Template-annealing-assisted fabrication of Au/TiO_2/Ni nanopetal arrays as ultrasensitive and reproducible SERS substrates with super long-term stability

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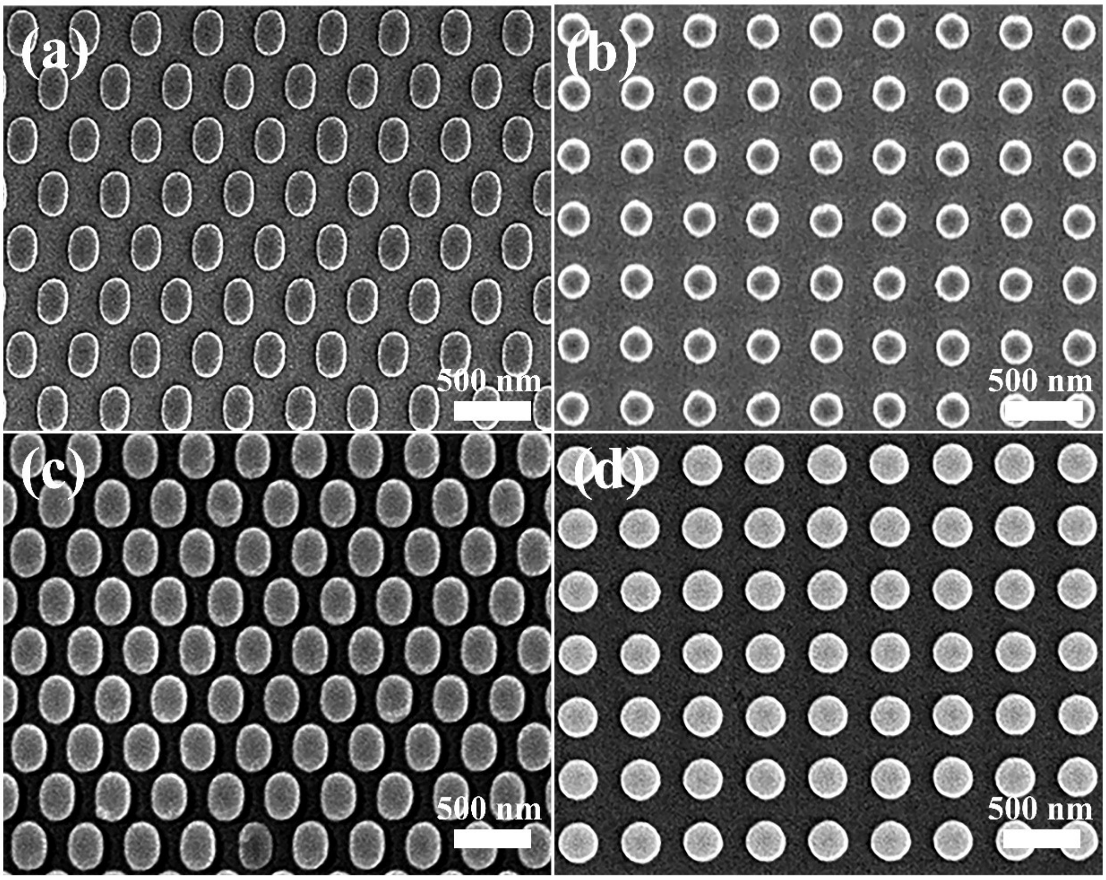

Fig. S1. SEM images of (a) H- and (b) S-Ni nanopillar arrays, and the corresponding (c) H- and (d) S-TiO_2/Ni nanopillar arrays.

