

# Hotspots on the Move: Active Molecular Enrichment by Hierarchically Structured Micromotors for Ultrasensitive SERS Sensing

Xingce Fan, Qi Hao, Mingze Li, Xinyuan Zhang, Xiaozhi Yang, Yongfeng Mei, and Teng Qiu\*



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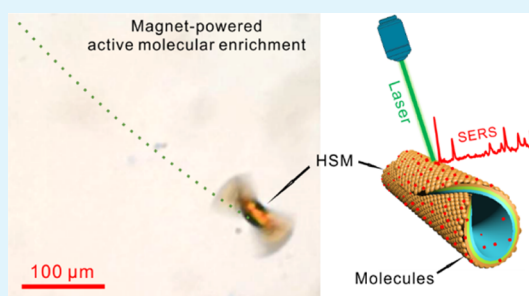
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Supporting Information

**ABSTRACT:** Surface-enhanced Raman scattering (SERS) is recognized as one of the most sensitive spectroscopic tools for chemical and biological detections. Hotspots engineering has expedited promotion of SERS performance over the past few decades. Recently, molecular enrichment has proven to be another effective approach to improve the SERS performance. In this work, we propose a concept of “motile hotspots” to realize ultrasensitive SERS sensing by combining hotspots engineering and active molecular enrichment. High-density plasmonic nanostructure-supporting hotspots are assembled on the tubular outer wall of micromotors via nanoimprint and rolling origami techniques. The dense hotspots carried on these hierarchically structured micromotors (HSMs) can be magnet-powered to actively enrich molecules in fluid. The active enrichment manner of HSMs is revealed to be effective in accelerating the process of molecular adsorption. Consequently, SERS intensity increases significantly because of more molecules being adjacent to the hotspots after active molecular enrichment. This “motile hotspots” concept provides a synergistical approach in constructing a SERS platform with high performance. Moreover, the newly developed construction method of HSMs manifests the possibility of tailoring tubular length and diameter as well as surface patterns on the outer wall of HSMs, demonstrating good flexibility in constructing customized micromotors for various applications.

**KEYWORDS:** surface-enhanced Raman scattering, active molecular enrichment, hotspots engineering, micromotor, rolling origami, nanoimprint



## 1. INTRODUCTION

Surface-enhanced Raman scattering (SERS), featuring high sensitivity and specificity, has been recognized as one of the most powerful spectroscopic tools for ultrasensitive sensing applications.<sup>1–6</sup> Generally, plasmonic nanostructures are designed to generate intense localized surface plasmon resonance when excited by light and provide concentrated electromagnetic fields at their interstitial junctions.<sup>7–9</sup> These junctions, called “hotspots”, can dramatically amplify the Raman signals of surrounding analytes. To date, diverse strategies have been proposed to achieve excellent SERS sensitivity with enhancement factors exceeding  $10^5$ . The strategies can be classified into two categories: hotspots engineering and molecular enrichment.

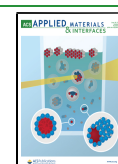
Hotspots engineering is recognized as the most efficient strategy to acquire high-performance SERS substrates, and various techniques have been developed ranging from top-down methods like lithography<sup>10,11</sup> to bottom-up methods like chemical growth,<sup>12,13</sup> self-assembly,<sup>14,15</sup> and template-assisted assembly.<sup>16–19</sup> Because SERS intensity is theoretically proportional to the number of attached molecules in proximity of plasmonic nanostructures, molecular enrichment is an emerging approach beyond hotspots engineering to further improve the SERS performance.<sup>20</sup> The methodology of mainstream is to

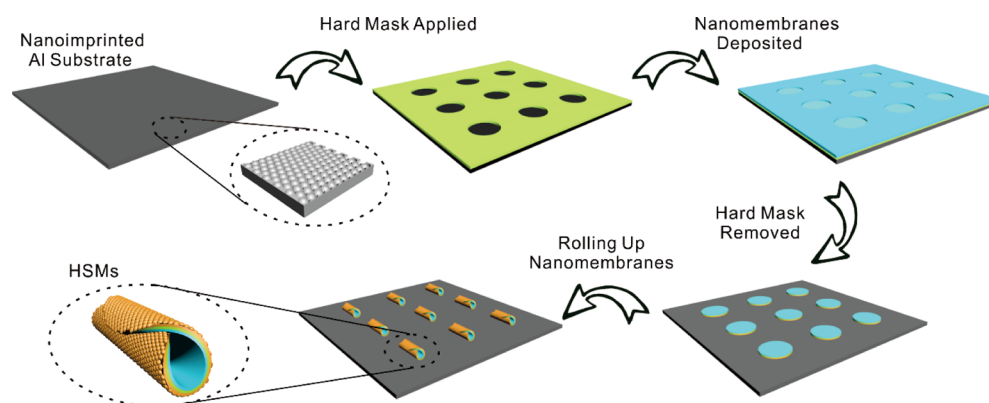
increase the molecular concentration adjacent to the plasmonic surface. Currently, there are three widely studied enrichment approaches: chemical analyte directing capture,<sup>21–23</sup> superhydrophobic surface-induced concentration,<sup>24–28</sup> and sorbent material-incorporated concentration.<sup>29–32</sup> The chemical analyte directing capture approach employs specific chemical reactions to selectively capture molecules, but grafting of Raman tags may cause interference in distinguishing the Raman signal of captured molecules from the overlapped spectrum. The superhydrophobic surface-induced concentration approach utilizes nonwetting substrates to concentrate aqueous analytes, while construction of the superhydrophobic surface tends to be complex and costly. The sorbent material-incorporated concentration approach involves secondary sorbent materials to enrich molecules, but it is challenging to position molecules

