SUPPLEMENTARY INFORMATION

Colloid preparation

$AgNO_3$ and $HAuCl_4$ were purchased from Sigma Aldrich UK, all salts were purchased from Avocado Research Chemicals Ltd and propranolol hydrochloride was purchased from Fisher Scientific UK. All reagents were used without further purification.

Five colloids were prepared as follows:

1. Reduction of $AgNO_3$ by citrate ions[1]. 90 mg $AgNO_3$ was dissolved in 500 mL of deionised H_2O (dH_2O). The solution was then heated until boiling, stirring continuously. Following this 10 mL of a 1% sodium citrate solution was added dropwise and stirred vigorously. The solution was then left to boil for a further 60 min and a colour change from clear to grey-green was noted. The solution was then stored in a dark cupboard until use.
2. Reduction of $AgNO_3$ by hydroxylamine ions[2]. 52 mg $AgNO_3$ was dissolved in 270 mL of dH_2O, 63 mg of hydroxylamine hydrochloride was dissolved in 15 mL dH_2O and 13.5 mL of 0.10 M of NaOH was added dropwise. The two solutions were then combined and a grey-brown solution resulted. The solution was stored in a dark cupboard until use.
3. Reduction of $AgNO_3$ by borohydride ions[3]. 14 mg $NaBH_4$ was dissolved in 300 mL dH_2O to which 38 mL of a 2×10^{-3} M $AgNO_3$ was added dropwise with continuous stirring where the colour changed from clear to yellow. The resulting solution was stirred for a further 45 min and kept in an ice bath at all times before storage at 4 °C. During analysis this colloid was kept in an ice bath to maintain its temperature.
4. Reduction of gold (III) chloride ($HAuCl_4$) by borohydride ions[1]. 49 mg $HAuCl_4$ was dissolved in 25 mL of cooled dH_2O and 6 mg $NaBh_4$ was dissolved in 75 mL of cooled dH_2O. The two solutions were added together and a red colour was noted. The colloid was stored at 4 °C. During analysis the colloid was kept in an ice bath to maintain its temperature.
5. Reduction of $HAuCl_4$ by citrate ions[4]. 97 mg $HAuCl_4$ was dissolved in 200 mL dH_2O and boiled. 6 mL of a 1% sodium citrate solution was then added dropwise while boiling. The solution was left boiling for a further 30 min with continuous stirring and a dark red colour was noted. After cooling the colloid was kept in a dark cupboard until use.

Instrumentation

SERS spectra were recorded on four different instruments:

1. NIR Advantage Series Raman spectrometer (DeltaNu, Laramie, WY, USA) emitting up to ~ 60 mW of 785 nm radiation with 23 s integrations;
2. Advantage 200A Series Raman spectrometer (DeltaNu, Laramie, WY, USA) emitting up to ~ 3 mW of 633 nm radiation with 23 s integrations;

   Data acquired on the above two instruments was saved in the NuSpec ASCII XY format
3. Ocean Optics spectrometer, (Dunedin, FL, USA) emitting up to ~ 77 mW of 532 nm radiation with 23 s integrations, for which the data was saved as csv format via RSI Scan software;
4. ChiralRAMAN spectrometer (BioTools Inc., Jupiter, FL, USA) emitting up to ~ 500 mW of 532 nm radiation with 32 scans (23 s integrations) measured, where the data were saved as ASCII txt format via Critical Link LLC software.

Spectra were measured as triplicate repeat sample condition for all four instruments. The data from all four instruments were exported to a PC running Windows 7 and converted to xls format and csv format where required, for analysis and data processing.

Scaling factors for comparison of intensities.

During the study we had to consider how best to compare the results from each laser excitation wavelength impartially. In order to do this we considered different scaling factors and present the reasons for our choice:

Initially, data were analyzed without any scaling factor being applied. However, it was clear that the results observed overwhelmingly favoured the ChiralRAMAN spectrometer. Presumably this was due to the laser power at the sample compared to the Raman probes which emitted radiation at least eight times lower intensities than the ChiralRAMAN spectrometer.

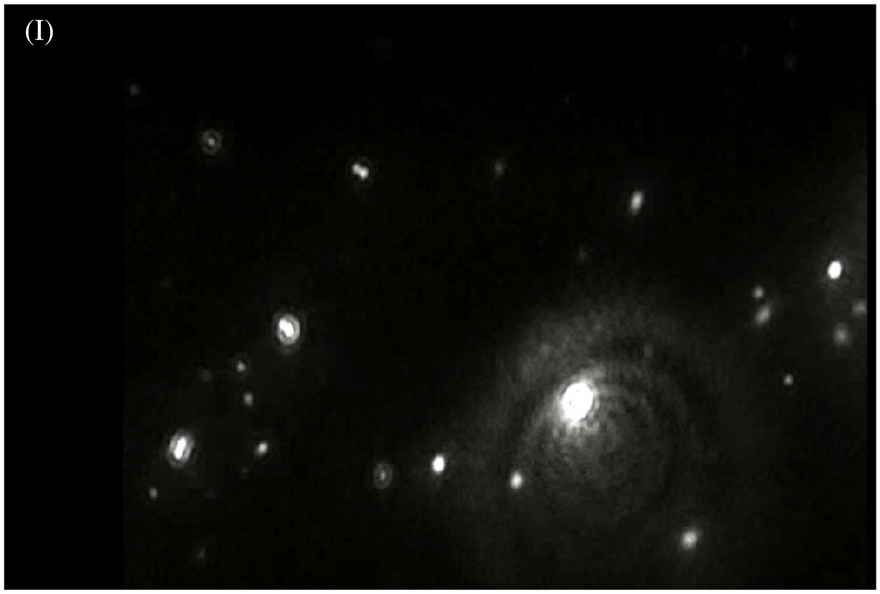
Taking this important difference forward we scaled the data by multiplying the data observed for the Advantage 200A Series spectrometer and the NIR Advantage Series spectrometer (the Ocean Optics spectrometer was not used at this point) by appropriate scaling factors to normalize them to the intensities measured using the ChiralRAMAN spectrometer. The SERS intensities measured using the Advantage 200A spectrometer were scaled by a factor of 8.33, and the SERS intensities measured using the NIR Advantage instrument by 166.67. However, the results then greatly favoured the Advantage NIR spectrometer, indicating that this scaling factor was inappropriate.

Scaling factors were then determined based on effective scattering intensities measured on each spectrometer for a reference compound, pure ethanol. This yielded scaling factors of 5200 for the 785 nm excitation wavelength and 285 for the 633 nm laser excitation wavelength. However, these scaling factors again led to favouring the Advantage NIR spectrometer.

