Electronic Supplementary Material (ESI) for Environmental Science: Nano.

SEED MEDIATED GROWTH OF GOLD NANOPARTICLES AT ROOM TEMPERATURE: MECHANISTIC INVESTIGATIONS AND LIFE CYCLE ASSESMENT

*Weinan Leng, Paramjeet Pati, and Peter J Vikesland **

Department of Civil and Environmental Engineering, Virginia Polytechnic Institute and State University, 418 Durham Hall, Blacksburg, VA 24060-0246

Electronic Supplemental Information (ESI)

Table S1: Volumes (V) of nanopure water, $HAuCl_4$, seed suspension, and trisodium citrate (Na_3Ctr) used in the seed-mediated synthesis of the different sized nanoparticles.

AuNPs	intended particle size / nm	V_{water} / mL	V_{HAuCl4} ^{a} / mL (c = 44.7 mM)	V_{seed} / mL (d = 14 nm, c = 6.54 $\times 10^{12}$ particles/ml)	Final seed conc./ µg/mL	V_{Na3Ctr} / mL (c = 38.8 mM)
A	22.7	36.220	0.227	3.377	16.632	0.176
B	34.2	38.786	0.227	0.811	3.994	0.176
C	45.7	39.270	0.227	0.327	1.610	0.176
D	57.1	39.432	0.227	0.165	0.813	0.176
E	68.6	39.502	0.227	0.095	0.468	0.176
F	80.0	39.537	0.227	0.060	0.296	0.176
G	91.4	39.557	0.227	0.040	0.197	0.176
H	102.9	39.569	0.227	0.028	0.138	0.176
I	114.3	39.577	0.227	0.020	0.099	0.176

[a]Final mass concentration for gold is 50 µg/mL

Table S2. Inputs for 1 mg of the following custom-defined processes in SimaPro: a) chloroauric acid, b) trisodium citrate, and c) AuNP 'seeds'

[Custom defined] Chloroauric acid		
Gold [1]| production | Alloc Def, S	0.72	mg
Hydrochloric acid, without water, in 30% solution state {RER}| hydrochloric acid production, from the reaction of hydrogen with chlorine | Alloc Def, S	0.13	mg
Chlorine, gaseous {RER}| sodium chloride electrolysis | Alloc Def, S	0.39	mg
[Custom defined] Trisodium citrate		
Citric acid {GLO}| market for | Alloc Def, S	0.51	mg
Soda ash, light, crystalline, heptahydrate {GLO}| market for | Alloc Def, S	0.66	mg
[Custom defined] AuNP 'seeds'		
[Custom defined] Chloroauric acid	1.73	mg
[Custom defined] Trisodium citrate	5.08	mg
Water, deionised, from tap water, at user {CH}| production | Alloc Def, S	505.08	g
Tap water {CH}| market for | Alloc Def, S	30.00	g
Sodium hydroxide, without water, in 50% solution state {GLO}| market for | Alloc Def, S	0.41	mg
Cleaning solvents		
Hydrochloric acid, without water, in 30% solution state {RER}| hydrochloric acid production, from the reaction of hydrogen with chlorine | Alloc Def, S	1.81	mg
Nitric acid, without water, in 50% solution state {RER}| nitric acid production, product in 50% solution state | Alloc Def, S	0.72	mg
[Stirring] Electricity, medium voltage {NPCC, US only}| market for | Alloc Def, S	0.01	MJ
[Heating] Electricity, medium voltage {NPCC, US only}| market for | Alloc Def, S	0.08	MJ

