Electronic Supplementary Material

Ag-NPs@Ge-Nanotapers/Si-Micropillar Ordered Arrays as Ultrasensitive and Uniform Surface Enhanced Raman Scattering Substrates

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Part S1. The function of GO.

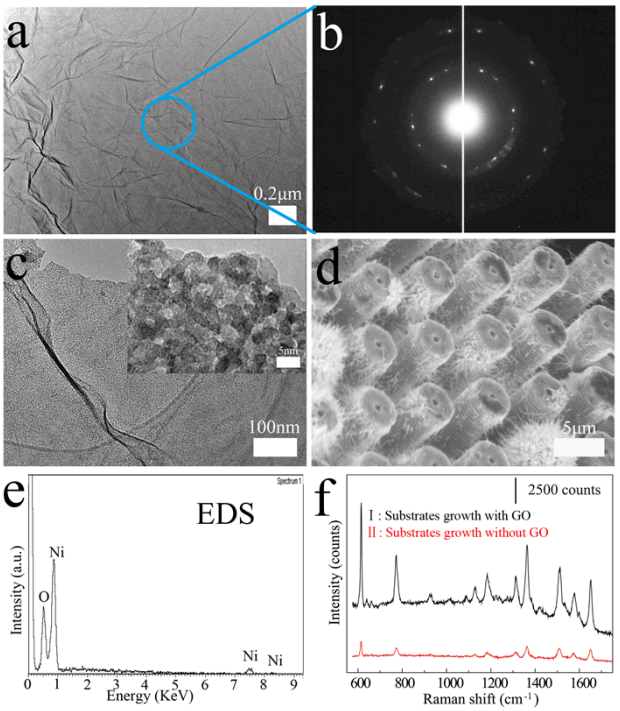

Fig. S1. TEM image (a) and SAED pattern (b) of GO. (c) TEM image of GO loading with NiO and the inset is the close-up view. (d) SEM image of Ge-nanotapers/Si-micropillars achieved without using GO. (e) The EDS spectrum of GO loading with NiO. (f) SERS spectroscopy of 10^{-7} M R6G adsorbed on the Ag-NPs@Ge-nanotapers/Si-micropillar arrays (with $AgNO_3$ immersing duration for 9 min) achieved with (Ⅰ) and without (Ⅱ) using GO.

Fig. S1a-b are TEM image and selected area electron diffraction (SAED) pattern of GO respectively, demonstrating that the GO were multilayer. In order to reveal the function of the GO, the mixed solution of $Ni(NO_3)_2$ and GO was centrifuged and the precipitations were annealed in argon gas at 330℃ for 5min. The TEM image and EDS spectrum of the above-treated samples demonstrate that GO loaded with a huge number of NiO (as shown in Fig. S1c and e respectively). It verifies that GO plays an important role in decorating sufficient catalyst precursor onto the surfaces of Si-micropillar arrays, contributing to the growth of flocky Ge-nanotapers. There is no N element in the EDS spectrum because that $Ni(NO_3)_2$ were decomposed into NiO solid and NO_2 gas at the high temperature. And NO_2 gas was discharged finally. Without using GO, only few Ge-nanotapers were grown onto the Si-mircopillars unevenly (Fig.

S1d). The SERS performance of Ag-NPs@Ge-nanotapers/Si-micropillar arrays achieved by using GO was higher than that achieved without using GO, as shown in Fig. S1f.

Part S2. TEM images of Ge-nanotaper and Ag-NPs@Ge-nanotaper.

