Supporting information: Influence of organic compounds on the sulfidation of copper oxide nanoparticles

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Tables

Table S1: Characteristics of the raw wastewater sample (0.4 µm filtered, aerated)

Parameter	Value	Unit
DOC	536	mg L^{-1}
Cl	214	mg L^{-1}
Na	42.2	mg L^{-1}
K	7.7	mg L^{-1}
Ca	77.4	mg L^{-1}
Mg	10.6	mg L^{-1}
Cu	0.89	mg L^{-1}

Table S2: LCF results along with statistical parameters for samples collected at increasing reaction times of the sulfidation of CuO NP with HS^- (1.3 mM CuO, 4 mM HS^-) in the presence or absence of different organic compounds, obtained from XANES spectra between 8964 and 9064 eV.

Time [min]	Organic compound	Concentration [mg L^{-1}]	CuO	LCF error	Cu_xS primitive	LCF error	CuS (Covellite)	LCF error	Sum	R-factor	Red. χ^2	χ^2
0	None	0	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	None	0	0.51	0.00278	0.39	0.01188	0.10	0.01337	1.01	1.32E-04	2.28E-05	3.79E-03
5	None	0	0.28	0.00430	0.51	0.01848	0.21	0.02079	1.03	3.09E-04	5.40E-05	8.21E-03
15	None	0	0.19	0.00523	0.52	0.02240	0.28	0.02520	1.02	5.05E-04	8.11E-05	1.35E-02
60	None	0	0.10	0.00409	0.34	0.01758	0.55	0.01979	1.01	2.94E-04	4.89E-05	7.44E-03
180	None	0	0.01	0.00480	0.09	0.02055	0.90	0.02312	1.02	4.26E-04	6.83E-05	1.13E-02
0	BSA	1000	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	BSA	1000	0.54	0.00330	0.39	0.01421	0.08	0.01599	1.02	1.72E-04	3.19E-05	4.86E-03
5	BSA	1000	0.45	0.00298	0.37	0.01283	0.17	0.01444	1.01	1.46E-04	2.60E-05	3.96E-03
15	BSA	1000	0.43	0.00254	0.41	0.01091	0.16	0.01228	1.01	1.06E-04	1.88E-05	2.86E-03
60	BSA	1000	0.36	0.00362	0.42	0.01556	0.22	0.01751	1.01	2.20E-04	3.83E-05	5.82E-03
180	BSA	1000	0.32	0.00316	0.36	0.01361	0.32	0.01531	1.01	1.68E-04	2.93E-05	4.45E-03
300	BSA	1000	0.29	0.00649	0.53	0.02706	0.19	0.03093	1.04	6.72E-04	1.25E-04	1.68E-02
0	ALG	1000	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	ALG	1000	0.43	0.00323	0.43	0.01389	0.14	0.01564	1.02	1.72E-04	3.06E-05	4.64E-03
5	ALG	1000	0.28	0.00355	0.53	0.01528	0.19	0.01720	1.02	2.15E-04	3.70E-05	5.62E-03
15	ALG	1000	0.22	0.00358	0.52	0.01538	0.26	0.01730	1.01	2.21E-04	3.75E-05	5.70E-03
60	ALG	1000	0.11	0.00350	0.39	0.01506	0.50	0.01694	1.01	2.14E-04	3.59E-05	5.45E-03
180	ALG	1000	0.04	0.00283	0.11	0.01218	0.86	0.01371	1.01	1.40E-04	2.35E-05	3.57E-03
0	PAA	1000	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	PAA	1000	0.46	0.00565	0.32	0.02429	0.23	0.02734	1.03	5.05E-04	9.34E-05	1.43E-02
5	PAA	1000	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

