

## Electronic Supplementary Information (ESI):

### Chemometric Analysis of Spectroscopic Data on Shape Evolution of Silver Nanoparticles Induced by Hydrogen Peroxide

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To demonstrate the capability of the proposed method to return correct values of component fractions, an additional experiment was performed by mixing the pure component synthesized at mole ratio of H<sub>2</sub>O<sub>2</sub>/Ag being equal 0 (Ag nanospheres) and 35 (Ag nanoplates). Characteristic LSPR bands show up presented at 400 and 575 nm for pure Ag nanospheres and Ag nanoplates, respectively. A single plasmon band reveals that the components were prepared with the high purity (Fig. S1A).

The different mole fractions of the two pure components are adjusted for 21 ratios with the interval ratio of 0.05. The extinction intensity at 400 and 575 nm are directly related to the mole fractions of Ag nanospheres:Ag nanoplates. At higher mole ratio of Ag nanoplates, the intensity in extinction spectra of Ag nanospheres decreases, while the extinction intensity of Ag nanoplates increases, and vice versa (Fig. S1B).

In MCR-ALS calculation, the factor analysis and error indicator function were performed to determine the number of main components in the data matrix as shown in Table S1.

**Table S1** Factor analysis and error indicator functions on the UV-visible spectral data matrix.

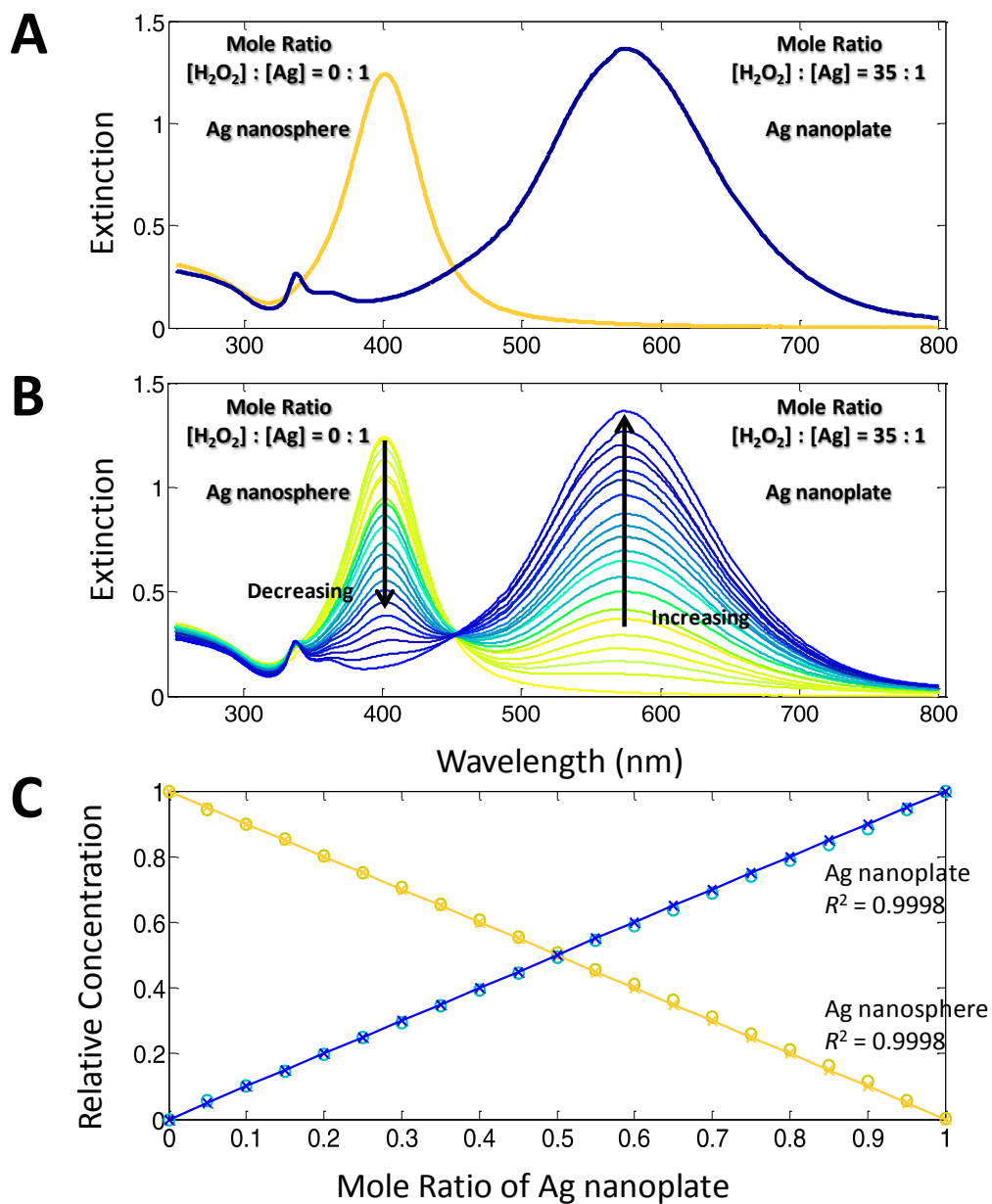
Factor	EV <sup>a</sup>	Log EV <sup>b</sup>	EVR <sup>c</sup>	RSS <sup>d</sup>	RSD <sup>e</sup>	RPV <sup>f</sup>
1	5745.55	3.76		992.44	0.1716	14.64
2	982.19	2.99	0.17	10.24	0.0101	0.33
3	1.17	0.07	0.00	9.07	0.0008	63.88
4	0.85	-0.07	0.72	8.23	0.0007	59.19
5	0.38	-0.42	0.45	7.85	0.0006	68.99

