Double Beam Interference Femtosecond Laser Fabrication of Large Area Periodic Au Nanoparticle Arrays by Spatial Light Modulation

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Abstract: We propose a simple and efficient method for preparing large-area periodic Au nanoparticle arrays by dual-beam interference femtosecond laser by spatial light modulation. The Au film sample is double-exposed by successively loading the interference phases perpendicular to each other, then the large-area periodic Au nanoparticle array structure can be directly obtained, which only take one step. This method not only adjusts the period of the nanoparticle array through the phase period, but also flexibly regulates the size of the nanoparticles by the laser energy and the number of pulses, the minimum nanoparticle diameter achieved in this paper is 338 nm. In addition, we also analyse the mechanism of Au pattern morphological changes during the heating of the auxiliary muffle furnace, which provided a new idea for the preparation of gold nanoparticle arrays.

1. Introduction

Recently, metal nanostructures have important applications in the fields of optics, chemistry, and biomedicine[1-4]. And noble metal nanoparticle structure is attracting more and more scientific attention due to their unique optical and electromagnetic properties. This structure is capable of exciting localized surface plasmon resonance (LSPR), so it can effectively manipulate and amplify incident electromagnetic waves[5], and is often used in biological and chemical sensing, renewable energy, fluorescent enhancement and nonlinear optics, and data storage[6]. Some preparation methods have been proposed for the preparation of noble metal nanoparticles, such as electron beam processing, focused ion beam processing, photolithography, laser processing[7-8]. Among them, the femtosecond laser is considered to be an irreplaceable technology in the field of nanofabrication due to its unique characteristics of extremely high peak power and extremely short pulse duration, and is widely used in the preparation of nanoparticles.

Femtosecond laser-induced forward transfer was a typical method for preparing nanoparticle arrays[9-11]. By melting a local metal film, it was detached from the bulk material and form nanoparticles on the surface of the substrat. However, this method can only process one nanoparticle at a time, which was inefficient for the preparation of large-area array structures. Some

group realized the preparation of large-area metal nanoparticle structures by laser direct writing[12], which effectively improved the processing efficiency. However, this method also had the insufficiency of regulating the size and spacing of nanoparticles, which limited the application of structures. Mask-assisted laser irradiation could effectively control the size and spacing of nanoparticles while meeting the needs of large-area preparation[13-14]. Unfortunately, there were many steps in this method. In summary, a simple and efficient preparation method was still a challenge for large-area precious metal nanoparticle array structures with adjustable size and spacing.

In this paper, a simple and efficient method is proposed for preparing large-area periodic Au nanoparticle arrays by dual-beam interference femtosecond laser by spatial light modulation. The Au film sample is double-exposed by successively loading the interference phases perpendicular to each other, then the large-area periodic Au nanoparticle array structure can be directly obtained, which only one step. This method not only adjusts the period of the nanoparticle array through the phase period, but also flexibly regulates the size of the nanoparticles by the laser energy and the number of pulses.

2. Experimental Section

A commercial Spitfire laser with a central wavelength of 800 nm, pulse width of 35 fs and repetition rate of 1000 Hz was used to be shaped by Spatial Light Modulation(SLM), to form double beam interference light for processing of Au nanoparticle arrays. The schematic diagram of the experimental device is shown in Figure 1 Femtosecond laser was incident on SLM after through a HW plate, attenuator and the shutter. By loading the two-beam interference phase, the femtosecond laser was shaped to double-beam interference light and reflected by SLM, then carried by the 4f lens group and reflected by the mirror, and finally focused on the sample surface by the 20x objective microlens， when processing with a two-beam interference region, the sample needed to be lifted by 60 μm. The illustrations in the Figure 1 (a) represented the two-beam interference phase loaded by SLM (left) and the intensity distribution of double beam interference light before focused (right).