15	PAA	1000	0.23	0.00390	0.47	0.01677	0.29	0.01887	1.02	2.63E-04	4.45E-05	6.81E-03
60	PAA	1000	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
180	PAA	1000	0.03	0.00401	0.12	0.01724	0.85	0.01940	1.02	2.83E-04	4.70E-05	7.20E-03
0	HA	600	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	HA	600	0.48	0.00580	0.50	0.02419	0.00	0.02765	1.00	5.52E-04	9.97E-05	1.36E-02
5	HA	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15	HA	600	0.22	0.00836	0.75	0.03487	0.07	0.03985	1.08	1.06E-03	2.07E-04	2.82E-02
60	HA	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
180	HA	600	0.06	0.00740	0.41	0.03085	0.54	0.03525	1.04	9.13E-04	1.62E-04	2.20E-02
0	BSA	100	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	BSA	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	BSA	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15	BSA	100	0.28	0.00356	0.51	0.01531	0.21	0.01723	1.01	2.17E-04	3.71E-05	5.67E-03
60	BSA	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
180	BSA	100	0.09	0.00332	0.30	0.01430	0.61	0.01609	1.02	1.94E-04	3.24E-05	4.95E-03
0	ALG	100	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	ALG	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	ALG	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15	ALG	100	0.21	0.00399	0.53	0.01707	0.26	0.01920	1.02	2.89E-04	4.71E-05	7.82E-03
60	ALG	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
180	ALG	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
0	HA	100	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	HA	100	0.48	0.00820	0.53	0.03418	0.00	0.03906	1.05	1.06E-03	1.99E-04	2.71E-02
5	HA	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15	HA	100	0.21	0.00866	0.74	0.03609	0.04	0.04124	1.03	1.27E-03	2.22E-04	3.02E-02
60	HA	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
180	HA	100	0.02	0.01109	0.37	0.04622	0.64	0.05283	1.08	2.01E-03	3.64E-04	4.95E-02
0	BSA	10	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	BSA	10	0.44	0.00325	0.44	0.01393	0.11	0.01567	1.01	1.86E-04	3.14E-05	5.21E-03
5	BSA	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15	BSA	10	0.19	0.00400	0.53	0.01712	0.28	0.01926	1.02	2.94E-04	4.74E-05	7.87E-03
60	BSA	10	0.11	0.00331	0.37	0.01422	0.53	0.01600	1.02	1.90E-04	3.21E-05	4.87E-03
180	BSA	10	0.02	0.00423	0.16	0.01809	0.82	0.02035	1.02	3.30E-04	5.29E-05	8.78E-03
0	ALG	10	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	ALG	10	0.43	0.00339	0.50	0.01450	0.07	0.01631	1.02	2.03E-04	3.40E-05	5.64E-03
5	ALG	10	0.29	0.00330	0.49	0.01421	0.22	0.01599	1.01	1.86E-04	3.19E-05	4.86E-03
15	ALG	10	0.20	0.00383	0.54	0.01639	0.26	0.01844	1.02	2.69E-04	4.34E-05	7.21E-03
60	ALG	10	0.10	0.00366	0.29	0.01572	0.61	0.01769	1.01	2.33E-04	3.91E-05	5.95E-03
180	ALG	10	0.03	0.00424	0.14	0.01814	0.83	0.02041	1.02	3.32E-04	5.32E-05	8.83E-03
0	PAA	10	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	PAA	10	0.46	0.00339	0.47	0.01452	0.07	0.01633	1.01	2.02E-04	3.41E-05	5.66E-03
5	PAA	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15	PAA	10	0.17	0.00436	0.54	0.01867	0.29	0.02100	1.02	3.52E-04	5.63E-05	9.35E-03
60	PAA	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
180	PAA	10	0.02	0.00495	0.12	0.02120	0.87	0.02385	1.03	4.50E-04	7.27E-05	1.20E-02
0	HA	10	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00			
0.25	HA	10	0.47	0.00385	0.44	0.01649	0.09	0.01855	1.02	2.59E-04	4.40E-05	7.30E-03

5	HA	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15	HA	10	0.20	0.00405	0.53	0.01732	0.27	0.01948	1.02	3.00E-04	4.85E-05	8.05E-03
60	HA	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
180	HA	10	0.01	0.00430	0.10	0.01838	0.89	0.02068	1.02	3.42E-04	5.47E-05	9.07E-03
0	FW	536	1.00	0.00199	0.00	0.00000	0.00	0.00000	1.00	0.00E+00	0.00E+00	0.00E+00
0.25	FW	536	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	FW	536	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15	FW	536	0.30	0.00313	0.48	0.01347	0.22	0.01516	1.01	1.67E-04	2.87E-05	4.36E-03
60	FW	536	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
180	FW	536	0.06	0.00376	0.16	0.01617	0.78	0.01820	1.02	2.46E-04	4.14E-05	6.29E-03

n.d.: Not determined

Table S3: LCF results for samples collected at increasing reaction times of the sulfidation of CuO NP with HS^- (1.3 mM CuO, 4 mM HS^-) in the presence or absence of different organic compounds, obtained from EXAFS data between 3 and 8 $Å^{-1}$.

Time [min]	Organic compound	Concentration [mg L^{-1}]	CuO	Cu_xS primitive[1]	CuS (Covellite)	Sum
0	None	0	1.00	0.00	0.00	1.00
0.25	None	0	0.49	0.42	0.14	1.06
5	None	0	0.24	0.67	0.25	1.16
15	None	0	0.34	0.84	0.05	1.23
60	None	0	0.14	0.55	0.46	1.15
180	None	0	0.00	0.26	0.94	1.21
0	BSA	1000	1.00	0.00	0.00	1.00
0.25	BSA	1000	0.56	0.58	0.03	1.17
5	BSA	1000	0.48	0.54	0.05	1.07
15	BSA	1000	0.46	0.43	0.14	1.03
60	BSA	1000	0.38	0.66	0.08	1.12
180	BSA	1000	0.36	0.45	0.28	1.09
300	BSA	1000	0.27	0.70	0.12	1.09
0	ALG	1000	1.00	0.00	0.00	1.00
0.25	ALG	1000	0.43	0.33	0.23	1.00
5	ALG	1000	0.27	0.69	0.13	1.09
15	ALG	1000	0.27	0.67	0.14	1.08
60	ALG	1000	0.14	0.62	0.39	1.15
180	ALG	1000	0.03	0.24	0.91	1.19
0	PAA	1000	1.00	0.00	0.00	1.00
0.25	PAA	1000	0.50	0.51	0.00	1.01
5	PAA	1000	n.d.	n.d.	n.d.	0.00
15	PAA	1000	0.30	0.68	0.14	1.11
60	PAA	1000	n.d.	n.d.	n.d.	0.00
180	PAA	1000	0.04	0.41	0.72	1.17
0	HA	600	1.00	0.00	0.00	1.00
0.25	HA	600	0.40	0.60	0.00	1.00