<sup>a</sup> Eigenvalue, <sup>b</sup> Logarithm of Eigenvalue, <sup>c</sup> Ratio of the *i*th eigenvalue, <sup>d</sup> Residual sum of square, <sup>e</sup> Residual standard deviation, <sup>f</sup> Residual percent variance

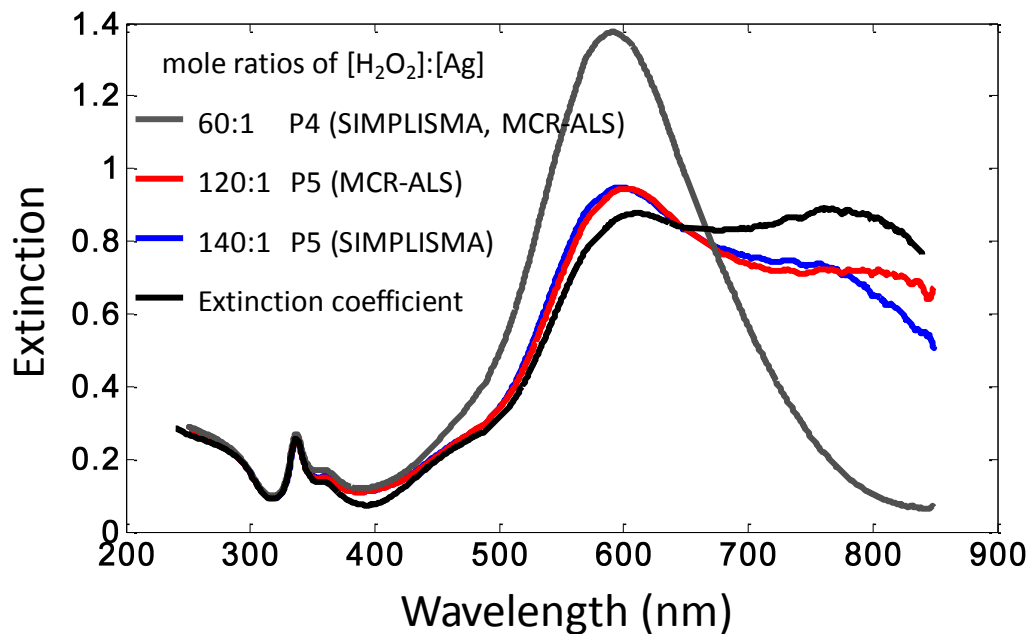
The number of significant component in the data matrix will be indicated by yellow labels in the table. From Table 1, the two components is significantly determined by finding the break of statistical value (EV, EVR, and RSD), the point will be flatted (RSS), and the optimum point with the minimum error (RPV). Only Log EV give the different answer (= 3 components). However, the majority reported that only 2 significant components correspond to the systematic

variance in the data matrix. It is in good agreement with the presetting species corresponding to Ag nanosphere and nanoplate in the experiment.

