Supporting information

Transformation of Ag ions to Ag nanoparticles-loaded AgCl microcubes in the plant root zone

Huiyuan Guo,[†] Chuanxin Ma,[§] Lauren Thistle,[†] My Huynh,[†] Chenghao Yu,[†] Dan Clasby,[#] Benny Chefetz,[‖] Tamara Polubesova,[‖] Jason C. White,[§] Lili He,[‡,] Baoshan Xing[†,*]*

† Stockbridge School of Agriculture, University of Massachusetts, Amherst, MA 01003, USA

‡ Department of Food Science, University of Massachusetts, Amherst, MA 01003, USA

§ Department of Analytical Chemistry, The Connecticut Agricultural Experiment Station, New Haven, CT 06511, USA

Civil and Environmental Engineering, University of Massachusetts, Amherst, MA 01003, USA

‖ Department of Soil and Water Sciences, Hebrew University of Jerusalem, Rehovot 76100, Israel

*Corresponding Authors

Dr. Baoshan Xing, Tel.: +1 413 545 5212; Fax: +1 413 577 0242; E-mail: bx@umass.edu

Dr. Lili He, Tel.: +1 413 545 5847; Fax: +1 413 545 1262; E-mail: lilihe@foodsci.umass.edu

Methods

Section 1. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) analysis

The particle suspension was placed on a silicon wafer and dried in a dark laminar flow hood. In order to minimize the charging interference and acquire high resolution images, a thin layer of gold (2-3 nm) was coated on the sample before SEM-EDS analysis.

Section 2. Raman spectroscopy and Fourier-transform infrared spectroscopy (FTIR)

For both characterization methods, the particles in 0.5 mL sample were collected after centrifugation (13,500 rpm, 30 min) and re-suspended in 30 µL of nanopure water. Prior to Raman measurements, 5 µL of particle suspension was deposited on a clean gold slide, dried in a dark laminar flow hood and analyzed by a DXR Raman Spectro-microscope (Thermo Scientific, Madison, WI). The analysis was performed with a 789 nm laser at 5 mW, a 10 × confocal microscope objective, 50 µm slit aperture, 2 s integration time, 3 µm spot diameter, and 5 cm^{-1} spectral resolution in a range of 400-3400 cm^{-1}. In addition, the formation of nAg in the samples was confirmed by using a surface-enhanced Raman spectroscopy (SERS)-based method that was previous established in our group[1] with minor revision. The approach involves using ferbam as an indicator molecule; the enhanced signals of the indicator-nAg complex can are readily detectable by SERS.[1] Briefly, ferbam (5 µL, 10 mg/L in H_2O) was placed on the top of dried particles on the gold slides. After air-drying in a dark laminar flow hood, the sample was analyzed by SERS using the same settings as described above.

The attenuated total reflectance (ATR)-FTIR spectra were obtained using Perkin-Elmer Spectrum One FTIR Spectrometer equipped with a Lithium tantalate ($LiTaO_3$) detector and a one-reflection

horizontal ATR accessory with a diamond Zn/Se crystal (Shelton, CT). Atmospheric background subtraction and baseline correction were achieved through Spectrum software. The samples (2 µL) were dropped on the small crystal (~1 cm) and air-dried. To ensure sufficient sample on the crystal, this process was repeated two additional times. Finally, the sample was analyzed for 200 scans with a resolution of 8 cm^{-1} and a scan speed of 1.0 cm/s in the range of 650-4000 cm^{-1}.

