Research article

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Shaped femtosecond laser induced photoreduction for highly controllable Au nanoparticles based on localized field enhancement and their SERS applications

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Abstract: Gold nanoparticles (Au NPs) have a wide range of applications because of their localized surface plasmon resonance properties. Femtosecond laser is considered to be an effective method for preparing Au NPs because of its characteristics of ultrashort irradiation periods and ultrahigh intensities. In this study, a novel method is proposed to produce an Au NP-attached substrate using the spatially and temporally shaped femtosecond laser. Laser-induced periodic surface structures (LIPSS) are designed to obtain the localized optical field enhancement, which leads to the femtosecond laser spatially reshaping, enabling the deposition of Au NPs by photoreduction on silicon substrates. The Au NPs prepared by this method exhibit morphological controllability and chemical stability, especially excellent spatial selectivity and uniformity, resulting in the tunable and stable surface-enhanced Raman scattering (SERS) applications. Also, the temporally shaped femtosecond pulses are introduced to further increase the enhancement factors of the SERS. This method successfully achieves the controllable morphology synthesis and selective deposition of Au NPs on the substrate simultaneously, which provides a promising candidate for SERS substrates fabrication, and holds potential applications in optoelectronics, such as molecular detection and biosensors.

Keywords: shaped femtosecond laser; photoreduction; localized field enhancement; Au nanoparticles deposition; surface-enhanced Raman scattering (SERS).

1 Introduction

Noble metal (e.g. gold (Au), platinum, and silver) nanoparticles (NPs) exhibit more favorable plasmon-dominated optical properties than conventional bulk metal because of the resonance of conduction electrons with the incident light [1–3]. This phenomenon is termed as localized surface plasmon resonance [4, 5]. Among the various noble metal NPs, Au NPs have a wide range of applications such as catalysis, molecular detection, and medicine because of their excellent chemical stability [6–8].

So far, much effort has been devoted to produce diverse Au NPs, such as chemical reduction, electrochemical deposition, and film thermal treatment [9–11]. Besides, because of the unique interaction mechanism between femtosecond laser and materials (different from traditional laser or sun light), femtosecond laser created a lot of exciting new possibilities in micro/nano structure fabrication [12–16]. In general, two primary methods (top-down and bottom-up) are currently available for fabricating Au NPs by femtosecond laser. Among these two methods, the top-down approach involves that the pulse laser irradiates the Au target (including bulk, powders, and precursors) through solution. Au NPs are sputtered and then dispersed in the solution [17–19]. In this technique, the laser beam propagates through the solution at first and then irradiates the interface between target and liquid, which occurs complex physical and chemical processes at the same time [20, 21]. The size of the product can be controlled by changing the laser parameters and the solutions. Through this method, small and pure Au NPs are generally yielded, but the morphology controllability of the prepared Au NPs remains limited [22, 23].

In addition, the bottom-up approach can also be utilized to prepare Au NPs. It is a photoreduction process initiated by laser and the solution containing Au³⁺ ions

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and other additives, which always occurs in the region of the laser focus. In the process, the focused laser irradiates the solution containing Au^{3+} ions to form the Au seeds [24, 25]. The seeds are dispersed in the solution and further grown to the Au nanocluster, whose morphology can be controlled under the influence of the surfactants and the surrounding environment [26, 27]. However, some surfactants are difficult to be degraded and are harmful to the environment. Therefore, this method always requires a complicated purification procedure before the specific application [28].

These two main-stream methods both can achieve size-controllable Au NP preparation. However, both of the aforementioned methods meet a common challenge that the Au NPs are always dispersed in the solution. In certain applications, such as surface-enhanced Raman scattering (SERS) detection, substrates are required to carry the prepared nanostructures [29]. Hamad et al. prepared NP-embedded SERS structures by femtosecond laser ablation of Si in acetone solution and then drop casted or plated the metal NPs on them, which has wide application in a variety of molecule test [30]. Ran et al. prepared silver NPs on the Si substrates by femtosecond laser-induced plasma, and it was found to have high sensitivity [31]. Powell et al. used femtosecond laser direct writing and physical deposition to prepare Si-Au particle composite structures on Si surface, which have been widely used in biological detection [32]. They contributed to the preparation of SERS substrate by using femtosecond laser to fabricate a micro-nano composite structure of metal and substrate. But the uniformity, stability, and controllability of SERS substrate are still needed to be improved. Therefore, a cost-effective, efficient method of the Au NP-attached SERS substrate fabrication containing a controllable position and morphology remains challenging.