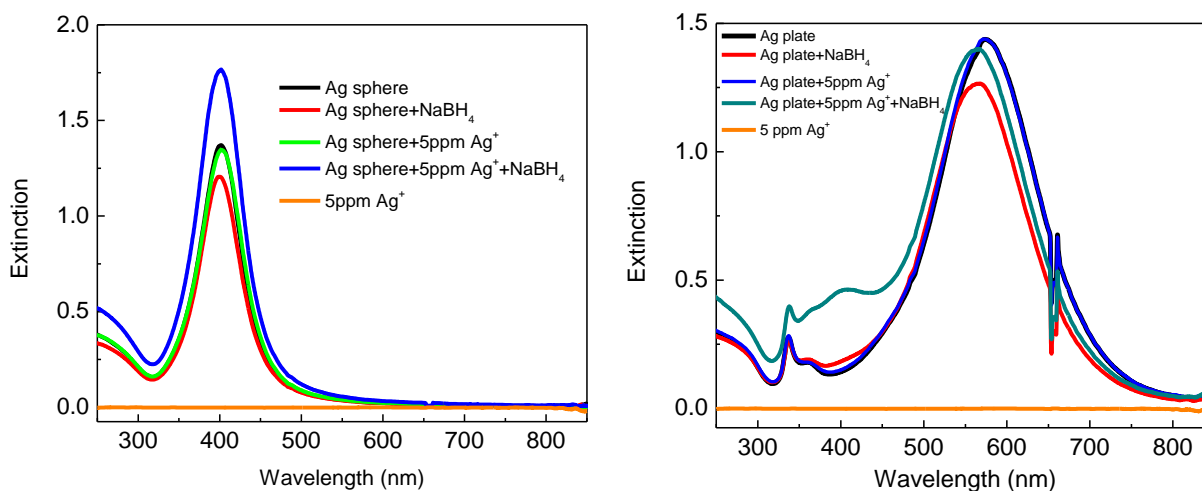
After the number of major component was determined, SIMPLISMA was performed in order to obtain an initial estimation of the concentration profile and pure spectra of the detected component as a function of the mole ratio of Ag nanoplate. The initial purest spectra of Ag nanosphere and nanoplate are the spectrum at the mole ratio of Ag nanoplate equal to 0 (the purest Ag nanosphere) and 1 (purest Ag nanoplate), respectively as identical to Fig S1A. In MCR-ALS calculation, the non-negative constraint (NNLS) to control the output with only positive values and closure constraint to control the total overall mass equal to 1 (the purest fraction ratio) were applied in the calculation. The resolved concentration profiles of the 2 major components are shown in Fig. S1C. The predicted concentrations of each component are perfectly fitted with the presetting concentration with  $r^2 = 0.998$  for both Ag nanospheres and Ag nanoplates. This shows that our proposed technique with the appropriate constraints can return correct values of component fractions in analysis of the mixtures.



**Fig. S1** (A) Extinction spectra of the pure component synthesized at mole ratio of  $H_2O_2/Ag$  being equal 0 and 35 corresponding to the Ag nanospheres and Ag nanoplates, respectively. (B) Extinction spectra of colloids with different mole fractions of the Ag nanospheres:Ag nanoplates. (C) The resolved concentration profiles of the components represented by circle (o) compared with the presetting concentration value represented by solid line (-).



**Fig. S2** The UV-visible spectra of colloids with the mole ratio of  $[\text{H}_2\text{O}_2]:[\text{Ag}]$  at 140 and 120 for component P5 selected by SIMPLISMA and MCR-ALS calculation, respectively, compared to the calculated extinction spectra of component P5.



**Fig. S3** Extinction spectra of the Ag sphere and Ag plate conversion by the addition of a reducing agent (NaBH<sub>4</sub>)

The complete conversion (unity Ag nanoparticles) was proven by the addition of a reducing agent (NaBH<sub>4</sub>) into Ag colloids. Two colloids (initial Ag nanosphere colloid and one of Ag nanoplate colloids) were chosen to demonstrate this situation. If Ag<sup>+</sup> ion remains in the colloids, the intensity in extinction spectra (at 400 nm) will increase. In Fig. S3, only small blueshift with a little decrease in the intensity can be observed after the addition of NaBH<sub>4</sub> in both Ag nanospheres and Ag nanoplates, which can be explained by the aggregation/deaggregation of Ag nanoparticles due to the electrical stabilization of BH<sub>4</sub><sup>-</sup> [ref. 1]. Any increase in the intensity cannot be noticed. Furthermore, the colloids with existing Ag ions were simulated by adding small amount of Ag<sup>+</sup> (5 ppm) into the original one. Then, the Ag<sup>+</sup>-added colloids were added by NaBH<sub>4</sub>. It is noticed that the absorption of small amount (5 ppm) of Ag<sup>+</sup> in UV–visible region cannot be detected. The results show an increase in the intensity at ~400 nm in spectra of both cases (Ag nanospheres and Ag nanoplates), which indicates the generation of new Ag nanospheres. From these results, we believe that the unity nanoparticle yield in our procedures is demonstrated at the measurement time.