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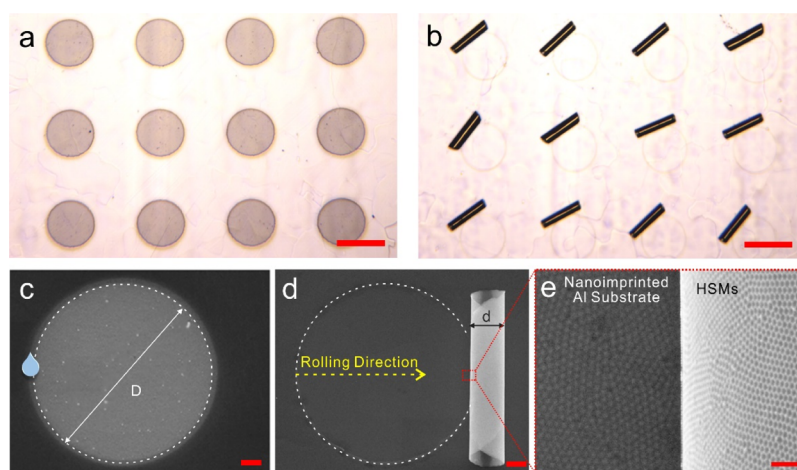
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**Figure 1.** Schematics of fabrication procedures of HSMs via rolling origami.



**Figure 2.** Optical image of (a) planar prestrained Au/SiO/Fe nanomembrane arrays and (b) HSM arrays rolled up via rolling origami. (c) The SEM image of planar prestrained Au/SiO/Fe nanomembranes with marked trigger point of rolling up. (d) The SEM image of one rolled up HSM. (e) The SEM image of the magnified view of HSM and the corresponding nanoimprinted Al substrate. Scale bars: (a,b) 100  $\mu\text{m}$ ; (c,d) 10  $\mu\text{m}$ ; and (e) 400 nm.

within the working distance of plasmonic structures. Particularly, these three enrichment approaches all present a passive molecular adsorption manner, which generally leads to low capturing probability and long capturing duration.

Recently, catalytic micromotors<sup>33–38</sup> have received widespread investigation because of their self-propelled behavior in the presence of fuels to complete various tasks, such as cargo delivery,<sup>39,40</sup> water remediation,<sup>41,42</sup> detoxification,<sup>43–46</sup> and biochemistry detection.<sup>47–53</sup> The active movement of catalytic micromotors has been shown to impart efficient micromixing and enhance mass transfer.<sup>54–56</sup> Our group first proposed an active molecular enrichment strategy to achieve better SERS performance<sup>57</sup> in which bubble-propelled SERS-active micromotors are utilized to enrich molecules in fluid, consequently leading to significantly enhanced Raman intensity. Active locomotion of micromotors can increase probability of contact between micromotors and analytes, enabling quick and effective molecular enrichment on the plasmonic surface. Meanwhile, we realized that active molecular enrichment approach needs large amount of fuel, typically hydrogen peroxide, to guarantee sufficient time of molecular capture, which may cause oxidation of molecules and destruction of the plasmonic surface. To solve the problem, the power source should be replaced.

Herein, we propose a concept of “motile hotspots” to realize ultrasensitive SERS sensing by combining the superiorities of hotspots engineering and active molecular enrichment. High-

density plasmonic nanostructure-supporting hotspots are assembled on the outer wall of micromotors via nanoimprint and rolling origami techniques. The micromotor with a nanostructured outer wall is termed as the hierarchically structured micromotor (HSM). Meanwhile, the Fe layer is incorporated into the tubular wall of HSMs to realize controllable motion in an external magnetic field. Consequently, the dense hotspots carried on these HSMs can be magnet-powered to actively enrich molecules in fluid. The active enrichment manner of HSMs is revealed to be effective in accelerating the process of molecular adsorption. The increased number of molecules adjacent to the hotspots leads to dramatically enhanced SERS intensities. This “motile hotspots” strategy provides a promising approach in designing a SERS platform of high performance. Besides, the newly developed construction method of HSMs manifests the possibility of tailoring tubular length and diameter as well as surface patterns on the outer wall of HSMs, demonstrating good flexibility in constructing customized micromotors for various applications.

