Phase-Selective Synthesis of Bornite Nanoparticles

Alex M. Wiltrout, Nathaniel J. Freymeyer, Tony Machani, Daniel P. Rossi, and Katherine E. Plass[a*]

Supporting Information:

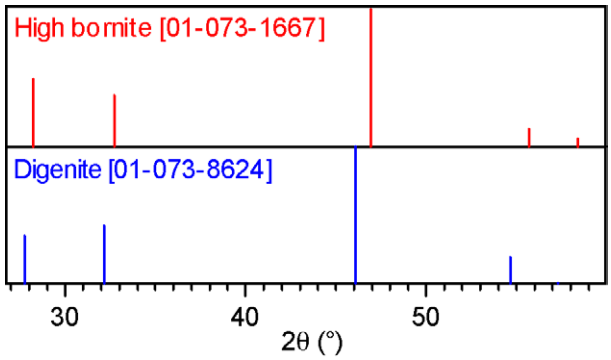

Figure S1. ICDD database PXRD patterns of high bornite [01-073-1667] and digenite [01-073-8624].

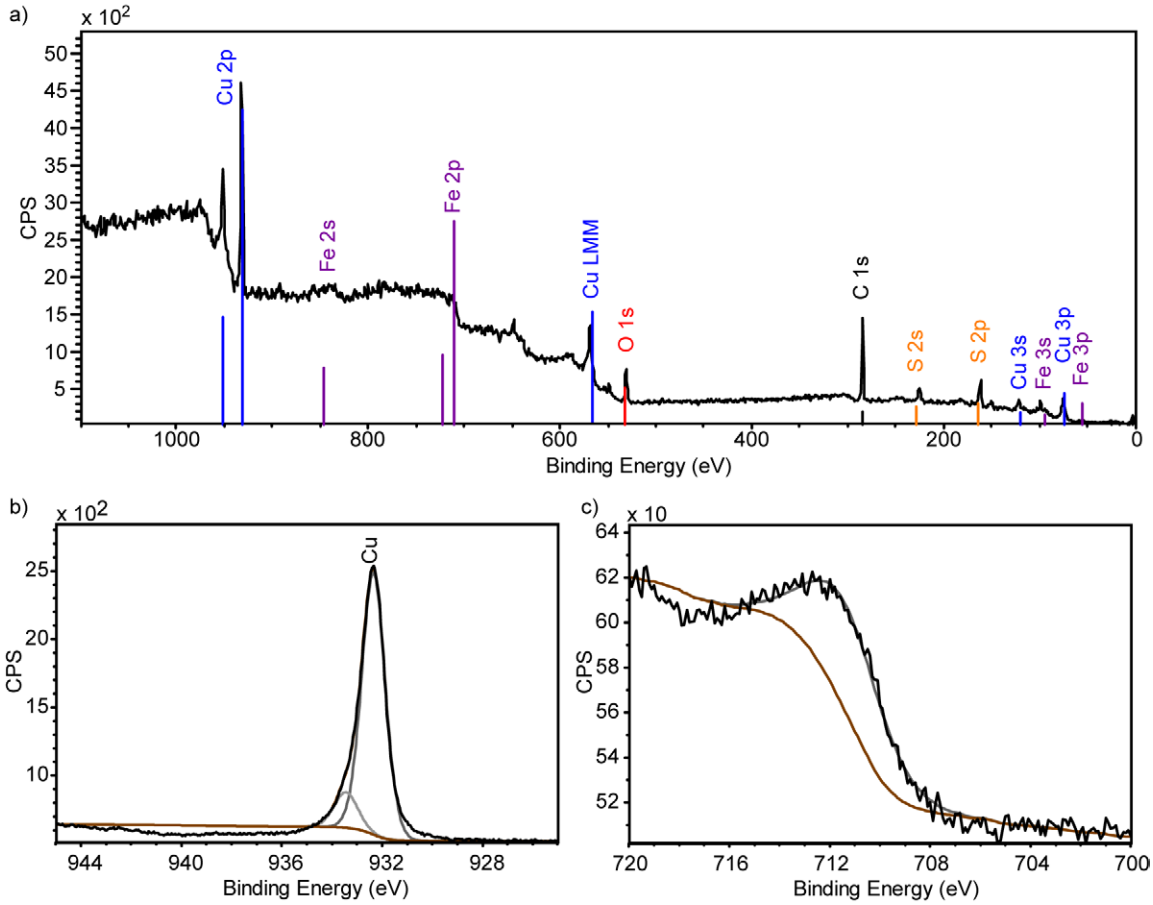

Figure S2. X-ray photoelectron spectra of bornite nanoparticles. a) Survey scan shows the presence of Fe, Cu, S, and C as expected for 1-dodecanethiol-coated bornite particles. O is present as well, suggesting that oxidation of the surface may have occurred to some degree. b) The Cu 2p 3/2 region shows primarily a peak centered at 932.3 eV, which is expected of Cu^{+} species. A shoulder peak reveals the presence of a small amount of Cu^{2+}. c) The Fe 2p 3/2 region shows a broad peak that extends from 708 eV to 716 eV, encompassing the range of values observed for the Fe ion in FeS, Fe2O3, and CuFeS2. (Wagner, C. D.; Naumkin, A. V.; Kraut-Vass, A.; Allison, J. W.; Powell, C. J.; Rumble, J. R., NIST Standard Reference Database 20, Version 3.5. 2003.)