Figures

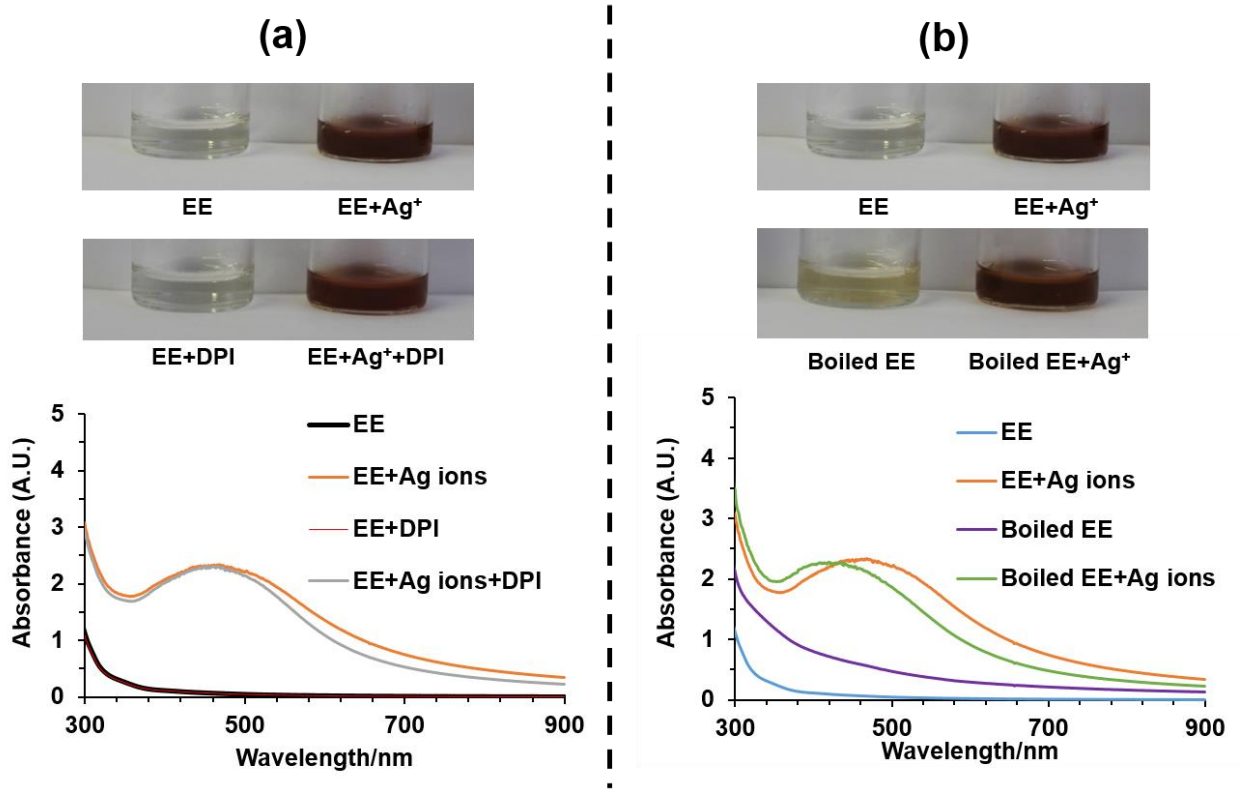


Figure S1. (a) Influence of DPI (1 µM) as a dehydrogenase inhibitor on the reduction of Ag^+ (1 mM) by the root enzyme extract (EE). (b) Formation of nAg as affected by deactivation of the root EE through boiling.

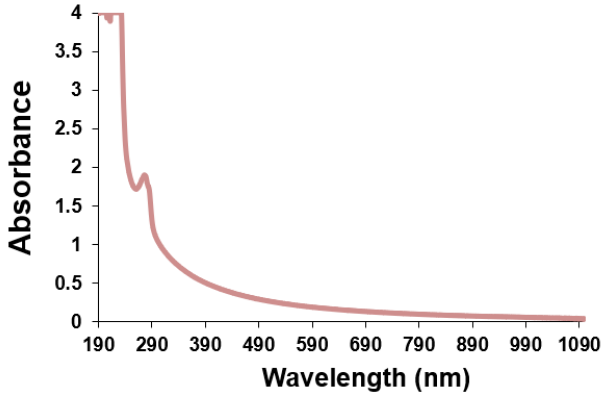


Figure S2. UV-Vis spectrum of TX-114 (1%, v/v) demonstrates an absorbance peak at 280 nm.