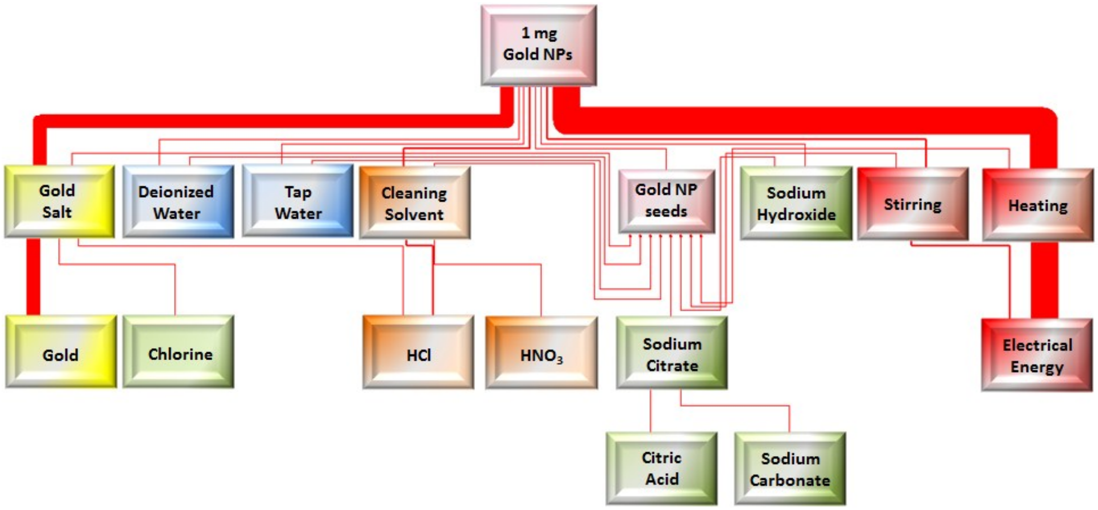

Figure S1. Energy flows (cumulative energy demand) of 1 mg AuNP synthesis at 100 °C. (Flow lines show individual contributions of different inputs.)

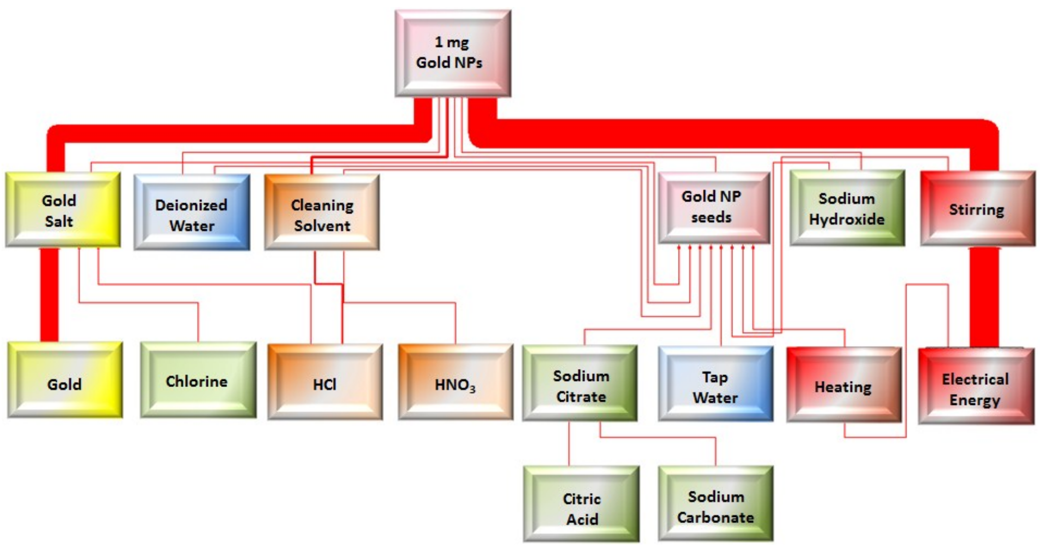

Figure S2. Energy flows (cumulative energy demand) for 1 mg AuNP synthesis at room temperature. (Flow lines show individual contributions of different inputs.)

Table S3. Inputs for 1 mg of seed-mediated, citrate reduced AuNPs synthesized under boiling conditions

[Custom defined] Chloroauric acid	1.94	mg
Water, deionised, from tap water, at user {CH}| production | Alloc Def, S	444.13	g
Tap water {CH}| market for | Alloc Def, S	25.40	g
[Custom defined] AuNP 'seeds'	0.03	mg
Sodium hydroxide, without water, in 50% solution state {GLO}| market for | Alloc Def, S	0.03	mg
[Custom defined] Trisodium citrate	0.09	mg
Cleaning solvents		
Hydrochloric acid, without water, in 30% solution state {RER}| hydrochloric acid production, from the reaction of hydrogen with chlorine | Alloc Def, S	1.81	mg
Nitric acid, without water, in 50% solution state {RER}| nitric acid production, product in 50% solution state | Alloc Def, S	0.72	mg
[Stirring] Electricity, medium voltage {NPCC, US only}| market for | Alloc Def, S	0.08	kWh
[Heating] Electricity, medium voltage {NPCC, US only}| market for | Alloc Def, S	0.97	kWh