5	HA	600	n.d.	n.d.	n.d.	0.00
15	HA	600	0.22	1.00	0.00	1.22
60	HA	600	n.d.	n.d.	n.d.	0.00
180	HA	600	0.06	0.54	0.51	1.11
0	BSA	100	1.00	0.00	0.00	1.00
0.25	BSA	100	n.d.	n.d.	n.d.	0.00
5	BSA	100	n.d.	n.d.	n.d.	0.00
15	BSA	100	0.32	0.66	0.14	1.12
60	BSA	100	n.d.	n.d.	n.d.	0.00
180	BSA	100	0.10	0.60	0.49	1.19
0	ALG	100	1.00	0.00	0.00	1.00
0.25	ALG	100	n.d.	n.d.	n.d.	0.00
5	ALG	100	n.d.	n.d.	n.d.	0.00
15	ALG	100	0.26	0.71	0.16	1.12
60	ALG	100	n.d.	n.d.	n.d.	0.00
180	ALG	100	n.d.	n.d.	n.d.	0.00
0	HA	100	1.00	0.00	0.00	1.00
0.25	HA	100	0.44	0.56	0.04	1.03
5	HA	100	n.d.	n.d.	n.d.	0.00
15	HA	100	0.21	0.63	0.15	0.99
60	HA	100	n.d.	n.d.	n.d.	0.00
180	HA	100	0.02	0.23	0.88	1.13
0	BSA	10	1.00	0.00	0.00	1.00
0.25	BSA	10	0.45	0.51	0.09	1.06
5	BSA	10	n.d.	n.d.	n.d.	0.00
15	BSA	10	0.25	0.72	0.16	1.13
60	BSA	10	0.11	0.67	0.38	1.16
180	BSA	10	0.02	0.46	0.74	1.23
0	ALG	10	1.00	0.00	0.00	1.00
0.25	ALG	10	0.46	0.40	0.17	1.03
5	ALG	10	0.30	0.69	0.13	1.13
15	ALG	10	0.24	0.76	0.16	1.16
60	ALG	10	0.14	0.63	0.40	1.17
180	ALG	10	0.00	0.30	0.89	1.19
0	PAA	10	1.00	0.00	0.00	1.00
0.25	PAA	10	0.44	0.39	0.17	1.00
5	PAA	10	n.d.	n.d.	n.d.	0.00
15	PAA	10	0.21	0.61	0.29	1.11
60	PAA	10	n.d.	n.d.	n.d.	0.00
180	PAA	10	0.06	0.32	0.79	1.17
0	HA	10	1.00	0.00	0.00	1.00
0.25	HA	10	0.47	0.68	0.00	1.14
5	HA	10	n.d.	n.d.	n.d.	0.00
15	HA	10	0.21	0.70	0.21	1.12
60	HA	10	n.d.	n.d.	n.d.	0.00
180	HA	10	0.01	0.27	0.88	1.17
0	FW	536	1.00	0.00	0.00	1.00

0.25	FW	536	0.34	0.78	0.00	1.13
5	FW	536	n.d.	n.d.	n.d.	0.00
15	FW	536	0.11	0.37	0.68	1.15
60	FW	536	n.d.	n.d.	n.d.	0.00
180	FW	536	0.14	0.15	0.76	1.05