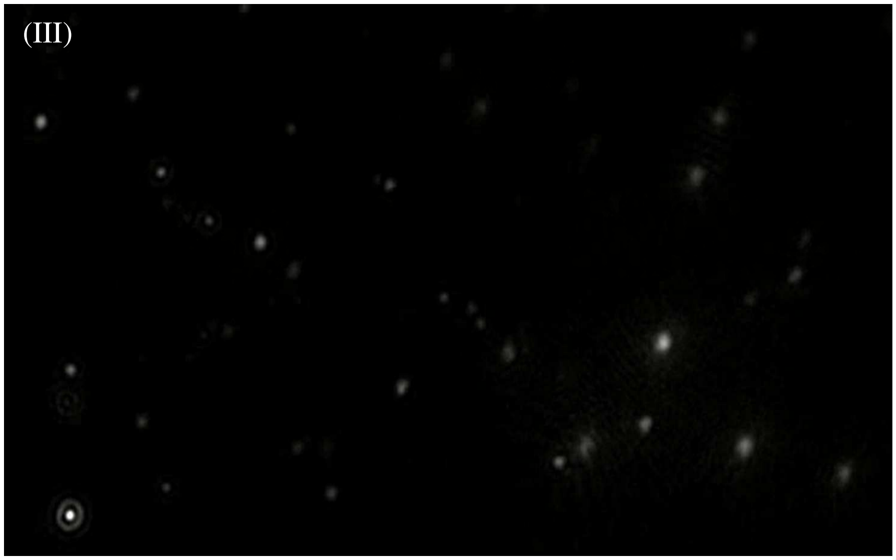
In order to remove this uncertainty over appropriate scaling factors we therefore scaled the data to between 0 and 1 for all instruments, 0 being the lowest point observed for the spectrum. This negates the effect of variable instrument parameters (such as excitation wavelength, quantum efficiency of the detector and the efficiency of the optical alignment) which can dramatically differ from spectrometer-to-spectrometer and so makes our approach applicable to any SERS experiment.

References

(1) Lee P.C.; Meisel D. *J. Phys. Chem.* **1982**, *86*, 3391-3395.
(2) Leopold N.; Lendl B. *J. Phys. Chem. B* **2003**, *107*, 5723-5727.
(3) Creighton J.A.; Blatchford C.G.; Albrecht M.G., *J. Chem. Soc. Faraday Trans. 2* **1979**, 75, 790-798.
(4) Grabar K.C.; Freeman R.G.; Hommer M.B.; Natan N.J. *Anal. Chem.* **1995**, *67*, 735-743


(I)


(II)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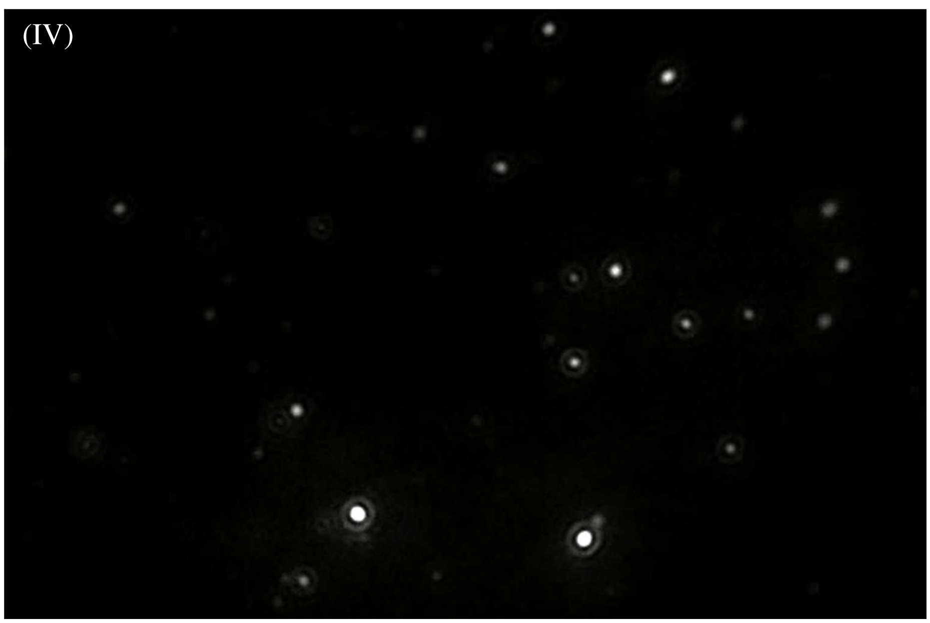
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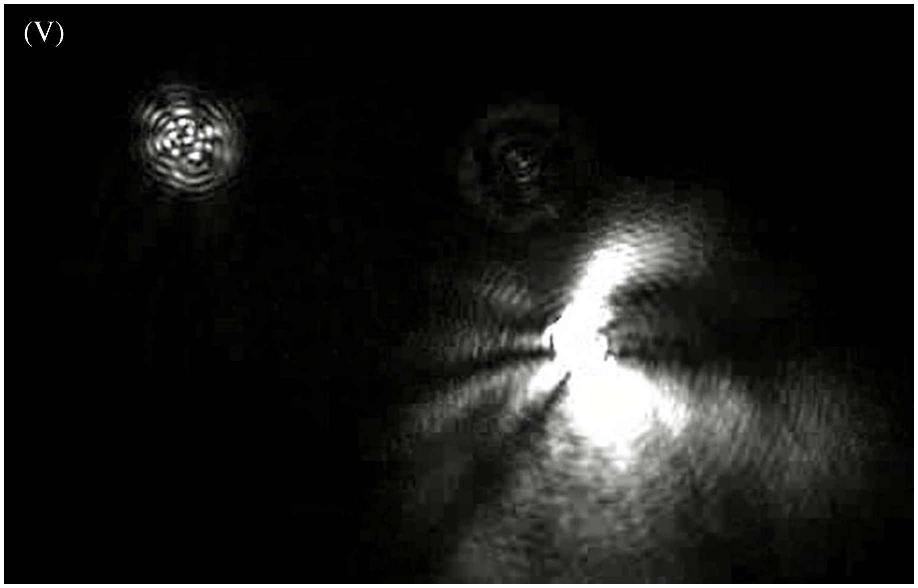


Fig. S1 Representative images of colloids measured using a Nanoparticle Tracking Analysis (NTA) Version 2.0 Test Version Build 0252 (NanoSight Ltd. Amesbury, UK), in order to characterize colloid size and density in the sol:

(I) Borohydride reduction of $AgNO_3$, ~90 % of the metal particles were at least 41 nm in diameter and there were 3.70 x 10^8 particles/mL.

(II) Citrate reduction of $AgNO_3$, ~90% of the metal particles were at least 76 nm in diameter and there were 3.87 x 10^8 particles/mL.

(III) Citrate reduction of $HAuCl_4$, ~90% of the metal particles were at least 81 nm in diameter and there were 4.94 x 10^8 particles/mL.

(IV) Borohydride reduction of $HAuCl_4$, ~90% of the metal particles were at least 57 nm in diameter and there were 5.56 x 10^8 particles/mL.

(V) Colloids produced by hydroxylamine reduction of $AgNO_3$ were too large to be measured using NTA.

