

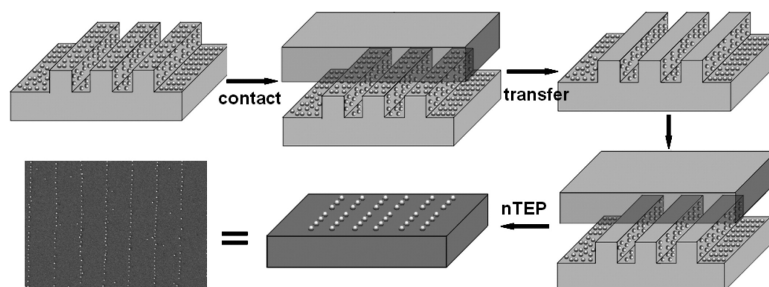
Letter

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## Transfer Printing of Metal Nanoparticles with Controllable Dimensions, Placement, and Reproducible Surface-Enhanced Raman Scattering Effects

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This paper describes the fabrication of single, multiple strand, and three-dimensional patterning of metal nanoparticles by nanotransfer edge printing (nTEP), a method comprising nanoparticle self-assembly, nanotransfer printing (nTP), and edge lithography. In the process proposed here, 20 nm Au nanoparticles (AuNPs) are deterministically arranged in precise placement by manipulating a topographically patterned poly(dimethylsiloxane) (PDMS) stamp, and Ag nanoparticles are conjugated with AuNP patterns to construct surface-enhanced Raman scattering (SERS)-active substrate to detect trace amounts ( $10^{-13}$  mol/L) of biological molecules such as thrombin with enhancement up to  $10^{10}$ . The simple, convenient, and inexpensive procedure has extended nTP and nTEP from using evaporated thin metal film to using self-assembled nanoparticles, and may stretch to other organic and inorganic species to find broad applications in many areas.

### Introduction

Metal nanoparticles are of great interest for broad applications, ranging from magnetic memory arrays and catalysts for the growth of nanowires or nanotubes, to quantum optoelectronic logic circuits and plasmonic devices.<sup>1</sup> Nanoparticles of noble metals such as Au and Ag can produce highly magnified local electromagnetic fields when they are coupled with light, and the enhancement in local field and strong scattering is useful for subwavelength optical waveguiding, surface-enhanced Raman scattering (SERS), biolabeling, biosensing, as well as medical diagnosing.<sup>2–4</sup> For instance, SERS, occurring when molecules are adsorbed on nanostructured surfaces such as metallic nanoparticles or rough electrodes, has been used to detect biological molecules (DNA, protein) with single-molecule capability.<sup>5</sup> Although many previous reports have demonstrated the SERS effect (up to  $10^{14}$  enhancement) for different biochemical molecules,<sup>6,7</sup> sample preparation continues to limit the practical implementation of SERS-active substrates because it is too difficult to control the reproducible aggregation of solution-phase nanoparticles.<sup>8</sup> Although bulk syntheses of colloids produce metal nanoparticles efficiently with unique and useful properties,<sup>9</sup> there remains the challenge for assembling and positioning the nanoparticles in desired locations to construct complex,

higher-order functional structures,<sup>10</sup> especially for the fabrication of large areas and high-accuracy patterns with good reproducibility and low cost.

Structures of metal nanoparticles are typically formed using either top-down or bottom-up approaches. Bottom-up solution-phase synthesis can form nanoparticles with tunable size, shape, composition, and structure (e.g., solid or shell), while the integration of these nanoparticles into functional devices is generally achieved by top-down lithography.<sup>11</sup> Conventional top-down methods such as electron beam lithography and focused ion beam lithography can exquisitely control the interparticle spacing of surface-bound metallic nanostructures with excellent reproducibility;<sup>12</sup> for example, Kraus et al.<sup>13</sup> have reported a method to print nanoparticles with high accuracy and single-strand resolution using e-beam lithography defined gravure printing plates. However, because of the high capital and operating costs, the facilities of these methods are only accessible for limited users. Dip-pen nanolithography has been widely used to pattern nanoparticles in sub-50 nm resolution for applications in protein arrays and DNA assays, but the method of pick-and-position using AFM tips is generally extremely time-consuming which hampers its future applications.<sup>14</sup>

