Supporting information

Thermal and Photo-induced Reduction of Ionic Au(III) to Elemental Au Nanoparticles by Dissolved Organic Matter in Water: Possible Source of Naturally Occurring Au Nanoparticles

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Number of pages: 23

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Dialysis of River Waters.

The dialysis of river water samples was performed in a regenerated cellulose membrane dialysis bags (molecular weight cutoffs of 1000 Da, Roth, Germany) and the procedure was the same with our previous study.¹

UV-vis Spectroscopy. UV-vis spectrums were recorded on a Beckman Coulter DU 800 UV/Vis Spectrophotometer (Brea, CA). The maximum absorbance of well-dispersed AuNPs was at ~522 nm, indicating the concentration of AuNPs²,³ increased almost linearly with heating time. The apparent kinetics of AuNPs formation can be written as: \( \Delta A = r \times t \), in which \( \Delta A \) is the increased absorbance maximum absorbance of AuNPs at 522 nm, and \( r \) is the formation rate of AuNPs. Under the constant concentration of \( \text{AuCl}_4^- \), the formation of AuNPs under heating fits the pseudo-first-order reaction kinetics for concentration of HA, \( r = k_{\text{obs}}[\text{HA}] \), in which \( k_{\text{obs}} \) is the apparent formation rate constant. Besides AuNPs solution, river water samples were also characterized by UV-vis spectroscopy. Chromophoric dissolved organic matter (CDOM) absorption was estimated according to the following equation:⁴

\[
a(\lambda) = 2.303 \times \frac{A(\lambda)}{L}(m^{-1})
\]

where \( a(\lambda) \) is the absorbance and \( L \) the path length of the cuvette (0.01 m). The absorption at 355 nm was chosen as a proxy of CDOM.

Fluorescence Spectroscopy of the River Waters.

The river water samples were characterized by fluorescence spectroscopy on a fluorescence spectrophotometer (F-4500, Hitachi, Japan) with excitation wavelength at 370 nm and emission wavelength at 400 nm-600 nm. The excitation and emission bandwidths were set at 5 nm. The fluorescence emission intensity at 460 nm was used as a proxy for CDOM.⁵
Transmission Electron Microscopy (TEM).

TEM images, coupled with an energy dispersive spectrometer (EDS) and selected area electron diffraction (SAED) were obtained from a TEANAI G² 20-200 kV (FEI, Hillsboro, OR) or JEOL 2011 (Herts, England) transmission electron microscope. The specimen for TEM characterization was prepared by evaporation of solution onto an ultra-thin carbon-coated copper grid (T11032, Xinxing Bairui, Beijing, China) in vacuum at room temperature. The average particle size of the formed AuNPs was analyzed using a particle size analysis software, Nano Measurer 1.2, which is based on the TEM micrograph and utilizes an image ruler to measure the particle sizes of dispersed particles.

X-ray Diffraction (XRD).

The prepared AuNP solution in the Chaobai river water was centrifuged at 8000 rpm. The sedimentation solution was collected, dropped on Si slide, dried in the vacuum desiccators at room temperature and then characterized by XRD. XRD patterns were recorded with an X’pert PRO instrument (PANalytical, Almelo, Netherlands) using Cu Kα radiation (λ=0.15418 nm) with the diffraction angle (2θ) at a range of 30-90°.

Ultrafiltration for enrichment of AuNPs.

Ultrafiltration was employed to enrich and facilitate the following characterization of ultra-low concentration of AuNPs in river water by TEM. Briefly, into the 15 mL centrifugal ultrafilter devices (Amicon Ultra-15 10 kD, Millipore) was added 10 mL river water containing the photo-synthesized AuNPs. After centrifugation for 30 min at 8000 rpm, the filtrate was discarded and another 10 mL river water sample was added for centrifugation. Totally, 50 mL river water was subjected for ultrafiltration. Then, the upper solution, kept in the filter device, was used to prepare TEM samples to characterize the photo-formed AuNPs.
Cloud Point Extraction (CPE) for enrichment of AuNPs.

