Laser Direct Fabrication of Three-dimensional Microstructures Using Photocatalyst Nanoparticles

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Abstract:
The purpose of this research is to develop a new concept of micromachining technique based on photocatalysis, allowing us to fabricate three-dimensional (3-D) microstructures. In order to verify the feasibility of the proposed technique, a microstructure fabrication system with in-process visualization units was developed and several experiments were performed. A SEM-EDX analysis showed that photocatalytic deposition of silver can be performed only at the position of the beam waist of the converging laser beam with the wavelength of 405 nm in silver nitrate solution by using the brookite TiO_2 nanoparticles. And several demonstrational fabrication experiments suggested that the proposed method has a possibility of fabricating complex functional 3-D microstructures with a size scale of several 10 μm.

Keywords: Micromanufacturing processes, Three-dimensional micro structures, Laser direct fabrication, Photocatalyst

1. Introduction

Recently, micromachining technology has been developing along with increasing demand. In particular, micro devices such as Micro Electro Mechanical System (MEMS), Micro Total Analysis System (μ-TAS) and microscopic optical devices as typified by a photonic crystal are in huge demand. So many novel 3-D microstructure fabrication methods, having a potential of fabricating these functional micro devices, have been developing based on various principles [1-3]. For the purpose of realizing such a micromachining method, we propose a new concept of microstructure fabrication technique, which is characterized by reduction of metal ions using photocatalyst nanoparticles, allowing us to directly fabricate 3-D metal microstructures by using a low power continuous wave laser [4]. In this paper, in order to verify the feasibility of the proposed concept, a basic 3-D microstructure fabrication system based on the proposed principle was developed and several basic experiments analyzing the fabrication characteristics and fabricating complex 3-D microstructures were carried out.

2. Concept of Laser Direct Fabrication using Photocatalyst Nanoparticles

Our propoosed microfabrication technique is based on the photocatalytic oxidation-reduction (redox) reaction. When a photocatalyst absorbs light energy that is greater than its bandgap energy, electrons in the valance band transfer to the conduction band. In this study, we selected a TiO_2 photocatalyst [5-6], because it is very active and stable throughout the redox reaction. TiO_2 absorbs light with wavelength that is shorter than about 400nm, and then it generates pairs of holes and electrons. The holes are so oxidative that they can break apart the water molecules to form hydrogen gas and hydroxyl radicals. And the electrons can reduce oxygen molecules to form super oxide anions (Fig. 1). If excitation of TiO_2 occurs in ionic solution of noble metal, ionicity of which is lower than H^+, reduction of the metal ions is possible. Actually, it was reported that when TiO_2 was illuminated with UV-light, it caused deposition of metal, such as silver [7] and platinum [8]. However, the conventional microfabrication techniques using TiO_2 photocatalysis was limited to be 2-D microfabrication [8-9].

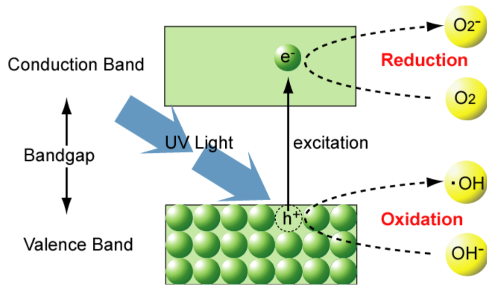

Figure 1: Photocatalytic mechanism.

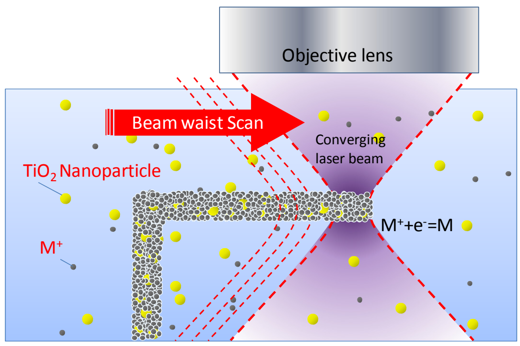

Figure 2: Concept of 3-D microstructure fabrication by photocatalyst nanoparticles.

