A high-performance and low cost SERS substrate of plasmonic nanopillars on plastic film fabricated by nanoimprint lithography with AAO template

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As a powerful spectroscopy technique, surface-enhanced Raman scattering (SERS) can provide non-destructive and sensitive characterization down to a single molecular level. Aiming to the main challenges of high-performance SERS-active substrates for their real-world applications involving the ultra-sensitive and reproducible signals detection and signal uniformity with large-area, herein, a facile and reliable strategy based on combination of thermal imprinting polycarbonate (PC) film with porous anodic aluminum oxide (AAO) mold and E-beam evaporation of gold is provided to fabricate a high-quality SERS-active substrate consisting of ultra-dense hot-spots with large-area uniformity. Two kinds of sub-10 nm gaps were obtained, including the nanogaps between the neighboring gold coated PC-nanopillars and those between gold on the top of the nanopillars and that on the base, which actually build up a three-dimensional (3D) hot-spot network for high-performance SERS detection. The effect of structural parameters on SERS enhancement was investigated numerically and experimentally, and by optimizing the structural parameters, a remarkable average SERS enhancement factor up to of 1.4×10^8 is achieved and it shows an excellent reproducibility with a relative standard deviation of 18%, which allows for enhanced practicability in the application of quantitative biochemical detection. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4985270]

I. INTRODUCTION

Noble metallic nanostructures have attracted considerable interest in recent years due to their unique optical properties and great potentials for highly effective nanoscale optoelectronic devices in the fields of nanophotonics,1 photothermics2,3 or photovoltaics,4 photocatalysis5,6 and biosensing.7 Specifically, it has been greatly demonstrated that the metallic nanostructures with strongly enhanced local electric field bears the advantages of being non-destructive, highly-sensitive and label-free bio-sensor.8–10 Of particular interest is the combination of metallic nanostructures and Raman spectroscopy that would provide a powerful analytical technique, namely, surface-enhanced Raman scattering (SERS) for the ultra-sensitive bio-chemical detection even to a single molecular level.11–17 A large number of studies have focused on boosting SERS-active sites or creating so-called

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“hot-spots” on metallic nanostructure to realize a high-performance SERS substrate.\textsuperscript{16,17} It has already been accepted extensively that the excitation of the localized surface plasmon resonances (LSPRs) of the noble metal nanostructures give rise to extraordinarily large enhancements of the Raman scattering spectra of absorbed or adjacent molecules, which is actually the main contribution to the enhancement factor ($EF$) of SERS.\textsuperscript{18,19}

It has been demonstrated that metal colloidal particles and rough metal films could effectively enhanced the Raman signals of target molecules.\textsuperscript{20–22} When noble metal nanoparticles are close enough, the coupling of their LSPRs emerges and leads to a new localized electromagnetic distribution with strong field intensity, which usually consequently results in dramatically enhancing Raman $EF$ up to $10^{11}$, even sufficient for single-molecule detection.\textsuperscript{23} However, the sparse hot-spots and lack of the uniformity and reproducibility in EF for the random nanostructures limit their practical applications.\textsuperscript{24} Alternatively, to control and immobilize the SERS-active sites, various types of ordered nanostructure such as nanodots and nanoholes arrays have been proposed, which could improve the reliability and reproducibility of the SERS measurement. The top-down approaches such as electron-beam lithography (EBL) and focused-ion-beam (FIB) offer high fidelity and high controllability to produce the metallic nanostructure arrays with patterned SERS hot-spots, but its high cost hinders the fabrication over a large-area for practical application in SERS.\textsuperscript{25,26} On the other hand, self-assembly approaches, such as nanosphere lithography and block copolymer lithography\textsuperscript{27–29} are cost effective to produce high-resolution nanostructures over a large-area, but it is still limited to obtain highly controllable structures with well-designed symmetries across whole area. Therefore, the urgent challenge to SERS for the real applications is how to fabricate large-area and uniform SERS-active substrate with high density controllable hot-spots through a cost efficient and reproducible way.