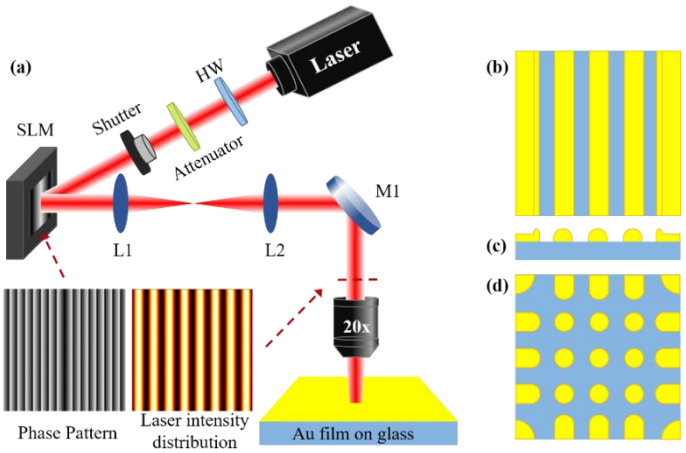

Figure 1: The schematic diagram of the experimental device and the preparation principle. (a) The schematic diagram of the experimental device, illustrations represent the two-beam interference phase loaded by SLM (left) and the intensity distribution of double beam interference light before focused (right); (b-d) descript the principle of preparing large-area nanoparticle periodic array by orthogonal interference phase.

A 10 nm Au film based on glass was selected as the preparation material for nanoparticle array, the transverse interference phase and the longitudinal interference phase are loaded one after the other. Due to the dewetting of Au film, fabrication of large-area periodic nanoparticle arrays was possible. Figure 1(b-d) descript the preparation principle. After the longitudinal interference light interacts with the Au film, the Au film under strong light intensity was removed, under weak light intensity was retained and the material at the interface was bulge by the extrusion to form a recast layer. Finally, the Au film formed a patterned longitudinal stripe distribution on the surface of the substrate, as shown as Figure 1(b). Figure 1(c) is schematic diagram of the side profile. Next, loading a transverse interference phase perpendicular to the previous phase to form lateral interference light. The new light field interacts with the longitudinal stripe distribution of the Au film, eventually forming a large-area periodic array of nanoparticles, as shown as Figure 1(d).

3. Results & Discussion

The laser spot size before phase modulation was determined to be 7 mm, at which laser power was measured. Figure 2 shows the morphological characterization of the surface structure of the Au film after successively loading mutually perpendicular interference phases with laser power of 6.5 mW and pulse number of 30. After loading the longitudinal interference phase as shown in Figure 2 (a), the surface morphology of the Au film is shown as the SEM images of Figure 2 (b), the high-resolution SEM image in the upper right corner of Figure 2 (b) shows the recast layer edge of the structure similar to "pizza" due to extrusion. Then loading the lateral interference phase who perpendicular to the previous phase, as shown in Figure 2 (c). At last, the large-area nanoparticle periodic array prepared by the orthogonal processing of phase in both directions, as shown as Figure 2 (d), the size of nanoparticle is 360nm.

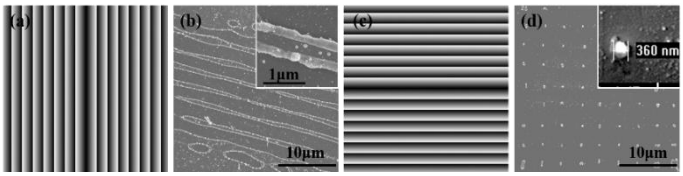

Figure 2: (a), (c) Two-beam interference phase pattern with directions perpendicular to each other; (b), (d) SEM images of the surface structure of the Au film after successively loading mutually perpendicular interference phases.

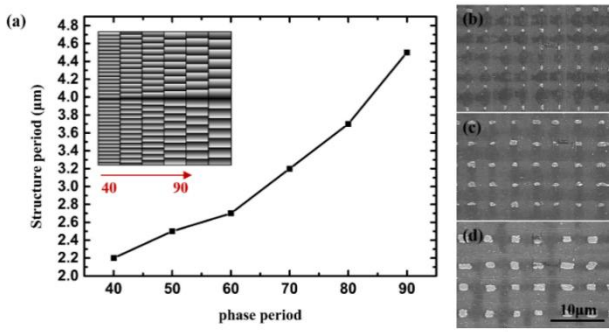

Figure 3: (a) the change in the structural period when the phase period changes from 40 to 90; (b-d) SEM image of Au nanoparticle periodic array with a phase pattern period of 40.70.90, respectively.