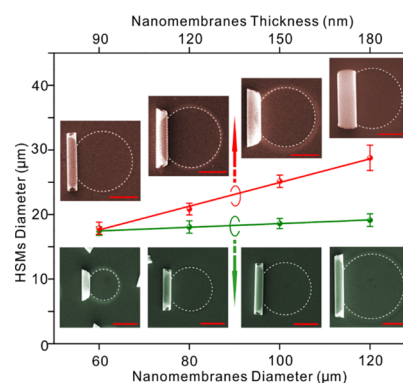
## 2. RESULTS AND DISCUSSION

**2.1. Design and Fabrication of HSMs.** The construction of HSMs is the prerequisite for achieving “motile hotspots” to promote the SERS performance. The constructing procedures of HSMs are schematically illustrated in Figure 1. The nanoimprinted Al foil serves as a substrate to duplicate

nanopattern on the outer wall of micromotors. First, the polished Al foil is nanoimprinted by anodic aluminum oxide (AAO) stamps, whose structural flexibility and mechanical hardness offer multiple choices to pattern the Al substrate with the customized surface morphology.<sup>58,59</sup> The detailed nanoimprint process can be found in the [Supporting Information](#) (Notes S1, S2 and Figures S1–S3). Subsequently, the nanoimprinted Al substrate is covered by the hard mask with designed circular opening arrays. This step intends to define shape of deposited planar prestrained nanomembranes. Then, Au/SiO/Fe multilayer nanomembranes are deposited layer by layer via electron beam evaporation. This material selection is based on the feasibility of the roll-up process and the designed functions of active molecular enrichment and plasmonic sensing. Au, featuring distinct plasmonic response within the visible range<sup>9</sup> and van der Waals adhesion on the Al substrate, is selected as the first deposited material, serving as the outer wall after rolling up. SiO and Fe layers provide HSMs with additional strain during the roll-up process and structural robustness to avoid damages during active molecular enrichment. Moreover, the incorporation of the Fe layer provides magnetic control over the motion of HSMs in fluid. This selection effectively avoids molecule oxidation when using catalytic micromotors to enrich molecules. After deposition, the hard mask is peeled off, leaving well-defined arrays of circular nanomembranes ([Figure 2a](#)). Finally, the planar prestrained nanomembranes are released from the nanoimprinted Al substrates to form 3D tubular hierarchical structures by immersion in ethanol. In [Figure 2b](#), the optical image illustrates the constructed HSMs of uniform length and diameter, elucidating successful massive production of HSMs via rolling origami.

In a rolling up process, droplet intercalation between the Au layer and Al substrate plays an important role,<sup>60</sup> where the rolling behavior is triggered from the edge of nanomembranes ([Figure 2c](#)), and then, the planar nanomembranes continue to roll up into the 3D tubular structure with the help of their internal strain gradient ([Figure 2d](#)). In this case, the tubular walls of HSMs are strong enough to maintain their 3D configuration after drying rather than collapsing into the flat structure. Rolling origami enables lift-up of the planar structure to form a curved surface, which is favorable in sensing applications owing to the diminished impact of substrates.<sup>61</sup> [Figure 2e](#) shows the magnified view of HSMs with the nanobowl-arrayed outer wall copied from the pore-side-imprinted Al substrate. The result demonstrates feasibility of rolling origami in assembling plasmonic nanoarrays on 3D structures. It should be highlighted that no sacrificial layer or wet etching is evolved during construction of HSMs, and they can be readily transferred for on-chip or out-of-chip applications. By comparison, traditional methods<sup>57,62,63</sup> always involve sacrificial layer patterning and wet etching steps, tending to bring complexity in fabrication and damages to the constructed structures. Moreover, micromotors acquired via traditional methods are generally fixed on the substrate firmly, and transfer of the micromotors might cause unexpected damages to the tubular structure.

The main body of HSMs consists of thin tubular wall, which responds to external rotating magnetic fields during active molecular enrichment. The tubular geometric parameters of HSMs (diameter and length) are crucial for the state of movement in fluid. Flexible tunability of tubular diameter and length is of significance in cater to their applications in different fluids. As shown in [Figure 3](#), the tubular diameter and length can be readily modified by adjusting thickness and diameter of the