Unconventional techniques have attracted increasing attention in nanoparticles patterning because they are capable of patterning large areas in parallel at low cost. Block copolymer lithography has been applied to guide nanoparticles self-assembly with nanoscale resolution and rich patterns;<sup>15</sup>

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spontaneous formation of nanoparticle stripe patterns through dewetting, reported by Huang et al.,<sup>16</sup> can simply and experimentally conveniently pattern nanoparticles in large area although the lithography-free method can only produce limited stripe patterns such as simple lines. Soft-lithography, a typical unconventional top-down technique, has been widely used for the patterning of soft matter, including organic or inorganic compounds, polymers, biomaterials, metals, and nanoparticles with different geometries and length scales, and find broad application in many areas.<sup>17–19</sup>

In our previous study, we have developed a nanotransfer edge printing (nTEP) method,<sup>20,21</sup> which is the combination of metal thin-film deposition, edge lithography, and nanotransfer printing (nTP);<sup>19</sup> this method can generate nanometer scale metallic structures on hard substrate by peeling the metal film left on the sidewall of topographically patterned poly (dimethylsiloxane) (PDMS) stamp after nTP procedure. The width of the metal nanowire is equal to the thickness of as-deposited thin metal film that is determined by the time and speed of magnetic sputtering. Herein we further our effects in exploring metal nanoparticle patterning techniques based on the nTEP method. Commercially available metal nanoparticles are self-assembled into a monolayer on PDMS stamp to substitute evaporating metal thin film, and transfer printed onto another flat substrate to single, multiple strand, or three-dimensional micro-/nanostructures. The metal nanoparticle patterns can serve as stable SERS-active substrates, and are proved to be highly sensitive and reproducible for the detection of trace amount of biomolecules, for example, thrombin in this paper.

## Experimental Section

**Materials.** All materials and chemicals were purchased commercially and used without further purification. Au colloid (20 nm in diameter), (3-mercaptopropyl)-trimethoxysilane, and 1,8-octanedithiol were purchased from Sigma-Aldrich, and other reagents were purchased from Sinopharm Chemical Reagent Beijing Co.

**Preparation of Au and Ag Sols.** AgNO<sub>3</sub> (90 mg) was dissolved in 500 mL water and heated to boiling. A solution of 1% sodium citrate (10 mL) was added. The solution was kept on boiling for catalyzing 1 h. The Ag sols prepared by this procedure was greenish yellow and had absorption maximum at 420 nm.<sup>22</sup> Scanning electron microscopy (SEM) images show the diameter of as-synthesized Ag nanoparticles (AgNPs) around 150 nm. Au nanoparticles (Au NPs) with diameter around 100 nm were synthesized by a similar procedure by adding sodium citrate into HAuCl<sub>4</sub> solution.

**nTP and nTEP of AuNPs.** Soft lithography and rapid prototyping were used to fabricate features in SU-8 (Micro-Chem Corp.), which were subsequently replica-molded using a PDMS prepolymer to fabricate the flexible stamps. The obtained stamps were first plasma-treated for 10 min to be hydrophilic and then immediately immersed into 20 nm Au colloid for 24 h. Silicon wafer was treated with 30% H<sub>2</sub>O<sub>2</sub> + 70% H<sub>2</sub>SO<sub>4</sub>

and washed with deionized water, and then coated with (3-mercaptopropyl)-trimethoxysilane in 10 mM ethanol solution at 60 °C for less than 1 h. The AuNP-coated PDMS stamp and self-assembled monolayer (SAM)-coated silicon wafer were put in contact with each other without additional pressure, and were separated to achieve the AuNP arrays on the silicon substrate. The nTEP process is almost identical to the first nTP step: after the AuNPs were transferred from the protruding part of the PDMS stamp, the AuNPs left on the sidewall (sharp edge) of the PDMS stamp were subsequently transferred to another SAM-coated Si wafer to finish the second nTP, or nTEP procedure. The images of the AuNP patterns were recorded by SEM (JEOL 7401).