To facilitate the characterization of ultra-low concentration of AuNPs by TEM, cloud point extraction, an effective enrichment protocol for nanomaterials, was employed to concentrate AuNPs in river water. Briefly, into the 12 mL centrifuge tube was added 10 mL river water containing the photo-synthesized AuNPs, 0.1 mL of 3.5 mol L\(^{-1}\) NaNO\(_3\) and 0.2 mL of 10% (w/v) Triton X-114. The mixture was adjusted to pH 4.5 with diluted HNO\(_3\). After incubation in a 40°C water bath for 30 min, the mixture was centrifuged at 2000 rpm (~640 g) at room temperature for 5 min to facilitate the phase separation. The Triton X-114-rich phase with the concentrated AuNPs obtained in the first CPE, was re-dispersed and performed CPE twice. Then, the obtained Triton X-114-rich phase with the concentrated AuNPs was diluted by 5 mL 1:1 (v/v) water/methanol solution for TEM and EDS characterization.

X-ray Photoelectron Spectroscopy (XPS).

The prepared solution (in matrix of river water or HA solution) was dropped on Si wafer and then dried in the vacuum desiccators at room temperature. The XPS characterization was carried out in an ESCALAB 250 spectrometer (Thermo Scientific, UK) using monochromatic Al Kα radiation of energy 1486.6 eV. Core level binding energies were determined and corrected for substrate charging using C1s peak at 284.8 eV as the reference.

REFERENCES

(1) Yin, Y. G.; Liu, J. F.; Jiang, G. B. Sunlight-induced reduction of ionic Ag and Au to metallic nanoparticles by dissolved organic matter. *ACS Nano* 2012, 6, (9), 7910-7919.


Figure S1. High-resolution TEM (a) and EDS (b) characterization of the AuNPs in Chaobai river water 1 after cloud point extraction. The concentration of spiked AuCl₄⁻ is 0.1 µmol L⁻¹ (19.8 µg L⁻¹ Au) and cumulative PAR is 8.52 E m⁻².
Figure S2. Particle size distribution of the formed AuNPs in Figure 4b.
Figure S3. UV-vis spectra of AuNPs formed in Chaobai river water 1 with and without dialysis by spiking 200 µmol L$^{-1}$ AuCl$_4^-$ under sunlight and thermal irradiation. Note: The pH of river water after dialysis decreased from pH 8.17 to pH 7.51.
Figure S4. X-ray photoelectron survey spectra of Chaobai River water 1 spiked with AuCl$_4^-$ under sunlight. The concentration of spiked AuCl$_4^-$ is 200 µmol L$^{-1}$ and cumulative PAR is 7.06 E m$^{-2}$. 
Figure S5. Stability studies of the AuNPs formed in Chaobai river water 1 under natural sunlight or 65 °C heating. The cumulative PAR for synthesis of AuNPs was 30.94 E m⁻². The time for heating was 36 h. Absorption spectra of the AuNPs were acquired after 0 and 12 days.
Figure S6. The reduction of Au(I/III) to AuNPs by HA under heating at 65 °C. (a) UV-visible spectrums of the reduction of Au(I/III) to AuNPs by various HA under 65 °C for 36 h. (b) Time-resolved evolution of absorption at 522 nm of the reduction of Au(I/III) to AuNPs by various HA under 65 °C. The concentration of AuCl₄⁻ or Au(S₂O₃)₂³⁻ and HA are 250 µmol L⁻¹ and 50 mg DOC L⁻¹, respectively.
Figure S7. Effect of pH, concentration of HA and AuCl$_4^-$ on the formation of AuNPs under simulated sunlight. Conditions: (a) 5 mg DOC L$^{-1}$ Aldrich HA, 1000 µmol L$^{-1}$ AuCl$_4^-$. (b) 1000 µmol L$^{-1}$ AuCl$_4^-$, pH 8.1. (c) 5 mg DOC L$^{-1}$ Aldrich HA, pH 8.1.
Figure S8. Effect of pH, concentration of HA and AuCl₄⁻ on the formation of AuNPs under heating. Conditions: (a1-2) 50 mg DOC L⁻¹ Aldrich HA, 250 µmol L⁻¹ AuCl₄⁻, 65 °C. (b1-2) 250 µmol L⁻¹ AuCl₄⁻, pH 8.1, 65 °C. (c1-2) 50 mg DOC L⁻¹ Aldrich HA, pH 8.1, 65 °C.
Figure S9. TEM images of the formed AuNPs in HA solution under simulated sunlight: (a1-2) 5 mg DOC L$^{-1}$ SRHA, 250 µmol L$^{-1}$ AuCl$_4^-$ (b1-2) 5 mg DOC L$^{-1}$ Aldrich HA, 250 µmol L$^{-1}$ AuCl$_4^-$ (c1-2) 5 mg DOC L$^{-1}$ Aldrich HA, 1000 µmol L$^{-1}$ AuCl$_4^-$ (d1-2) 20 mg DOC L$^{-1}$ Aldrich HA, 1000 µmol L$^{-1}$ AuCl$_4^-$. 
Figure S10. TEM images of the formed AuNPs in solution under 65 °C heating for 36 h: (a1) 250 µmol L\(^{-1}\) AuCl\(_4^-\), 50 mg DOC L\(^{-1}\) SRHA, (b1) 250 µmol L\(^{-1}\) AuCl\(_4^-\), 20 mg DOC L\(^{-1}\) Aldrich HA, (c1) 250 µmol L\(^{-1}\) AuCl\(_4^-\), 50 mg DOC L\(^{-1}\) Aldrich HA, (d1) 1000 µmol L\(^{-1}\) AuCl\(_4^-\), 50 mg DOC L\(^{-1}\) Aldrich HA.
Figure S11. Particle size distribution of the formed AuNPs in Figure S10a1.
Figure S12. Effect of heating temperature on the formation of AuNPs: (a) UV-visible spectrums of formed AuNPs by Aldrich HA for 36 h. (b) time-resolved evolution of absorption of AuNPs at 522 nm. The concentration of HA and AuCl₄⁻ are 50 mg DOC L⁻¹ and 250 µmol L⁻¹ AuCl₄⁻, respectively.
Figure S13. Effects of heating temperature and HA concentration on the formation of AuNPs.