Nanoimprint lithography (NIL) provides a gateway to largely solve the above mentioned issues of conventional fabrication techniques, which is a high-throughput and low-cost fabrication technique capable of replicating nanopatterns from a master mold over large-area with nanometer precision.\textsuperscript{30,31} Up to present, various noble metal nanostructures aiming at the enhanced SERS effect have been successfully fabricated by NIL. For example, the gold coated flexible polymer nanofingers array prepared via UV-curing NIL could be driven together by capillary force, which created reliable hot-spots at the tiny gaps among the fingertips for SERS to detect the trapped molecule.\textsuperscript{32} And recently, to obtain a dense and uniform hot-spots array for large-area and high-performance SERS substrate, a novel three-dimensional (3D) plasmonic nanoantenna array is fabricated through a typical NIL approach, which exhibited a remarkable field enhancement by coupling a 3D microcavity mode with the LSPR modes excited by individual nanodots.\textsuperscript{33} However, as we know, the desired stamping mold is one of the critical bottlenecks to NIL process by virtue of EBL and FIB method, which actually is very tedious and time-consuming.

Anodic aluminum oxide (AAO) templates with hexagonal arrays of nanopores have some significant advantages including their large working areas (>100 cm$^2$) and narrowly distributed pore size which can be freely tuned from 5 to 500 nm by changing the oxidation condition. Due to those merits, AAO templates have been applied as nanoimprint mold to exploit nanodots arrays in various fields such as data storage,\textsuperscript{34} sensing,\textsuperscript{35} photovoltaics\textsuperscript{36} and super-hydrophobic surfaces.\textsuperscript{37} Nevertheless, the inevitable non-flatness of AAO templates, which causes large area defects in conventional thermal imprint because of the non-conformal contact between the template and flat target substrate, would severely hinder its use as a practical mold for commonly used NIL process. In this work, we present a simple and low-cost method to fabricate a large-area gold coated nanopillars arrays on flexible polycarbonate films by utilizing the thermal nanoimprint technique with an AAO template and followed by a thin gold layer deposition. The key structural parameters such as the diameters of the gold coated nanopillars and the gap distance between the neighboring nanopillars are easily tuned by changing the AAO molds with different pore sizes and pore-to-pore distance. And also, the fine control of the gap distance could be achieved through the gold film deposition process. The as-prepared highly uniform and dense gold coated nanopillars arrays not only provided dense hot-spots, and also permitted more target molecules to access these hot-spots, which achieved remarkable performance on enhancement of Raman signal of these molecules. Especially, by optimizing the structural parameters of PC nanopillars arrays and the gold deposition thickness, a SERS substrate with the pillars diameter of 90 nm, inter-rod spacing of 20 nm and gold thickness of 90 nm could achieve
A highest average Raman EF up to $1.4 \times 10^8$. Such an extraordinary SERS performance is owing to the existence of the highly-dense nanogaps created not only between the neighboring gold coated nanopillars but also between the gold-caps on the tops of the PC-nanopillars and the gold film at the bottom of the nanopillars arrays. Strong local electromagnetic fields due to the excited LSPs of gold coated nanopillars and their couplings appear in these sub-10 nm nanogaps, which has been verified by the numerical simulations. Moreover, the 3D plasmonic hot-spots network shows an excellent SERS uniformity with a relative standard deviation (RSD) of 15%, which might be very potential for quantitative biochemical detection.

II. EXPERIMENTAL SECTION

A. Materials

Three AAO templates with different nanopores diameters ($d$) and their average spacings ($s$) ($\{d, s\} = \{50, 40\}, \{70, 40\}, \{90, 20\}$ in unit of nanometer) were purchased from Shanghai Shangmu Technology Co. Ltd. Polycarbonate (PC) films with 0.3 mm thickness were purchased from Corp. of DuPont. Trichloro(1H,1H,2H,2H-perfluorooctyl)siilane was purchased from Gelest, Inc. Trans-1,2-bis(4-pyridyl)ethylene (BPE) was purchased from Sigma-Aldrich Co.

