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Additive and subtractive manufacturing of gold micro/nanostructures by using laser trapping and ablation

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A B S T R A C T

Gold micro/nanostructures were additively manufactured by using laser trapping of gold nanoparticles in an aqueous solution. Gold wire composed of sintered compacted nanoparticles with spatial resolution of 470 nm was fabricated. Influence factors for wire fabrications were also studied systematically. In order to investigate the fabrication capacity of this technology for three-dimensional structures, several microstructures were fabricated. A new additive and subtractive hybrid manufacturing technology by using laser trapping and ablation was proposed and realized to further improve the spatial resolution of the fabricated structures. A gold microring with line width of 37 nm was fabricated through precisely controlling fabrication parameters. This hybrid manufacturing technology has great application prospects in the fabrication of high spatial resolution nanostructures.

1. Introduction

Gold micro/nanostructures have attracting characters compared with other metal micro/nanostructures. They have been extensively used in micro/nano-electronics [1], plasmonic optical devices [2,3], metamaterials [4], and surface enhanced Raman scattering [5,6]. Usually, gold and other metal micro/nanostructures are fabricated by combining photoresist lithography with metal deposition or etching [7,8]. This fabricating process is complicated, inefficient, and costly. A few of metal direct-writing technologies which can overcome these disadvantages have been developed in the past two decades [9–11]. Compared with other direct-writing technologies, laser trapping fabrication is a technology with simple principle and process [12,13]. Bahns et al. have fabricated C-Au microstructures with spatial resolution of about 3 μm by using this technology [14]. Xu et al. reported fabricating gold wires with about 600 nm spatial resolution by using femtosecond laser trapping [15]. However, spatial resolution of fabricated structures still need to be improved, and influencing mechanisms of different parameters have not been systematically investigated. Three-dimensional gold micro/nanostructures have more significant applications, but their fabrication by using laser trapping is still a challenge. In this paper, the influence of femtosecond laser wavelength to laser trapping additive manufacturing of gold micro/nanostructures was systematically investigated. Gold micro/nanostructure with spatial resolution of 470 nm was additively manufactured using a 400 nm femtosecond laser. Several 3D microstructures which can embody the fabrication ability of this technology were also fabricated.

Laser ablation is a widely used technology for microstructure fabrication in laser process field. A lot of metallic micro/nanostructures have been fabricated by using this technology [16,17]. By combining the two-photon polymerization and multiphoton ablation, Xiong et al. have reported simultaneous additive and subtractive of polymer micro/nanostructures [18]. The spatial resolution is one of the most significant parameters for the fabricated gold micro/nanostructure. In order to further improve that of the laser additive manufacturing with laser trapping, a new additive and subtractive hybrid manufacturing technology by combining laser trapping with laser ablation was investigated and realized in this paper. A gold microring with line width of about 37 nm, about one-eleventh of the laser wavelength at 400 nm, was fabricated by using this hybrid technology.

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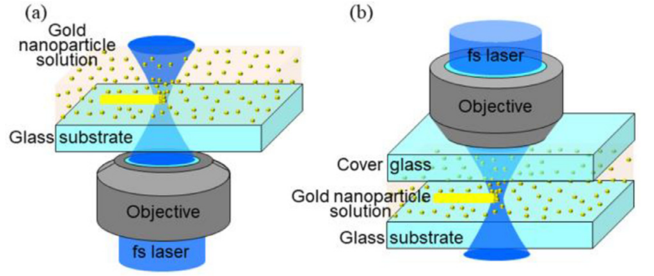

Fig. 1. (a) Schematic diagram of inverted laser irradiating optical experimental setup for additive and subtractive manufacturing of gold micro/nanostructures. (b) Schematic diagram of upright laser irradiating optical experimental setup for additive manufacturing of three-dimensional gold micro/nanostructures.

