Research Article

Bromide-Assisted Anisotropic Growth of Gold Nanoparticles as Substrates for Surface-Enhanced Raman Scattering

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We report herein a one-step synthesis of gold nanoparticles (Au NPs) of various shapes such as triangles, hexagons, and semispheres, using 5-hydroxyindoleacetic acid (5-HIAA) as the reducing agent in the presence of potassium bromide (KBr). Anisotropic Au NPs have received ever-increasing attention in various areas of research due to their unique physical and chemical properties. Numerous synthetic methods involving either top-down or bottom-up approaches have been developed to synthesize Au NPs with deliberately varied shapes, sizes, and configurations; however, the production of templateless, seedless, and surfactant-free singular-shaped anisotropic Au NPs remains a significant challenge. The concentrations of hydrogen tetrachloroaurate (HAuCl_4), 5-HIAA, and KBr, as well as the reaction temperature, were found to influence the resulting product morphology. A detailed characterization of the resulting Au NPs was performed using ultraviolet-visible (UV-Vis) spectroscopy, scanning electron microscopy (SEM), and Raman spectroscopy. The as-prepared Au NPs exhibited excellent surface-enhanced Raman scattering (SERS) properties, which make them very attractive for the development of SERS-based chemical and biological sensors.

1. Introduction

Raman spectroscopy, based on molecular vibrational transitions, has long been regarded as a valuable tool for the identification and quantification of chemical and biological species [1, 2]. While it is well known that signals in normal Raman spectroscopy are extremely weak, great progress has been made since the discovery of surface-enhanced Raman scattering (SERS) [3–5]. A great deal of recent research has been delving into how effective Au NPs are as SERS substrates. The surface chemistry of gold is quite versatile, as it can easily be manipulated into a variety of sizes and shapes [6–10]. The electron cloud plasmons and the wavelength where that metal nanoparticle absorbs photons are directly affected by the type, shape, size, and structure of the metal nanoparticle. If it is possible to match the plasmon absorption wavelength of Au NPs with the excitation wavelength of the laser, resonance Raman, yet another boost to the Raman signal, is possible. Therefore, being able to manipulate the size and shape of a gold nanoparticle would allow for simple

and easy modifications to analytical devices that utilize SERS technology that would greatly improve sensitivity and selectivity.

It has been shown that Au NPs can be synthesized in any number of sizes or shapes quite easily. The Au NPs that have been synthesized are nanoflowers [1, 11], planar triangles (or prisms) [12–14], planar hexagons [12], nanorods [13, 15, 16], spheres [17, 18], octahedra, and cubes [19], to name just a few. Even though the toxicity of Au NPs has been widely studied, they have not been shown to be toxic to humans [9]. With this in mind, Au NPs can be utilized for a broad range of biomedical sensing, diagnostics, or other biomedical-based applications [12].

Herein, we report a facile approach for the synthesis of anisotropic Au NPs of various shapes such as triangles, hexagons, and semispheres, using 5-hydroxyindoleacetic acid (5-HIAA) as the reducing agent in the presence of potassium bromide (KBr). The concentrations of hydrogen tetrachloroaurate (HAuCl_4), 5-HIAA, and KBr, as well as the reaction temperature, were found to influence the resulting

product morphology. A detailed characterization of the resulting Au NPs was performed using ultraviolet-visible (UV-Vis) spectroscopy, scanning electron microscopy (SEM), and Raman spectroscopy. The as-prepared Au NPs exhibited excellent SERS properties, which make them very attractive for the development of SERS-based chemical and biological sensors.

2. Materials and Methods

2.1. Chemicals. Hydrogen tetrachloroaurate (1% w/v) was obtained from Ricca Chemical Company, 5-hydroxyindole-3-acetic acid (5-HIAA, 99%) and crystal violet were obtained from Acros Organics, and potassium bromide (KBr, 99% FT-IR grade) was obtained from Sigma-Aldrich. All solutions were prepared with high purity deionized water (resistivity $\geq 18 \text{ M}\Omega\cdot\text{cm}$) from a Picopure®2 ultrapure water purification system (Hydro, Inc.).

2.2. Synthesis of Anisotropic Gold Nanoparticles in the Absence of KBr. A 0.75 mM solution of 5-HIAA was created by adding 7.17 mg of 5-HIAA to 50 mL of dH_2O (DI). The solution was sonicated for about 1 minute until there was no longer any visual evidence of the solid 5-HIAA. On a stir plate, 44.42 mL of DI, 5 mL of 0.75 mM 5-HIAA, and 579.2 μL of 1% HAuCl_4 were mixed at approximately 300 rpm for 30 minutes under ambient conditions. The color turned gray about a minute after addition of the 5-HIAA. At the end of the 30-minute period, the sample started to turn to a salmon-pink color.