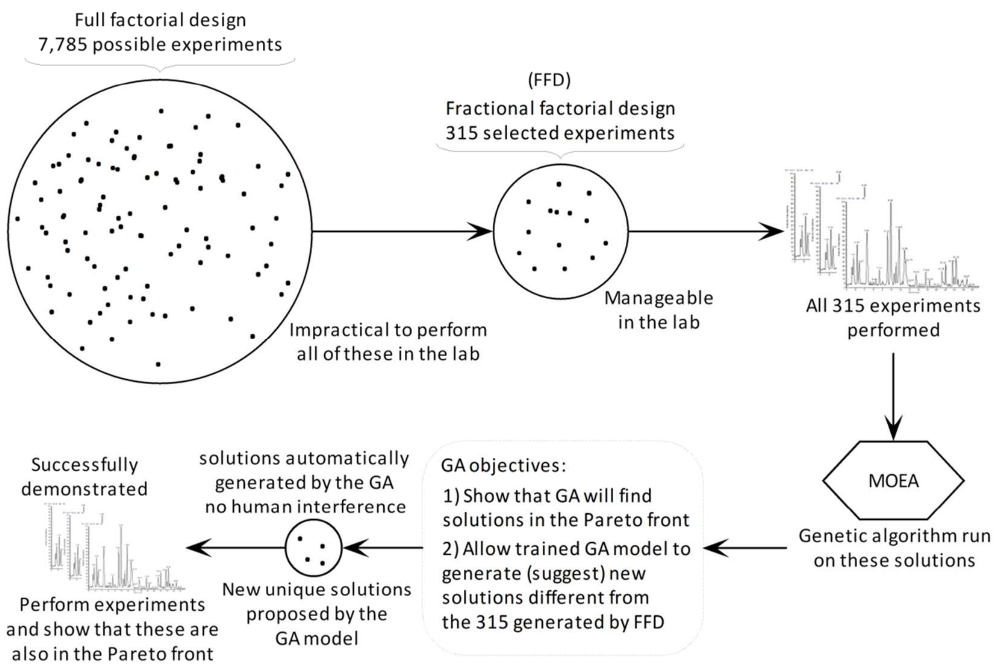


Fig. S2 A summary of the MOEA workflow.

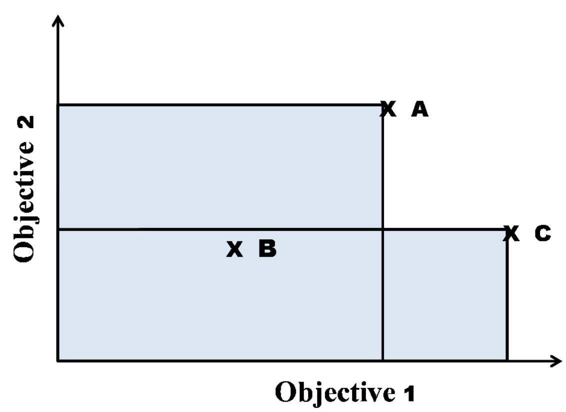


Fig. S3 Pareto optimality for two objective functions - Point A dominates point B in both objectives but only dominates point C in objective 2. Therefore as no solution dominates all the others in both objectives, solutions A and C would be acceptable solutions that sit on the Pareto Front

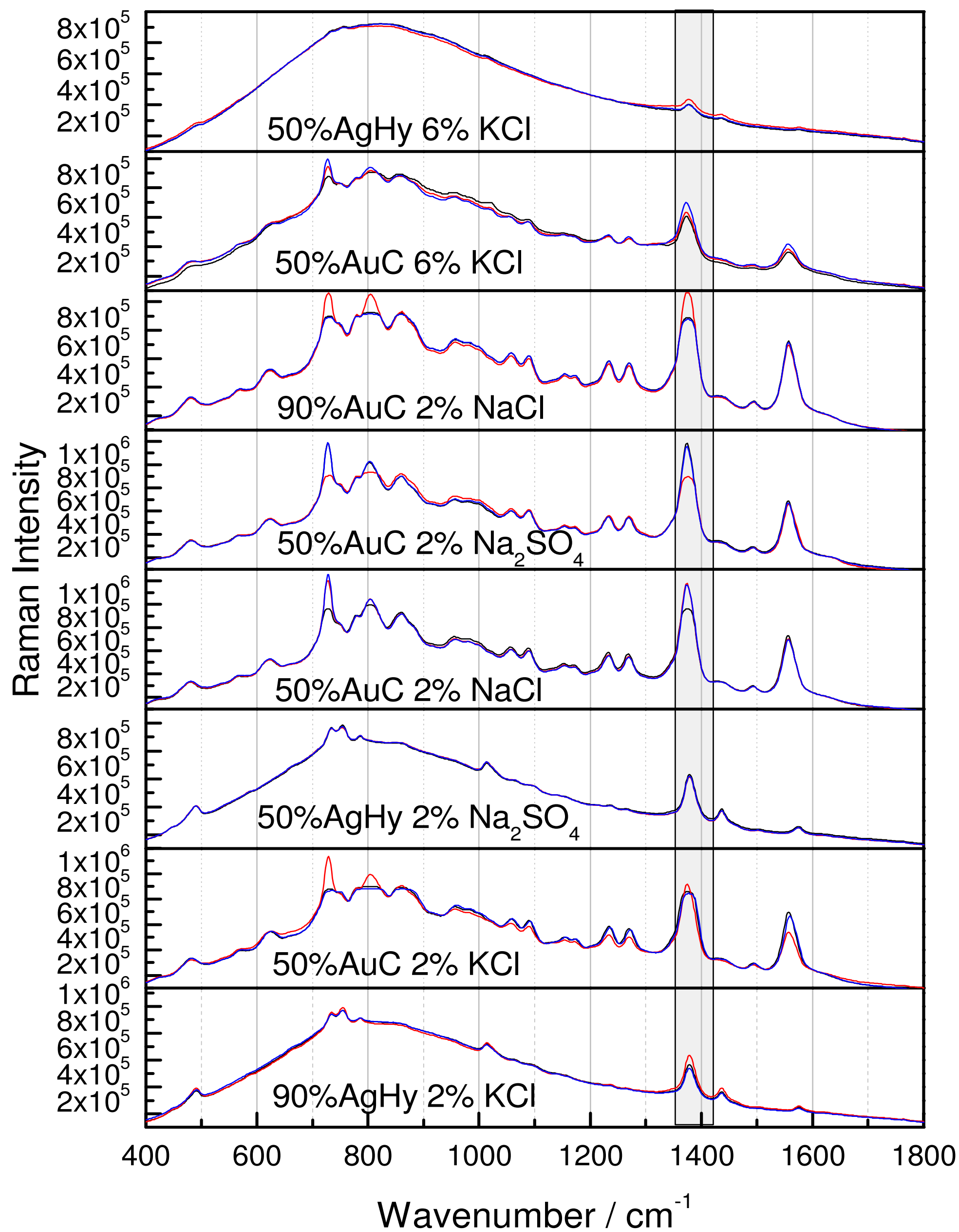
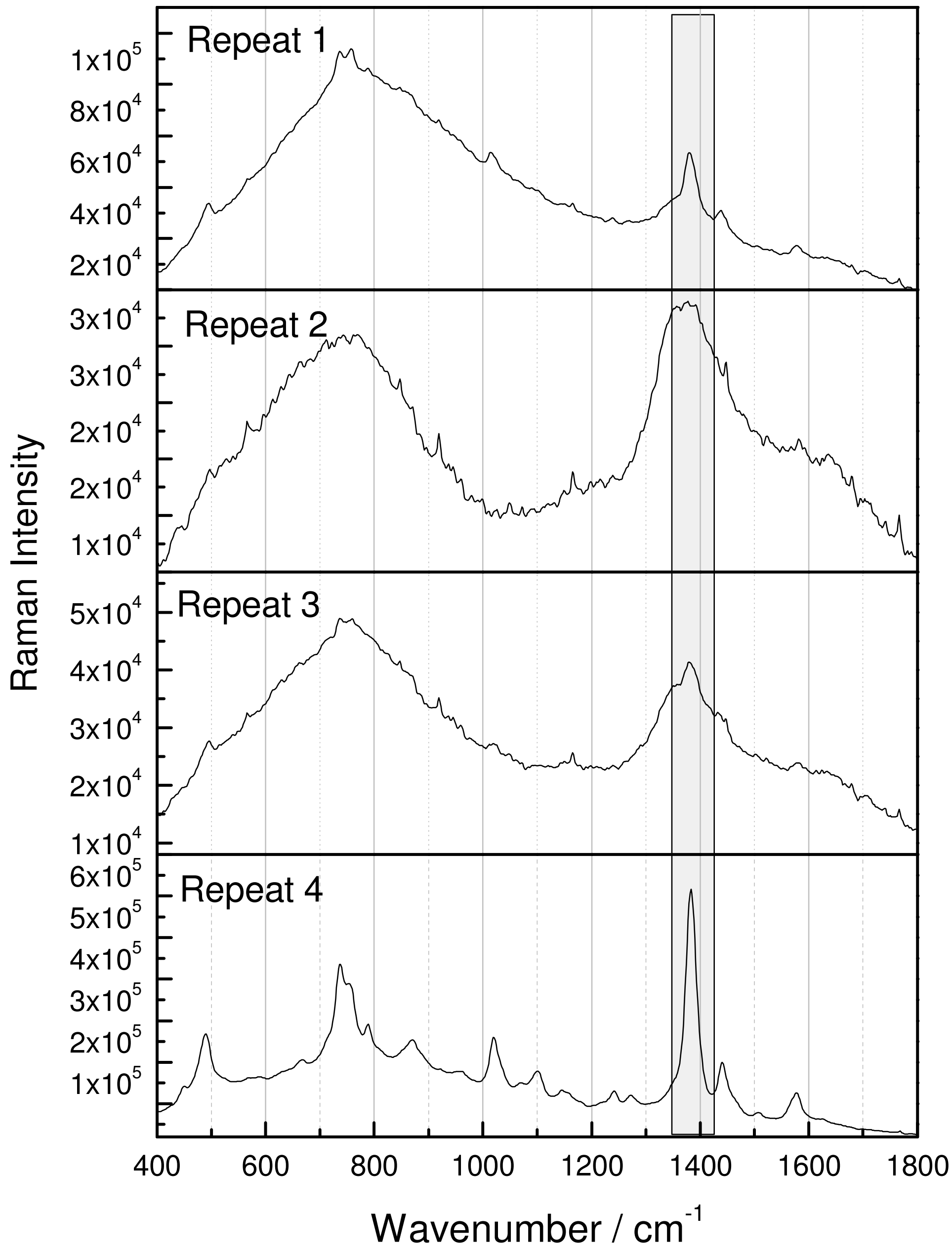