The Au film sample is double-exposed by successively loading the interference phases perpendicular to each other, then the large-area periodic Au nanoparticle array structure can be

directly obtained. The period of Au nanoparticle array can be changed by adjusting the gray period of the phase pattern (the number of pixels required for a set of bright stripes) loaded by the SLM to adjust the incident angle of the two interference lights to change the period of the interference fringes. Figure 3(a) shows the change in the structural period when the phase period changes from 40 to 90. The larger the phase period is, the smaller the incident angle of the two beams is formed, and the longer the fringe period formed after the interference, so the longer the structural period formed by the action of the Au film is. When the phase period is 40, the structural period is 2.2 μm; when the phase period is increased to 90, the structural period is increased to 4.5 μm. Figure 3 (b-d) shows SEM image of large-area Au nanoparticle periodic array formed by double-exposure processing Au film with a phase pattern period of 40.70.90, respectively. The loaded phase period is 40, the interference laser energy is 6.5 mW, and the number of laser pulses is 1.

Further verification of the regulation of laser energy on the morphology and size of Au nanoparticles. Figure 4(a) shows the change in size of a single Au nanoparticle, in the case of a single pulse with a phase period of 40 and laser energy change from 3 mW to 6.5 mW, the size decreases as laser energy increases. The illustration in Figure 4(a) shows the SEM image of a single Au nanoparticle. When the laser energy increases, the interaction range with the Au film increases, resulting in more Au film removal, smaller area retention. In addition, the thermal effect of the deposition exacerbates the dewetting and recast layer phenomenon, therefore the size of the retained Au film is kept smaller and has a tendency to gather toward the center, when the laser energy is 6.5 nm, the Au film pattern size is 721 nm.

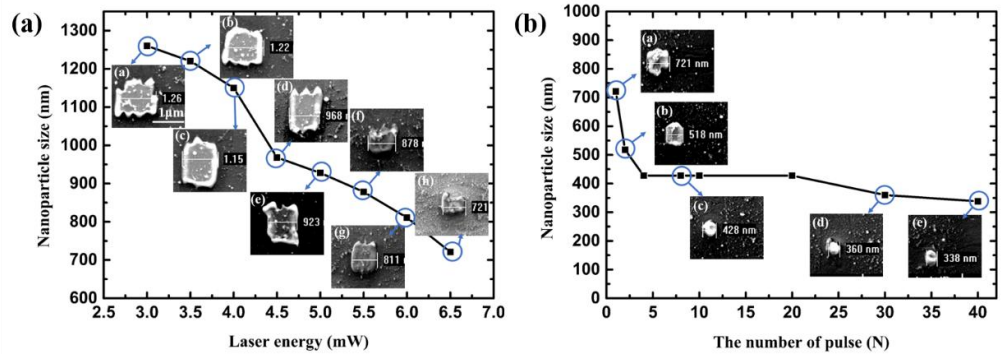

Figure 4: (a) the change in size of a single Au nanoparticle with the laser energy change from 3 mW to 6.5 mW. (b) The size and morphology of Au nanoparticles vary with the number of pulses.

Due to the single-pulse processing, the laser and Au film have a very short action time, the process has been completed without the crystal lattice being heated, resulting in a small thermal effect. Therefore, the Au film pattern remains in the square after laser removal, and does not aggregate into a spherical shape. In this paper, by increasing the number of pulses, the laser energy is effectively precipitated, and the thermal effect accumulation is enhanced to obtain the ideal shape of the Au nanoparticles. The size and morphology of Au nanoparticles vary with the number of pulses as shown in Figure 4(b), the loaded phase period is 40 and the laser energy is 6.5 mW. When the number of pulses increases from 1 to 4, the shape of the Au pattern changes rapidly from square to spherical, this is due to the accumulation of thermal effects caused by the increase in the number of pulses, which causes the edge of the Au pattern dewetting, the liquid phase material recrystallizes to form a sphere under the action of extrusion and surface tension, and the size also drops to 428nm rapidly. When the number of pulses continues to increase until 40, the morphology of Au nanoparticles does not change significantly, and the size decreases to 338nm slightly, because the Au nanoparticle size is smaller than the interference laser irradiatable region, the laser cannot directly act on the Au nanoparticle, and the silica substrate has poor thermal conductivity and the

laser energy transfer effect is not good. Therefore, further increasing the number of pulsed lasers has limited contribution to the regulation of Au nanoparticle size.