n.d.: Not determined

Figures

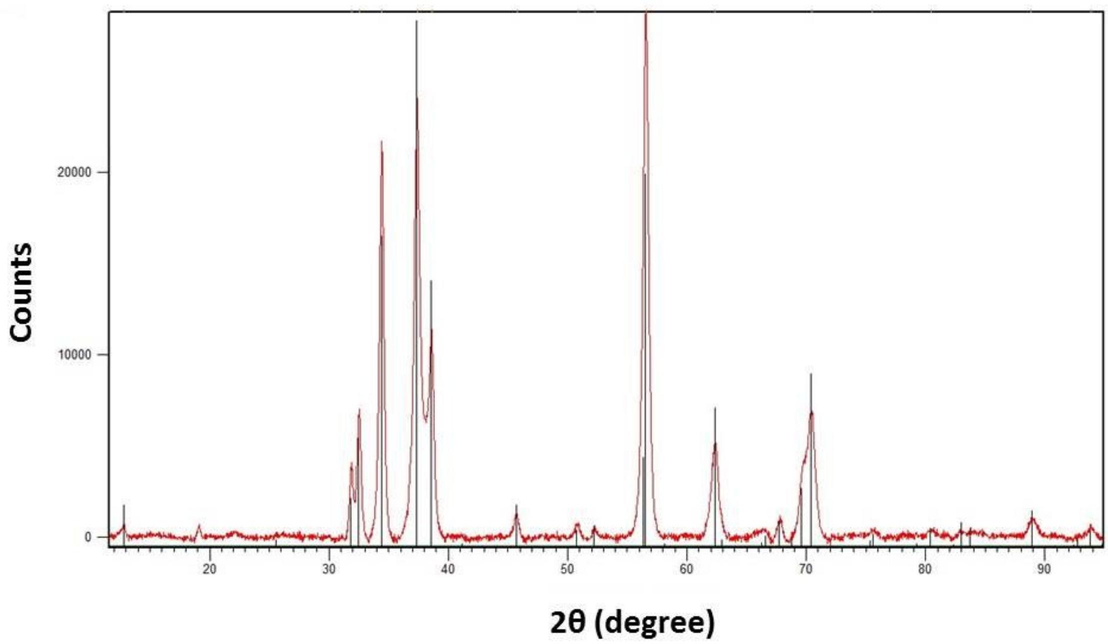

Fig. S1: X-ray powder diffractogram of the CuS reference material (red line). Vertical black lines are peak matches for a covellite reference diffractogram.

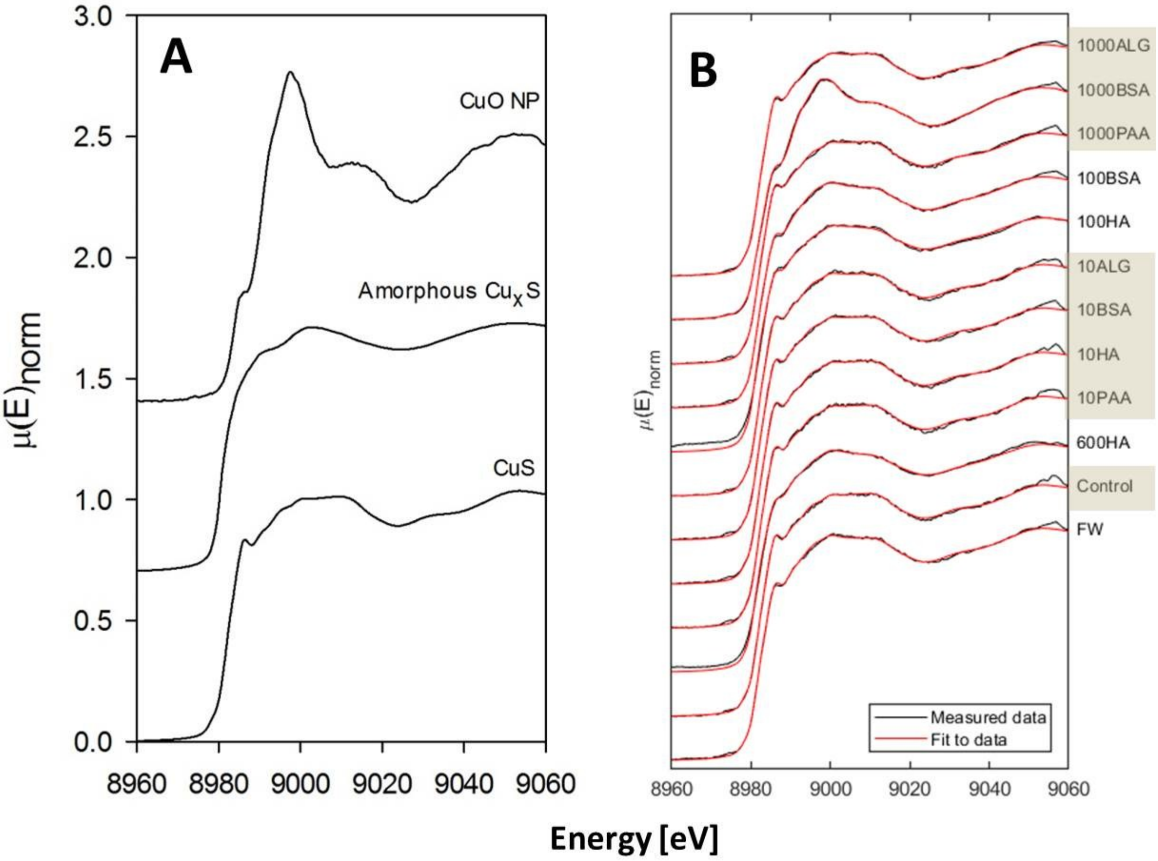

Fig. S2: (A) Normalized XANES spectra of the references used for the LCF analyses .The reference spectrum for amorphous Cu_xS was obtained from Pattrick et al. (see ref[1] Figure 3, 2n – blue/black primitive). (B) Experimental spectra at t = 3 h (solid black lines). "Control" refers to the experiment conducted in the absence of organic compounds. Corresponding LCF fits for each experimental spectrum are shown in solid red lines.

