Supporting Information

A Two-dimensional Ag Nanoparticle Tetramer Array for Surface-enhanced Raman Scattering Measurements

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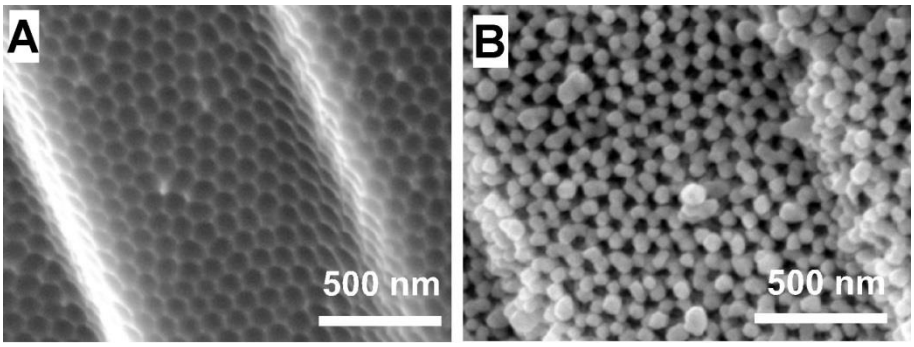

Figure S1. FESEM images of (A) the wrinkled porous Al substrate and (B) the wrinkled AgNP array prepared by electrodeposition.

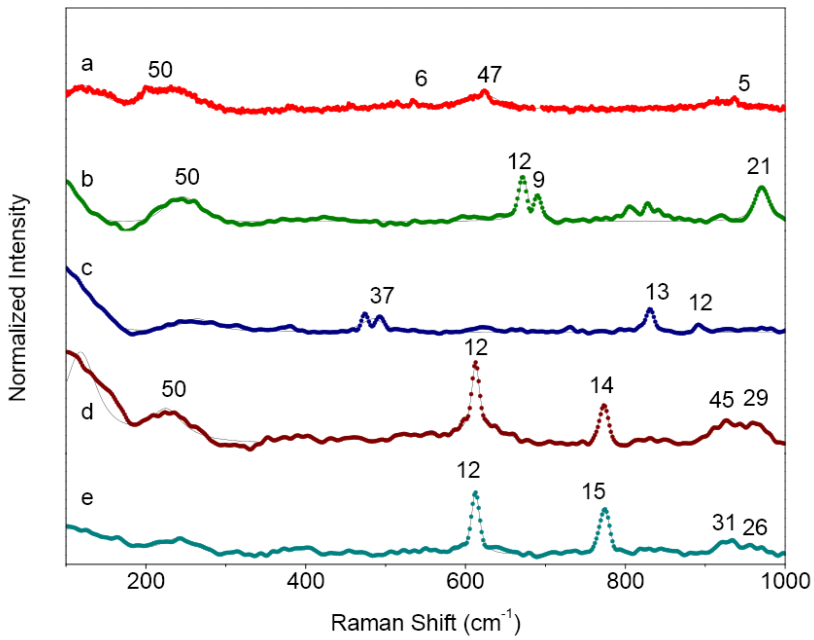

Figure S2. SERS lineshapes in the 100–1000 cm^{-1} regime for R6G on 2D AgNP array in various concentrations and under different laser irradiation. (a) 2×10^{-15} M: $\lambda_{ex} = 633$ nm, $P_{acq} = 0.1$ mW, $t_{acq} = 10$ s (red). (b) 2×10^{-15} ML: $\lambda_{ex} = 514$ nm, $P_{acq} = 0.05$ mW, $t_{acq} = 10$ s (green), in one sampling spot. (c) 2×10^{-15} M: $\lambda_{ex} = 514$ nm, $P_{acq} = 0.05$ mW, $t_{acq} = 10$ s (blue), in another sampling spot. (d) 2×10^{-12} M: $\lambda_{ex} = 514$ nm, $P_{acq} = 0.5$ mW, $t_{acq} = 1$ s (brown). (e) 2×10^{-8} M: $\lambda_{ex} = 514$ nm, $P_{acq} = 0.5$ mW, $t_{acq} = 1$ s (dark cyan). The FWHM for each SERS feature is indicated. Spectra have been fitted and background-subtracted. Colored dots are the experimental data and the gray lines are the fitted features. All spectra are normalized to the maximum feature intensity. The FWHM values in parentheses indicate the uncertain results caused by their background fitting and subtraction.

