FDTD simulation of the optical properties for gold nanoparticles

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Abstract

The optical properties of gold nanoparticles such as strong extinction and surface plasmon resonance can be adjusted by altering the structure, which was used widely in the surface enhanced Raman scattering (SERS). In this paper, the optical properties of gold nanoparticles were investigated by using the Finite-Difference Time-Domain (FDTD) method. The influences of AuNP-size and NP-NP-spacing on the local electric field and extinction properties were analyzed in detail. The results showed that the electric field intensity of AuNPs increased rapidly with the increasing size. Meanwhile, the formant appeared blue shift and the peak intensity increased first and then decreased with the increase of NP-NP-spacing. The theoretical calculation results are concordant with experimental results. The FDTD simulation results of this paper have a guiding significance in SERS areas.

1. Introduction

Gold nanoparticles (AuNPs) have been widely adopted in the field of biosensors, surface enhanced Raman scattering (SERS) and medical diagnosis because of the unique physical and chemical properties [1–4]. Recently, it has been developed that Au particles exhibit many new and excellent properties after being reduced to nanoscale [5–7]. For example, local surface plasmon resonance (LSPR) can enhance the local electric field greatly due to the resonance generated by electron oscillation and photon vibration on the surface [8]. Under the LSPR effect of metal nanoparticles, the scattering effect, fluorescence and Raman scattering of molecules around the particles will be significantly enhanced [9–12]. LSPR characteristics are related to the size and structure of nanomaterials and metal nanometers [13, 14]. Recently, He et al. have constructed a \( \Delta \lambda_{\text{LSPR}} \)-based catalytic nucleic acid biosensor, which relied on DNA-mediated control of the structure of gold nanorods (GNRs). By taking advantage of the LSPR properties from the morphological evolution of the GNR, the \( \Delta \lambda_{\text{LSPR}} \)-based biosensor exhibited promising detection [15]. LSPR characteristics of gold nanostructures are of great controllability. Therefore, an in-depth study of LSPR characteristics is of positive and important significance.

When the incident laser is irradiated to the molecule on the surface of a good metal conductor, the Raman scattering signal is significantly stronger than the ordinary signal. This optical phenomenon is Surface enhanced Raman scattering (SERS) effect. SERS technology provides rich molecular characteristic peaks for rapid qualitative analysis of the components. SERS can be used to detect analytes in trace chemistry and biochemistry with high sensitivity and rapid reaction [16, 17]. Most recently, Foscan M et al. have reported a plasmonic biosensor for specific dual LSPR-SERS immuno-detection. The immune sensor used the specificity of SERS to recognize human IgG-anti-human IgG [18]. Based on the LSPR model of electromagnetic enhancement mechanism, when electromagnetic fields generated by nanoparticles and molecular scattering overlap, the local enhanced electric field of nanoparticles radiation can be used for molecules scattering, thus enhancing the Raman scattering of molecules. These regions can generate strong Raman signals, thus achieving high sensitivity detection of the components adsorbed on the substrate. The LSPR electric field intensity of nanoparticles is effectively improved to maximize SERS output.

Finite-difference time-domain (FDTD) method has become one of the important numerical methods of the electromagnetic field [19, 20]. Besides, FDTD can obtain simulate the light scattering from metal particles [21, 22]. To further study the coupling effect between nanoparticles and quantify the SERS enhanced effect of...
LSPR, FDTD was used to simulate the LSPR characteristics of gold nanoparticles. In this paper, the refractive index of the medium was adjusted by changing the factors affecting the LSPR of metal nanoparticles, focusing on the LSPR optical properties of Au nanoparticles, and using FDTD method to calculate the extinction cross-section.

2. Experiment

2.1. Structural models in FDTD simulation
FDTD solution was used to set up the structure and calculate the digital simulation. The wavelength range of the simulation is set between 400 nm and 700 nm, which is the visible light range. The source type adopted a Total-field scattered-field (TSFT) source, which is often used to study the scattering characteristics of nanoparticles. And Perfectly matched later (PMI) boundary was utilized to calculate the absorption cross-section.