B. Fabrication of gold coated nanopillar arrays

The surface of the AAO templates were first cleaned by O$_2$ plasma, and then coated with a self-assembled monolayer of Trichloro(1H,1H,2H,2H-perfluorooctyl)siilane by vapor-phase deposition. Fig. 1 shows the schematic of the preparing process of the gold coated nanopillars arrays. In brief, a PC film was thermally imprinted by an AAO template at 165 °C under a pressure of 0.6 MPa for 5 mins using an air-pressure imprinter (Corp. of ImprintNano, China). After removing the AAO template, a thin gold layer was deposited on the imprinted PC film by e-beam evaporation. The sizes of the two kinds of gold nanogaps formed by the neighboring gold/PC nanopillars and interstices between top and bottom gold could be determined by the geometries of the AAO template and the subsequent gold deposition process.

C. Characterizations

All the scanning electron microscope (SEM) images were taken using field-emission scanning electron microscope (ZEISS ULTRA-55). To characterize the surface hydrophobic properties

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**FIG. 1.** A schematic process of the preparation of gold/PC nanopillars array nanostructures.
of the metallic microstructures, the contact angle measurements were performed using a contact angle meter (JC2000 CS). To illustrate the performance of as-prepared SERS-active substrates, the Raman spectra were acquired using a Renishaw inVia Raman microscope system with a laser excitation at wavelength of $\lambda = 633$ nm with 0.6 mW laser output power, and the Raman signals were collected during just one-second of integration time via a 50x magnification objective. The spot size of exciting laser was about 2 $\mu$m$^2$. Before Raman measurements, all the samples were soaked in the prepared BPE solutions with known concentrations for 1 h, and subsequently dried in air as well.

III. RESULTS AND DISCUSSIONS

Before the thermal imprinting process, it is crucial to modify the surface of AAO templates with an anti-stick agent trichloro(1H,1H,2H,2H-perfluorooctyl)silane to reduce the surface energy for mold separation. The AAO template was treated by the O$_2$ plasma to clean its surface and expose the hydroxyl groups on it. Then trichloro(1H,1H,2H,2H-perfluorooctyl)silane monolayer was covalently bonded to the AAO template via the reaction of a chlorosilane group with the hydroxyl groups on the surface of aluminum oxide. Fig. 2(a) and (b) show the water contact angle measurement of the AAO template before and after surface modification, respectively. The contact angle increased from 79.0° to 135.3°, which indicated the surface-treated AAO template was much more hydrophobic.

Normally, thermal imprinting may not make a perfect replica of the pattern of AAO template to a conventional hard substrate like silicon wafer due to the non-flatness of AAO foils. This issue can be addressed by using a flexible PC film as a target substrate, which allows a conformal contact with the non-flat AAO template under a uniform air pressure. As we know, PC has a glass transition temperature of about 145°C. In our experiments, to make it easily thermformed and molded, PC film was thermally imprinted at the temperature of 165 °C. Fig. 2(c) shows the photograph of a typical AAO template (20x20 mm$^2$), of which the diameter (d) of nanopores is about 90 nm with an average nanopore spacing (s) of 20 nm. Using this AAO template as a mold, a large-area gold/PC nanopillars array could be obtained through a thermal imprint process combined with a subsequent metal physical deposition. As shown in Fig. 2(d), the as-prepared gold/PC nanopillars array on PC flexible film exhibits a uniform black color without

![FIG. 2. Water contact angle measurement of the AAO template before (a) and after (b) surface modification with an anti-stick agent. Photographs of (c) an AAO template, and (d) corresponding imprinted PC film after deposition of 90 nm gold layer.](image-url)
obvious defects, indicating its excellent optical response of broadband light absorption in the visible regime.