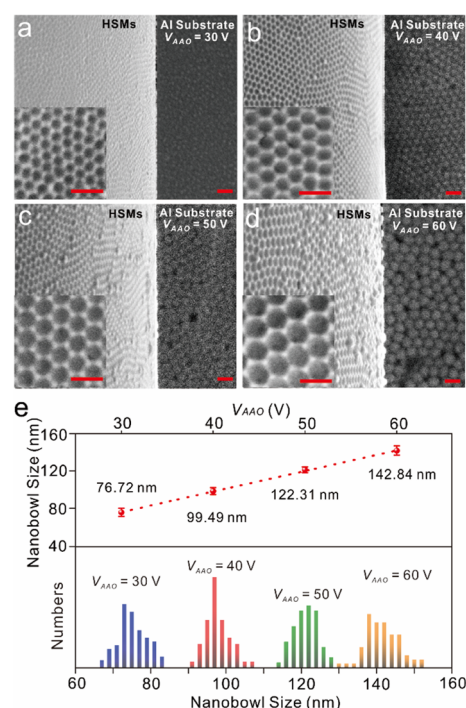


**Figure 3.** Top panel: SEM images of HSMs by rolling up Au/SiO/Fe nanomembranes of different thicknesses (left-to-right: 30/30/30, 40/40/40, 50/50/50, and 60/60/60 nm); the red line shows the linear relationship between average tubular diameter of HSMs and total nanomembrane thicknesses. Bottom panel: SEM images of HSMs by rolling up Au/SiO/Fe nanomembranes of different diameters  $D$  (left-to-right: 60, 80, 100, and 120  $\mu\text{m}$ ); the green line shows relationship between average tubular diameter of HSMs and nanomembranes diameter. Scale bars: 50  $\mu\text{m}$ .

planar prestrained nanomembranes, respectively. For demonstrating controllable modification of the tubular diameter, each layer of nanomembranes is of the same thickness (30/30/30, 40/40/40, 50/50/50, and 60/60/60 nm for Au/SiO/Fe), while diameter  $D$  of the initial planar prestrained nanomembranes is fixed as 100  $\mu\text{m}$ . The statistical tubular diameter  $d$  values are plotted, as shown in [Figure 3](#) (red dots), based on twenty constructed HSMs for each set of thickness parameters. The SEM of a single HSM is shown in the top panel of [Figure 3](#), and the SEM images of HSM arrays are shown in [Figure S4](#). The 3D geometric microstructures obtained via rolling origami is determined by elastic properties and strain gradient of deposited multilayer nanomembranes.<sup>60</sup> According to the calculation based on the elastic mechanism, the diameter of tubular structures is proportional to the total thickness of nanomembranes when the thickness of each layer is equal.<sup>60</sup> Therefore, a linear fitting is shown as the red line in [Figure 3](#). The results prove that the adjustment of deposition parameters is feasible in controllably modifying the tubular diameters of HSMs via rolling origami. Furthermore, the tubular length of HSMs is determined by diameter  $D$  of planar nanomembranes. The SEM images shown in the bottom panel of [Figure 3](#) present HSMs of different lengths: 60, 80, 100, and 120  $\mu\text{m}$ . At this time, the thickness of each layer of the Au/SiO/Fe nanomembranes is 30 nm. The precise change in tubular length indicates the feasibility of rolling origami in constructing HSMs with the customized tubular length. However, whether the change in the HSM length is influential to its tubular diameter remains unknown. In this regard, the tubular diameters  $d$  of HSMs with different lengths are statistically studied, as shown in [Figure 3](#) (green dots), based on twenty HSMs, as shown in [Figure S5](#). In this case, the statistical tubular diameter  $d$  of HSMs (the green line, as shown in [Figure 3](#)) is almost proportional to the tubular length. A slight increase in the tubular diameter results from increased winding numbers when rolling up longer HSMs. Nevertheless, this slight change in tubular diameter is negligible. Hence, the modification of the tubular length is regarded independent to the tuning of its tubular diameter, which enables flexible selection of tubular geometries in cater to specific applications.

