

## Supporting Information for

### **Reduction of silver ions to form silver nanoparticles by redox-active organic molecules: Coupled impact of redox state and environmental factors**

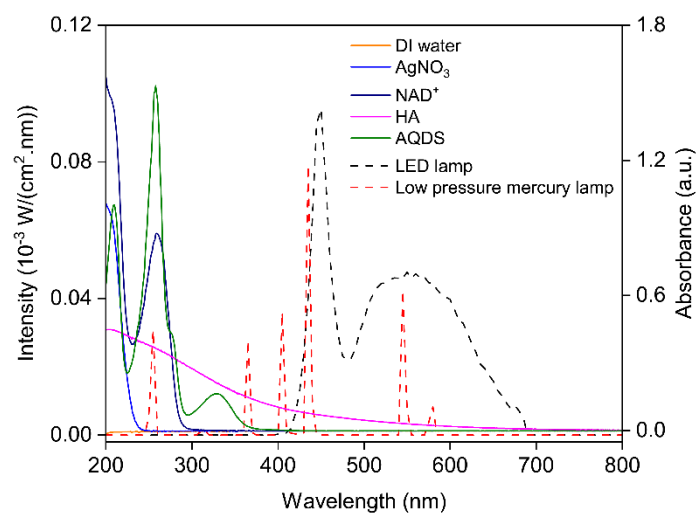
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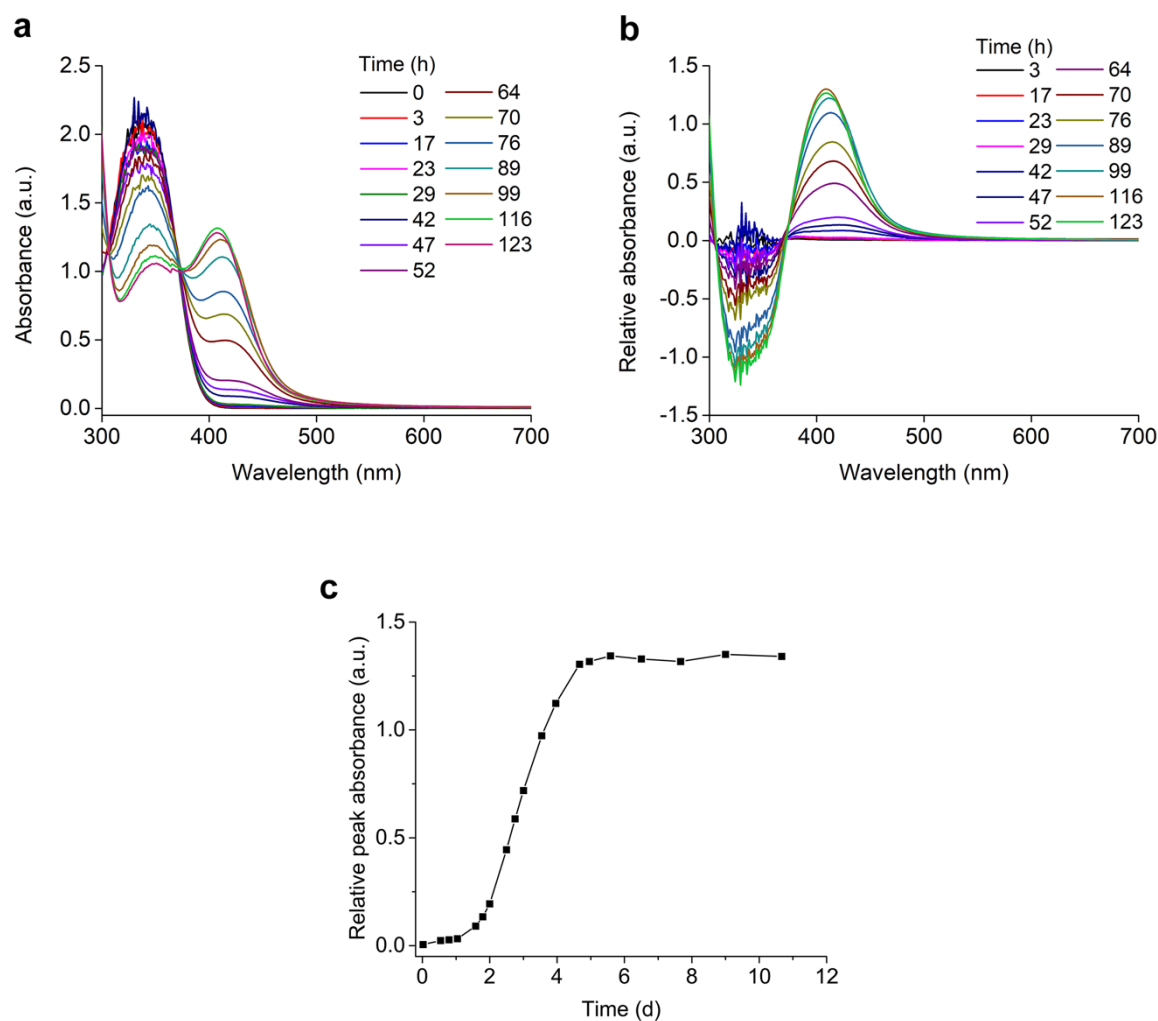
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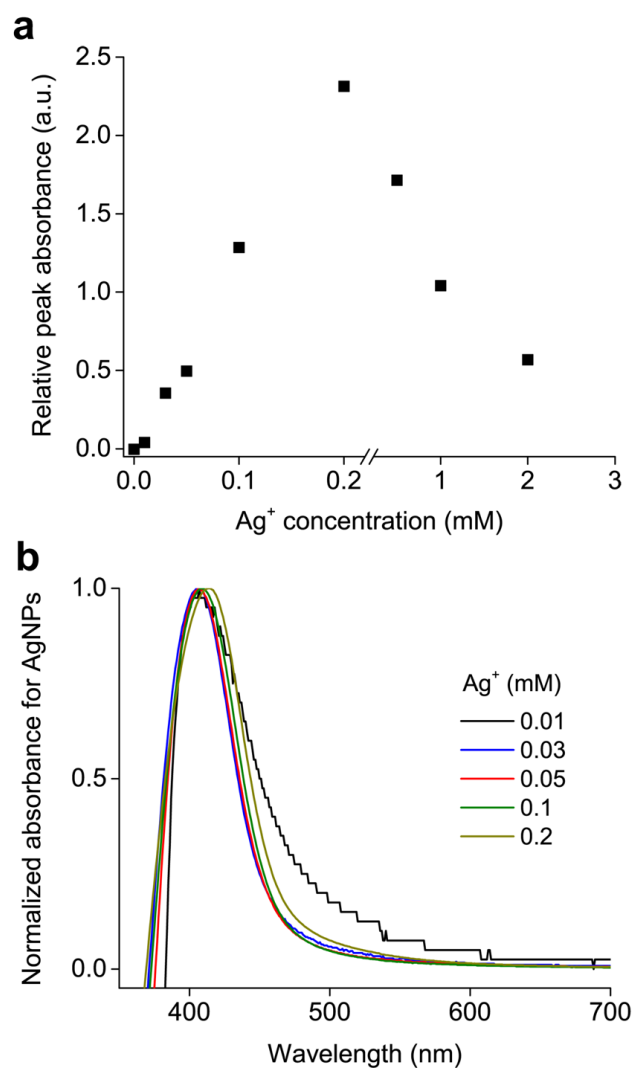
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**Fig. S1.** Spectra of the light emitted by the light-emitting-diode light (LED) and low pressure mercury vapor lamps (left y-axis), and UV-Vis absorption spectra of  $\text{AgNO}_3$  (0.1 mM),  $\text{NAD}^+$  (0.05 mM), AQDS (0.025 mM), and humic acid (HA, 10 mg/L) between 200 and 800 nm (right y-axis). DI water was measured as a control.