**Orderly Arrangement of Au–Ag Nanoparticle (Au–AgNP) Conjugated System.** AuNP disk arrays with 300 nm spacing were prepared by the method mentioned above. The silicon wafer with the AuNP arrays was plasma oxidized for 10 min and then immediately immersed into 10 mM 1,8-octanedithiol solution at 60 °C for less than 2 h. A piece of freshly peeled flat PDMS was first plasma-treated for 1 min and then immediately immersed into 150 nm Ag colloid for 24 h. Then AgNP-coated PDMS stamps were contacted with silicon wafers with AuNP arrays to complete the conjugation of Ag–AuNP three-dimensional patterning. SEM and optical microscopy images were obtained on a JEOL 7401 and Renishaw Invia Microscope.

**Detection of Thrombin on SERS-Active Substrate.** Raman measurements were performed using a Renishaw Invia Raman Microscope spectrometer equipped with a diode laser (633 nm). A laser power of 1 mW was used at the samples. The concentration of thrombin was set as 1 nmol/L for SERS spectra of thrombin on AuNP structures and 0.8 pmol/L for the conjugated Ag–AuNP system.

## Results and Discussion

**Patterning AuNPs by nTP.** Figure 1 (left column) shows the general nTP procedure used to fabricate AuNP microstructures, which is the combination of AuNP self-assembly and transfer printing. The topographically patterned PDMS substrates were first plasma-treated to become hydrophilic and then were immediately immersed into Au colloid for 24 h in a sealed chamber. In this step, the formation of the AuNP monolayer was facilitated by the electrostatic adsorption occurring on the plasma-treated PDMS surface and the capillary force effect caused by the natural volatilization of the solvent after AuNP assembly. Then we deposited (3-mercaptopropyl)-trimethoxysilane onto a piranha solution-treated silicon wafer, resulting in a SAM on the silicon wafer. The elastomeric PDMS stamp coated with AuNPs and the silicon wafer coated with SAMs were put in contact with each other. No additional pressure was actualized to the two substrates during this process; the pattern transfer process was completed after the stamp was removed from the Si substrate. During the separation, the AuNP monolayer was transferred from the raised plateaus of the PDMS stamp to the SAM-coated silicon wafer, because the covalent bond between gold and sulfur from SAM is much stronger than the electrostatic force between the AuNP and the PDMS stamp.

Figure 2 shows a set of SEM images of the AuNP microstructures on a silicon wafer after nTP. Before transferring, the AuNP monolayer was evenly spread on the topographically patterned PDMS stamp after AuNPs were electrostatically self-assembled from the Au colloid. During the separation, the AuNPs were transferred to the SAM-coated silicon wafer by the covalent bond between gold (AuNPs)