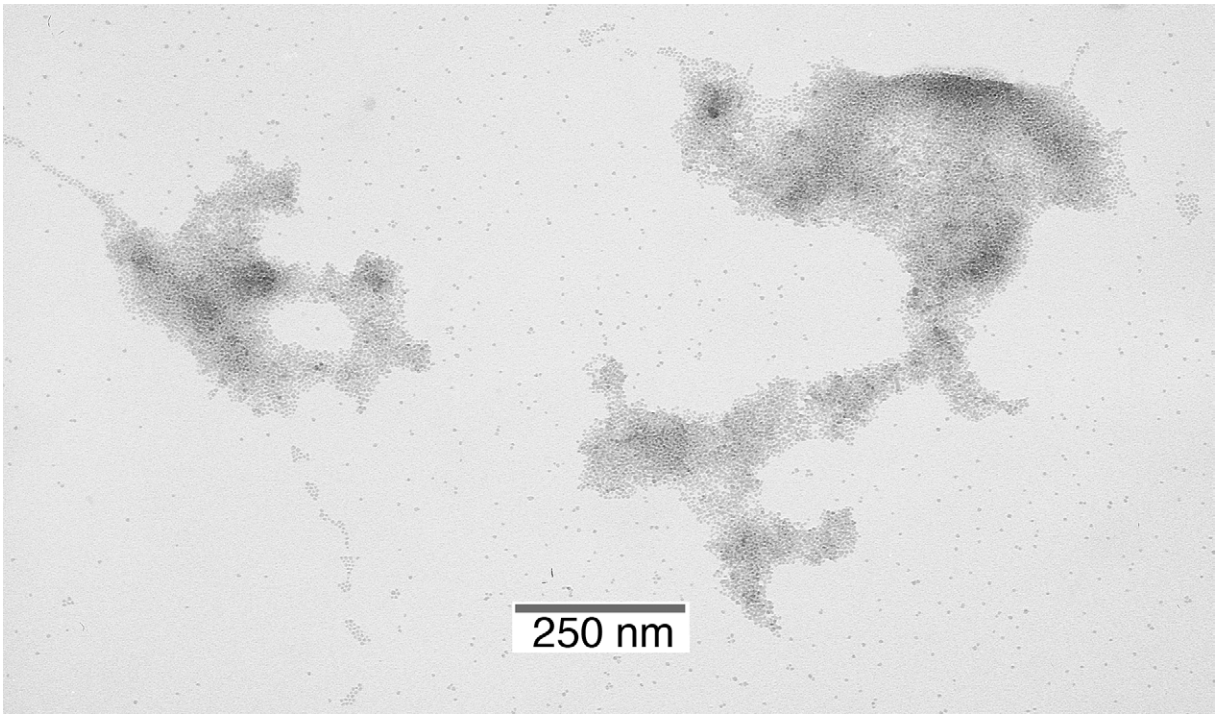

Figure S3. TEM image (50,000x) of high bornite nanoparticles obtained at 180 °C.

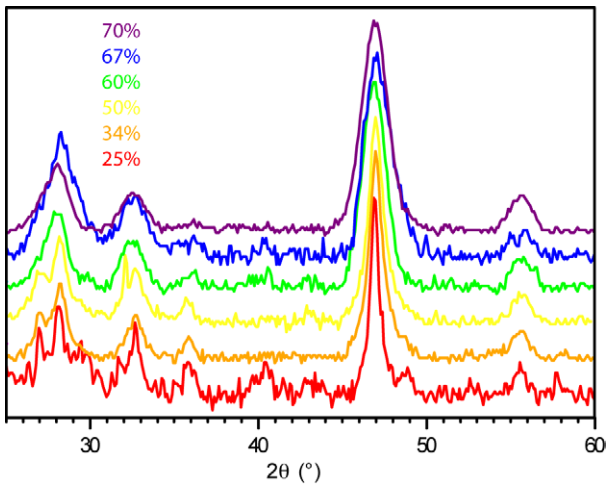

Figure S4. PXRD patterns of nanoparticles obtained from 80 mM of S, 50 mM Cu(II)$(acac)_2$, and 10 mM Fe(III)$(acac)_3$ in solutions of various 1-dodecanethiol/oleic acid ratios. The percentage of 1-dodecanethiol is shown in the legend. The peak at 47° 2θ increases in width with the amount of 1-dodecanethiol, independently from the particle size (at 34% 1-dodecanethiol the particle diameter was 9.4 ± 2.7 nm while at 65% 1-dodecanethiol the particle diameter was 9.3 ± 3.2 nm).

