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Supplementary Information

Size tunable elemental copper nanoparticles: extracellular synthesis by thermoanaerobic bacteria and capping molecules.

Gyoung Gug Jang[a], Christopher B. Jacobs[b], Ryan G. Gresback[b], Ilia N. Ivanov[b], Harry M. Meyer III[c], Michelle Kidder[d], Tommy J. Phelps[a], Pooran C. Joshi[c], Gerald E. Jellison Jr[c], David E. Graham[a], Ji-Won Moon[a*]

[a] Biosciences Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831, USA

[b] Center for Nanophase Materials Sciences Division, ORNL, Oak Ridge, TN 37831

[c] Materials Science and Technology Division, ORNL, Oak Ridge, TN 37831

[d] Chemical Science Division, ORNL, Oak Ridge, TN 37831

Table S1. Summary of various bio-synthesized Cu NPs

Cu NPs	Reaction time	Surfactant (In situ) (wt.%)	Surfactant (post dose)	XRD analysis	CuNPs	Reaction time	Surfactant (In situ)	Post dose (In situ)	XRD analysis
AbCu	48hr		N/A	Cu^0 (>100nm)	**CuNO**	48hr	Ole_0.1		No reduction
	48hr		NTA_0.1	Cu^0(>100nm)		48hr		NTA+Ole_0.1	Cu^0(70nm)
	48hr		ASC_0.1	Cu^0(>100nm)		**48hr**		**NTA+Ole_0.2**	**Cu^0(28nm)**
	48hr		Cys_0.1	Cu^0(>100nm)		48hr		NTA+Ole_0.5	Cu0 + Partial Phase transition to Cu_2O
	48hr		Ole_01	Cu^0(>100nm)					
BCu	40hr		N/A	Amorphous	**CuNA**	48+1hr		Asc_0.1	Cu^0 + Cu_2O(>100nm)
	48hr		N/A	Amorphous		**48+1hr**		**NTA_0.1+ Asc_0.1**	**Cu^0(53nm)**
	56hr		N/A	Cu^0 + Cu_2O(>100nm)		48+1hr		NTA_0.1+ Asc_0.2	Cu^0 + Cu_2O(71nm)
	64hr		N/A	Cu^0(>100nm)		48+1hr		NTA_0.1+ Asc_0.5	Cu^0 + Cu_2O(44nm)
	72hr		**N/A**	**Cu^0(>100nm)**	**CuNC**	**48+1hr**		**L-cysteine**	**No reduction**
CuN	0hr	NTA_0.2		No crystallization		**48+1hr**		**NTA+cys_0.2**	**Cu^0(62nm)**
	48hr	NTA_0.2		No crystallization	**CuNM**	48+1hr		Oleylamin_0.2	No reduction
	72hr	NTA		No crystallization		48+1hr		**NTA+Olem_0.2**	**Cu^0(55nm)**
	48+1hr		**NTA_0.1**	**Cu^0 + Cu_2O(50nm)**	CuNS	48+1hr		(NH4)2S_0.1	CuS
	48+1hr		NTA_0.2	Cu^0 + Cu_2O(54nm)					
	48+1hr		NTA_0.5	Phase transition to amorphous Cu_2O					

- Abiotic Cu crystallites (AbCu), Biotic Cu crystallites (BCu), NTA addition to BCu (CuN), L-cysteine addition to CuN (CuNC), Ascorbic acid addition to CuN (CuNA), Oleic acid addition to CuN (CuNO), Oleylamine addition to CuN (CuNM
- Optimized elemental Cu NP formation condition was represented to boldening.