In this study, a novel method was proposed to produce an Au NP-attached substrate using a spatially and temporally shaped femtosecond laser. Laser induced periodic surface structures (LIPSS) were designed to obtain the localized optical field enhancement (LOFE), which led to femtosecond laser reshaping, enabling the deposition of Au NPs on silicon substrates with excellent spatial selectivity and uniformity. Also, the finite difference time domain (FDTD) was used to simulate optical fields, which demonstrated the existence of LOFE. In our method, the morphology of the Au particles can be easily controlled by adjusting the laser parameters, which was classified into cluster-like, transitional-state, and sphere-like structures. Au NP-attached substrates with various particle morphologies and spatial distributions were used for SERS detection, which performed sensitive and tunable activity

under the synergistic effect of physical enhancement and chemical enhancement: The enhancement factors (EFs) can be further improved to 4.3×10^7 by introducing temporally shaped femtosecond laser, and the Au NP-attached substrates exhibit excellent chemical stability with the intensity deviation of 5.3% in the atmosphere for 2 months. This new method facilitates the efficient, low-cost, and mask-free manufacturing of SERS substrates. Also, this new method provides a new strategy to fabricate Au NP-attached SERS substrate and holds great potential application in molecular detection and biosensors.

2 Experimental section

2.1 Preparation of precursor solution and substrates

At room temperature, 0.05 M HAuCl_4 and 0.05 M $\text{KNaC}_4\text{H}_4\text{O}_6$ aqueous solutions were configured. The precursor solution for Au NPs fabrication was prepared by mixing stock solutions of $[\text{AuCl}_4]^-$ and $\text{KNaC}_4\text{H}_4\text{O}_6$ in equal parts. The sample substrate was silicon (crystal orientation: 100). Before the experiment, the samples were ultrasonically and sequentially bathed with ethanol and deionized water for 10 min each.

2.2 Fabrication process

Figure 1 shows the schematic of this process. The detailed experimental setup is provided in Figure S1. In the atmosphere, a uniform ripple structure was obtained by a femtosecond laser (Figure 1A). In the mixed solution of $[\text{AuCl}_4]^-$ and $\text{KNaC}_4\text{H}_4\text{O}_6$, a secondary scan was performed on the primary uniform periodic section to produce Au particles through photoreduction (Figure 1B). Furthermore, the morphology of particles can be varied by adjusting laser parameters. Therefore, Au particles were attached to the periodic area from the previous treatment, whereas the untreated area did not contain any deposition (Figure 1C).

A linear polarized femtosecond laser pulse from Ti:sapphire laser system with a duration of 35 fs, a repetition rate of 1000 Hz, and a center wavelength of 800 nm was adopted for the fabrication process. A laser pulse was divided into two pulses by a Michelson interferometer and focused at the interface between the solution and the substrate by a 10× Olympus microscope objective lens ($\text{NA}=0.3$). The diameter of the laser spot size at focus is

Figure 1: Schematic process of the Au NP-attached substrate fabrication.

(A) A uniform ripple structure was obtained by femtosecond laser in the air environment. (B) Femtosecond laser induced photoreduction process in the solution. (C) Shape-controlled Au NPs decorated on the treated Si substrate.

approximately $6.12 \mu\text{m}$, and the Rayleigh length of the objective in our experiment is approximately $36.67 \mu\text{m}$. The laser fluence and interval were 0.5 J/cm^2 and $2 \mu\text{m}$, respectively. The samples were translated using a six-axis translation stage. The positioning accuracy is $1 \mu\text{m}$ in the X and Y directions. The positioning accuracy in the Z direction is $0.5 \mu\text{m}$. The Au NP-attached substrates were rinsed with distilled water after the experiment.

