

Electronic Supplementary Information (ESI) for

Aqueous Photoproduction of Au Nanoparticles by Natural Organic Matter: Effect by NaBH₄ Reduction

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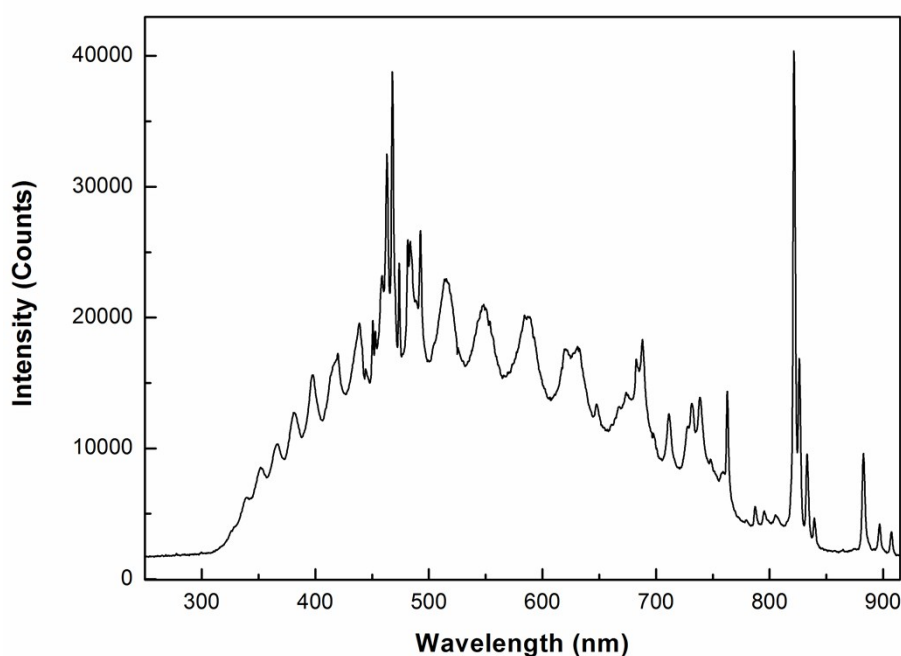


Fig. S1. Spectral irradiance of the 250 W Xe lamp used in this study.

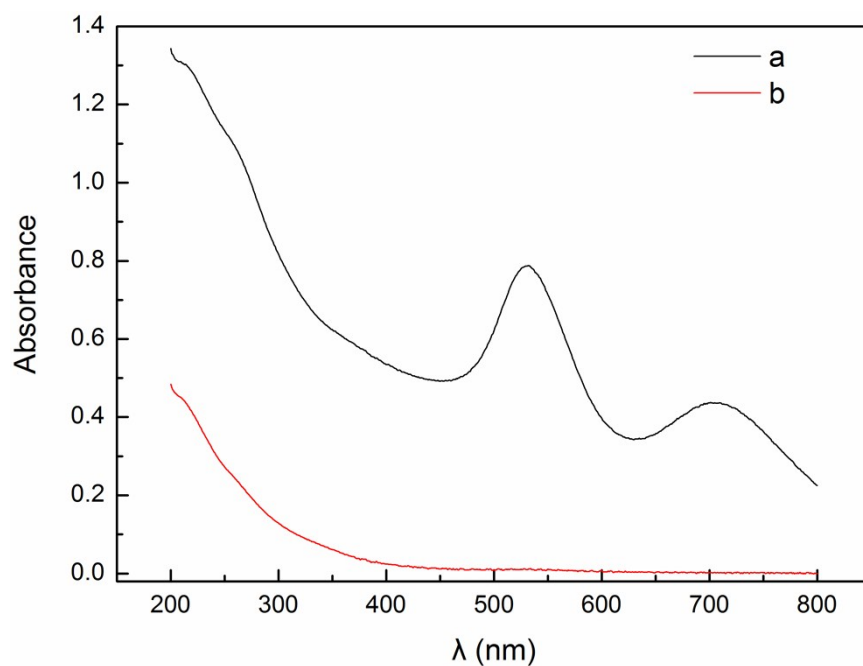


Fig. S2. The UV-vis spectra of AuNPs solution after 1-hour-long exposure under simulated sunlight in the presence of 0.2 mM HAuCl_4 and 10 mg C/L SRHA: (a) UV-vis spectra of original solution, (b) UV-vis spectra of the supernatant after centrifugation.

