Supplementary material

Formation mechanism of micro-sized Cu plates using Br ions as basal plane-specific adsorbent and their application in the preparation of highly conductive and flexible Cu films

Yusaku Noda, [a] Shun Yokoyama, *[a] Takashi Ito [b] and Balachandran Jayadevan [a]

[a] Graduate School of Environmental Studies, Tohoku University, 6-6-20, Aramaki, Aoba-ku, Sendai, 980-8579, Japan

[b] Frontier Research Institute for Interdisciplinary Sciences, Tohoku Univdersity, Aramaki aza Aoba 6-3, Aoba-ku, Sendai 980-8578, Japan

*Corresponding author. E-mail: shun.yokoyama.c2@tohoku.ac.jp

Tel: +81-22-795-3871 Fax: +81-22-795-7392

Content:

Table S1. Stability constants for constracting pH–potential diagrams at 25°C.

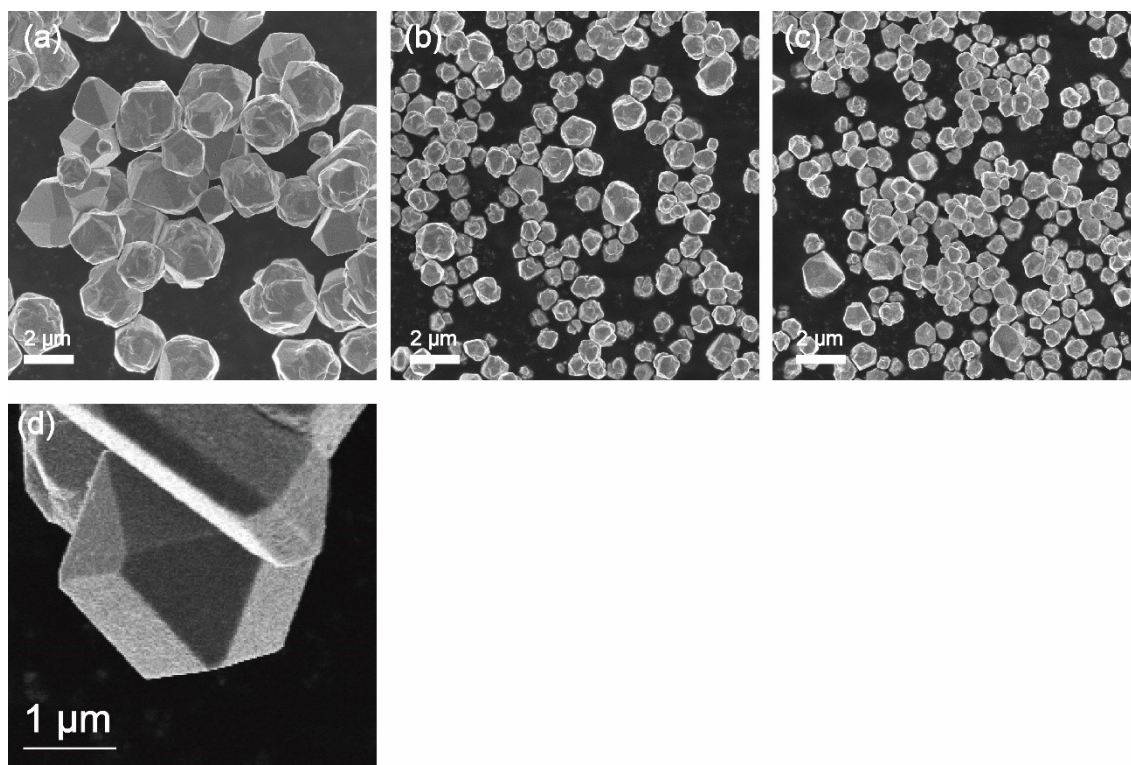| Reaction	Log K
$H_2O = H^+ + OH^-$	14.002
$H^+ + L^- = HL$	-3.81
$Cu^{2+} + L^- = CuL^+$	2.45
$Cu^{2+} + 2L^- = CuL_2$	4.08
$Cu^{2+} + 2L^- = Cu(H_{-1}L)L^- + H^+$	-2.87
$Cu^{2+} + 2LA^- = Cu(H_{-1}L)_2^{2-} + 2H^+$	-11.82
$Cu^{2+} + 2e^- = Cu$	11.395
$Cu^{2+} + H_2O + e^- = 2H^+ + Cu_2O$	7.155
$Cu^{2+} + Br^- + e^- = CuBr$	11.133