2.3 Characterization

The morphology of the prepared substrate was characterized through SEM (Hitachi S-4800, Ibaraki, Japan). Three-dimensional morphology was obtained using an AFM (Dimension Edge PSS, Bruker, Inc., Karlsruhe, Germany). SERS measurements were performed by Micro-Raman spectroscopy (inVia reflex, Renishaw, Gloucestershire, London, UK). XPS was performed using a PHI Quantera X-ray photoelectron spectrometer (Physical Electronics GmbH, Ismaning, Germany).

3 Results and discussion

3.1 Selective deposition of Au NPs

Figure 2A presents the schematic of fabricating the periodic structures on Si substrate in air, and the arrow indicates the direction of the laser movement. The formation mechanism of periodic surface structures is as follows: One of the main properties of femtosecond lasers is the ultra-short time scale. During the process of femtosecond laser irradiation onto the silicon, the surface becomes metallic instantaneously when the number of excited

electrons increases to a critical amount, thus producing surface plasmons (SPs). The surface plasmon polaritons (SPPs) will be generated by a superposition of the incident laser and the SPs. Finally, with the initial laser-SPPs interference and the subsequent grating-assisted SPPs-laser coupling effect [33], near-subwavelength ripples were formed on the silicon surface [34]. Figure 2B is a scanning electron microscopy (SEM) image of near-subwavelength ripples generated by the femtosecond laser. The SEM image indicates that the corrugated structure has a period of approximately 650 nm . The structure also provides a uniform carrier for the adhesion of Au NPs. Also, the surface with the corrugated Si can absorb the incident light more effectively than the planar Si, which has a LOFE effect of the subsequent laser. Therefore, we designed the corrugated Si to reshape the femtosecond laser optical field, which enables the tunable deposition of Au NPs on silicon substrates. Figure 2C depicts the schematic of the production of Au atoms through photoreduction in the solution, and the arrow indicates the direction of laser movement during the process. Figure 2D is a schematic of the reduction of Au^{3+} through LOFE. In conventional photoreducing process, a relatively high pulse energy is required to obtain Au NPs without reductant, which may cause irreversible damage and eruption debris on the substrate [35]. In this study, the laser energy required for photoreduction on the substrate was reduced because the corrugated structure processed in the first step can achieve LOFE, thus enabling the reduction in the corrugated structure with low pulse energy without destroying the substrate. Hydrogen radicals were generated due to the multiphoton ionization of water, causing Au^{3+} to be gradually reduced to Au atoms. In this way, selective deposition of Au NPs on the LOFE area was achieved. Therefore, the proposed design of surface periodic structures is imperative to obtain the spatial selectivity deposition of Au NPs.

Figure 2: Schematic and the results of Au³⁺ reduction in two steps.

(A) Femtosecond laser irradiation in air. (B) SEM image of periodic surface structures, with a scale bar of 5 μm. (C) Femtosecond laser irradiation in a solution containing Au³⁺. (D) Reduction of Au³⁺ because of LOFE. (E) SEM image of the square array, with a scale bar of 100 μm. (F) SEM image of the “BIT” shape, with a scale bar of 500 μm.

To evaluate the effects of this processing method, three sets of comparative experiments were performed (more details are provided in the Supplementary Material and Figure S2). The results indicated that the selective deposition of Au particles cannot be achieved by only using a reducing agent (Figure S2A) or directly writing on the solid-liquid interface (Figure S2B). On the basis of the comparative experiment, a two-step process, as proposed in this study, is advantageous for selectively depositing uniform Au particles. It is worth noting that the flexible pattern-deposition of Au particles can be realized because of the direct writing characteristics of the femtosecond laser [36]. Figure 2E and F show the SEM images of the square array and “BIT” shape fabricated using this new method, respectively.

