

Supporting information

Silicon Nanowire Based Single-Molecule SERS Sensor

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S1, A series of Si nanowires coated with compact aggregates of silver nanoparticles (AgNPs) have been controllably fabricated.

AgNPs can be controllably deposited on silicon nanowires (SiNWs) through adjusting the concentration of AgNO₃ and cetyltrimethyl ammonium bromide (CTAB). The surface-enhanced Raman scattering (SERS) enhancement is greatly affected by the density of AgNPs. It was found that when the formed AgNPs are smaller (<20 nm), standing alone (Figure S1a) or having few aggregations (Figure S1b), their enhancement effect is lower and the resulting SERS spectrum of R6G is weak (Figures S2a and S2b). When the AgNPs are about 34 nm, and with an average interparticle spacing of < 7 nm (Figure S1c), SERS spectra can be collected with fine spectroscopic fingerprinting (Figure S2c). However, while AgNPs are forming a continuous film (Figure S1d), the sensitivity and resolution of the SERS spectra are decreased by the presence of a continuum background (Figure S2d).

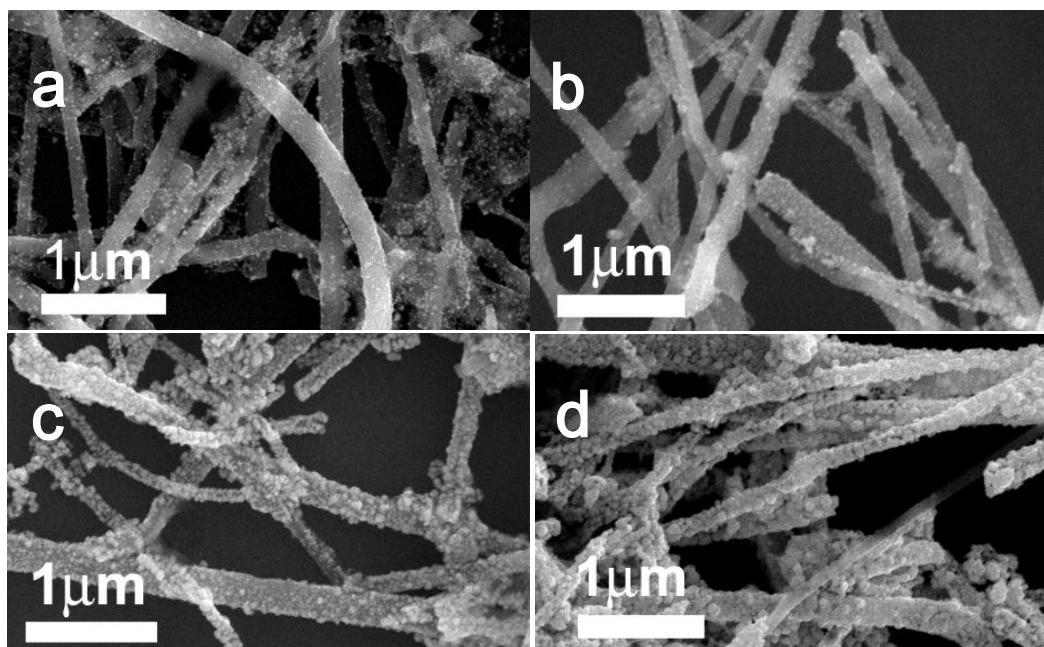


Figure S1. TEM images of AgNPs modified SiNWs synthesized by adding X mL of 1 mM AgNO₃ solution to 1 mL of SiNWs-CTAB dispersion. a) X=0.5; b) X=1.0; c) X=3.0; d) X=4.0.

