) in back scattering mode, using a laser particle sizer (Malvern 110 Zetasizer Nano ZS, equipped with a He–Ne laser at 633 nm, 5 mW). For this assay, particle samples were diluted in Milli-Q water to a final concentration of 0.01 mg/ml. Data were analyzed by the Malvern Proprietary Software. Raman scattering measurements were performed over a wide wavenumber range between 300 and 3000 cm^{-1} by means of a microprobe set-up (Horiba-Jobin-Yvon, model Aramis) consisting of a He–Ne laser operating at 633 nm (power 20 mW), a narrowband edge filter, a 46 cm focal length spectrograph using a 1800 grooves/mm holographic grating and a charge-coupled device (CCD) detector.

2.5. Modeling

Numerical simulations were carried out for AuNS, using the Discrete Dipole Approximation method (DAA). Water was considered as the external medium ($n = 1.33$) and the experimental values from Johnson and Christy for the dielectric function of gold were used [15]. Simulations were performed by using a Cone–Sphere–Cone geometry composed by a central sphere with a radius of 22 nm and two conical tips with a length of 6 nm and a tip curvature of 2 nm.

3. Results and discussion

In a typical preparation, a solution of $HAuCl_4$ in Milli-Q water was added to hydroxylamine water solution at pH 12 adjusted by sodium hydroxide under vigorous stirring. The color of the solution changed instantaneously from transparent to deep blue (see supporting information video). The nanoparticles were purified by repeated centrifugation (three times) to remove the NaOH and finally redispersed in Milli-Q water. In Fig. 1A–D representative transmission and scanning electron microscopy images of the gold nanoparticles are shown. The NPs showed a non-spherical geometry with protrusions on the surface and a mean size (tip to tip) of around 60 nm (Fig. 1E). The statistical distribution calculated by the TEM images indicates an average core diameter of 42 (±5) nm and an average branch length of 8 (±3) nm. The Selected Area Electron Diffraction (SAED, Fig. 1F) revealed the classical ring structures ascribable to the gold diffraction pattern. The low magnification SEM image revealed a good uniformity in size of the AuNS (Fig. S1), also confirmed by the hydrodynamic size distribution obtained by DLS (Fig. S2).

The formation of AuNS could be attributed to the direct reduction of $HAuCl_4$ by the hydroxylamine since no other reducing agent was present in the system. It is worth pointing out that the pH of solution can play a fundamental role in the formation of gold nanostructures. To better understand the reducing capacity of hydroxylamine, the reaction was carried out at different pH from 7 to 14. The results are summarized in Table S1. It is known from the literature that the reductive activity of hydroxylamine increases at elevated