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# Femtosecond Laser Near-Field Reduction for Fabrication of 3D Gold Nanocluster Array Assisted by $MoS_2$ Quantum Dots

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Laser-induced near-field effect, which confines the laser energy in a nano scale region to be enhanced, allows the laser fabrication with a resolution much smaller than the wavelength. Owing to such a high fabrication resolution, the laser-induced near-field fabrication has been attracting much attention as a tool for the surface nanostructuring. In this report, we introduce a novel method based on the laser-induced near-field reduction using a femtosecond laser by which gold nanocluster arrays are formed on substrates with the assistance of self-assembled silica microspheres. In the laser near-field reduction, the incident laser is focused in the vicinity of the backside of the silica microspheres to initiate synthesis of gold nanoparticles, followed by creation of gold nanoclusters by continuous growth of the gold nanoparticles along the silica microsphere surfaces. In addition, laser-treated $MoS_2$ quantum dots are mixed in the gold precursor to increase the reduction efficiency for the formation of spherical gold nanoclusters. The gold nanocluster arrays provide potential applications for plasmonic devices.

**Keywords: laser reduction, microsphere, nanodot, near-field, nanocluster**

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## 1 INTRODUCTION

Near-field induced by microsphere-assisted laser processing is an attractive method to fabricate nanostructures with a high fabrication resolution far beyond the optical diffraction limit. The laser beam can be tightly focused by the microsphere when its diameter is close to the laser wavelength [1]. The near-field is usually confined in much smaller space than the laser wavelength where the electric field is locally enhanced. Based on the near-field effect, the materials can be accurately processed in the near-field with pulsed (nanosecond or shorter pulse) laser irradiation [2]. Till now, the laser near-field ablation utilizing the monolayer of silica microspheres is used for the fabrication of periodic nanostructures for surface nanopatterning. For example, Khan et al. used a contact particle lens array combined with laser scanning to control the wettability of silicon substrate [3]. The ablation depth depended on the laser processing parameters such as number of laser shots, laser pulse energy and laser wavelength [4]. However, there's few works on the femtosecond laser near-field processing to build up three-dimensional (3D) nanostructures by an additive scheme. Recently, we reported that based on femtosecond laser near-field processing, the silver superstructure array could be fabricated by photonic reduction, by which the plasmon peak of array could be tuned by adjusting the period of superstructure. The fabricated silver superstructure array was used for the trace-detection of