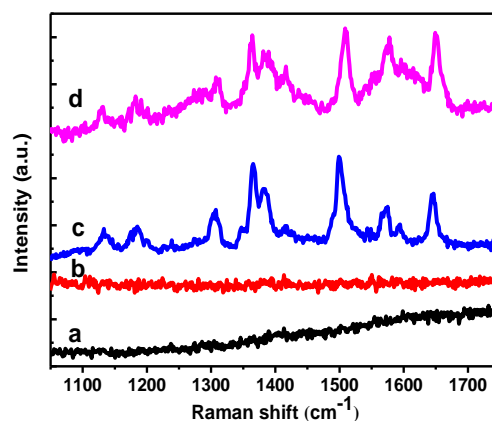


Figure S2. SERS spectra recorded from single AgNPs@SiNW. Spectra a, b, c, and d were collected respectively from samples a, b, c, and d as shown in Figure S1. The concentration of R6G is 5×10^{-9} M.

S2, Quantitative evaluation of the enhancement factor.

The SERS enhancement factor (EF) was calculated with $EF_{\text{SERS}} = I_{\text{SM-SERS}} N_{\text{bulk}} / I_{\text{bulk}} N_{\text{SM-SERS}}$, where $I_{\text{SM-SERS}}$ and I_{bulk} are the intensities of the band at 1648 cm^{-1} from the AgNPs@SiNW and that of bulk solid sample, respectively. $N_{\text{SM-SERS}}$ and N_{bulk} are the number of molecules on the surface of the area irradiated by the laser and in the bulk with the volume of irradiation. The experiment was performed under the same laser power (0.05 mW) and acquisition time (10 s). The weak incident laser power and short acquisition time were used to avoid photobleaching.

1) Determining the I_{bulk} and N_{bulk} and calculating $N_{\text{bulk}}/I_{\text{bulk}}$.

Since the Raman spectrum of R6G solution with high concentration is overlapped by fluorescence, the I_{bulk} and N_{bulk} were measured with R6G molecule thin film. 0.05 mL R6G solution (2.8×10^{-2} M) was dropped into a circular glass tank ($\phi=8.5$ mm). After evaporating the water in air, the bottom of the glass tank was covered by a thin R6G film. $50 \times$ objective (NA= 0.5, effective laser focus cross section was $1.3 \mu\text{m}$ in diameter) was used to collect Raman spectrum. The intensity (498.25 counts) at 1648 cm^{-1} was obtained after Gaussian fitting the spectrum with the “Wire 3.0 peak fit tools” of the Raman spectroscope.

The total molecule number on the bottom of the glass tank can be obtained:

$$N_{\text{total}} = C \cdot V \cdot NA = 2.8 \times 10^{-2} \times 0.05 \times 10^{-3} \times 6.02 \times 10^{23} = 8.43 \times 10^{17} \text{ (NA is the Avogadro's Number)}$$

The molecule number of the bulk in the volume of irradiation is:

$$N_{\text{bulk}} = (A_{\text{ex}}/A_{\text{total}}) \times N_{\text{total}} = 1.97 \times 10^{10} \text{ (} A_{\text{ex}} \text{ and } A_{\text{total}} \text{ are the area of the laser focus and the glass tank)}$$

Then, $N_{\text{bulk}}/I_{\text{bulk}} = 3.95 \times 10^7$

2) Determining the $I_{\text{SM-SERS}}$ and $N_{\text{SM-SERS}}$ and calculating $I_{\text{SM-SERS}}/N_{\text{SM-SERS}}$.

100 Raman spectra of 5×10^{-9} M R6G solution were selected ($N_{\text{SM-SERS}}=1.18$) to calculate the SM-SERS intensity, in which the spectrum of R6G is definite. The average, maximum and minimum SM-SERS intensity are 123.3, 736.4 and 11.2 counts, respectively.

Then $(I_{\text{SM-SERS}}/N_{\text{SM-SERS}})_{\text{average}} = 104.49$; $(I_{\text{SM-SERS}}/N_{\text{SM-SERS}})_{\text{max}} = 624.07$; and $(I_{\text{SM-SERS}}/N_{\text{SM-SERS}})_{\text{min}} = 9.49$.

Based on the above analysis, the average EF_{SERS} for the single-molecule detection in our experiment is 4.12×10^9 , and the maximum and minimum are 2.47×10^{10} and 3.75×10^8 , respectively.

S3, Single AgNPs@SiNW system has a higher SERS sensitivity and better stability than AgNPs on Si wafer system.