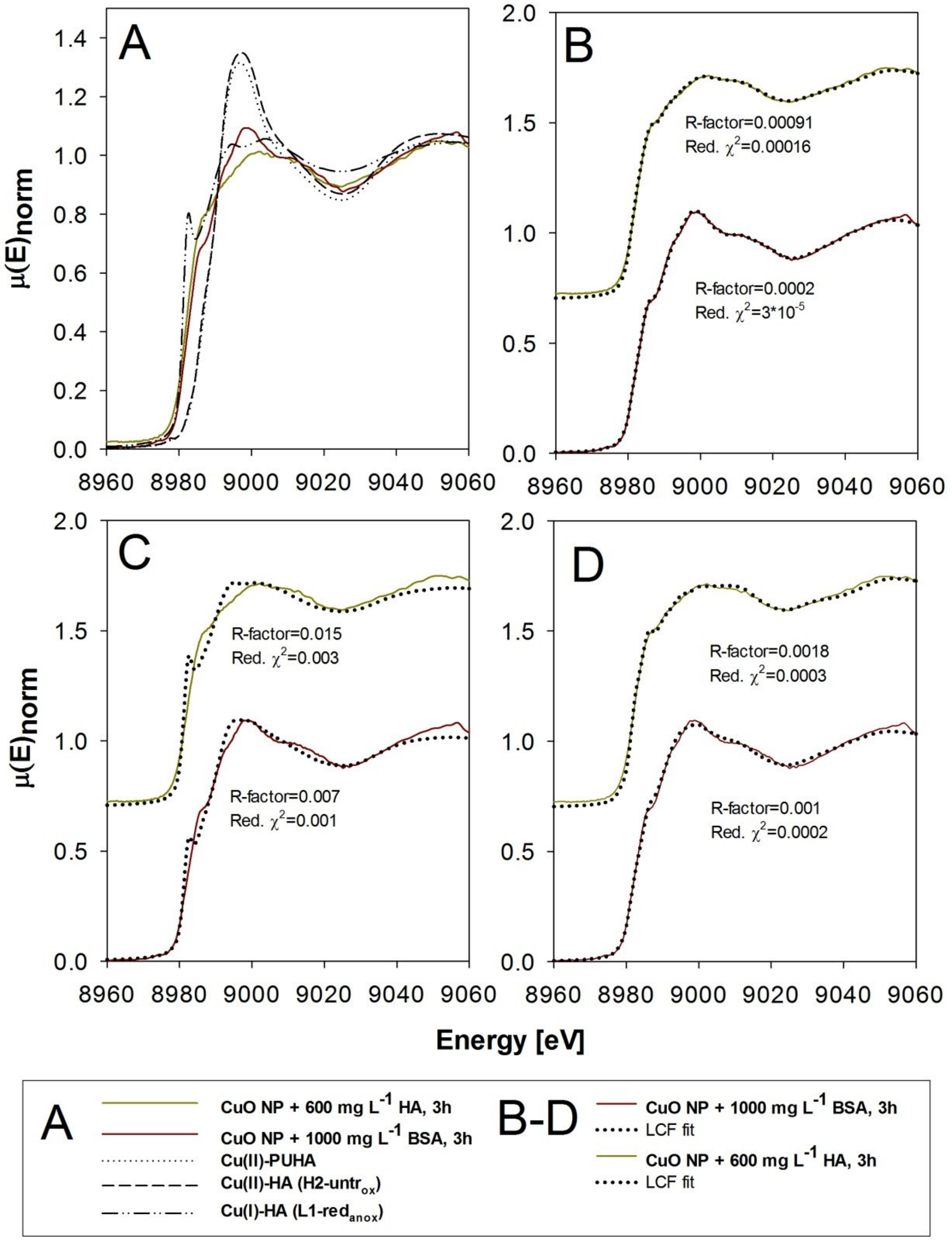

Fig. S3: (A) Normalized XANES spectra of CuO-NP reacted with 1000 mg L^{-1} BSA (dark red line) and 600 mg L^{-1} HA (dark yellow line) at t = 3 h together with references for Cu(II) or Cu(I) complexed to humic acid from Fulda et al.[2] (H2-untr$_{ox}$ and L1-red$_{anox}$, measured at 4 K). Cu(II)-PUHA was measured at room temperature and prepared by mixing 20 mL of a 2.27 gTOC L^{-1} purified Unterrickenzopfen humic acid (PUHA) with 400 µL 0.5M $NaNO_3$, adjusting to pH 6 with 0.1M NaOH, adding 800 µL 50mM $CuCl_2$, shaking slowly for 1h and subsequent freeze drying. (B) LCF fit results for CuO-NP reacted with 1000 mg L^{-1} BSA and 600 mg L^{-1} HA at t = 3 h using the CuO-NP/amorphous Cu_xS and CuS reference shown in Figure S1. (C) LCF fit results using only the three Cu-humic acid complexes shown in A. (D) LCF fit results using the three Cu-humic acid complexes shown in A together with the amorphous Cu_xS and CuS (for BSA) or the CuO and CuS (for HA) reference shown in Figure S1. Statistic parameters (R-factor and reduced χ^2) are given below the graphs. If references for CuO and and for Cu^{2+} complexed to HA were both included in addition to Cu_xS and CuS in the LCF analyses, the reference of CuO was always preferred over Cu^{2+} complexed to HA.

