Supporting information

New insight into naturally formed nanosilver particles: role of plant root exudates

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Methods

Section 1. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) analysis and high-resolution TEM (HRTEM) with a selected area electron diffraction (SAED)

Before SEM-EDS analysis, the particle suspension was dried on a silicon chip in a dark laminar flow hood. The sample was coated by a thin layer of gold (2-3 nm) to minimize the charging interference and acquire high-resolution images. For HRTEM-SAED, the sample was dropped onto a lacey carbon supported copper grid and dried in a dark laminar flow hood before analysis.

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

Prior to characterization by Raman spectroscopy or FTIR, the formed particles in 0.5 mL RE were isolated by centrifugation (13,500 rpm, 30 min). After removing the supernatant, the particles were re-suspended in Milli-Q water (30 μ L). For Raman analysis, 5 μ L of particle suspension was placed on a clean silicon chip and dried in a dark laminar flow hood. The Raman measurements were performed using a DXR Raman Spectro-microscope (Thermo Scientific, Madison, WI) with a 789 nm laser at 5 mW, a 10 × confocal microscope objective, 50 μ m slit aperture, 2 s integration time, 3 μ m spot diameter, and 5 cm⁻¹ spectral resolution. In addition, ferbam was used as an indicator to confirm the formation of nAg based on a previously developed surface-enhanced Raman spectroscopy (SERS) method in our group³ with minor modification. Briefly, the particles were mixed with ferbam (5 μ L, 10 mg/L in H₂O) on the gold slides and detected by SERS using the same settings as described above.

The attenuated total reflectance (ATR)-FTIR spectra of the formed particles were detected using Perkin-Elmer Spectrum One FTIR Spectrometer equipped with a Lithium tantalate (LiTaO₃) detector and a one-reflection horizontal ATR accessory with a diamond Zn/Se crystal (Shelton, CT). Prior to analyzing the samples, baseline was corrected with atmospheric background subtraction through Spectrum software. The spectra were collected with a resolution of 8 cm⁻¹, a scan speed of 1.0 cm/s and totally 200 scans in the range of 650-4000 cm⁻¹.

Figures



Figure S1. The formation of nAg by pristine RE under photoirradiation followed a pseudo-firstorder reaction kinetics. At and A_{max} represent the UV-Vis absorbance at time t and at the stabilized point (12 h), respectively.



Figure S2. Surface-enhanced Raman spectroscopy (SERS) detection of the formed particles (8 h) by pristine RE under photoirradiation with the assistance of ferbam. Compared with negative control (ferbam alone) and positive control (standard nAg), the enhanced signals of ferbam by particles in RE confirmed the formation of nAg.



Figure S3. Characterization of the spherical nanoparticles (4 h) formed by pristine RE under photoirradiation using high resolution TEM (HRTEM) (a, b), EDS (c) and selected area electron diffraction (SAED) (d).



Figure S4. SEM images and size distribution of the formed nanoparticles by pristine RE under photoirradiation at different time points (0 h, 0.5 h, 4 h, and 12 h). The size distribution was based on the length measurements of 261-421 individual particles.

Figure S5. Zeta potential (mV) of the particles induced by pristine RE under photoirradiation at different time intervals (0-12 h).

Figure S6. Characterization of the formed particles by pristine RE after 0 h, 0.5 h, 4 h, and 12 h of photoirradiation using Raman spectroscopy in a Raman shift range of 200-3000 cm⁻¹ (left panel). To show the relatively weak peaks (800-1000 cm⁻¹) more clearly, the Raman shift scale was narrowed down to 800-1800 cm⁻¹ (middle panel). The assignments of Raman peaks at 12 h are listed in the right panel, except for the two peaks (518 and 935 cm⁻¹) from silica chip (substrate used for sample preparation). *Infrared and Raman spectroscopy: principles and spectral interpretation/Peter Larkin. ISBN: 978-0-12-386984-5.

Figure S7. Characterization of the particles formed by pristine RE after 0 h and 12 h of photoirradiation using FTIR with spectra shown at the left panel and the peak assignments at the right panel. *Infrared and Raman spectroscopy: principles and spectral interpretation/Peter Larkin. ISBN: 978-0-12-386984-5.

Figure S8. SEM-EDS (a and b) and XRD data (c) demonstrate that both nAg and AgCl are present in the formed particles by pristine RE after 12-h light exposure.

Figure S9. UV-Vis spectrum of wheat root exudates without addition of Ag^+ . The high absorbance at around 280 nm indicates that amino acids of chromophores with light absorbance at 280 nm are present.

Figure S10. UV-Vis absorbance spectra demonstrate the photo-induced formation of nAg by boiled (a) vs pristine (b) RE over time (0-8 h). The light intensity was 6800 ± 124 lux. The comparison of the absorbance peak (450 nm) between boiled and pristine RE (c) indicates that proteins in RE did not play a significant role in the photo-induced transformation of Ag⁺ to nAg. The image (d) shows the observation of samples at 8 h.

Figure S11. The molecules detected in pristine RE by GC-MS and their relative abundance (%).

Figure S12. (a) Pristine RE was purged with air for 1 hour to increase the dissolved O_2 prior to interacting with Ag^+ (1 mM) while another group was purged with pure nitrogen to remove the dissolved O_2 . After 8-h incubation with Ag^+ , the sample color and UV-Vis absorbance were compared with the group without purge. (b) SOD (150 U/mL and 600 U/mL) was added into pristine RE to remove superoxide radical before reaction with Ag^+ (1 mM).¹ The nAg formation over time was monitored by a UV-Vis spectrophotometer. The light intensity was 4439 ± 145 lux.

Figure S13. (a-c) The UV-Vis spectra of the formed nAg from 0 h to 8 h by pristine RE in presence of different concentrations (0 mM, 5 mM and 20 mM) of Na⁺ under light irradiation. (d) The time-dependent change of UV-Vis absorbance at 450 nm. Lines were made based on eyes and used to show the general trend of the transformation. (e) Images of samples at 8 h.

Figure S14. The UV-Vis spectra of the formed nAg from 0 h to 8 h by pristine RE in presence of different concentrations (0.05 mM, 0.1 mM and 0.33 mM) of Ag⁺.