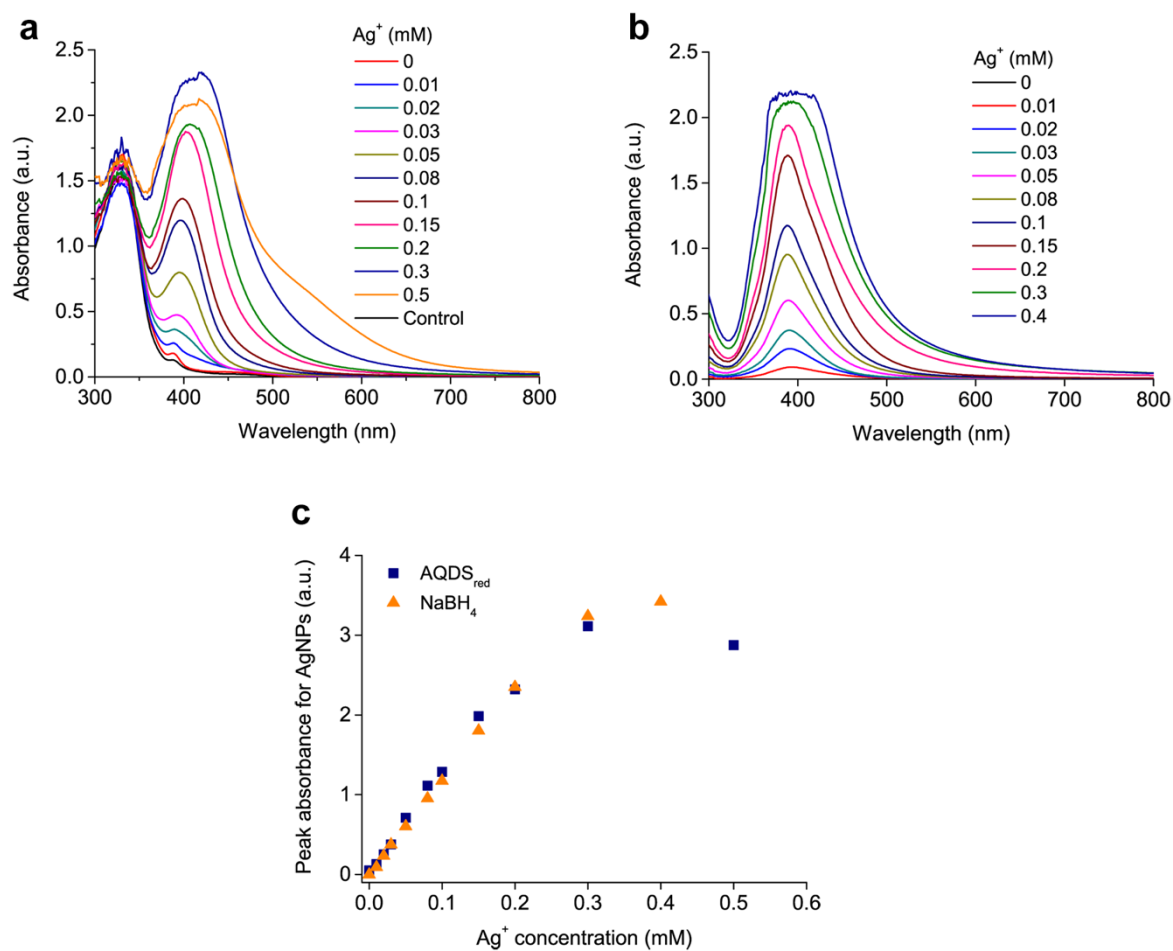


**Fig. S2.** Kinetics of silver nanoparticle (AgNP) formation when reducing 0.1 mM  $\text{Ag}^+$  with 0.5 mM NADH under anaerobic conditions. **(a)** UV-Vis absorption spectrometry (UVAS) curve for the mixture as a function of time. **(b)** Relative absorbance of AgNPs, obtained by subtracting the absorbance of NADH from that of the mixture. The increasing absorbance between 380 and 500 nm, which features the local surface plasmon resonance (LSPR) of AgNPs, indicated the reduction of  $\text{Ag}^+$ . The decreasing absorbance at around 330 nm suggested the oxidation of NADH to  $\text{NAD}^+$  over the reaction. **(c)** Peak absorbance for AgNPs as a function of time. The increase of relative peak absorbance indicated the increase of AgNPs produced from the reaction.

