Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Electrochemical Surface-Enhanced Raman Spectroscopy (EC-SERS): A Tool for the Identification of Polyphenolic Components in Natural Lake Pigments

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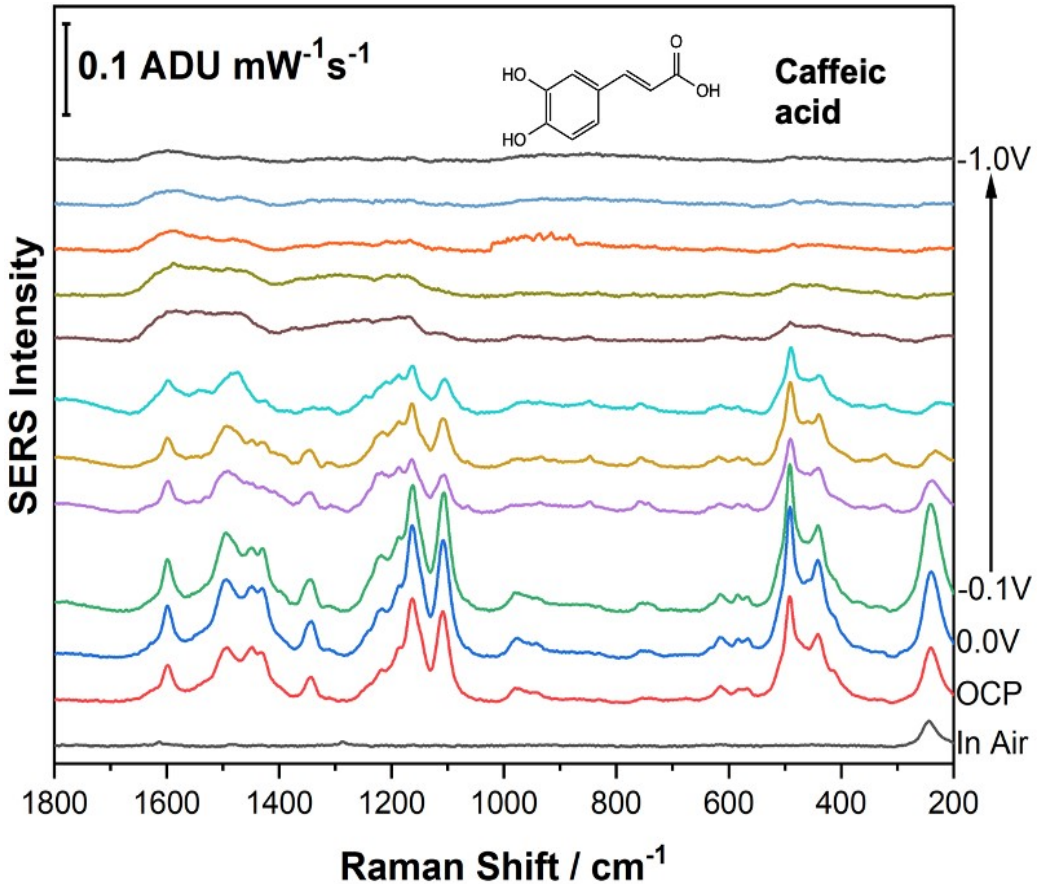
0.1 ADU mW-1s-1
Caffeic acid
HO
HO
O
OH
-1.0V
-0.1V
0.0V
OCP
In Air
SERS Intensity
1800
1600
1400
1200
1000
800
600
400
200
Raman Shift / cm-1