Table S4. Inputs for 1 mg of seed-mediated, citrate reduced AuNPs synthesized at room temperature

[Custom defined] Chloroauric acid	1.94	mg
Water, deionised, from tap water, at user {CH}| production | Alloc Def, S	444.13	g
[Custom defined] AuNP 'seeds'	0.03	mg
Sodium hydroxide, without water, in 50% solution state {GLO}| market for | Alloc Def, S	0.03	mg
[Custom defined] Trisodium citrate	0.09	mg
Cleaning solvents		
Hydrochloric acid, without water, in 30% solution state {RER}| hydrochloric acid production, from the reaction of hydrogen with chlorine | Alloc Def, S	1.81	mg
Nitric acid, without water, in 50% solution state {RER}| nitric acid production, product in 50% solution state | Alloc Def, S	0.72	mg
[Stirring] Electricity, medium voltage {NPCC, US only}| market for | Alloc Def, S	0.76	kWh

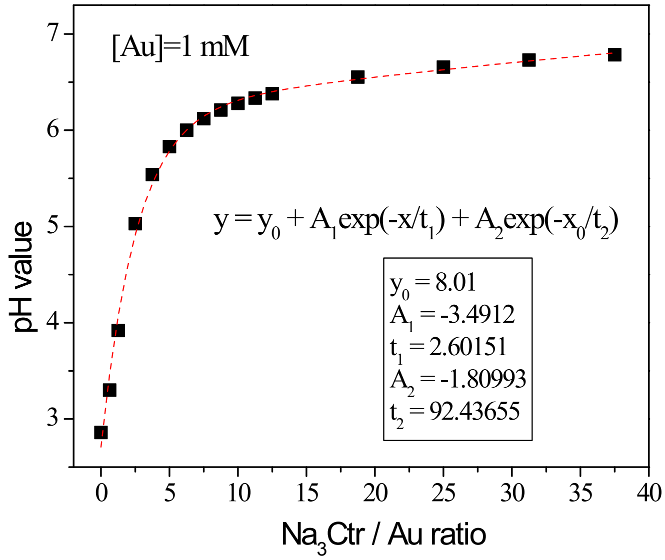

Figure S3. pH value at room temperature against the concentration ratio of Na_3Ctr and Au^{III} for a fixed 1 mM Au^{III} concentration.

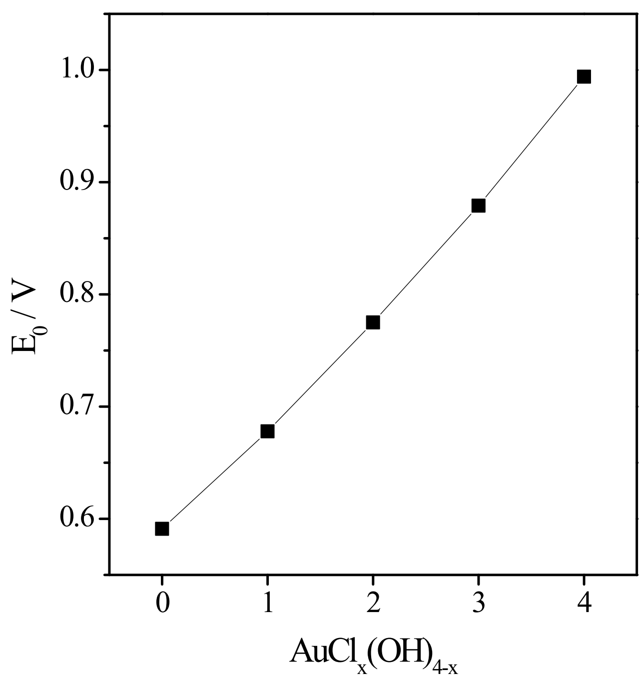

Figure S4. The standard reduction potential (E^0) for $Au^{III} \rightarrow Au^0$ for the gold solution species $AuCl_X(OH)_{4-X}$ (x=0-4). E^0 was calculated using the Nernst equation of $\Delta G^0 = -nFE^0$, where Gibbs free energy (ΔG^0) of $AuCl_X(OH)_{4-X}$ (x=0-4) was reported by Machesky et al.[2]