Fig. S4 Observed SERS spectra for the second generation of experiments (experimental conditions are listed in Table S3) which were performed in triplicate. An EMSC was applied to all spectra prior to analysis.

(I)



Repeat 1
Repeat 2
Repeat 3
Repeat 4
Raman Intensity
Wavenumber / cm-1

(II)

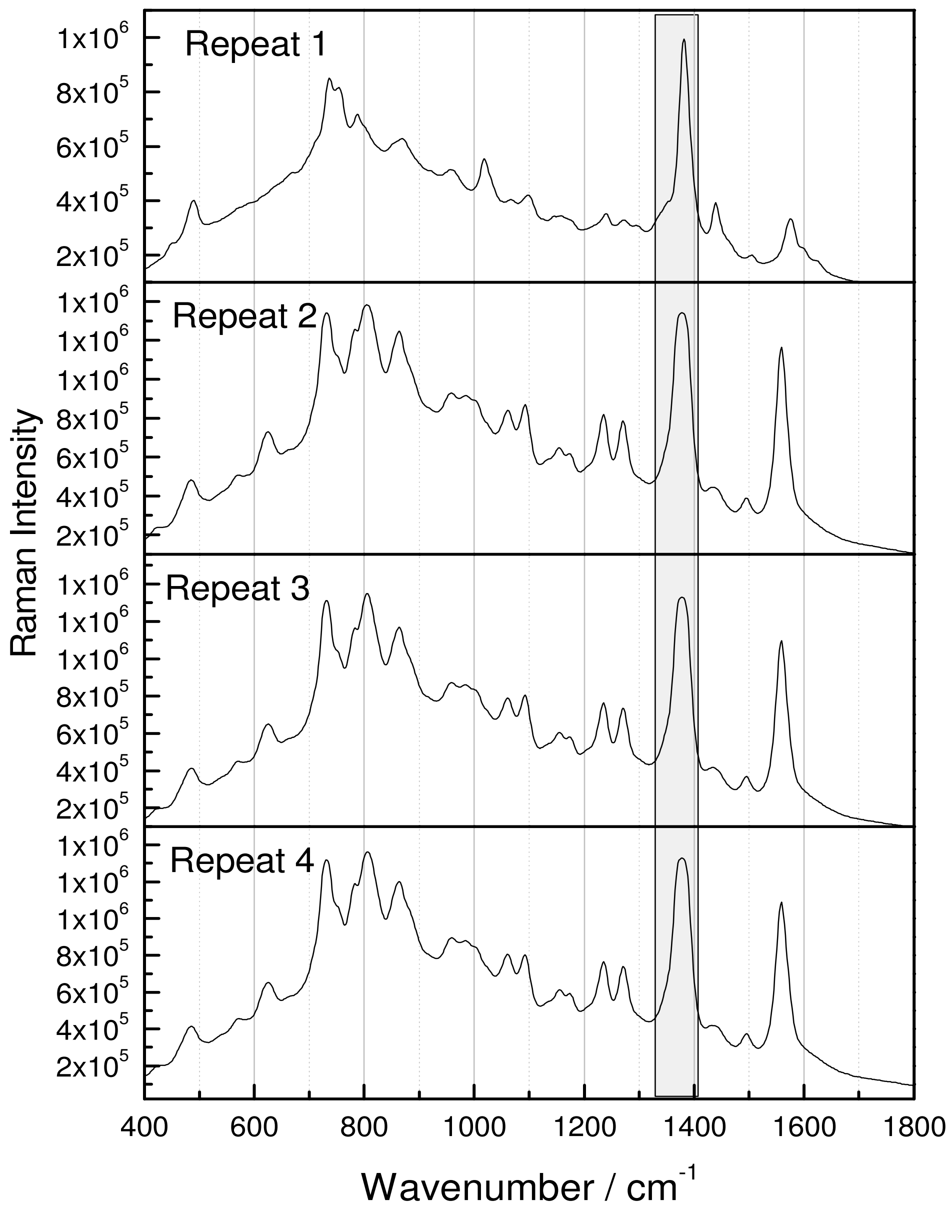


Fig S5 Representative SERS spectra demonstrating the relative differences in reproducibility in: (I) in the absence of an aggregating agent for hydroxylamine reduction of $AgNO_3$, and (II) in the absence of an aggregating agent for citrate reduction of $HAuCl_4$. These spectra illustrate that more consistent results were obtained for citrate reduction of $HAuCl_4$.

