Tunability and stability of gold nanoparticles obtained from chloroaauric acid and sodium thiosulfate reaction

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Abstract

In the quest for producing an effective, clinically relevant therapeutic agent, scalability, repeatability, and stability are paramount. In this paper, gold nanoparticles (GNPs) with precisely controlled near-infrared (NIR) absorption are synthesized by a single-step reaction of HAuCl4 and Na2S2O3 without assistance of additional templates, capping reagents, or seeds. The anisotropy in the shape of gold nanoparticles offers high NIR absorption, making it therapeutically relevant. The synthesized products consist of GNPs with different shapes and sizes, including small spherical colloid gold particles and non-spherical gold crystals. The NIR absorption wavelengths and particle size increase with increasing molar ratio of HAuCl4/Na2S2O3. Non-spherical gold particles can be further purified and separated by centrifugation to improve the NIR-absorbing fraction of particles. In-depth studies reveal that GNPs with good structural and optical stability only form in a certain range of the HAuCl4/Na2S2O3 molar ratio, whereas higher molar ratios result in unstable GNPs, which lose their NIR absorption peak due to decomposition and reassembly via Ostwald ripening. Tuning the optical absorption of the gold nanoparticles in the NIR regime via a robust and repeatable method will improve many applications requiring large quantities of desired NIR-absorbing nanoparticles.

Keywords: gold nanoparticles, gold colloid, gold nanoplates, near-infrared absorption, surface plasmon resonance, sodium thiosulfate, core-shell structure

Background

Metal nanoparticles are one of the basic building blocks of nanotechnology. Gold nanoparticles (GNPs) have attracted enormous attention in chemistry, biomedicine, and electronics due to their very small size, oxide-free surfaces, bio-conjugation properties, good biocompatibility, and unique optical properties. Specifically, because of their optical activity in the near infrared (NIR), GNPs are extensively utilized in immunosassays [1,2], drug delivery systems [3] as well as imaging, detection, and thermal therapy of cancer [4-6]. These applications have sparked great interest in the development of synthetic methods for preparing different gold-based nanostructures. The anisotropy in nanoparticle shape offers high near-infrared absorption and improved Raman scattering [7]. Based on Mie scattering theory, shifts in the surface plasmon resonance (SPR) [8] occur when the particles deviate from spherical geometry. Non-spherical gold nanoparticles present multiple absorption bands correlating with their multiple axes, and they can support both propagating and localized surface plasmon resonances [7]. The number of SPR peaks usually increases as the symmetry of nanoparticles decreases; spherical nanoparticles exhibit only one peak, whereas two and three peaks are often observed in nanorods, nanodisks, and triangular nanoplates, respectively. Many anisotropic gold nanostructures like gold nanotubes [9,10], nanocages [11], gold nanoshells [6], gold nanorods [12], and gold triangular nanoprism [13,14] have been developed and demonstrate enhanced and adjustable absorption in the NIR region. However, most of these gold nanostructures require a complicated multistep and time-
consuming synthesis process, which includes shaping the particles by use of templates, kinetically controlling the facet growth rates of seeds with assistance of capping reagents, and assembly of preformed spherical colloid nanoparticles [7].

In this work, GNPs with controllable NIR absorption were synthesized by the reaction of chloroauric acid and sodium thiosulfate. This reaction was derived from the reaction of chloroauric acid and sodium sulfide that Zhou et al. first reported, whereby a proposed core-shell-type Au$_2$S nanoparticle structure was produced via a two-step reduction of HAuCl$_4$ by Na$_2$S [15,16]. Later, Norman et al. proposed that the resulting optical properties are simply from aggregation of gold nanoparticles [15,17]. In molecular sensor studies based on scattering spectroscopy, Raschke et al. reported that gold products from Na$_2$S reaction showed great improvement in scattering compared to solid GNPs, and those particles have a dielectric nanocrystal property and behave like gold nanoshells [18]. Subsequent investigations revealed that this reaction lacks reproducibility because the Na$_2$S solution requires an aging process, and the aging time and reaction conditions required for this process were not well defined [19]. Schwartzberg et al. mentioned that the Na$_2$S solution is not chemically stable during the aging process. Na$_2$S may convert to different compounds, and sodium thiosulfate is one of the final compounds producing GNPs [20]. These findings encouraged us to attempt to reveal the key factor that dominates the nanostructure formation and the stability of the GNPs in the HAuCl$_4$/Na$_2$S$_2$O$_3$ reaction. We found that the NIR absorption of the gold products from this reaction can be well controlled and show good reproducibility when the molar ratio of HAuCl$_4$/Na$_2$S$_2$O$_3$ is in a suitable range. The instability of the GNPs is affected by the reaction conditions, resulting in the diversification of the nanostructures.