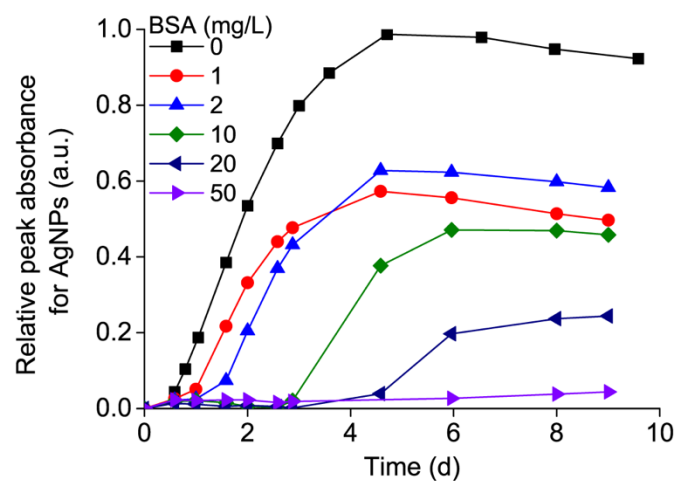


**Fig. S3.** Kinetics of silver nanoparticle (AgNP) formation when reducing varying concentrations of  $\text{Ag}^+$  with 0.5 mM NADH in anaerobic environments. **(a)** Peak absorbance of UV-Vis absorption spectrometry (UVAS) curves for AgNPs as a function of  $\text{Ag}^+$  concentrations after 10 days of reaction. The peak absorbance increased linearly with  $\text{Ag}^+$  concentrations in the range of 0–0.2 mM and decreased at  $\text{Ag}^+$  concentrations  $> 0.2$  mM. **(b)** Normalized UVAS curves of the AgNPs. The LSPR band of AgNP suspension was normalized by dividing the peak absorbance ( $A_{\text{peak}}$ ) by the absorbance at a specific wavelength of the UV-Vis absorption spectrum curve. The difference between 0.01 mM and

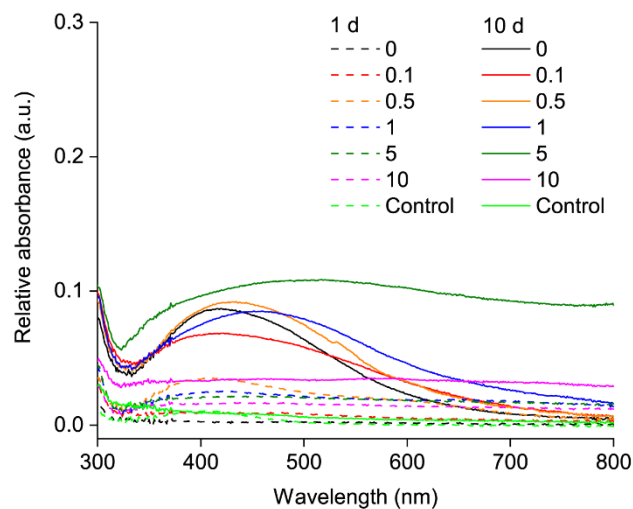
other concentrations was likely attributed to the relatively low signal/noise ratio of the AgNPs formed at small  $\text{Ag}^+$  concentrations. No apparent difference of the UVAS curves were observed for the AgNPs formed when reducing 0.03–0.2 mM  $\text{Ag}^+$ .



**Fig. S4.** Kinetics of silver nanoparticle (AgNP) formation when reducing Ag<sup>+</sup> with AQDS or NaBH<sub>4</sub>. UV-Vis absorption spectrometry (UVAS) curves for the mixtures when reducing varying concentrations of Ag<sup>+</sup> with (a) 0.5 mM chemically reduced AQDS (AQDS<sub>red</sub>), or (b) 0.5 mM NaBH<sub>4</sub>. (c) Peak absorbance values of the UVAS curves in Panel (a) and (b). The amounts of AgNPs generated in AQDS<sub>red</sub> were close to that in NaBH<sub>4</sub>. The peak absorbance values were proportional to Ag<sup>+</sup> concentrations at 0–0.3 mM.

