Study on the Particle Characteristics and Stability of Ag-NPs Naturally Generated in Soil Matrix

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This document contains: 8 pages, 1 text, 5 figures and 6 tables.

Text S1. Steps of the iterative algorithm for data processing

The steps of iterative algorithm were outlined as follows: the standard deviation (σ) and mean value (μ) of total raw dataset were calculated and the outliers which exceeding the value of (μ + 5σ) were removed. Subsequently, μ and σ of the remaining fraction were recalculated and the procedure was repeated until no dataset could be removed, that was, convergence was achieved. Then iteration process end and the background signals were identified in this way. The particle events were identified and their intensities were recorded in succession. All target particles detected were assumed to be spherical and zero-valent for each event. The nanoparticle number concentration N_{NP}, particle mass m_{NP} and nanoparticle diameter d_{NP} could be calculated as described in equation (1), (3) and (4), respectively.

$$f_{NP} = N_{NP} Q_{sam} \eta_n \qquad (1)$$

$$W = \eta_n Q_{sam} t_{dwell} C \qquad (2)$$

$$m_{NP} = f_m^{-1}\left[\frac{\left(I_{NP} - I_{bgd}\right) * \eta_i}{m}\right] \qquad (3)$$

$$d_{NP} = \sqrt[3]{\frac{6m_{NP}}{\pi\rho}} \qquad (4)$$

Where, f_{NP} is frequency of pulse events (pulse per event), Q_{sam} is the sample flow rate (mL·min^{-1}), η_n is transport efficiency, W is the mass flux equation (mass per event), t_{dwell} is the dwell time (ms per event), C is analytical element of ionic calibration curve equation, I_{NP} is nanoparticle signal intensity (cps), I_{bgd} is background signal intensity (cps), f_m is the mass fraction of analytical element, η_i is the particle ionization efficiency, m is the slope of the calibration curve for the dissolved ion (cps·μg^{-1}·L), ε_{neb} is the nebulization efficiency, and ρ is the particle density (g·cm^{-3}). Background signal includes instrument noise and signal from dissolved metal ions.

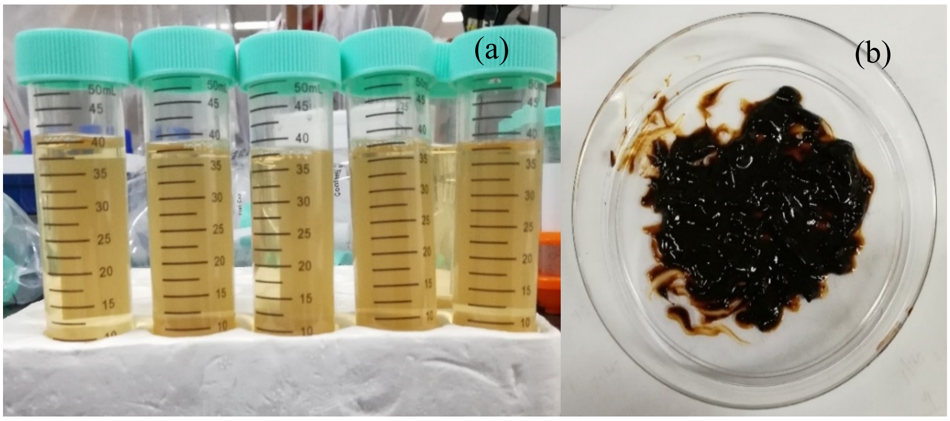

Figure S1. (a) Fulvic acid and (b) humus extracted from the environmental soil.

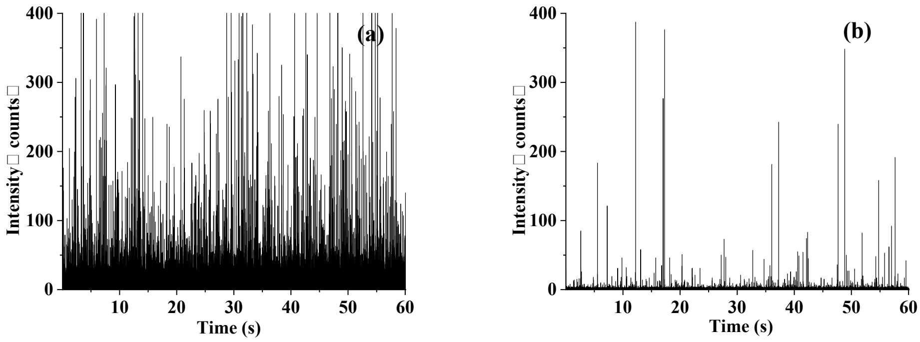

Figure S2. Time scans of Ag-NPs (a) with (b) without cloud point extraction.