**Ref 1:** Solomon S.D., Bahadory M., Jeyarajasingam A.V., Rutkowsky S.A., and Boritz C., *Journal of Chemical Education*, 2007, **84**, 322-325.

The rank analysis methods evolving Eigenvalue (EV), Logarithm of Eigenvalue (Log EV), Ratio of the *i*th eigenvalue (EVR), Residual sum of square (RSS), Residual standard deviation (RSD) and Residual percent variance (RPV) are performed on the added noise data matrices with noise level at 0.1%, 1%, 2% and 5%, respectively. The number of significant components is determined by finding the break of statistical value (for EV, Log EV, EVR, RSD) or the point will be flatted (for RSS), while for RPV, it is determined by the optimum point that gives the minimum error. The obtained results are shown in Table S2.1 –S2.4 below. The number of significant component in the data matrix will be indicated by yellow labels in the table, while no label refers to the uncertain answer.

**Table S2.1** Rank analysis methods on the added noise matrix with **0.1% noise level**

Factor	EV	Log EV	EVR	RSS	RSD	RPV
1	16856.29	4.23		2573.72	0.2069	13.20
2	1421.20	3.15	0.08	1152.52	0.1382	44.54
3	925.91	2.97	0.65	226.61	0.0601	18.89
4	166.16	2.22	0.18	60.45	0.0288	22.93
5	48.21	1.68	0.29	12.25	0.0145	2.48
6	0.89	-0.05	0.02	11.36	0.0002	27.31
7	0.15	-0.83	0.17	11.21	0.0002	55.51

**Table S2.2** Rank analysis methods on the added noise matrix with **1% noise level**

Factor	EV	Log EV	EVR	RSS	RSD	RPV
1	16863.64	4.23		2588.46	0.2071	13.21
2	1423.56	3.15	0.08	1164.91	0.1383	44.55
3	925.23	2.97	0.65	239.68	0.0604	19.09
4	167.37	2.22	0.18	72.31	0.0292	23.32
5	48.51	1.69	0.29	23.79	0.0163	4.68
6	0.92	-0.03	0.02	22.87	0.0005	61.19
7	0.19	-0.72	0.20	22.68	0.0005	87.04

**Table S2.3** Rank analysis methods on the added noise matrix with **2% noise level**

Factor	EV	Log EV	EVR	RSS	RSD	RPV
1	16861.06	4.23		2623.76	0.2073	13.23
2	1417.81	3.15	0.08	1205.95	0.1388	44.84
3	928.81	2.97	0.66	277.14	0.0612	19.41
4	167.98	2.23	0.18	109.16	0.0305	24.91
5	49.80	1.70	0.30	59.36	0.0100	10.65
6	1.07	0.03	0.02	58.28	0.0009	81.90
7	0.32	-0.49	0.30	57.96	0.0009	93.38