2. Materials and experimental setup

The gold nanoparticle solution was synthesized referring to a reported method (see the supplementary material for preparation of gold nanoparticles) [19]. Average diameter of synthesized gold nanoparticles is 21 nm with concentration of about 9 mg/ml. Fig. 1 shows the schematic diagram of the experimental setup for laser additive and subtractive manufacturing. As shown in Fig. 1(a), an inverted laser irradiating optical structure was adopted for two dimensional micro/nanostructure fabrication. A expanded laser beam coming from the laser source entranced the objective lens (Olympus, oil immersed, 100 ×, 1.49). It was focused at the interface of the gold nanoparticle solution and glass substrate. In the fabrication process, gold nanoparticles in the laser light were driven to the laser focus and printed on the glass substrate. The inverted laser irradiating optical structure can favor the fabrication of gold micro/nanostructures with high spatial resolution. However, an upright laser irradiating optical structure was applied to fabricate three-dimensional structures [Fig. 1(b)] in order to avoid the shielding effect caused by the fabricated structure. The convergent femtosecond laser from objective lens passed through the cover glass and gold nanoparticle solution, and was focus on the top surface of the glass substrate. Micro/nanostructures were fabricated on the top surface of the glass substrate. After fabrication, the glass substrate was rinsed with ultrapure water and dried naturally in ambient air. The fabricated gold micro/nanostructures are strongly bonded to the glass substrates. Their morphology can't be changed even in ultrasonic washing process. In the experiment, a piezostage (Physik Instrumente, P-563.3CD) was employed to move the specimen and realize fabricating the two or three dimensional patterns. A femtosecond laser (Spectra Physics, MaiTai HP 100 fs, 80 MHz) and its nonlinear frequency converter (Spectra Physics, Inspire Auto 100) were used as laser sources.

3. Results and discussion

Fig. 2(a) shows the calculated trapping force in radial direction for an 800 nm femtosecond laser with a power of 1 mW at focal spot (see the supplementary material for calculations on force caused by different laser). The position of r=0 nm, z=0 nm is the center of laser focus at the interface of solution and glass substrate. The laser beam propagates in vertical upward (positive z) direction in gold nanoparticle solution as shown in Fig. 1(a). Trapping forces F_r in radial direction all point to the negative r direction, the maximum trapping force is 5.30×10^{-15} N at the position of r=110.2 nm, z=0 nm. Laser trapping forces are greatly influenced by the laser wavelength. With laser wavelength changes from 800 to 400 nm, the trapping force increases rapidly. As shown in Fig. 2(b), the maximum trapping force is 8.94×10^{-15} N for the 700 nm laser with a power of 1 mW at focal spot, and it is about 1.7 times that of at 800 nm. However, the maximum trapping force is 3.83×10^{-14} N for a 400 nm laser with the same power at focal spot [Fig. 2(b)], which is about 7.2 times that of 800 nm laser. In the laser trapping process, the

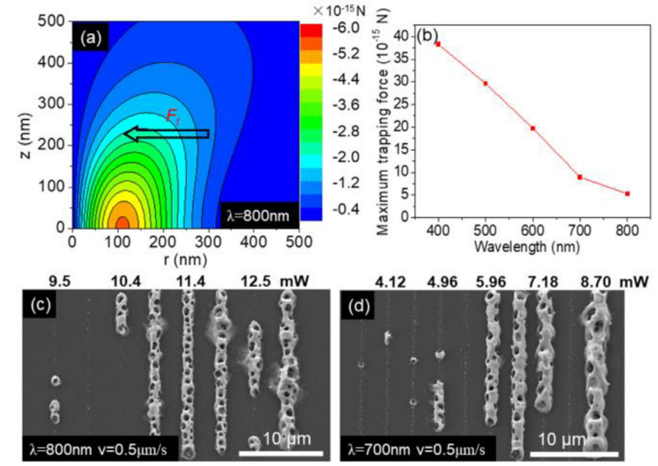

Fig. 2. (a) Trapping force in radial direction caused by laser light with a power of 1 mW at focal spot. (b) The maximum trapping force vs laser wavelength. (c) SEM image of gold wires additively manufactured using an 800 nm laser with incident laser power from 9.5 to 13.2 mW. (d) SEM image of gold wires additively manufactured using a 700 nm laser with incident laser power from 3.76 to 8.70 mW.

