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Supplemental Material for "Electrodeposition of nanowires of a high copper content thiourea precursor of copper sulfide"

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Table of Contents

Cyclic staircase voltammetry **3**

Copper electrodeposition and dissolution from an electrolyte containing Copper Sulfate, HCl and Thiourea 3

Voltage dependent copper electrodeposition and dissolution from an electrolyte containing Copper Sulfate, HCl and Thiourea 3

Frequency and voltage dependent study of current fluctuations **4**

Report about Rietveld refinement **6**

References **8**

Cyclic staircase voltammetry (CV)

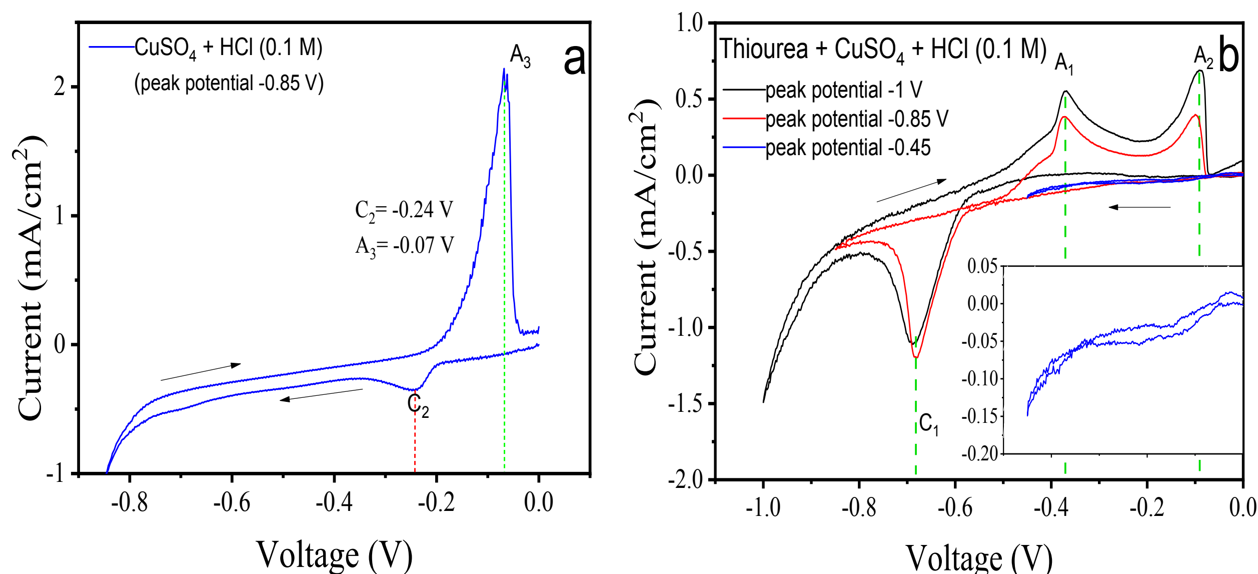

Figure S1: Cyclic voltammograms obtained from an 0.1 M HCl solution containing (a) copper-sulfate (potential range 0 to -0.85 V) (b) copper sulfate and thiourea for different potential ranges, the lower inset is the magnified view of the voltammogram recorded with the peak potential of -0.45 V.

Copper electrodeposition and dissolution from an electrolyte containing Copper Sulfate, HCl

Copper electrodeposition from a thiourea free acidic solution of copper sulfate occurs at -0.24 V (C_2), shown in Figure S1 a as reported by *Ghahremaninezhad.* et.al.[1] The dissolution of deposited copper occurs at at -0.07 V (A_3).

Voltage dependent copper electrodeposition and dissolution from an electrolyte containing Copper Sulfate, HCl and Thiourea

The solution containing thiourea reveals a copper deposition peak at -0.68 V (C_1), two dissolution/reaction peaks at -0.37 V (A_1) and -0.01 V (A_2), which are shown in Figure S1 b. Peak C_1 corresponds to the deposition of copper from an acidic solution containing thiourea. The deposition and dissolution/reaction processes were confirmed after comparing with the CV data from the copper sulfate solution without thiourea. This study is consistent with the study by *Ghahremaninezhad et.al.*[1,2].

Voltage dependent copper electrodeposition and dissolution from an electrolyte containing Copper Sulfate, HCl and Thiourea

In order to confirm the dissolution channels we compared the CV measurements obtained using different potential scan ranges (0 V to the peak potential) from a thiourea containing acidic solution of copper sulfate. In Figure S1b, we presented three cyclic voltammograms of the solution corresponds to three different peak potentials -0.45 V, -0.85 V and -1 V, respectively. The reason behind the choice of -0.45 V is that the voltage scanning range still remain below the copper deposition potential (-0.68 V) of thiourea containing solution but the voltage scanning range still covers the potential for the dissolution (-0.37 V, -0.01 V). The

magnified voltammogram (inset of Figure S1b) corresponds to peak potential of -0.45 V reveals neither deposition peak nor any dissolution peak. Further repetitions of the cycle as well reveal no peaks. This observation clearly confirms that the dissolution is causally connected with the deposition. On the other hand, if we increase the peak potentials from -0.85 V to -1 V not only the deposition of copper increases, the area of dissolution peaks also increases, as shown in Figure S1b.