**Table S2.4** Rank analysis methods on the added noise matrix with **5% noise level**

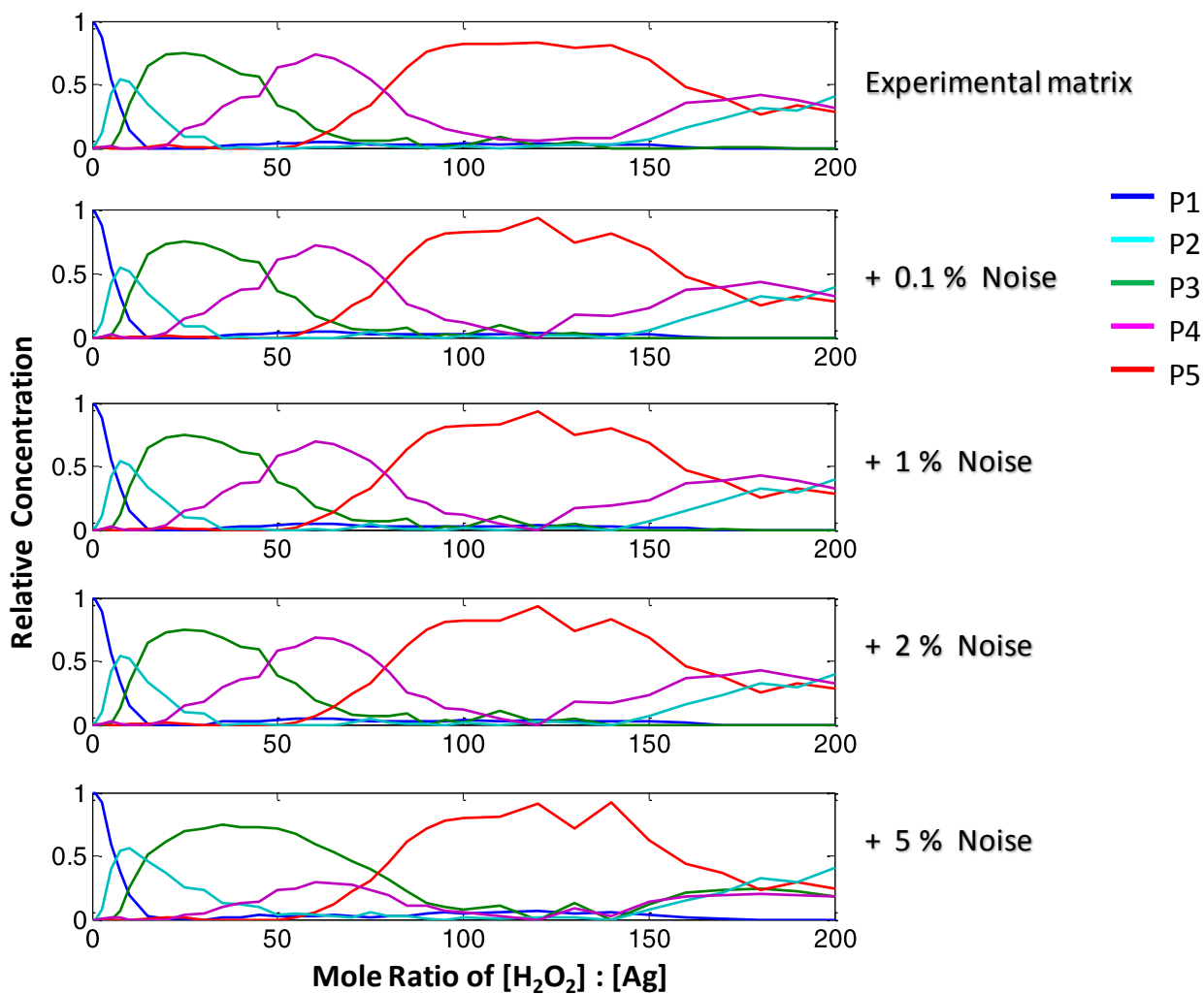
Factor	EV	Log EV	EVR	RSS	RSD	RPV
1	16869.70	4.23		2917.71	0.2102	13.55
2	1438.55	3.16	0.09	1479.15	0.1419	45.58
3	937.31	2.97	0.65	541.84	0.0669	12.21
4	178.04	2.25	0.19	363.80	0.0387	33.47
5	59.08	1.77	0.33	304.72	0.0226	34.03
6	1.98	0.30	0.03	302.73	0.0219	93.49
7	1.30	0.12	0.66	301.43	0.0214	95.42

The added noises will be affected to the systematic variance, especially for the later significant components in the data matrix. Therefore, the majority reported statistical data suggests that there are 5 major components for the data matrix with added noise  $\leq 2\%$ , while there is uncertain answer for the data matrix with 5% added noise (it can be either 3, 4, or 5 from the rank analysis). However, 5 major components are selected for the consistency data analysis in the further steps.

After the rank analysis, SIMPLISMA was performed in order to obtain an initial estimation of pure spectra of the detected components. In case of the data matrix with added noise  $\leq 2\%$ , the initial purest spectra of each specie obtained from SIMPLISMA is identical to that obtained from the original data matrix (the spectrum at the ratios  $[\text{H}_2\text{O}_2]:[\text{Ag}]$  of 0:1, 7.5:1, 25:1, 60:1, and 140:1, respectively.). On the other hand, the initial pure spectra obtained from the data matrix with and without 5% noise are different (for 5% added noise matrix, the initial pure spectra are selected at the ratios  $[\text{H}_2\text{O}_2]:[\text{Ag}]$  of 0:1, 1:1, 5:1, 20:1, and 140:1, respectively). In MCR-ALS calculation, the number of significant component was set to 5. The non-negative constraint (NNLS) to control the output with only positive values and closure constraint to



control the total overall mass equal to 1 (relative value) were applied in the MCR-ALS calculation. The resolved concentration profiles of the 5 major components are shown in Fig. S4.



**Fig. S4** The resolved concentration profiles of each component (P1-P5) by MCR-ALS calculation on the experimental matrix, matrices with the additional noise levels of 0.1, 1, 2, and 5%.