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Gold Nanofingers for Molecule Trapping and Detection

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Abstract: Here we demonstrate a molecular trap structure that can be formed to capture analyte molecules in solution for detection and identification. The structure is based on gold-coated nanoscale polymer fingers made by nanoimprinting technique. The nanofingers are flexible and their tips can be brought together to trap molecules, while at the same time the gold-coated fingertips form a reliable Raman hot spot for molecule detection and identification based on surface enhanced Raman spectroscopy (SERS). The molecule self-limiting gap size control between fingertips ensures ultimate SERS enhancement for sensitive molecule detection. Furthermore, these type of structures, resulting from top-down meeting self-assembly, can be generalized for other applications, such as plasmonics, meta-materials, and other nanophotonic systems.

Understanding and controlling the hot spots for ultrahigh Raman scattering enhancement, with the ultimate goal of detecting and identifying single molecules reliably, have been a major focus of the surface enhanced Raman spectroscopy (SERS) research community for the past few decades.[1] One of the critical issues for achieving reproducible hot spots has been the control of the gap size between plasmonic structures with sub-nanometer precision in order to maximize the electric field experienced by a molecule.[2] Even though such small gaps have been observed in aggregates of pre-synthesized nanoparticles[3] as well as break junctions formed by electromigration,[4] they were difficult to produce uniformly. On the other hand, various fabrication approaches have been applied in order to produce hot spots uniformly over a large area,[5] but achieving sub-nanometer critical dimension control is beyond the capability of existing fabrication techniques. Furthermore, molecules might not land inside hot spots even if they could be precisely prefabricated.

Here we show a nanoscale structure with gold-coated flexible polymer fingers that can close to trap molecules and at the same time form reliable hot spots at the fingertips for molecule detection based on SERS. Since the molecules trapped by the fingertips dictate the gap size, a hot spot with an ultrahigh field enhancement is ensured. The nanofingers were deterministically fabricated with a high density over a large surface area with nanoimprint lithography.[6] The fingers can self-close driven by the microcapillary force under exposure to liquid. These structures can provide a generic platform for molecule trapping and SERS sensing with high sensitivity and uniformity, which can help to transform SERS into a practical analytical technique.

As illustrated in Figure 1a, we have fabricated high-density square arrays of free-standing polymer nanofingers on substrate surfaces using nanoimprint lithography. A scanning electron microscope (SEM) image of a gold-coated nanofinger array is shown in Figure 1c; the typical diameter of each finger is 100 nm,

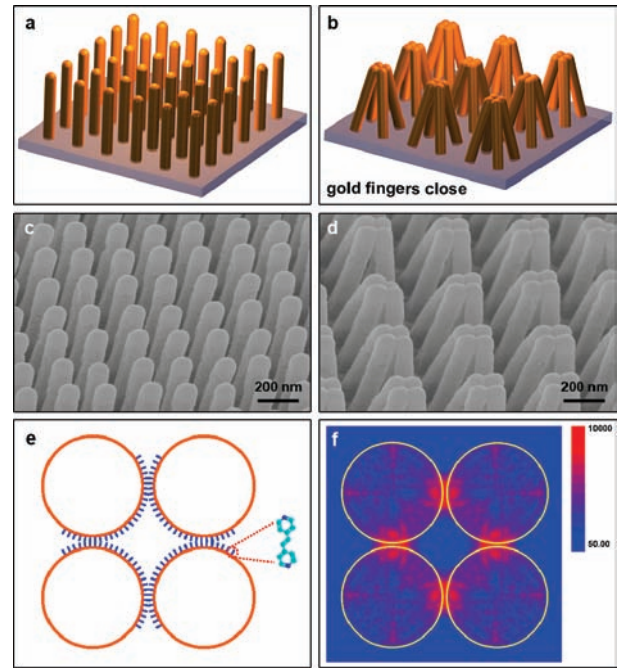

Figure 1. Gold nanofingers. (a,b) Schematic of capillary-force-driven self-closing of the gold fingers. (c,d) SEM images of open fingers vs closed fingers after molecule trapping. (e) Schematic of molecules trapped in the nanogaps of the fingers. (f) Distribution of electric field intensity $|E(r)|^2$ (indicated by color bar) at 750 nm for the four Au spheres of 68 nm radius.

the height is 700 nm, and the area density is ~25 fingers/μm^2. After the arrays were exposed to analyte solutions and air-dried, the fingers closed together in groups of four, as shown schematically in Figure 1b and in the SEM image of Figure 1d. If molecules sit between the fingertips, they are the primary factor that determines the gap size, which is below the SEM resolution. The finger closure is driven by capillary forces during the liquid drying step. As the solvent evaporates from the array, neighboring fingers are pulled toward each other while the analyte molecules are wicked up the fingers and trapped between the fingertips after the evaporation is complete. This capillary-force-induced structural deformation, especially for high-aspect-ratio micro- or nanostructures, has been observed within the microelectromechanical systems (MEMS) community, where it has mostly been considered a nuisance; only recently was it harnessed to make self-assembled hierarchical structures.[7]