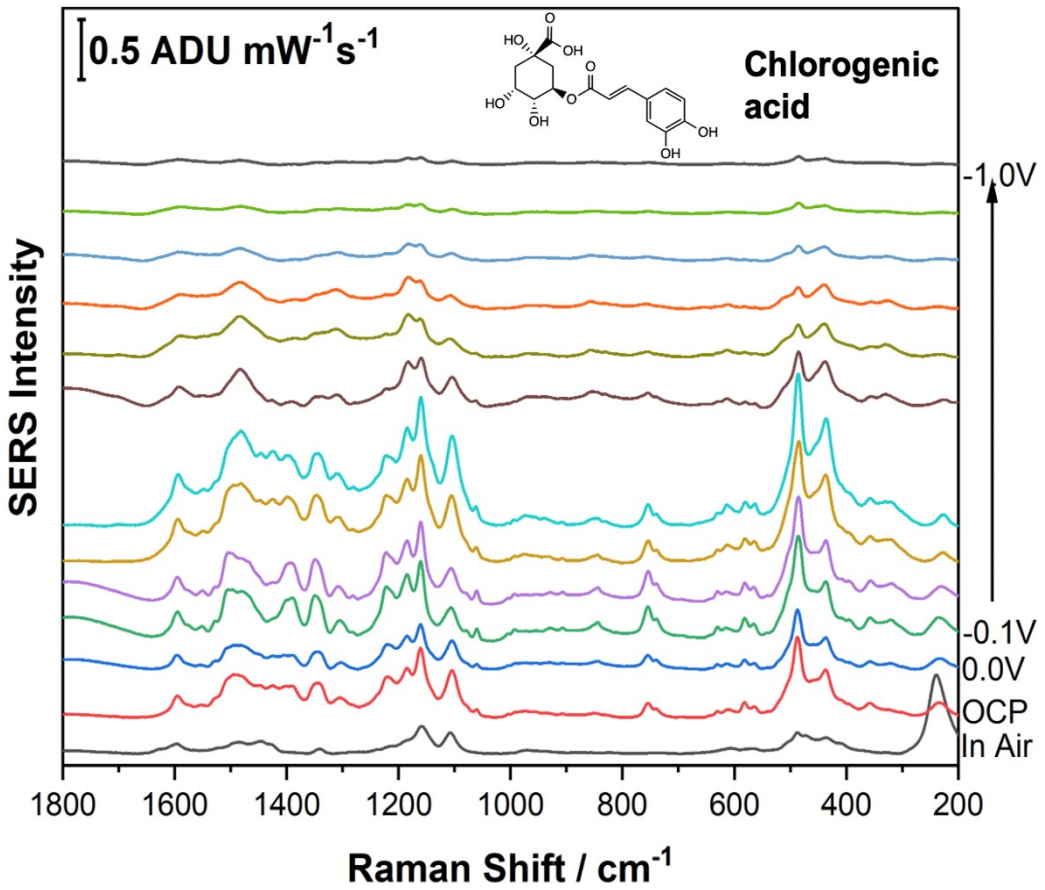

Figure S-1: Cathodic EC-SERS spectra for 2000 ppm caffeic acid and 2000 ppm chlorogenic acid on the surface of the AgNP coated screen-printed electrode in 0.1 M NaF supporting electrolyte. Applied voltage was stepped in the cathodic direction in 100 mV increments. Laser excitation was 780 nm. Power at the sample was 80 mW, and acquisition time was 30 s.

Table S-1: Discriminant peaks of apigenin, luteolin, quercetin, rhamnetin, kaempferol, emodin, caffeic acid and chlorogenic acid