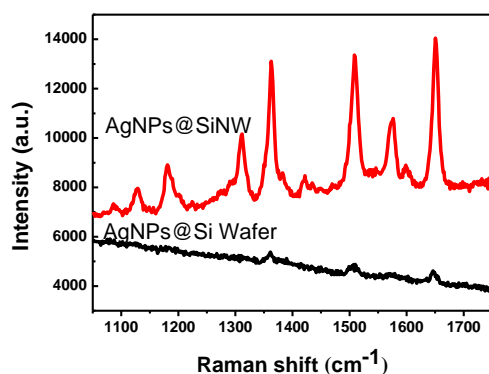


Figure S3. SERS spectra of 5×10^{-8} M R6G solution collected respectively from Ag NPs-deposited Si wafer and single AgNPs@SiNW under a $50 \times$ objective (NA=0.5) with the same experiment conditions. Morphology of AgNPs on Si wafer is shown in the Figure S4a.

AgNPs coated on Si wafer have an average diameter of 44 nm in the range of 27–56 nm. Its particle density is $180/\mu\text{m}^2$ (Figure S4a). AgNPs on the SiNWs have an average diameter of 34 nm (in the range of 25–53 nm). Its linear particle density is $132.5/\mu\text{m}$ (Figure S4b). The confocal laser spot of the $50 \times$ objective (NA=0.5) is $1.3 \mu\text{m}$ in diameter, which means the area of the laser spot will be $1.33 \mu\text{m}^2$. Based on this, the number of AgNPs within the laser spot is 239.4 and 172.3 for Si wafer and SiNWs, respectively.

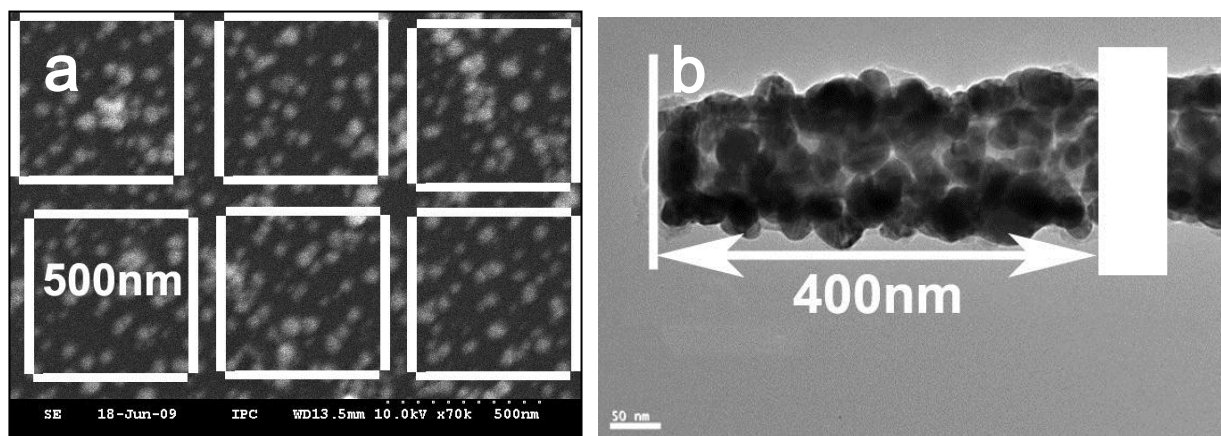


Figure S4. a) SEM and b) TEM images of AgNPs on Si wafer and SiNWs, respectively.

Table 1. The number of AgNPs and the intensity at 1648 cm^{-1} from AgNPs-coated Si wafer and SiNWs.

AgNPs	Diameter (nm)	Density	Area of the laser spot	Number	I_{1648}
On Si Wafer	44 nm (27-56 nm)	$180/\mu\text{m}^2$	$1.33\mu\text{m}^2$	239.4	466.3
On Si nanowires	34 nm (25-53 nm)	$132.5/\mu\text{m}$	$1.3\mu\text{m}$	172.3	5910.6

Above results show that the band intensity at 1648 cm^{-1} (aromatic stretching vibrations) collected from AgNPs@SiNW is about 10 times stronger than that from AgNPs-coated Si wafer (Figure S3), although the number of Ag nanoparticles on SiNW within the sampling probe are less than that on the Si wafer (Table 1). In

addition, AgNPs on Si wafer system show unstable morphology after being immersed in D. I. water for 24 hours.