Discrete dipole approximation (DDA) was used to model the gold fingertips (Figure 1e). The plan view of the electric field map through the four gold spheres for 750 nm unpolarized incident radiation is shown in Figure 1f. (See Supporting Information for more details.) The strongest fields are concentrated in the four gaps

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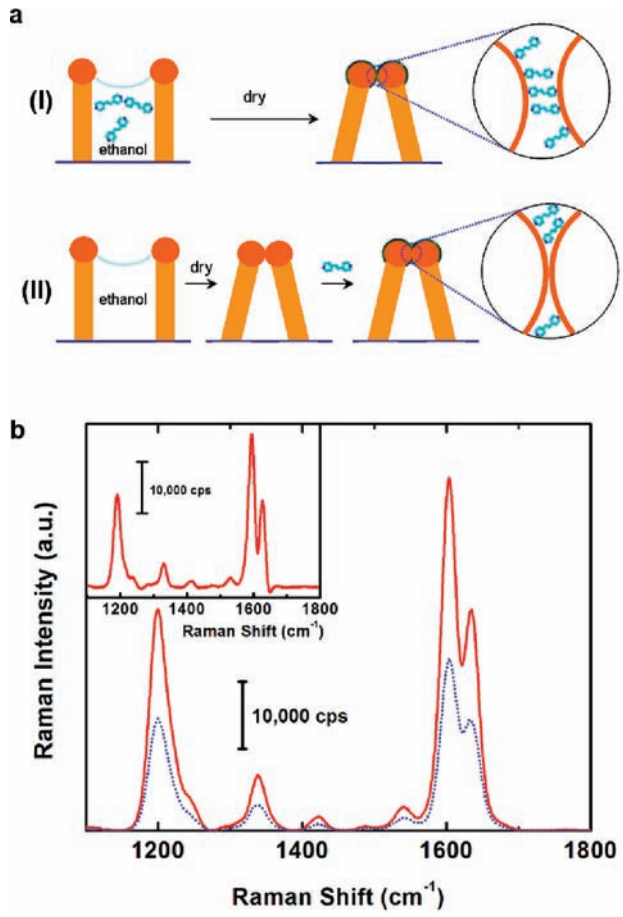

Figure 2. Demonstration that molecules were trapped in the fingertips. (a) Schematic illustrations: (I) fingers immersed in analyte solution and dried to close the fingers and (II) fingers immersed in pure ethanol to close the fingers prior to exposure to analyte solution. The insets show the presumed details at the fingertips for both cases. (b) Comparison of Raman spectra of the analyte molecules from case I (red spectrum) and case II (blue spectrum). The inset shows the difference spectrum of the red and the blue spectra, indicating the net contribution from the molecules trapped in the fingertips.

of the spheres, with the maximum enhancement of $|E|^2$ about $10000\times$ that of the incident field.

In order to test our molecule trapping and Raman enhancement hypothesis, we examined three widely used molecules for SERS studies, *trans*-1,2-bis(4-pyridyl)ethylene (BPE), 4-mercaptophenol (4MP), and Rhodamine 6G (R6G) (data shown in Figure S1 in Supporting Information). All spectra were collected with the same micro-Raman setup through a $100\times$ objective; the Raman intensity of the closed versus open finger structures was a factor of 10 higher for BPE and 4MP, and a factor of 30 higher for R6G, demonstrating that fingertips in proximity were more effective at enhancing the spectral intensity than isolated fingers. Multiple points on the finger arrays were measured over a sample area of 1 in.^{2} with the variation of the Raman intensity <10% from point to point, which demonstrated good uniformity of the enhancement.

Nonetheless, did we actually trap molecules between the gold fingertips? In order to address this question, we performed the experiment illustrated schematically in Figure 2a. We cleaved a sample into two pieces with the same finger array on both parts. One piece was immersed in 1 mM BPE ethanolic solution for 10 min, removed, and air-dried as before; the other piece was immersed in pure ethanol for 10 min, removed, and air-dried to induce finger closing, and then re-immersed in the 1 mM BPE ethanolic solution for 10 min to adsorb BPE onto the fingers. Both samples were rinsed extensively with pure ethanol before collecting Raman spectra. The Raman signal from the sample initially immersed in the solution (red spectrum) was more than twice as intense as that observed from the sample initially immersed in ethanol (blue spectrum), as shown in Figure 2b. The inset in Figure 2b shows the difference spectrum, derived by subtracting the blue spectrum from the red spectrum, and we assign this increased intensity to molecules trapped between the fingertips. Thus, the trapped molecules contributed almost 60% of the total Raman signal of the sample initially immersed in solution.