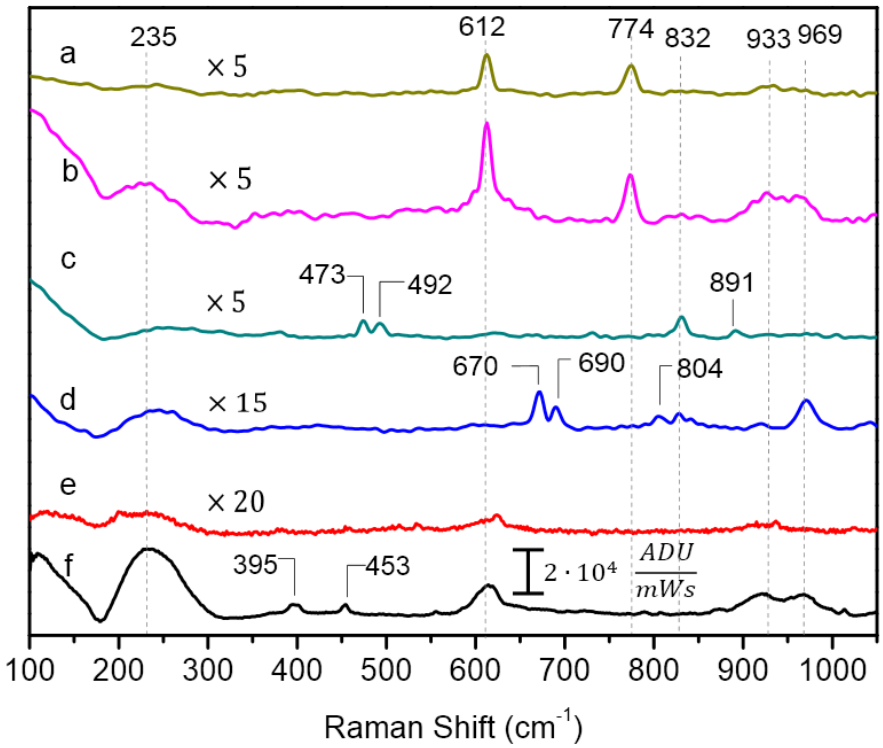

Figure S3. SERS spectra of various R6G concentrations on the 2D AgNP array in the regime of 100 - 1000 cm^{-1}. (a) 2×10^{-8} M (brown) and (b) 2×10^{-12} M (pink) : λ_{ex} = 514 nm, P_{acq} = 0. 5 mW, t_{acq} = 1 s, (c) and (d) 2×10^{-12} M in two different sampling spots (blue and green): λ_{ex} = 514 nm, P_{acq} = 0.05 mW, t_{acq} = 10 s, (e) and (f) 2×10^{-15} M in two sampling spots: λ_{ex} = 633 nm, P_{acq} = 0.1 mW, t_{acq} = 10 s (red and black). All spectra are background-subtracted and smoothed.

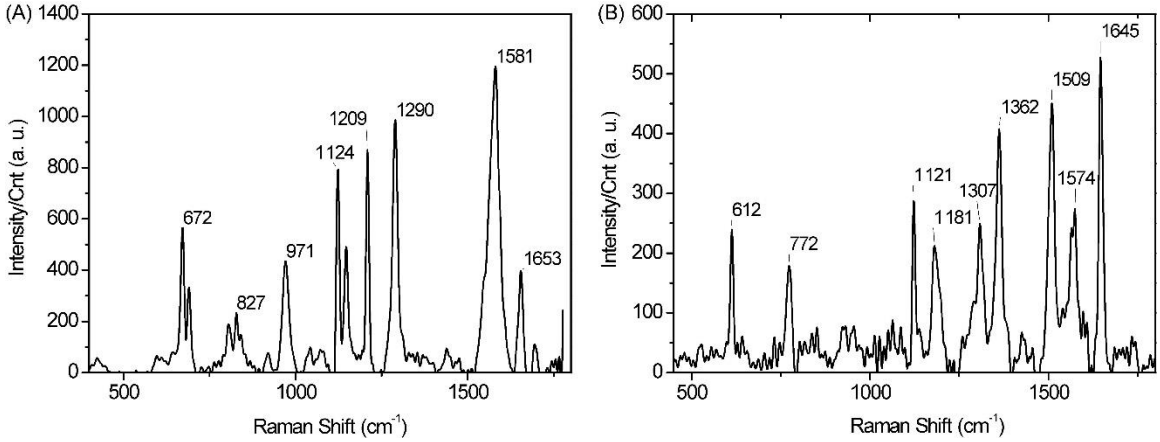

Figure S4. (A) Comparison of SERS spectra of 2×10^{-15} M R6G on the AgNP substrate. λ_{ex} = 514 nm, P_{acq} = 0.05 mW, t_{acq} =10 s and (B) Raman spectra of 10^{-3} M R6G collected on electrochemically deposited Ag film on Al substrate. λ_{ex} = 514 nm, P_{acq} = 0. 5 mW, t_{acq} = 1 s.