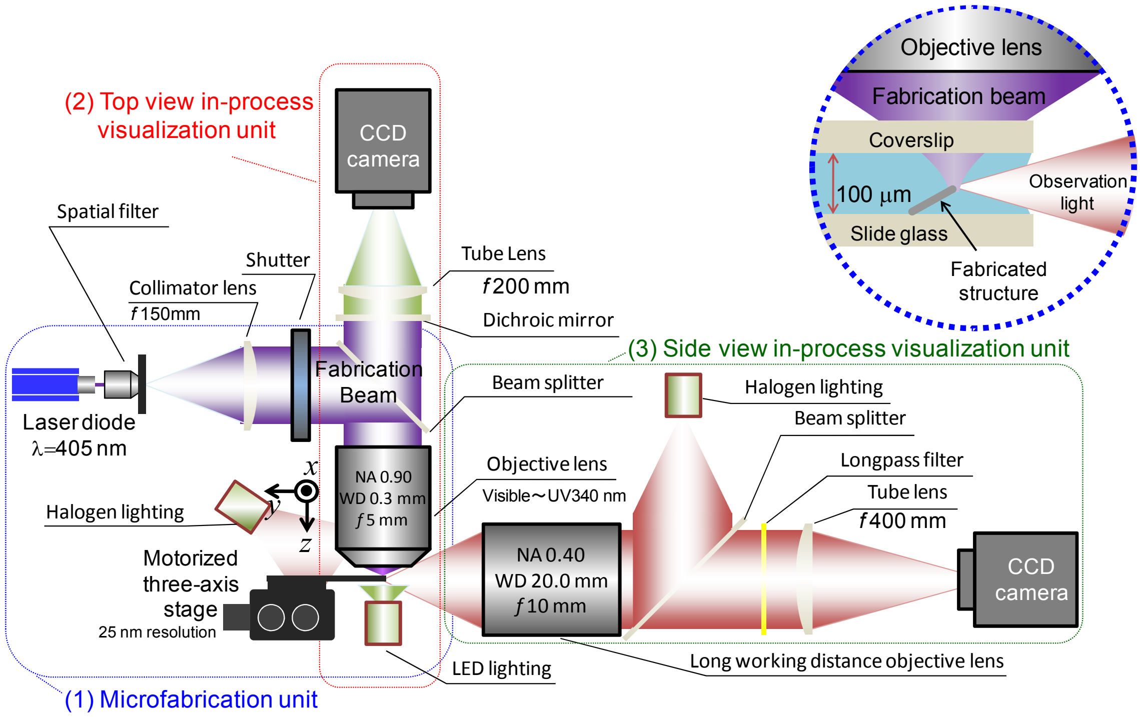

Figure 3: 3-D microstructure fabrication system by photocatalyst nanoparticles.

Figure 2 shows the concept of our proposed method. In order to achieve 3-D microfabrication, we used suspension of TiO_2 nanoparticles. If the TiO_2 nanoparticles in the metal ion solution are three-dimensionally locally excited by a converging laser beam, the photocatalytic redox reaction of TiO_2 nanoparticles causes a cluster of metal to appear just at the localized light energy in the suspension. In this case, by scanning this 3-D localized light energy in the 3-D space, it is expected to fabricate the desired complex 3-D metal microstructure as the laser direct writing method.

