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Preparation of Gold Crown-Like Nanoparticles by the Seed-Mediated Growth Method

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The aim of this work is to present results on the preparation of gold crown-like nanoparticles by the seed-mediated growth method, using cetyltrimethylammonium bromide as a capping agent. By means of this method of synthesis we show that the size and morphology of the nanoparticles can be modified only by varying gold seed amount in the growing solution. The particles generated could range from spheroidal with an average particle size of 24 nm, to crown-like with an average particle size of 60 nm. Due to the capacity of change in size and morphology of the as-synthesized Au nanoparticles, the optical absorption band, a result of the surface plasmon resonance response, can be tuned in the visible-near infrared range. This is very important in terms of the their potential applications, which can cover from biophotonics to solar cells. Gold nanoparticles were characterized by ultraviolet-visible spectroscopy and transmission electron microscopy.

Keywords: Gold Nanocrowns, Visible-Near Infrared Absorption, TEM.

1. INTRODUCTION

Gold nanoparticles (Au NPs) are of great importance in technology applications. Their application includes areas, such as electronics, optics, medicine, catalysis, biology, etc.[1–6] It is well known that the optical properties of the metal nanoparticles are determined by their morphology and size. For this reason, it is crucial to control these two parameters in each synthetic method. Au NPs can be synthesized in organic media, have narrow size distribution and are monodisperse; however, it is difficult to obtain Au NPs with different morphology rather than spheres. Thus, synthesis in aqueous media is more prevalent because it is simple, rapid, environmentally friendly, and allows the generation of anisotropic Au NPs.[7] There have been many break throughs in the preparation of Au NPs like the one introduced by Turkevitch in 1951, which is based on a single phase water reduction reaction of a gold salt using citrate. This method was further improved by Frens in 1973, which allows high control over particle size.[8] However, such methods only produced spherical or quasi-spherical particles.

The morphology of nanomaterials is an important factor when developing devices with desired functions. Hence, efforts have been invested into the synthesis of materials of different shapes in the nanoscale. Anisotropic nanostructures present properties that are in function of the direction, and more than one structural parameter is needed to describe them. Their particular and controlled physical and chemical properties turns them into interesting candidates for the design of new applications.[9]

Murphy's and El-Sayed's research groups produced Au nanorods through a seed-growth method.[10,11] This method has become the basis for anisotropic generation of Au NPs like nanostars, nanotriangles, branched nanoparticles,

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etc.[12–14] Anisotropic Au NPs particles have unique optical properties. Restricted mobility of electrons, holes, excitons, phonons, and plasmons with respect to the morphology of a material is the explanation for the change in properties.[9] Optical properties can be tuned from the visible to the infrared regions of the spectrum, as a function of their shape. Anisotropic Au NPs in particular show intense surface plasmon resonance (SPR), that is a function of aspect ratio, probably because of their different surface areas and crystallographic facets.[9, 15] Because of this property, there is a growing interest in anisotropic Au NPs in cancer photothermal therapy,[4] as well as in development of optical antennas, fluorescence, photovoltaics, etc.[15–17] Due to their potential use in bio-sensing, imaging and vivo implementation, another highly desired morphology is branched gold nanoparticles.[18]

Great amount of efforts have been used to produce these structures, like gamma-irradiation, photochemical reduction.[18] However, wet chemical reduction synthesis was limited to nanospherical, rods, triangular/hexagonal/sphere mixtures, and cubes. Not many reports focused on branched-like morphologies.[19] In the last years, the use of cetyltrimethylammonium bromide (CTAB) during chemical reduction has allowed the formation of nanopods, L-shaped, I shaped and V-shaped bipods, T-shaped, Y-shaped and regular triangular tripods, and cross-like tetrapods.[20] The seed mediated method allows an easier control over particle size and shapes of Au NPs. It takes place in two steps. During the first step, Au NPs seeds are prepared, and during the second step, the seeds are added to a growth solution containing the gold salt precursor, the stabilizing and reducing agents. Using this last method, the size, shape, and surface properties are controlled by the amount and nature of the gold precursor, reducing agent and stabilizer.[20]

In this work, based on the Murphy's[10] seed-mediated approach we obtained Au nanocrowns by varying Au precursor concentration. Au NPs present a broad optical absorption that covers UV-Vis-NIR range that makes these structures suitable for many optical applications.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of Au NPs