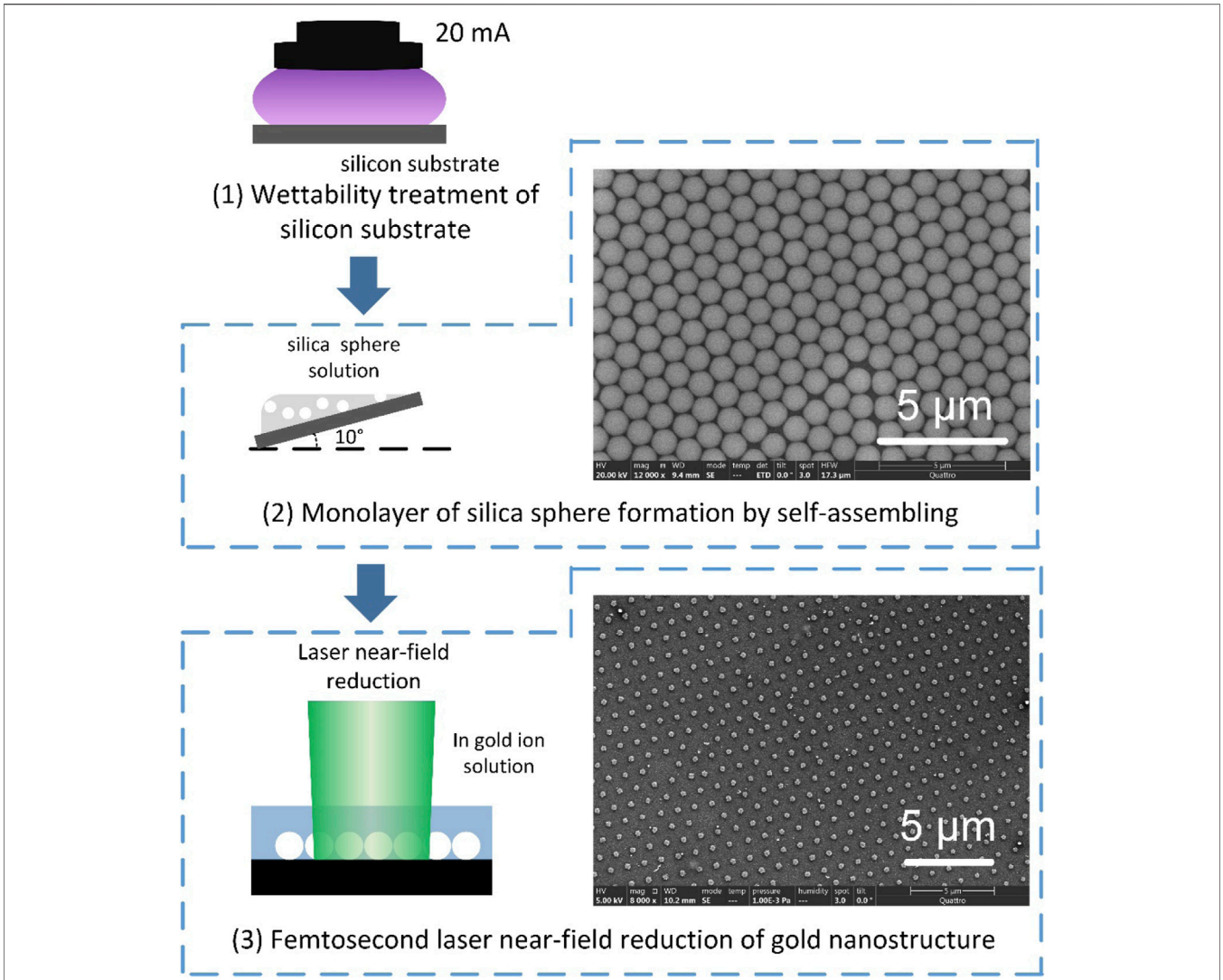


**FIGURE 1 |** Fabrication procedure of the femtosecond laser near-field reduction for formation of periodic gold nanostructures with SEM micrographs of samples at (2) self-assembling of monolayer of silica sphere array and (3) formation of 2D periodic gold nanostrictures.

fluorescent toxic substance (perfluorooctanoic acid) by surface-enhanced Raman scattering (SERS) [5]. The gold superstructure array would generate different plasmon peak to provide better SERS performance for detection of such fluorescent substances. However, the reduction efficiency was too low to build up 3D gold nanostructure by femtosecond laser irradiation.

In this report, we present the laser near-field reduction to build up 3D gold nanoclusters with porosity, which are composed of gold nanoparticles. An array of the gold nanoclusters is fabricated in hydrogen tetrachloroaurate solution with the assistance of self-assembled silica nanospheres. To increase the reduction efficiency and thereby to create spherical gold nanoclusters, laser-treated $MoS_2$ quantum dots are introduced in the gold precursor. We further found addition of citrate and polyvinylpyrrolidone (PVP) enables the anisotropic growth of gold nanoplates on the silica microshperes to create an array of nanoclusters composed of gold nanoplates. The nanocluster array provides potential applications for plasmonic devices.

## 2 METHODS

Trisodium citrate (Junsei Chemical Co. Ltd), PVP (K-90, NACALAI TESQUE, INC), hydrogen tetrachloroaurate tetrahydrate (NACALAI TESQUE, INC) and molybdenum disulfide (SIGMA-ALDRICH) were used for preparation of an aqueous gold ion precursor for laser near-field reduction. Typically, 43 mM $C_6H_5Na_3O_7$ and 20 mM $HAuCl_4$ in 2 ml deionized water were mixed with 80 mg PVP in a glass vessel. First, surface of silicon substrate (n-type, 12.8–15.7 Ω•cm) was treated to improve wettability by plasma etching with a pressure of 20 Pa and a discharge current of 20 mA (PIB-20, Vacuum Device) [**Figure 1**(1)]. Monolayer of silica spheres of 1 μm in diameter