Table S1. Mass percent measurements used for calculation of stoichiometries.

	low bornite nanoparticles			high bornite nanoparticles		
	S mass %	Fe mass %	Cu mass %	S mass %	Fe mass %	Cu mass %
1	15.43	10.13	74.45	29.10	6.70	64.20
2	28.3	7.80	63.91	27.77	7.20	65.03
3	22.26	8.29	69.44	26.19	7.41	66.41
4	33.06	8.82	58.12	30.74	6.48	62.78
5	30.36	8.74	60.89	25.95	6.74	67.31
6	29.57	8.55	61.88	29.78	7.38	62.84
7	33.06	8.82	58.12	28.61	8.03	63.36
8	30.36	8.74	60.89	24.41	7.71	67.88
9	29.57	8.55	61.88			
Average	29.57	8.54	61.89	27.82	7.21	64.98
Standard Deviation	3.39	0.35	3.62	2.15	0.54	2.02

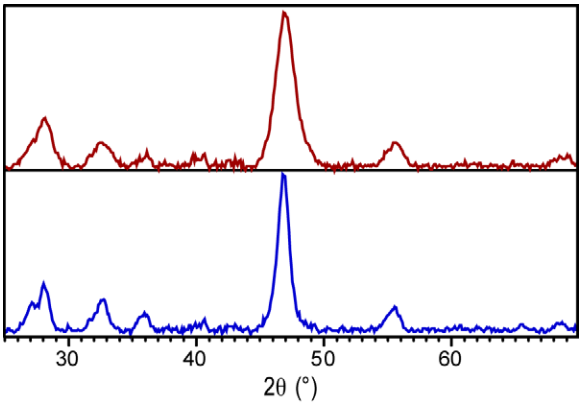

Figure S5. PXRD patterns of low bornite particles obtained after 6 hours with 50 mM (top) and 80 mM (bottom) of S, 50 mM Cu(II)(acac)$_2$, and 10 mM Fe(III)(acac)$_3$.

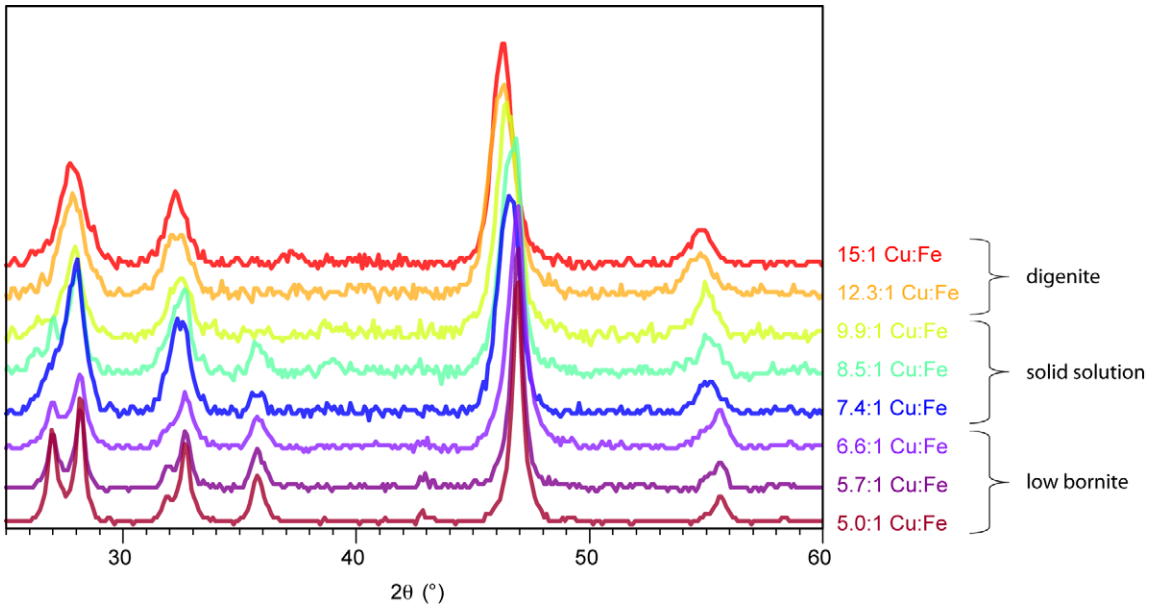

Figure S6. PXRD patterns of nanoparticles obtained with 80 mM of S and 10 mM Fe(III)$(acac)_3$, and varying amounts of Cu(II)$(acac)_2$ in the mole ratios given above.