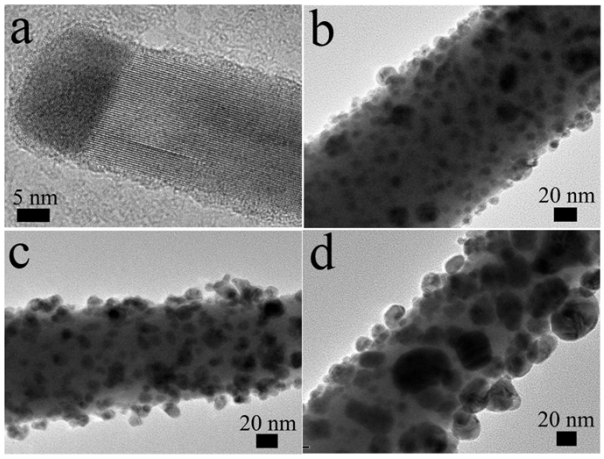

Fig. S2. TEM images of Ge-nanotaper with Ni nanoparticle catalyst tip (a), Ag-NPs@Ge-nanotaper with $AgNO_3$ immersing durations of 6 min (b), 9 min (c) and 12 min (d).

From the TEM images of Ag-NPs@Ge-nanotaper with different $AgNO_3$ immersion durations (6, 9, 12 min) (Fig S2 b-d), we can see that the variation of the size of Ag-NPs is little (the disparities are within 15 nm). The average diameters of Ag-NPs with immersing durations of 6, 9 and 12 min are 10, 12 and 22 nm respectively.

Part S3. SERS performance of Ag-NPs@Ge-nanotapers/Si-micropillar arrays with varied Ge-nanotaper growth durations.

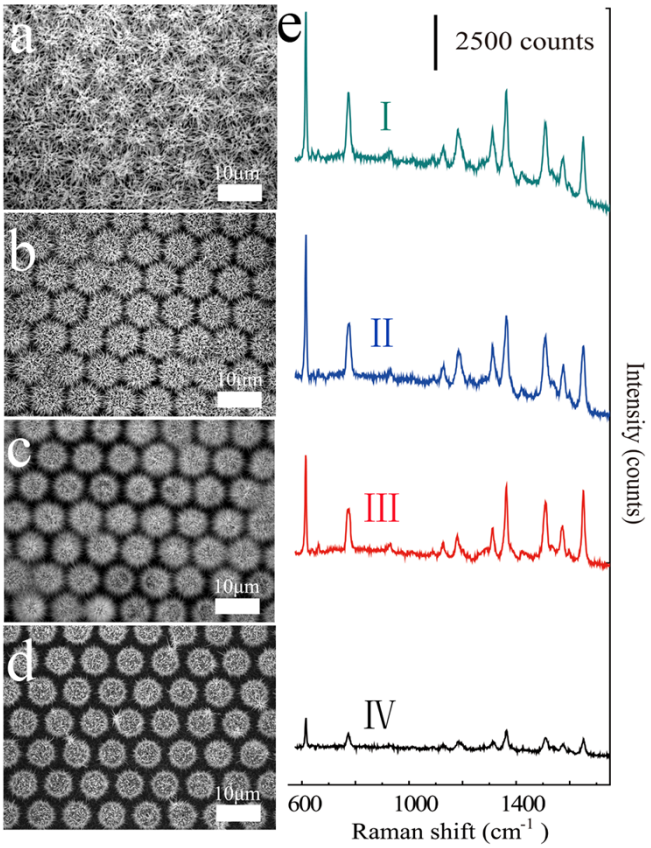

Fig. S3. SEM images of Ge-nanotapers/Si-micropillar arrays with CVD durations of 40 (a), 30 (b), 20 (c) and 10 (d) min. (e) SERS spectroscopy of 10^{-7} M R6G adsorbed on the Ag-NPs@Ge-nanotapers/Si-micropillar arrays (with $AgNO_3$ immersing duration of 7 min) with CVD durations of 40 (Ⅰ), 30 (Ⅱ), 20 (Ⅲ) and 10 (Ⅳ) min.

Part S4. Calculation of the enhancement factor (EF) for detecting PATP.