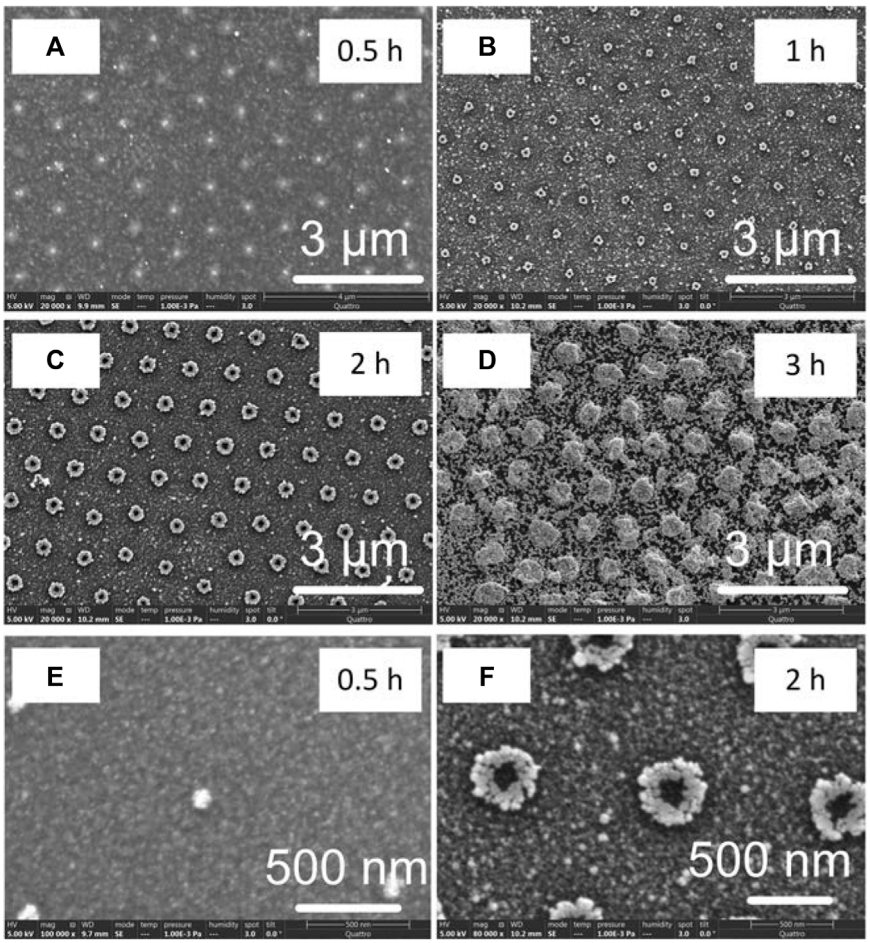


**FIGURE 2 | (A)—(D)** SEM images of periodic gold periodic nanostructures formed at the reduction times of 0.5 h, 1 h, 2 h and 3 h, respectively **(E)** and **(F)** High magnification SEM images of **(A)** and **(C)**, respectively.

(SIGMA-ALDRICH) was self-assembled on the treated silicon substrate [**Figure 1**(2)] which was then immersed in the gold ion precursor for laser near-field reduction. In order to form the monolayer of silica spheres, the substrate was tilted at 10° which illustrated in the previous works [6, 7]. A second harmonic (515 nm) converted from femtosecond (fs) laser with a pulse width of 223 fs and a wavelength of 1030 nm by a lithium triborate (LBO) crystal was loosely focused by a convex lens to achieve a spot diameter of 1 mm on the sample surface [**Figure 1**(3)]. The laser pulse energy and the repetition rate were set at 1 nJ and 1 MHz, respectively. After the laser near-field reduction, the sample was treated with hydrofluoric acid (HF) to completely etch away silica spheres, resulting in formation of gold nanodot or hollow nanocluster arrays. The fabricated gold nanostructure array was observed by an environmental scanning electron microscope (SEM).

