

# Molecule-sensitive and selective gap plasmon-enhanced Raman sensing platform with ultrahigh-density one-nanometer gaps

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## Abstract

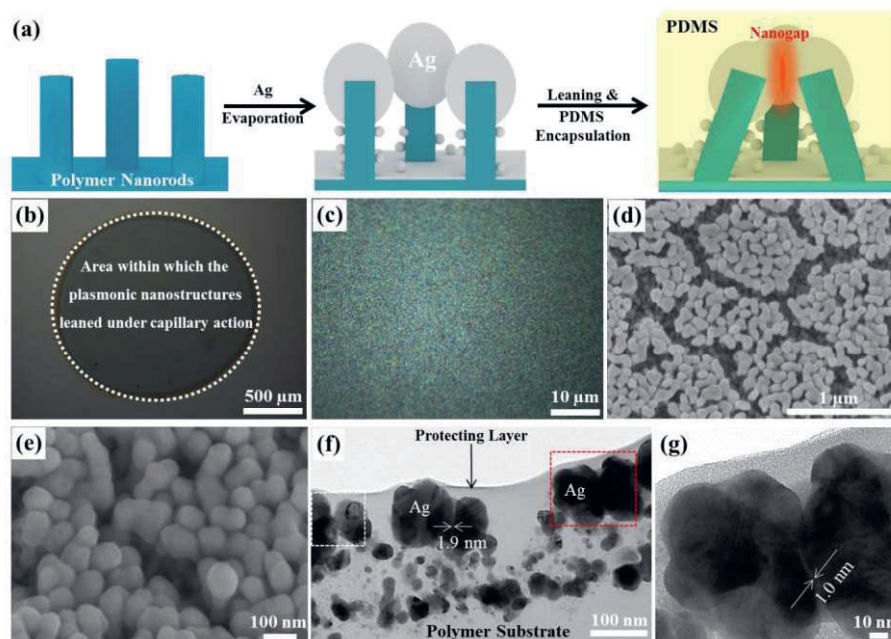
We report a molecule-sensitive and selective nanogap-enhanced plasmonic detection platform with ultrahigh-density one nanometer gaps. We developed a simple method for generating ultrahigh-density plasmonic nanogaps through a direct maskless plasma treatment of a polymer surface in conjunction with the surface tension-driven assembly of freestanding metal nanoparticles. We confirmed that the nanogap size was on the one-nanometer scale. These structures produced an enhanced near-field interaction via coupled localized surface plasmon resonance among Ag nanoparticles. The high areal density of the small nanogaps yielded both a high plasmonic detection performance, with an average Raman enhancement factor (EF) of  $1.5 \times 10^7$ , and a small standard deviation of 11.4%. Inspired by the selective permeation of target substances through cell membranes, the encapsulation of plasmonic nanostructures within nanofiltration membranes enables the selective filtration of molecules based on the degree of membrane swelling and molecular size. Nanofiltration membrane-encapsulated plasmonic substrates do not require pretreatment to exclude large particles or debris in real applications; therefore, they provide a simple and highly effective method of detecting hazardous and toxic molecules using Raman spectroscopy.

**Key words:** surface-enhanced Raman spectroscopy, sensors, gap plasmon, nanogap, nanofiltration

Gap plasmons generated at junctions (so-called "hot spots") between metallic nanostructures enable the single molecule detection of plasmon-enhanced optical sensors.[1][2] The near-field interactions between the plasmonic nanostructures create an enhanced electromagnetic (EM) field due to the coupled localized surface plasmon resonance (LSPR). [3][4] This enhancement of the EM field has been exploited in many plasmon-mediated applications. Therefore, significant efforts have been dedicated toward fabricating high-density plasmonic nanogaps. Among the many fabrication methods tested, the capillary action-induced leaning of metallic nanorods offers a simple and efficient strategy for generating nanogaps.[3] The capillary-driven leaning method relies on attractive forces among proximal upright metallic structures during solvent evaporation, inducing contact among two or more nanorods. Target molecules may then be trapped among the bundled nanostructures. It is possible to capture analyte

molecules within the nanogaps to produce highly sensitive surface-enhanced Raman spectroscopy (SERS) sensors.

Here, we report a new method for generating ultrahigh-density one-nanometer nanogaps through the direct maskless dry etching of soft polymer surfaces combined with capillary leaning effects. Molecular selectivity was provided by the physical molecular size exclusion effects of the nanofiltration membrane-encapsulated plasmonic nanostructures. We utilized a simple nanolithography-free two-step process (i.e. direct generation of polyethylene terephthalate (PET) nanorods via maskless dry etching and the subsequent deposition of Ag onto the PET nanorods) to fabricate freestanding Ag NPs deposited onto high aspect ratio polymer nanorods. The plasmonic substrates were coated with ultrahigh-density ( $53/\mu\text{m}^2$ ) free-standing Ag NPs. The capillary-driven leaning effects applied to the free-standing Ag NPs led



**Fig. 1** Fabrication of high-density free-standing Ag nanoparticles (NPs) with one nanometer gaps. (a) Schematic illustration of the nanolithography-free fabrication process used to prepare free-standing Ag NPs. (b) Optical image of the area within which the Ag NPs leaned under capillary action (inside the dotted circle), and the as-prepared upright free-standing Ag NPs (outside the dotted circle). (c) Bright field image of the leaning Ag nanostructures, showing strong Rayleigh scattering from the Ag NPs. White light was used to illuminate the surface, and wavelength-selective Rayleigh scattering was observed. Scanning electron microscopy images of the leaning Ag NPs: (d) top view, and (e) tilted view. The SEM image shows the area density of Ag NPs, calculated to be  $53/\mu\text{m}^2$ . (f, g) Cross-sectional transmission electron microscopy (TEM) images of the leaning Ag NPs. The TEM images showed that the leaning Ag NPs formed nanometer gaps with the adjacent NPs (red dotted rectangles in (f) and (g)), and some of the NPs contacted two or more proximal NPs (white dotted rectangle in (f)).

to the assembly of high-density plasmonic nanogaps with a one nanometer or subnanometer gap size. These nanogaps provided a strong SERS effect with an average enhancement factor (EF) of  $1.5 \times 10^7$  and a high signal uniformity with a small standard deviation of 11.4%. We also found that the deposition of a thin inorganic ZnO layer (8.4 nm thick) onto the polymer nanorods improved the mechanical strength of the nanorods, which led to greater structural stability, even after applying the capillary force. Molecular selectivity was obtained by taking advantage of the polydimethylsiloxane (PDMS) membrane swelling properties in a nonpolar organic solvent. A plasmonic sensing platform was obtained with a molecular selectivity that depended on the degree of swelling of the nanofiltration membrane as well as molecular size effects. The molecular selectivity was demonstrated by observing that small methylene blue (MB, molecular weight (MW) of 319.85 g/mol) molecules dissolved in chloroform diffused into the hot spot region, whereas the large rhodamine 6G (MW of 479.02 g/mol) molecules were excluded; however, dissolving the MB molecules in deionized (D.I.) water resulted in the exclusion of even the small MB molecules because the

PDMS membrane did not swell in D.I. water. The nanofiltration membrane-encapsulated plasmonic substrates could be used for molecular detection in organic solvent, indicating that this sensing platform might facilitate environmental monitoring and hazardous molecule detection, especially in the chemical and food industries, where large amounts of organic solvents are used.

## References

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