Formation of gold nanoplates and nanorods. The formation of gold nanoplates and nanorods was observed in the seeded growth approach, especially when the seed concentration was less than 1.6×10^{10} particles/mL (AuNPs D – I in Table S1). Under this condition, AuNP growth is reliant primarily on the individual seeds, and the interaction between seeds is minimal. Figure S5 shows the growth process of 111 nm gold nanoparticles. The formation of rod or triangular-shaped nanoparticles has previously been attributed to the presence of rod or triangular-shaped seed particles.[3] The nanoparticles gradually grow by adding Au atoms or ions onto more energetically favorable faces than (111).[4] This process results in the formation of nanoplates, nanorods, and hexagonally-shaped nanoparticles.[3,5] Alternatively, citrate ions and its oxidation product – ACDC may selectively adsorb on the (111) facets and hinder the crystal growth in those directions. The average numbers of particles with different shapes were counted and listed in Table S5.

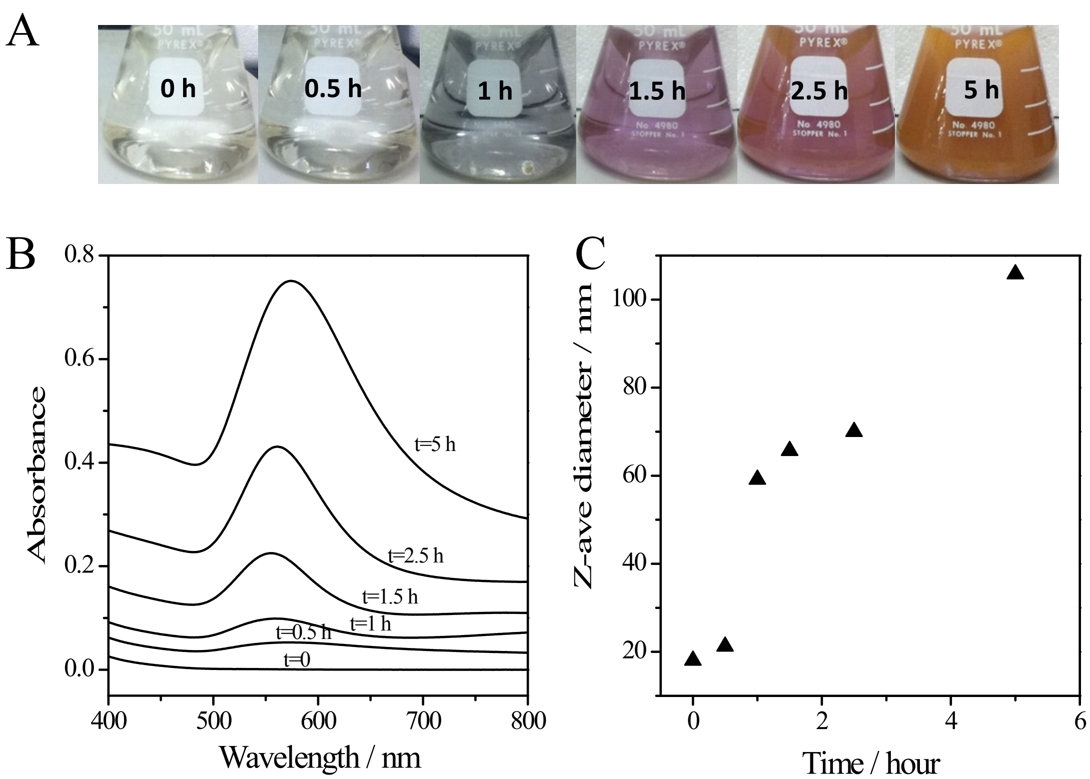

Figure S5. Seed mediated growth with mixed solution of $HAuCl_4$ (0.254 mM), Au seeds (3.3×10^9 particles/mL), and Na_3Ctr (0.17 mM) at room temperature. (A) optical images, (B) absorption spectra and (C) hydrodynamic diameter of growth solutions in different times.

Table S5. The percentage of nanoplates and nanorods in AuNP sample D – I.