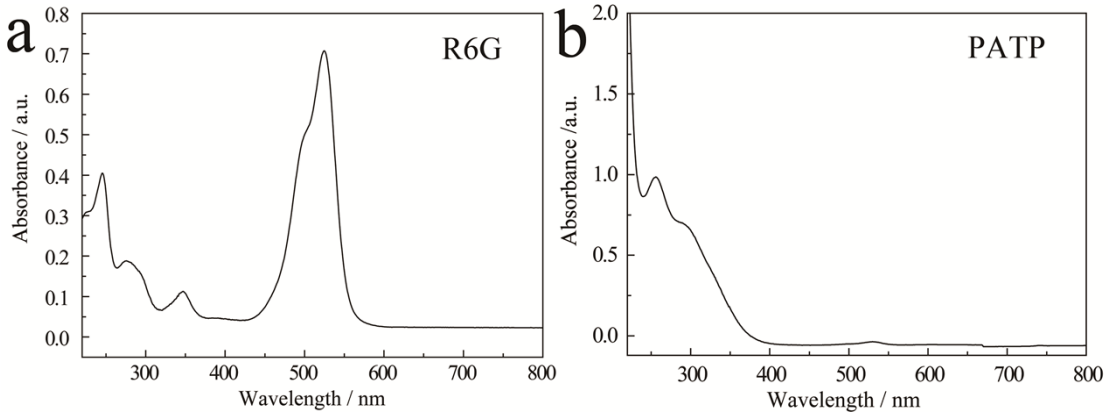

Fig. S4. Absorption spectra of analytes. (a) The UV-vis absorption spectrum of R6G aqueous solution, (b) the UV-vis absorption spectrum of PATP ethanol solution.

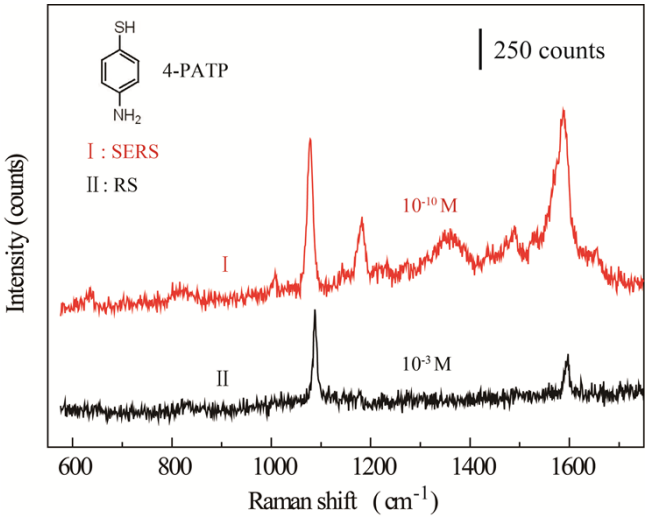

Fig. S5. (I) SERS spectrum of 50 μL 10^{-10} M PATP ethanol solution dispersed on 40 mm^2 Ag-NPs@Ge-nanotapers/Si-micropillar arrays. (II) Raman spectrum of 100 μL 10^{-3} M PATP ethanol solution dispersed on 70 mm^2 glass substrate.

The absorption peak of R6G is at ~525 nm, which is near the laser line 532 nm in the Raman measurements (Fig. S4a). To avoid the overestimation of the enhancement factor caused by the resonance enhancement, 4-aminothiophnol (PATP) which has no absorption peak near the 532 nm, was used as analytes to estimate the enhancement factor (Fig. S4b).

The EF of the Ag-NPs@Ge-nanotapers/Si-micropillar arrays can be calculated by:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{Nor}/N_{Nor}} = \frac{I_{SERS}}{I_{Nor}} \times \frac{N_{Nor}}{N_{SERS}}$$

Where I_{SERS} and I_{Nor} correspond to the intensity of the 1080 cm^{-1} band of PATP of SERS spectrum and normal Raman spectrum, respectively. N_{SERS} and N_{Nor} represent the corresponding number of molecules in the focused incident laser spot. Herein, 50 μL 10^{-10} M PATP were dispersed on 5×8 mm^2 Ag-NPs@Ge-nanotapers/Si-micropillar arrays for SERS experiment, and 100 μL 10^{-3} M PATP were dispersed on 7×10 mm^2 glass film for nomal Raman spectra. (In terms of Raman spectrum, PATP powder and dried PATP on the glass substrate are the same. We dispersed PATP ethanol solution onto the glass substrate in order to estimate the number of PATP molecules in the focused incident laser spot.) Thus, the value of N_{nor}/N_{SERS} was about