2.2. Principle of extinction properties
The incident source has been used to detach two distinct regions from the computation region—one contains the total field (the sum of the incident field and the scattered field), while the second region contains only the scattered field [23]. The scattering cross-section $\sigma_{\text{scat}}$ can be represented by the following formula [24]:

$$\sigma_{\text{scat}}(\omega) = \frac{P_{\text{cat}}(\omega)}{I_{\text{int}}(\omega)}$$ (1)

Where $P_{\text{cat}}(\omega)$ and $I_{\text{int}}(\omega)$ are respectively represented the total scattered power and the intensity of the incident source. The total scattered power is obtained by adding the power of the scattered area power monitors. In addition, the absorption cross-section can be calculated using the following equation:

$$\sigma_{\text{abs}}(\omega) = \frac{P_{\text{abs}}(\omega)}{I_{\text{inc}}(\omega)}$$ (2)

Where $P_{\text{abs}}(\omega)$ is the total power absorbed by Au nanoparticles, which can be obtained by calculating the sum of the power flowing into the monitors located in the full field area. According to the scattering field and total field obtained by numerical simulation, the extinction cross-section $\sigma_{\text{ext}}$ is obtained by using the following formula [25]:

$$\sigma_{\text{ext}}(\omega) = \sigma_{\text{abs}}(\omega) + \sigma_{\text{scat}}(\omega)$$ (3)

From the above function, the extinction cross-section $\sigma_{\text{ext}}$ is the summation of the scattering cross-section $\sigma_{\text{scat}}$ and absorption cross-section $\sigma_{\text{abs}}$. 

Figure 1. Structural model of the Au nanoparticle in the FDTD simulation.
2.3. Raman spectra

AuNPs were prepared by the conventional wet chemical method for reducing a 50 ml 0.01 wt% chloroauric acid (HAuCL4) solution, in DI water, with a 0.5 ml 1 wt% trisodium citrate (Na3C6H5O7) at 100 °C. And the solution reacted for 20 min at 100 °C with vigorous stirring. Then the solution was concentrated by centrifugal separation at 12000 rpm for 4 min. The supernatant was removed. The reducing agent and its concentration are the main ingredients controlling the resultant AuNPs size. A colloidal solution of AuNPs in water is thus obtained.

4-Aminothiophenol (4-ATP) was chosen as the probe molecule. 5 μl 4-ATP (10⁻⁵M) was added into 0.5 ml AuNPs under vigorous stirring and stood at room temperature for 20 min. When 4-ATP was adsorbed on AuNPs substrate, Raman spectral mapping was performed. SERS measurements were performed on a Raman spectrometer with the 785 nm helium-neon excitation laser. The laser beam was focused onto the sample with an exciting power of 0.1 W and the exposure time at each and every pixel was 10 ms.

3. Results and discussion

3.1. Effect of AuNP-size on the electric field and extinction properties

According to Mie theory [27], only the dipole effect can be considered when sizes of nanoparticles are smaller than light waves. As the AuNP-size changes, the electromagnetic field of particles changes and the multipole effect cannot be ignored. Different AuNP-sizes (10, 20, 30, 40, 50, 60 nm) were calculated to investigate their influences on optical properties and the electric field distribution. In the simulation environment in figure 1, the
local electric field of six AuNP-sizes ranging from 10 nm to 60 nm was simulated under 510 nm laser excitation. As shown in figures 2(a)–(f), for single spherical Au nanoparticles, the electric field intensity varied as the sample size increased. As can be seen from figure 2(g), the highest electric field intensity of AuNPs was achieved at a radius of 60 nm, which is twice as strong as that of 40 nm. Figure 2(f) illustrated that the peak intensity of extinction increased significantly with increasing the radius. Meanwhile, a slight red shift of the extinction position was also observed.
When the particle radius is 10 nm, the incident light can penetrate the entire nanoparticle, and the boundary between the surface plasmon and the volume plasmon will disappear. So the extinction cross-section is relatively small. In addition, the scattering effect of the dipole and the multi-dipole of particles with a radius of 50 nm is similar. Then the extinction, scattering and absorption cross-sectional area of the particles were calculated under 510 nm laser excitation. As shown in figure 3, the peak positions of the three spectral lines of Au nanosphere were consistent.