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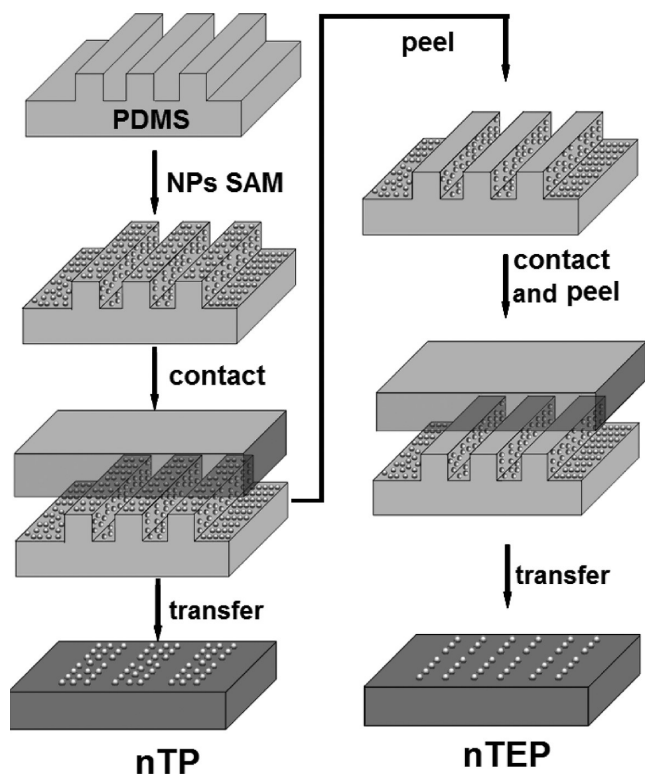
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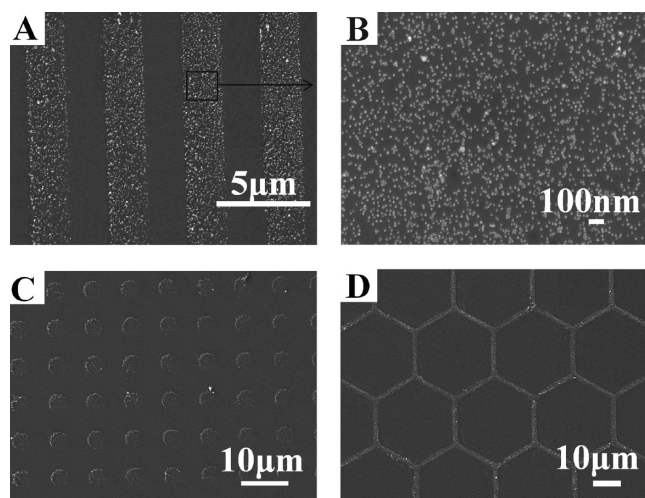
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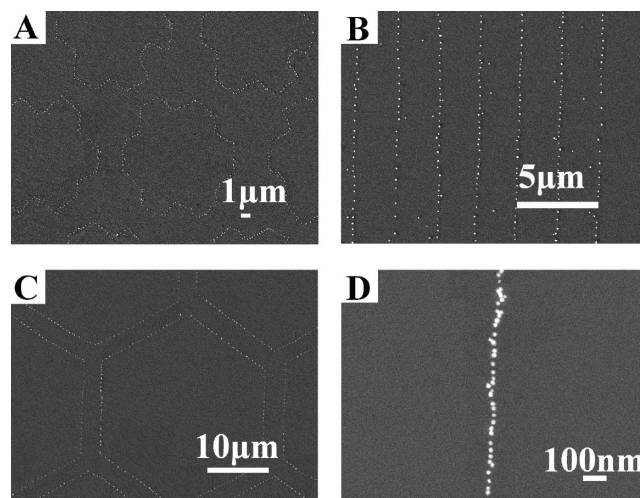


**Figure 1.** Schematic strategy for fabricating designed AuNP microstructures by nTP and nTEP. The procedures contain the following processes: Au NPs were self-assembled onto a PDMS stamp, then contacted with a SAM-coated Si wafer and separated to finish the first transfer printing process (nTP, the left column); Au NPs left on the sidewall of the PDMS stamp were contacted with another SAM-coated Si wafer and separated to complete the second transfer printing process (nTEP, the right one)



**Figure 2.** SEM images of patterns of AuNPs on Si wafer after nTP exhibiting different geometries and length scale. Panel B shows the magnified view of the parallel AuNP arrays in panel A.

and sulfur from SAM. The shape and spacing of the as-fabricated AuNP microstructures were determined by the features of the PDMS stamp, as shown in Figure 2A,C,D. The distance between two adjacent AuNPs was determined by the diameter of the AuNP and the time of electrostatic assembly. The surface coverage nearly reached up to 40% after Au colloid assembled on it for 24 h, as shown in