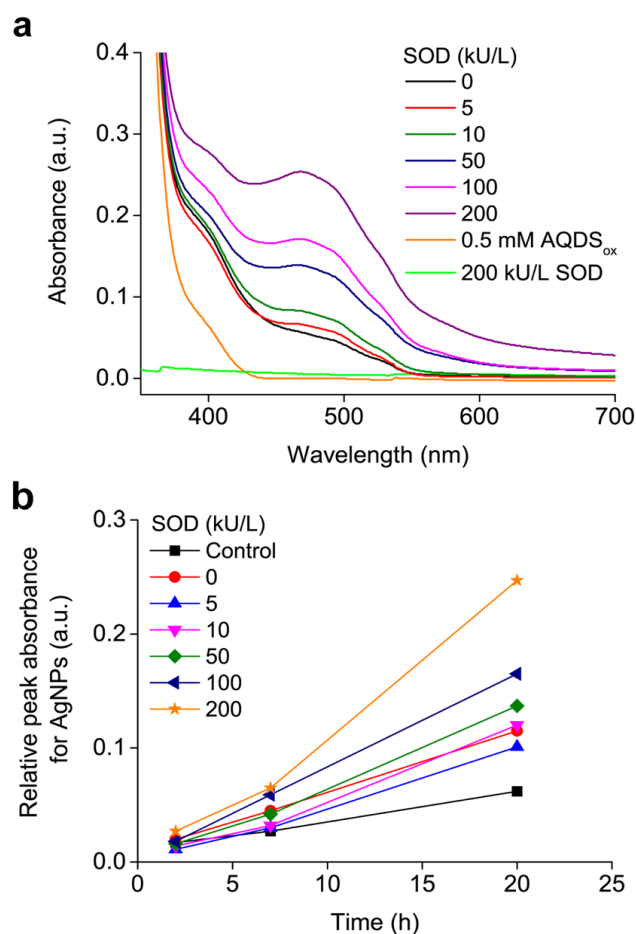


**Fig. S5.** Kinetics of silver nanoparticle (AgNP) formation when reducing 0.1 mM Ag<sup>+</sup> with 0.5 mM NADH in the presence of varying concentrations of bovine serum albumin (BSA) in anaerobic environments. The addition of BSA inhibited Ag<sup>+</sup> reduction in a dose-dependent pattern.