Table S1 Experimental conditions for the fractional factorial study

Exp.	% Metal	Metal	% Salt	Salt	% Analyte	H_2O	Laser (nm)
1	20	AgBh	1	NaCl	5	74	532
2	20	AgBh	7	NaCl	5	68	532
3	70	AgBh	1	KNO_3	5	24	532
4	70	AgBh	7	KNO_3	5	18	532
5	20	AgBh	1	NaCl	5	74	785
6	20	AgBh	7	NaCl	5	68	785
7	70	AgBh	1	KCl	5	24	785
8	70	AgBh	7	KCl	5	18	785
9	20	AgBh	1	Na_2SO_4	5	74	532
10	20	AgBh	7	$Na_2 SO_4$	5	68	532
11	70	AgC	1	K_2SO_4	5	24	532
12	70	AgC	7	K_2SO_4	5	18	532
13	20	AgC	1	KNO_3	5	74	785
14	20	AgC	7	KNO_3	5	68	785
15	70	AgC	1	$MgSO_4$	5	24	785
16	70	AgC	7	$MgSO_4$	5	18	785
17	20	AgC	1	KCl	5	74	532
18	20	AgC	7	KCl	5	68	532
19	70	AgC	1	Na_2SO_4	5	24	532
20	70	AgC	7	Na_2SO_4	5	18	532
21	20	AgHy	1	K_2SO_4	5	74	785
22	20	AgHy	7	K_2SO_4	5	68	785
23	70	AgHy	1	NaCl	5	24	785
24	70	AgHy	7	NaCl	5	18	785
25	20	AgHy	1	$MgSO_4$	5	74	532
26	20	AgHy	7	$MgSO_4$	5	68	532
27	70	AgHy	1	KCl	5	24	532
28	70	AgHy	7	KCl	5	18	532
29	20	AgHy	1	Na_2SO_4	5	74	785
30	20	AgHy	7	Na_2SO_4	5	68	785
31	70	AuBh	1	K_2SO_4	5	24	785
32	70	AuBh	7	K_2SO_4	5	18	785
33	20	AuBh	1	NaCl	5	74	532
34	20	AuBh	7	NaCl	5	68	532
35	70	AuBh	1	KNO_3	5	24	532
36	70	AuBh	7	KNO_3	5	18	532
37	20	AuBh	1	KCl	5	74	785
38	20	AuBh	7	KCl	5	68	785
39	70	AuBh	1	Na_2SO_4	5	24	785
40	70	AuBh	7	Na_2SO_4	5	18	785
41	20	AuC	1	K_2SO_4	5	74	532
42	20	AuC	7	K_2SO_4	5	68	532
43	70	AuC	1	NaCl	5	24	532
44	70	AuC	7	NaCl	5	18	532
45	20	AuC	1	KNO_3	5	74	785
46	20	AuC	7	KNO_3	5	68	785
47	70	AuC	1	$MgSO_4$	5	24	785
48	70	AuC	7	$MgSO_4$	5	18	785
49	20	AuC	1	Na_2SO_4	5	74	532
50	20	AuC	7	Na_2SO_4	5	68	532
51	10	AuBh	0	0	5	85	532
52	50	AuBh	0	0	5	45	532
53	90	AuBh	0	0	5	5	532

Table S1 Cont.

Exp.	% Metal	Metal	% Salt	Salt	% Analyte	H_2O	Laser (nm)
54	10	AuC	0	0	5	85	532
55	50	AuC	0	0	5	45	532
56	90	AuC	0	0	5	5	532
57	10	AgBh	0	0	5	85	532
58	50	AgBh	0	0	5	45	532
59	90	AgBh	0	0	5	5	532
60	10	AgC	0	0	5	85	532
61	50	AgC	0	0	5	45	532
62	90	AgC	0	0	5	5	532
63	10	AgHy	0	0	5	85	532
64	50	AgHy	0	0	5	45	532
65	90	AgHy	0	0	5	5	532
66	10	AuBh	0	0	5	85	633
67	50	AuBh	0	0	5	45	633
68	90	AuBh	0	0	5	5	633
69	10	AuC	0	0	5	85	633
70	50	AuC	0	0	5	45	633
71	90	AuC	0	0	5	5	633
72	10	AgBh	0	0	5	85	633
73	50	AgBh	0	0	5	45	633
74	90	AgBh	0	0	5	5	633
75	10	AgC	0	0	5	85	633
76	50	AgC	0	0	5	45	633
77	90	AgC	0	0	5	5	633
78	10	AgHy	0	0	5	85	633
79	50	AgHy	0	0	5	45	633
80	90	AgHy	0	0	5	5	633
81	10	AuBh	0	0	5	85	785
82	50	AuBh	0	0	5	45	785
83	90	AuBh	0	0	5	5	785
84	10	AuC	0	0	5	85	785
85	50	AuC	0	0	5	45	785
86	90	AuC	0	0	5	5	785
87	10	AgBh	0	0	5	85	785
88	50	AgBh	0	0	5	45	785
89	90	AgBh	0	0	5	5	785
90	10	AgC	0	0	5	85	785
91	50	AgC	0	0	5	45	785
92	90	AgC	0	0	5	5	785
93	10	AgHy	0	0	5	85	785
94	50	AgHy	0	0	5	45	785
95	90	AgHy	0	0	5	5	785
96	10	AuBh	10	K_2SO_4	5	75	532
97	10	AuBh	10	KNO_3	5	75	532
98	10	AuBh	10	$MgSO_4$	5	75	532
99	10	AuBh	10	Na_2SO_4	5	75	532
100	10	AuC	10	NaCl	5	75	532
101	10	AuC	10	$MgSO_4$	5	75	532
102	10	AuC	10	KCl	5	75	532
103	10	AgBh	10	K_2SO_4	5	75	532
104	10	AgBh	10	KNO_3	5	75	532
105	10	AgBh	10	KCl	5	75	532
106	10	AgC	10	K_2SO_4	5	75	532
107	10	AgC	10	NaCl	5	75	532

Table S1 Cont.