Sample	D	E	F	G	H	I
n (# of nanoplates and nanorods)	21	14	15	32	16	17
N (total # of particles counted)	216	148	156	343	126	213
Percentage / (n/N) × 100%	9.7	9.5	9.6	9.3	12.7	8.0

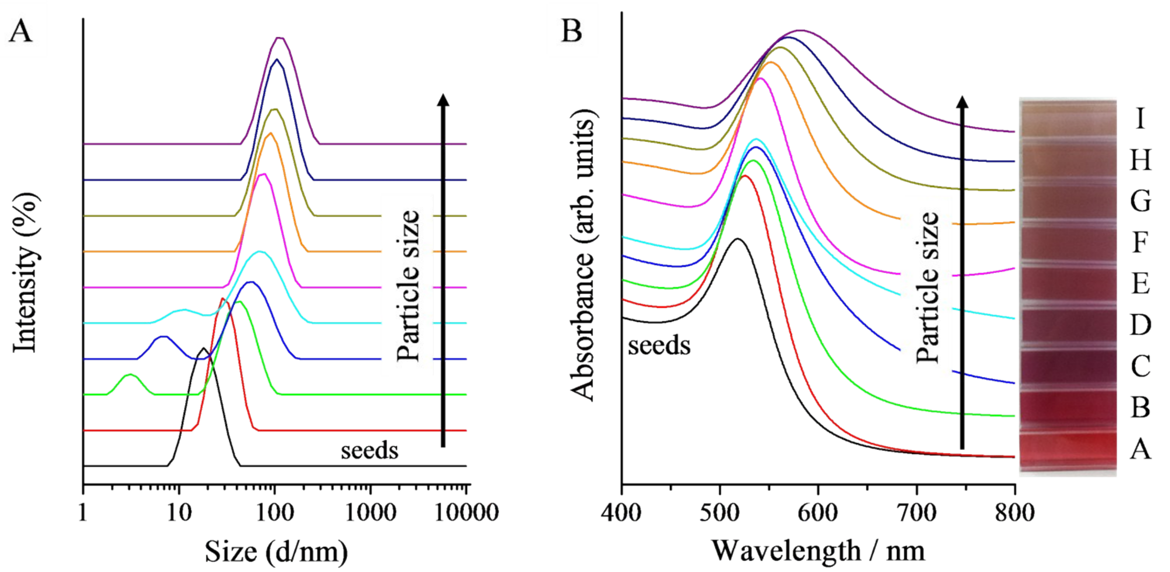

Figure S6. (A) Size distributions by intensity (DLS) and (B) absorption spectra of a set of seeded growth prepared samples with increased size and shifted SPR.