Au NPs were synthesized base on a sequential growth process reported by the Murphy's group.[10] An aqueous seed suspension was prepared in a 10 mL flask involving 57 μL of 44 mM $HAuCl_4$ $3H_2O$ (Sigma-Aldrich, 99.99%) stock solution, 250 μL of a 10 mM trisodium citrate (Sigma-Aldrich) solution, 600 μL of 0.1 M $NaBH_4$ (Fluka, 99%) solution, and graduated to 10 mL with deionized (DI) water. The reaction mixture was left under magnetic stirring, and undisturbed for 4 h at room temperature. Growth suspension was prepared in a 100 mL flask by adding 568 μL of 44 mM $HAuCl_4$ $3H_2O$ (Sigma-Aldrich, 99.99%) solution and graduated with DI water. Then, 3 g of CTBA (Sigma-Aldrich, 99%), 1.5 mL of cyclohexane (Tecsiquim, 99%), and 2 ml of acetone (Sigma-Aldrich, 99%) were mixed in the previous flask under magnetic stirring at 60 °C. Next, the resulting solution was allowed to cool at room temperature. In order to obtain gold nanocrown-like particles with different size, eight flasks were used varying the gold seed volume (1000, 500, 250, 125, 90, 60, 30 and 15 μL), and adding 10 mL of gold growth solution, 500 μL of 0.1 M ascorbic acid (Sigma-Aldrich, 99%) solution, and 5 μL of 10 mM $AgNO_3$ (Fluka) solution under magnetic stirring at room temperature (Table I). The solution was left undisturbed for 12 h.[10] The resulting suspensions were placed in dialysis during 3 days at 40 °C to remove excess CTAB. Afterwards, the suspensions were centrifuged at 4000 rpm during 30 min, and the supernatant was removed. Au NPs were washed with 5 mL of isopropanol and re-centrifuged at the same conditions. Finally, Au NPs were re-dispersed in 5 mL of DI water.

Table I. Synthesis conditions for the generation of anisotropic Au NPs.

Sample	Seed suspension volume (μL)	Growth solution volume (mL)	Ascorbic acid volume (mL)	$AgNO_3$ volume (μL)
S1′	1000	10	10	5
S1	500	10	10	5
S2′	250	10	10	5
S2	125	10	10	5
S3′	90	10	10	5
S3	60	10	10	5
S4′	30	10	10	5
S4	15	10	10	5

3. CHARACTERIZATION

UV-Vis absorption spectra of Au NPs were obtained using a Thermo Scientific GENESYS 10S ultraviolet-visible (UV-vis) spectrophotometer. Each spectrum was measured in the 300–1000 nm range. Transmission electron microscopy (TEM) images were acquired with a JEOL JEM-2010. For its study, the samples were prepared by placing one drop of a dilute suspension of Au NPs onto a carbon coated copper grid and allowing the solvent to evaporate at room temperature. Particle size was estimated by using the Image J software.

4. RESULTS AND DISCUSSION

As was described in the experimental section, the generation of Au NPs was achieved by adding different amounts of the seed suspension to the reaction mixture. In Table I, it can be noticed the volume of the seed suspension that was used to prepare the samples named S1′, S1, S2′, S2, S3′, S3, S4′, S4. As it can be observed, the volume of growth solution, ascorbic acid and $AgNO_3$ were kept constant. From the naked eye, the final suspensions presented different tones of blue color (not shown here). UV-Vis