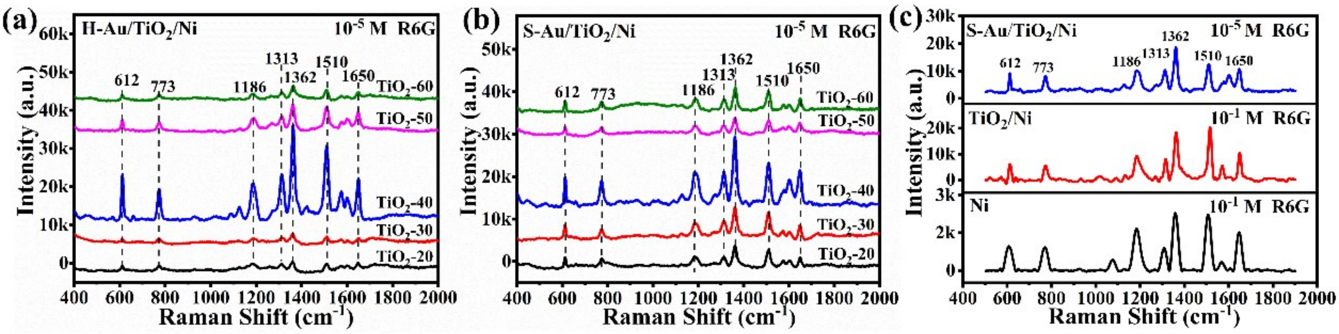

Fig. S2. SERS spectra of 10^{-5} M R6G molecules on (a) H-Au/TiO_2/Ni and (b) S-Au/TiO_2/Ni nanopillar arrays with different TiO_2 thicknesses of 20, 30, 40, 50 and 60 nm. (c) Comparisons of SERS response among S-Au/TiO_2/Ni, S-TiO_2/Ni and the original S-Ni nanopillar arrays to R6G molecules.

EF calculation

To explain the improvement of SERS sensitivity after the deposition of TiO_2 and Au, enhancement factors (EFs) of Au/TiO_2/Ni compared to TiO_2/Ni, and that of TiO_2/Ni compared to Ni were roughly estimated (using the SERS intensities *I* and molecule concentrations *C* shown in Fig. S2c) using the following formulas:

$EF_1=(I_{TiO2/Ni}/I_{Ni})\times(C_{Ni}/C_{TiO2/Ni})$

$EF_2=(I_{Au/TiO2/Ni}/I_{TiO2/Ni})\times(C_{TiO2/Ni}/C_{Au/TiO2/Ni})$

Tab. S1. Enhanced factors (EF_1, EF_2) calculated at main characteristic peaks.

Peak position (cm^{-1})	EF_1	EF_2	I_{Ni}	$I_{TiO2/Ni}$	$I_{Au/TiO2/Ni}$
612	6.27	1.50×10^4	968.565	6074.76	9102.55
773	6.07	1.45×10^4	920.564	5590.59	8120.65
1186	5.54	1.11×10^4	1662.63	9215.47	10219.9
1313	9.00	1.29×10^4	888.915	7999.78	10298.4
1362	8.05	1.01×10^4	2287.13	18409.8	18654.1
1510	9.22	0.61×10^4	2216.4	20428.6	12414.6
1650	6.88	1.02×10^4	1515.96	10421.8	10676.7