local heating caused by the laser absorptions of nanoparticles can also give rise to thermal convection, and it helps to transport nanoparticles to the laser trapping [14,20,21]. The thermal convection and laser trapping force both make contributions to the additive manufacturing of gold micro/nanostructures. Fig. 2(c) is the SEM image of gold wires additively manufactured by using the 800 nm femtosecond laser. Laser power was changed from 9.5 to 13.2 mW with a scanning speed of 0.5 μm/s. Most of fabricated wires were composed of dispersed nanoparticles when the laser power was equal to or small than 10.4 mW. Several short wires were also found on scanning tracks. Relatively continuous wires were fabricated with laser power greater than 10.4 mW. However, there were many holes on the fabricated wires, which were caused by thermal effect at high laser power. This phenomenon greatly influenced the spatial resolution, accuracy and morphology of the fabricated gold structures, and the stability of fabrication condition. Fig. 2(d) shows gold wires additively manufactured using the 700 nm femtosecond laser with power changing from 3.76 to 8.70 mW and the scanning speed of 0.5 μm/s. Fabricated wires were also mainly composed of dispersed nanoparticles when the laser power was smaller than 5.96 mW. However, there were more gold nanoparticles on scanning tracks. When the laser power was equal to or bigger than 5.96 mW, continuous wires could be fabricated. The threshold laser power for fabricated continuous wire was much smaller than that of the 800 nm laser. There were also less holes caused by laser thermal effect on the fabricated wires. Therefore, the short wavelength laser favors reducing the laser power for fabricating continuous wires and improving the fabricated wire morphology. This phenomenon identifies well with the calculation on the trapping force shown in Fig. 2(b).

According to Fig. 2(b), a femtosecond laser beam with a wavelength of 400 nm from a nonlinear frequency converter was used to trap nanoparticles and additively manufacture gold wires. Fig. 3(a) shows gold wires fabricated with laser power from 2.50 to 5.47 mW. The scanning speed was 1 μm/s. when the laser power was 3.52 mW or less, fabricated wires were still composed of scattered nanoparticles. However, there were much more nanoparticles on tracks, compared with those fabricated with the 700 nm and 800 nm lasers. Account of nanoparticles on the track also had obvious increase with the increase of laser power. Continuous gold wires composed of sintered compacted nanoparticles were fabricated when the laser power was bigger than 3.52 mW. They also had small holes, but their spatial resolution, accuracy and morphology were much better than those of wires fabricated with longer