Excimer coupling happens near the contact point of double spherical gold nanoparticles, resulting in a ‘hot spot’. The pole characteristics have been completely masked because of the strong coupling effect. As the increase of particle size, the ‘hot spot’ position will move to each side, the surface plasmon vibration mode becomes complex. Therefore, the electric field and extinction spectrum of Au particles with particle radius of 40 nm, 50 nm and 60 nm were further studied. Figure 4 showed electric field distribution and extinction properties of a pair of AuNPs with three AuNP-sizes, where NP-NP-spacing was 2 nm. As shown in figures 4(a)–(c), the intensity of ‘hot spot’ increased with the increase of NP-size. For two gold particles with constant spacing and increasing particle size, the electric field intensity increased due to the enhancement of their local

Figure 5. FDTD simulated the electric field when the NP-NP-spacing was increased from 0 nm to 6 nm in (a)–(d). The inset of (e) showed distribution of the electric field by different Au-sizes. The extinction cross-sections were calculated when the different NP-NP-spacing with a radius in (f).
electromagnetic field interaction (see figure 4(d)). The superimposition of multiple dipole effects appeared when the radius of particles was over 40 nm in figure 4(e). According to Drude model [28], the position of the LSPR format is mainly determined by the metal composition and the optical properties of the medium around the nanoparticles. When the refractive index of the medium around the nanoparticles changes slightly, a large shift the LSPR peak may be obtained in the corresponding spectrum. As the increase of AuNP-size of double spherical gold particles, the extinction position appeared red shift in figure 4(e). The reason might be that the refractive index of the external medium increased.

3.2. Effect of NP-NP-spacing on the electric field and extinction properties

In order to know the relationship between the particle coupling electric field enhancement and NP-NP-spacing, double gold particles model was simulated. The electric field and extinction properties have been displayed in figure 5. The enhancement was greatly influenced by NP-NP-spacing (see figures 5(a)–(d)). The coupling enhanced electric field of double spherical gold particles was stronger than that of single spherical gold nanoparticles. There are distance conditions for the electric field coupling between particles. Only the surface plasmon of double spherical Au nanoparticles is in the appropriate location, the optimal coupling effect is obtained. The coupling effect decreases rapidly with the increase of the NP-NP-spacing. The optimized enhancement effect was achieved when the NP-NP-spacing was 2 nm as shown in figure 5(e). Besides, the ‘hot spot’, with the strongest local electric field intensity, can significantly enhance the fluorescence or Raman signal of the molecule.

Figure 5(f) showed the extinction spectra calculated by FDTD when NP-NP-spacing was increased to 6 nm (AuNP-size is 50 nm). With the increase of NP-NP-spacing, blue shift happens for local surface plasmon resonance. When the distance between two gold nanoparticles is near together, two peaks will appear. There is no split peak and the coupling effect is weak when the two particles are far apart. The formant positions are in the long-wavelength region with small spacing. This phenomenon represents that the coupling becomes weaker with the larger spacing (less density). Therefore, LSPR can be controlled based to achieve regulation of the spectral response range and realize a wider application.

3.3. Spectra of AuNPs at different concentrations

The near-field coupling effect between adjacent gold nanoparticles plays a key role in the SERS electromagnetic field enhancement. The charge between the particles exchange as they approach. Then the enhancement effect of surface plasmon resonance is weakened, resulting in a decrease of SERS activity of the substrate. 4-Aminothiophenol (4-ATP) is a common Raman label molecule used in the SERS measurement and was chosen as the probe molecule. The sample was excited by a 785 nm laser with an exciting power of 0.1 W.
Figure 6 showed the Raman spectra of 4-ATP on AuNPs with different concentrations (different NP-NP-spacing). Au1 was a gold sol, which was prepared by concentrating 1 ml of the synthetic solution synthesized into 0.1 ml water. Experimental results confirmed that the spacing of Au nanoparticles has a great effect on the Raman signal. With the concentration of AuNPs increasing, the Raman signal increases significantly. The increasing concentration of gold nanoparticles increased the adsorption of the 4-ATP molecule, which makes it fully interact with gold nanoparticles and improves the SERS effect.

In summary, the optical properties of AuNPs structures have been studied using FDTD simulation. For a single gold nanoparticle, the result of electric field enhancement with the increase of AuNP-size is consistent with Mie theory. In the case of double spherical Au nanoparticles, the main factor affecting the extinction spectrum is the spacing of the spheres under the constant radius. Under the 510 nm laser, the coupling phenomenon occurs between the spheres. And the extinction position appears blueshift with the increase of the NP-NP-spacing. By controlling the number of Au nanoparticles and the distance between the particles can be implemented to enhance the optical properties of LSPR control. The simulated results have a certain guiding significance for the realization of Au nanoparticles in the future, and are convenient for research with SERS substrates.

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