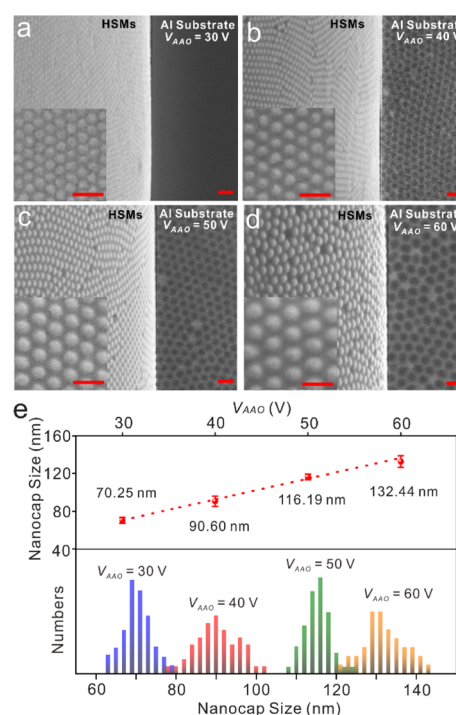


Other than tubular geometries, the rolling origami technique enables facile assembly of plasmonic nanostructures on the outer wall of HSMs, offering versatile selections in engineering plasmonic hotspots on HSMs. In this work, the nanoarrays on the outer wall of HSMs are duplicated from nanoimprinted Al substrates. It is convenient to modify the parameters of hierarchical nanoarrays on HSMs by the rational design of nanopatterns on Al substrates. The Al substrates with various nanopatterns are nanoimprinted by tuning the surface morphology of AAO stamps, as well as selecting either the pore-side or the barrier-side of the stamp during nanoimprint.<sup>64</sup> The average unit size of AAO stamps can be proportionally tuned by adjusting the anodic voltage  $V_{\text{AAO}}$ ,<sup>65</sup> which enables the precise modification of nanoarrays on the outer wall of HSMs. In Figure 4a–d, the nanobowl-arrayed outer wall of HSMs with



**Figure 4.** HSMs with the nanobowl-arrayed outer wall. SEM images of HSMs rolled up on pore-side-imprinted Al substrates with  $V_{\text{AAO}}$  values of (a) 30, (b) 40, (c) 50, and (d) 60 V. Insets of (a–d): corresponding magnified view of the nanobowl-arrayed outer wall. (e) Statistical results of nanobowl size shown in the insets of (a–d); the red line is the linear fitting of the average nanobowl size against the  $V_{\text{AAO}}$  value. Scale bars: 200 nm.

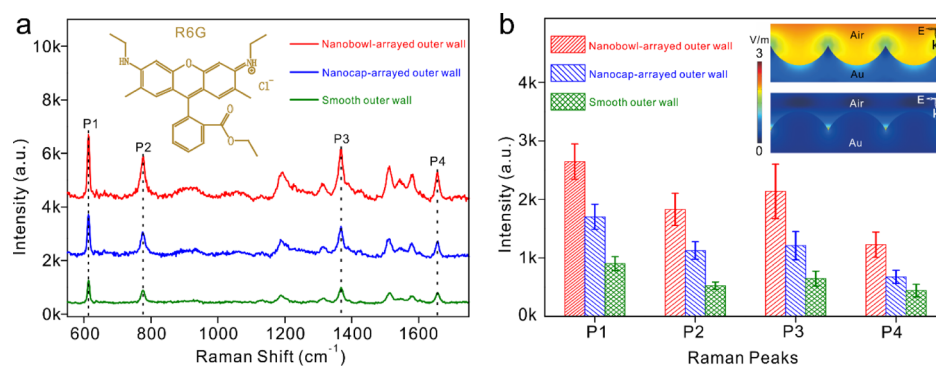
different unit sizes are illustrated, where the corresponding nanoimprinted Al substrates are also presented. To show the nanobowl-arrayed patterns on HSMs more clearly, the magnified views are displayed in the insets of Figure 4a–d, from which the size distributions of nanobowls are statistically studied (as shown in Figure 4e). The result demonstrates the linear relationship between the average nanobowl size and the  $V_{\text{AAO}}$  value, which is in agreement with the case of AAO stamps. Different from HSMs with the nanobowl-arrayed outer wall, the ones with the nanocap-arrayed outer wall are constructed by releasing planar prestrained nanomembranes from barrier-side-imprinted Al substrates (as shown in Figure 5a–d). The magnified view of nanocap arrays on HSMs is shown in the inset of Figure 5a–d, from which the average nanocap sizes are



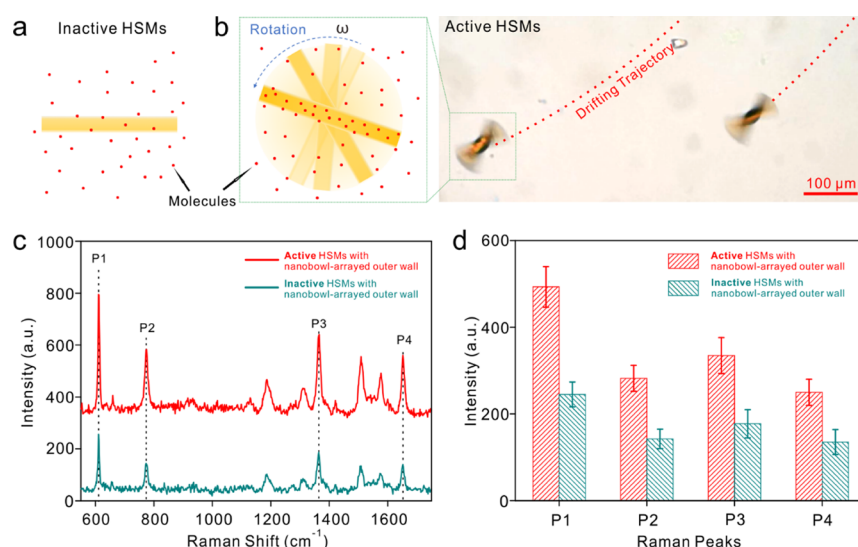
**Figure 5.** HSMs with the nanocap-arrayed outer wall. SEM images of HSMs rolled up on barrier-side-imprinted Al substrates with  $V_{\text{AAO}}$  values of (a) 30, (b) 40, (c) 50, and (d) 60 V. Insets of (a–d): corresponding magnified view of the nanocap-arrayed outer wall. (e) Statistical results of the nanocap size shown in the insets of (a–d); the red line is the linear fitting of the average nanocap size against the  $V_{\text{AAO}}$  value. Scale bars: 200 nm.