Fig. S1. SEM micrographs of Cu particles obtained at pH (a) 3.5, (b) 4.5, and (c) 5.5 without Br ions. (d) SEM micrograph of 14-hedral particles observed at pH 5.5.
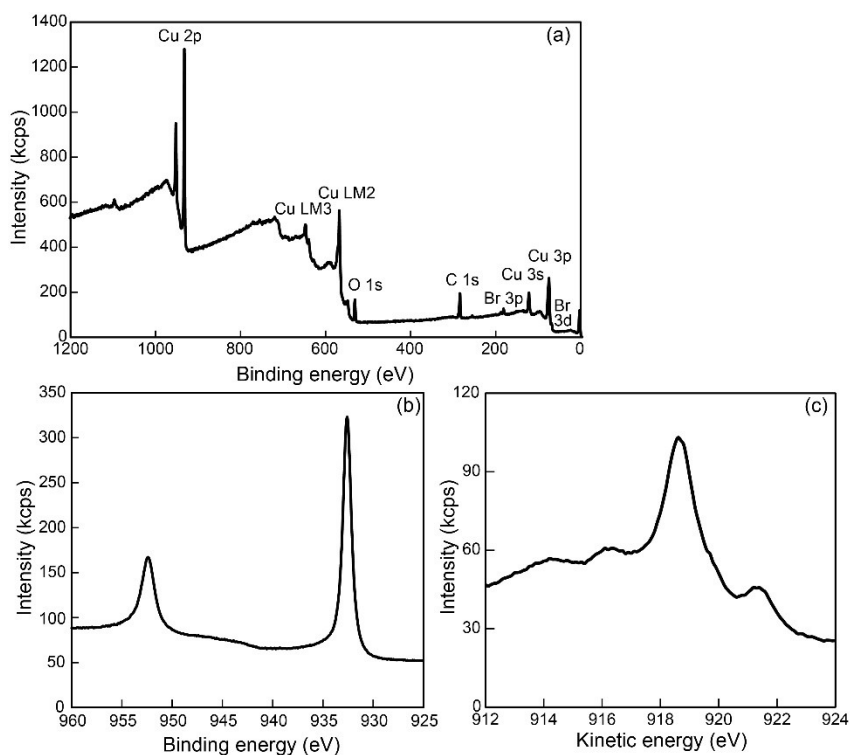
Fig. S2. XPS profiles in (a) the wide scan, (b) the Cu 2p, and (c) the Cu LMM region of Cu particle synthesized at pH 5.5 with Br ions.

Table S2. Peak area ratio of deconvoluted C 1s peaks to C1 of Cu particles obtained at various conditions with Br ions and reference materials.

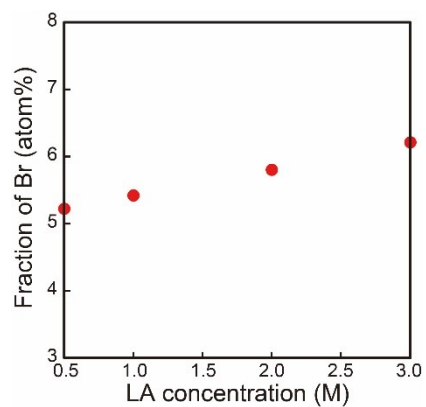| Synthesis condition	C1	C2	C3	C4	C5
pH 3.5, LA 0.50 mol/l	1	0.18	0.17	0.12	0.05
pH 5.5, LA 0.50 mol/l	1	0.15	0.11	0.07	0.03
pH 7.5, LA 0.50 mol/l	1	0.14	0.12	0.07	0.04
pH 5.5, LA 1.0 mol/l	1	0.13	0.11	0.05	0.03
pH 5.5, LA 2.0 mol/l	1	0.10	0.11	0.05	0.03
pH 5.5, LA 2.0 mol/l	1	0.09	0.11	0.05	0.02
Reference					
Silver lactate	1	0.72	-	0.62	-
Reference					
Ascorbic acid	1	-	38	-	7.7