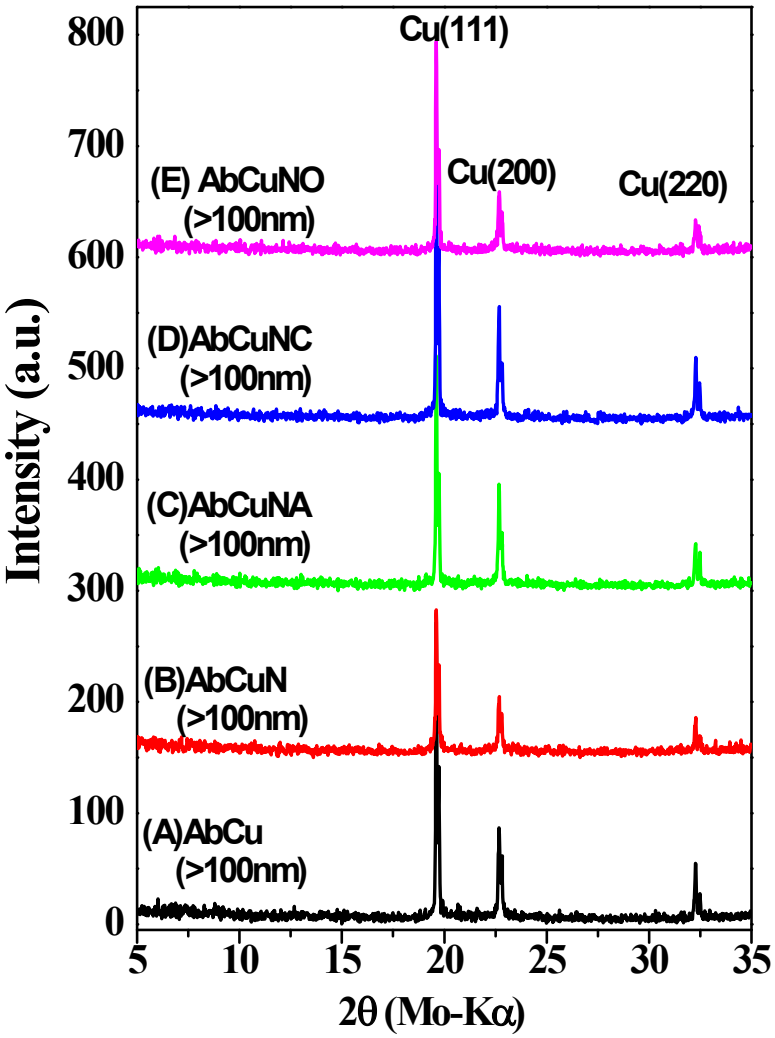

Fig. S1 XRD patterns of abiotic Cu crystallites which formed at 1 day incubation via addition of additives. In order to reduce crystallite size with < 100 nm, various surfactants were added at 0 and 1 day abiotic Cu incubation. However, it did not show elemental Cu reduction at 0 day (not shown) and formed crystallites with >100 nm at 1 day. (A) Abiotic Cu crystallites (**AbCu**) (B) NTA added Abiotic Cu crystallites (**AbCuN**) (C) NTA and Ascorbic acid added abiotic Cu NP (**AbCuNA**) (D) Cu+NTA+L-cysteine (**AbCuNC**) (E) Cu+NTA+Oleic acid (**AbCuNO**)