Exp.	% Metal	Metal	% Salt	Salt	% Analyte	H_2O	Laser (nm)
108	10	AgC	10	$MgSO_4$	5	75	532
109	10	AgC	10	Na_2SO_4	5	75	532
110	10	AgHy	10	NaCl	5	75	532
111	10	AgHy	10	KNO_3	5	75	532
112	10	AgHy	10	KCl	5	75	532
113	10	AuBh	10	K_2SO_4	5	75	633
114	10	AuBh	10	NaCl	5	75	633
115	10	AuBh	10	KNO_3	5	75	633
116	10	AuBh	10	$MgSO_4$	5	75	633
117	10	AuBh	10	KCl	5	75	633
118	10	AuBh	10	Na_2SO_4	5	75	633
119	10	AuC	10	K_2SO_4	5	75	633
120	10	AuC	10	NaCl	5	75	633
121	10	AuC	10	KNO_3	5	75	633
122	10	AuC	10	$MgSO_4$	5	75	633
123	10	AuC	10	KCl	5	75	633
124	10	AuC	10	Na_2SO_4	5	75	633
125	10	AgBh	10	K_2SO_4	5	75	633
126	10	AgBh	10	NaCl	5	75	633
127	10	AgBh	10	KNO_3	5	75	633
128	10	AgBh	10	$MgSO_4$	5	75	633
129	10	AgBh	10	KCl	5	75	633
130	10	AgBh	10	Na_2SO_4	5	75	633
131	10	AgC	10	K_2SO_4	5	75	633
132	10	AgC	10	NaCl	5	75	633
133	10	AgC	10	KNO_3	5	75	633
134	10	AgC	10	$MgSO_4$	5	75	633
135	10	AgC	10	KCl	5	75	633
136	10	AgC	10	Na_2SO_4	5	75	633
137	10	AgHy	10	K_2SO_4	5	75	633
138	10	AgHy	10	NaCl	5	75	633
139	10	AgHy	10	KNO_3	5	75	633
140	10	AgHy	10	$MgSO_4$	5	75	633
141	10	AgHy	10	KCl	5	75	633
142	10	AgHy	10	Na_2SO_4	5	75	633
143	10	AuBh	10	K_2SO_4	5	75	785
144	10	AuBh	10	KNO_3	5	75	785
145	10	AuBh	10	$MgSO_4$	5	75	785
146	10	AuBh	10	Na_2SO_4	5	75	785
147	10	AuC	10	NaCl	5	75	785
148	10	AuC	10	$MgSO_4$	5	75	785
149	10	AuC	10	KCl	5	75	785
150	10	AgBh	10	K_2SO_4	5	75	785
151	10	AgBh	10	KNO_3	5	75	785
152	10	AgBh	10	KCl	5	75	785
153	10	AgC	10	K_2SO_4	5	75	785
154	10	AgC	10	NaCl	5	75	785
155	10	AgC	10	$MgSO_4$	5	75	785
156	10	AgC	10	Na_2SO_4	5	75	785
157	10	AgHy	10	NaCl	5	75	785
158	10	AgHy	10	KNO_3	5	75	785
159	10	AgHy	10	KCl	5	75	785
160	50	AuBh	6	K_2SO_4	5	39	532
161	50	AuBh	6	NaCl	5	39	532
162	50	AuBh	6	KNO_3	5	39	532
163	50	AuBh	6	$MgSO_4$	5	39	532

Table S1 Cont.

Exp.	% Metal	Metal	% Salt	Salt	% Analyte	H_2O	Laser (nm)
164	50	AuBh	6	KCl	5	39	532
165	50	AuBh	6	Na_2SO_4	5	39	532
166	50	AuC	6	K_2SO_4	5	39	532
167	50	AuC	6	NaCl	5	39	532
168	50	AuC	6	KNO_3	5	39	532
169	50	AuC	6	$MgSO_4$	5	39	532
170	50	AuC	6	KCl	5	39	532
171	50	AuC	6	Na_2SO_4	5	39	532
172	50	AgBh	6	K_2SO_4	5	39	532
173	50	AgBh	6	NaCl	5	39	532
174	50	AgBh	6	KNO_3	5	39	532
175	50	AgBh	6	$MgSO_4$	5	39	532
176	50	AgBh	6	KCl	5	39	532
177	50	AgBh	6	Na_2SO_4	5	39	532
178	50	AgC	6	K_2SO_4	5	39	532
179	50	AgC	6	NaCl	5	39	532
180	50	AgC	6	KNO_3	5	39	532
181	50	AgC	6	$MgSO_4$	5	39	532
182	50	AgC	6	KCl	5	39	532
183	50	AgC	6	Na_2SO_4	5	39	532
184	50	AgHy	6	K_2SO_4	5	39	532
185	50	AgHy	6	NaCl	5	39	532
186	50	AgHy	6	KNO_3	5	39	532
187	50	AgHy	6	$MgSO_4$	5	39	532
188	50	AgHy	6	KCl	5	39	532
189	50	AgHy	6	Na_2SO_4	5	39	532
190	50	AuBh	6	K_2SO_4	5	39	633
191	50	AuBh	6	NaCl	5	39	633
192	50	AuBh	6	KNO_3	5	39	633
193	50	AuBh	6	$MgSO_4$	5	39	633
194	50	AuBh	6	KCl	5	39	633
195	50	AuBh	6	Na_2SO_4	5	39	633
196	50	AuC	6	K_2SO_4	5	39	633
197	50	AuC	6	NaCl	5	39	633
198	50	AuC	6	KNO_3	5	39	633
199	50	AuC	6	$MgSO_4$	5	39	633
200	50	AuC	6	KCl	5	39	633
201	50	AuC	6	Na_2SO_4	5	39	633
202	50	AgBh	6	K_2SO_4	5	39	633
203	50	AgBh	6	NaCl	5	39	633
204	50	AgBh	6	KNO_3	5	39	633
205	50	AgBh	6	$MgSO_4$	5	39	633
206	50	AgBh	6	KCl	5	39	633
207	50	AgBh	6	Na_2SO_4	5	39	633
208	50	AgC	6	K_2SO_4	5	39	633
209	50	AgC	6	NaCl	5	39	633
210	50	AgC	6	KNO_3	5	39	633
211	50	AgC	6	$MgSO_4$	5	39	633
212	50	AgC	6	KCl	5	39	633
213	50	AgC	6	Na_2SO_4	5	39	633
214	50	AgHy	6	K_2SO_4	5	39	633
215	50	AgHy	6	NaCl	5	39	633
216	50	AgHy	6	KNO_3	5	39	633
217	50	AgHy	6	$MgSO_4$	5	39	633
218	50	AgHy	6	KCl	5	39	633
219	50	AgHy	6	Na_2SO_4	5	39	633

Table S1 Cont.

Exp.	% Metal	Metal	% Salt	Salt	% Analyte	H_2O	Laser (nm)
220	50	AuBh	6	K_2SO_4	5	39	785
221	50	AuBh	6	NaCl	5	39	785
222	50	AuBh	6	KNO_3	5	39	785
223	50	AuBh	6	$MgSO_4$	5	39	785
224	50	AuBh	6	KCl	5	39	785
225	50	AuBh	6	Na_2SO_4	5	39	785
226	50	AuC	6	K_2SO_4	5	39	785
227	50	AuC	6	NaCl	5	39	785
228	50	AuC	6	KNO_3	5	39	785
229	50	AuC	6	$MgSO_4$	5	39	785
230	50	AuC	6	KCl	5	39	785
231	50	AuC	6	Na_2SO_4	5	39	785
232	50	AgBh	6	K_2SO_4	5	39	785
233	50	AgBh	6	NaCl	5	39	785
234	50	AgBh	6	KNO_3	5	39	785
235	50	AgBh	6	$MgSO_4$	5	39	785
236	50	AgBh	6	KCl	5	39	785
237	50	AgBh	6	Na_2SO_4	5	39	785
238	50	AgC	6	K_2SO_4	5	39	785
239	50	AgC	6	NaCl	5	39	785
240	50	AgC	6	KNO_3	5	39	785
241	50	AgC	6	$MgSO_4$	5	39	785
242	50	AgC	6	KCl	5	39	785
243	50	AgC	6	Na_2SO_4	5	39	785
244	50	AgHy	6	K_2SO_4	5	39	785
245	50	AgHy	6	NaCl	5	39	785
246	50	AgHy	6	KNO_3	5	39	785
247	50	AgHy	6	$MgSO_4$	5	39	785
248	50	AgHy	6	KCl	5	39	785
249	50	AgHy	6	Na_2SO_4	5	39	785
250	90	AuBh	2	NaCl	5	3	532
251	90	AuBh	2	$MgSO_4$	5	3	532
252	90	AuBh	2	KCl	5	3	532
253	90	AuC	2	K_2SO_4	5	3	532
254	90	AuC	2	KNO_3	5	3	532
255	90	AuC	2	KCl	5	3	532
256	90	AuC	2	Na_2SO_4	5	3	532
257	90	AgBh	2	K_2SO_4	5	3	532
258	90	AgBh	2	NaCl	5	3	532
259	90	AgBh	2	$MgSO_4$	5	3	532
260	90	AgBh	2	Na_2SO_4	5	3	532
261	90	AgC	2	NaCl	5	3	532
262	90	AgC	2	KNO_3	5	3	532
263	90	AgC	2	KCl	5	3	532
264	90	AgHy	2	K_2SO_4	5	3	532
265	90	AgHy	2	KNO_3	5	3	532
266	90	AgHy	2	$MgSO_4$	5	3	532
267	90	AgHy	2	Na_2SO_4	5	3	532
268	90	AuBh	2	K_2SO_4	5	3	633
269	90	AuBh	2	NaCl	5	3	633
270	90	AuBh	2	KNO_3	5	3	633
271	90	AuBh	2	$MgSO_4$	5	3	633
272	90	AuBh	2	KCl	5	3	633
273	90	AuBh	2	Na_2SO_4	5	3	633
274	90	AuC	2	K_2SO_4	5	3	633
275	90	AuC	2	NaCl	5	3	633