**Methods**

GNPs were prepared by mixing 1.71 mM HAuCl$_4$ (Au 49.50%; Alfa Aesar, Ward Hill, MA, USA) with 3 mM Na$_2$S$_2$O$_3$ (99.999%; Aldrich, St. Louis, MO, USA) solution. The Na$_2$S$_2$O$_3$ solution is quickly added into the HAuCl$_4$ solution with the desired volume ratio and vortexed for 20 s for uniform mixing. The water used in the experiments was purified by a Thermo Scientific Easypure II system (18.2 MΩ cm; Thermo Scientific Corp., Logan, UT, USA). GNPs were purified and separated by an Allegra® X-12 Series Centrifuge (Beckman Coulter Inc., Brea, CA, USA). The as-synthesized GNP suspensions were centrifuged at 1,000 x g for 20 min, and then, the pellets were dispersed in deionized (DI) water for further study. The optical absorbance and intensity of nanoparticles were measured by a UV-visible-IR spectrophotometer (Cary-50Bio, Varian, Palo Alto, CA, USA). The hydrodynamic size of the nanoparticles was measured by a Zetasizer (Nano-ZS90, Malvern Instruments Ltd., Worcestershire, UK). An FEI Tecnai F20 transmission electron microscope (TEM; FEI Company, Hillsboro, OR, USA) operated at 200 KV was used to determine the shape and size of the GNPs.

**Results and discussion**

**NIR absorption of the gold nanoparticles from sodium thiosulfate reaction**

Gold ions are electropositive and can be reduced by various reducing agents such as borohydride, amines, alcohols, and carboxylic acids. The most common methods use sodium citrate, sodium borohydrate, and ascorbic acid and usually produce spherical GNPs. Sodium thiosulfate, as a common reagent, has been used in many applications, such as silver recovery in photographic process and leaching of gold from mines. In the gold-leaching process, sodium thiosulfate works as a complexing agent. The reaction is complicated but can be briefly expressed as the following equation [21]:

$$4Au + 8S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 4[Au(S_2O_3)_2]^{3-} + 4OH^-$$

(1)

Sodium thiosulfate solution is weakly alkaline and was reported as a reducing reagent both in alkaline [22] conditions for silver nanoparticle formation and in moderately acidic conditions [23] for the preparation of selenium nanoparticles, as shown in Equations 2 and 3:

$$S_2O_3^{2-} + 6H^o \rightarrow 2SO_4^{2-} + 3H_2O + 4e^- (-0.57V)$$

(2)

$$S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8e^- (-1.5V)$$

(3)

In the reaction of HAuCl$_4$ and Na$_2$S$_2$O$_3$, sodium thiosulfate has the ability to reduce Au$^{3+}$ to Au$^0$. In order to interpret the mechanism of this reaction, nine representative samples were presented. They were synthesized by mixing 2.2, 2.0, 1.8, 1.6, 1.4, 1.2, 1.0, 0.8, and 4.0 mL (samples 1 through 9, respectively) of 3.0 mM Na$_2$S$_2$O$_3$ with 5 mL of 1.71 mM HAuCl$_4$. Within the first minute of adding Na$_2$S$_2$O$_3$ to HAuCl$_4$, all the samples showed a dark yellow color. As time progressed, the solution presented different colors. After a few minutes, the color of samples 1 to 6 turned purple, and this color was retained afterwards. Samples 7 and 8 showed the same purple color at 40 min, but after a few hours, the color had differentiated from a purple to bright brown. After dilution, these samples showed reddish to pink color when light was viewed through the sample. Sample 9 showed a quick color.
change to dark yellow after a few minutes and then retained this color afterwards. These colors indicate the formation of GNP samples with different optical properties. Figure 1 shows the photos of these GNP samples after mixing Na$_2$S$_2$O$_3$ and HAuCl$_4$ solutions at 1 h and 1 day, respectively. To clearly distinguish the colors, the product solutions were diluted five times with water. Figure 2 shows the optical spectra of the nine GNP samples at 1 h. In samples 1 to 8, two plasmon resonance peaks are clearly observed. The first SPR peak centered at around 530 nm is the characteristic SPR of the spherical gold structures [24,25], and the second peak SPR component at the higher NIR wavelength is attributed to the multiple SPR band from the non-spherical gold nanostructures. We can see the tendency that the NIR peak wavelength increases with increasing the HAuCl$_4$/Na$_2$S$_2$O$_3$ molar ratio (samples 6 to 8, the NIR peaks are close or above 1,100 nm, beyond the measurement limit of our UV-visible (UV–vis)-NIR spectrometer). Unlike samples 1 to 8, in sample 9, where the HAuCl$_4$/Na$_2$S$_2$O$_3$ molar ratio is extremely low (approximately 0.71), only one weak SPR peak at 530 nm can be seen.