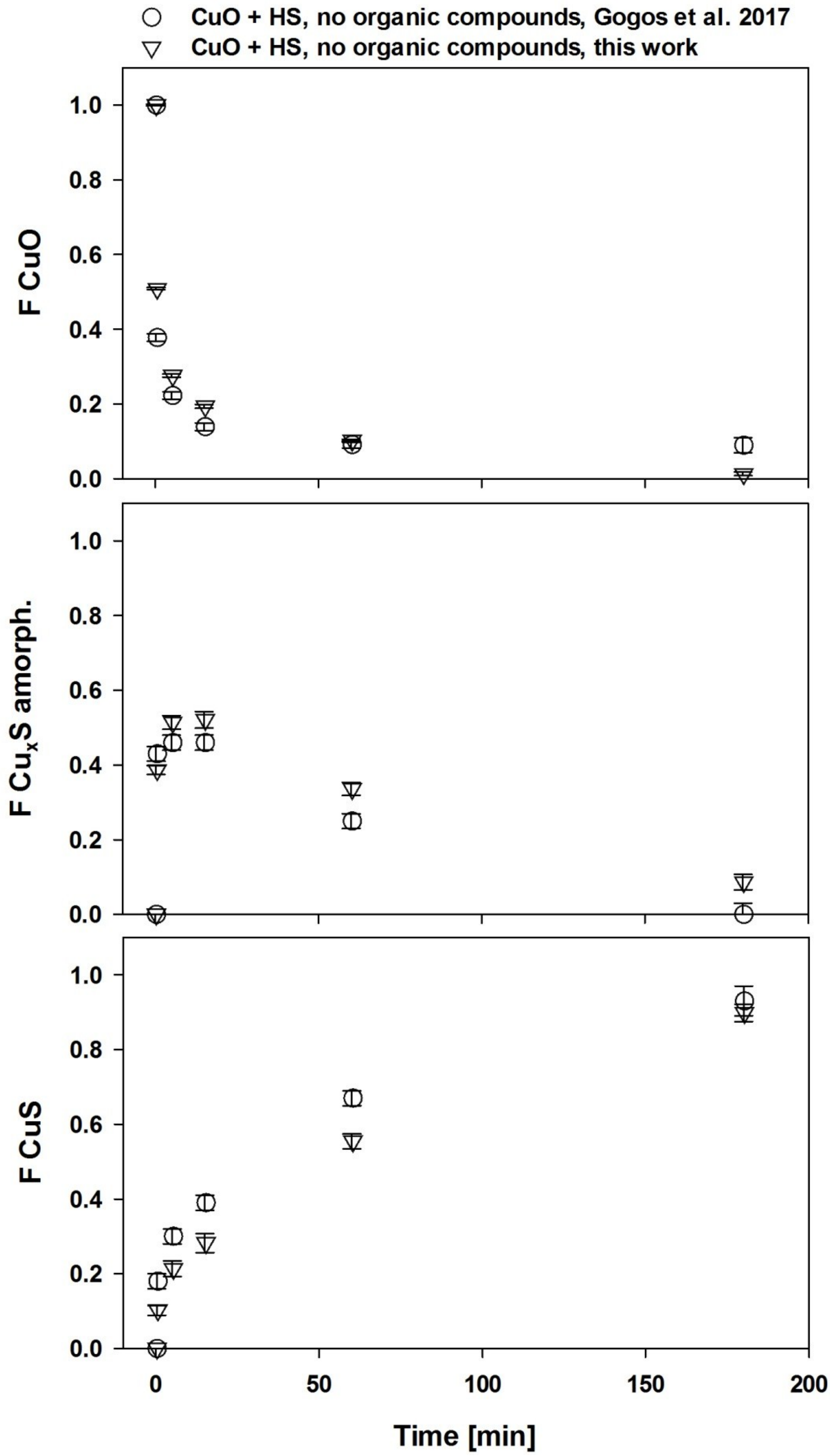

Fig. S4: Fraction of CuO, amorphous Cu_xS and CuS determined at increasing reaction times using LCF analyses of XANES spectra (starting conditions 1.3 mM CuO, 4 mM HS^- (3.2 mM effective concentration)) determined in this work (open triangles) and in Gogos et al.[3] (starting conditions 1.3 mM CuO, 4.2 mM HS^-, open circles). Error bars in the center of the symbols represent the error returned from LCF analysis.