Dye	Raman Shift (cm^{-1})			Ref	
	In Air	**OCP**	**-1.0V**		
Apigenin	1178 w	1168 w	1166 w, 831 m	29	-
Luteolin	1504 m, 510 w, 468 w	1504 m, 510 w, 468 w	512 w	29	-
Quercetin	-	1598 s, 1516 m, 1463 m, 1408 m, 1334 m, 1248 m, 1214 m, 1203 m, 1103 w, 1087 m, 1007 w, 962 w, 845 w, 680 w, 634 w, 586 w, 567 sh, 481 s, 417 m	1595 w, 1461 w, 1207 w,1101 w, 844 w, 427 w	30	42
Rhamnetin	1101 w,1001 w	1598 m , 1516 w, 1465 w, 1406 w, 1346 w, 1318 w, 1252 w, 1207 w, 1163 w, 1135 w, 1103 w, 1088 w, 963 w, 676 w, 633 w, 590 w, 568 w, 553 w, 477 m, 463 sh, 437 w, 402 w, 321 w	1465 w, 1409 w, 1310 w, 844 w, 643 w, 604 w	-	-
Kaempferol	-	1169 w, 967 w, 480 m	1583 w	42	
Emodin	1321 w, 1278 w, 1262 w, 641 w, 471 w	1323 w, 1281 w, 1263 w, 942 w, 91 w, 642 w, 472 w	1557 w, 1364 w	42	43
Caffeic acid	1613 w, 1287 w	1598 m, 1492 m, 1448 m, 1432 m, 1343 w, 1163 s, 1109 s, 980 w, 614 w, 573 w, 491 s, 441 s	-	44	-
Chlorogenic acid	1596 w, 1108 m, 487 w, 436 w	1595 w, 1220 m, 1185 m, 754 w, 564 w, 487 s, 436 m, 358 w	1184 w, 485 w, 437 w	45	-

Abbreviations used: s, strong; m, medium; w, weak; sh, shoulder

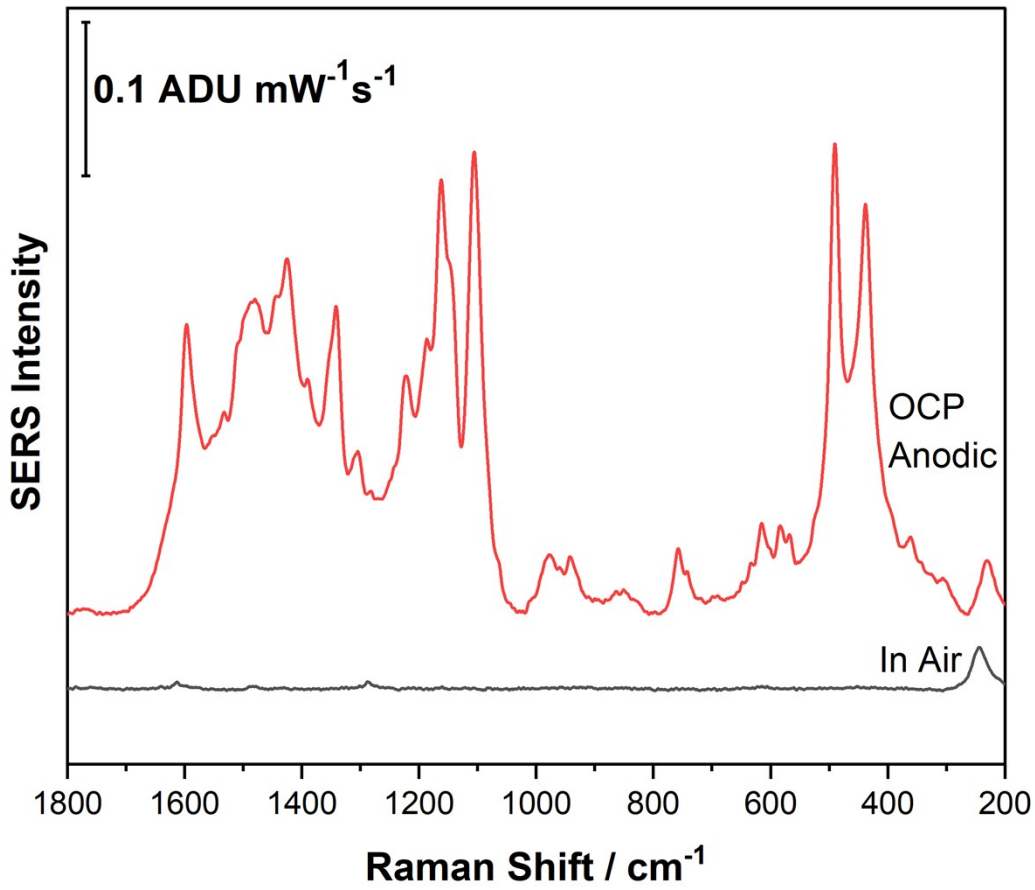

Figure S-2: Comparison of EC-SERS spectra of in air and at the voltage that gives the best SERS signal of caffeic acid.