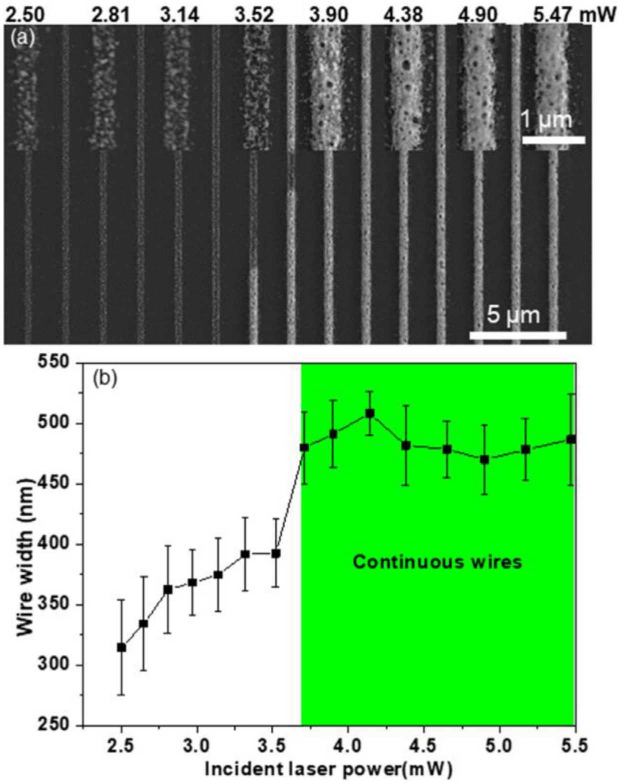

Fig. 3. (a) SEM image of gold wires additively manufactured using a 400 nm laser with incident laser power from 2.50 to 5.47 mW. (b) Gold wire width vs incident laser power of the 400 nm laser.

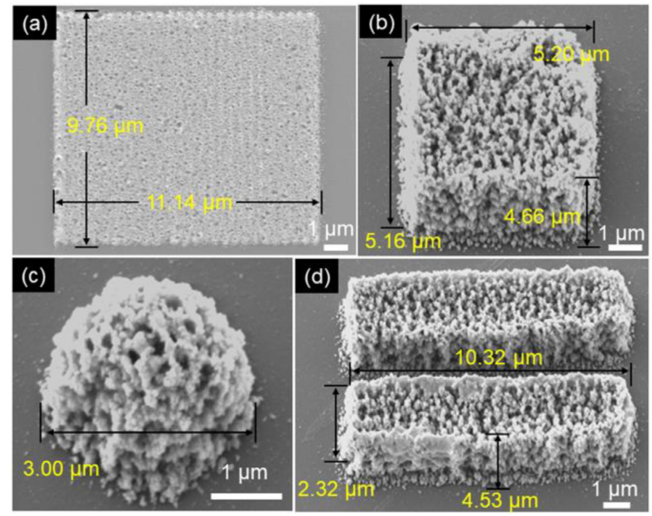

Fig. 4. (a) SEM image of two dimensional rectangular plane microstructure fabricated with an incident laser power of 4.31 mW and a scanning speed of 1 μm/s. (b) SEM image (25° tilted view) of gold cube microstructure fabricated with an incident laser power of 5.69 mW and a scanning speed of 1 μm/s. (c) SEM image (25° tilted view) of gold hemispheroidal microstructure fabricated with an incident laser power of 6.67 mW and a scanning speed of 1 μm/s. (d) SEM image (25° tilted view) of gold cuboid microstructures fabricated with an incident laser power of 6.67 mW and a scanning speed of 1 μm/s.

wavelength lasers. The dependency of gold wire width on incident laser power of the 400 nm laser is shown in Fig. 3(b). The wire width increases with laser power when the laser power is equal to or smaller than 4.14 mW, but has an obvious decrease with laser power changing from 4.14 to 4.90 mW. The increase of fabricated wire width under smaller laser power may mainly be caused by the increase of trapped nanoparticle amount. The decrease of wire width at laser power from 4.14 to 4.90 mW should mainly arise from compacted combination between nanoparticles caused by the bigger trapping force and melting of nanoparticles at high laser power. The increase of wire width with laser power greater than 4.90 mW is also resulted from the increase of trapped nanoparticle amount. Finest gold wires composed of scattered nanoparticles and sintered compacted nanoparticles with average widths of 314 nm and 470 nm were obtained, respectively. With application of a higher gold nanoparticle concentration solution, wires composed of sintered compacted nanoparticles with much smaller widths may be additively manufactured by using lower laser power.