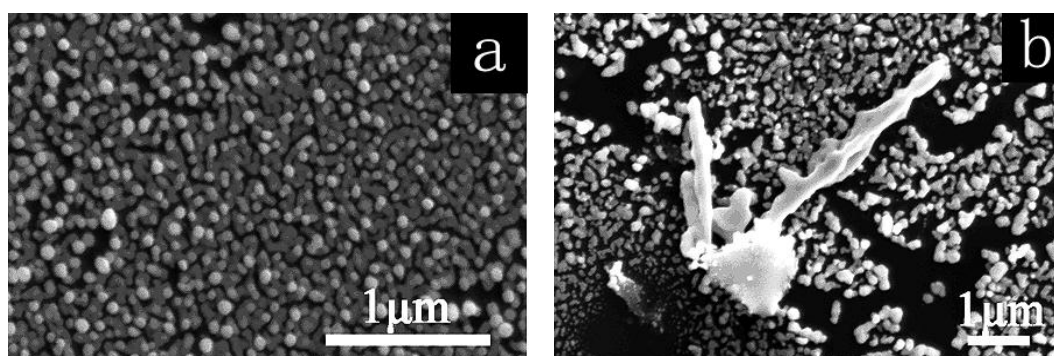


Figure S5. Morphology change of AgNPs on Si wafer before a) and after b) being immersed in D. I. water.

S4, AgNPs@SiNWs has stronger photoabsorption and Raman scattering intensity than aggregated AgNPs colloids.

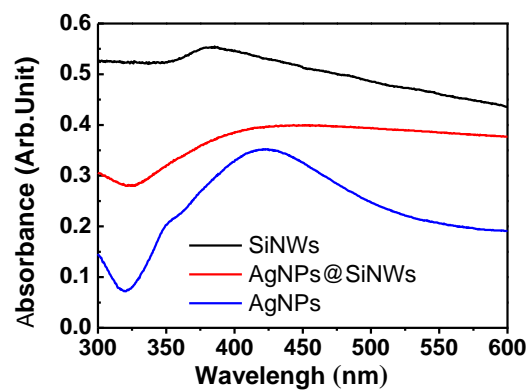


Figure S6. UV-Vis absorption spectra of SiNWs, AgNPs@SiNWs, and AgNPs (measured by HiTachi U-3010 spectrometer).

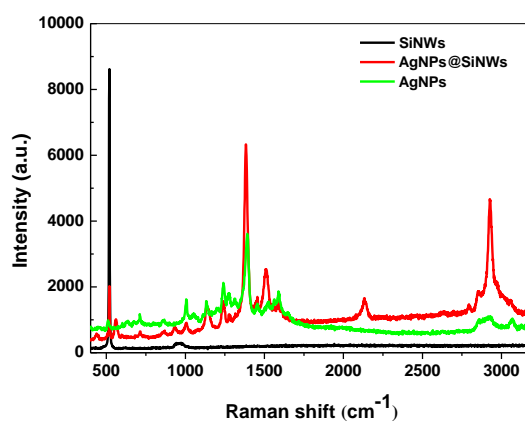


Figure S7. Raman spectra collected from SiNWs, AgNPs@SiNWs, and AgNPs. The AgNPs@SiNWs show stronger Raman intensity than AgNPs.