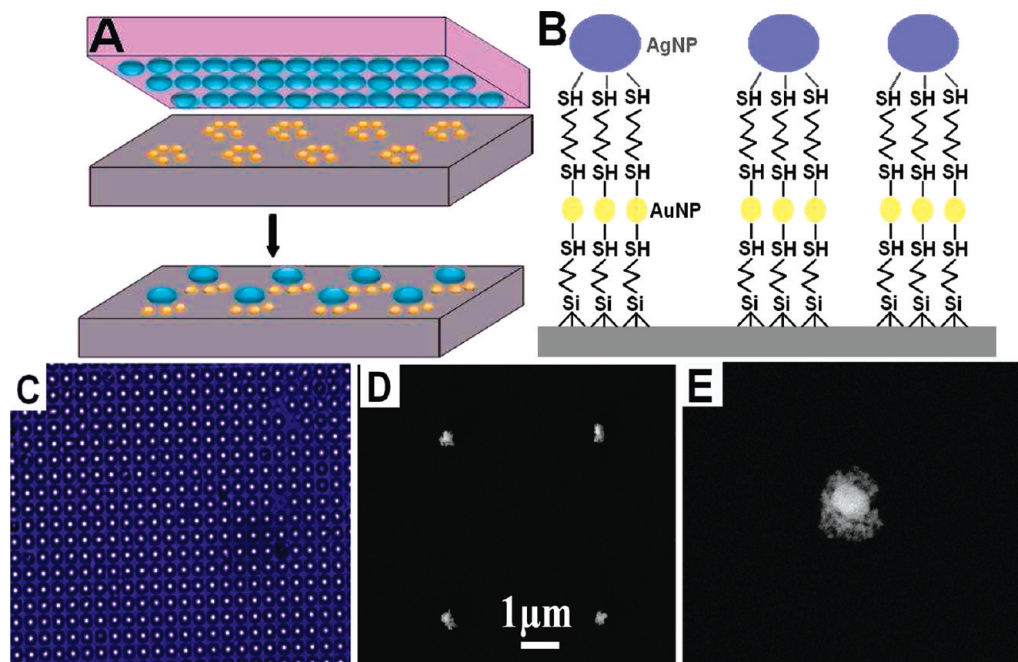
**Figure 3.** SEM images of single strand AuNPs on a Si wafer after nTEP.

Figure 2B, and no severe aggregation of AuNPs was observed during the process because the solvent volatilization is very slow self-assembly in a closed chamber.

**Patterning AuNPs with Single-Particle Resolution by nTEP.** The right column in Figure 1 shows the typical procedure of nTEP, which is almost identical to the nTP process, except that the stamp has variations: after the first nTP step, the AuNPs on the raised plateaus of the PDMS stamp were completely removed, and AuNPs were only left on the sidewall and the trench of the PDMS stamp. During the second nTP process or nTEP procedure, the PDMS stamp was contacted with another fresh SAM-coated Si wafer, and only the AuNPs from the sidewall of PDMS stamp can reach the SAM on the Si wafer to form a Au–S covalent bond and be transferred onto the Si substrate.

Figure 3 shows the SEM images of the AuNP microstructures on a silicon wafer after nTEP. The shape and spacing of AuNP microstructures were determined by the features of the PDMS stamp, which is quite similar to the nTP process. The diameter of the AuNPs (bought from Aldrich Co.) in Figure 3D is around 20 nm, while 100 nm AuNPs (synthesized by our group) are used in Figure 3A–C to make them clearly observed in a large area under SEM.

Unlike the nTP procedure, the AuNP microstructures in Figure 3 show rigorous single-particle resolution, and few particles are observed on the bare Si wafer between two adjacent AuNP lines. This unique phenomenon is attributed to its inimitable fabricating procedure: AuNPs on the raised plateaus of PDMS were transferred away during the first nTP process, and the AuNPs on the trench of the PDMS stamp can not reach the Si wafer to form a covalent bond. Only the AuNPs on the upper part of the sidewall of the PDMS stamp can be conformally contacted with the SAM-coated Si wafer to complete the nTEP process, and only one narrow line of nanoparticles is located at the edge of the PDMS stamp to transfer print onto the Si substrate. According to our knowledge, besides the fact that AFM tips can arrange nanoparticles using the pick-and-position method, e-beam lithography can create predefined gravure plates for high placement accuracy positioning of sub-100 nm nanoparticles, and our method provides a simple and low-cost alternative for the large-area printing of 20 nm metal nanoparticles with high efficiency and excellent positioning (by manipulating the PDMS stamp).