1.1×10^7. Fig. S4 shows the SERS spectrum and the Raman spectrum of PATP from the above-mentioned substrates. For the band at 1080 cm^{-1}, I_{SERS}/I_{Nor} was about 1.5. Hence, $EF=1.5\times1.1\times10^7=1.65\times10^7$.

Part S5. Finite element modeling of Ag-NPs@Ge-nanotaper.

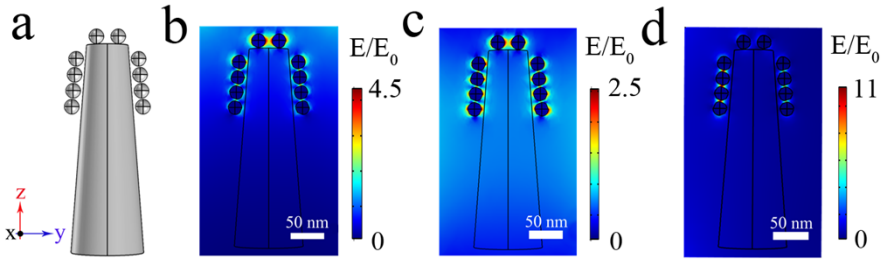

Fig S6. Finite element modeling of the Ag-NPs@Ge-nanotaper. (a) The simulation model. The calculated electric field distribution of the Ag-NPs@Ge-nanotaper with a 532 nm linear polarized plane wave illuminated along the z-axis (b) x-axis (c) and y-axis (d), respectively.

Part S6. Uniformity of SERS sensitivity of the optimal Ag-NPs@Ge-nanotapers/Si-micropillar hierarchical arrays.

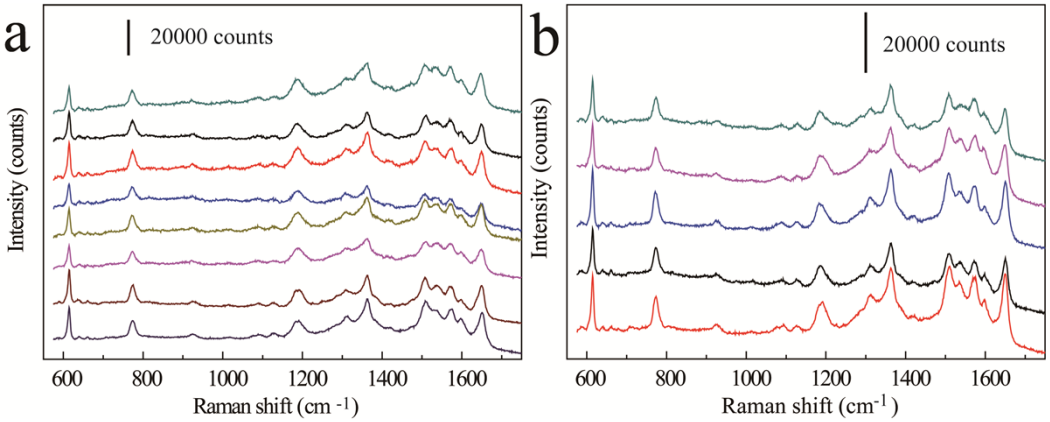

Fig. S7. SERS signals of 10^{-6} M R6G on eight randomly chosen points from one Ag-NPs@Ge-nanotapers/Si-micropillar SERS substrate (a) and points from five Ag-NPs@Ge-nanotapers/Si-micropillar SERS substrates of different batches (b).

Part S7. SERS mapping.