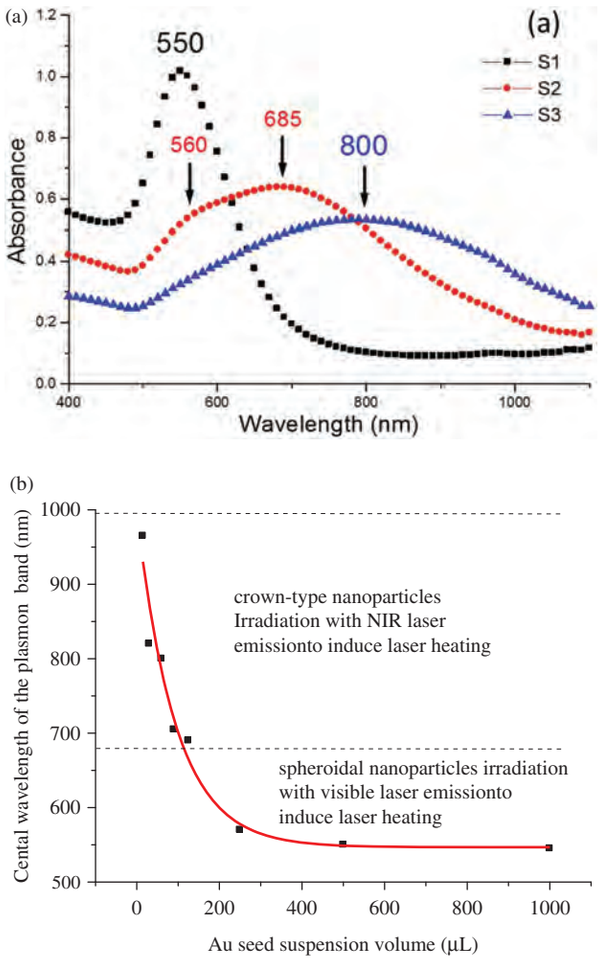

Figure 1. UV-Vis spectra of Au NPs generated in S1, S2 and S3 (see Table I) (a); and shift of the central wavelength of plasmon band as a function of seed suspension volume occupied in the synthesis (b).

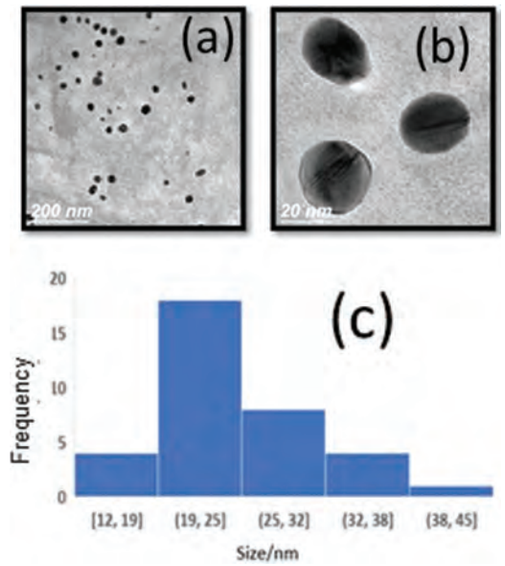

Figure 2. TEM images of samples: S1 (nanospheroids). The scale bar is 20 nm (a) and 200 nm (b); particle size distribution is also shown (c).

spectra were recorded to establish a probable shape and size for the Au NPs generated in all the reactions.

All samples web characterized by UV-Vis spectroscopy. UV-Vis spectra for S1, S2, and S3 samples are shown in Figure 1(a) as representative examples of the optical properties of Au NPs suspensions. As one can observe, for sample S1 a narrow peak appears with a maximum absorption peak at $\lambda_{max} = 560$ nm. This maximum corresponds to the SPR of the Au NPs. The fact that the peak is narrow and symmetrical implies that particles size distribution is also narrow. Since only one peak is observed, it can be assumed that Au NPs are spherical or spheroidal.[10] When analyzing the UV-Vis spectrum for S2 two maxima absorption peaks appear at $\lambda_{max\,1} = 570$ nm and $\lambda_{max\,2} = 690$ nm. The maxima are not separated enough to confirm a rod-like morphology. In the literature, this kind of response has been observed for nanoprism, nanostars, octahedral, jack-shaped, and aggregated nanoparticles.[12, 13] For S3 UV-Vis spectra, only one band is present at $\lambda_{max} = 800$ nm. It is extremely broad, which could be explained by various reasons. Particles size distribution could be broad and a heterogenous morphology of Au NPs could be present.

In Figure 1(b), it can be seen the shift of the central wavelength of the plasmon band as a function of the seed suspension volume used in the preparation of Au NPs. As it can be observed, the central band positions and the spectral form of the band depend on seed suspension volume. Then this parameter lets to control the optical properties of the Au NPs suspensions.

