Supporting Information

Highly Sensitive, Reproducible, and Stable SERS Sensors Based on Well-Controlled Silver Nanoparticles–Decorated Silicon Nanowire Building Blocks

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S1. Microscopic Characterization of as-prepared AgNPs@SiNWs



Figure S1. SEM images of AgNPs@SiNWs prepared in the absence (a) and presence (b) of CTAB, with other conditions same.



Figure S2. HR-TEM image of as-prepared AgNPs@SiNW. The dot rectangular indicates the interface between AgNPs ans SiNW.



S2. A series of AgNPs@SiNW prepared with varied concentration of AgNO₃.

Figure S3. TEM images of a series of AgNPs@SiNW prepared with varied AgNO₃ concentration as follows: (a) 0.2 mM, (b) 0.6 mM, (c) 1.5 mM. (a1), (b1), and (c1) are their corresponding size distribution graph. The case of 1.0 mM AgNO₃ in this experiment is the same as Figure 2c, hence not shown here.

S3. Calculation of the enhancement factor of single AgNPs@SiNW.

The SERS enhancement factor (EF) was calculated with the commonly used formula: $EF_{SERS}=I_{SERS}N_{bulk}/I_{bulk}N_{SERS}$.^[1,2] In this expression, I_{SERS} and I_{bulk} denote the integrated intensity for band of R6G molecules (vibration at 1648 cm⁻¹ was selected in our system) absorbed on SERS substrate and those of bulk sample, respectively. N_{SERS} and N_{bulk} are the number of molecules illuminated by the laser spots under SERS and normal Raman of bulk sample condition, respectively.

Normal Raman spectra of bulk R6G: 0.05mL R6G solution $(2.8 \times 10^{-2} \text{ M})$ was dropped into a circular glass tank (\emptyset =8.5 mm). After evaporating the water in air, the bottom of the glass tank was covered by a thin R6G film. 50 × objective (NA= 0.5, effective laser focus cross section was 1.3 µm in diameter) was used to collect Raman spectrum and the number of molecules excited by laser was calculated as 1.97×10^{10} . 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.

Single molecule SERS (SM-SERS) spectra: $100 \times \text{objective}$ (NA=0.89) was used to collect Raman spectra of 5×10^{-9} M R6G solution from AgNPs@SiNWs. The efficient scattering volume

was estimated to 0.39 μ m³ (the diameter of laser focus spot of 0.5 μ m and the depth of 2 μ m), and hence an average of 1.18 R6G molecules are present in the sampling volume. 100 Raman spectra were selected to calculate the SM-SERS intensity. The average, maximum and minimum SM-SERS intensity are 123.3, 736.4 and 11.2 counts, respectively.

Therefore, the obtained average EF_{SERS} for the approximately single R6G molecule in our experiment is 4.12×10^9 , and the maximum and minimum are 2.47×10^{10} and 3.75×10^8 , respectively.

[1] S. Gupta, M. Agrawal, M. Conrad, N. A. Hutter, P. Olk, F. Simon, L. M. Eng, M. Stamm, R. Jordan, *Adv. Funct. Mater.* **2010**, *20*, 1756-1761.

[2] M. L. Zhang; X. Fan; H. W. Zhou; M. W. Shao; J. A. Zapien; N. B. Wong; S. T. Lee, J. Phys. Chem. C 2010, 114, 1969.

S4. Schematic of the giant SERS enhancement from AgNPs@SiNW under irradiation.



Figure S4. Schematic of the giant SERS enhancement effect from AgNPs@SiNW system under irradiation.

S5. The UV-vis spectra of SiNWs, AgNPs, AgNPs@SiNWs, and AgNPs@Si wafer and Raman spectra comparison from R6G molecules absorbed on AgNPs@SiNWs and AgNPs@Si wafer.



Figure S5. UV-Vis absorption spectra of AgNPs@SiNWs, Ag colloidal NPs, and AgNPs@Si wafer.



Figure S6. Raman spectra of R6G molecules adsorbed on single AgNPs@SiNW and AgNPs@Si wafer. R6G concentration 5×10^{-8} M, $50 \times$ objective, excited wavelength 532 nm, laser power 50 μ w, acquisition time 10 s.

S6. SERS spectra collected from AgNPs@SiNWs prepared in the absence of CTAB and their SEM images.

As comparison, we collected SERS spectra of R6G molecules from single AgNPs@SiNW prepared in the absence of CTAB. The spectra recorded from seven different sites on a single AgNPs@SiNW are shown in Fig. S7a. Although the characteristic Raman peak of R6G can be observed in all of the spectra, the intensities (1650 cm⁻¹) of SERS signal vary largely with RSD of about 40 %–80%. In addition, much larger variation can also be observed when collecting spectra from randomly selected 20 different NWs (with RSD of ~140%). Some NWs cannot even produce observable SERS signal. These unreproducible SERS signals are related to the morphology of AgNPs on SiNWs. As shown in Fig. S7b and c, the formed AgNPs aggregate randomly and distribute nonuniformly on the entire wire surface. Even if increasing the concentration of reactive AgNO₃, it is still difficult to load uniform AgNPs on the entire wire surface (Fig. S7d). This random aggregation and nonuniform distribution of AgNPs on SiNWs undoubtedly induce dramatic variation in the SERS response not only from different sites on a single AgNPs@SiNW but also between different wires. Thus reproducible and sensitive detection with such single AgNPs@SiNW cannot be achieved.



Figure S7. a) Raman spectra recorded at seven different sites on a single AgNPs@SiNW prepared in the absence of CTAB. b) SEM image of AgNPs@SiNWs prepared through direct reduction of Ag⁺ ions on SiNWs without using CTAB. c) SEM image of AgNPs@SiNWs from (b). d) SEM image of AgNPs@SiNWs prepared with 0.1 M AgNO₃ solution.

S7. UV-vis absorption spectra of AgNPs@SiNWs that stored in D.I. water for different period of time.



Figure S9. UV–vis absorption spectra of AgNPs@SiNWs that stored in D.I. water for different period of time.

S8. Raman spectra of R6G molecules from sample before and after stored in D.I. water or exposed in air.

The SERS spectra from AgNPs@SiNWs after immersed in D.I. water for one week shows negligible changes in the intensities and positions of Raman vibration bands (Figure S10). After exposing the sample in air for 3h, the SERS spectra of R6G molecules also changes little (Figure S11). These results reveal that the oxidation of our AgNPs@SiNW in air or an aqueous environment has a slight influence on the measured SERS signal. Additionally, no significant changes can be observed in the SERS spectra of R6G absorbed on sample stored in ethanol for 3 months but only a reduction by ~20% in the spectra intensity.



Figure S10. The Raman spectra of R6G molecules from both freshly prepared AgNPs@SiNWs and stored in D.I. water for about one week, conditions same as figure S6.



Figure S11. The Raman spectra of R6G molecules absorbed on AgNPs@SiNW, a) before and b) after exposed in air for 3h.