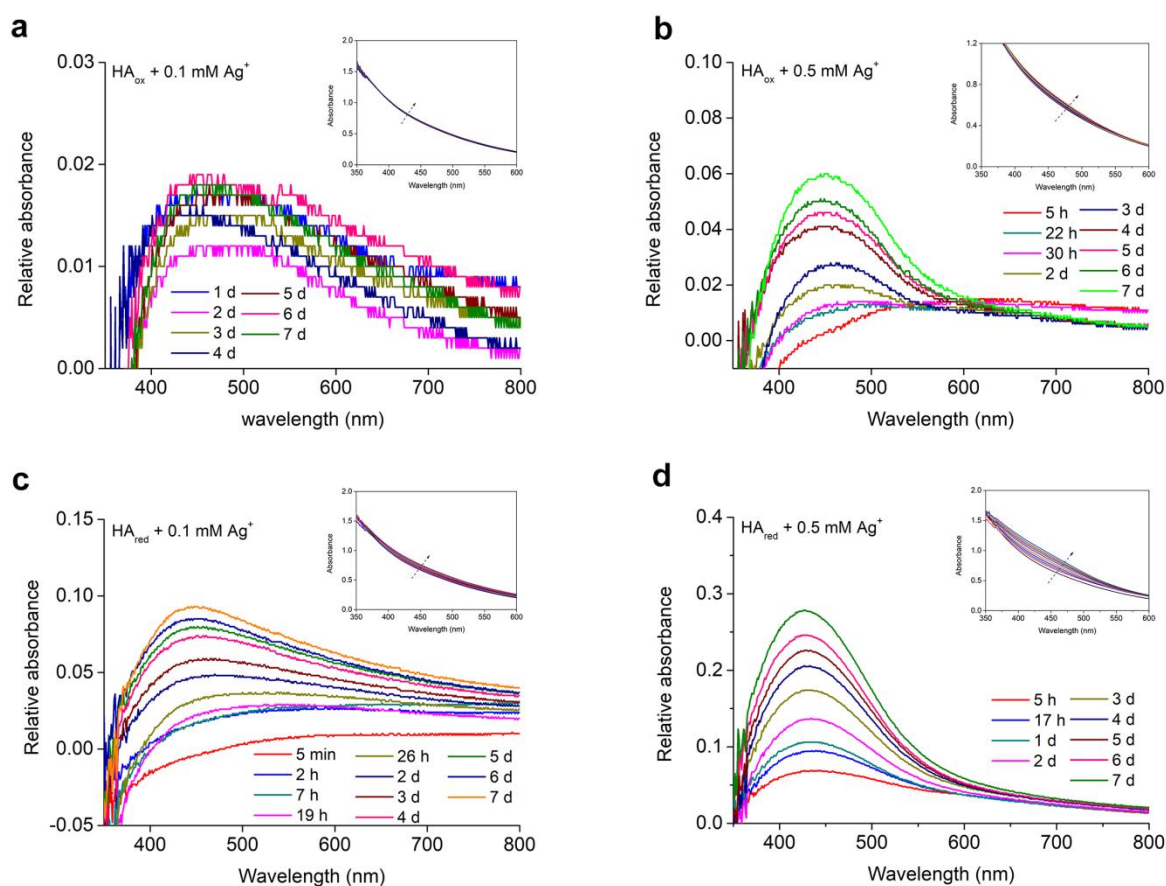


**Fig. S6.** Reduction of Ag<sup>+</sup> under UV light radiation in the presence of various concentrations of H<sub>2</sub>O<sub>2</sub>. The AgNO<sub>3</sub> (0.1 mM) and H<sub>2</sub>O<sub>2</sub> (0–10 mM) mixtures were exposed to UV light under anoxic condition. The UV-Vis absorption spectra of the mixtures were measured on 1 and 10 d, respectively. The relative absorbance was obtained by subtracting the absorbance of the mixture at time ‘0’ from that on day 1 and 10, respectively.