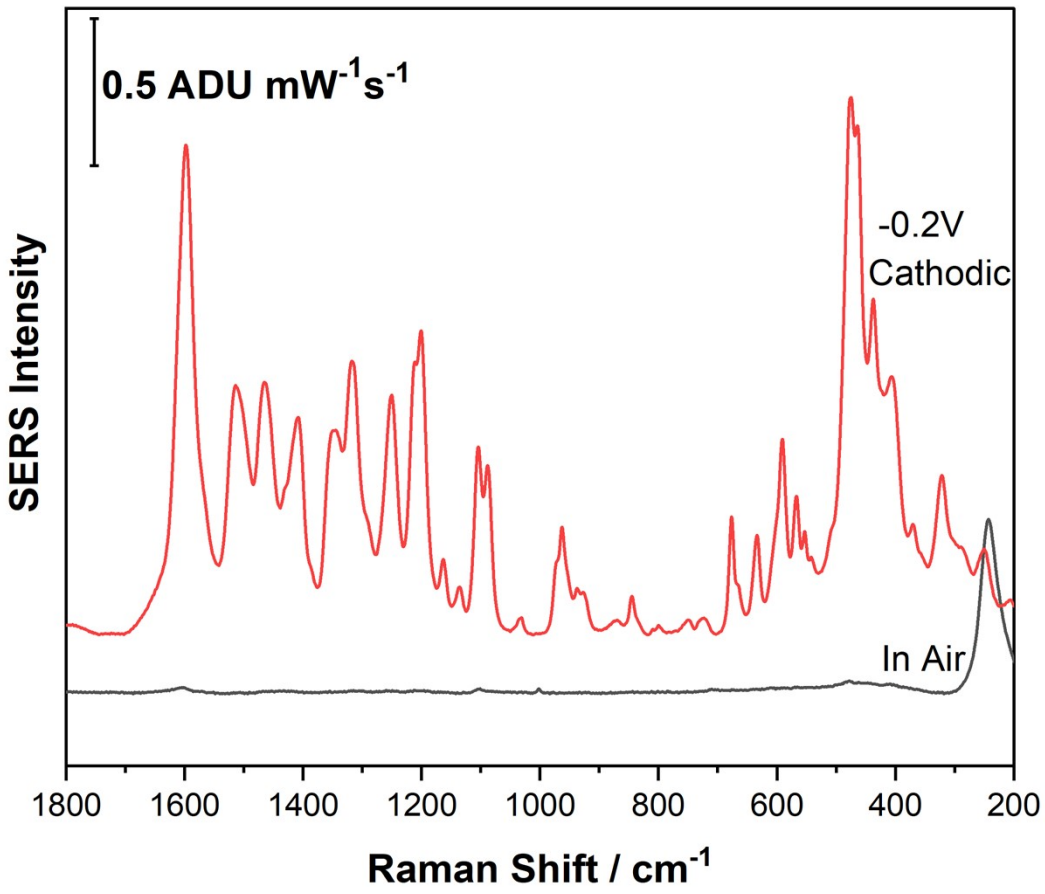

Figure S-3: Comparison of EC-SERS spectra of in air and at the voltage that gives the best SERS signal of rhamnetin.