As shown in Fig. 4(a), the two dimensional rectangular plane microstructure with length of 11.14 μm and width of 9.76 μm was fabricated to investigate the manufacturing ability of additive manufacturing for large area microstructure. The irradiated laser power was 4.31 mW with scanning speed of 1 μm/s. Many holes were found on the fabricated rectangular plane. However, the rectangular plane was intact. Therefore, gold three-dimensional structures can be additively manufactured layer by layer by using trapping of gold nanoparticles in solution. As shown in Fig. 1(b), an upright laser irradiating optical structure in which the laser irradiates the substrate from the top is used for fabrication of three-dimensional structures. Fig. 4(b) shows the 25° tilted view of a gold cube microstructure fabricated with an incident laser power of 5.69 mW and a scanning speed of 1 μm/s. Length, width and height of the cube microstructure are 5.20, 5.16 and 4.66 μm, respectively, which are in good consistency with the designed sizes of 5.0, 5.0 and 5.0 μm. The cube microstructure is composed of sintered gold nanoparticles (see the supplementary material for EDX mapping) with a lot of holes between them. A hemispheroidal microstructure [Fig. 4(c)] and two cuboid microstructures [Fig. 4(d)] were also fabricated by using this technology. They are all fabricated with a laser power of 6.67 mW and a scanning speed of 1 μm/s. The diameter of the hemisphere is 3.00 μm. Length, width and height of cuboid microstructures are 10.32, 2.32 and 4.53 μm, respectively. They are also in good consistency with designs. The hemispheroidal microstructure and cuboid microstructures have similar roughness with the cube structure. These microstructures may have significant applications in SERS and catalysis. More complicate three-dimensional microstructures with neat surface could be fabricated by using the solution with higher concentration of gold nanoparticles and a better experimental setup to avoid the laser light pass through the whole solution layer before arriving the glass substrate.

In gold micro/nanostructure additive manufacturing process, nanoparticles in solution are trapped by laser light and guided to the laser focal center. They combine and form micro/nanostructure on the glass substrate as shown in Fig. 5(a). However, the formed micro/nanostructure blocks the focused laser light which irradiates from the glass substrate and causes the absorption of laser light. The absorbed laser light gives rise to thermal effect on the fabricated micro/nanostructures. If the fabricated micro/nanostructures are exposed to the laser light with an enough exposed dose, its center where is exposed with the highest intensity because of Gauss distribution of laser light will be melted and got rid of by the thermal effect [Fig. 5(a)]. This new additive and subtractive hybrid manufacturing technology provides a method for fabricating gold micro/nanostructure with higher resolution. Fig. 5(b) shows the SEM image of a two-dimensional microring array fabricate by using this technology. Each microring was fabricated with an incident laser power of 5.47 mW and an exposed time of 4000 ms. They have good consistency in morphology, but there are also several microrings having many residual nanoparticles at their center. A high resolution SEM image of the fabricated microring is shown in Fig. 5(c). The diameter of microring is 910 nm. The minimum width of microring line is 143 nm, but the maximum of that is 192 nm. Therefore, it fluctuates a little big. In order to reduce the fluctuation of micror-