Frequency and Voltage dependent copper electrodeposition and dissolution from an electrolyte containing Copper Sulfate, HCl and Thiourea

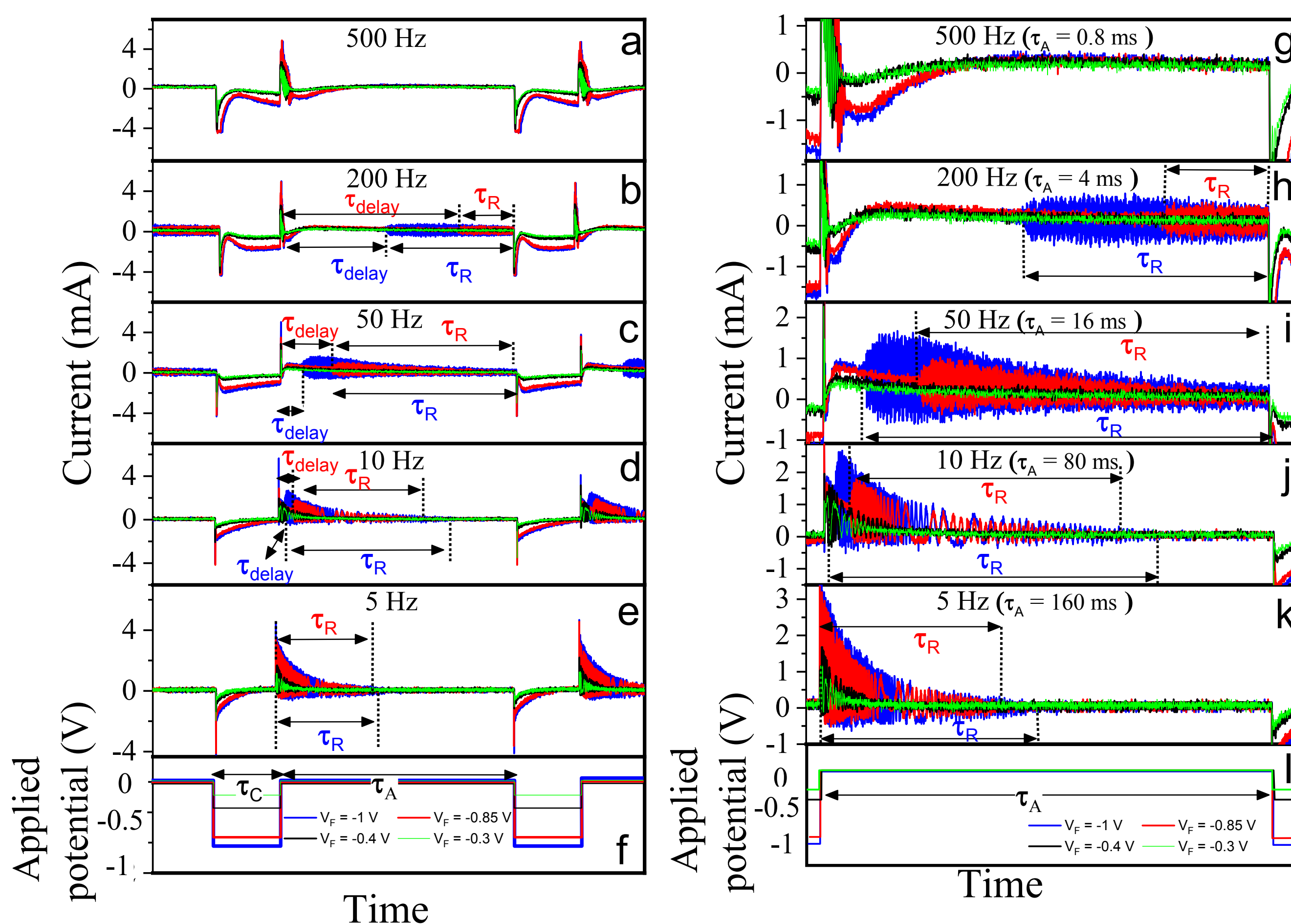

Figure S2: Current pulses recorded during the synthesis of CTC nanowires using frequencies (a) & (g) 500 Hz, (b) & (h) 200 Hz, (c) & (i) 50 Hz, (d) & (j) 10 Hz, (e) & (k) 5 Hz of the rectangular voltage pulses of four different amplitudes between -1 and -0.3 V as illustrated in (f) & (g). For each of the frequencies the current was recorded for four different pulses having different deposition potentials -1 V (blue line), -0.85 V (red line), -0.4 V (black line) and -0.3 V (green line).

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Table S1: Analyzed parameters tabulated from Figure S2.