In order to obtain the morphology of the corrugated structure more comprehensively, atomic force microscopy (AFM) characterization was carried out. Figure 3A and B present the AFM image and cross-sectional view of the corrugated structure, which indicate that the corrugated structure has an approximately 650 nm period and 150 nm depth. The results also confirm the aforementioned SEM results (Figure 2B). To verify the LOFE property of the uniform periodic surface structure processed in the first step, the localized optical field was simulated based on FDTD method using a commercial software program (FDTD solutions). In the simulation process, we used the characterization results (period and depth) from the AFM

image and simplified the femtosecond laser and ripples with the plane wave and the periodic rectangular structure, respectively (the schematic diagram of effective focal spot size position above the LIPSS surface is provided in the Supplementary Material and Figure S3). Figure 3C and D present two views of the field enhancement of the uniform periodic surface structure. Under femtosecond laser excitation, a reinforcing region can be observed, and the optical field enhancement area is present in the region that is approximately 0.4 μm above the trough of the periodic surface structure (Figure 3D). FDTD demonstrates the existence of LOFE, which is considered to cause the photoreduction under low pulse energy.

In this study, we not only analyzed the enhancement effect of light field but also fully studied the photoreduction process of the Au NPs. The reduction process of Au ions can be attributed to the direct multiphoton interaction with a laser field-induced radical-mediated reaction. The reaction process of specific chemical reductions can be explained as follows: Free electrons and H[•] were produced by the multiphoton absorption of water, which induced a reduction of the Au³⁺ ions. Multiphoton absorption of water leads to optical breakdown, and then free electrons and H[•] are released (Reaction 1) [37]. The reaction of reducing radicals and hydrated electrons with ionic Au is generally the mechanism that initially reduces Au³⁺. Moreover, hydrogen atoms can reduce the complexity of Au³⁺ [38, 39]. The disproportionation reaction of Au²⁺ is essential to

Figure 3: FDTD simulations of a local electric field induced by a plane wave ($\lambda = 800$ nm) that is vertically incident on periodic surface structures.

(A) AFM image of periodic surface structures, with a scale bar of 5 μm . (B) Sectional view of the AFM image, with a scale bar of 2 μm . (C) XY section of the periodic surface structures. (D) XZ section of the periodic surface structures.

the reaction process, and Au atoms are finally obtained through stepwise reduction (Reaction 2) [40]. During this process, numerous Au ions with different valences coexist in the solution. When Au^0 finally reaches supersaturation, the Au atoms coalesce with each other, self-assemble, and aggregate to form Au seeds (Reaction 3). In the reduction process, the hydroxyl group in sodium potassium tartrate can also assist in the reduction of Au ions in the solution [41]. During this process, $\text{KNaC}_4\text{H}_4\text{O}_6$ acts as a kind of auxiliary reducing agent, and more details are shown in the Supplementary Material and Reaction S1.

Multiphoton absorption of water

Reduction of Au^{3+}

Atomic Au coalescence

3.2 Morphological changes of Au NPs

The morphology of Au NPs has a significant impact on their photoabsorption and physical/chemical properties. Therefore, the synthesis of Au NPs with morphological controllability is essential. As shown in Figure 4A–E, the specific morphologies of the Au particles deposited on the silicon substrate surface can be observed through SEM (see the details about energy dispersive X-ray spectroscopy (EDX) mapping results of sediments in the Supplementary Material and Figure S4) [42]. In photoreduction processing, we achieve many kinds of Au NPs morphologies through controlling the scanning speeds, which are classified into three types: Type I: At a scanning speed of 160 $\mu\text{m/s}$, cluster-like Au structures composed of slice were generated. The diameter of a single cluster is 800 nm to 1 μm , and the spacing between clusters is close to the diameter of the cluster. Type II: With the decrease in scanning speed, the edge of cluster-like structures

Figure 4: SEM images of Au structures formed at different scanning speeds.

(A) Type I: cluster-like structure. (B–D) Type II: cluster-like to sphere-like transitional state. (E) Type III: sphere-like Au NPs. The scale bars are 500 nm. Au 4f spectral regions on (F) Type I and (G) Type III structures were further studied through XPS. The scale bars of the illustrations are 250 nm.

exhibited a passivation tendency, and the clusters were gradually dispersed. We believe that Type II is a transitional state between Type I and Type III. In Type II, the size of a single cluster slightly reduces with an increase in scanning speed. Type III: When the scanning speed is approximately 20 μm/s, the cluster-like Au structures were mutated to the sphere-like Au NPs, and the sizes of Au particles were also sharply reduced. Spherical Au NPs have a relatively uniform diameter distribution of approximately 50 nm, and the particles are closely arranged (the histogram of Au NPs diameters distribution is shown in Figure S5). Therefore, by adjusting the scanning speed during the photoreduction process, morphologies of Au particles can be controlled flexibly, which paves the way for the tunable SERS application.