2.3. Synthesis of Anisotropic Gold Nanoparticles in the Presence of KBr. A 0.75 mM solution of 5-HIAA was created by adding 7.17 mg of 5-HIAA to 50 mL of dH_2O (DI). The solution was sonicated for about 1 minute until there was no longer any visual evidence of the solid 5-HIAA. A 0.60 mM solution of KBr was made by adding 3.57 mg of KBr to 50 mL of DI. Synthesis was performed using increasing volumes of KBr. In a beaker, 4 mL, 5 mL, and 6 mL of 0.60 mM KBr, 5 mL of 0.75 mM 5-HIAA, and 579.2 μL of HAuCl_4 (1% w/v) were mixed with DI water in a solution of 50 mL. The solutions were mixed on a stir plate set at approximately 300 rpm for 30 minutes under ambient conditions. The color turned yellow about a minute after addition of the 5-HIAA and then to gray and purple after about 5 minutes.

2.4. UV-Vis Spectrophotometry. The UV-Vis spectra were obtained using an Evolution 220 UV-Vis spectrophotometer. The spectra measured absorbance from 400 to 750 nm, with a 100% T baseline correction. Samples were analyzed in a standard quartz cuvette.

2.5. Scanning Electron Microscopy (SEM) Analysis. SEM images were obtained using a FEI XL-30 Field Emission SEM. The accelerating voltage used was 30 kV with a spot size of 2. A working distance of around 7 mm was used to optimize the magnification using the through-the-lens detector (TLD). Samples were prepared on a silicon wafer.

2.6. Raman Spectroscopy. Raman spectra were acquired using a Renishaw RM1000 Raman microspectrometer (with a 20x objective). The Raman system was coupled to an Olympus BH-2 microscope and equipped with a 785 nm diode laser, an edge filter with 200 cm^{-1} cutoff, 1200-line/mm grating, and a thermoelectrically cooled CCD detector. The system is operated using Renishaw WIRE™ software (version 3.3).

3. Results and Discussion

3.1. Effect of Varied Order and Manner of Addition. In order to determine the best order and manner of addition, a series of 4 samples all began by adding 44.42 mL of DI on a stir plate. Sample 1 was performed by adding 5 mL of 0.75 mM 5-HIAA, followed by simple addition of 579.2 μL of 1% HAuCl_4 . Sample 2 was the same as sample 1, but with dropwise addition of HAuCl_4 . Sample 3 was performed by adding 579.2 μL of 1% HAuCl_4 , followed by dropwise addition of 5 mL of 5-HIAA. Sample 4 was the same as sample 3, but with simple addition of 5-HIAA. From the resulting SEM images seen in Figure 1, it was observed that all of the variations were successful in creating gold nanoparticles. The simple addition of HAuCl_4 to the solution of 5-HIAA was the method that garnered the most gold nanoparticles.

3.2. Effect of Varied Mixing Parameters. In order to determine the optimal mixing parameters, the two conditions tested were to gently agitate synthesis solution on a platform agitator and to vigorously agitate on a stir plate set at around 300 rpm. From the resulting SEM images seen in Figure 2, it was observed that both variations were successful in creating gold nanoparticles of the same size and shape. In general, the results showed that there were more nanoparticles seen using the vigorous mixing parameter.

3.3. Effect of Reaction Temperatures. The gold nanoparticle synthesis was performed with variances in the temperature at which the synthesis was performed, either in a 15°C bath, at room temperature, or in a 45°C bath. From the resulting SEM images seen in Figure 3, it was observed that all three variations were successful in creating gold nanoparticles, but the shapes and sizes were different in each temperature set. The lower temperature set did not create as many gold nanoparticles, and there seemed to be some residual unreacted material. The heated synthesis showed more nanoparticles, but the edges and forms were less defined. The results showed that the room temperature synthesis was the most successful in creating gold nanoparticles.

3.4. Effect of Varied Concentrations of Reactants. The gold nanoparticle synthesis was performed with variances in the concentrations of both HAuCl_4 and 5-HIAA. Specifically, the first concentration variation was to the 0.75 mM of 5-HIAA. The initial volumes of DI were varied to compensate for the variations of 5-HIAA added. In samples 1 through 5, 10 mL, 5 mL, 2.5 mL, 1.67 mL, and 1.25 mL of 0.75 mM 5-HIAA were added. The volume of 1% HAuCl_4 added remained constant at 579.2 μL . A second set of syntheses were performed as stated

FIGURE 1: SEM images showing results from gold nanoparticle synthesis with variances in manner and order of addition. (a) Simple addition of HAuCl_4 to solution of 5-HIAA. (b) Dropwise addition of HAuCl_4 . (c) Dropwise addition of 5-HIAA to solution of HAuCl_4 . (d) Simple addition of 5-HIAA to solution of HAuCl_4 .

FIGURE 2: SEM images showing results from gold nanoparticle synthesis with variances in mixing parameters. (a) Vigorous mixing at around 250 rpm and (b) gentle mixing on a platform agitator.

in Section 2.2, but with a variation in the concentrations of HAuCl_4 . The initial volumes of DI were varied to compensate for the variations of HAuCl_4 added, while the volume of 0.75 mM 5-HIAA remained constant at 5 mL. In samples 1 through 4, 678.0 μL , 579.2 μL , 482.6 μL , and 386.1 μL of 1% HAuCl_4 were added. The resulting SEM images seen in Figure 4 were from the variances in 5-HIAA. It was

observed that all variations were successful in creating gold nanoparticles, but the shapes and sizes were different for each concentration of 5-HIAA.