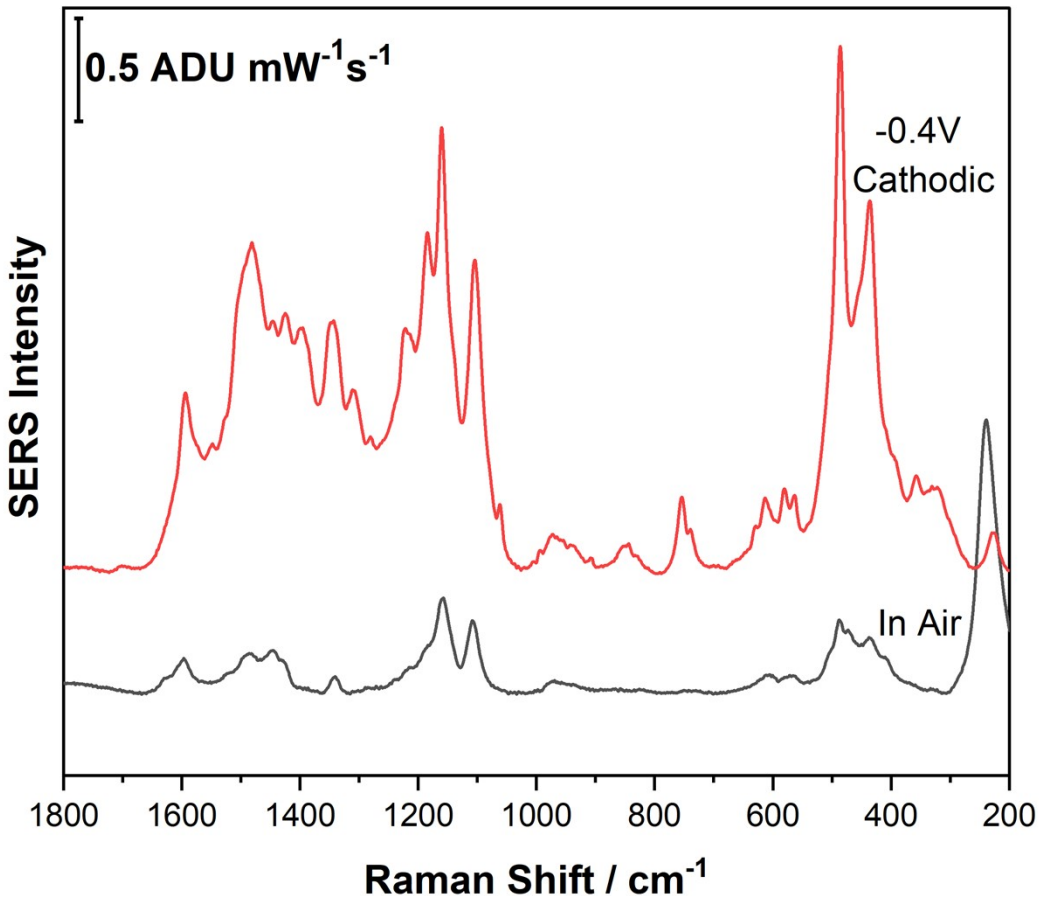

Figure S-4: Comparison of EC-SERS spectra of in air and at the voltage that gives the best SERS signal of chlorogenic acid.