Conditions: (a) 250 $\mu$mol L$^{-1}$ AuCl$_4^-$ with various HA concentrations under 75 °C incubation, (b) 250 $\mu$mol L$^{-1}$ AuCl$_4^-$ with various HA concentrations under 85 °C incubation, (c) show a linear relationship between HA concentration and formation rate of AuNPs.
Figure S14. The photo-reduction of Au(III) to AuNPs by HA under natural sunlight. Conditions:

5 mg DOC L⁻¹ HA, 250 µmol L⁻¹ AuCl₄⁻, pH 8.1. The cumulative PAR was 68.35 E m⁻².
Figure S15. TEM images of the formed AuNPs in Aldrich HA solution under natural sunlight.

Conditions: 5 mg DOC L$^{-1}$ Aldrich HA, 250 µmol L$^{-1}$ AuCl$_4^-$, pH 8.1. The corresponding cumulative PAR for (a1-2), (b1-2), (c1-2), (d1-2) were 16.57, 36.65, 53.01 and 221.25 E m$^{-2}$, respectively.
Figure S16. XPS spectra of Au species in Aldrich HA solution. Conditions: (a) 5 mg DOC L$^{-1}$ Aldrich HA, 200 µmol L$^{-1}$ AuCl$_4^-$, 96 h simulated sunlight irradiation, (b) 50 mg DOC L$^{-1}$ Aldrich HA, 200 µmol L$^{-1}$ AuCl$_4^-$, 36 h heating at 65 °C.
Table S1. Characteristics of the sampled river waters.

<table>
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<tr>
<th>Location</th>
<th>DOC (mg L⁻¹)</th>
<th>Fluorescence values at Ex370 nm/Em440 nm</th>
<th>pH</th>
<th>ORP (mV)</th>
<th>(a_{CDOM}(355 , \text{nm})) (m²)</th>
<th>Ca²⁺ (mg L⁻¹)</th>
<th>Mg²⁺ (mg L⁻¹)</th>
<th>K⁺ (mg L⁻¹)</th>
<th>Na⁺ (mg L⁻¹)</th>
<th>Total Fe (mg L⁻¹)</th>
<th>NO₂⁻ (mg L⁻¹)</th>
<th>NO₃⁻ (mg L⁻¹)</th>
<th>SO₄²⁻ (mg L⁻¹)</th>
<th>Cl⁻ (mg L⁻¹)</th>
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<td>Chaobai river water 1</td>
<td>N 40°10'18.76&quot;, E 116°40'39.43&quot;</td>
<td>30.29</td>
<td>1.46×10⁶</td>
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<td>-</td>
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-, not determined.
Table S2. Effect of heating temperature and Aldrich HA concentration on the formation rate (ΔA/t) of AuNPs.

<table>
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<th>85 °C</th>
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