Using the common method for calculating the enhancement factor (EF),[1] we estimated a conservative EF for the molecules between the closed fingertips to be $\mathrm{EF} = (I_{\mathrm{SERS}}/N_{\mathrm{SERS}})/(I_{\mathrm{bulk}}/N_{\mathrm{bulk}}) \approx 2 \times 10^{10}$, where within the $\sim 2\ \mu\mathrm{m}^2$ laser spot there were 50 fingers, with $\sim$5 molecules/finger gap (a more detailed description is in the Supporting Information). A more accurate way to quantify the number of molecules trapped between the fingertips will be required to provide an improved value for EF. Recently, a study of the Raman hot-spot distribution on silver-coated close-packed polystyrene spheres revealed that a small fraction of molecules adsorbed on hot-spot sites with enhancement factor $>10^{10}$ contributed about 7% of the total SERS signal.[8] Since the molecules trapped in the fingertips of our structures contributed $\sim$60% of the total Raman signal, active trapping appears to significantly improve the SERS enhancement.

By using imprint lithography to fabricate the nanofinger arrays, we can duplicate the same structures inexpensively over a large area. Imprinting also enables the use of a variety of substrate materials and shapes, such as polymers, glass, and curved surfaces, and also allows facile integration with optical components such as mirrors, prisms, and lenses. Since we do not depend on the fabrication technique to control the precise gap size, the critical dimension of the imprint process is not critical for reliable formation of the assembled structures. Furthermore, the plasmonic properties of the self-closed finger assemblies can be easily tuned by coating the fingers with different metals as well as dielectric shells. Finally, the concept of using top-down meeting self-assembly can be generalized to form various two-dimensional and three-dimensional functional structures that self-assembly alone cannot achieve. Therefore, we expect this finger structure concept not only can be a generic platform for molecule trapping, detection and identification with high sensitivity and uniformity based on SERS, but also can be generalized for other functional plasmonic structures[9] and metamaterials[10] as well as other nanophotonic systems.[11]

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Supporting Information Available: Full experimental details and characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Van Duyne, R. P.; Kneipp, K.; Kneipp, H.; Schatz, G. C. *Surface-Enhanced Raman Scattering - Physics and Applications*; Springer: Berlin/Heidelberg, 2006. (b) Moskovits, M. *J. Raman Spectrosc.* **2005**, *36*, 485–496. (c) Nie, S.; Emory, S. R. *Science* **1997**, *275*, 1102–1106.
(2) (a) Jiang, J.; Bosnick, K.; Maillard, M.; Brus, L. *J. Phys. Chem. B* **2003**, *107*, 9964–9972. (b) Camden, J. P.; et al. *J. Am. Chem. Soc.* **2008**, *130*, 12616–12617.
(3) Lim, D. K.; Jeon, K. S.; Kim, H. M.; Nam, J. M.; Suh, Y. D. *Nat. Mater.* **2010**, *9*, 60–67.
(4) Ward, D. R.; Grady, N. K.; Levin, C. S.; Halas, N. J.; Wu, Y.; Nordlander, P.; Natelson, D. *Nano Lett.* **2007**, *7*, 1396–1400.

(5) (a) Hulteen, J. C.; Van Duyne, R. P. *J. Vac. Sci. Technol. A* **1995**, *13*, 1553–1558. (b) Tao, A. R.; Sinsermsuksakul, P.; Yang, P. *Nature Nanotechnol.* **2007**, *2*, 435–440. (c) Tang, J.; et al. *Appl. Phys. A: Mater. Sci. Process.* **2009**, *96*, 793–797. (d) Diebold, E. D.; Mack, N. H.; Doorn, S. K.; Mazur, E. *Langmuir* **2009**, *25*, 1790–1794.
(6) (a) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *J. Vac. Sci. Technol. B* **1996**, *14*, 4129–4133. (b) Chen, Y.; et al. *Nanotechnology* **2003**, *14*, 462–468. (c) Wu, W.; Hu, M.; Ou, F.-S.; Li, Z.; Williams, R. S. *Nanotechnology* **2010**, *21*, 255502.
(7) (a) Segawa, H.; et al. *Appl. Phys. A: Mater. Sci. Process.* **2006**, *83*, 447–451. (b) Chandra, D.; Yang, S. *Langmuir* **2009**, *25*, 10430–10434.
(8) Fang, Y.; Seong, N. H.; Dlott, D. D. *Science* **2008**, *321*, 388–392.
(9) Mertens, H.; Biteen, J. S.; Atwater, H. A.; Polman, A. *Nano Lett.* **2006**, *6*, 2622.
(10) Pendry, J. B.; Schurig, D.; Smith, D. R. *Science* **2006**, *312*, 1780.
(11) Engheta, N. *Science* **2007**, *317*, 1698.

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