[Supporting Information]

Nanoparticle-Coated PDMS Elastomers for Enhancement of Raman Scattering

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Experimental Section

Materials

Gold (III) chloride trihydate ($HAuCl_4 \cdot 3H_2O$), silver nitrate ($AgNO_3$), sodium citrate (Na_3Ct), sodium borohydride ($NaBH_4$), 98 % sulfuric acid (H_2SO_4), 30 % hydrogen peroxide (H_2O_2), acetone, 3-aminopropyltriethoxysilane (APTES), *p*-aminothiophenol (PATP), and methylene blue (MB) were purchased from Sigma-Aldrich Pte Ltd. (Singapore). Silicone elastomer and silicone elastomer curing agent (Sylgard® 184 silicone elastomer kit) were purchased from Dow Corning Corporation (Midland, MI). Silicon wafers were purchased from Bonda Technology, Singapore. All chemicals were used as received without further purification. Milli-Q water (Milli-Q System, Millipore, Billerica, MA) was used in all experiments.

Synthesis of Au and Ag nanoparticles (NPs)

The Au NPs and Ag NPs used in this work were synthesized using a two-step method.[1,2] Briefly, 13 nm Au NPs was prepared by boiling of $HAuCl_4$ (0.5 mM) and Na_3Ct (1 wt%) for 20 min.[3,4] The as-prepared Au NP seeds (different amount) were added into 20 mL solution of $HAuCl_4$ (0.5 mM) and heated to boiling, followed by addition of 2 mL Na_3Ct (1 wt%), to obtain the bigger Au NPs.

The Ag seed was firstly synthesized by addition of 60 μL of $NaBH_4$ (0.1 M) into 2 mL mixed solution of Ag NO_3 (0.5 mM) and Na_3Ct (1.5 mM), followed by aging for 2-5 h. Then the as-prepared Ag NP seeds (different amount) were added into 20 mL Ag NO_3 (0.5 mM) and heated to boiling, followed by addition of 2 mL Na_3Ct (1 wt%), to obtain bigger Ag NPs.

The size of synthesized Au or Ag NPs was measured by TEM. These synthesized Au or Ag NPs were used directly in the following experiments.

Preparation of Ag or Au substrate

Silicon wafers were firstly sonicated in acetone for 10 min and rinsed with Milli-Q water, then immersed into a freshly prepared piranha solution ($V(H_2SO_4):V(H_2O_2)= 7:3$) at 100 ^oC for 30 min. After the cleaned substrates were rinsed with Milli-Q water and dried with N_2 flow, they were coated with 3 nm Ti as an adhesion layer and subsequently with 30 nm Ag or Au using a magnetron sputtering system (base pressure $< 1 \times 10^{-5}$ Torr). The surface roughness (root-mean-square, RMS) of a 1×1 μm^2 Ag surface is 6.2 nm, measured by tapping mode atomic force microscopy (TMAFM, Dimension 3100, Veeco, CA, USA).

Fabrication of micropatterns of PATP and MB for Raman mapping

The micropatterns of PATP and MB were fabricated *via* microcontact printing (μCP) of PATP on Ag substrates followed by passivation with MB. A PDMS stamp was first inked with 2 mM PATP ethanolic solution for 10 s. After drying it with N_2 gas, it covered on a fresh Ag surface for 60 s. The PATP-patterned Ag substrate was then passivated with MB by immersing it into a 1 mM ethanol solution of MB for 10 s, followed by rinsing thoroughly with ethanol and drying with N_2.

Fabrication and characterization of nanoparticle-coated polydimethylsiloxane (PDMS) elastomers

Thin PDMS elastomers were fabricated by pouring a mixture of Sylgard® 184 elastomer and curing agent (w/w = 10:1) on a flat Si substrate and heating at 70 ºC for 12 h after degassing.[5] The as-prepared PDMS elastomers were treated with O_2 plasma (Harrick Plasma PDC-32G-2) at a pressure of 200 mTorr and a power of 6.8 W for 30 s, and then immersed in an aqueous solution of APTES (1 wt%) for 10 min,[6] followed by thoroughly rinsing with Milli-Q water and drying with N_2. The APTES-modified PDMS elastomer was immersing in the respective Au or Ag NP solutions for 10 min, followed by thoroughly rinsing with Milli-Q water and drying with N_2. The Au or Ag NP-coated PDMS elastomer was employed as an efficient and convenient tool for Raman detection by simply covering it onto the detected substrate.

Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6340F field-emission scanning electron microanalyzer at an accelerating voltage of 5 kV. Prior to SEM imaging, the Au or Ag NP-coated PDMS was coated with 10 nm Pt film. The Raman detection was carried out on a WITec CRM200 confocal Raman microscopy system with the excitation line of 633 nm and an air cooling charge coupled device (CCD) as the detector (WITec Instruments Corp, Germany). The Raman band of a silicon wafer at 520 cm^{-1} was used as a reference to calibrate the spectrometer.

Supplementary Results

1. Ag NP-coated PDMS elastomers for Raman detection

Besides Au NPs, Ag NPs can also be adsorbed onto the APTES-modified PDMS elastomers for highly sensitive Raman detection. Figures S1D-E show the Raman intensity of MB and PATP after covering the Ag NP-coated PDMS elastomers on MB or PATP coated Ag substrates. The 18±6 nm Ag NP-coated PDMS elastomer (Figure S1A) gives poor Raman enhancement, which is only 7.5 times increased for MB (band at 1625 cm^{-1}) (curve a in Figure S1D). However, the 42±12 and 68±20 nm Ag NP-coated PDMS elastomers (Figures S1B-C) provide 47 and 71 times increase of Raman signal for MB (band at 1625 cm^{-1}), respectively (curves b and c in Figure S1D). Similarly, the Raman intensity of PATP pre-coated on Ag surface is also dramatically enhanced (Figure S1E) after covering the Ag NP-coated PDMS elastomers.

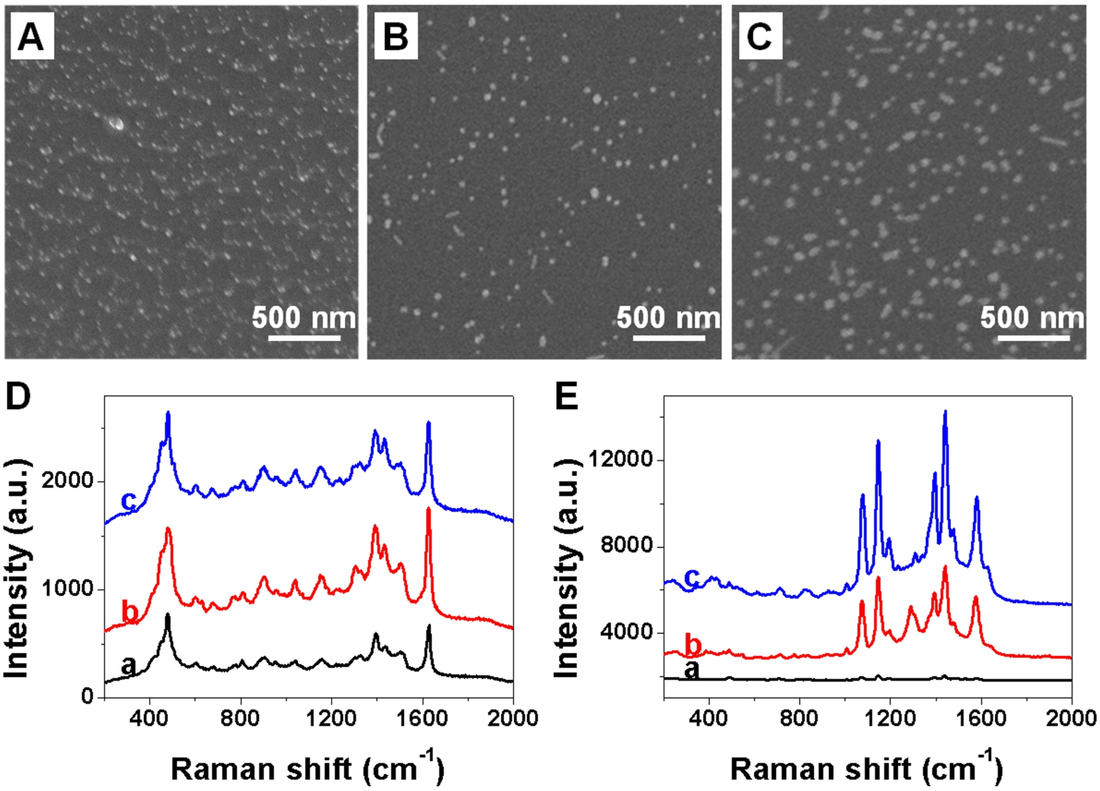

Figure S1. SEM images of Ag NPs with size of (A) 18±6, (B) 42±12 and (C) 68±20 nm adsorbed on PDMS elastomers which were coated with 10 nm Pt film. Raman detection of (D) MB and (E) PATP on Ag substrates which were covered by the Ag NP-coated PDMS elastomer. Curves (a-c) were obtained with different sized Ag NPs (A-C) coated PDMS elastomers.

