

Flexible SERS active Substrates from Ordered Vertical Au Nanorod Arrays

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Supporting Information

Au nanorod synthesis

Seed Solution (Nanorods 11×41 nm)

CTAB solution (5 mL, 0.2 M) was mixed with 5.0 mL of 0.5 mM HAuCl₄. To the stirred solution 0.6 mL of ice-cold 0.01 M NaBH₄ was added, which resulted in the formation of a pale brown solution. Vigorous stirring of the seed solution was continued for 2 min. Solution was kept at 30 °C until further use.

Growth of Nanorods (11 × 41 nm)

CTAB (25 mL, 0.2 M) was added to 1 mL of 4 mM of AgNO₃ at 30 °C. To this solution, 25 mL of 1 mM HAuCl₄ was added, and after gentle mixing 0.35 mL of 0.0788 M ascorbic acid was added. Upon addition of ascorbic acid the solution color changed from intense orange to colorless. Finally, 70 μL of seed solution were added at 30 °C. The color of the solution gradually changed from colorless to intense red (10-20 min). The solution was stirred at 30 °C until growth process was complete (90-120 min).

Growth of Nanorods (20 × 61 nm)

Nanorods 20 × 61 nm were obtained by overgrowth of previously synthesized nanorods (11×41 nm). Specifically, 0.0788 M ascorbic acid was added dropwise (5 μL/5 min) to 15 mL of nanorod solution previously synthesized. Growth rate was monitored by measuring solution UV-vis spectra every 4/5 ascorbic acid additions. Ascorbic acid was added until no spectroscopic changes were detected (ca. 15 additions).

Organic solvent transfer

Au nanorods in water solution were centrifuged and redispersed in water so that the final CTAB concentration was lower than 0.2 mM. Mercapto-succinic acid (3 mL, 10 mM) was added to 3 mL of aqueous nanorod solution. The pH was adjusted to 9 under vigorous stirring. To this solution 1.5 mL of a 50 mM solution of TOAB in chlorobenzene was added. The resulting mixture was left under vigorous stirring for 30 min until the water phase discoloured and the organic phase became intense red.

Stamping of Au Nanorods

Ordered nanorod arrays were formed by droplet deposition on rigid (glass or SiO₂) surfaces. Figure S11 shows vertical arrays formed on SiO₂. Nanorods assembled in tightly packed hexagonal arrays.

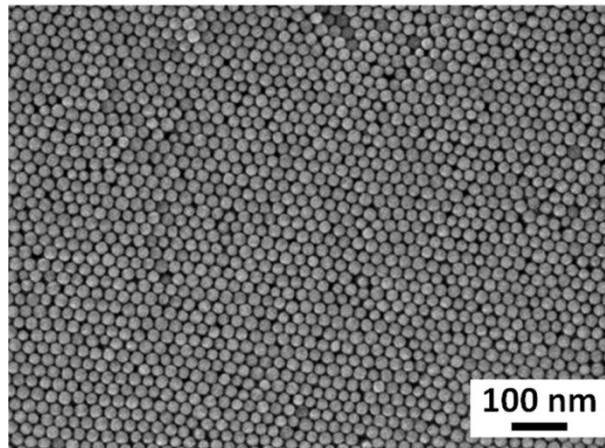


Figure S11. SEM image of Au nanorods droplet deposited on SiO₂ surfaces from chlorobenzene solutions after evaporation of the drop.

EF calculations

The sampling volume used to obtain the Raman spectrum of neat 4-ABT powder was calculated assuming that the laser spot formed a cylinder of 5 μm in diameter and 40 μm in length (penetration depth). Therefore illuminated volume was: $V = \pi r^2 h = 3.14 \times (2.5)^2 \times 40 = 7.8 \times 10^{-10} \text{ cm}^3$.

Since the density of 4-ABT is $d = 1.18 \text{ g/cm}^3$ and its molecular weight (MW) is 125.19 g/mol, the number of 4-ABT molecules illuminated by the laser light is equal to $N_{\text{RN}} = (V \cdot d) / (\text{MW} \cdot \text{AN})$ where V is the illuminated volume, d is the density of 4-ABT, MW is the molecular weight and AN is Avogadro's number 6.022×10^{23} . Accordingly, the calculated N_{RN} is 4.4×10^{12} .