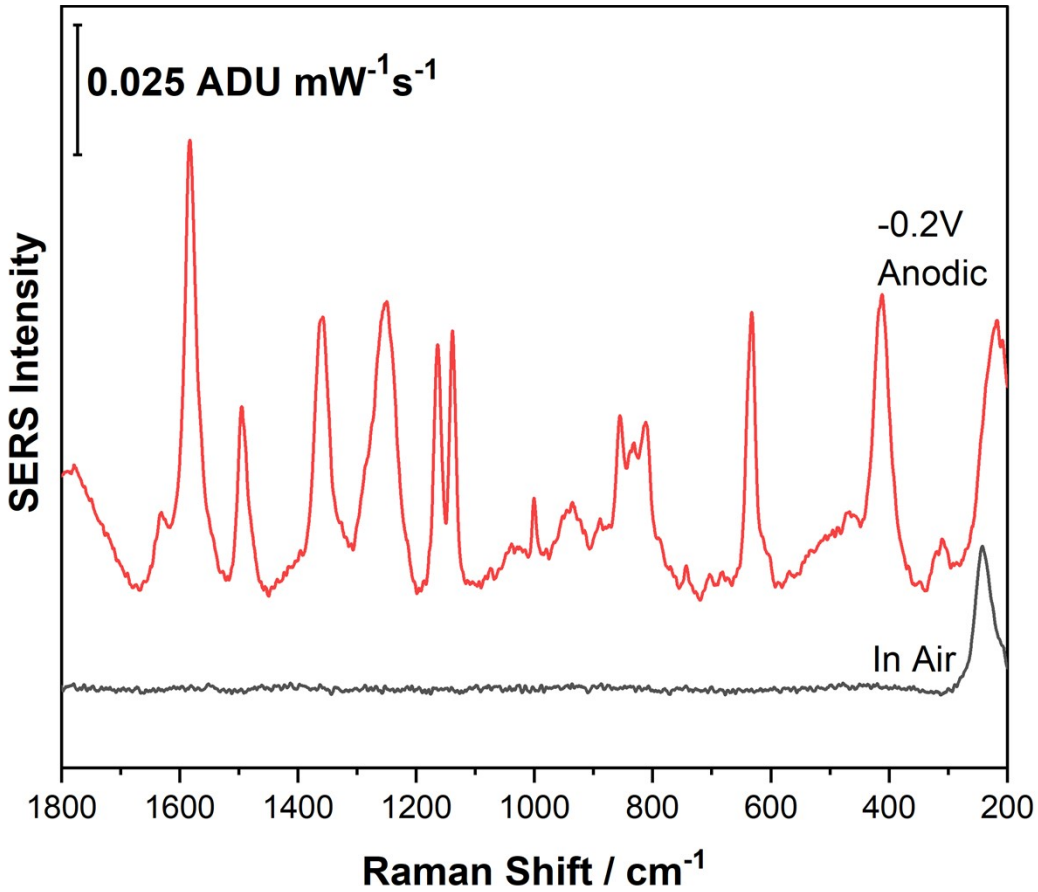

Figure S-5: Comparison of EC-SERS spectra of in air and at the voltage that gives the best SERS signal of kaempferol.