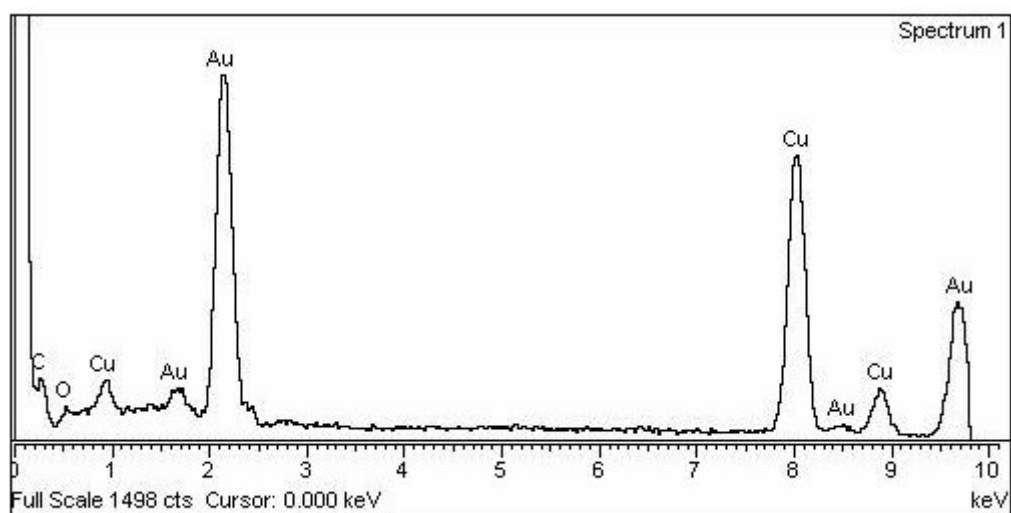


Fig.S3. Formation of gold nanoparticles was evidenced by energy-dispersive spectroscopy (EDS).

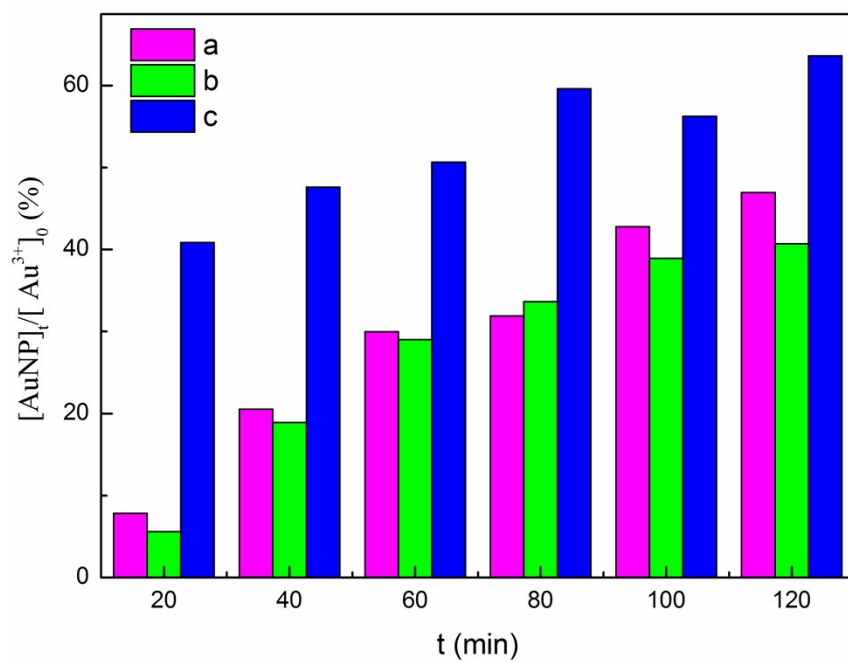


Fig. S4. Temporal reduction ratio of Au³⁺ to AuNPs by different mixture of quinones. Solution conditions: 12.5 μM HAuCl₄ and 3 mg C/L (a) original quinones solution, (b) reduced quinones solution which had been adjusted pH back to original value, (c) reduced quinones without adjusting pH.

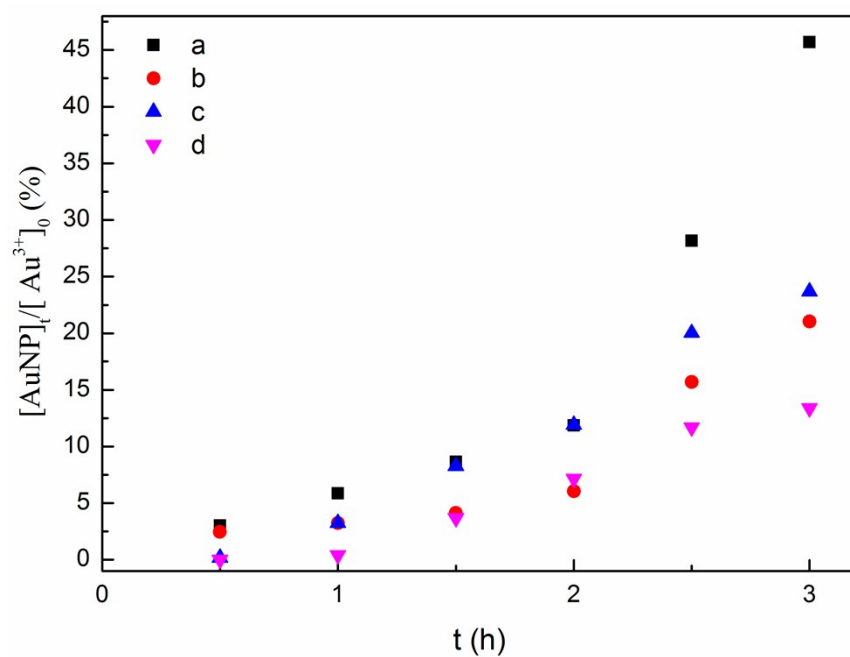


Fig. S5. Reduction ratio of Au^{3+} to AuNPs versus time using: (a) original AHA, (b) original AHA with 150 U/mL SOD, (c) reduced AHA, (d) reduced AHA with 150 U/mL SOD. Solution conditions: 0.2 mM HAuCl_4 and 10 mg C/L AHA.