statistically studied, as shown in Figure 5e. The average nanocap size presents linear relationship versus  $V_{\text{AAO}}$  as well.

**2.2. Active Molecular Enrichment by HSMs for Ultra-sensitive SERS Sensing.** SERS experiments are conducted to verify the effectiveness of the “motile hotspots” strategy in realizing ultrasensitive SERS sensing. First, the SERS performance of HSMs with nanobowl- and nanocap-arrayed outer walls ( $V_{\text{AAO}} = 40$  V) are evaluated to confirm the contribution of hotspots engineering. The micromotor featuring smooth outer wall is selected as a reference, which is rolled up on the flat Al substrate. The SEM image of the micromotor with a smooth outer wall is shown in Figure S6. Rhodamine 6G (R6G) is selected as the probe molecule for its well-studied Raman properties.<sup>66,67</sup> Micromotors with smooth, nanobowl-arrayed, and nanocap-arrayed outer walls are transferred into R6G solutions separately. In this case, it does not involve any external power source; therefore, R6G molecules are passively adsorbed on HSMs. The passive adsorption manner depends largely on passive diffusion of molecules from the bulk phase to vicinity of the plasmonic surface; therefore, longer molecular capturing duration is always required for establishing adsorption/desorption equilibrium. As shown in Figure 6a,b, four characteristic Raman peaks of R6G are monitored, marked as P1 (612  $\text{cm}^{-1}$ ), P2 (773  $\text{cm}^{-1}$ ), P3 (1365  $\text{cm}^{-1}$ ), and P4 (1650  $\text{cm}^{-1}$ ). P1 and P2 can be assigned to in-plane and out-of-plane bending motions of carbon and hydrogen atoms of the xanthene skeleton, respectively; P3 and P4 correspond to the aromatic C–C stretching vibration modes. By monitoring P2, the HSMs with nanobowl- and nanocap-arrayed outer walls show  $\sim 3.5$  and  $\sim 2.2$  times stronger Raman intensity when compared with the micromotor with smooth outer wall, respectively. The increased



**Figure 6.** Verification of contribution of hotspots engineering to ultrasensitive SERS sensing. (a) SERS spectra of R6G acquired from micromotors with different outer wall morphologies: smooth, nanobowl-arrayed ( $V_{AAO} = 40$  V), and nanocap-arrayed ( $V_{AAO} = 40$  V); the concentration of R6G:  $10^{-5}$  M; four characteristic Raman peaks of R6G are marked as P1 ( $612\text{ cm}^{-1}$ ), P2 ( $773\text{ cm}^{-1}$ ), P3 ( $1365\text{ cm}^{-1}$ ), and P4 ( $1650\text{ cm}^{-1}$ ). (b) Raman intensity histograms of P1, P2, P3, and P4 derived from the SERS spectra in (a); inset: simulated two-dimensional electromagnetic field distribution map of the nanobowl and the nanocap array.



**Figure 7.** Confirmation of active HSMs in accelerating the process of molecular adsorption. (a) Schematics of passive molecular adsorption of inactive HSMs in fluid. (b) Optical image of magnet-powered HSMs during active molecular enrichment; rotation of HSMs is schematically shown, and drifting trajectories are marked as red dashed lines. For full video, please refer to the [Supporting Information Movie](#). (c) SERS spectra acquired from inactive and active HSMs after molecular enrichment (the concentration of R6G:  $5 \times 10^{-8}$  M). (d) SERS intensity histograms of R6G characteristic Raman peaks derived from (c).

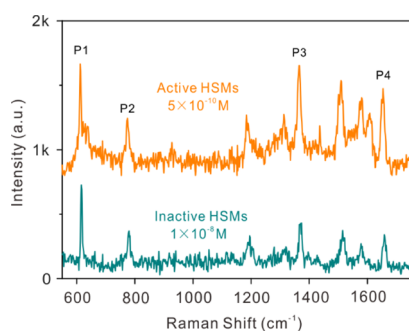
SERS intensity originates from the plasmonic hotspots on the outer wall of HSMs, indicating the effectiveness of hotspots engineering in boosting the SERS performance. The finite-differential time-domain (FDTD) simulations are also conducted to further confirm the contribution of hotspots engineering (inset of [Figure 6b](#)) in which the enhanced near-fields are observed in the center of nanobowls and the gaps between adjacent nanocaps (the incident wavelength is set as  $532\text{ nm}$ ).