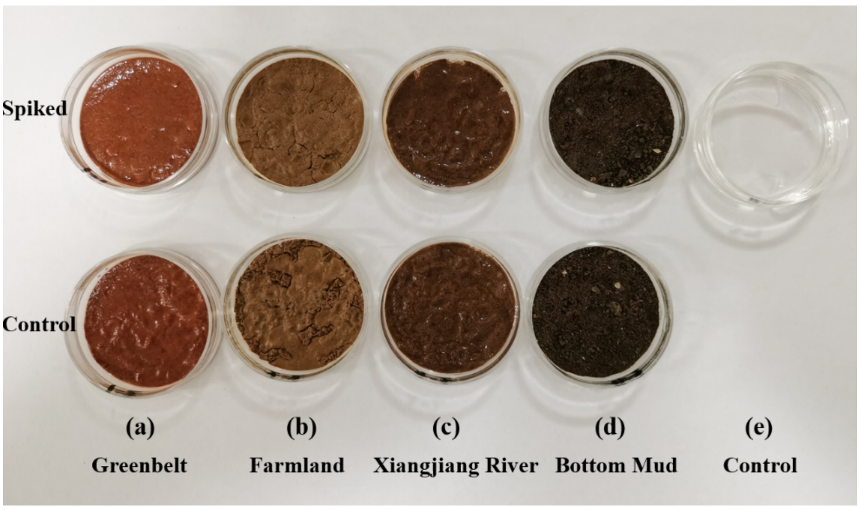

Figure S3. Visual observation of the generation of Ag-NPs in (a) Greenbelt, (b) Farmland, (c) Xiangjiang River, (d) Bottom Mud and (e) Control group.