3. Development of 3-D Microstructure fabrication System using Photocatalyst Nanoparticles

In order to verify the concept of the proposed method, a basic 3-D microstructure fabrication system based on the proposed principle as outlined in the previous chapter was developed. This microfabrication system mainly consists of a microfabrication unit (1), a top view in-process visualization unit (2), and a side view in-process visualization unit (3) as shown in Fig. 3. The microfabrication unit (1) is mainly consisting of a laser diode with 405 nm wavelength as a light source (LDM Series Blue, Omicron Laserage, 55 mW), high-power objective lens with a numerical aperture of 0.90, and a motorized three-axis stage with about 100 nm positioning accuracy. This unit was designed so that laser spot, which causes photocatalytic reduction locally inside the TiO_2 nanoparticles suspension, could be automatically manipulated in all three-directions under computer control. By sharing the high-power objective lens, the top view in-process visualization unit (2) allows us to observe the fabricated structures with the magnification of 40 times from above. On the other hand, the side view in-process visualization unit (3), by using a

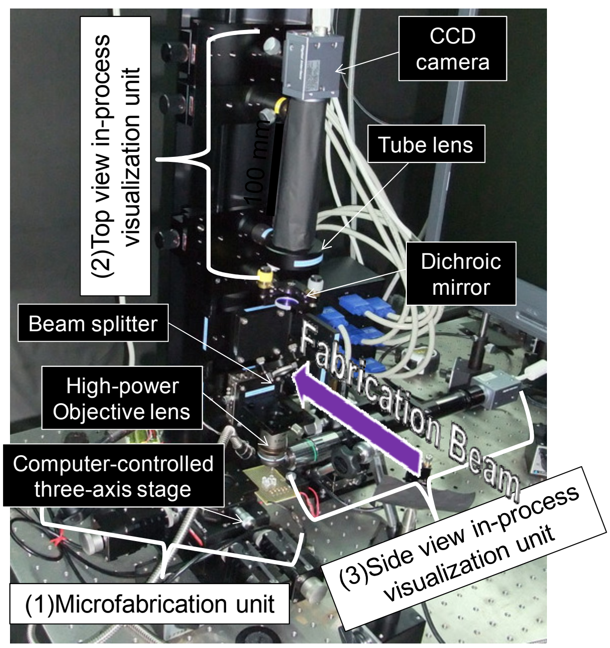

Figure 4: Photograph of developed 3-D microstructure fabrication system.

long working distance objective lens and a tube lens with the focal length of 400 mm, allows us to observe the fabricated structures with also 40 times from side. By both in-process visualization units, the microfabrication process can be microscopically observed. The fabrication region was set between a glass substrate and a coverslip with a gap of about 100 µm, in which the metal ion solution including TiO_2 nanoparticles is maintained by surface tension (upper right, Fig. 3). Figure 4 indicates the photograph of the developed system. The whole system is located on a vibration isolation table.

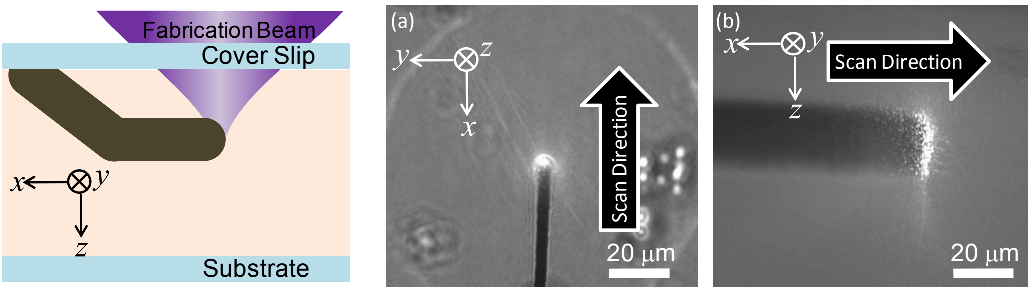

Figure 5: In-process visualization of the proposed microfabrication method.
(a) With the top view unit. (b) With the side view unit.