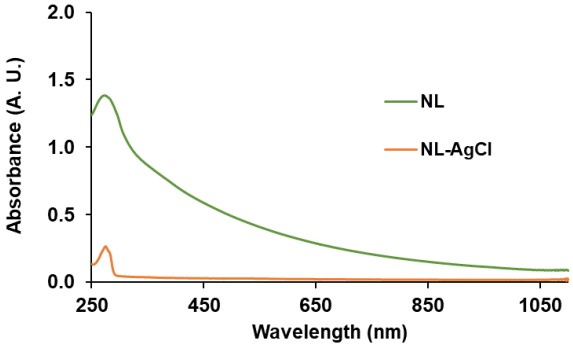


Figure S3. UV-Vis absorbance of the formed AgCl particles before (NL) and after removal of AgCl (NL-AgCl).

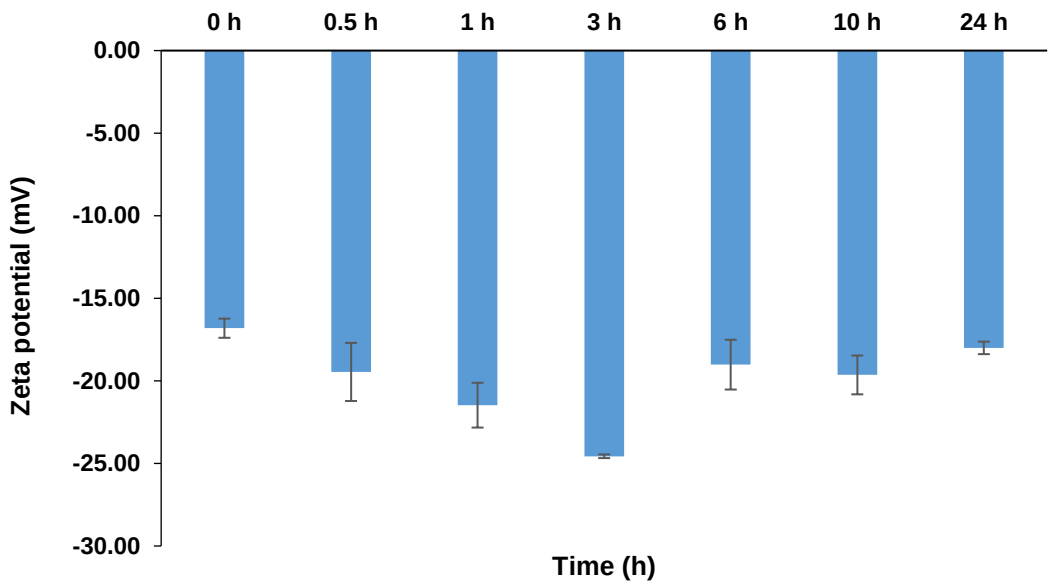
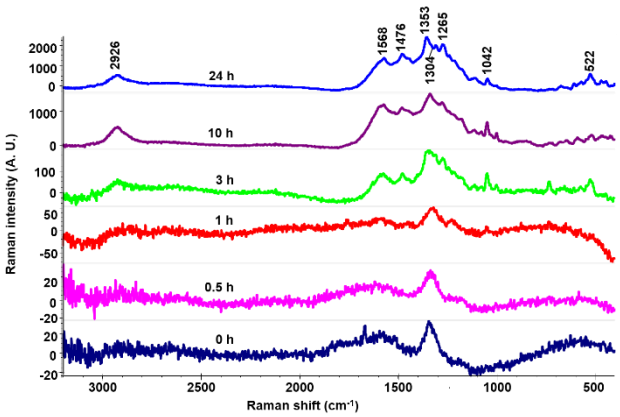
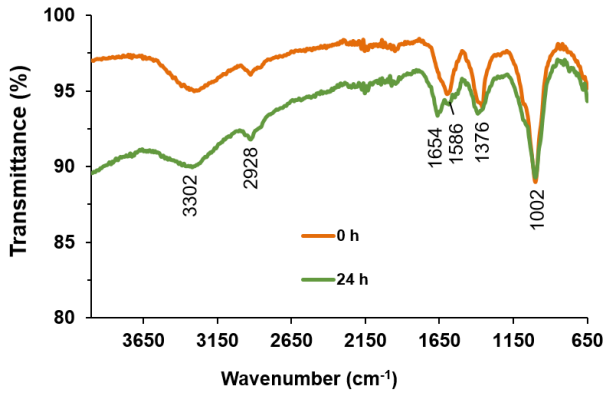


Figure S4. Zeta potential (mV) of the formed particles at different time intervals (0-24 h).