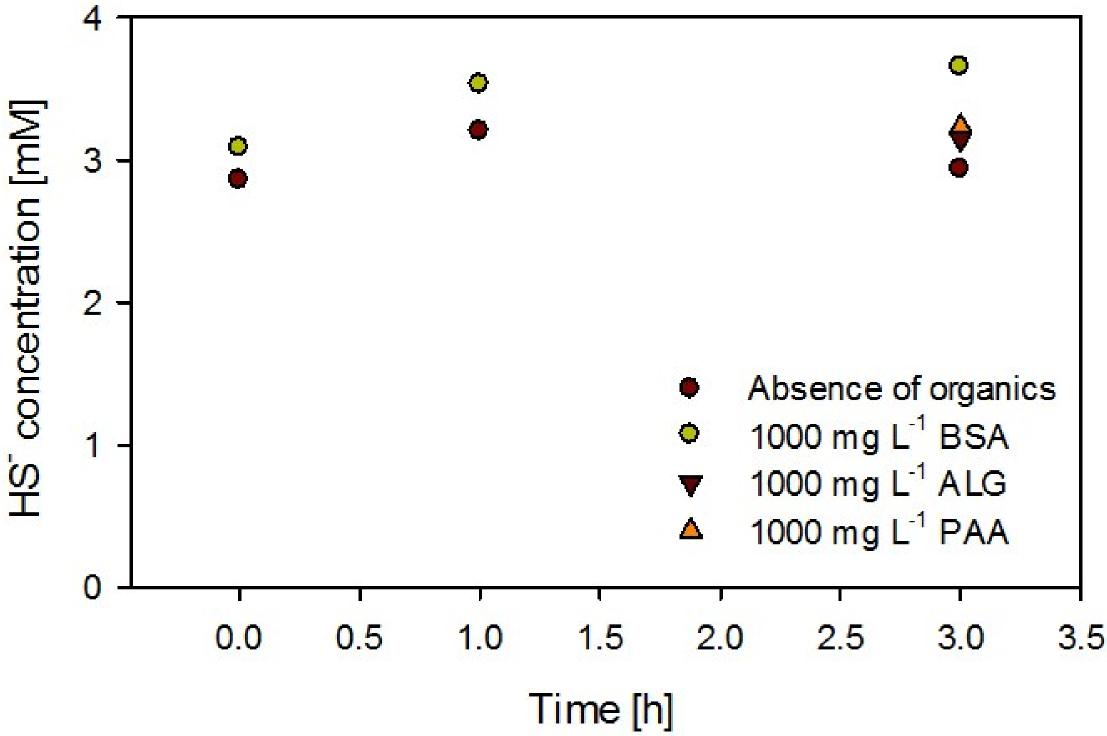

Fig. S5: Bisulfide (HS^-) concentration over time in the absence or presence of organic compounds at 1000 mgL^{-1}. The HS^- concentration was determined in the absence of CuO NP.

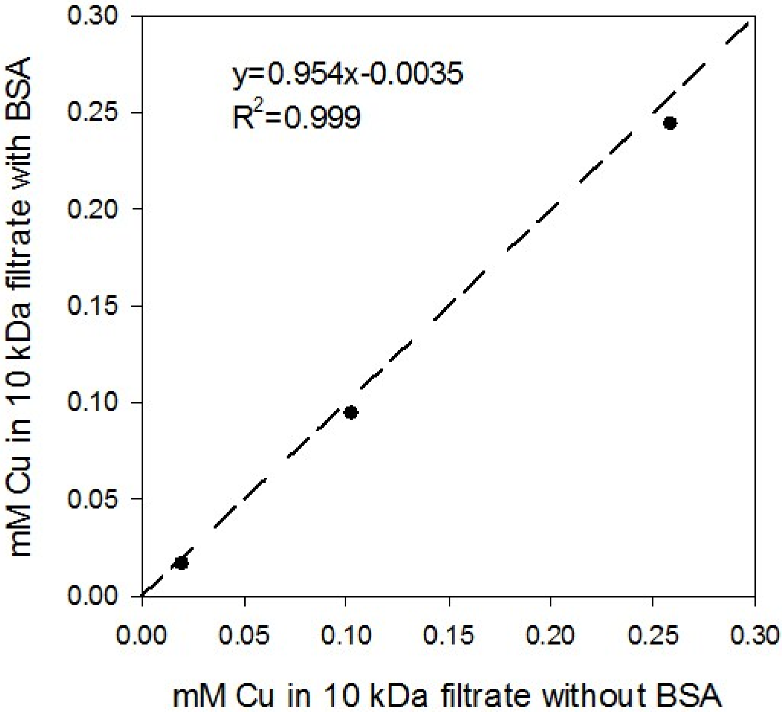

Fig. S6: Cu concentration in 10 kDa filtrates with and without 1000 mg L^{-1} BSA. The experiment was conducted as follows: 200 µL of 0.1, 0.5 and 1.3 mM Cu^{2+} (Cu-nitrate) solutions were prepared in Tris-HCl (50 mM, pH 8) with and without 1000 mg/L BSA, mixed thoroughly and equilibrated for 15 minutes. The resulting solutions were diluted 1:5, resulting in concentrations of 0.02, 0.1 and 0.26 mM Cu^{2+}, and subsequently filtered as described for the experimental samples. The filtrates were then diluted further in 2% HNO_3 for Cu determination using ICP-MS. The dashed line in the graph represents the 1:1 line.

