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Synthesis and Deposition of Irregular and Complex Gold Nanostructures

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Abstract

It is a short report about the synthesis of complex shaped (sperm-like and ribbon-like) gold nanoparticles that have been achieved by using bottom up chemical synthesis technique. These methods are not only simple in approach, but it gives some new irregular shapes of gold nanoparticles. Sperm-like particle are showing some sharp edges, rounded, and twist/ turns within a single nanostructure. Instead of their irregular structure, such particles have been observed self- assembled in the best possible sterically orientations. Similarly, ribbon-like nanostructures are showing analogous UV-vis peaks like nano rods, but their structure seems to be disrupted and shaped like a ribbon. Moreover, since these nanoparticles are comprising of twisted and sharp edges could be helpful in many applications associated with such complex building blocks.

Keywords: Coffee-stain ring; Gold nanocrystals; Convective flow; Ribbons; Sperm like

Introduction

Currently, metal nanocrystals are typically investigated owing to their unique optical properties. These optical properties are linked with localized plasmon resonances (LPR) that associated with metal nanoparticles and such unique optical induced quantum effects have become a source for variety of applications [1,2]. Theoretical approximations of the optical properties of plasmonic nanoparticles, typically consumes spherical shape approximation for the analytical solution of the optical and plasmonic properties is well recognized [3]. On the other hand, synthesis methods of just about monodisperse nanoparticles with sharp corners have now been developed. Especially, nanocrystals of high symmetrical shapes with sharp and well define sharp edges are synthesized recently [4,5].

It is well understood that the fundamental properties associated with nanomaterials are strong related to their different sizes and shapes. The presence of surfactant layers is also equally significant, as these surfactant molecules not only stabilizes the nanoparticles but also allows nanocrystals compatibility with various biomedical techniques. Hence, alteration in size and shapes of the nanostructures undoubtedly offers significant influence and have key position in clinical uses.

For that reason, it should be important to realize the plasmonic properties of nanostructures comprises of sharp-edges and having complex structures. There may not exist any sharp edges, also in simulations it is often impossible to smooth all boundaries because several domains made of different materials may contact at one point or along a line which leads to a sharp corner of one or more domains [6]. As a result, the consideration of nanoparticles with sharp edges are very important as well for simulations consideration of such complex systems. The description of the objects with sharp-edges and complex structures are considered very complicated from the theoretical point of view [7,8]. Therefore, understanding of complex nanostructures is very much open field for various experimental, simulation, and theoretical studies.

Multi-dimensional elongation and thinness of nanoparticles possesses manifold nanoscale domains of materials within a single nanoparticle. The configurations of such complex structures typically asymmetric, which give them significance. In fact, alterations in dimension also changes the relevant properties associated with such complex structures. Such unique nanostructures and their fascinating properties [9,10], may offer potential cutting-edge applications such as chiral separation [11], DNA detection [12,13], asymmetric catalysis [14], and novel optical properties [15]. However, synthesis of complex nanostructures is still challenging because these complex nanostructures does not occur in nature.

Here complex nanostructure is synthesis by using one step synthesis technique. Gold nanostructures obtained comprises of thick-thin regions within a particle. These regions also show sharp-edges and twisted round and faceted regions. Size of these nanoparticles varies with concentration of $AgNO_3$. Furthermore, evaporation induced deposits within the ring like structure showed that these particles self-assembles in a close packed layer of particles. Their unique nanostructure could be useful in many relevant applications.

In this paper we demonstrate the synthesis of complex-shaped Au nanoparticles using wet chemical approach for synthesis. These nanoparticles are shown consistency in shapes for $AgNO_3$ concentration of less than 90 µl. These particles show sharp ends and twisted regions could useful for various analysis relevant to the sharp edges of plasmonic nano entities. Likewise, ribbon-like gold nanoparticles are synthesized with help of concentrated HCl. These nanoparticles show some interesting features such as undeveloped surfaces and deviation from symmetrical geometry. However, some of features like crystal structure, crystallographic composition over the various ends, and diffraction patterns of these structures etc. are still open for future research.

Experimental

Materials

Sodium borohydrate ($NaBH_4$, 99%, Aldrich), hydrogen tetrachloroaurate ($HAuCl_4.3H_2O$, 99.999%, Aldrich), sodium hydroxide (NaOH, Merck), hydrochloric acid (HCl, 37%, Merck), ascorbic acid (AA, 99%, Merck), cetyltrimethylammonium bromide (CTAB, Aldrich, 98%), and silver nitrate ($AgNO_3$, 99%, Acros) were used. Synthesis were performed using Milli-Q quality water (18.2 Mcm) produced in a Simplicity 185 system (Millipore).