Raman peak/cm^{-1}	Intensity	Assignment*
522	m	C-C=O bending
1042	m	C-O stretching
1265	s	Imidazole ring in-phase breathing mode
1304	w	
1353	s	CH_3 bending or COO^- stretching
1476	s	C-H stretching
1568	s	COO^- stretching or NH_2 deformation
2926	s	C-H stretching in -CH_3 and -CH_2-

Figure S5. Raman spectra of the formed particles at different time points (left panel) and the main peak assignment at 24 h (right panel). *Infrared and Raman spectroscopy: principles and spectral interpretation/Peter Larkin. ISBN: 978-0-12-386984-5.



Wavenumber/cm^{-1}	Intensity	Assignment*
1002	s	C-O stretching
1376	s	CH_3 deformation or COO^- stretching
1586	w	COO^- stretching or NH_2 deformation
1654	s	C=O stretching
2928	m	C-H stretching in -CH_3 and -CH_2-
3302	s	O-H stretching

Figure S6. FTIR spectra of the formed particles at 0 h and 24 h (left panel) and the main peak assignments at 24 h (right panel) *Infrared and Raman spectroscopy: principles and spectral interpretation/Peter Larkin. ISBN: 978-0-12-386984-5.

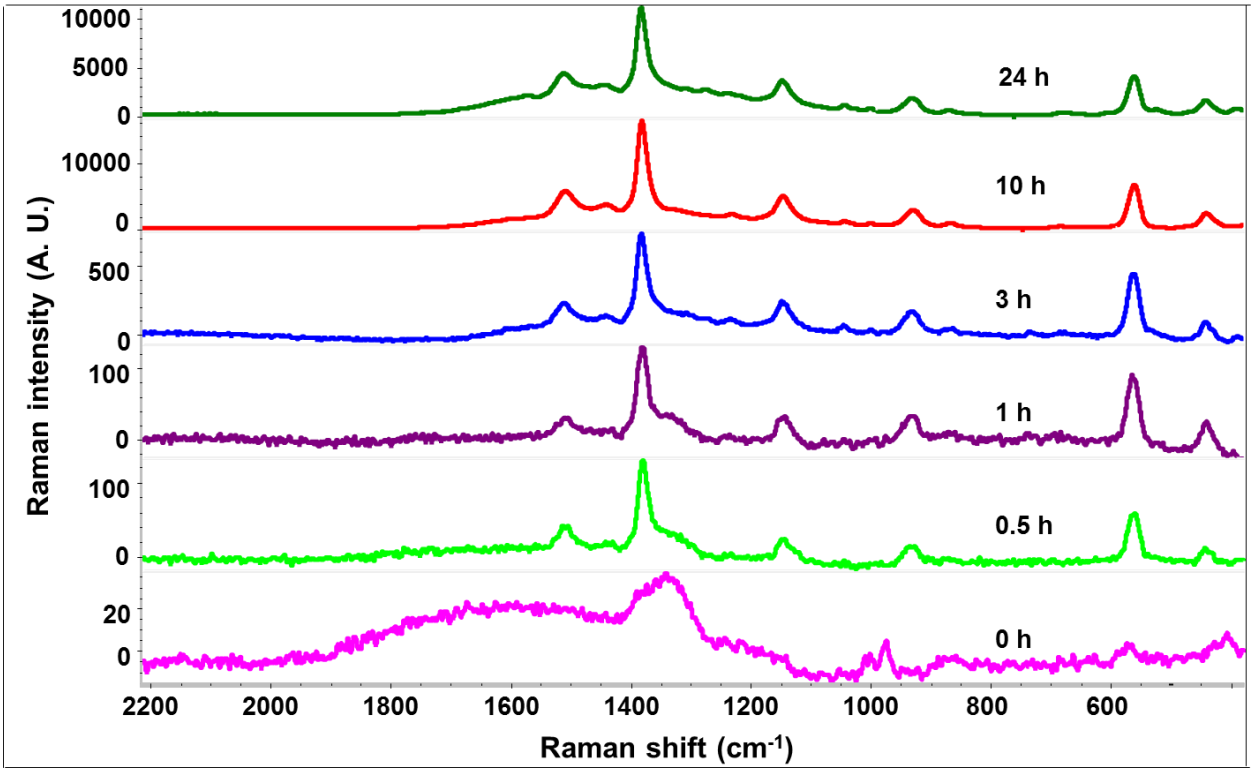


Figure S7. Surface-enhanced Raman spectroscopy (SERS) detection of the formed nAg by using ferbam (10 mg/L) as an indicator.

Rate equation:

$2AgCl \longrightarrow 2Ag + Cl_2$

$r=k[AgCl]^2$

$-d[AgCl]/dt = r = k[AgCl]^2$

$$\frac{1}{[AgCl]t}=\frac{1}{[AgCl]0}+2kt$$

$[AgCl]_t=[AgCl]_0-[Ag]_t$

$$\frac{1}{[AgCl]0-[nAg]t}=\frac{1}{[AgCl]0}+2kt$$

$k=1.11\ mM^{-1}.h^{-1}$

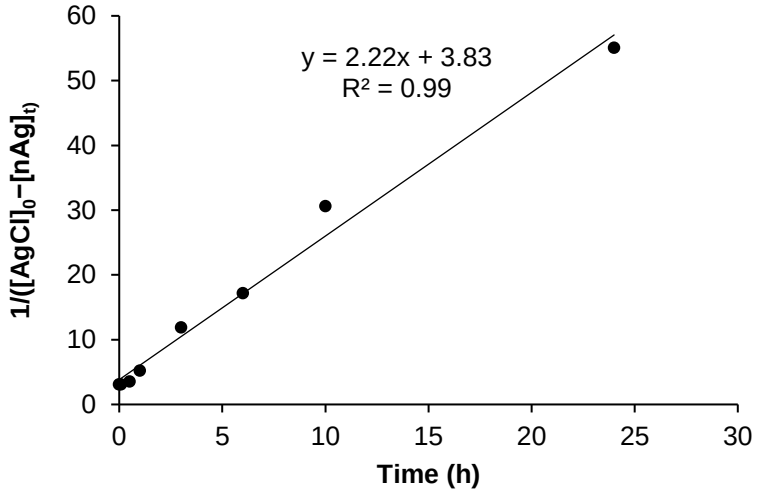
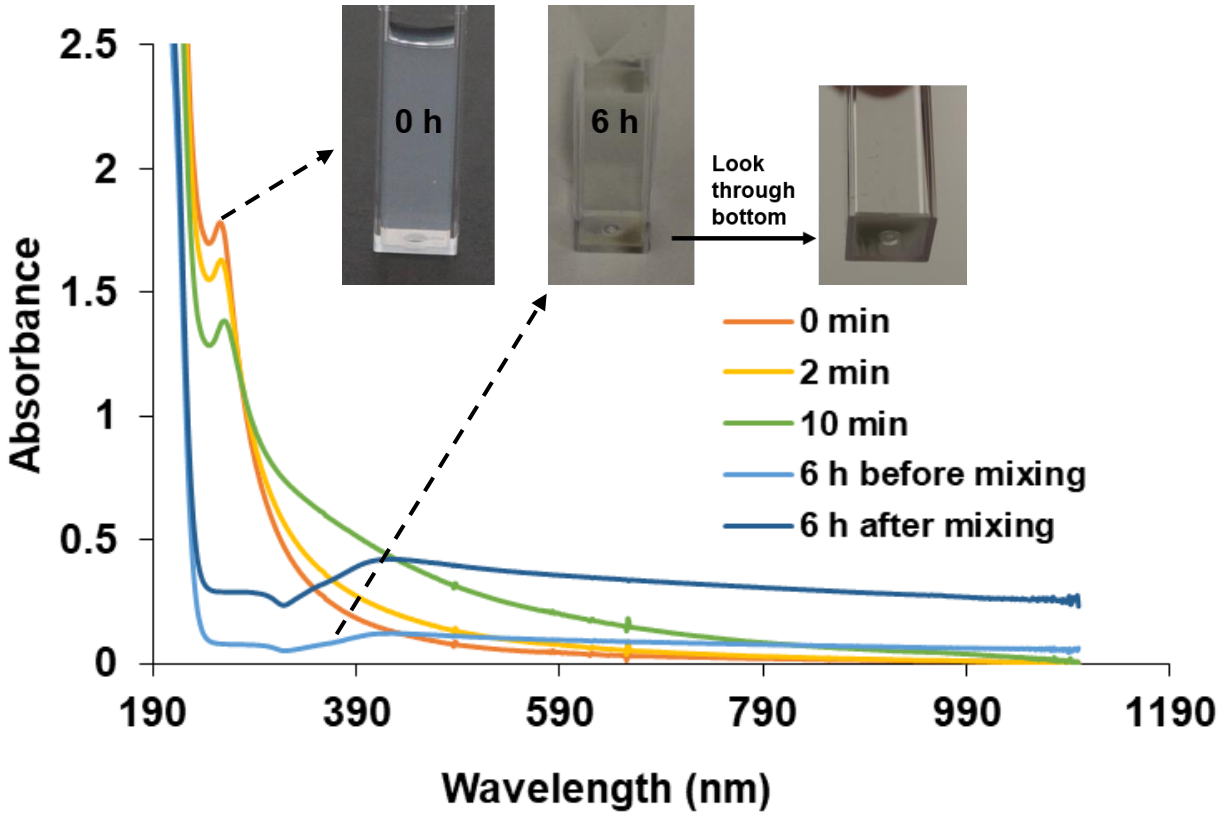