A higher concentration seemed to hinder the reaction, where the concentration in the literature resulted in gold nanoparticles more consistent with previous results. The lower concentrations created gold nanoparticles with less

FIGURE 3: SEM images showing results from gold nanoparticle synthesis with variances in the temperature at which the synthesis was performed. (a) 15°C bath, (b) room temperature, and (c) 45°C bath.

defined edges and inconsistent shapes. The resulting SEM images seen in Figure 5 were from the variances in HAuCl_4 . It was observed that all variations were successful in creating gold nanoparticles of similar shapes and sizes. The concentration of the HAuCl_4 did not seem to be as strong of a determining factor in the synthesis. There does seem to be a lower threshold, as the lowest concentrations still created gold nanoparticles, but with less of a population.

3.5. Effect of Potassium Bromide. Figure 6 shows the SEM images of the resulting gold nanoparticles when increasing concentrations of KBr were added to the synthesis. All three variations show that gold nanoparticles were successfully created. The lower concentration of KBr seemed to hinder the synthesis. The higher concentration of KBr created many planar shapes, but the edges of the nanoparticles were worn away, as seen in the inset picture of Figure 6(c). The synthesis involving the introduction of 0.075 mM KBr showed a great increase of planar shapes as compared to the synthesis in the absence of KBr. The synthesis with the addition of 0.075 mM KBr seemed to lead to the intended direction of more planar shapes as compared to the original synthesis. KBr is, in and of itself, a reducing agent [19]. The dependence of nanoparticle morphology on bromide concentration may be explained based on the preferential adsorption of bromide on the (111)

crystal facet of Au, as it was previously shown that halide ions adsorb on gold surfaces with binding energies that scale with crystal facet ((111) > (110) > (100)) [18, 20].

3.6. Characterization and Analytical Applications of Anisotropic Au NPs. Figure 7 shows two aspects of the synthesis: (1) visual images of the resulting gold nanoparticle solutions in the absence of KBr (left) and in the presence of 0.075 mM KBr (right) and (2) their corresponding UV-Vis spectra. Typical UV-visible absorption values for this kind of gold nanoparticle synthesis are around 540 nm [21]. The synthesis without KBr was close to this value, with the KBr-mediated synthesis nanoparticles showing absorption at wavelengths a bit longer. UV-Vis absorption spectrum could not be obtained for the as-prepared Au NP solution with the addition of 0.090 mM KBr, as all the Au NPs sank to the bottom of the cuvette.

Figure 8 shows the Raman spectra of crystal violet (1 mM) obtained from these two syntheses with 785 nm excitation. Top spectrum was measured from Batch 1 Au NPs solution which contained 0.075 mM KBr and gives a much higher signal for this excitation wavelength. An estimated enhancement factor of 5.4×10^6 was obtained on the basis of the intensity of the band centered at 724 cm^{-1} in the crystal

FIGURE 4: SEM images showing results from gold nanoparticle synthesis with variances in concentration of 5-HIAA. (a) 0.150 mM, (b) 0.075 mM, (c) 0.038 mM, (d) 0.025 mM, and (e) 0.019 mM.

violet Raman spectra. Postsynthesis isolation of individual shapes of gold nanoprisms via techniques such as sucrose gradient separation [21] is currently underway in our group.

4. Conclusions

We have demonstrated the facile synthesis of anisotropic Au NPs, which did not involve the use of any templates, seeds, surfactants, or polymers. Temperature, order and manner of addition, and ratio of chloroauric acid to reducing agent are extremely important. The most successful procedure which

led to the production of the largest number of Au nanoprisms within a batch of nanoparticles is as follows. 5 mL of 5-HIAA (0.75 mM), 579.2 μ L of HAuCl_4 (1% w/v), and 5 mL of KBr (0.75 mM) were mixed with DI water to form a solution of a total volume of 50 mL. The solutions were mixed on a stir plate set at approximately 300 rpm for 30 minutes under ambient conditions. The as-prepared Au NPs exhibited excellent Raman enhancement when tested with a Raman-active compound (i.e., crystal violet) and showed great potential as a novel substrate for SERS-based chemical and biological sensors.

FIGURE 5: SEM images showing results from gold nanoparticle synthesis with variances in concentration of HAuCl_4 . (a) 0.40 mM, (b) 0.30 mM, (c) 0.25 mM, and (d) 0.20 mM.

FIGURE 6: SEM images showing results from gold nanoparticle synthesis with variances in KBr concentrations. (a) 0.060 mM KBr, (b) 0.075 mM KBr, and (c) 0.090 mM KBr with inset of zoomed-in section.

FIGURE 7: Image of the resulting gold nanoparticle solutions prepared in the absence of KBr (left) and in the presence of 0.075 mM KBr and their corresponding UV-Vis spectra.

FIGURE 8: SERS spectra of crystal violet (1mM) from different batches of Au NPs. Batch 1: Au NPs prepared in the presence of 0.075 mM KBr. Batch 2: Au NPs prepared in the absence of KBr.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

Acknowledgments

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