Synthesis

Gold nano sperm-like particles: To synthesize gold nanoparticles of asymmetric complex structure resembles with sperm shape that comprises of rounded head and a tail region with smallest width, 25 µl (0.1M) ascorbic acid was introduced in a solution containing 10 ml (0.2M) of cetyltrimethylammonium bromide (CTAB) and 20 µl (0.1M) of $HAuCl_4$. After this, AA was introduced which turned yellowish aqueous mixture of CTAB/$HAuCl_4$ into colorless. Next, NaOH was added to rise the pH value of the solution. Finally, various amounts of $AgNO_3$ was added. UV-vis plots for different amount of $AgNO_3$ are shown in Figure 1A. UV-Vis spectrum shows that increase in $AgNO_3$ concentration leads to smaller transverse peak, showing that these nanoparticles becoming more rounded in shape as the amount of $AgNO_3$ increases.

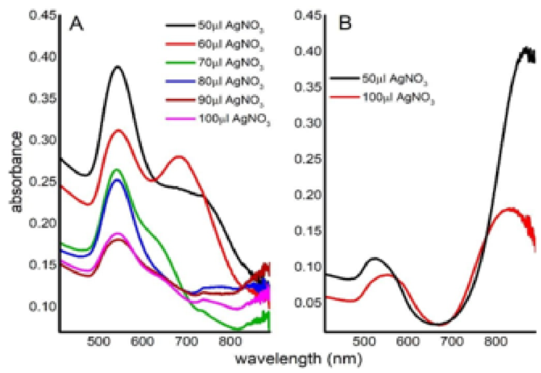

Figure 1: UV-vis spectrum of (A) sperm-like gold nanoparticles synthesized using various concentrations of $AgNO_3$, and ribbon-like gold nanoparticles for two different values of $AgNO_3$.

Gold nanoribbons like particles: Two-step seed mediated method explained by Nikoobakht and El-Sayed [16] to make the gold nanostructures used for this study. To begin with, CTAB coated seed nanoparticles were prepared by mixing 25 µl of $HAuCl_4$ (0.1M) in 10 ml of CTAB (0.1M). After that 60 µl of ice cold $NaBH_4$ (0.1M) was added with constant stirring for 5 minutes. The solution swiftly turns light brown, indicative of the creation of gold seeds. The resulting solution was set aside at room temperature for 2 hours.

In second step, for the synthesis of gold nanorods, the growth solution was prepared by mixing 50 µl of $HAuCl_4$ (0.1M) with 10 ml of CTAB (0.1M). This solution was set aside at 27°C for 30 minutes to dissolve the CTAB completely with continues stirring. After this, various amount of $AgNO_3$ (0.01M) was subsequently added at room temperature. Followed by 70 µl of ascorbic acid (0.1M) and 50 µl of HCl (37% without dilution). Lastly, 24 µl of seed solution was introduced into the growth solution and was left undisturbed for overnight at room temperature. UV-vis spectrum for different concentration of $AgNO_3$ are shown in Figure 1B. Where two peak positions confirm elongated shape of gold nanoparticles in suspension. Moreover, increase of $AgNO_3$ concentration seems to shift the transverse peak towards the higher value of the wavelength.

Deposit on the substrate: Droplet drying technique has been used for nanoparticles deposition over the substrate. Two substrates where used for nanoparticles deposition. SiO_2 was used for both type of particles used in this work whereas hydrophilic/hydrophobic stripes are used for ribbon-like nanoparticles.

Results and Discussion

SEM images in Figure 2 shows various complex shapes of gold nanoparticles comprises of rounded and sharp narrow edges (sperm-like structure).

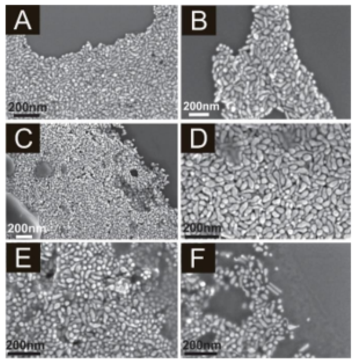

Figure 2: (A-F) SEM images of sperm-like gold nanoparticles synthesized using various concentrations of AgNO3, begin with 5 µl and ends with 100 µl respectively.

SEM image, Figure 1A shows gold nanoparticles for $AgNO_3$ concentration of 50 µl. Most of these particles are around 20-30 nm in elongated axis whereas width varies along the whole length from ~10 nm to ~3 nm. Some of these particles are turned and twisted at the thin ends. All particles are not elongated in shape, some particles are rounded but showing no thin neck like regions. Similarly, Figure 2B shows nanoparticles synthesized with $AgNO_3$ amounts to 60 µl, 50-100 nm elongated length have been observed whereas 5-20 nm is width distribution as one moves from thin-neck region to thicker rounded end of these nanoparticles. Analogous shapes are observed for silver nitride concentration of 70 µl and 80 µl as depicted in Figure 2C and 2D respectively. However, such shapes become more rounded for $AgNO_3$ concentration amounts to 90 µl and 100 µl as shown in Figure 2E and 2D.