Figure S8. Plot of $1/([AgCl]_0-[nAg]_t)$ versus time illustrates that the formation of nAg followed a second order reaction.



121 Figure S9. Sunlight-induced transformation of AgCl (0-6 h) in nanopure water as shown in the

122 images and UV-Vis absorbance.

123

124

125

126

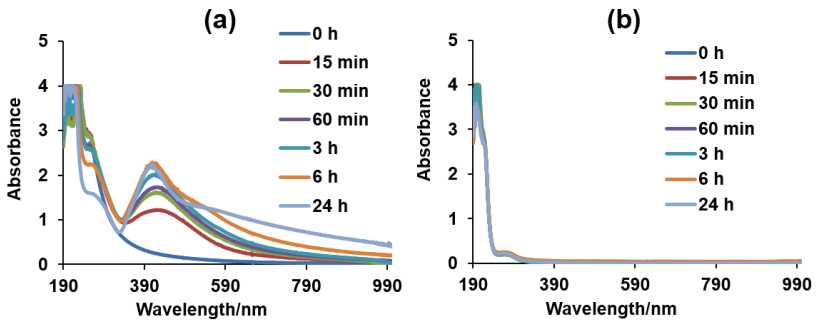


Figure S10. The transformation of Ag^+ over 24 h of light irradiation in the presence of organic molecules with (b) and without (a) removal of Cl^- in root exudates. The root exudates were collected from wheat plant roots exposed to 0.5 mM Ag^+. After root exudate collection, additional Ag^+ was added to ensure that Cl^- ions were completely transformed to AgCl and further removed by filtration through 100 kDa ultra-centrifugal filter membranes. It was noted that the small peak in (b) at around 270 nm is the common optical adsorption peak of amino acids and proteins[2,3] in root exudates and not from remaining AgCl, because it was also observed in root exudates without adding Ag^+ (Figure S11).