Figure 3 shows the scanning transmission electron microscopy (STEM) Z-contrast images of three typical samples from the reaction. Figure 3a,b is the TEM image of samples 1 and 5, which has their second NIR SPR band at 750 and 950 nm, respectively. These products are the mixtures of gold particles with different shapes and sizes: the non-spherical gold crystals are interspersed among smaller colloidal GNPs. The spherical colloid GNPs are less than 5 nm. The non-spherical gold crystals contain the pseudo-spherical structures, such as truncated octahedron, pentagons, and cuboctahedron, as well as the anisotropic nanostructures with lower symmetry, including triangular and truncated triangular-shaped plate structures. Since the Z-contrast STEM image is the high-annular dark-field image, the intensity of the Rutherford scattered beam is directly proportional to $Z^2$, where $Z$ is the atomic number of the scattering element. The pseudo-spherical particles show higher brightness than the nanoplates in TEM images due to their higher apparent atomic number resulting from larger thickness. In Figure 3a, the pseudo-spherical crystals have diameters in the range of 15 to 30 nm, and the edges of the nanoplates are in the range of 40 to 60 nm. In Figure 3b, the size of pseudo-spherical particles increases to 30 to 45 nm, and the edge of triangular nanoplates increases to 45 to 90 nm. The thickness of the nanoplate structures, estimated from Z-contrast STEM images, is about 8.5 ± 1.5 nm. A rough approximation was made here that the dark field contrast changes linearly with the GNP thickness [26], and the data from a number of smaller pseudo-spherical nanoparticles were used for the calibration. The TEM image of sample 9 is shown in Figure 3c. This sample contains only spherical colloid GNPs with an average size around 3 nm, which correlates with only one SPR band at 530 nm. Figure 3d,e,f,g shows the high-resolution TEM images of the typical species of GNPs in the product: cuboctahedrons, pentagons, truncated triangle plates, and colloidal gold particles, respectively. Figure 4 shows the hydrodynamic size from dynamic light scattering (DLS) measurements and the NIR peak wavelengths as functions of the molar ratio of HAuCl$_4$/Na$_2$S$_2$O$_3$.
In the DLS spectra, the size of small spherical colloid GNPs and the size of non-spherical gold particles can be monitored. Figure 4 shows the DLS average sizes of non-spherical gold particles, and the measurements are consistent with the TEM observation. The SPR of noble metal nanoparticles is dominated by their particle size [27] and shape [15,28]. The key feature of this synthesis method is that the optical properties of the GNPs vary with their size and the population of different non-spherical particles. It is easy to tune their NIR absorption wavelengths by adjusting reaction conditions and further separation.

Crystal structure of the gold nanoparticles
To separate the larger NIR-absorbing particles from the smaller colloidal gold particles, a centrifugation process was used to purify the synthesized products. Figure 5 shows the UV–vis-NIR spectra of GNPs before and after the centrifugation process. For comparison, samples were diluted to 1 optical density (OD). After centrifugation, the NIR peak of the GNPs shifted from 850 to 890 nm, accompanying a great decrease in the intensity of the SPR band at 530 nm. Figure 6a shows the Z-contrast STEM images after purification. Different species of gold particles are clearly present. Most of the small spherical colloid GNPs were removed after centrifugation. Figure 6b shows the diffraction pattern obtained from the purified GNPs, with rings corresponding to the (111), (200), (220), (311), and (222) reflections of the face-centered-cubic (fcc) structure of gold.