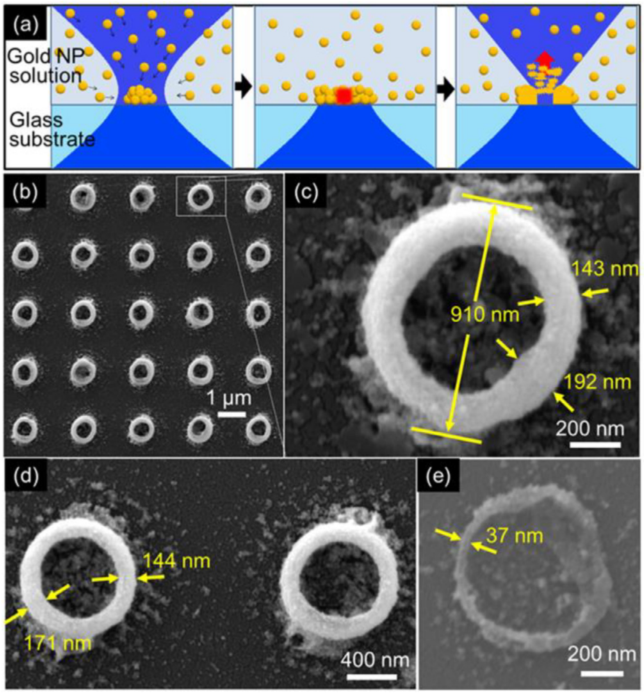

Fig. 5. (a) Schematic diagram of additive and subtractive manufacturing by using laser trapping and ablation. (b) SEM image of gold microrings fabricated using additive and subtractive manufacturing with an incident laser power of 5.47 mW and an exposed time of 4000 ms. (c) High-resolution SEM image of the fabricated gold microring. (d) SEM image of gold microrings fabricated using additive and subtractive manufacturing with an incident laser power of 5.77 mW and an exposed time of 4000 ms. (e) SEM image of gold microring fabricated using additive and subtractive manufacturing with an incident laser power of 9.40 mW and an exposed time of 500 ms.

ing line width, several microrings were fabricated with a bigger laser power of 5.77 mW at the same exposed time. Fig. 5(d) is the SEM image of fabricated microrings. The minimum and maximum width of the microring are 144 nm and 171 nm, respectively. Compared with microrings shown in Fig. 5(b) and (c), the fluctuation is much smaller. These fabricated microrings has application at plasmonics, SERS and metametials [22–25]. Kuchmizhak et al. and Syubaev et al. have reported the fabrication of similar gold microrings by nanosecond laser ablating and argon-ion beam etching the pre-deposited gold film. Toriyama et al. reported the fabrication of silver rings by using multiphoton photoreduction of pre-coated precursor film with a circular polarization femtosecond laser beam, and accompanied by developing with an alkaline NaOH solution. Here, the gold microrings were directly fabricated by using a hybrid method of laser trapping and ablation in the gold nanoparticle solution. This is a simple, flexible and environmentally friendly method, and it is also beneficial to the fabrication of more complicated micro/nanostructures, even three-dimensional structures.

Widths of fabricated microring lines were still bigger than 100 nm when they were fabricated with a laser power of about 5 mW and an exposed time of 4000 ms. However, microrings with line width smaller than 100 nm could be obtained by precisely regulating the irradiate laser power and exposed time to control the additive and subtractive manufacturing process of laser trapping and ablation. Fig. 5(e) shows the microring with the smallest line width of 37 nm fabricated with an incident laser power of 9.40 mW and an exposed time of 500 ms. Although morphology of this microring was not very well, and the width of microring line fluctuated largely at different parts, this fabricated microring provides an example for fabricating the gold micro/nanostructure with feature size at nanoscale by using additive and subtractive hybrid manufacturing of laser trapping and ablation. This method can also be used in fabrication of other gold nanoscale structures with more complexity.

4. Conclusions

In conclusion, gold micro/nanostructure with spatial resolution of 470 nm was additively manufactured by using laser trapping of gold nanoparticles in aqueous solution. A new additive and subtractive hybrid manufacturing technology by using laser trapping and ablation was investigated to further improve the spatial resolution of the fabricated structures. Gold microring with line width of 37 nm, which is one-eleventh of the used laser wavelength, was fabricated through precisely controlling fabrication parameters. This result exhibits the potential of this technology in high spatial resolution gold and other metallic nanoscale structure fabrication. Several three-dimensional gold microstructures were fabricated by using additive manufacturing of laser trapping, and the fabricated structures demonstrate the fabricating capacity of this technology for three-dimensional structures. More complicated and accurate three-dimensional micro/nanostructures can also be fabricated by further improving the experimental setup and gold nanoparticle solution. The fabricated structures have significant applications in SERS, micro/nanoelectronics, MEMS, and catalysis. This work also provides a new additive and subtractive hybrid manufacturing method for fabrication of high spatial resolution metal nanostructures and a protocol for fabrication of three-dimensional metal microstructures by using laser trapping.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.optlaseng.2022.106959.

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