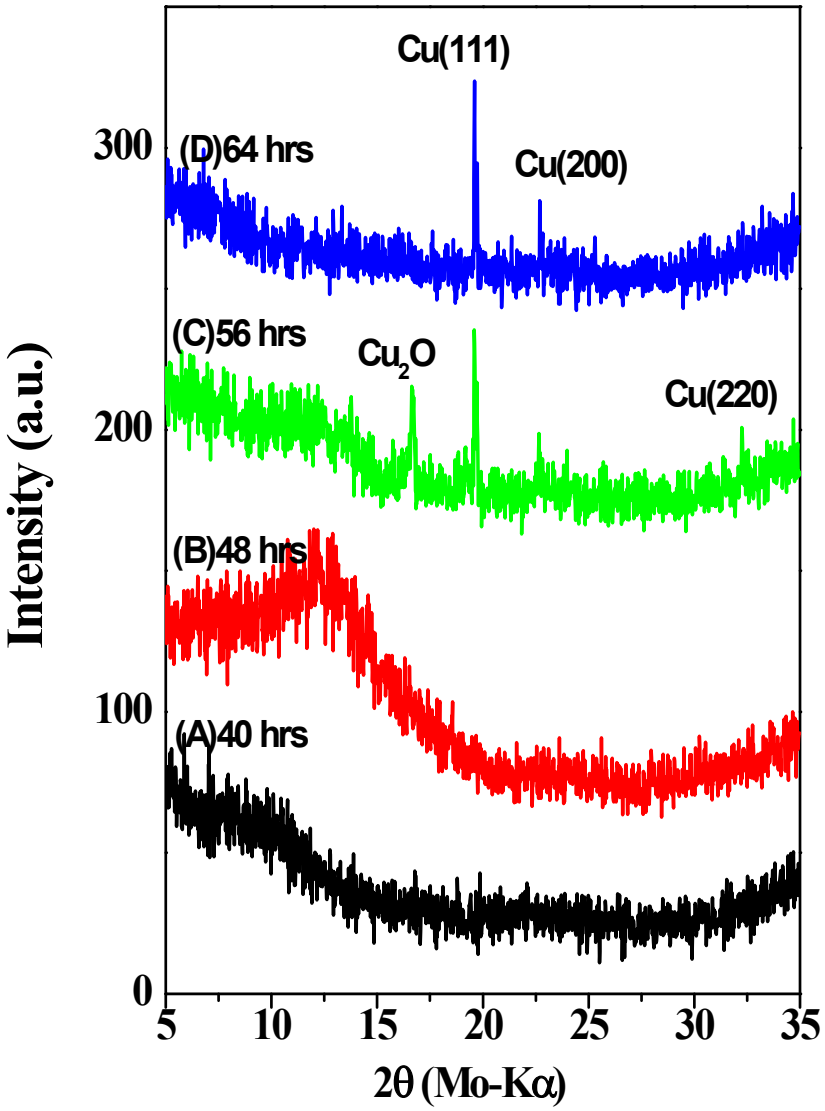

Fig. S2. XRD patterns of biotic Cu (BCu) crystallites. For crystallite growth and size confinement, samples were prepared by various incubation times for 40, 48, 56 and 64 hrs after Cu inoculation. BCu crystallites was produced after 56 hrs, however did not showed average crystallite size (ACS) confinement to less than 100 nm. Both ACS of (C) and (D) were >100 nm. The uncapped biotic Cu crystallite ((C) 56 hrs incubation) appeared to be oxidized during XRD measurement (~30 min).