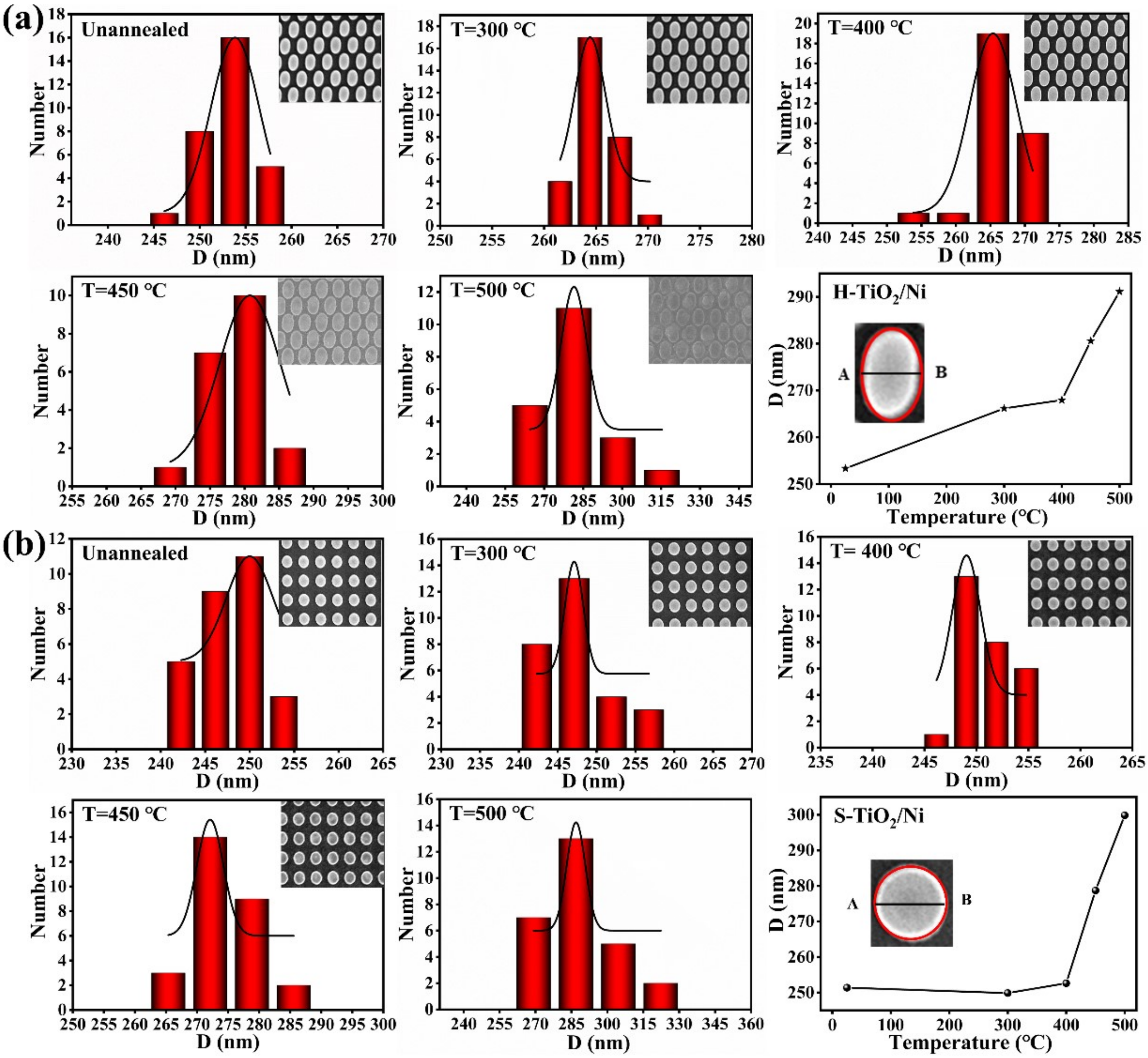

Fig. S3. Distributions of nanopillar diameter (D) of (a) H-TiO_2/Ni and (b) S-TiO_2/Ni nanoarrays at different temperatures.

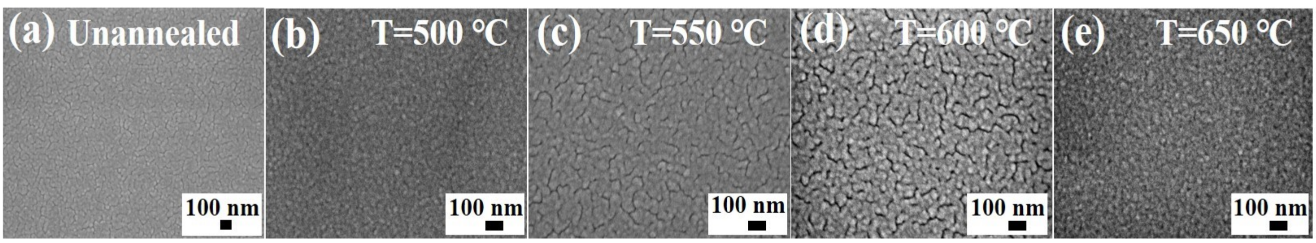

Fig. S4. SEM images of (a) unannealed and (b-e) annealed Au/TiO_2/Si nanoarrays at 500℃–650℃.