Figure 4 Hydrodynamic size from dynamic light scattering measurements and the NIR peak wavelengths. NIR peak wavelength and the hydrodynamic size of gold nanoparticles as functions of the molar ratio of HAuCl₄/Na₂S₂O₃ (only shows samples 1 to 6 with NIR peaks in the UV–vis-NIR measurable range).
resolved (111)-type crystallographic planes (measured D-spacing of about 2.35 Å, as shown in Figure 7b), which run parallel to the long sidewalls of the structures. Figure 7c shows the selected area electron diffraction (SAED) pattern of a typical nanoplate. The pattern has a six-fold symmetry indicating the {111} zone axis, in agreement with the indexing, which can be performed self-consistently on the fcc gold structure using {220} (box-selected) and weak (1/3) {422} (triangle-selected) spots. The lattice spacing of the (220) planes measured from this pattern agrees very well with the value of 2.039 Å reported for gold. The presence of weak (1/3) {422} spots is most likely due to {111} twin planes within the nanoplates [29]. These nanoplates have the same structure as gold triangular nanoplates synthesized with the assistance of surfactants as capping agents [13,14], gold nanoplates prepared from lemon-grass extract [30], and the silver nanoplate structures [31].

Unstable gold nanoparticles and mechanism
Optical absorption measurements indicate that the suitable range of the HAuCl4/Na2S2O3 molar ratio for producing stable non-spherical GNPs is between 1.3 and 2.0, corresponding to the particles’ NIR absorption wavelength from 750 to 950 nm. When the molar ratio is higher than 2, the gold nanostructures become unstable. Figure 8a,b,c shows the time evolution of the optical absorption spectrum of samples 1, 5, and 8 during the reaction, respectively. Samples 1 and 5 presented in Figure 8a,b show similar behavior. After 5 min, two clear peaks belonging to the transverse SPR and multiple SPR band can be clearly seen at 530 nm and at a higher NIR region. The intensity of both peaks increases while the reactions progress, and after around 40 min, the increasing of intensity becomes extremely slow, indicating that the GNPs are formed and stabilized in the early 40 min. A typical unstable sample is presented in Figure 8c, which displays the NIR peak above 1,100 nm. Unlike the stable samples, the reaction takes much longer, and both SPRs shift with time. After 1 day, the peak at 530 nm shifts to 550 nm, and the NIR SPR bands disappear.

With the assistance of TEM analysis, the evolution of the unstable particle structure and the quenching mechanism of NIR absorption can be interpreted. Figure 9 compares the morphology of sample 8, prepared by mixing 5 mL of 1.71 mM HAuCl4 with 0.8 mL of 3.0 mM Na2S2O3, after 40 min, 2 h, 4 h, and 1 day (Figure 9a,b,c, d, respectively). At 40 min, the solution contains a high

![Figure 5](https://example.com/fig5.png)

**Figure 5** UV–vis-NIR spectra of gold nanoparticles shown before and after purification via centrifugation. The sample is separated at 1,000 x g for 20 min.

![Figure 6](https://example.com/fig6.png)

**Figure 6** TEM image and electron diffraction pattern of the purified gold nanoparticles. (a) TEM image showing the morphology of the gold crystals. (b) Electron diffraction pattern from the GNPs showing the (111), (200), (220), (311), and (222) reflections of gold.
density of colloid particles in addition to nanoplates and pseudo-spherical GNP s, as shown in Figure 9a. Typically, nanoparticles tend to aggregate during their synthesis, and the stabilizers, such as surfactant, small organic molecules, or polymers, play the role to protect nanoparticles after their formation through steric hindrance, thereby preventing aggregation. The Na2S2O3 solution is a complex system, which may contain many sulfur-based compounds. Besides the SO4^{2−} and SO3^{2−} species listed in Equations 2 and 3, the self oxidation-reduction of Na2S2O3 may produce trace S^{2−} and S^{0} (S2O3^{2−} → SO4^{2−} + S^{2−} or S2O3^{2−} → SO4^{2−} + S^{0}) and further convert to other sulfur derivatives [32]. Some of these species possibly function as ‘capping reagents’ or stabilizer, which direct crystal shape during the crystallization and stabilize the GNP s. For high molar ratios of HAuCl4 and Na2S2O3, the lack of capping reagents disturbs the crystallization process. Meanwhile, since the molar ratio of Cl− and H+ ions to the freshly formed GNP s is higher, Ostwald ripening will affect these nanostructures. Ostwald ripening is a thermodynamically driven process in which smaller crystals are sacrificed by transition of atoms from the surface to the solution and then deposited onto larger crystals. This is driven by the higher surface energy of the smaller particles and the favored energy state of the larger particles. As can be seen, at 2 h and later, the colloid is already absent from the solution and is found to decorate larger GNP s (Figure 9b,c, 9d, and 9e).

Figure 7 High-resolution TEM image of the vertex of one of the nanoplate structure (a). Its enlarged section (b) and SAED pattern (c) of the gold nanoplate structure.