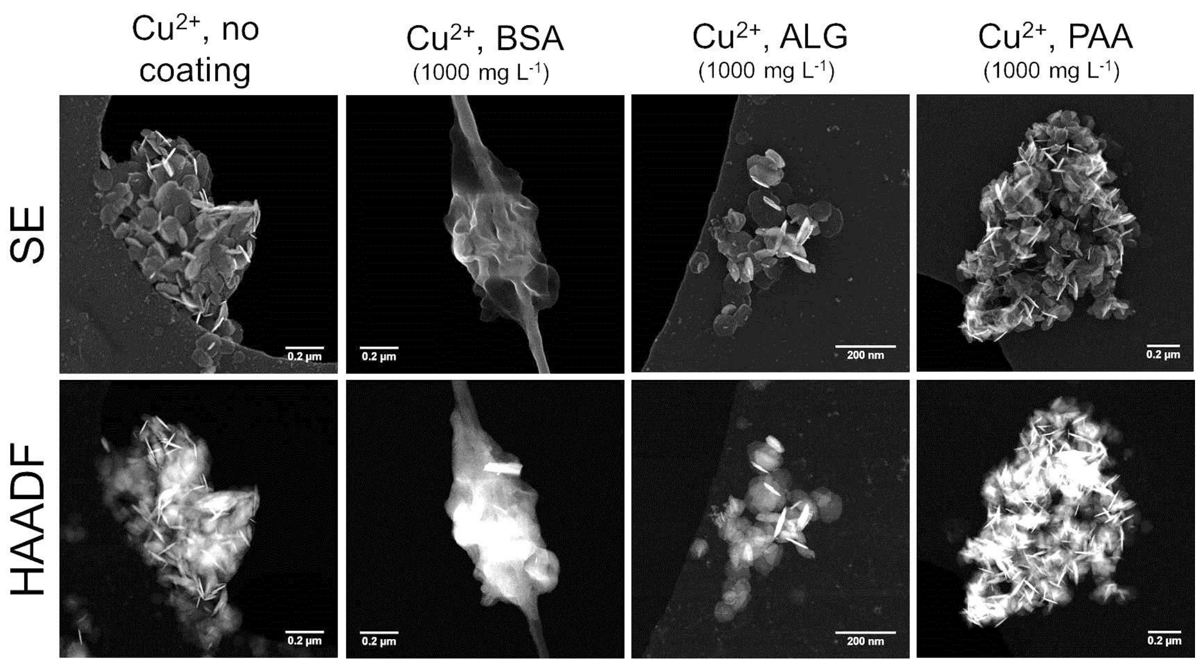

Fig. S7: STEM – SE (upper panel) and corresponding STEM – HAADF (lower panel) micrographs showing reaction products of 1.3 mM Cu^{2+} (from $CuNO_3$) and 4 mM HS^-

after 1 h reaction time in the presence of 1000 mg L^{-1} BSA, ALG and PAA, 600 mg L^{-1} HA and without added organic compounds.

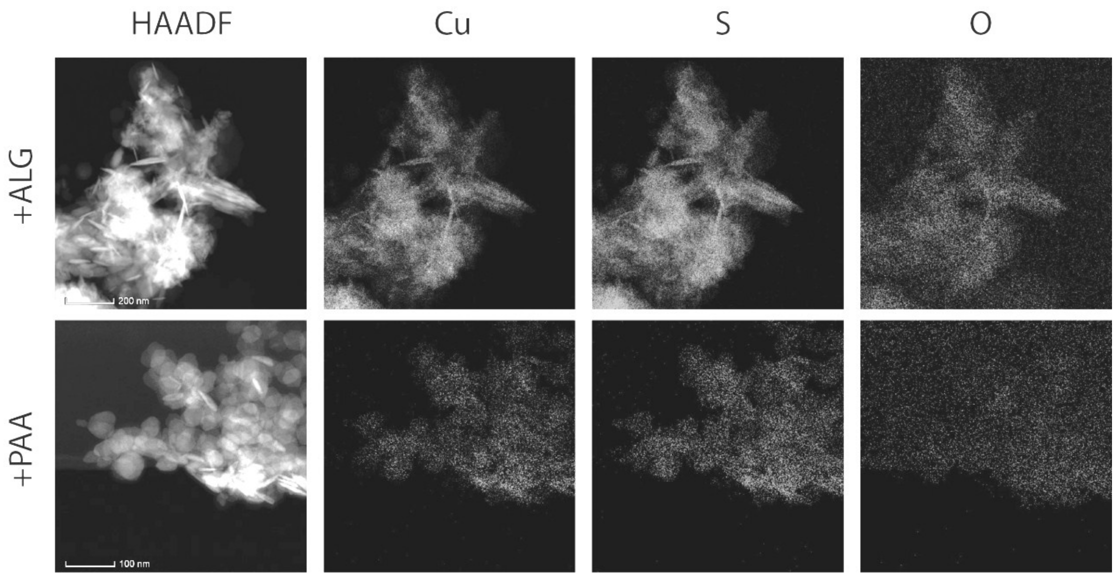

Fig. S8: STEM – HAADF (left) micrographs and EDX elemental distribution maps showing agglomerated particles after 3 h of sulfidation in the presence of 1000 mg L^{-1} ALG and PAA.

References

1. R. Pattrick, J. Mosselmans, J. Charnock, K. England, G. Helz, C. Garner and D. Vaughan, The structure of amorphous copper sulfide precipitates: An X-ray absorption study, *Geochimica et Cosmochimica Acta*, 1997, **61**, 2023-2036.
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3. A. Gogos, B. Thalmann, A. Voegelin and R. Kaegi, Sulfidation kinetics of copper oxide nanoparticles, *Environmental Science: Nano*, 2017, **4**, 1733-1741.