## 3 RESULTS AND DISCUSSION

According to Mie theory, the sphere will focus the laser when its diameter is slightly larger than wavelength, otherwise the laser will be scattered. Since the diameter (1 μm) of silica microspheres in experiments is larger than the laser wavelength (515 nm), the laser beam can be focused on the backside of silica microspheres to enhance the electric field in near-field. The photo-induced reduction is confined in the vicinity of backside of silica microspheres because the two-photon absorption takes place for the near-field reduction due to enhanced laser intensity:

$$3C_6H_5Na_3O_7 + AuCl_4^- + H^+ \xrightarrow{2h\nu} 3C_5H_4Na_3O_5 + 3CO_2 + Au + 4HCl \quad (1)$$

Minor reduction by hydrated electrons is also induced by femtosecond laser [8]:

$$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^- \quad (2)$$

According to **Eqs. 1**, **2**, the gold nanoparticles are synthesized at the backside of silica microspheres, forming a nanodot array as shown in a right side photo of **Figure 1**(3). The formed gold nanodots act as the nucleus for the continuous reduction, resulting in the growth of gold

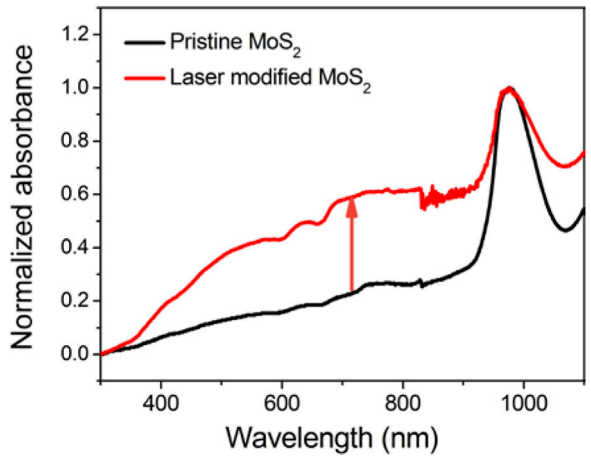


**FIGURE 3 |** Absorption spectra of pristine $MoS_2$ and laser modified $MoS_2$.

nanoparticles along the surface of silica microspheres to create gold nanoclusters [9]:

$$nAu \rightarrow Au_n \tag{3}$$

Geometry of created gold nanostructures can be controlled by the reduction time. **Figure 2** shows gold nanostructure array with different geometries created at the reduction time from 0.5 h to 3 h. The smallest nanodot with a diameter of ~104 nm is generated at 0.5 h (**Figure 2A**), which grows to nanobowl with a diameter of ~800 nm as the reduction time increases to 3h (**Figure 2D**). **Figure 1** E and F show the magnified SEM images of nanodot and nanobowl array. Because the gold nanoparticles are generated at the backside of the silica microsphere, the center of nanodot and nanobowl has a void where the silica microspheres contact to the silicon substrate. As the reduction time increases, the gold nanoparticles grow along the surface of silica microsphere to form the nanobowls. According to **Eq. 3**, the gold nanoparticles are reduced and aggregated in the near-field. Since the nanobowl is composed of gold nanoparticles, it has a porous structure. The growth mechanism of gold nanostructure induced by femtosecond laser was shown in **Supplementary Figure S1**. Due to near-field effect, the gold nanoparticles are synthesized at the backside of silica spheres. The synthesized gold nanoparticles enhance the electric field of incident laser beam due to localized surface plasmon resonance to further grow the gold nanoparticles along the surface of silica sphere. HF etching after entire growth of the gold nanoparticles along the surface of silica sphere eventually leaves hollow nanoclusters. However, the reduction efficiency is not sufficiently high for the creation of gold microsphere because PVP greatly suppresses the reduction of gold ions [10]. To increase the efficiency, $MoS_2$ quantum dots are added to the gold precursor.