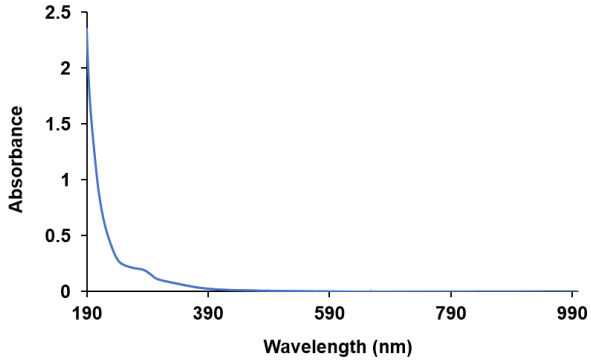


Figure S11. UV-Vis spectrum of wheat root exudates without adding Ag^+.

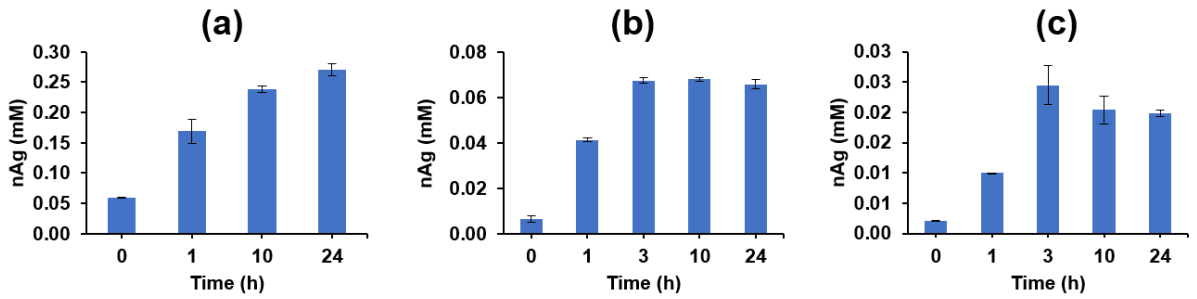


Figure S12. Formation of nAg under sunlight irradiation (0-24 h) in root exudates that were collected from live aquatic plants (*Lolium multiflorum*) treated with initial [Ag^+] of (a) 0.5 mM, (b) 0.1 mM, (c) 0.05 mM.

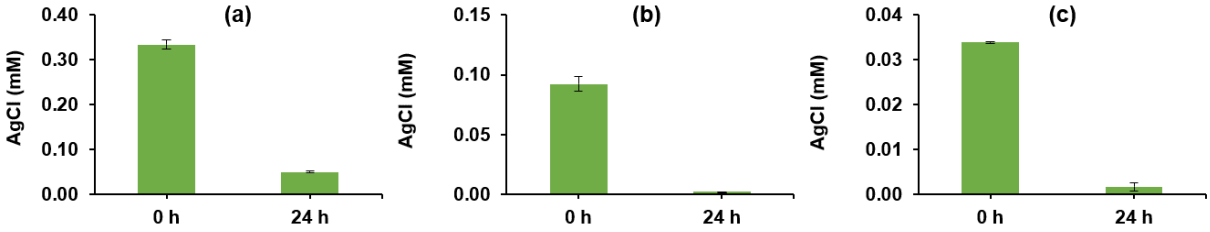


Figure S13. Photoreduction of AgCl at 0 h and 24 h of sunlight irradiation in root exudates that were collected from live aquatic plants (*Lolium multiflorum*) treated with initial [Ag^+] of (a) 0.5 mM, (b) 0.1 mM, (c) 0.05 mM.

References

1 H. Guo, Z. Zhang, B. Xing, A. Mukherjee, C. Musante, J. C. White and L. He, *Environ. Sci. Technol.*, 2015, **49**, 4317–4324.

2 A. Aitken and M. Learmonth, *Protein Determination by UV Absorption*, Humana Press, Totowa, NJ, 2009.

3 H. Nakano, N. Tamai, M. Nii, M. Tsukamoto and N. Abe, *J. Laser Micro Nanoeng.*, 2007, **2**, 100–102.

155