Table S1 Cont.

Exp.	% Metal	Metal	% Salt	Salt	% Analyte	H_2O	Laser (nm)
276	90	AuC	2	KNO_3	5	3	633
277	90	AuC	2	$MgSO_4$	5	3	633
278	90	AuC	2	KCl	5	3	633
279	90	AuC	2	Na_2SO_4	5	3	633
280	90	AgBh	2	K_2SO_4	5	3	633
281	90	AgBh	2	NaCl	5	3	633
282	90	AgBh	2	KNO_3	5	3	633
283	90	AgBh	2	$MgSO_4$	5	3	633
284	90	AgBh	2	KCl	5	3	633
285	90	AgBh	2	Na_2SO_4	5	3	633
286	90	AgC	2	K_2SO_4	5	3	633
287	90	AgC	2	NaCl	5	3	633
288	90	AgC	2	KNO_3	5	3	633
289	90	AgC	2	$MgSO_4$	5	3	633
290	90	AgC	2	KCl	5	3	633
291	90	AgC	2	Na_2SO_4	5	3	633
292	90	AgHy	2	K_2SO_4	5	3	633
293	90	AgHy	2	NaCl	5	3	633
294	90	AgHy	2	KNO_3	5	3	633
295	90	AgHy	2	$MgSO_4$	5	3	633
296	90	AgHy	2	KCl	5	3	633
297	90	AgHy	2	Na_2SO_4	5	3	633
298	90	AuBh	2	NaCl	5	3	785
299	90	AuBh	2	$MgSO_4$	5	3	785
300	90	AuBh	2	KCl	5	3	785
301	90	AuC	2	K_2SO_4	5	3	785
302	90	AuC	2	KNO_3	5	3	785
303	90	AuC	2	KCl	5	3	785
304	90	AuC	2	Na_2SO_4	5	3	785
305	90	AgBh	2	K_2SO_4	5	3	785
306	90	AgBh	2	NaCl	5	3	785
307	90	AgBh	2	$MgSO_4$	5	3	785
308	90	AgBh	2	Na_2SO_4	5	3	785
309	90	AgC	2	NaCl	5	3	785
310	90	AgC	2	KNO_3	5	3	785
311	90	AgC	2	KCl	5	3	785
312	90	AgHy	2	K_2SO_4	5	3	785
313	90	AgHy	2	KNO_3	5	3	785
314	90	AgHy	2	$MgSO_4$	5	3	785
315	90	AgHy	2	Na_2SO_4	5	3	785

AgHy, Hydroxylamine reduction of $AgNO_3$; AgC, Citrate reduction of $AgNO_3$; AgBh,Borohydride reduction of $AgNO_3$; AuC, Citrate reduction of $HAuCl_4$; AuBh, Borohydride reduction of $HAuCl_4$

Table S2 Experimental conditions, RFWHM and Reproducibility values for the top 35 experiments for each laser excitation wavelength.

Exp	% Metal	Metal	% Salt	Salt	Laser (nm)	% H_2O	RFWHM	Reproducibility
1	20	AgBh	1	NaCl	532	74	0.0007818	0.9860563
2	20	AgBh	7	NaCl	532	68	0.0003823	0.9694903
3	70	AgBh	1	KNO_3	532	24	0.0008868	0.9935829
4	70	AgBh	7	KNO_3	532	18	0.0011649	0.9110733
9	20	AgBh	1	Na_2SO_4	532	74	0.0013439	0.9578850
10	20	AgBh	7	Na_2SO_4	532	68	0.000248	0.9011291
11	70	AgC	1	K_2SO_4	532	24	0.0008765	0.8205746
12	70	AgC	7	K_2SO_4	532	18	0.0019134	0.9885939
17	20	AgC	1	KCl	532	74	0.0012186	0.4584051
18	20	AgC	7	KCl	532	68	0.0016668	0.9491515
19	70	AgC	1	Na_2SO_4	532	24	0.0002739	0.9731962
25	20	AgHy	1	$MgSO_4$	532	74	0.0072671	0.9806879
26	20	AgHy	7	$MgSO_4$	532	68	0.0033792	0.9919365
27	70	AgHy	1	KCl	532	24	0.0046555	0.9738544
28	70	AgHy	7	KCl	532	18	0.0029686	0.9582929
58	50	AgBh	0	None	532	45	0.0006888	0.9737556
59	90	AgBh	0	None	532	5	0.0007729	0.7314980
60	10	AgC	0	None	532	85	0.0003099	0.7663300
61	50	AgC	0	None	532	45	0.0006293	0.6599318
62	90	AgC	0	None	532	5	0.0010444	0.7256348
63	10	AgHy	0	None	532	85	0.0005966	0.9529210
64	50	AgHy	0	None	532	45	0.0004972	0.9042508
65	90	AgHy	0	None	532	5	0.0079598	0.9880928
20	70	AgC	7	Na_2SO_4	532	18	0.0010242	0.9927537
103	10	AgBh	10	K_2SO_4	532	75	0.0002664	0.9362621
104	10	AgBh	10	KNO_3	532	75	0.0005739	0.9977370
105	10	AgBh	10	KCl	532	75	9.04E-17	0.7136317
106	10	AgC	10	K_2SO_4	532	75	0.0026595	0.9853837
107	10	AgC	10	NaCl	532	75	0.0029707	0.9981194
108	10	AgC	10	$MgSO_4$	532	75	0.0021527	0.9955688
109	10	AgC	10	Na_2SO_4	532	75	0.0063402	0.8938766
111	10	AgHy	10	KNO_3	532	75	0.0017837	0.8014731
172	50	AgBh	6	K_2SO_4	532	39	2.13E-17	0.9902685
174	50	AgBh	6	KNO_3	532	39	0.0014734	0.9078552
179	50	AgC	6	NaCl	532	39	0.0081306	0.9915709
67	50	AuBh	0	None	633	45	0.00124	0.9973015
68	90	AuBh	0	None	633	5	0.001716	0.9979812
70	50	AuC	0	None	633	45	0.0017893	0.9985373
71	90	AuC	0	None	633	5	0.0034376	0.9987074
73	50	AgBh	0	None	633	45	0	0.9997801
74	90	AgBh	0	None	633	5	5.65E-05	0.9984665
75	10	AgC	0	None	633	85	0.0003076	0.9963967
76	50	AgC	0	None	633	45	0.0004458	0.9840583
77	90	AgC	0	None	633	5	0.0003379	0.9907843
78	10	AgHy	0	None	633	85	0.0002767	0.9793328
79	50	AgHy	0	None	633	45	0.0009037	0.9950422
80	90	AgHy	0	None	633	5	0.0024011	0.9989047
131	10	AgC	10	K_2SO_4	633	75	0.0013233	0.9959887
132	10	AgC	10	NaCl	633	75	0.0006301	0.9947151

Table S2 Cont.