The detailed surface chemical properties of Type I and Type III were further studied using X-ray photoelectron spectroscopy (XPS). The Au 4f spectra for Type I (Figure 4F) and Type III (Figure 4G) regions exhibit two

peaks at 84 and 87.6 eV, which confirms the existence of Au⁰ rather than other valence in the test area. That means the structures are formed by the native Au instead of HAuCl₄ crystal. Figure 4F–G present magnified views of the typical morphology of Type I and Type III structures, respectively. In addition, we also studied the deposition rate of Au particles by adjusting the scanning speed (see more details in the Supplementary Material and Figure S6).

The mechanism of size reduction with a decrease in scanning speed could be analyzed in this experiment. Photothermal ablation, near-field enhancement, and Coulomb explosion are the three probable mechanisms [43–46]. Photothermal ablation may occur when low irradiation fluence and high repetition rate are adopted, because high repetition rate may cause the heat accumulation, which is characterized by the melting and evaporation of the surface of particles [44, 47]. Near-field enhancement mechanism frequently requires high laser

fluence and produces intermediates [43, 45]. In Coulomb explosion, numerous electrons are ejected to generate multiple ionized NPs that undergo spontaneous fission because of charge repulsion. The Coulomb explosion mechanism is generally considered to be a dominant factor in femtosecond fragmentation [48, 49].

In this study, when the femtosecond laser fluence was constant, with a decrease in scanning speed, the morphology and size of the Au structures varied dramatically. The Coulomb explosion is considered as the main mechanism of the size mutation in this research. The detailed reasons are as follows: (1) The size of Au particles was drastically reduced. Scanning speed reduction indicates that the material surface undergoes more laser irradiation doses per unit area. If there is no phase change causing fragmentation, as the soaking time increases, the size of Au clusters would increase rather than reduce sharply. (2) The laser fluence was 0.5 J/cm^2 , which is less than the energy required to generate a near-field enhancement. (3) The sphere-like Au NPs are relatively uniform in size. Compared with photothermal ablation and near-field enhancement, the particles produced by the Coulomb explosion do not exist intermediates any more. This change is generally considered as indirect evidence of the Coulomb explosion mechanism.

According to the above mechanism analysis, the whole process can be summarized in Figure 5. Figure 5A–D show

the primary growth process of cluster-like Au structures at a scanning speed of $160 \text{ }\mu\text{m/s}$. First, under the combined action of the femtosecond laser and reducing agent, Au ions dispersed in the mixed solution are reduced and formed Au seeds gradually (Figure 5A). Subsequently, the Au seeds further adsorb the surrounding Au atoms in the solution and form large aggregations (Figure 5B). Aggregations grow under the influence of the surrounding environment, and the contact between seed particles at the accurate crystallographic alignment then results in oriented attachment forming plate-like structures (Figure 5C) [50]. Finally, the aggregations of small plates with additional seeds form cluster-like Au particles upon the continuous action of free radicals in the solution (Figure 5D). The constant femtosecond laser energy with the decreasing scanning speed indicates an increase in the laser power density. The Au seeds are then completely grown into cluster-like structures at the same position, and the edge is passivated by subsequent pulses. With the further reduction in the scanning speed, the Coulomb explosion occurs when the scanning speed is approximately $20 \text{ }\mu\text{m/s}$. Figure 5E–H show the schematic of the Coulomb explosion process. Taking one of the Au nanosheets as an example, an Au nanosheet absorbs photon energy during the continuous injection of the laser pulse at a low scanning speed (Figure 5E). Subsequently, a large amount of electrons are rapidly injected

Figure 5: Schematic of the morphological transformation of Au particles.