Fig. 3 presents the SEM images of PC nanopillars arrays made from three typical original AAO nanoporous templates with different nanopore diameters and their average spacings \(d, s\) = \{50, 40\}, \{70, 40\} and \{90, 20\} in unit of nanometer (shown in Fig. 3(a)–(c)) through the thermal nanoimprint process. And the middle and bottom rows of Fig. 3 are the top-view and cross-section SEM images of the PC nanopillars arrays with the corresponding diameter of nanopillar \(d\) and the average distance between the neighboring nanopillars \(s\). In fact, it was difficult to break the PC film even cooled in liquid nitrogen for taking SEM image of the cross-section due to its flexibility and toughness. Instead, the cross-sections of the PC nanopillars arrays were obtained from the 180 nm thick PC films which were spin-coated on silicon wafers by a PC/chlorobenzene solution and imprinted by the same AAO template. It can be obtained from the cross-section SEM images that the height of the PC nanopillars is about 100nm.

Followed by depositing a gold layer onto the PC nanopillars arrays described above via an e-beam evaporation, a gold coated PC nanopillars array could be obtained. Basically, the outer diameter \(D\) of gold-caps should be larger than the diameter of PC nanopillars due to this metal deposition process. As expected, the quantity of the metal deposition on the PC nanopillars array would provide an alternative effective way to control the distance between the neighboring gold/PC nanopillars, which might strongly influence plasmonic properties of these metallic nanostructures. Fig. 4 shows SEM images of the above-mentioned PC nanopillars arrays coated with different thicknesses \(h\) of gold. In the bottom row of Fig. 4, the cross-section SEM images of the gold PC nanopillar arrays with different gold deposition thickness are presented, which are made from the AAO templates with \(d, s\) = \{90, 20\} in unit of nanometer. Two kinds of nanogaps could be obtained due to the physical deposition process of metal, including the nanogaps between the neighboring gold-caps on the top of PC nanopillars as well as those between the gold-caps and the gold film on the base, of which the gap-sizes are defined as \(l_1\) and \(l_2\), respectively. The sizes of both nanogaps got smaller as the gradual increase of the gold deposition at the bottom and expanding of the diameters of gold coated
FIG. 4. (a–l) Top view SEM images of gold/PC nanopillars arrays with \( (d, s) = \{50, 40\} \) in unit of nanometer, the gold deposition thickness \( h \) is (a, e, i) 30 nm, (b, f, j) 60 nm, (c, j, k) 90 nm, (d, f, l) 120 nm respectively, the scale bars represent 200 nm. (m – p) Cross-sectional SEM images of gold/PC nanopillars arrays with \( (d, s) = \{90, 20\} \) in unit of nanometer, and \( h \) is (m) 30 nm, (n) 60 nm, (o) 90 nm, (p) 120 nm, respectively, the scale bars represent 400 nm.

PC nanopillars. Therefore, in regard to different PC nanopillars arrays templates, dense sub-10 nm gold nanogaps could be achieved by controlling the thickness of the deposited gold layer. In Fig. 4, it’s clear that the gold on the nanopillars tended to merge into a continuous film after the gold deposition thickness exceeded \( h = 120 \) nm.

IV. SERS ENHANCEMENT EFFECTS

The nanogaps between the neighboring gold coated nanopillars as well as those between the gold caps on the tops of the nanopillars and the gold film at the bottom of the nanopillars arrays can be considered as the hot-spots for enhancing Raman intensity. As we know, the SERS EF could be expressed approximately as \( EF \propto |E/E_0|^4 \), where \( |E| \) is the amplitude of the enhanced local electric field and \( |E_0| \) is the amplitude of incident electric field. To well evaluate the SERS enhancement effects of as-prepared gold/PC nanopillars arrays, 3D numerical simulations were performed with a simplified metalldielectric model by using commercial software package (COMSOL Multiphysics) based on finite-element method. Here, we assumed that the gold-capped PC nanopillars constituted a 2D hexagonal lattice. The calculation domain comprised one complete and four-quarter gold/PC nanopillars in the \( x-y \) plane defined as Fig. 5. The periodic boundary conditions were applied to the four sides of the rectangular simulation domain to fit the periodicity of the whole structure. In the simulation, a plane wave with linear polarization was illuminated normally on the modeled microstructure. The refractive index of the PC was set as 1.59 and the permittivity of gold was described as a dispersive medium with the complex dielectric parameters taken from experimental data by Johnson and Christy.