Assuming that the surface illuminated by the laser is $\pi r^2 = 3.14 \times (2.5)^2 = 2 \times 10^{-7} \text{ cm}^2$ and that each 4-ABT molecule occupies an area of ca. 0.2 nm^2 at the full coverage limit on Au, the number of 4-ABT molecules illuminated by the laser light will be 9.8×10^7 ($2 \times 10^{-7} \text{ cm}^2 / 0.2 \times 10^{-14} \text{ cm}^2$) (N_{SERS}).

Since the calculated number of nanorods/ μm^2 is 1262 (experimentally counted), the number of nanorods in the illuminated area is 2.5×10^5 ($2 \times 10^{-7} \text{ cm}^2 \times 1262$). The calculated surface area of one nanorod is 3202 nm^2 , assuming a cylinder of 40 nm length and two semicircles of 20 nm diameter. The total nanorod surface area in the laser spot is $7.9 \times 10^7 \text{ nm}^2$ ($2.5 \times 10^5 \times 3202$). Considering that each 4-ABT molecule occupies an area of ca. 0.2 nm^2 the effective number of molecules illuminated by the laser light is 4.0×10^8 (N_{SERS}). ($7.9 \times 10^7 / 0.2$).

The intensity ratio of the 7a bands at 1080 cm^{-1} in Figure 2, red curve and Figure 2, black curve was measured to be 12 (13150/1080). Recalling that the number of 4-ABT molecules illuminated by the laser light was 4.4×10^{12} the enhancement factor (EF) should be 5.5×10^5 ($13150 / 9.8 \times 10^7$) / ($1080 / 4.4 \times 10^{12}$). However, the actual number of 4-ABT molecules on Au nanorods under the laser spot is 4.0×10^8 , and the calculated EF is 1.4×10^5 ($5.5 \times 10^5 / (4.0 \times 10^8 / 9.8 \times 10^7)$).

Following analogous calculations EF of 9.2×10^4 was obtained for PVC active substrates.

PPET and PVC nanorod stamped substrate reproducibility

Uniformity of the fabricated arrays necessary to provide reproducible results was evaluated by measuring 4-ABT SERS spectra in 4 random points over an area of 5 mm diameter of a perpendicular array stamped on pPET and PVC, respectively. Illumination from a laser at 514 nm was used, the illumination power was 7.5 mW. The obtained spectra are shown in Figure SI2. The intensity change of the Raman band at 1074 cm^{-1} was used to calculate the relative standard deviation of the intensity from 4 points. Values of 14% and 24 % were obtained for pPET and PVC, respectively.

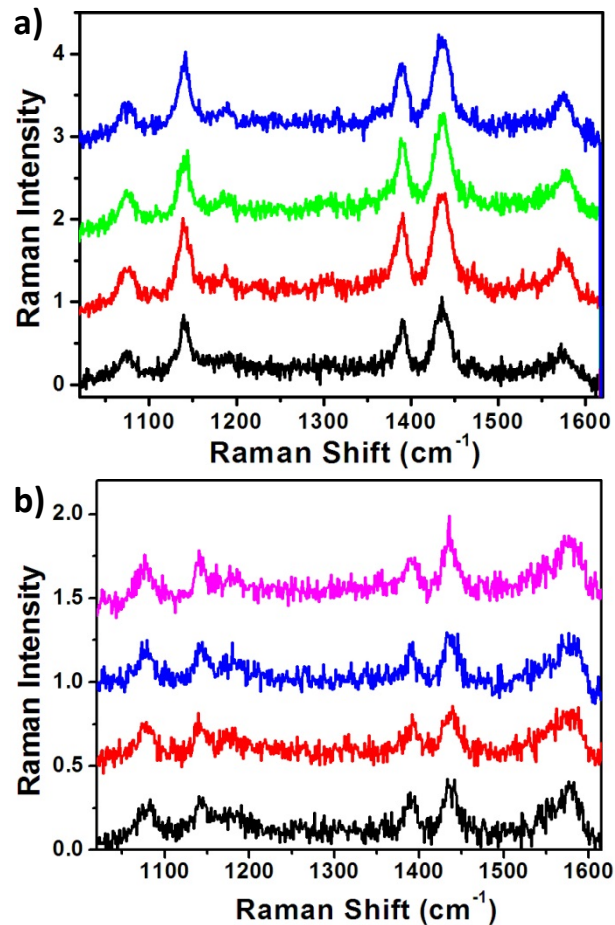


Figure S12) Variation of intensity of 4-ABT C-S stretching band, ν_{7a} , measured in 4 random points across a 5 mm diameter perpendicular array stamped on a) pPET, (SD = 14%) and b) PVC, (SD = 24%).