The above explores the effects of laser energy and pulses number on the morphology and size of the nanoparticles, demonstrating that high-energy multi-pulses help to form spherical and small-sized nanoparticles. At the same time, the nanoparticle size can be controlled by adjusting the phase pattern period, the SEM image of Au nanoparticle is shown in Figure 5(a-c), in which laser energy is 6.5 mW, pulses number is 30 and the loaded phase pattern periods are respectively 40,70,90, the particle sizes are 360 nm, 486 nm, and 532 nm, respectively. The SLM-based interference femtosecond laser preparation method can realize flexible and controllable Au nanoparticle size.

In addition, for the Au pattern which does not aggregate into a spherical shape under low laser energy, this paper proposes a method of assisting muffle furnace heating to realize the morphological transformation of Au pattern to Au nanoparticles. Figure 5(d-e) shows the results of the interference processing in the case where the phase period is 40, and the number of pulses is 30, and the laser energy is respectively 4.5 mW and 3 mW. Figure 5(d) Au pattern size is about 600-700 nm, the shape is almost circular but does not present a sphere, Figure 5(e) Au pattern size is about 900-1000 nm, showing a thin intermediate, thick surrounding square. The structure of Figure 5(d-e) was placed in a muffle furnace at a temperature of 800° for two hours and naturally cooled to obtain the structural morphology as shown in Figure 5(f-g), respectively. Au pattern in Figure 5(d) is heated by high temperature and converted from a solid phase material to a liquid phase material. Due to the surface tension, the liquid phase material will self-assemble into sphere, and after cooling, it will recrystallize into the Au nanoparticle shown in Figure 5(f), the diameter is about 500nm. However, due to the unique structure thin in the middle and thick around of Au pattern in Figure 5(e), heat unevenness occurs when it is heated, the middle temperature is higher than the surrounding temperature of Au pattern. The liquid metal movement speed is affected by the temperature gradient, which is easier to move from the high temperature region to the low temperature region[15-16]. Therefore, the Au pattern will split from the middle to the periphery, self-assembling into two or more nanoparticles as shown in Figure 5(g).

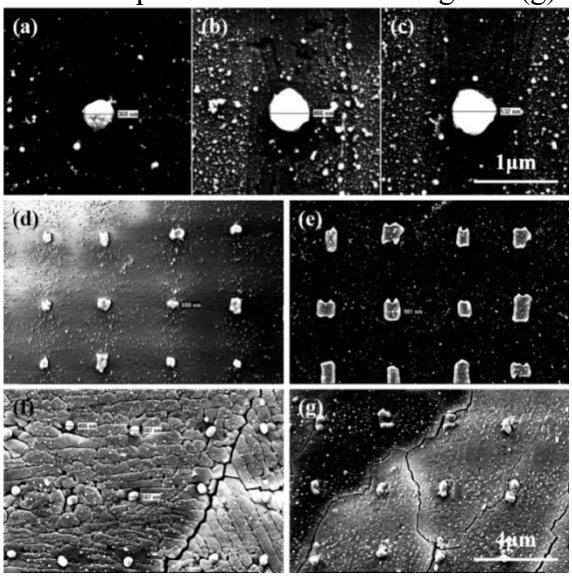

Figure 5: (a-c) the SEM image of Au nanoparticle with different phase pattern periods, respectively 40, 70, 90. (d-e) the SEM image of Au nanoparticle with different laser energy, respectively 4.5 mW and 3 mW. (f-g) the SEM image of Au nanoparticle which have been placed in a muffle furnace at a temperature of 800° for two hours.

4. Conclusion

In conclusion, we propose a simple and efficient method for preparing large-area periodic Au nanoparticle arrays by dual-beam interference femtosecond laser by spatial light modulation. The Au film sample is double-exposed by successively loading the interference phases perpendicular to each other, then the large-area periodic Au nanoparticle array structure can be directly obtained, which only one step. This method not only adjusts the period of the nanoparticle array through the phase period, but also flexibly regulates the size of the nanoparticles by the laser energy and the number of pulses, the minimum nanoparticle diameter achieved in this paper is 338 nm. In addition, we also analyse the mechanism of Au pattern morphological changes during the heating of the auxiliary muffle furnace, which provided a new idea for the preparation of gold nanoparticle arrays.

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