**Figure 4.** (A) Schematic illustration of the AgNP transfer printing onto the AuNP patterns. (B) The covalent bonds bridging the Si substrate, AuNPs, and AgNPs. (C) The optical image of the Ag–AuNPs after transfer printing. (D) The SEM image of the conjugating Ag–AuNPs after printing. (E) Magnified view of panel D.

**Constructing the Au–AgNP Conjugating System.** Well-positioned metal nanoparticle microarrays are intrinsically important and useful in electronics, optics, and biology, and there are great demands for the fabrication of conjugated metal nanoparticle microstructures in order that the unique interaction of coupled metal nanoparticles with electromagnetic radiation could produce a giant “hot spot” effect in surface plasmon resonances (SPR) or SERS. The procedure of either nTP or nTEP as shown in Figure 1 cannot produce conjugated Ag–AuNPs because it is very difficult to control the different nanoparticles’ self-assembly electrostatically onto the PDMS stamp with desired placement, thus we work out another strategy to construct a conjugated Au–AgNP patterning method.

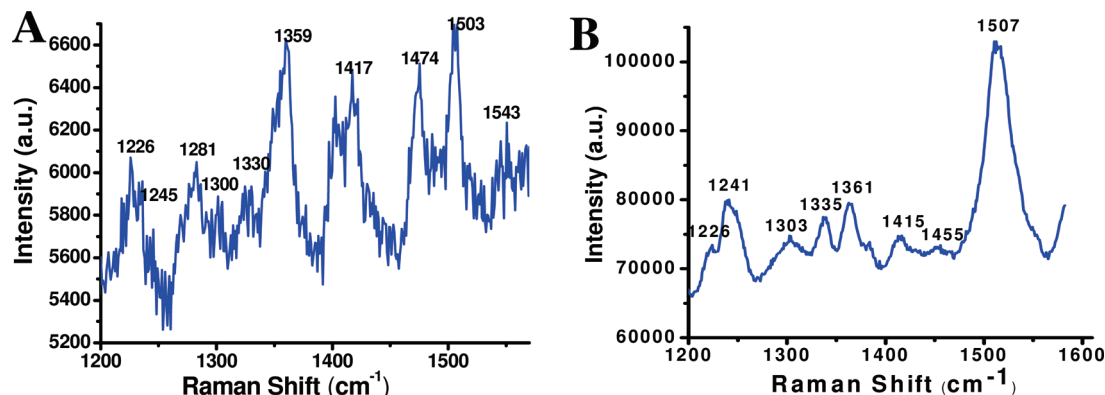
As shown in Figure 4A, a microarray of 20 nm AuNPs was fabricated onto a Si substrate using the same nTP method as shown in Figure 1, then the rest of the SAM of (3-mercaptopropyl)-trimethoxysilane on the Si wafer was removed by oxygen-plasma. After this step, the silicon wafer with the AuNP microarray was immediately immersed into the 1,8-octanedithiol solution to assemble another SAM on AuNPs. At the same time, a piece of freshly peeled flat PDMS was first plasma-treated and then immediately immersed into 150 nm of Ag colloid for 24 h to get the AgNP monolayer on the flat PDMS surface. Then AgNP-coated PDMS slab was conformally contacted with patterned AuNP-coated silicon wafers and separated thereafter. The pattern transfer (Figure 4A) was achieved through the spontaneous formation of  $-S-Au-S-(CH_2)_n-S-Ag$  bonds (as shown in Figure 4B) at the interface between Ag and AuNPs. Finally the Au–Ag conjugated microstructures were fabricated onto the silicon substrate with desired geometry and spacing.

The optical image in Figure 4C shows a large area observation of Ag–Au conjugated microstructures, and the SEM images in Figure 4D,E show the same area with different magnifications. From these images, we can find

that only one or two AgNPs were transferred onto the top of one area of the AuNP array; this fact is mainly attributed to the relative size of the disk pattern of AuNPs (the template is around 300 nm) to AgNPs.