Fig. S3. XPS elemental composition of Br and Cu calculated from the peaks in the Cu 2p and Br 3d region of Cu particles synthesized at pH 5.5 and various LA concentrations.
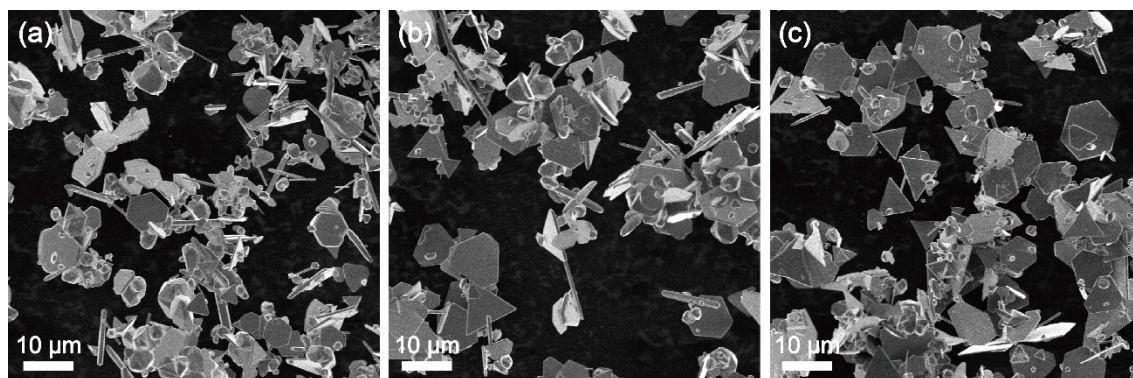

