Synthesis of Hexagonal Gold Nanoparticles and Study of its Optical and Near-field Distribution Properties by Discrete Dipole Approximation

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Abstract: Anisotropic nanostructures with unique physical and chemical properties have been widely applied in optical, electronic, magnetic, and catalytic fields. This paper described the synthesis of hexagonal gold nanoplates (HAuNPs) by trisodium citrate and ascorbic acid. The optical and near-field distribution properties of hexagonal gold nanoplates were studied by discrete dipole approximation method. Simulation results showed that due to the shape anisotropy of HAuNPs, the optical properties of HAuNPs were significant differences between the horizontal orientation and vertical orientation.

1. Introduction
Hexagonal gold nanoplates (HAuNPs) were a kind of anisotropic nanostructures that have attracted considerable attention in the past few decades since their potential applications in nanophotonics, surface-enhanced Raman scattering (SERS), biosensors and optoelectronics. There's more than one way to synthesize of hexagonal gold nanoparticles. Neretina and co-workers [1] prepared periodic arrays of hexagonal Au nanoplates by using a combination of nanoimprint lithography (NIL), vapor-phase directed assembly and liquid-phase epitaxy methods. The synthetic strategies demonstrated the viability of plasmon-mediated growth modes and a new building block for the design of photoactive surfaces. Yuan et al [2] studied the biosynthesis of gold nanoparticles (AuNPs) using persimmon fruit extract. The hexagonal gold nanoparticles were also synthesized at a certain amount of chloroauric acid, however, the yield of HAuNPs was very low despite more than 97% of Au$^{3+}$ ions were converted to AuNPs. Chung et al [3] developed an environmentally friendly method for the synthesis of triangular and hexagonal AuNPs. The cytotoxicity of the as-prepared AuNPs was evaluated using 3T3-L1 adipocytes and a well biocompatibility of nanoparticles was obtained. The plants extract mediated growth method for preparing HAuNPs and nanomaterials was a viable method. In addition, the humus basidiomycetes and soil bacteria were also employed to prepare the hexagonal gold and silver nanoparticles [4]. Because of the high polydispersity and low yields for synthesis of HAuNPs by the current synthetic protocols such as photochemical process, biological reaction and wet chemical reduction methods. Zubarev et al [5] proposed a new seed-mediated synthesis of HAuNPs using hydroquinone as a weak reductant and poly (vinylpyrrolidone) (PVP) as a shape-directing additive. The synthesis of small HAuNPs presented an over 90% shape yield and a long-term shape stability.

The controllable synthesis of HAuNPs is one of the important aspects of nanotechnology. Another important aspect is to study the optical characteristics of nanostructures. The noble metals nanostructures such as Au (gold), Ag (silver), and Pt (platinum), etc. showed unusual optical properties because of the
collective charge oscillations. Many numerical simulation methods such as finite element method (FEM), finite difference time domain method (FDTD) and discrete dipole approximation (DDA) have been used to describe the optical properties of different nanostructures. Since DDA was able to calculate the extinction of electromagnetic waves by objects with arbitrary geometries and complex refractive indexes. The surface plasmon resonance (SPR) of silver nanoparticles and AuNPs in the proximity of graphene flakes or embedded in graphene structures were studied by Amendola [6]. Wriedt et al [7] investigated the plasmonic response of gold nanospheres using DDA method. The results were in good agreement with those of FEM and FDTD methods. Pileni et al [8] compared the absorption spectra of two-dimensional (2D) assemblies of Ag or Au nanocrystals (NCs) with DDA method. There were no SPR bands splitted for 2D assemblies of Au NCs, which were well reproduced by DDA simulation. However, only few researches were related to the near field distribution properties of gold nanoparticles by DDA method so far.

In this study, we demonstrated the fabrication of HAuNPs by using only ascorbic acid and trisodium–citrate mixture solution in mild condition. The optical properties and near-field distribution properties of HAuNPs employed the most popular method of DDA were researched in detail.

2. Materials and Methods

2.1 Material and Instrumentation
Chloroauric acid (HAuCl₄·3H₂O, 99.9%), sodium citrate dihydrate (trisodium citrate or Na₃Cit, 99%), ascorbic acid (AA, 99%) were purchased from Shanghai Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were of analytical grade and used as received without any further purification. Ultrapure water (Resistivity > 18.25 MΩ·cm) was used for all solution preparation and throughout the experiments. The shapes and sizes of the HAuNPs were characterized by scanning electron microscopy (SEM, Nova NanoSEM 250, FEI Company, Hillsboro, USA) with an accelerating voltage of 30 kV.