Paper SERS active substrates

In order to further explore the potential of our developed technique we decided to stamp arrays of nanorods into low-cost commercial flexible substrates like thin film chromatography (TLC) plates and filter paper. The use of adsorbing substrates allowed exploring sampling detection by physical swabbing, which is an efficient method for rapid and accurate sample collection and detection from a real-world surface. In the proposed method the analyte is brought to the detection area by capillary action through paper substrate partially immersed in solvent.

To obtain swabbing SERS spectra flexible support with stamped nanorod arrays were cut into 2 cm stripes. 4-ABT was dissolved in MeOH and spotted on a microscope glass surface. After the sample has dried, the stamped flexible substrates were firmly wiped over the glass slide. In both cases, after the swab had dried the stripe was placed into a vial containing 2 mL of MeOH so that its bottom was in touch with the solvent. MeOH moved up the swab by capillary action collecting analyte from the bulk of the sample and concentrating it into the stamped detection area at the top of the stripe. After ca. 20 min running time the swab was removed from the MeOH, dried and scanned for SERS signals.

Figure SI2 shows SERS spectra from 6 μg of 4-ABT swabbed on TLC plates and filter paper respectively and collected by lateral-flow concentration. Spectra were collected using laser excitation wavelengths 633 and 514 nm for TLC and paper substrates, respectively. Interestingly, both spectra displayed only a_1 bands with the absolute scattering intensity peaks from TLC substrates more intense than those obtained from paper. A summary of peak positions and assignments obtained for TLC stamped substrates is reported in Table SI 1. The low intensity of bands obtained from stamped paper might be ascribed to the partial dissolution of Au nanorods in the paper fibers following lateral-flow concentration. On the other hand lateral flow concentration of Au nanorods stamped on TLC plates likely caused nanorods to penetrate and mix with the dried silica layer constituting the plates resulting in SERS peaks of higher intensity.

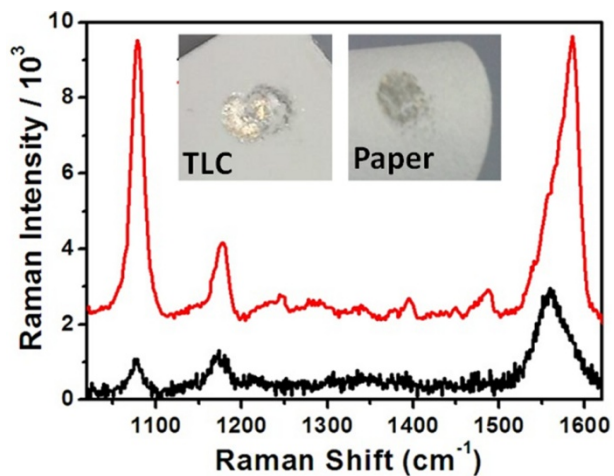


Figure S12. SERS spectra of 4-ABT obtained by swabbing and capillary collection obtained with TLC (red curve) and chromatographic paper (black curve) active substrates.

Peak Position 4-ABT powder	Peak Position 4-ABT/TLC	Assignments*
1591	1585	ν CC, 8a (a_1)
1569		ν CC, 8b (b_2)
1495	1488	ν CC + dCH, 19a (a_1)
		ν CC + δ CH, 19b (b_2)
	1394	δ CH + ν CC, 3 (b_2)
		ν CC + δ CH, 14b (b_2)
1178	1178	δ CH, 9a (a_1)
		δ CH, 9b (b_2)
1086	1079	ν CS, 7a (a_1)
1007		γ CC + γ CCC, 18a, (a_1)

Table S11. Raman band frequencies of bulk 4-ATP and SERS band frequencies of 4-ABT adsorbed on pPET active SERS substrates; [*] ν = stretching, δ , γ = bending, π = wagging. Letters in parenthesis indicate the vibrational symmetry.