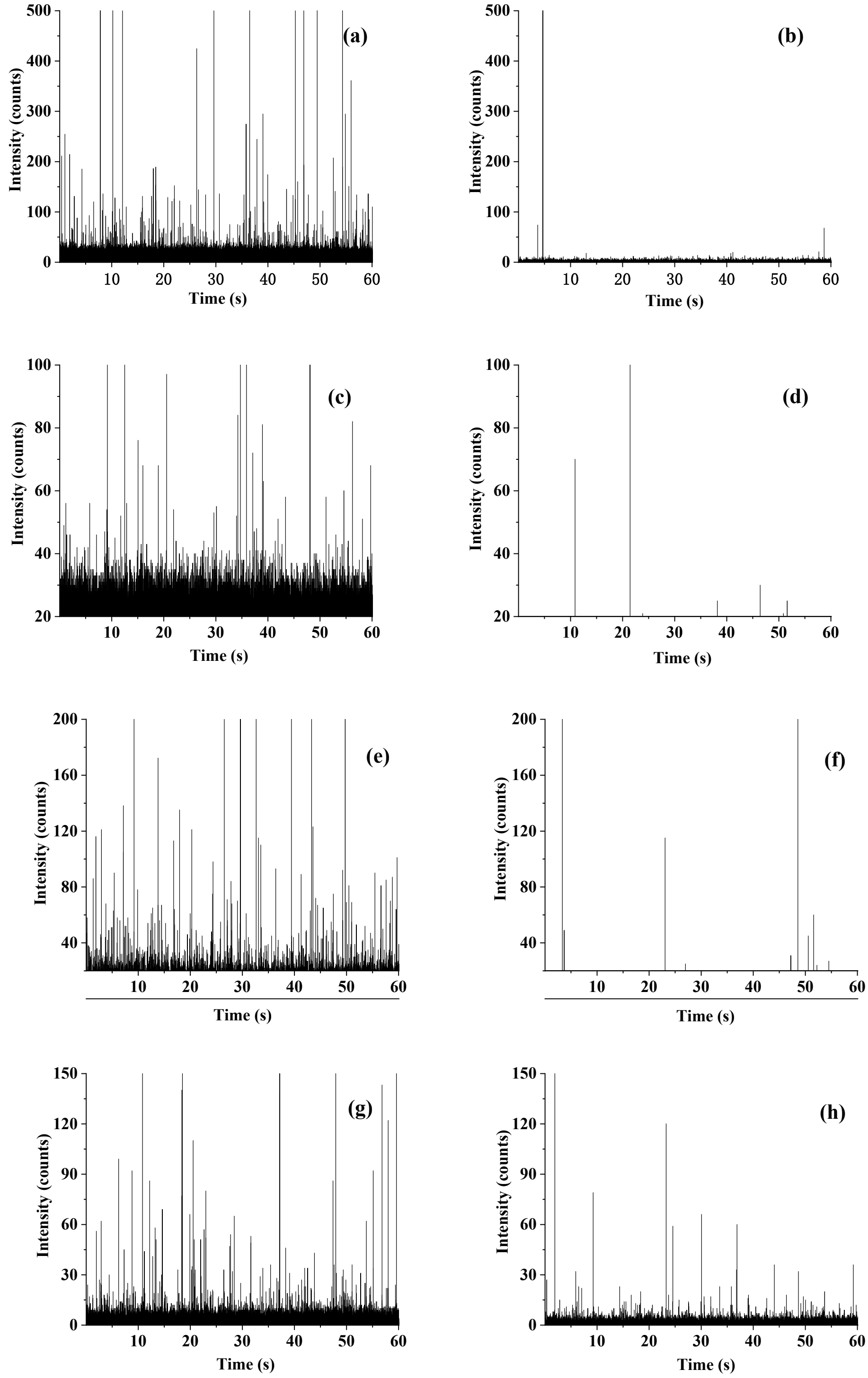

Figure S4. Time scans of Ag-NPs generated in Greenbelt (a) with (b) without, Farmland (c) with, (d) without, Xiangjiang River (e) with, (f) without, Bottom Mud (g) with and (h) without Ag^{+} added, respectively ($1.6 * 10^{4}$ times diluted).

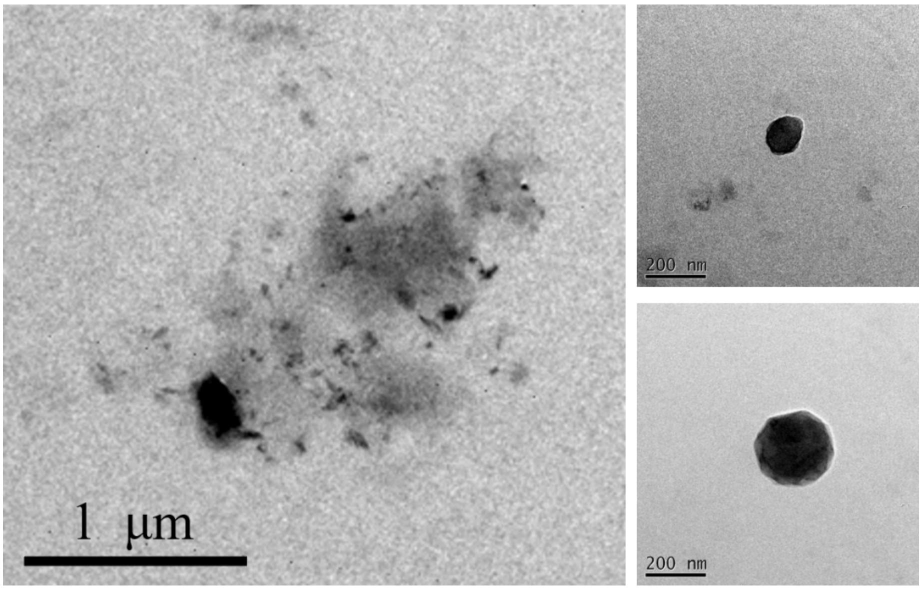

Figure S5. TEM images of the Ag-NPs generated in the soil.