Fig. 6(a–d) show the calculating models of gold/PC nanopillars arrays used for simulations. The structural parameters for our theoretical simulation models were all based on those in the real fabricated samples. To be clear, the structural parameters of the as-prepared samples were summarized
FIG. 5. (a) Schematics of gold/PC nanopillars arrays and the absorption spectra dependent on the gold deposition thickness \((h)\) with different parameters (b) \(d = 50\) nm, (c) \(d = 70\) nm, (d) \(d = 90\) nm. Other structural parameters for simulation were shown in Table 1.

in Table 1. \(d\) and \(s\) are the average diameters of the PC nanopillars and their average spacings which are determined by the original commercial AAO templates. The nominal thickness \((h)\) of deposited gold, which actually could be described as the thickness of gold on top of PC nanopillars or that

FIG. 6. (a-d) Schematics of gold/PC nanopillars arrays used for simulations with \(d = 90\) nm, and (a) \(h = 30\) nm, \((l_1 = 15\) nm, \(l_2 = 70\) nm), (b) \(h = 60\) nm, \((l_1 = 12\) nm, \(l_2 = 40\) nm), (c) \(h = 90\) nm, \((l_1 = 9\) nm, \(l_2 = 10\) nm), (d) \(h = 120\) nm, \((l_1 = 7\) nm, \(l_2 = 0\) nm), respectively, and the corresponding maps of the electric field distributions at the wavelength of 633 nm along the \(x-y\) plane \((a'-d')\), and the \(x-z\) plane \((a''-d'')\).
TABLE I. Summarization of structural parameters of the as-prepared samples.

<table>
<thead>
<tr>
<th>{d, s} (nm)</th>
<th>(h) (nm)</th>
<th>(D) (nm)(^a)</th>
<th>(l_1) (nm)(^b)</th>
<th>(l_2) (nm)</th>
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<tbody>
<tr>
<td>{50, 40}</td>
<td>0</td>
<td>0</td>
<td>40 (i)(^b)</td>
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<td>120</td>
<td>103±5</td>
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\(^a\)Obtained by the statistical SEM analysis.
\(^b\)The spacing between the neighboring PC nanopillars.

on the PC bottom. \(D\) is the outer diameter of gold-caps on PC nanopillars, which was obtained by the statistical SEM analysis. \(l_1\) is the average size of the gap between the neighboring gold-caps on PC nanopillars, which was also obtained by the statistical SEM analysis. \(l_2\) is the average size of the gap between the rims of top gold-caps and the bottom gold film, which was deduced by the quantity of metal deposition and the height of PC nanopillars. The spectral absorption (\(A\)) which were defined as \(A = 1 - \text{Transmittance (T)} - \text{Reflectance (R)}\) for the samples with different \(h\) were plotted in Fig. 5. For all the modeled gold/PC nanopillars arrays with different diameters of original PC nanopillars (\(d\)), an absorption peak is obvious only for \(h = 90\) nm for each sample, which shows apparent red-shift as \(d\) increases. In particular, for \(d = 90\) nm, the absorption peak with intensity up to 80% could be tuned to 633 nm which is the typical exciting laser wavelength used in our experiment. Fig. 6(a′-d′) and Fig. 6(a′′-d′′) show the electric field distributions dependent on the gold deposition thickness along the x-y plane and x-z plane under the excitation of 633 nm for the typical samples made of PC nanopillars array with 90 nm in diameter, respectively. Here, the average gap-distance between the gold/PC nanopillars was evaluated from the SEM images of the gold/PC nanopillars arrays and it decreased with increasing the thickness of gold (\(h\)). It can be seen that dramatically field enhancement in the nanogaps between the neighboring gold/PC nanopillars as well as between the gold caps on the tops of the PC nanopillars and the gold film at the bottom of the nanopillars arrays are formed, which stems from the near-field coupling of the localized surface plasmon (LSP).