Figures 2 and 3 show the TEM images corresponding to S1, and S2 samples, respectively. It can observed that the shape in each case is different. The nanoparticles for the S1 sample are spheroids with an average particle size (d) of 24 ± 6 nm, while in the S2 sample have a crown-like morphology with $d = 60 \pm 14$ nm. Considering the particle synthetic conditions, it can be assumed that the average particle size increased with decreasing seed volume. Hence, given that the other reaction reagents and reaction conditions remained constant, it can be established that size and shape of Au NPs can be controlled by solely varying the seed volume of Au suspension in the reaction mixture. The increment in average particle size growth may be explained as follows. Au seed amount is lower in the reaction of S2 than for S1. Hence, fewer seeds are present in the reaction mixture that can consume the Au precursor present in the growth reaction mixture; allowing particles become bigger. On the other hand, in reaction of S1 the seed amount is higher and the amount of gold precursor is the same in all reactions. Due to this, the ratio between seed amount and gold precursor is lower

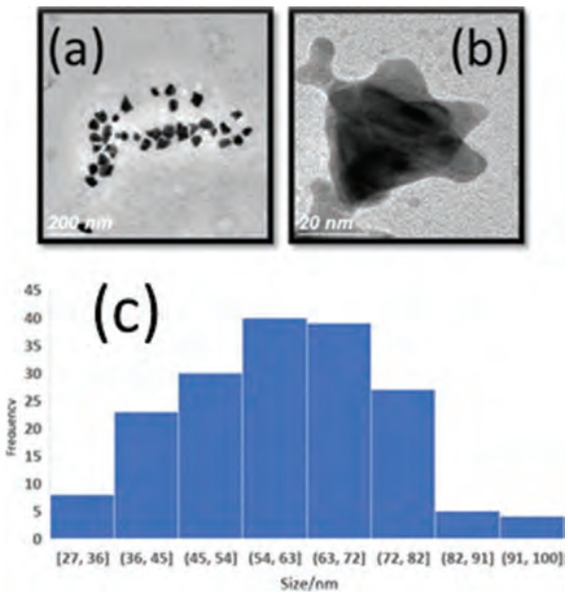

Figure 3. TEM images of samples: S2 (nanocrowns). The scale bar is 20 nm (a) and 200 nm (b); particle size distribution is also shown (c).

than for S2, resulting in a reduced increase in particle size.

On the other hand, as it was mentioned, particle morphology change is interesting. For cancer photothermal therapy applications the optical absorptions features of Au NPs are very important. For example, Mendoza-Nava H. has studied the laser heating induced in Au nanospheres functionalized with octreotide.[21] Thanks to the plasmon of spherical nanoparticles (see the optical absorption spectrum), they utilized a Nd-YAG laser emitting in 532 nm (green light) to perform their laser irradiation experiments. They conclude that the system presented properties suitable for plasmonic photothermal therapy in the treatment of cervical cancer.[22] For these applications, the optical properties of our Au NPs (nanocrown-like particles, see Fig. 1(b)) becomes relevant because one can perform experiments of laser heating with lasers emitting in the NIR window range (700 to 900 nm). In this interval water and hemoglobin are quite transparent and the Au NPs gives the optical absorption.[22]

The change in morphology is in function of several parameters. The shape and structure of the initial seeds and the composition of the growth solution are factors that play a crucial role for the development of anisotropic NPs. CTAB is used as a stabilizing agent to control the growth of anisotropic shape.[18] According to Kawamura, acetone and cyclohexane also play an important role.[23] Acetone brings the length of branches to increase, while cyclohexane causes the Au NPs shape branches to round.

Considering all the above data generated by optical characterization, the UV-Vis spectra show the characteristic SPR properties. The prepared anisotropic particles present a red shift in the UV-Vis spectra due to increase in particle size. The SPR can be attributed to the collective oscillation of free electrons at the gold particle surface. For this kind of morphology, the frequency of the oscillation reduces and spreads because of the preferential accumulation of surface charges at the corners. Hence, the peak absorptions present in the long wave region are due to the resonance coming from the sharp apices of the branches.[23]

5. CONCLUSIONS

We have successfully prepared spheroidal and crown-like nanoparticles by the seed-mediated growth method. Due to their morphology and size, these type of gold nanoparticles present optical properties, which can be controlled varying the seed suspension volume. The position of plasmon band can be tuned in the Vis-NIR range. Therefore, these Au crowns-like nanoparticles could have potential applications in photo thermal therapy, solar cells, SERS and so on.

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