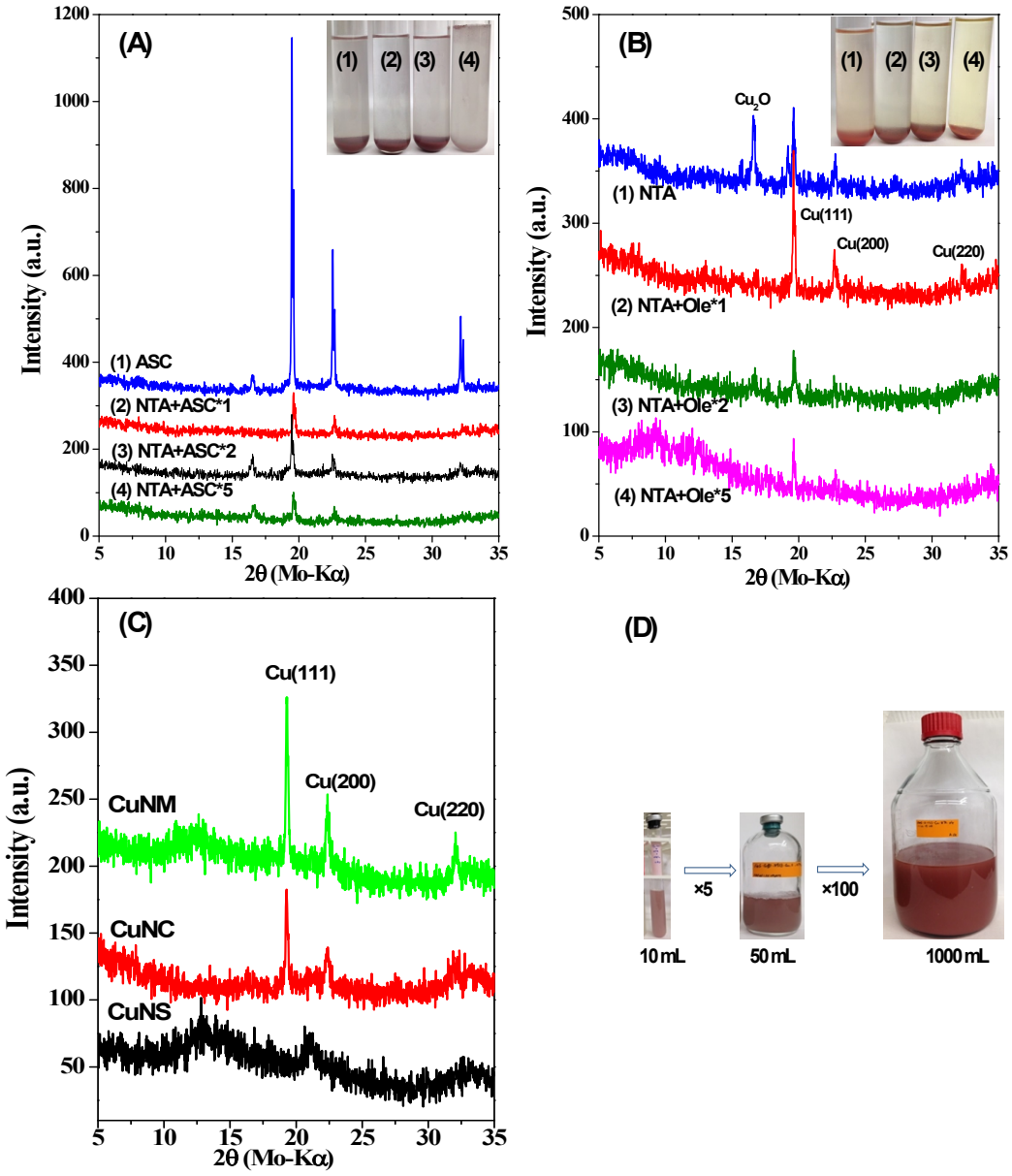

Fig. S3. (A) XRD patterns of ascorbic acid effect on biotic Cu NP formation; Addition of ascorbic acid formed micron size Cu crystallite without NTA. Addition of NTA and ascorbic acid exhibited size confinement and elemental Cu stabilization (CuNA), however increasing amounts of ascorbic acid was not effective at reducing crystallite size and stabilizing. (B) XRD patterns of Oleic acid effect on CuN NP formation; the optimized ratio of NTA and Oleic acid ((2) NTA+Ole*2) reduced size in nano-dimension and stabilize it (CuNO). (C) XRD patterns of Oleylamine, L-cysteine, and ammonium sulfide effects on CuN NP formation; Oleylamine (CuNM) and L-cysteine (CuNC) form nano-crystallites, however ammonium sulfide (CuNS) formed copper sulfide. (D) Scalability of microbially facilitated synthesis of elemental Cu NP with oleic acid was tested for increasing medium volume from 10 mL to 1000 mL reactor.

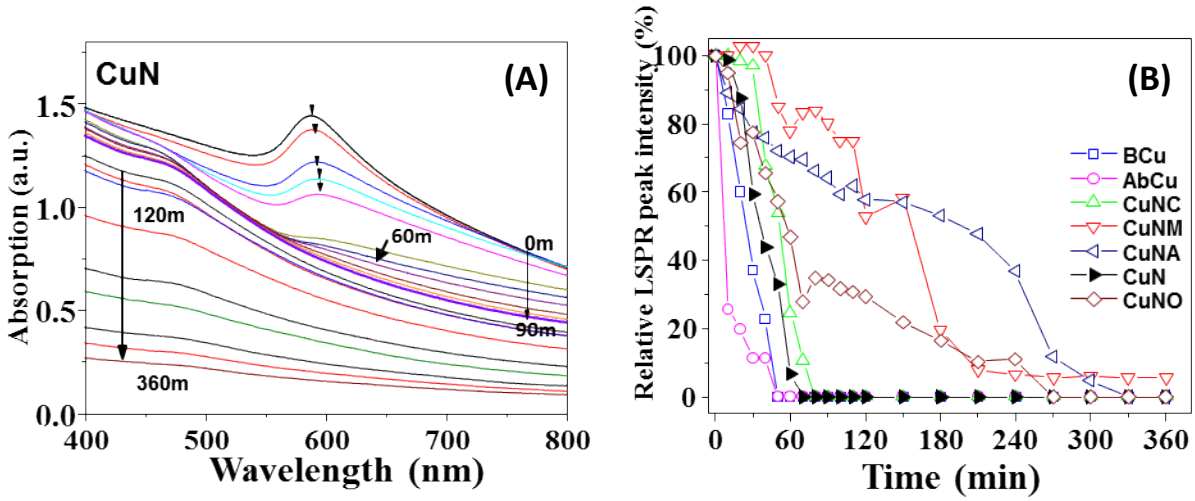

Fig. S4 (a) Corresponding spectra of CuN NPs changed as the NP oxidized (spectra were measured every 10 min for 120 min and every 30 min after 120 min). (b) The relative LSPR peak intensity (%) changed during the oxidation process.