(A) Au seeds are formed during irradiation. (B) Au seeds adsorb the surrounding Au atoms to form larger aggregates. (C) Contact between seed particles at the accurate crystallographic alignment results in oriented attachment, thus creating plate-like structures. (D) Au cluster-like structures were formed. (E–H) Schematic of the Coulomb explosion.

and multiple charged NPs are formed (Figure 5F). The charged NPs undergo fission because of charge repulsion (Figure 5G). Finally, small-sized sphere-like Au NPs are formed (Figure 5H).

3.3 Highly sensitive and tunable SERS applications for Au NPs

Au NPs are widely used in various fields. Among them, controllable Au NPs are always used for molecular detection [51]. In this study, we took the application of Au NPs in SERS as an example to study the properties of this highly controllable structure. The obtained shape-controlled Au NP-attached substrates were employed as SERS substrates. As can be seen from the full spectrum of XPS in the processing area (Figure S7), the result shows that the surface of the SERS substrate manufactured through this method was clean and the solution ions were easily removed. R6G aqueous solution was dropped onto the substrate, which was used as a detection molecule. The Raman spectra of R6G exhibited sharp peaks at 611, 776, 1180, 1360, 1509, and 1650 cm^{-1} . Three types of Au-silicon structures produced through the two-step process were dripping with R6G aqueous solution with a concentration of 1×10^{-6} M for Raman signal detection. For comparison, a smooth, bare silicon wafer that was used as a reference sample was dropped with R6G aqueous solution with a concentration of 1×10^{-2} M. According to the SERS spectra (Figure 6A), the Raman enhancement order for the structures with three morphologies is Type III > Type II > Type I. The signal for R6G was not apparent in the reference sample.

EFs were calculated using the Raman peak at 1360 cm^{-1} to quantitatively investigate the EFs on different substrates. The calculation formula is shown in Equation 4. I_{SERS} and I_{ref} indicate Raman intensities of Au NP-attached SERS substrates and reference samples, respectively. N_{SERS} and N_{ref} represent the number of molecules detected on Au NP-attached SERS substrates and reference samples, respectively [11, 52].

$$\text{EF} = \frac{I_{\text{SERS}}}{I_{\text{ref}}} \frac{N_{\text{ref}}}{N_{\text{SERS}}} \quad (4)$$

The calculated EFs for Types I, II, and III structures were 2.5×10^6 , 2.1×10^7 , 3.5×10^7 , respectively (the SERS results of different scanning speeds (lower than 20 $\mu\text{m/s}$) are provided in the Supplementary Material and Figure S8). For single molecule detection, the EFs of the substrates are always required to reach 10^6 [53]. Therefore, EFs of the controllable Au NP-attached substrates prepared in this new method are sufficiently high for molecular level measurements. The measured results demonstrate highly sensitive and tunable SERS applications [54].

The peaks of the three types were measured at 1360 cm^{-1} (Figure 6B) to study the relationship between morphologies and EFs. The spectra intensity of Type III surfaces is 1800% and 150% higher than that of Type I and Type II surfaces, respectively. Figure 6B illustrates SEM views of the microareas of the three types of substrates. To study the relationship between Raman EFs and different morphologies, the effects of the diameter of NP and nanogap were considered to evaluate SERS performance [55]. The size and spacing of Au NPs significantly affect

Figure 6: Raman spectra of R6G obtained on three types of substrates. (A–B) Comparison of the peak values of three different types. All scale bars are 200 nm.

local surface plasmon resonance. In Type III, spherical Au NPs are uniformly dispersed and have a small particles size. Strong coupling was observed between NPs because of a tight arrangement, which is conducive to the further enhancement of factors. To verify this supposition, FDTD was used to simulate the electric field enhancement of different NP diameters (D) and spacing (Figures S9 and S10).

To further study SERS substrates fabricated through this new method, temporally shaped femtosecond pulses were introduced in the second step of laser processing. As Figure 7A shows, the Raman spectra of R6G was obtained for Type III substrates with different pulse delays at 0, 200, 1000, 2000, and 5000 fs, respectively. We found that the EFs reach maximum at 200 fs pulse delay. For further comparison, we also tested the Type I substrates (Figure S11). The relationship between the pulse delay and EFs in two typical structures was plotted (Figure 7B). In particular, taking Type III substrate as an example, with the increase of pulse delay, the EFs increase rapidly until a

maximum of 4.3×10^7 at the pulse delay of approximately 200 fs. Then, with the increase of pulse delay, the EFs tend to decrease slowly. In order to explore the influence of femtosecond laser pulse delay on different types of Au NPs, Type I substrates were also analyzed. The EF trend of Type I substrates is similar to that of Type III. Therefore, we proved the significant improvement of the EFs by introducing temporally shaped femtosecond pulses. In addition, we also studied the limit of detection, repeatability, and reusability of the substrates. The results showed that the substrate processed by this method exhibited good sensitivity, repeatability, and reusability (please see more details in the Supplementary Material and Figure S12).