Fig. S4. SEM micrographs of Cu particles synthesized at LA concentration (a) 1.0 mol/l, (b) 2.0 mo/l and (c) 3.0 mol/l.
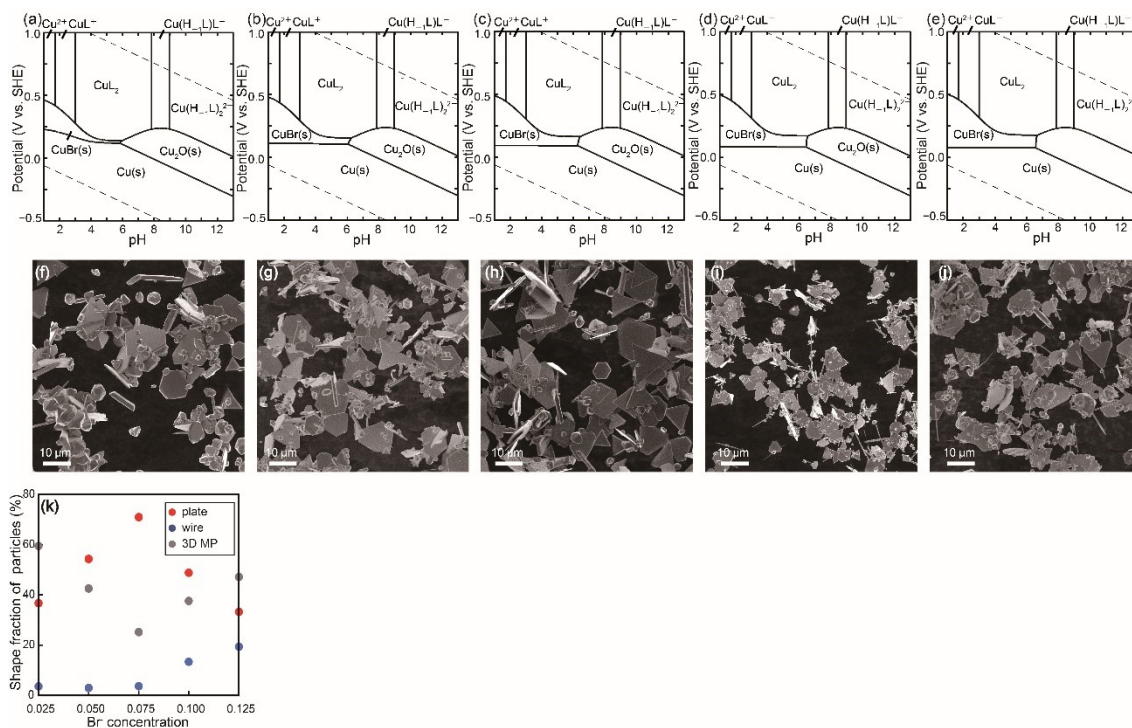
Fig. S5. The pH–potential diagram of the Cu–Br–LA–H$_2$O system at Cu^{2+} = 0.050 mol/l, LA = 3.0 mol/l and Br$^-$ = (a) 0.025, (b) 0.050, (c) 0.075, (d) 0.100, or (e) 0.125 mol/l. The dotted lines show the redox potential of water. HL stands for lactic acid, and H and L denote proton and ligand, respectively. SEM images of Cu particles obtained at pH 5.5, Cu^{2+} = 0.050 mol/l, LA = 3.0 mol/l and Br$^-$ = (f) 0.025, (g) 0.050, (h) 0.075, (i) 0.100, or (j) 0.125 mol/l. (k) The shape fractions determined from the SEM images.