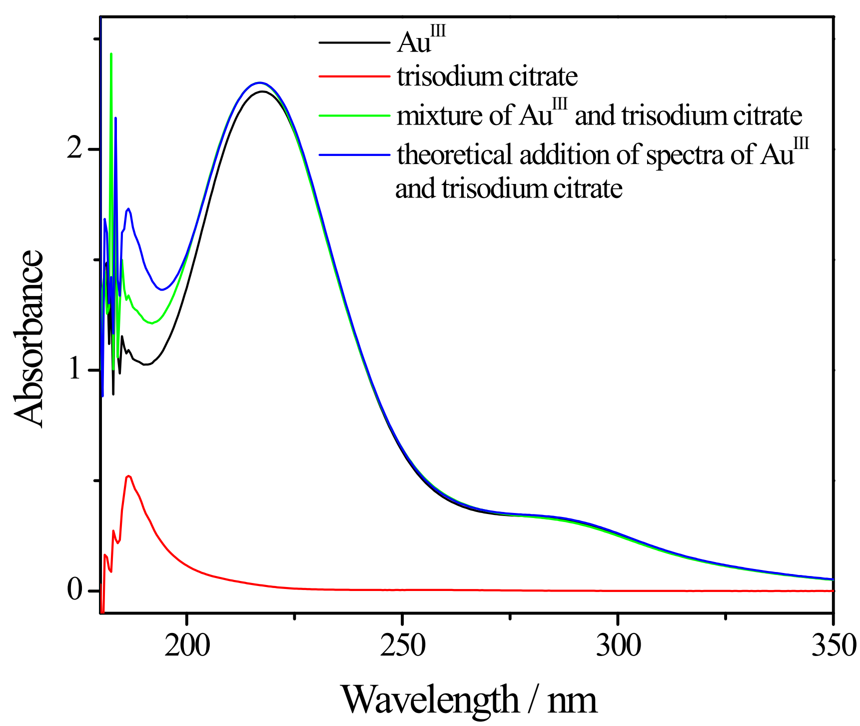

Figure S7. UV absorption spectra of $[AuCl_4]^-$ (0.127mM, black solid line), Na_3Ctr (0.088 mM, red line) and a mixture of the same volume of $[AuCl_4]^-$ and Na_3Ctr with final concentrations of 0.127 mM and 0.088 mM respectively (green line). Blue line is the expected spectrum for the mixture based upon the combination of the spectra for $[AuCl_4]^-$ and Na_3Ctr.

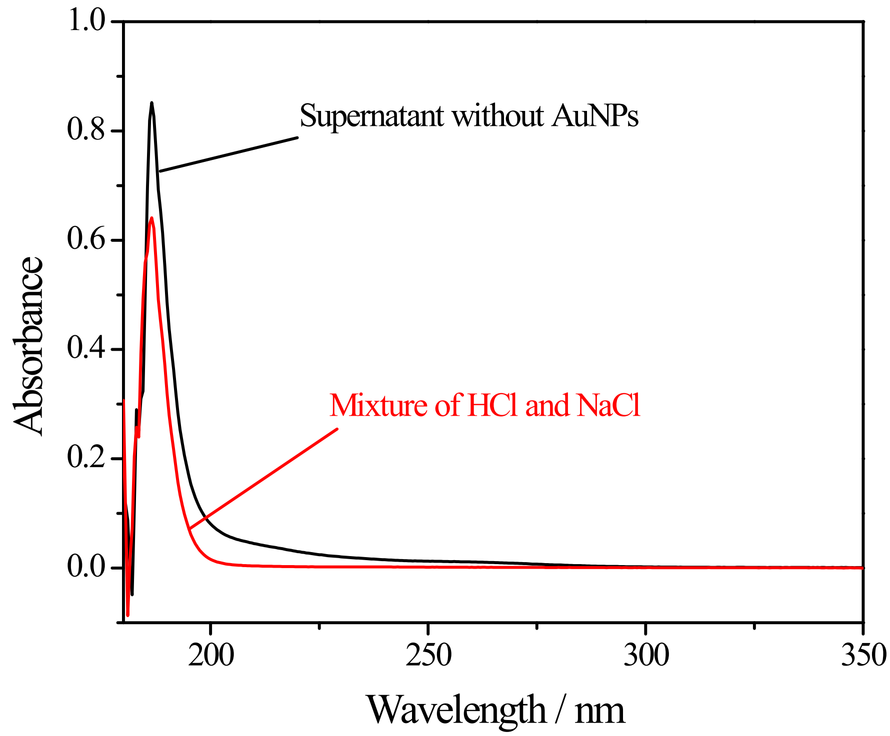

Figure S8. Comparison of UV absorbance between supernatant from a completely reacted Au solution and a simulation mixture of HCl and NaCl. The final concentrations of HCl and NaCl are based on the stoichiometry of equation 11.

46 nm seed mediated AuNPs prepared at 100 ^oC. In brief, 0.818 mL seed suspension and 0.44 mL of 38.8 mM Na_3Ctr were quickly added to a boiling solution of 100 mL of 0.254 mM $HAuCl_4$ under vigorous stirring. After a reaction period of 30 min, the AuNP suspension was cooled down at room temperature under stirring.