A brief analysis of the effects of double pulses is as follows: In the region illuminated by the femtosecond laser pulses, photon absorption efficiency is improved because of the synergistic effect of two pulses. This process generally occurs during the pulse delay of several

Figure 7: Raman spectra of R6G obtained for substrates.

(A) Raman spectra of R6G obtained for Type III substrates with different pulse delays. (B) EFs calculated for Type III and Type I substrates with different pulse delays. (C) Raman mapping image of the Type III substrate with a pulse delay of 200 fs. (D) Variations of Raman spectra over time on the Type III substrate with a pulse delay of 200 fs.

hundred femtoseconds. Therefore, within pulse delay of 1000 fs, the content of Au particles obtained by photoreduction was increased because of higher photon absorption efficiency, which led to an increase in the EFs compared with the simple femtosecond laser. However, when the pulse delay was further increased (>1000 fs), the electron decay term became significant. The free electron decay excited by the first subpulse disappeared before the second subpulse was exposed. In temporally shaped femtosecond pulses, the first beam pulse energy was less than the single pulse energy, thereby reducing the photon absorption efficiency. Therefore, a decrease in the content of Au particles per unit of substrate area was observed during photoreduction, and the particles spacing became larger. Hence, the coupling between the particles was weakened, which considerably reduced the EFs. To verify this phenomenon, EDX was performed for a component analysis of the regions with different pulse delays (Table S1). According to the semiquantitative detection, with an increase in pulse delay from 0 to 5000 fs, the content of the Au element per unit of the substrate area first increased and then decreased. The relationship between the rate of Au NPs deposition and pulse delay was also analyzed (more details are provided in the Supplementary Material and Figure S13), the two results are consistent, which can indirectly validate the speculation.

The stability and repeatability of the SERS substrate is also critical. In this study, SERS repeatability was measured using a region of the integral intensity of $20 \times 20 \mu\text{m}$ at 1360 cm^{-1} . A total of 441 data points were acquired with a uniform spacing of $1 \mu\text{m}$ in the selected area. The mapping result demonstrates the high uniformity of the EFs on the Au NP-attached substrates. The Au NP-attached substrates exhibited superior chemical stability with the highest intensity deviation of 5.3% on exposure to air environment for 2 months (Figure 7C and D).

4 Conclusions

In conclusion, a novel method was proposed to produce an Au NP-attached substrate using a spatially and temporally shaped femtosecond laser. LIPSS were designed to obtain the LOFE, which led to femtosecond laser reshaping, enabling the deposition of Au NPs on silicon substrates with excellent spatial selectivity and uniformity. FDTD was used to simulate optical fields, which demonstrated the existence of LOFE. Besides, the morphology of the Au particles can be easily controlled by adjusting the laser parameters, which was classified into cluster-like, transitional-state, and sphere-like structures. Au NP-attached substrates with

various particle morphologies and spatial distributions were used for SERS detection, which performed sensitive and tunable activity: The enhancement factors (EFs) can be further improved to 4.3×10^7 by introducing temporally shaped femtosecond laser, and the Au NP-attached substrates exhibit excellent chemical stability with the intensity deviation of 5.3% in the atmosphere for 2 months. This new method facilitates the efficient, low cost, and mask-free manufacturing of SERS substrates. This work explores the mechanism including formation and deformation of metal NPs in the process of photoreduction through femtosecond laser irradiation and facilitates people to deeply understand the process of the interaction between light and materials. Furthermore, this new method provides a new strategy to fabricate Au NP-attached SERS substrate and holds great potential application in molecular detection and biosensors.

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