**Detecting Trace Amounts of Biological Molecules on SERS-Active Substrate.** The controlled and reproducible fabrication of metallic nanostructures is of paramount importance since they can produce hot geometries where the trace amount (up to a femtomolar or even to single molecular level) of molecules can be detected through giant SERS effect, and Au and Ag nanoparticles are proved to have significant potential as nanoscale plasmonics. Although Au or Ag can produce giant enhancements (up to  $10^{14}$ ) at certain “hot spots” for using SERS as a sensitive molecular sensing tool, it is still hard to control the aggregation of solution-phase nanoparticles reproducibly. The microstructures of Au and Ag nanoparticles fabricated by nTP and nTEP as shown in this paper can be arbitrarily tuned with high efficiency and excellent positioning by manipulating the PDMS stamp, which opens a new way to test SERS effect on these patterned metal nanoparticle systems.

To further examine the as-fabricated nanoparticle microstructures’ application as SERS-active substrates, we chose thrombin as our model biological molecule. Thrombin is a multifunctional protease operated in the regulation of homeostasis, and its detection is extremely important for clinical diagnosis and biological research. Figure 5A shows the SERS spectra of thrombin detected on AuNP microstructures as shown in Figure 2A where AuNPs is loosely distributed into the microstructure without too many aggregated “hot spots”. An as low as 1 nmol/L thrombin solution was dropped onto the AuNP microstructure, and the SERS-active substrate could achieve the enhancement factor of  $10^7$ . As shown in Figure 5A, many peaks were distinctly observed in the spectra, and the bonds of the amide groups ( $1281\text{ cm}^{-1}$ ) and those assignable to tryptophan



**Figure 5.** SERS spectra of thrombin on AuNP structures (A) and a conjugated Ag–AuNP system (B). The concentration of thrombin is 1 nmol/L for panel A and 0.8 pmol/L for the system in panel B.

(Trp) residues can be clearly identified in the SERS spectrum of thrombin.<sup>23</sup>

Comparing with AuNP patterns, the conjugating Ag–AuNP microarrays show much better SERS effect when detecting thrombin. As shown in Figure 5B, thrombin with ultralow concentration ( $8 \times 10^{-13}$  mol/L) can be detected with excellent signal-to-noise ratio, and the SERS-active substrate can achieve an enhancement factor of  $10^{10}$ . Herein, the coupled Ag–AuNPs can produce localized plasmons or “hot spots” as electromagnetic nanoenvironment for giant SERS enhancements, and these plasmons can be described within the plasmon hybridization picture as dimmer resonance.<sup>24</sup> Unlike the random aggregation of solution-phase metal nanoparticles, the conjugating Ag–AuNP microstructures are fabricated with well-controlled dimensions and placement, thus they can produce highly reproducible SERS-active substrates with precisely designed “hot-spot” locations, where trace amount of biological species need to be detected efficiently and reliably.

From Figure 5, we can clearly find that the SERS spectrum of thrombin in a Ag–Au conjugated NP system is obviously different from that in AuNP substrate besides the SERS intensity; we are not knowledgeable enough at the current stage to fully understand the huge difference in Raman scattering caused by the different enhancement factors. However, the method to construct reproducible patterns

between well-positioned metallic nanoparticles should be useful for experts in the SERS field to investigate the deep physics problems behind the phenomenon.

### Conclusion

In summary, we proposed a simple, convenient, and inexpensive method to fabricate microstructures of metallic nanoparticles with controllable dimensions and placement. Comparing with conventional nTP or nTEP procedure, which uses evaporating metal thin film as transferring blocks, electrostatically self-assembled nanoparticles show their unique properties in constructing single, multiple strand, or three-dimensional conjugated patterns. We have demonstrate the detection of a trace amount of thrombin molecules through SERS-active substrates using as-proposed Ag–AuNP microstructures, which are highly reproducible with precisely designed “hot spots” for giant enhancement. For the sake of our limited infrastructures, we have not demonstrated the application of as-fabricated single strand metal nanoparticles which are too difficult or too expensive to make by using other methods, however, we believe these metal nanoparticle microstructures with single-particle resolution should find extremely important applications in electronics, optics, and biological fields.

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