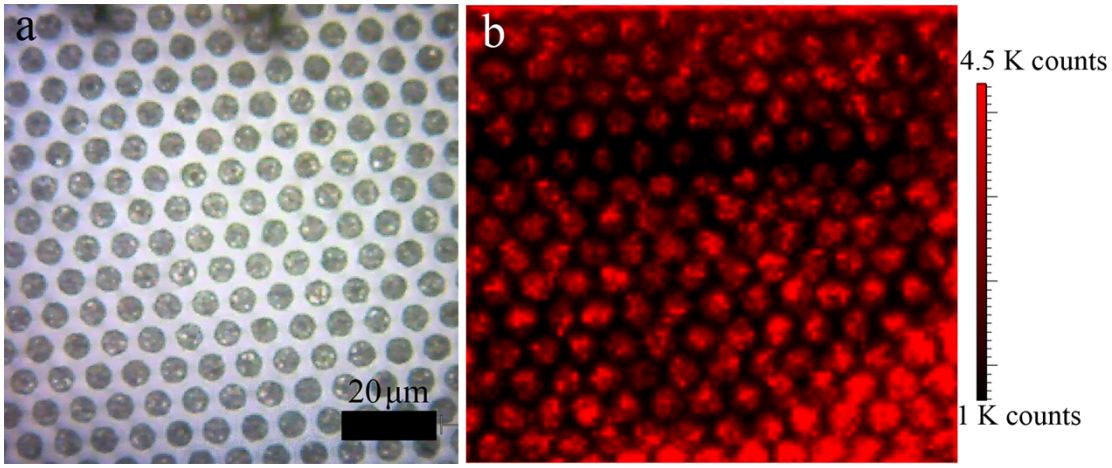

Fig. S8. (a) Optical image of Ag-NPs@Ge-nanotapers/Si-micropillar arrays with shorter Ge-nanotapers (CVD duration of 10 min). (b) SERS mapping of the substrate indicated by the optical image shown in (a) dispersed with 10^{-6} M R6G (614 cm^{-1} band).

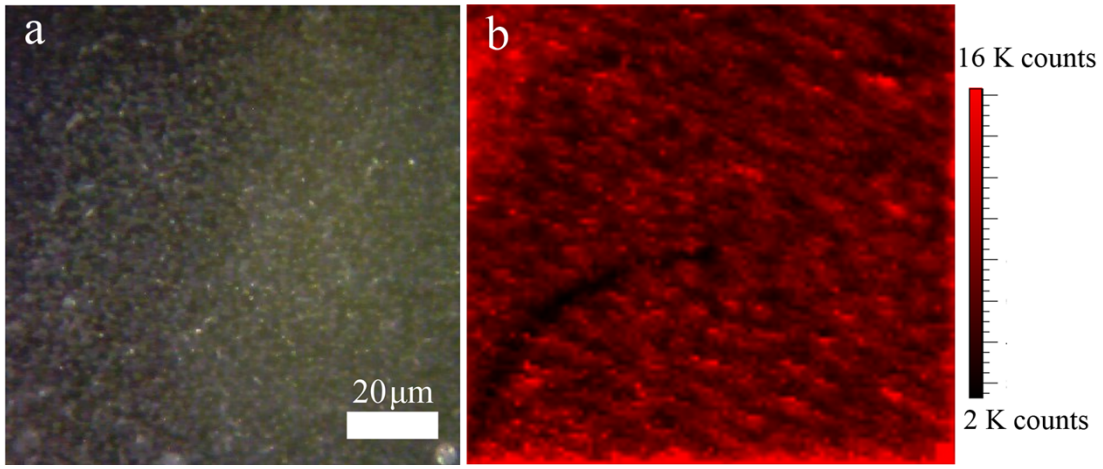

Fig. S9. (a) Optical image of Ag-NPs@Ge-nanotapers/Si-micropillar arrays with longer Ge-nanotapers (CVD duration of 30 min). (b) SERS mapping of the substrate indicated by the optical image shown in (a) dispersed with 10^{-6} M R6G (614 cm^{-1} band).