Subsequently, the HSMs with the nanobowl-arrayed outer wall ( $V_{AAO} = 40$  V) are selected to evaluate the efficiency of active molecular enrichment. As shown in [Figure 7a,b](#), the HSMs without an external power source are defined as “inactive,” while the ones powered by an external rotating magnetic field are defined as “active.” The inactive and active HSMs undergo different molecular adsorption processes in R6G solutions with the concentration of  $5 \times 10^{-8}$  M. For passive adsorption cases (inactive HSMs), the time of establishing adsorption–desorption equilibrium of R6G molecules on metallic surface is generally  $\sim 120$  min at room temperature.

The optical image of active HSMs in [Figure 7b](#) is taken from the [Supporting Information Movie](#), which presents their motion behaviors comprising rotation and drift. The rotation of active HSMs is schematically shown, and the drifting trajectories are also marked as red dashed lines. These two motion behaviors could significantly contribute to the micromixing effect and increase capturing probability of R6G molecules simultaneously. To prove the capability of active HSMs in accelerating the process of molecular adsorption, the molecular enrichment time of inactive and active HSMs are all set as 15 min, while the adsorption–desorption equilibrium of R6G molecules is not yet established for these two approaches. As shown in [Figure 7c,d](#), the increased Raman intensities can be observed on the active HSMs, showing 2.1 times higher than that on the inactive ones by monitoring P2. The enhanced Raman intensity on active HSMs strongly verifies that the active ones enrich more R6G molecules than inactive ones within the same time.

Next, the effectiveness of active molecular enrichment in further promoting the SERS performance is verified by comparing the detection limit of active and inactive HSMs

with the nanobowl-arrayed outer wall. As shown in Figure 8, the Raman signals of R6G can be observed down to  $5 \times 10^{-10}$  M for



**Figure 8.** Comparison of the detection limit of active and inactive HSMs. SERS spectra acquired from HSMs with the nanobowl-arrayed outer wall after active molecular enrichment in R6G solution with a concentration of  $5 \times 10^{-10}$  M and after inactive molecular adsorption in R6G solution with a concentration of  $1 \times 10^{-8}$  M.

active ones, while  $1 \times 10^{-8}$  M for inactive ones. The enhancement factor of active HSMs is calculated to be  $\sim 3.39 \times 10^7$  at the R6G concentration of  $5 \times 10^{-10}$  M, and inactive HSMs is calculated to be  $\sim 1.17 \times 10^6$  at the R6G concentration of  $1 \times 10^{-8}$  M. The detailed calculations of the enhancement factor are presented in Note S3. This evidence indicates that the active manner is more efficient in enriching analytes on the plasmonic surface compared with the passive adsorption way. In the case of active HSMs, the overall Raman enhancement results from the synergistical effect of hierarchical plasmonic nanoarrays on the outer wall and in active molecular enrichment manner, which successfully demonstrates the “motile hotspots” strategy of great effectiveness in realizing ultrasensitive SERS sensing.

### 3. CONCLUSIONS

In this work, we propose a concept of “motile hotspots” to realize ultrasensitive SERS sensing by combining the superiorities of hotspots engineering and active molecular enrichment. The construction of HSMs is the prerequisite for achieving “motile hotspots” in promoting the SERS performance. HSMs are fabricated in combination of nanoimprint and rolling origami techniques. The 3D tubular HSMs are constructed by rolling up planar prestrained nanomembranes on nanoimprinted Al substrates. No sacrificial layer or wet etching procedure is required during the construction, demonstrating a simple and clean approach eligible for massive production. The tubular diameter and length of HSMs can be tailored by designing thickness and diameter of the initial planar prestrained nanomembranes. Particularly, the rolling origami technique enables facile assembly of plasmonic nanostructures on the outer wall of HSMs, offering multiple choices in engineering dense plasmonic hotspots on HSMs. Eventually, the dense hotspots carried on the outer wall of HSMs are powered by an external rotating magnetic field to actively enrich molecules in fluid. The capabilities of active HSMs in accelerating the process of molecular adsorption and enriching more molecules are revealed. The increased number of molecules adjacent to the hotspots significantly contributes to the enhanced SERS intensities. Our demonstration provides a new concept to design a high-performance SERS platform in a synergistical way. Moreover, the construction methodology of HSMs may also

benefit the fields of bio-sensing, photocatalysis, and micro-battery.

## 4. EXPERIMENTAL SECTION

**4.1. Nanoimprint of Patterned Al Substrates.** AAO templates are utilized to nanoimprint periodic nanocap (or nanobowl) arrays on Al substrates. The nanoimprinted morphology of Al substrates can be readily modified by choosing either the pore-side or the barrier-side of AAO stamps, as well as tailoring the anodization voltage  $V_{AAO}$  during growth of AAO templates. The fabrication method of AAO templates and the detailed nanoimprint procedures can be found in the Supporting Information.