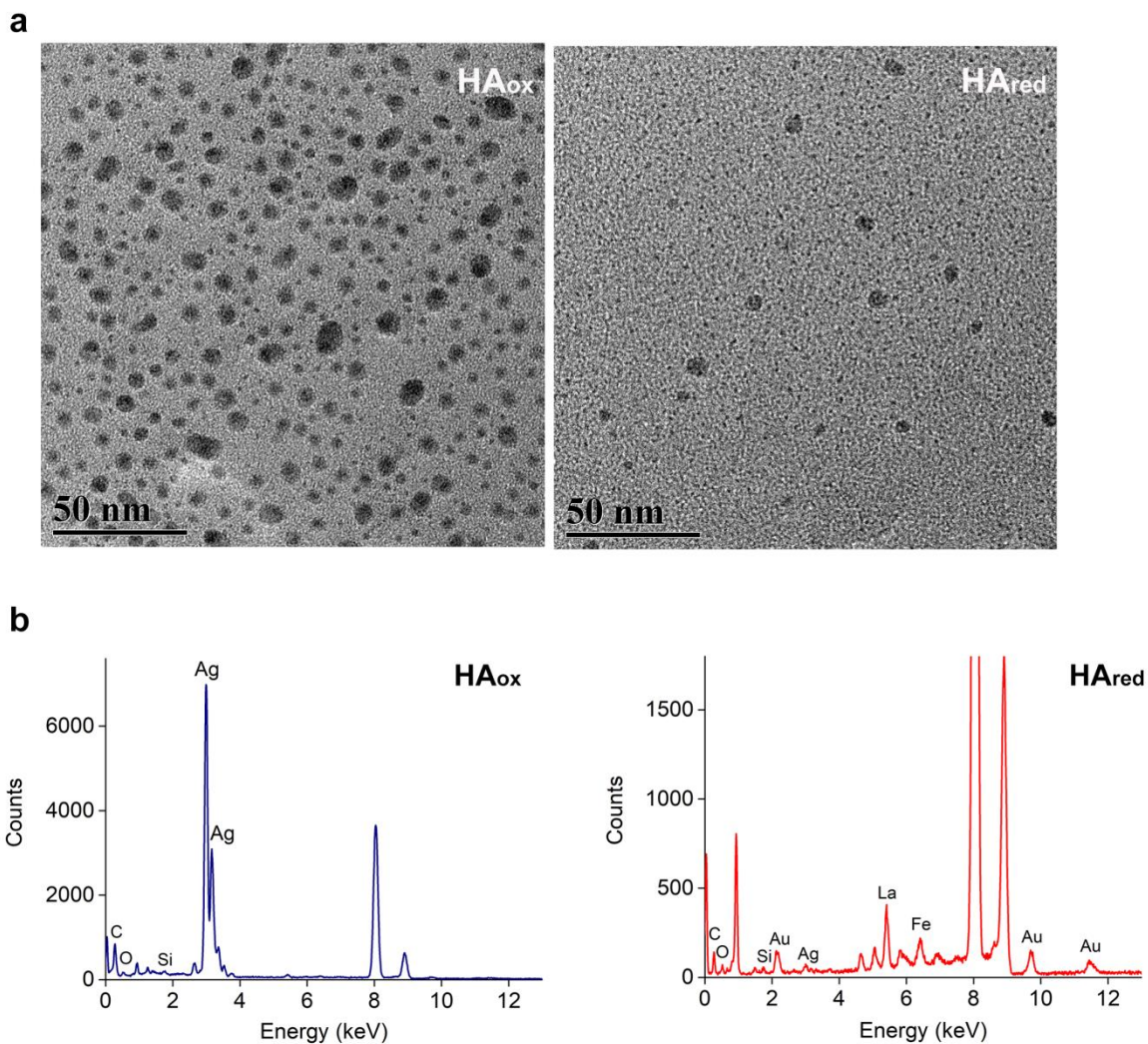




**Fig. S7.** Reduction of  $\text{Ag}^+$  by  $\text{AQDS}_{\text{ox}}$  under UV light irradiation in the presence of superoxide dismutase (SOD) at 30 °C. The experiment was performed in oxic environments by exposing the mixture to air. **(a)** UV-Vis absorption spectrometry (UVAS) curves for the mixtures after 20 h of reaction. The control was carried out with 0.5 mM  $\text{AQDS}_{\text{ox}}$  or 200 kU/L of SOD solution in  $\text{Ag}^+$ -free conditions. Increasing SOD concentration resulted in the increase of absorbance at around 465 nm. This may suggest that the presence of SOD did not have any negative impact on AgNP production. **(b)** Peak absorbance of the UVAS curve for AgNPs as a function of time in the presence of different concentrations of SOD. The control was conducted by 200 kU/L SOD solution in the absence of  $\text{Ag}^+$ . UV radiation may induce the change of dispersed SOD to cause the overlap of the absorbance at around 465 nm.



**Fig. S8.** Kinetics of silver nanoparticle (AgNP) formation when reducing 0.1 or 0.5 mM  $\text{Ag}^+$  with native ( $\text{HA}_{\text{ox}}$ ) or chemically reduced ( $\text{HA}_{\text{red}}$ ) humic acid (HA) in anaerobic environments, **(a)**  $\text{HA}_{\text{ox}} + 0.1 \text{ mM Ag}^+$ , **(b)**  $\text{HA}_{\text{ox}} + 0.5 \text{ mM Ag}^+$ , **(c)**  $\text{HA}_{\text{red}} + 0.1 \text{ mM Ag}^+$ , and **(d)**  $\text{HA}_{\text{red}} + 0.5 \text{ mM Ag}^+$ . The UV-Vis absorption spectrometry (UVAS) curves (relative absorbance) for AgNPs were obtained by subtracting the absorbance of HA from that of the mixtures. The inserts plot the UVAS curve of the mixture, with increase of the absorbance between 380 and 600 nm, indicating the AgNP-formation processes, as marked by the arrows.



**Fig. S9.** (a) Transmission electron microscopy (TEM) image of the AgNPs formed by reducing 0.1 mM Ag<sup>+</sup> with HA<sub>ox</sub> or HA<sub>red</sub> in anaerobic environments. (b) Energy dispersive X-ray spectrometry (EDS) spectra for the AgNPs shown in Panel (a). Because there were more AgNPs dispersed on the TEM grid for the HA<sub>ox</sub>-reduced sample, the count number at 2.99 keV, which refers to Ag, was larger for HA<sub>ox</sub> sample than that for HA<sub>red</sub> sample. This discrepancy was due to the uncertainty and variation in TEM sample preparation rather than the quantitative difference in the AgNPs formed in HA<sub>ox</sub> and HA<sub>red</sub>.