S5, Preparation of SiNWs

The SiNWs were synthesized using a high-temperature tube furnace, and this set up had been described previously. An Al₂O₃ boat with a mixture of 3.00 g SiO (Aldrich, 325mesh, 99.9%) and 0.50 g Sn was put in the center of an alumina tube, which was then mounted in the furnace. The system was pumped to 5×10^{-2} mbar before heated to 1320 °C at 40 °C/min then a mixture of argon (95%) and hydrogen (5%) at 350 mbar was kept flowing at a flow rate of 10 sccm. After about 7 h growth, the furnace was cooled to room temperature at 40 °C/min. A dark yellow product about 0.5 gram was obtained on the silicon wafer and the inside wall of the alumina tube at 750-850 °C zone of the downstream end, and the product yield can be increased through prolonging –the reaction time. The product was checked with scanning electron microscopy (SEM; Philips XL 30 FEG, Holland) and X-ray diffraction (XRD: Siemens D500). Some of the sample was dispersed in ethanol and a drop of the dispersion was put on a carbon-coated copper TEM sample grid for examination by transmission electron microscopy (TEM; Philips, CM20, operated at 200kV, Holland). To record the room-temperature photoluminescence spectrum, the sample was fixed between two pieces of crystal plates, and a 3941C-M1BB/Spitfire FF-1K/OPA-800CF-0.5 femto-second laser (300nm) was used as the excitation source.

S6, Spectrum blinking can only be found in single molecule detecting.

Three-dimensional Raman spectrum of single and multi-molecule had been compared as following: the spectrum of single molecule (5×10^{-9} M R6G, 100× objective, 1.17 molecules in the confocal laser spot) obviously showed blinking, while the multi-molecule (5×10^{-8} and 5×10^{-7} M R6G, 100× objective, 11.7 and 117 molecules in the confocal laser spot) showed gradual change. The result is consistent with the literatures.

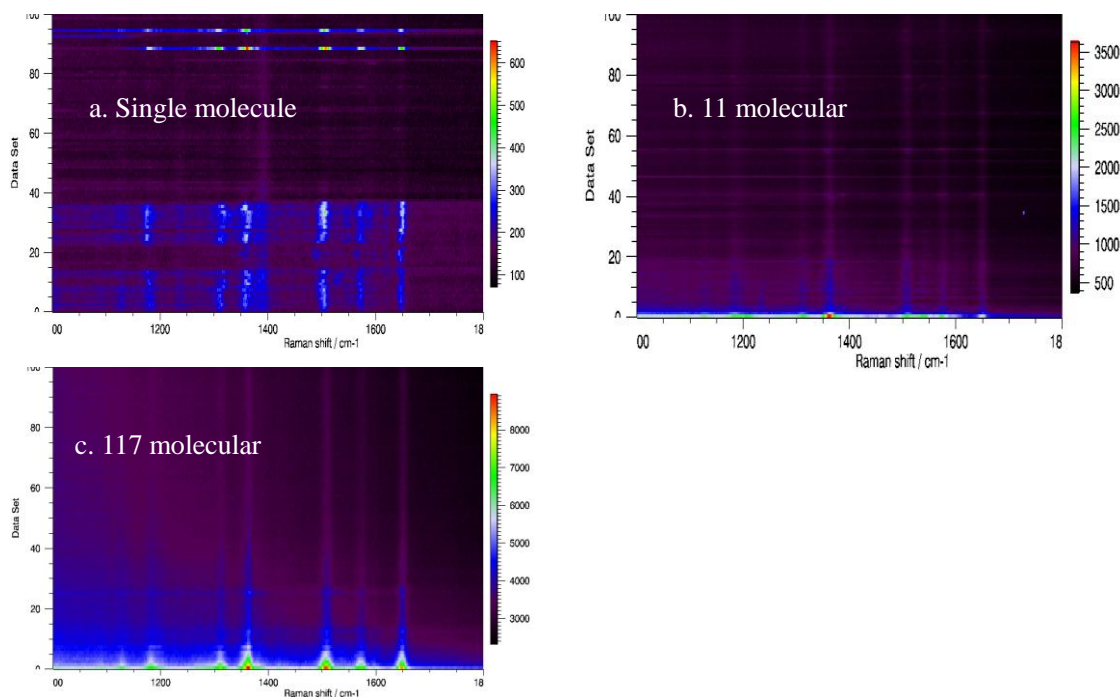


Figure S8. Three-dimensional Raman spectrum of single (a) molecule, 11 (b) and 117 (c) molecular. The 3-D spectrum composed 100 spectra that were collected in 40 minutes, respectively.