2. Raman detection of molecules on Au (or Ag) substrates after covering Au (or Ag) NP-coated PDMS elastomers

The Raman enhancements of molecules on Au or Ag substrates after covering Au or Ag NP-coated PDMS elastomers were studied (Figure S2). The Raman enhancement on both Ag and Au substrates achieved by covering the 42 nm Ag NP-coated PDMS elastomers (curves c and d in Figure S2) were larger than that achieved by covering 38 nm Au NP-coated PDMS elastomers (curves a and b in Figure S2). As shown in Figure 2C and S1B, the density of 38 nm AuNPs on PDMS elastomers was higher than that of 42 nm Ag NPs, indicating that the major reason for the larger Raman enhancement achieved by covering the Ag NP-coated PDMS elastomer is the stronger plasmon coupling between Ag NPs on PDMS elastomer and the underneath Ag or Au substrates. By covering the 38 nm Au NP-coated PDMS elastomer, the Raman enhancements of MB on both Au and Ag substrates are comparable (curves a and b in Figure S2) with slightly stronger Raman signals on Ag surface (curve b in Figure S2).

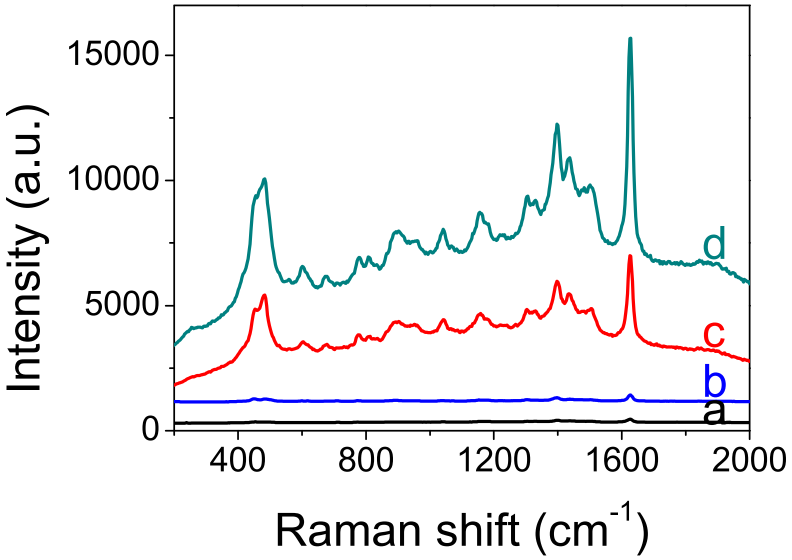

Figure S2. Raman spectra of MB on Au (curves a and c) and Ag (curves b and d) substrates after being covered by the 38 nm Au NP (curves a and b) and 42 nm Ag NP (curves c and d)-coated PDMS elastomers.

References

1. S. Schneider, P. Halbig, H. Grau and U. Nickel, *Photochem. Photobiol.*, 1994, **60**, 605-610.
2. U. Nickel, K. Mansyreff and S. Schneider, *J. Raman Spectrosc.*, 2004, **35**, 101-110.
3. K. C. Grabar, R. G. Freeman, M. B. Hommer and M. J. Natan, *Anal. Chem.*, 1995, **67**, 735-743.
4. G. Frens, *Nat. Phys. Sci.*, 1973, **241**, 20-22.
5. A. Kumar, H. A. Biebuyck and G. M. Whitesides, *Langmuir*, 1994, **10**, 1498-1511.
6. H. Li, J. Zhang, X. Z. Zhou, G. Lu, Z. Y. Yin, G. P. Li, T. Wu, F. Boey, S. S. Venkatraman and H. Zhang, *Langmuir*, 2010, **26**, 5603-5609.