Exp	% Metal	Metal	% Salt	Salt	Laser (nm)	% H_2O	RFWHM	Reproducibility
133	10	AgC	10	KNO_3	633	75	0.0019738	0.9982885
134	10	AgC	10	$MgSO_4$	633	75	0.0017023	0.9973875
136	10	AgC	10	Na_2SO_4	633	75	0.0025131	0.9954410
191	50	AuBh	6	NaCl	633	39	0.0006537	0.9992826
208	50	AgC	6	K_2SO_4	633	39	3.95E-18	0.9976212
209	50	AgC	6	NaCl	633	39	0.0016528	0.9661757
210	50	AgC	6	KNO_3	633	39	0.002025	0.9985192
211	50	AgC	6	$MgSO_4$	633	39	0.0027389	0.9994082
212	50	AgC	6	KCl	633	39	0.0013133	0.9821819
213	50	AgC	6	Na_2SO_4	633	39	0.0027377	0.9967578
268	90	AuBh	2	K_2SO_4	633	3	0.0015259	0.9990636
269	90	AuBh	2	NaCl	633	3	0.001998	0.9992729
270	90	AuBh	2	KNO_3	633	3	0.0017399	0.9989720
272	90	AuBh	2	KCl	633	3	0.0028638	0.9982551
273	90	AuBh	2	Na_2SO_4	633	3	0.0018061	0.9972161
275	90	AuC	2	NaCl	633	3	0.0015351	0.9988953
286	90	AgC	2	K_2SO_4	633	3	0.0020746	0.9989955
287	90	AgC	2	NaCl	633	3	0.000854	0.9620250
289	90	AgC	2	$MgSO_4$	633	3	0.0027859	0.9976735
290	90	AgC	2	KCl	633	3	0.0021716	0.9283899
291	90	AgC	2	Na_2SO_4	633	3	0.0039751	0.9973721
15	70	AgC	1	$MgSO_4$	785	24	0.0040283	0.9987636
23	70	AgHy	1	NaCl	785	24	0.0027722	0.9981028
47	70	AuC	1	$MgSO_4$	785	24	0.0054693	0.9903152
82	50	AuBh	0	None	785	45	0.0030403	0.9978472
83	90	AuBh	0	None	785	5	0.0039033	0.9989428
84	10	AuC	0	None	785	85	0.011085	0.9975688
85	50	AuC	0	None	785	45	0.0124174	0.9938986
86	90	AuC	0	None	785	5	0.005997	0.9991184
90	10	AgC	0	None	785	85	0.0021603	0.9988131
91	50	AgC	0	None	785	45	0.0006998	0.9985796
92	90	AgC	0	None	785	5	0.0002102	0.9997584
94	50	AgHy	0	None	785	45	0.0014439	0.7818621
95	90	AgHy	0	None	785	5	0.004342	0.9976340
155	10	AgC	10	$MgSO_4$	785	75	0.0022852	0.9966401
156	10	AgC	10	Na_2SO_4	785	75	0.0029586	0.9975039
227	50	AuC	6	NaCl	785	39	0.0100046	0.9996431
229	50	AuC	6	$MgSO_4$	785	39	0.006205	0.9987377
231	50	AuC	6	Na_2SO_4	785	39	0.0082573	0.9958329
241	50	AgC	6	$MgSO_4$	785	39	0.0023579	0.9963398
243	50	AgC	6	Na_2SO_4	785	39	0.0092114	0.9968489
245	50	AgHy	6	NaCl	785	39	0.0056831	0.9996215
249	50	AgHy	6	Na_2SO_4	785	39	0.0019541	0.9998693
298	90	AuBh	2	NaCl	785	3	0.0046969	0.9988741
299	90	AuBh	2	$MgSO_4$	785	3	0.0034221	0.9977913
300	90	AuBh	2	KCl	785	3	0.0043057	0.9965541
301	90	AuC	2	K_2SO_4	785	3	0.0038606	0.8921341
302	90	AuC	2	KNO_3	785	3	0.0051249	0.9948551
303	90	AuC	2	KCl	785	3	0.0104188	0.9976928
304	90	AuC	2	Na_2SO_4	785	3	0.0068583	0.9896388
309	90	AgC	2	NaCl	785	3	0.0060909	0.9995025

Table S2 Cont.

Exp	% Metal	Metal	% Salt	Salt	Laser (nm)	% H_2O	RFWHM	Reproducibility
311	90	AgC	2	KCl	785	3	0.0053014	0.9985426
312	90	AgHy	2	K_2SO_4	785	3	0.0058521	0.9988292
313	90	AgHy	2	KNO_3	785	3	0.0045641	0.9942991
314	90	AgHy	2	MgSO4	785	3	0.0005421	0.9998828
315	90	AgHy	2	Na_2SO_4	785	3	0.009227	0.9998469

AgHy, Hydroxylamine reduction of $AgNO_3$; AgC, Citrate reduction of $AgNO_3$; AgBh, Borohydride reduction of $AgNO_3$; AuC, Citrate reduction of $HAuCl_4$; AuBh, Borohydride reduction of $HAuCl_4$

Table S3: Second generation experimental conditions. The analyte concentration was fixed at 50µL 8.79 x 10^{-4}.

% Metal	Metal*	% Salt	Salt	Laser (nm)	% H_2O
90	AgHy	2	KCl	785	3
50	AuC	2	KCl	785	43
50	AgHy	2	Na_2SO_4	785	43
50	AuC	2	NaCl	785	43
50	AuC	2	Na_2SO_4	785	43
90	AuC	2	NaCl	785	3
50	AuC	6	KCl	785	39
50	AgHy	6	KCl	785	39

*AgHy, hydroxylamine reduction of $AgNO_3$;
AuC, citrate reduction of $HAuCl_4$

Table S4: Experimental conditions for the solutions observed on the Pareto front.

Exp. No.	% Metal	Metal type*	% Salt	Salt	Laser (nm)	% H_2O	RFWHM	Reproducibility
249	50	Aghy	6	Na_2SO_4	785	39	0.001514	0.999869
303	90	AuC	2	KCl	785	3	0.011416	0.997693
304	90	AuC	2	Na_2SO_4	785	3	0.012608	0.989639
227	50	AuC	6	NaCl	785	39	0.010005	0.999643
303	90	AuC	2	KCl	785	3	0.010419	0.997693
314	90	AgHy	2	$MgSO_4$	785	3	0.000627	0.999882

*AgHy, hydroxylamine reduction of $AgNO_3$;
AuC, citrate reduction of $HAuCl_4$