Figure 8 The evolution of the optical absorption spectrum of three samples. With different volume ratios of HAuCl4 and Na2S2O3 during the reactions: (a) 5 ml HAuCl4 + 2.2 ml Na2S2O3, (b) 5 ml HAuCl4 + 1.4 ml Na2S2O3, and (c) 5 ml HAuCl4 + 0.8 ml Na2S2O3. Samples were taken during the reaction and diluted five times with DI water then immediately measured by UV–vis–NIR spectrophotometer.
The size of the colloid on the larger GNP increases with time (Figure 9e,f,g,h) through the Ostwald ripening process. Notably, 1 day after the reaction, the nanoplates disappear completely from the sample. This agrees with the total quenching of NIR absorption shown in Figure 8c and can be understood as a result of the system free energy reduction. In brief, nanoplates initially formed during the reaction represent low free energy nanostructures due to their Au (111) facets. When the colloid particles start to decorate and roughen the nanoplate surfaces, their surface energy gradually increases and eventually leads to the decomposition of nanoplates and their reassembly into less anisotropic, more spherical, and lower energy nanostructures. The Ostwald ripening process, as well as the decomposition and reassembling of larger particles, is enabled by the efficient halide-assisted transport of Au atoms. The effect takes place in an environment containing large amounts of Cl\(^-\) and H\(^+\) ions, and ionic Au-Cl complexes serve as transport species, which accelerate the gold to redeposit on some crystal surfaces [33,34]. Ostwald ripening behavior in the gold-based nanostructure interface has been reported by a number of researchers. Liang et al. [35] observed that during the SiO\(_2\)/Au core-shell synthesis, the formation and morphology of gold nanoshell were affected by chloride-dependent Ostwald ripening. At low pH value, the gold shells reorganized to form different shaped structures. Zhao et al. [36] reported that due to intraparticle ripening, flower-shaped gold particles could be prepared by adjusting the pH and amount of
chlorine ions. Lou et al. [33] reported the encapsulation and Ostwald ripening of Au and Au–Cl complexes within the Au–silica structures, in which chlorine was found to be an efficient mediating ligand. Our study provides a basis to produce GNPs on a large scale in a short time. GNPs with good optical and chemical stability only formed within a narrow range in which the molar ratio of HAuCl₄/Na₂S₂O₃ ranged from 1.3 to 2.0 when the concentration of HAuCl₄ and Na₂S₂O₃ are fixed at 1.71 and 3 mM, respectively. Under the same reaction conditions (concentration, volume of the reagents), the NIR absorption peak of the GNP products can be duplicated. After purification by centrifugation, samples prepared at concentrations of 20 to 100 OD can be quickly dispersed in water with no changes in the optical absorption intensity or SPR shift even after prolonged storage at 4 °C. Tuning the optical absorption of the GNPs in the NIR region via a robust and repeatable method has great advantages reflected in the application of these GNPs in areas such as cancer therapy via photothermal ablation as well as cancer detection and imaging.

Conclusions
In summary, we report on a convenient synthesis process to precisely control the optical absorption within the NIR region and established the suitable range of concentrations to allow stable nanoparticle formation. In this procedure, a single-step reaction of HAuCl₄ and Na₂S₂O₃ was examined in details to analyze the products of self-assembly. The nanoparticles produced from this reaction include small spherical colloidal gold particles with resonance at 530 nm and anisotropic gold nanostructures with NIR resonance. We found that the placement of the peak resonance into the NIR is controllable and repeatable with increasing molar ratios of HAuCl₄/Na₂S₂O₃. From this, it was found that in order to achieve a peak resonance above 950 nm, a molar ratio of HAuCl₄/Na₂S₂O₃ > 2.0 was required and resulted in unstable nanoparticles. The instability appears to be due to Ostwald ripening behavior based on TEM analysis over time for reactants with molar ratio greater than 2.0. Our study outlines an easy way to produce GNPs with tunable NIR absorption on a large scale in a short time and serves as the basis for additional studies to improve the efficiency of the synthesis system. This work will benefit many applications in the physical, chemical, and biomedical fields where strong NIR-absorbing nanoparticles may be used for energy transfer to create heat.

Abbreviations
DLS: dynamic light scattering; GNPs: gold nanoparticles; NIR: near-infrared; OD: optical density; SAED: selected area electron diffraction; SPR: surface plasmon resonance; STEM: scanning transmission electron microscopy; TEM: transmission electron microscope.
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