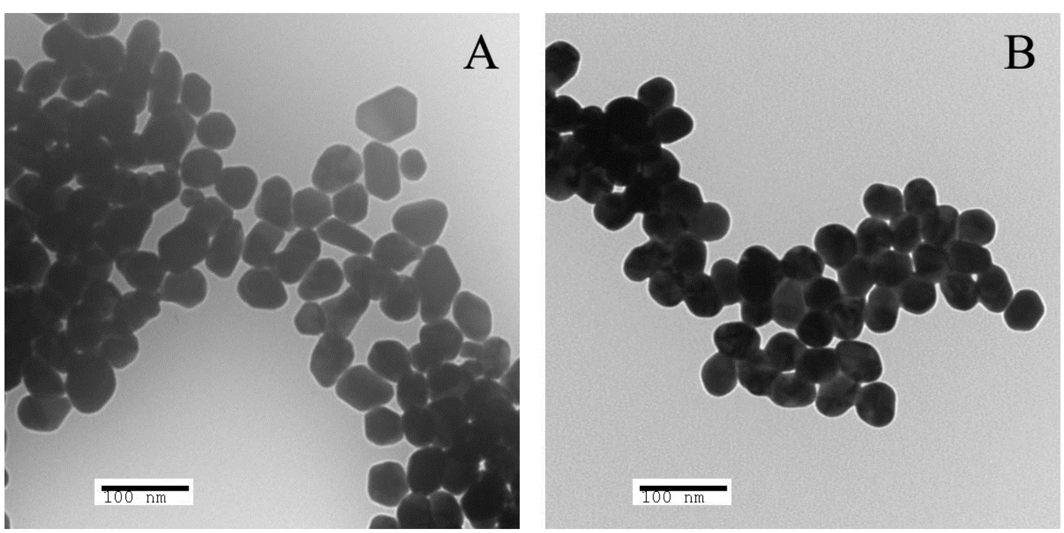

Figure S9. TEM images of seed mediated 46 nm AuNPs produced at room temperature (A) and at 100 °C (B).

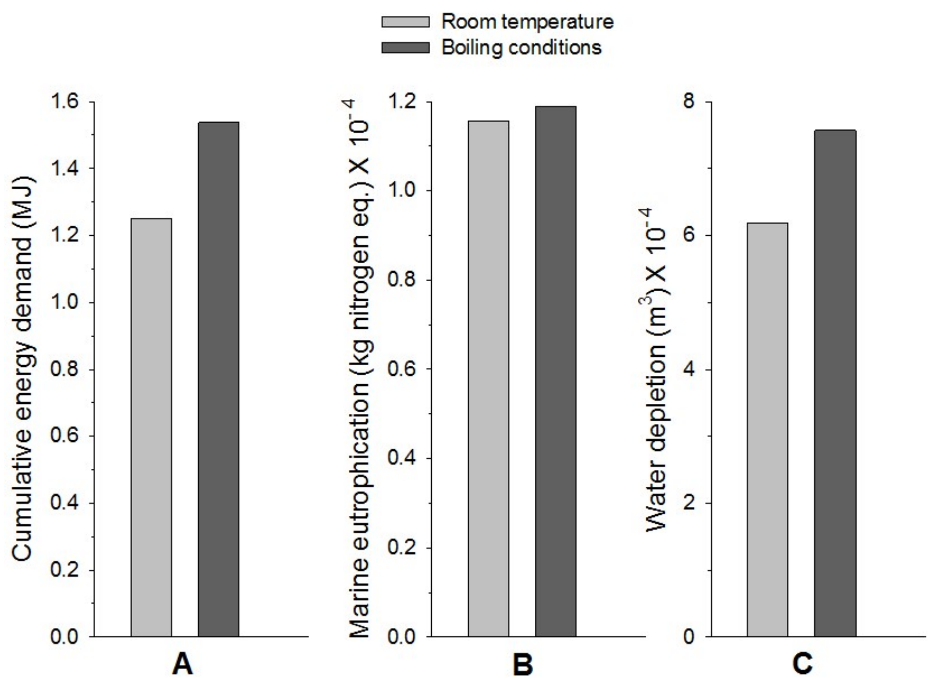

Figure S10. Cumulative energy demand (CED), marine eutrophication and water depletion for 1 mg of 46 nm AuNP synthesis at 100 °C vs. room temperature. AuNP synthesis at room temperature has lower environmental impacts than synthesis under boiling conditions,

Uncertainty analysis: LCA results typically involve *correlated* uncertainties. For example, some chemicals and processes from the life cycle inventories (such as gold, water, electricity etc.) are common to both synthesis methods - the room temperature AuNP synthesis and synthesis under boiling conditions. In such cases, the uncertainty for a chemical (say, gold) is common to both models, and therefore *correlated*[6]. In the case of correlated uncertainties, differences in results may be statistically significant, even if the error bars for their 95% confidence intervals overlap. Therefore, we have chosen to represent uncertainty in our LCA by comparing the actual Monte Carlo simulations instead of comparing 95% confidence intervals. As mentioned in the main manuscript, uncertainty analyses were performed using Monte-Carlo simulations for 1000 runs. As shown in Figure S7, a majority of those 1000 simulations showed that across all impact categories, AuNP synthesis at room temperature has a lower environmental impact than previously reported methods that involved boiling conditions.