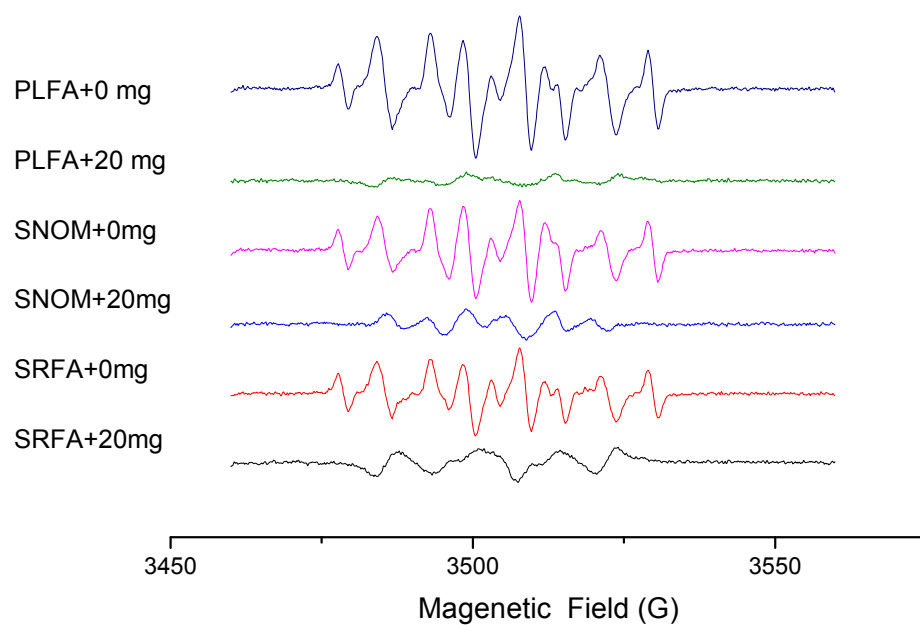


Fig S6. Corresponding DMPOO₂•⁻ EPR spectra of the original (0 mg) and NaBH₄-reduced (20 mg) NOMs (SNOM, SRFA and PLFA) after 4-minute-long simulated sunlight irradiation. Initial concentrations: 166.7 mg C/L NOM; 40 mM DMPO.

Table S1. Proposed mechanisms of the photoreduction of metal ions by NOM and validation methods in previous reports.

View	Validation Method	Metal Ion	Proposed Mechanism	Ref
Yes	O ₂ -dependent AgNPs formation and SOD inhabiting effect suggested O ₂ ^{•-} is the key reductant in DOM-induced photoreduction.	Ag ⁺	O ₂ ^{•-} produced by phenolic groups reduce Ag ⁺	13
No	O ₂ -independent formation of AgNPs suggested superoxide does not have a large role in photoreduction of Ag ions.	Ag ⁺	Ligand-to-metal charge transfer	16
Yes	XPS signal changes of Au and C suggested Au ³⁺ reduction should be ascribed to –OH (including phenolic, alcoholic groups).	Au ³⁺	Au(I) intermediate (produced by –OH)mechanism	14

Table S2. ¹³CNMR estimates of carbon distribution in NOM³⁶

Sample	Aliphatic	Hetero- aliphatic	Acetal	Aromatic	Carboxyl	Carbonyl
	0-60 ppm	90-60 ppm	110-90 ppm	165-110 ppm	190-165 ppm	220-190 ppm
NNOM	31	16	5	19	21	8
SRHA	29	13	7	31	15	6
SNOM	27	15	7	23	20	8
SRFA II	35	16	6	22	17	5
SRFA	33	11	5	24	20	7
PLFA	61	8.4	0.2	12	17	1.2

Table S3. Elemental Compositions of NOM³⁶

Sample	C	H	O	N	S	P
NNOM	53.17	5.67	nd	1.1	nd	nd
SRHA	52.63	4.28	42.04	1.17	0.54	0.013
SNOM	52.47	4.19	42.69	1.1	0.65	0.02
SRFA II	52.34	4.36	42.98	0.67	0.46	0.004
SRFA	52.44	4.31	42.20	0.72	0.44	<0.01
PLFA	52.47	5.39	31.38	6.51	3.03	0.55

“**nd**” means that an item was not determined.

Table S4. Rate constants of the pseudo–first–order part (k_1) of the plot of Au^{3+} reduction for the original and NaBH_4 -reduced NOMs.

	NNOM	SRHA	SRFA II	SNOM	PLFA	AHA	SRFA
k_o	1.58	1.78	1.25	1.23	1.10	1.36	1.36
k_r	0.52	1.70	1.08	unshown	unshown	unshown	unshown