SEM images in Figure 3A-3H are showing bunch of SEM images that display these unique gold nanostructures deposited at various locations of the substrate. Within such deposit these diverse shapes are arranged close-packed. Particularly, in isolated deposited islands these particles are monolayer and self-assembled in jam-packed manner with all their twists and turns oriented systematically. Close examination of such assemblies shows sterically favorable positions within the deposits.

Similarly, some structurally unique of nanoparticles showing various geometries such as thick, thin, turned, rounded and twisted regions within each individual nanoparticle are also observed. These self-generated structures within these arrays may be helpful in various studies owing to their sharp corners and ends [9,12,15].

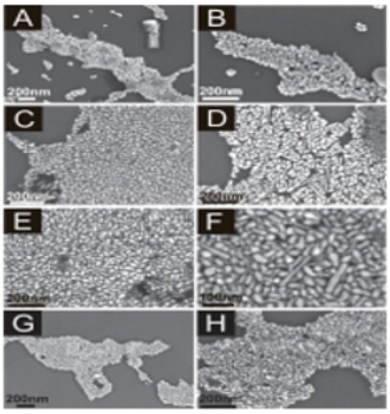

Figure 3: (A-H) Series of SEM images of sperm-like gold nanoparticles located at various positions of the deposited ring.

Ribbons-like structures are synthesized using concentrated hydrochloric acid showing that these nanostructures are 50-60 nm in length and 10 nm in width. The optical spectrum in Figure 1B clearly shows typically two peaks as observed for gold nanorods, which represents electron motion along long and short axis. Their irregular deposition over the surface could possibly owing to their uneven surfaces and light structure. SEM images in Figure 4A and 4B showing gold nanoribbons for 50 µl of $AgNO_3$ and 100 µl of $AgNO_3$ respectively.

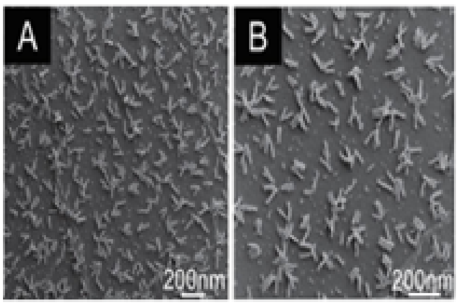

Figure 4: (A, B) SEM images of ribbon-like gold nanoparticles.

These nanoparticles are also dried on a substrate that comprises of alternating hydrophilic/hydrophobic linear stripes as shown in Figure 5A and 5C. As expected, these suspended nanostructures deposited merely over the hydrophilic region of the substrate as depicted in Figure 5B and 5D. Moreover, arrays of such nanostructures are like the deposits observed in Figure 4.

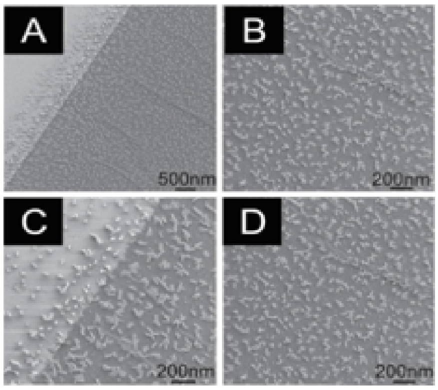

Figure 5: (A, C) SEM images of ribbon-like gold nanoparticles deposition on wetting stripe while nonwetting (hydrophobic) stripe is depleted from particles. (B, D) Deposits on hydrophilic stripes.

It is a short report about these novel nanostructures aiming to offer further investigations. Advance studies can also draw attention to new ways of consuming these structures in various fields. Furthermore, for future studies it is very much open to be investigated that in which manner gold atoms arranged within these structures? Similarly, formation of thin-thick regions within a single sperm-like nanoparticle and ribbons-like construction in the presence of CTAB, still open to be investigated.

Conclusion

In this article, it is presented that sperm-like and ribbon-like gold nonocomplex structures can also be made by using bottom-up chemical synthesis mechanism. In this preliminary work, it has been observed that gold nanostructures besides well-known structures like rods and spheres etc. there are possibilities that more complex structure can form by replacing HCl with NaOH is case of sperm-like nanoparticles whereas concentrated HCl can create ribbon-like nanoparticles. As these nanoparticles owing to their irregularity in structure provide various amplitudes of electron vibrations that results multiple peaks in UV-vis spectrum. However, ribbon-like nanoparticles, UV-vis spectrum shows two sharp peaks exactly matches with the one observed for gold nanorods. Images clearly reveals unique nanostructures of gold.

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