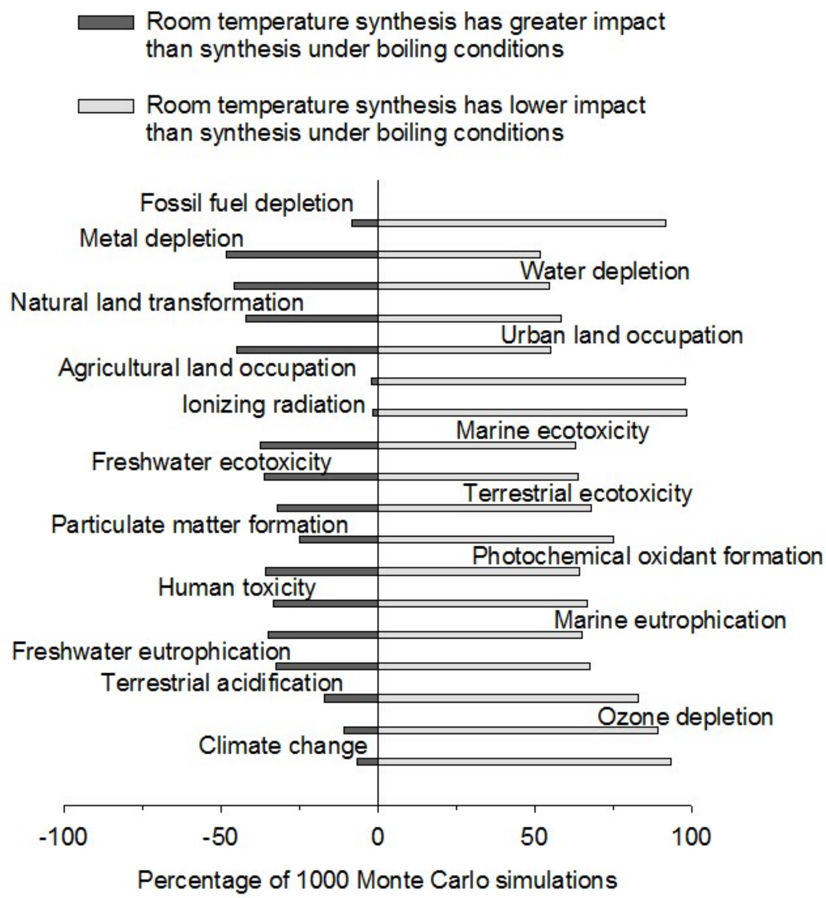

Figure S11. The percentage of 1000 Monte Carlo simulations showing that across all impact categories, most simulations show that the environmental impacts for room temperature AuNP synthesis are lower than those for synthesis under boiling conditions.

References:

1. Nanotechnology, V.T.C.f.S., In 2014.
2. Machesky, M.L.; Andrade, W.O.; Rose, A.W., Adsorption of Gold(Iii)-Chloride and Gold(I)-Thiosulfate Anions by Goethite. *Geochimica et Cosmochimica Acta* **1991,** *55*, (3), 769-776 (doi:10.1016/0016-7037(91)90340-B).
3. Xie, J.; Lee, J.Y.; Wang, D.I.C.; Ting, Y.P., Identification of Active Biomolecules in the High-Yield Synthesis of Single-Crystalline Gold Nanoplates in Algal Solutions. *Small* **2007,** *3*, (4), 672-682 (doi:10.1002/smll.200600612).
4. Brown, S.; Sarikaya, M.; Johnson, E., A Genetic Analysis of Crystal Growth. *J. Mol. Biol.* **2000,** *299*, (3), 725-735 (doi:10.1006/jmbi.2000.3682).
5. Shao, Y.; Jin, Y.; Dong, S., Synthesis of Gold Nanoplates by Aspartate Reduction of Gold Chloride. *Chemical Communications (Cambridge, United Kingdom)* **2004**, (9), 1104-1105 (doi:10.1039/b315732f).
6. Goedkoop, M.; Schryver, A.D.; Oele, M.; Roest, D.D.; Vieira, M.; Durksz, S., Simapro 7 Tutorial. *PRé Consultants* **2010**,