It is well known that laser-modified $MoS_2$ drives the reduction of gold ions to gold nanoparticles, resulting from the unbound sulfur formed on $MoS_2$ surface induced by femtosecond laser [11, 12]. The unsaturated active S atoms with dangling bonds have the chemical activity to directly reduce the $Au^{3+}$ ions. 200 μL $MoS_2$ quantum dots (4 wt%) were added into the aforementioned gold ion precursor to increase the efficiency of femtosecond laser-induced near-field reduction. To confirm the effectiveness of laser-modified $MoS_2$, we compared the absorption of pristine $MoS_2$ and the laser-modified $MoS_2$ as shown in **Figure 3**. In laser modification, the $MoS_2$ quantum dots solution was irradiated by 515 nm fs laser for 2 h. The laser fluence and repetition rate were set as same as the conditions for the fabrication of gold nanodot array. After modification, the absorption of $MoS_2$ in the visible region is increased because of a strong surface plasmon resonance (SPR). This increment of SPR in the visible region is attributed to the vacancy-induced free electrons in $MoS_2$, forming the redox pair with $AuCl_4^-$ to allow the spontaneous reduction of gold ions to nanoparticles [13].

Owing to the chemical activity of laser-treated $MoS_2$, the reduction efficiency is highly increased. As shown in **Figure 4A**, an array of periodic gold spheres with a porous structures is generated. For comparison, we also show the gold nanoparticles covering silica microsphere before hydrofluoric acid etching in **Supplementary Figure S2**. The diameter of

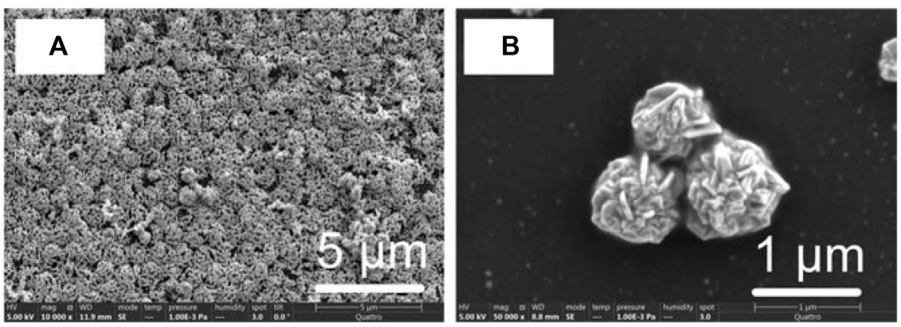


**FIGURE 4 | (A)** SEM image of gold nanocluster array formed at a reduction time of 1 h with the assistance of the laser-treated $MoS_2$ quantum dots **(B)** SEM image of gold nanocluster composed of gold nanoplates.

gold spheres is about one um since the one um silica spheres are used as the template for the femtosecond laser-induced near-field reduction. Therefore, the period of the gold spheres is dependent on the diameter of silicon spheres. In addition, the gold spheres shown in **Figure 4B** are composed of nanoplates, demonstrating the growth of gold nanomaterials with a specific crystal orientation. In the precursor, citrate and PVP are typical capping agents to control the synthesis of gold nanoparticles. The citrate is an ionic capping agent, which allows the crystal growth in 111) plane. Additionally, PVP (~3.6 wt%) selectively blocks the side faces of gold nanoplates in a high concentration to obtain the nanoplates composing nanoclusters [14, 15]. The nanocluster array consisting of an anisotropic structure has the potential applications for the plasmonic devices due to modulation of SPR [5, 16].

## 4 CONCLUSION

In this report, we presented a method of silica microsphere-assisted femtosecond laser near-field reduction for formation of gold nanocluster arrays. Owing to the microsphere, the laser was focused in the vicinity of backside of microspheres to reduce the gold ions. Since the reduction was confined in the near-field, the diameter of gold nanoparticle was about 100 nm (one-fifth of laser wavelength). The period of formed periodic structure was determined by the diameter of silica microsphere. To increase the reduction efficiency, laser-treated $MoS_2$ quantum dots were used to enhance the SPR in the visible regions. In addition, we found the PVP and citrate contributed to the synthesis of nanoplate, enabling creation of a unique feature of nanocluster. The nanocluster array will be of use for the plasmonic device in future work.

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding authors.

## AUTHOR CONTRIBUTIONS

SB conducted the experiments. KO prepared the materials. SB, and KS wrote the manuscript.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fphy.2022.917006/full#supplementary-material

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