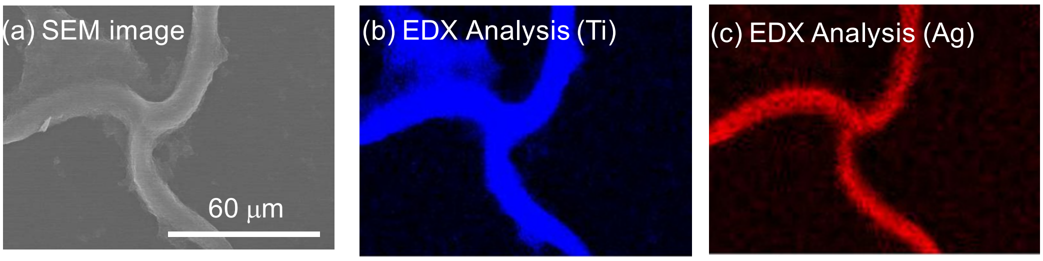

Figure 6: SEM-EDX anaysis. (a) SEM image. (b) EDX image of Ti. (c) EDX image of Ag.

4. Fundamental experimental analysis of deposition characteristics

In order to analyze the basic deposition characteristics of the proposed method, in-process visualization during a beam waist scanning and a SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-ray Spectrometer) analysis for the deposited clusters were performed.

4.1 Geometric property of deposited clusters

In experiments, as the metal ion solution, we employed silver nitrate solution (0.01 mol/l). And as photocatalysts, the brookite TiO_2 nanoparticles with a diameter of 10 nm (0.7 wt %, NTB-1, Showa Titanium Co., Ltd.) were employed. Output of laser before the objective lens and the scan velocity were adjusted at 2.0 mW and 1.0 μm/s, respectively.

Figure 5 shows the microscopically observed images with the in-process visualization unit during the beam waist scan, in which figure (a) and figure (b) mean the observation from above and from side, respectively. From this observation, it was confirmed that fabricated structures can be clearly observed with the developed in-process visualization units and the micro scale structure grew three dimensionally following the beam waist scan in the TiO_2 nanoparticles suspension. In this scanning experiment, 5μm width structure can be fabricated. This size mainly depends on the output of laser and the scanning speed. The vertical size is almost 4 times larger than the horizontal size. This ratio is almost equal to the ratio of three-dimensionally localized light energy of the beam waist caused by the employed objective lens of a numerical aperture. So it can be seen that a size of three-dimensionally localized light energy is one of the main factors deciding sizes of microstructures.

4.2 Material property of deposited clusters

Next, in order to analyze the material property of the fabricated clusters in detail, SEM observation with EDX were performed. From Fig. 6, the deposited clusters are mainly composed silver with titanium. This suggests that the proposed concept based on photocatalytic oxidation-reduction (redox) reaction is confirmed.

5. Demonstrational fabrication of 3-D microstructures

In order to estimate the potential fabrication ability for 3-D microstructures, fundamental demonstrational experiments were carried out. In this paper, we tried to fabricate a chain-like structure for complex 3-D microstructures ability and a micro-rotor for functional 3-D microstructures ability.

5.1 Complex 3-D microstructure fabrication

As an example of complex 3-D microstructures, we tried to fabricate a chain-like structure as shown in Fig. 7(a)-(b). This chain-like structure consists of two triangle elements (each side: 100 μm) and two rectangular elements (long side: 100 μm, short side: 40 μm). In this experiment, it takes about 30 minutes to fabricate the whole micro structures. Figure 7(c)-(d) show the fabricated chain-like structure, rolling over in the suspension flow. From this result, three-dimensionally complex chain-like structure can be also fabricated and the fabricated structures have a certain level of strength with which the structures keep their shape in the suspension flow.

5.2 Functional 3-D microstructure fabrication

As an example of functional 3-D microstructures, we tried to fabricate a micro-rotor structure as shown in Fig.8(a). This micro-rotor structure consists of a ring rotor with a diameter of 50 μm having two fins and a center shaft with a diameter of 12 μm. Figure 8(b) shows the fabricated micro-rotor. In this experiment, the center shaft was fabricated by laminating the deposited clusters. The