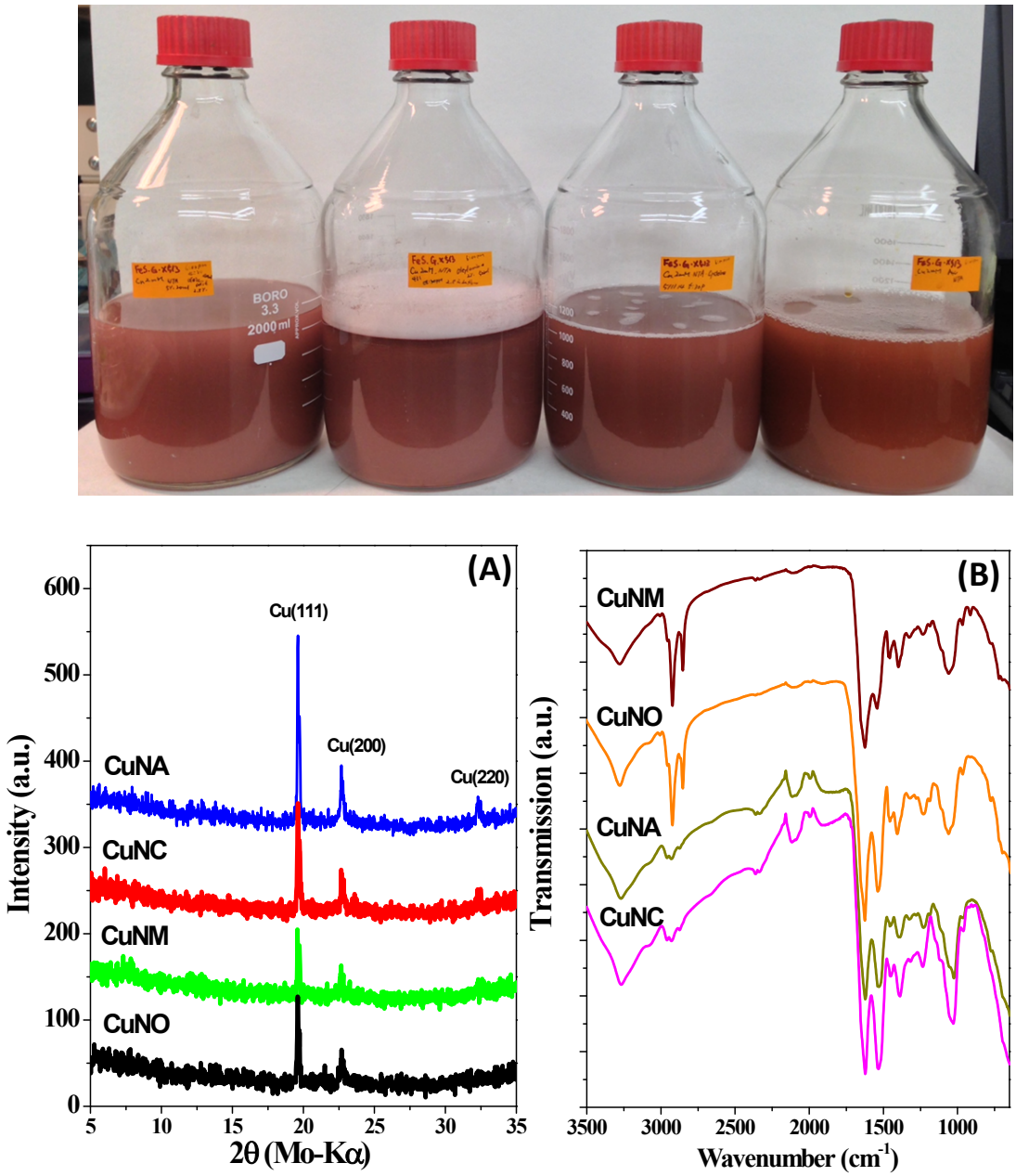

Fig. S5. Scale-up of elemental Cu NPs with ascorbic acid, L-cysteine, oleylamine and oleic acid for 1000 mL reactor. (A) XRD patterns of capped Cu NPs (B) FTIR spectra of indicated Cu NP. Scaling showed no significant influence on crystal structure and chemical surface structure. For CuNO, the bending mode of C=O at 1710 cm^{-1} disappeared after scale-up.