In our experiment, the trans-1,2-bis(4-pyridyl)ethylene (BPE) was used as probe molecular to characterize the SERS performance of the as-prepared gold/PC nanopillars arrays, 1.82 g BPE was dissolved with ethanol in 100 mL volumetric flask to form 10\(^{-1}\) M solution and followed by stepwise diluting to lower concentrations (10\(^{-2}\) M - 10\(^{-10}\) M). To compare the SERS enhancements of the blank Au film (50nm thick Au deposited on flat PC) and the different gold/PC arrays with various geometric parameters, the samples were soaked in ethanol solution of trans-1,2-bis (4-pyridyl)ethylen (BPE) with fixed concentration of 10\(^{-6}\) M for 1 h, and were subsequently dried in air.

All of the Raman spectra were measured under the same conditions. A 633 nm helium-neon (He-Ne) laser with power of 0.6 mW was used as the excitation source, and the acquisition time for Raman signal was 1 s. As shown in Fig. 7(a–c), in all cases with \(d = 50\) nm, 70 nm and 90 nm, the SERS intensity increased as the nominal thickness (\(h\)) of gold changed from 30 to 90 nm, and then decreased abruptly when \(h\) is about 120 nm, which fit with the trend of the electric field enhancement in the gaps very well as described in Fig. 7(d–f). It is worthwhile to note that the Raman intensities for the samples with \(h = 90\) nm were obviously much higher than the others. And the gold/PC nanopillars array
FIG. 7. Experimental SERS spectra of BPE molecules adsorbed on the samples with different nanopillars diameters (a) $d = 50$ nm, (b) $d = 70$ nm, (c) $d = 90$ nm. Experimental Raman signal intensity of BPE’s 1200 cm$^{-1}$ peak and corresponding calculated highest electric field enhancement versus gold thickness (d) $d = 50$ nm, (e) $d = 70$ nm, (f) $d = 90$ nm. The SERS spectra (a-c) are sequentially offset for clarity.

with optimal parameters of $d = 90$ nm and $h = 90$ nm could provide the largest SERS enhancement, which was illustrated with our experiments and corresponding simulations. When the thickness of gold was $h = 120$ nm, the electrical field enhancement was lower than the other cases, while the SERS enhancement in the experiment was still higher than the case for $h = 30$ nm and $h = 60$ nm. It was entirely possible that when $h = 120$ nm, the nanogaps between the gold caps on the tops of the nanopillars and the gold film at the bottom of the nanopillars arrays vanished in the simulation as shown in Fig. 5 and Fig. 6. However, in experiment, when the nanogaps between the neighboring nanopillars was narrow enough, gold will hardly deposit at the bottom, and thus some SERS hot-spots defined by interstice between the gold cap on the PC nanopillars and the bottom gold might be remained even if the gold/PC nanopillars were almost contact to one another. At the same time, discrepancy between the measured and calculated SERS EFs could also be attributed additionally to some other possible reasons. For example, the simulated nanostructures were largely simplified as shown in Fig. 6, and the actual nanostructures were much more complex, for example, the as-prepared nanopillars were not so regular as standard cylinders and the gold surface was not as smooth as that of the simulated cases.