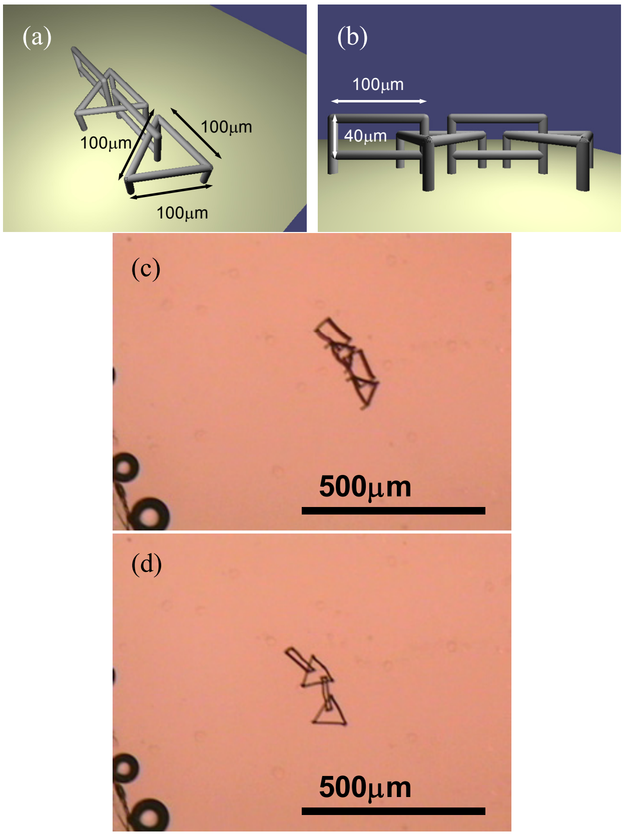

Figure 7: Fabrication of complex 3-D microstructures.
(a)-(b) Chain-like structure.
(c)-(d) Fabricated structure, rolling over in the suspension flow.

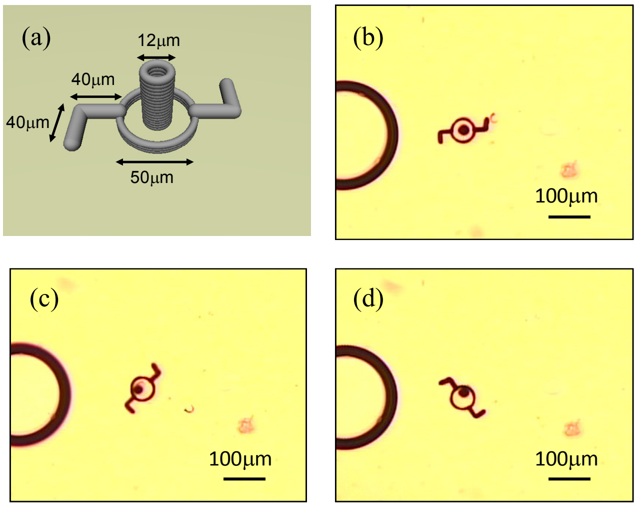

Figure 8: Fabrication of functional 3-D microstructures.
(a) Micro-rotor structure.
(b) -(d)Fabricated structure, which can rotate around the shaft.

fabrication time is also about 30 minutes. Fig. 8(b)-(d) mean that the fabricated rotor can rotate around the center shaft, which was caused by inducing vibration. This result suggests the proposed method allows us to fabricate functional 3-D microstructures.

6. Conclusion

We have proposed the new microfabrication technique based on photocatalytic deposition of silver. In order to verify the feasibility of this method, we developed the microfabrication system designed so that laser spot could be automatically manipulated in all three-directions under computer control, allowing us to fabricate 3-D metal microstructures. A SEM-EDX analysis that the fabrication clusters are composed silver with titanium verified the proposed concept using photocatalytic deposition. And the demonstrational experiments fabricating complex and functional 3-D microstructures suggest the proposed method has a potential ability to fabricate the micro functional structures with a size scale of several 10 μm. More quantitative analyses for both the fabrication characteristics such as the relationship between the scanning speed and the fabrication resolution and the property of fabricated structures such as strength property and electric property will be addressed in the future work.

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