Table S1. Basic physical and chemical properties of soil samples

Sample	pH (KCl)	Conductivity（μS cm^{-1}）	Ionic strength（mM）	Organic matter（%）	Ag concentration（mg kg^{-1}）
Greenbelt	7.13	315.0	4.0950	3.3791	0.0177
Farmland	6.43	158.2	2.0566	6.1909	0.0143
Xiangjiang River	7.41	107.3	1.3949	3.1963	0.0530
Bottom Mud	6.81	160.5	2.0865	12.7893	0.0128

Table S2. Operational Parameters for SP-ICP-MS Analysis

Instrumental parameters	Parameter values
RF power	1550
Plasma gas flow rate (L min^{-1})	15
Sample flow rate (mL min^{-1})	0.36
Spray chamber temperature (°C)	2
Data acquisition mode	TRA
Dwell time (ms)	3
Acquisition time (s)	60
Mass monitored	^{107}Ag

Table S3. Particle number concentration and size of Ag-NPs determined in the soil

Sample	Spiked sample			Control sample		
	Particle number concentration		Particle size(nm)	Particle number concentration		Particle size(nm)
	10^6 particles L^{-1}	10^6 particles g^{-1} soil		10^6 particles L^{-1}	10^6 particles g^{-1} soil	
Greenbelt	0.60	4.80	65	0.19	1.52	37
Farmland	0.09	0.72	50	0.22	1.76	30
Xiangjiang River	0.46	3.68	51	0.27	2.16	35
Bottom Mud	0.51	4.08	45	0.35	2.80	32

Table S4. Particle number concentration and average size of Ag-NPs

Sample	Particle number concentration (10^6 particles L^{-1})	Particle size (nm)
Control	0.23 ±0.17	37.94±3.01
Ag^+	1.43 ±0.13	41.55±3.77
Ag-NPs	4.33 ±0.41	32.26±2.20
Ag^+ and Ag-NPs	4.90 ±0.14	33.97±3.47

Table S5. The influence of illumination on the generation of Ag-NPs

<table>
<tr><th>Illumination intensity (μmol $m^{-2}\cdot s^{-1}$)</th><th>Illumination time (h)</th><th>Particle number concentration (10^6 particles L^{-1})</th><th>Particle size (nm)</th></tr>
<tr><td colspan="4">Illumination intensity</td></tr>
<tr><td>0</td><td rowspan="6">10</td><td>0.38±0.09</td><td>57.60±4.21</td></tr>
<tr><td>100</td><td>0.85±0.13</td><td>63.63±4.63</td></tr>
<tr><td>200</td><td>2.20±1.13</td><td>88.87±1.93</td></tr>
<tr><td>300</td><td>2.46±0.63</td><td>78.93±4.40</td></tr>
<tr><td>400</td><td>3.10±1.08</td><td>79.94±2.41</td></tr>
<tr><td>500</td><td>4.50±1.27</td><td>79.63±1.70</td></tr>
<tr><td colspan="4">Illumination time</td></tr>
<tr><td rowspan="6">300</td><td>0</td><td>0.24±0.03</td><td>61.55±1.08</td></tr>
<tr><td>5</td><td>0.86±0.12</td><td>72.29±0.35</td></tr>
<tr><td>10</td><td>5.50±1.27</td><td>81.65±3.09</td></tr>
<tr><td>24</td><td>5.83±0.78</td><td>80.95±3.14</td></tr>
<tr><td>48</td><td>6.63±0.55</td><td>78.44±1.10</td></tr>
<tr><td>72</td><td>6.50±0.76</td><td>82.14±1.36</td></tr>
</table>

Table S6. The influence of humic acid on the generation of Ag-NPs

Fulvic Acid (mg L^{-1})	Humus (mg g^{-1})	Particle number concentration (10^7 particles L^{-1})	Particle size (nm)
	Fulvic Acid		
0		0.43±0.09	33.38±2.09
1		0.81±0.16	35.15±3.31
2	/	1.02±0.13	45.96±1.29
5		5.80±1.25	79.06±1.41
10		7.43±0.64	80.16±1.19
20		6.16±1.36	76.67±4.43
	Humus		
	0.00	0.24±0.05	67.58±2.78
	0.01	1.61±0.19	45.02±1.81
	0.02	3.05±0.07	44.73±1.00
/	0.05	3.10±0.28	60.09±5.26
	0.10	2.54±0.21	46.73±4.61
	0.15	2.33±0.21	42.08±6.54