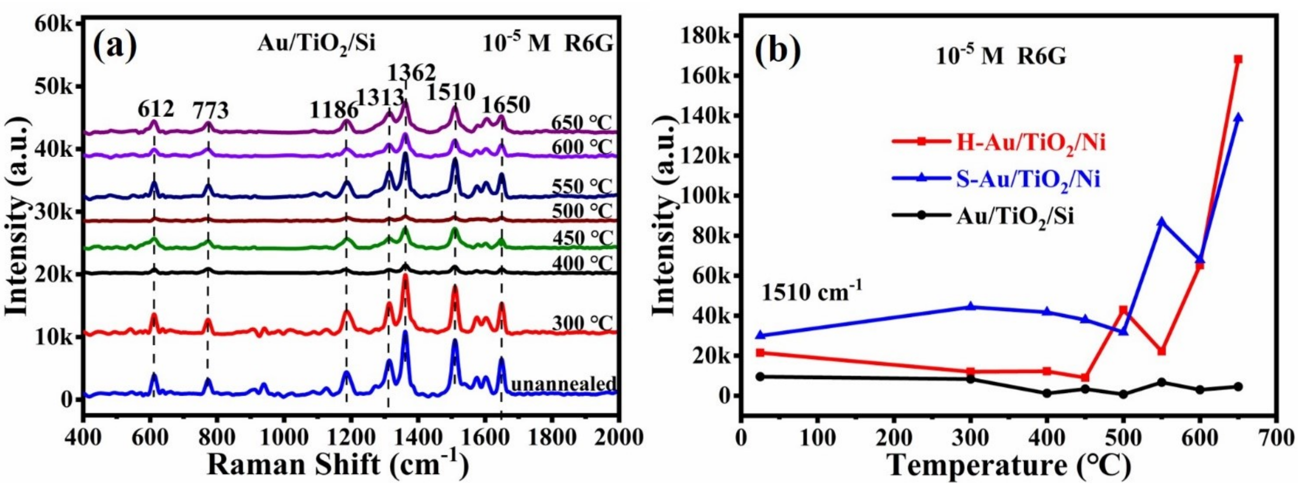

Fig. S5. (a) SERS spectra of 10^{-5} M R6G molecules on unannealed and annealed $Au/TiO_2/Si$ nanostructure at different annealing temperatures. (b) Comparisons of the variation trend of SERS response to 10^{-5} M R6G molecules with temperature among H-$Au/TiO_2/Ni$, S-$Au/TiO_2/Ni$ and $Au/TiO_2/Si$ structures at 1510 cm^{-1} peak.

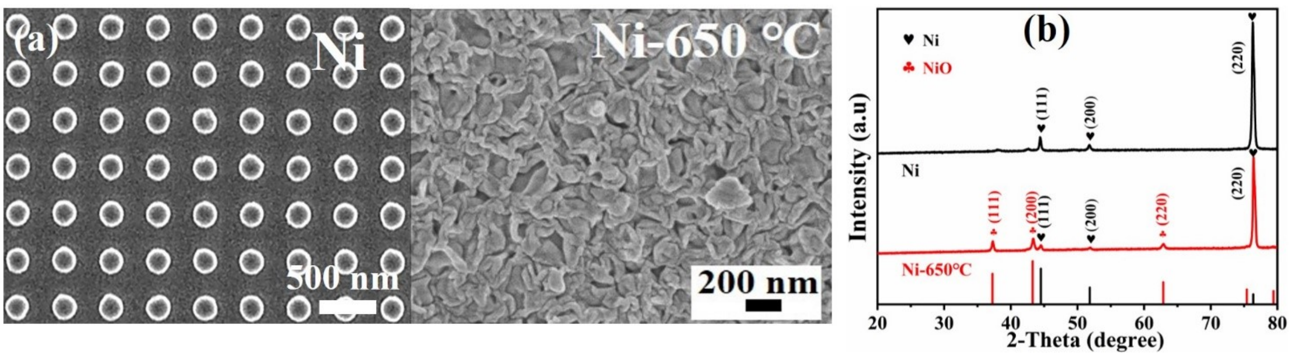

Fig. S6. (a) Comparison of SEM images of S-Ni nanoarrays before and after 650°C annealing. (b) Comparison of XRD patterns of S-Ni nanoarrays before and after 650°C annealing.

Tab. S2. Comparison of literature results on hybrid substrates of Au (Ag) and TiO_2 (ZnO) using R6G and CV as probe molecules.

Structure	Detection limit (mol/L)	Reference
Au@TiO_2 NRAs	10^{-7}（R6G）	[1]
TiO_2/Au NWAs	10^{-9}（R6G）	[2]
Au NPs coated amorphousTiO_2 nanotubes	10^{-6}（R6G）	[3]
Au/TiO_2 spheres	10^{-6}（R6G）	[4]
Au/ZnO	10^{-9}（R6G）	[5]
Au-decorated ZnO nanorod array	10^{-9}（R6G）	[6]
Ag/TiO_2	10^{-10}（CV）	[7]
Au Nanorods@TiO_2 Nanocomposites	10^{-9}（CV）	[8]
Au/TiO_{2-x}/NiO (Ni)	10^{-13}（CV）	This work
	10^{-12}（R6G）	This work

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