Table S1 Peak fitting with TD-DFT calculation results

Experiment				Theory[17]					
[1I]Position cm^{-1}	[1II]Position cm^{-1}	[2II]Position cm^{-1}	[3I]Position cm^{-1}	[1]Position cm^{-1}	PED value of vibrational modes (%)				
					Methyl	Xanthene	Ethyl	Phenyl	Ester
1649	1654		1648	1658*	8.9	89.6	1.3	0	0.2
1608	-	1608		1607	0	3.6	0	96.2	0.2
-	1579		1579	1579*	1.8	11.5	86.1	0.5	0
		1540	1557	1561*	1.3	73	24.2	1.5	0
		1509	1525	1515*	11.8	28.2	58.1	1.8	0.1
		1476	1473	1475	0	0	0	0	100
1452	-		1452	1450	0.3	2.1	1.3	95.9	0.4
-	1438			1441	37.8	11.6	47.9	2.7	0
1415[a]				1424*	37.9	30.3	17.1	14.5	0.2
1415[a]	-			1412	0	0	0	0.5	99.5
				1380	3.3	22.8	73.9	0	0
1347[a]	-	1361	1367	1356*	10.8	49.8	28.4	11.1	0
1306[a]				1314	0.4	9.1	87.5	3	0.1
-	1290			1298*	1	34	60.9	2.4	0.8
		1272	1256	1271	0.7	70	17.5	9.3	2.5
-	1209	1213	1192	1195*	0.4	61.2	38.3	0.1	0
		1183		1174	0	0	0	100	0
1145	1148		1142	1144	0.1	15.4	79.2	5.1	0.2
	1126[b]			1129*	13.5	27.5	40.5	16.1	2.4
1069	-			1049	92.8	7.1	0.1	0	0
-	995			989	0	0	0	99.9	0
-	971			959	16.8	18.2	3	62	0
936			931	925	1	40.8	32	22.8	3.4
-	827	830		826	0.2	98.2	1.6	0	0
				772*	16.8	42.3	39.7	1.1	0.2
-	672			669	22.5	71.7	5.8	0.1	0
624	-			632	0.4	66.8	3.7	25.7	3.4
		615	617	616*	3.5	39.2	6	51.1	0.1

Notes: 1) Methyl, Xanthene, Ethyl, Phenyl and Ester correspondingly refer to the methyl groups attached to the xanthene ring, the xanthene ring, the ethylamine groups attached to the xanthene ring (Ethyl), the phenyl ring, and the ester group attached to the phenyl ring. 2) Superscripts I and II refer to experimental results measured by the excitation laser of 633 nm and 514 nm in wavelength, respectively. 3) Superscript 'a' refers to the peaks which are also observed by LT-TERS, and big peaks in the TD-DFT spectra were marked by '*'.[17] 4) Superscript '#' marks that the peaks were observable in all Raman spectra collected with a 514 nm excitation laser. 5) Superscripted numbers, 1, 2 and 3, represent different sample sites where the Raman spectra were collected. Structures 2 and 3 are shown in Fig. S6.

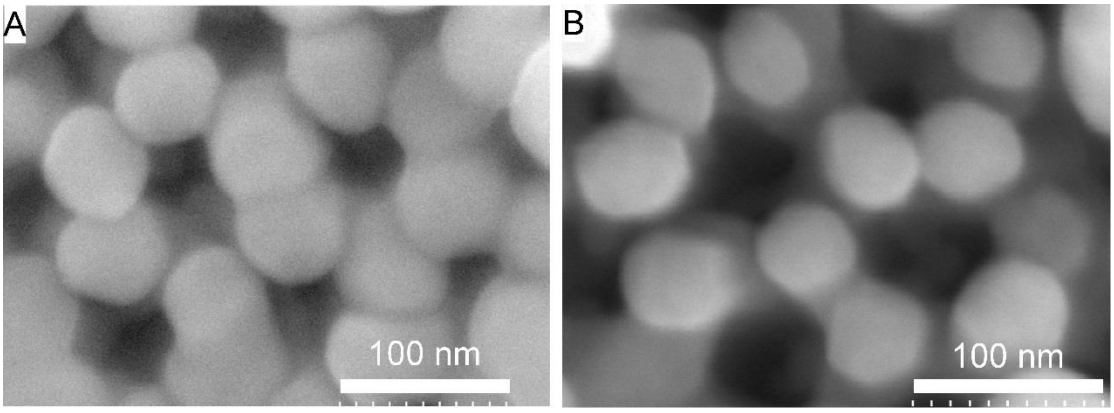

Figure S6. SEM images of structures 2 and 3 for SERS measurements of 10^{-15} R6G in Table S1.