2.2 Procedures and Methods
The experimental procedures were the same as those presented in our previous report [9]. In a typical experiment, 10 mL of the mixture containing trisodium citrate (w/v, 0.025%) and ascorbic acid (w/v, 0.05%) was dropwise added into 10 mL of 1 mM HAuCl₄ aqueous solution. This mixed solution continued to stir about 30 min. The completely mixed solution was placed in a fridge at 6 °C overnight (about 12 h). The hexagonal gold nanoplates were formed in solution despite many spherical nanoparticles were simultaneously produced.

The DDA method was employed to evaluated the optical properties and near field distribution properties of the HAuNPs [6, 7, 10, 11]. The DDA theory was described in detail in these reported papers. In this work, the free software ‘DDSCAT 7.3’ was used to carry out the DDA calculations. This open source software was usually used to calculate spectra of nanomaterials. The DDA started by dividing the object into a hexagonal prism of N-point dipoles. The interdipole spacing of d was 1 nm. The refractive index of the surrounding medium was set to the value n₀ = 1.33. The optical constants of Au adopted from the empirical values by Johnson and Christy.

3. Discussion
The previous study revealed that the several tens of microns of single-crystalline gold nanosheets were synthesized in an ethanol solution. The SERS performances of these nanostructures were studied [12]. In fact, we have used Na₃Cit and AA for synthesis of hexagonal AuNPs (HAuNPs) with average size of about 200 nm. The size and morphology of the as-prepared HAuNPs were examined using SEM. The SEM images in figure 1 illustrated that the HAuNPs with hexagonal morphologies which were marked with red regular hexagons. The average side size of the HAuNPs was 200 nm. In order to promote the application of HAuNPs in nanoscale, the optical properties and near field distribution properties of the HAuNPs were of importance to the nano science and technology. To simplify the calculation, we chose the 70 nm of HAuNPs as research model for carrying out the DDA calculation and demonstrating the
optical properties.

**Figure 1.** SEM images of synthesized HAuNPs with a certain concentration of Na₃Cit and AA. Scale bar: 1 μm. The inset image was a magnified image of single hexagonal gold nanostructure. Scale bar: 0.25 μm.

Because of the shape anisotropy of the HAuNPs, the anisotropic optical properties of the HAuNPs were investigated with DDA method. Figure 2a and 2b showed the dipole models of the 70 nm size of the HAuNPs. In the software of DDSCAT 7.3, the directions of the target frame (TF) was fixed by two orthogonal unit vectors. So, the dipole model of HAuNPs was chosen two different directions for the incident radiation. In each propagation modes, the incident radiation can be specified by three angles,
such as Θ, Φ, and β were specified in the file of ddsct.par. Figure 2c and 2d showed the optical properties of the HAuNPs. The two group of spectra curves represented the wavelength dependent absorption, scattering and extinction spectra of HAuNPs with side size 70 nm. The maximum extinction wavelength was observed at approximately 590 nm for the horizontal orientation of HAuNPs in figure 2c. For the vertical orientation of HAuNPs, there were at least two peak values in the calculation range with 400-800 nm. These spectra implied that this state of HAuNPs would be have stronger near field value. The high enhancement of near field may be benefit to the application of HAuNPs in SERS. The other incidence angles (such as oblique incidence) for different directions were not shown in the text. According to the previous reported, the maximum wavelength of the SPR band remained unchanged as the changing the incidence angles [8].

Figure 3 represented the two-dimensional field distribution of HAuNPs at different wavelength with different orientations. Despite the similar spectra values for horizontal orientation of HAuNPs at 532 nm and 785 nm. The visible enhancements in 785 nm incident radiation were obtained (Figure 3b). At excitation wavelength of 532 nm. The near-field distributions were relatively low values. These results were also presented in vertical orientation of HAuNPs. The results suggested that a longer wavelength would be conducive to the application of SERS.

**Figure 3.** Near-field distribution properties of HAuNPs with different wavelength of incident radiation. a) 532 nm for horizontal orientation, b) 785 nm for horizontal orientation, c) 532 nm for vertical orientation, d) 785 nm for vertical orientation.

**4. Conclusions**

In this paper, we have studied the preparation of hexagonal gold nanoplates and the calculation of the optical properties HAuNPs. In order to promote the application of hexagonal gold nanoplates in nanoscale, the 70 nm side size of gold hexagonal nanoplate was used as a model structure for studying. The discrete dipole approximation method was employed to analyse the optical and near-field distribution properties of hexagonal gold nanoplates. These results showed that the gold hexagonal nanoplates have different optical and near-field distribution properties with different orientation features. The hexagonal gold nanoplates would be applied in SERS field with better enhanced performances at longer wavelengths.
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