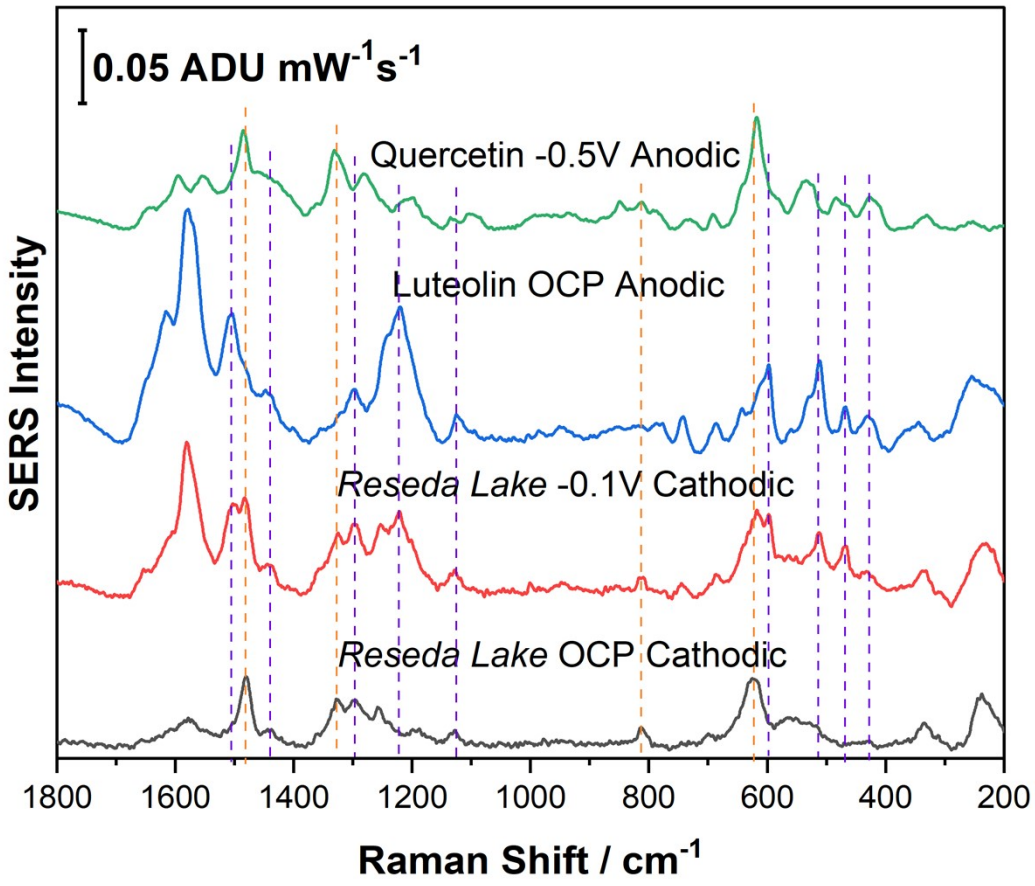

Figure S-6: Comparison of EC-SERS spectra of *Reseda Lake* extract at OCP and -0.1V cathodic, luteolin at OCP anodic and quercetin at -0.5V anodic. Laser excitation was 780 nm. Power at the sample was 80 mW, and acquisition time was 30 s. Orange dashed line indicates *Reseda Lake* OCP cathodic being compared to quercetin and purple dashed line indicates *Reseda Lake* -0.1V being compared to luteolin.