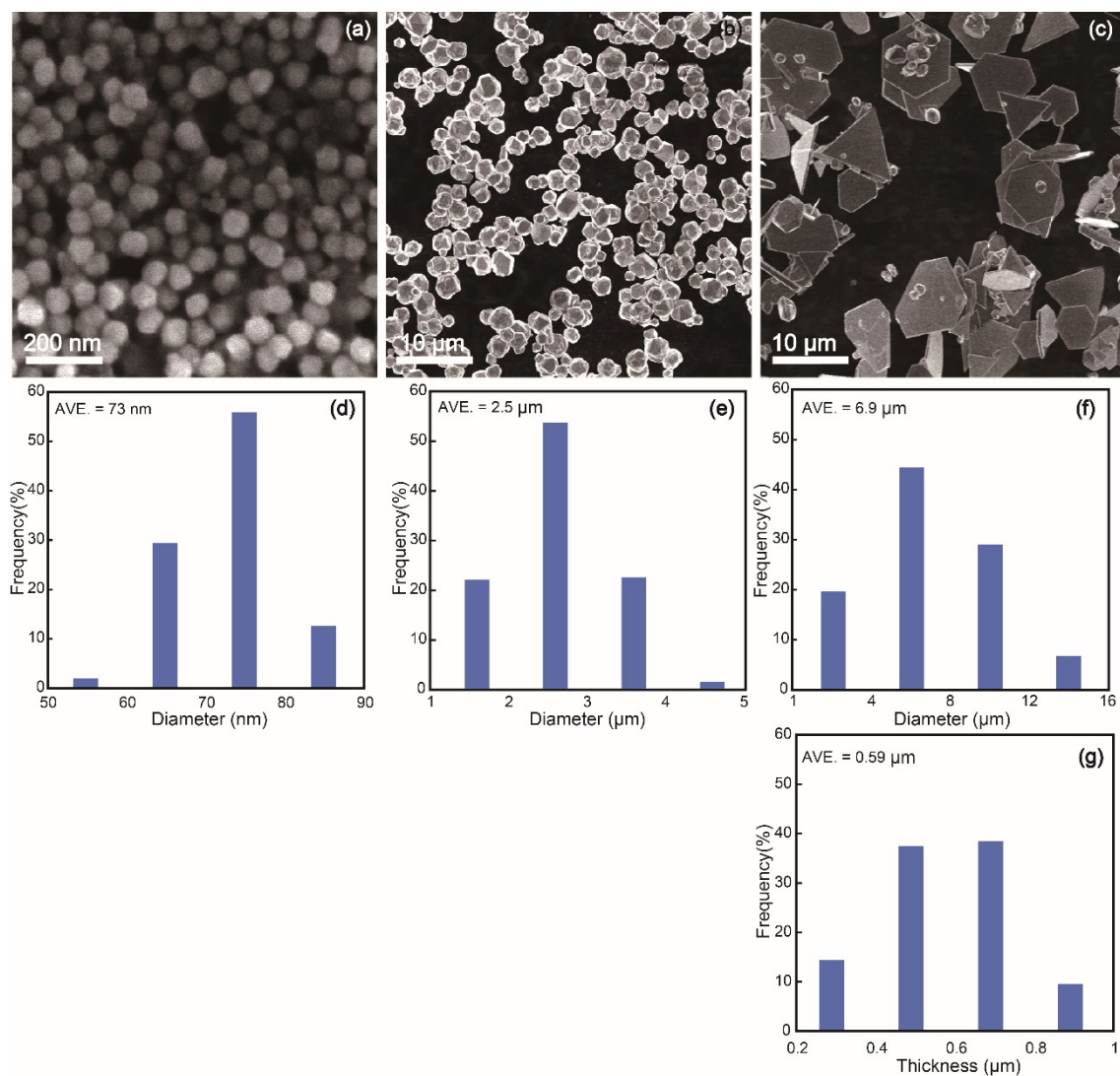
Fig. S6. SEM micrographs and size distributions of (a) and (d) Cu NPs, (b) and (e) 3D MPs, and (c), (f), and (g) MPLs used for evaluating their sintering properties.
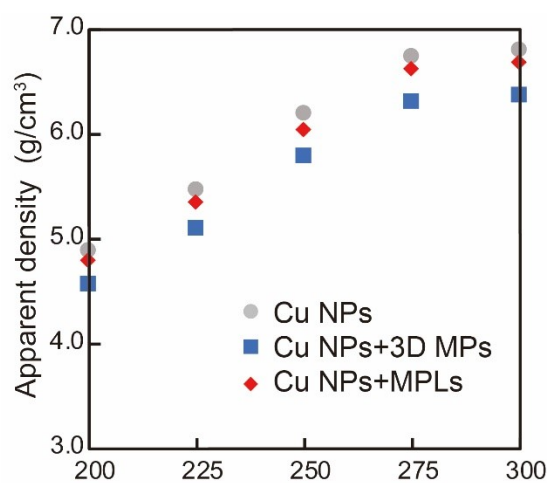
Fig. S7. Apparent density of thin Cu films after sintering at various temperatures.
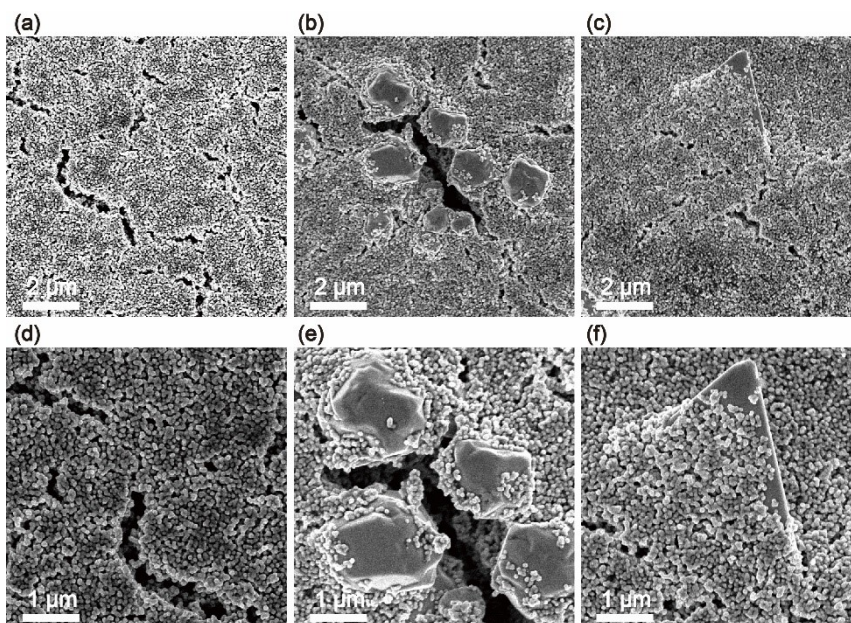

Fig. S8 SEM images of (a, d) Cu NPs, (b, e) mixture of Cu NPs and 3D MPs, and (c, f) mixture of Cu NPs and MPLs after sintering at 300 °C. (d), (e) and (f) are the enlarged view of (a), (b) and (c), respectively.