Considering the as-prepared sample with optimized parameters of $d = 90$ nm and $h = 90$ nm, the highest SERS enhancement can be acquired owing to the establishment of two kinds of highly-dense horizon and vertical nanogaps with sub-10 nm scale. Using the common method for calculating
FIG. 8. Experimental SERS spectra of BPE with different concentrations on the sample with \(d = 90\) nm, \(h = 90\) nm. The spectra are sequentially offset for clarity.

The enhancement factor,\(^{28,39}\) taking the 1200 cm\(^{-1}\) Raman peak into account, the SERS \(EF\) of the optimized metallic microstructure is estimated to be about \(1.4 \times 10^8\), showing a fairly high SERS activity (Details shown in supplementary material). To demonstrate the excellent SERS activity of the optimized metallic microstructure, we further measured its SERS spectra with the ethanol solutions of BPE from \(10^{-6}\) M to \(10^{-10}\) M with the above-described conditions. As shown in Fig. 8, the spectra clearly demonstrated the Raman characteristic of BPE probe molecules. The SERS spectrum of blank gold film with the ethanol BPE solution of \(10^{-1}\) M was also displayed in Fig. 8. Note that the Raman signal can still be distinguished when the concentration of BPE was down to \(10^{-10}\) M.

For the application of an SERS-active substrate, the uniformity and reproducibility of the Raman signal over a very large area are of great importance, which are associated with the uniformity of the SERS hot-spots. Six positions were selected randomly on the sample with \(d = 90\) nm and \(h = 90\) nm, and experimental SERS spectra of these points for BPE solution with low-concentration of \(10^{-7}\) M were collected, as shown in Fig. 9(a). In addition, Fig. 9(b) shows the SERS spectra for the \(10^{-7}\) M BPE solution using the five different as-prepared SERS substrates of gold/PC nanopillars array with \(d = 90\) nm and \(h = 90\) nm. The intensity of Raman signals from different positions of one substrate and from different substrates with optimal parameters \((d = 90\) nm and \(h = 90\) nm) were almost same. Here, we used the relative standard deviation (RSD) of SERS peak’s intensity around 1200 cm\(^{-1}\) to estimate the uniformity and reproducibility of the SERS signals. The RSD values are calculated to be about 15% and 18%, respectively, which means that the gold/PC nanopillars arrays demonstrates excellent SERS signal uniformity and reproducibility.

FIG. 9. (a) SERS spectra of \(10^{-7}\) M BPE from six randomly selected positions of one sample. (b) SERS spectra of \(10^{-7}\) M BPE from five randomly selected samples. Here, all the samples are prepared with optimal parameters \((d = 90\) nm and \(h = 90\) nm). The spectra are sequentially offset by 1000 counts for clarity.
V. CONCLUSION

In conclusion, we proposed and demonstrated a fairly simple, and low-cost way to fabricate a high-performance SERS substrates consisting of gold/PC nanopillars array, which is based on the combination of AAO templating and nanoimprint lithography, followed by a physical deposition process for metal. The optical properties could be easily tuned by changing the parameters of the AAO templates and the quantity of the gold deposition. Two kinds of highly-dense horizon and vertical nanogaps were formed and could be controlled to sub-10 nm, which would provide plenty of hot-spots for SERS. We numerically and experimentally investigated the effect of geometrical parameters of the gold/PC nanopillars arrays on SERS enhancement, and found that the highest average SERS EF could reach up to $1.4 \times 10^8$ when the structural parameters of the as-prepared gold/PC nanopillars arrays, such as diameter of PC nanopillars and thickness of gold, are optimized as $d = 90$ nm and $h = 90$ nm. Our purposed SERS-active substrate demonstrated excellent SERS signal uniformity and reproducibility. In addition, since the gold/PC nanopillars arrays were actually supported on flexible plastic PC films, physical forces such as bending and twisting could provide another degree of freedom to tune the SERS properties, and that might bring a wider application of the SERS substrates.

SUPPLEMENTARY MATERIAL

See supplementary material for the SERS enhancement factor calculation.

ACKNOWLEDGMENTS

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