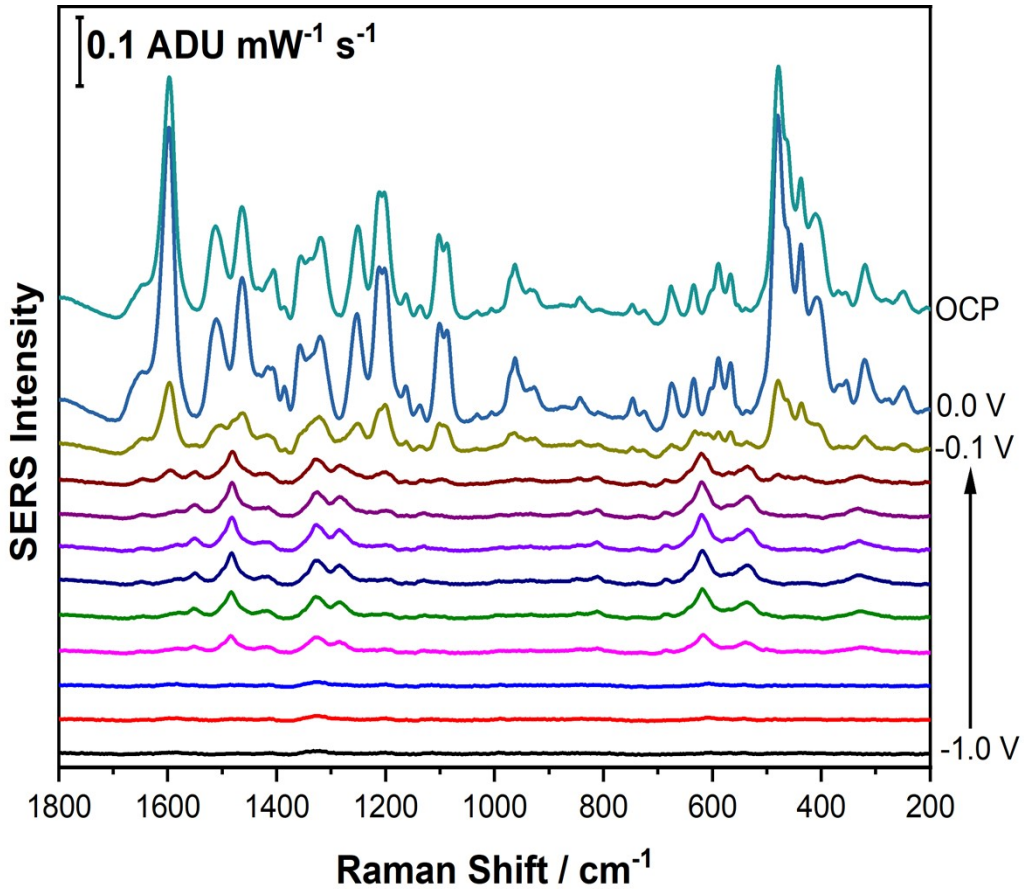

Figure S-7: Anodic progression of EC-SERS spectra for 2.0 mg *Stil de Grain* extract. Laser excitation was 780 nm. Power at the sample was 80 mW, and acquisition time was 30 s.

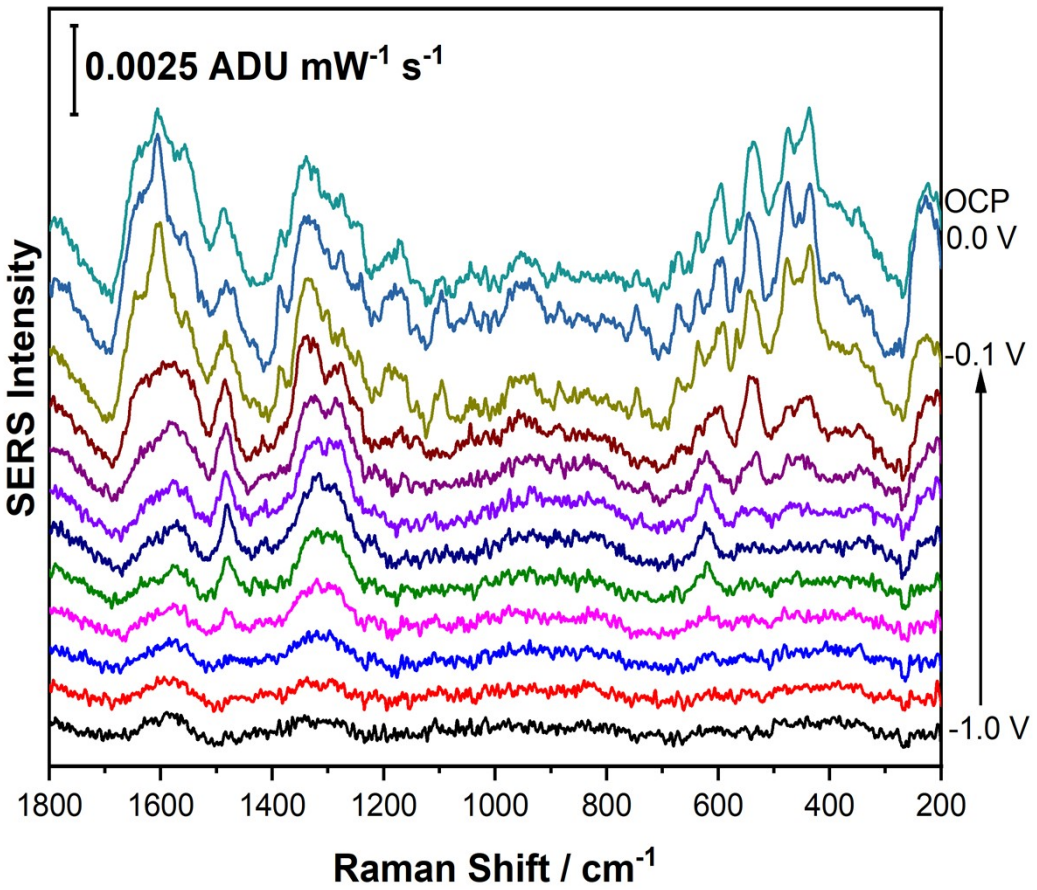

Figure S-8: Anodic progression of EC-SERS spectra for simulated *Stil de Grain* art sample extract. Laser excitation was 780 nm. Power at the sample was 120 mW, and acquisition time was 60 s.