**4.2. Rolling Up of HSMs.** The nanoimprinted (or polished) Al substrates are covered by hard masks with periodic circular opening arrays. Subsequently, Au/SiO/Fe multilayer nanomembranes with thicknesses of 30/30/30 nm (40/40/40, 50/50/50, or 60/60/60 nm) are deposited layer by layer on the nanoimprinted (or polished) Al substrates via electron beam evaporation. The deposition rates for each layer are maintained at 1.0/1.5/2.5 Å  $s^{-1}$  separately. Then, the hard masks are removed for reusing. Finally, the fresh-deposited planar prestrained nanomembranes are immersed into ethanol for 1 min and then taken out and dried.

**4.3. Magnet-Powered Active Molecular Enrichment.** R6G ethanol solution (10  $\mu$ L) with a concentration of  $10^{-7}$  M is first dropped on the Si substrate, and then, a droplet of ethanol (10  $\mu$ L) containing HSMs is transferred into R6G solution. The average amount of HSMs in each droplet is about 6. The HSMs are powered by an external rotating magnetic field for active molecular enrichment. The rotating speed of the external magnetic field is set at 500 rpm. At this time, the HSMs can only move within the droplet because of the confinement of the droplet edge. After molecular enrichment, exceeding amount of R6G solution is removed, and HSMs are dried for Raman measurements. The molecular adsorption time is 15 min for verifying the effectiveness of active HSMs in accelerating the process of molecular adsorption. The molecular adsorption time is 120 min for testing the detection limit of inactive and active HSMs.

**4.4. Instrumentation and Data Acquisition.** Optical images and movies are acquired on an optical microscope (Olympus BX51). The SEM images are acquired on a field-emission scanning electron microscope (FEI Inspect F50). Atomic force microscopy (Bruker Dimension Icon) is used to investigate the surface morphology. Image-Pro Plus is used to conduct the statistical analysis of the size of nanobowl and nanocap on HSMs. The Raman measurements are performed at room temperature on a Jobin Yvon Lab RAM HR 800 micro-Raman spectrometer with a 532 nm excitation laser. The laser power density is about  $1.40 \times 10^6$  mW  $cm^{-2}$ . The FDTD simulations are carried out on COMSOL, where the Drude model is adopted. The unit size of nanocap and nanobowl is set to be 100 nm. The domain size is set to be  $300 \times 200$  nm (length and height). Periodic boundary conditions are applied to the left and right domains; a scattering boundary condition is applied on the top domain; and a perfect conducting boundary condition is applied on the bottom domain. Plasmonic modes are excited by a plane-wave source with incident direction perpendicular to the plane of the structure. The incident light wavelength is 532 nm, and its electric field intensity is 1 V/m. The optical constants of Au are set as  $\epsilon' = -4.68$  and  $\epsilon'' = 2.43$ .

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c05371>.

Preparation of AAO stamps, nanoimprint of patterned Al substrates, calculation of enhancement factors, SEM images of AAO pore-side and AAO barrier-side and corresponding nanoimprinted Al substrates, SEM images of HSMs with different tubular diameters and lengths, and



SEM images of magnified view of micromotors with smooth outer wall (PDF)

Magnet-powered active molecular enrichment process of HSMs in fluid (MP4)

## AUTHOR INFORMATION

### Corresponding Author

Teng Qiu – School of Physics, Southeast University, Nanjing 211189, China; [orcid.org/0000-0002-1160-2619](https://orcid.org/0000-0002-1160-2619); Email: [tqiu@seu.edu.cn](mailto:tqiu@seu.edu.cn)

### Authors

Xingce Fan – School of Physics, Southeast University, Nanjing 211189, China; [orcid.org/0000-0002-2508-3063](https://orcid.org/0000-0002-2508-3063)

Qi Hao – School of Physics, Southeast University, Nanjing 211189, China

Mingze Li – School of Physics, Southeast University, Nanjing 211189, China

Xinyuan Zhang – Department of Materials Science, Fudan University, Shanghai 200433, China

Xiaozhi Yang – School of Physics, Southeast University, Nanjing 211189, China

Yongfeng Mei – Department of Materials Science, Fudan University, Shanghai 200433, China; [orcid.org/0000-0002-3314-6108](https://orcid.org/0000-0002-3314-6108)

Complete contact information is available at:

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### Author Contributions

X.F. and T.Q. conceived and designed experiments. X.F., X.Z., and X.Y. fabricated the samples. X.F. and Q.H. analyzed the data. X.F. and M.L. performed the simulations. The manuscript was primarily written by X.F. and revised by Q.H., Y.M., and T.Q. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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