Frequency	Available deposition time	Deposition potential	Available reaction time	Reaction potential	Delay before reaction start	Afforded Reaction time	Reaction status
Hz	τ_C (ms)	V	τ_A (ms)	V	τ_{delay} (ms)	τ_R(ms)	
500	0.2	- 0.3	0.8	0	NA	NA	
		- 0.4		0	NA	NA	
		- 0.85		0			(Not started) No current fluctuations
		- 1		0			(Not started) No current fluctuations
200	1	- 0.3	4	0	NA	NA	
		- 0.4		0	NA	NA	
		- 0.85		0	3	1.0	(Not completed) Current fluctuations remain until the pulse end
		- 1		0		2.2	(Not completed) Current fluctuations remain until the pulse end
50	4	- 0.3	16	0	NA	NA	
		- 0.4		0	NA	NA	
		- 0.85		0	3.4	12.3	(Completed) Current fluctuations amplitude decays to the base level noise before the pulse end
		- 1		0		14.5	Not completed
10	20	- 0.3	80	0	NA	NA	
		- 0.4		0	NA	NA	
		- 0.85		0	4.4	48	Completed
		- 1		0	2.2	50.2	Completed
5	40	- 0.3	160	0	NA	NA	
		- 0.4		0	NA	NA	
		- 0.85		0	5	64.6	Completed
		- 1		0		70	Completed

The dynamics of the copper electrochemical dissolution by probing current fluctuation is a well-established technique[3–5]. The feature of the current oscillations which corresponds to the dynamical behavior is collectively determined by reaction kinetics, mass transfer coefficient, electrode size, electrolyte etc[4,5].

As previously mentioned in the manuscript that during the synthesis of CTC nanowires we used rectangular periodic pulse where the duty cycle for the deposition (V_F) of copper is 20 %

and the rest 80% time is for the dissolution/ reaction of the deposited copper as shown in Figure S2 f. The existence of the current fluctuations is the indication of reaction/dissolution process.

During the study we varied the frequency of the rectangular pulse (maintaining fixed duty cycle 1:4) and probed the current fluctuations during the allowed dissolution period. Our aim for the study was to find the time in each cycle of the pulse which is necessary to complete the dissolution/reaction of the copper which was deposited in the cycle.

The measurement is shown in Figure S2 and the detailed analyzed parameter is tabulated in Table S1. In our main manuscript we incorporated the same measurement corresponds to 33 Hz rectangular waveform (Figure 8b). From the measurement we concluded that for the particular concentration of the electrolyte and for the deposition potential of -0.85 V we should not use the pulse frequency more than 50 Hz. If we use the pulse frequency more than 50 Hz then there is always a possibilities of remaining unreacted copper.

In each frequency of the applied waveform we compared the current fluctuations correspond to four different deposition potentials (V_F), as shown in Figure S2. We observed that the current fluctuations amplitude and the extension of current fluctuations is proportional the applied deposition potential. For a particular frequency, not only the current fluctuation amplitude is higher for the pulse for which the deposition potential (V_F) is higher but also the extension of the current fluctuations is for longer period. We also observed that the dissolution/reaction (current fluctuations) required a delay period (3 ms - 5 ms) which is confirming again that the dissolution/reaction process of the deposited copper from a solution containing thiourea is slow compare to the deposition process[6]

Rietveld refinement report of transformed nanowires

The reflection positions match very well with the Covellite phase (ICSD_CollCode26968) and a $Cu_{1.8}S$ phase (ICSD_CollCode57213.cif), therefore an attempt was made to perform a Rietveld refinement on the data.

The background was modelled with Chebychev polynoms, whereas the two copper sulphide phases were treated with Rietveld refinement. In this Rietveld refinement, only lattice parameters, crystallite size (and partially strain) for the FWHM of the reflections as well as atomic positions were allowed to vary. Displacement parameters and occupancies were fixed to the values in the CIF files, since they were not able to model the intensities correctly.

As the powder is arranged in form of a nanowire, one could expect that the reflections suffer from a rather complicated preferred orientation effect, as the nanowires are assumed to be confined within the plane in which they lie. Therefore spherical harmonics of 6th order had to be used in order to model the intensities correctly. Although the order of the spherical

harmonics is rather high, the stability of the refinement of the atomic positions suggests, that this approach is justified.

In the following, the refined results are presented:

R-Values

```
Rexp : 13.44   Rwp : 56.31    Rp  : 35.88  GOF : 4.19
Rexp`: 13.62   Rwp`: 57.09    Rp` : 37.68  DW  : 1.05
```

Quantitative Analysis - Rietveld

```
   Phase 1  : Covellite                        37.645 %
   Phase 2  : Cu1.8S                           62.355 %
```

Background

```
   Chebychev polynomial, Coefficient  0      2.304725
                                      1      -9.672732
                                      2      -2.628227
                                      3      0.8108488
```

Corrections

```
   Zero error                                0.02787164
   LP Factor                                 0
```

Miscellaneous

```
   X Calculation Step                        0.002
   Start X                                   3
   Finish X                                  17.4
```

Covellite (CuS)

```
   Phase name                                Covellite
   R-Bragg                                   100.000
   Spacegroup                                P63/mmc
   Scale                                       2.30675e-006
   Cell Mass                                 573.666
   Cell Volume (Å^3)                         206.83013
   Wt% - Rietveld                            37.645
   Double-Voigt|Approach
      Cry size Lorentzian                    25.5
      k:  1  LVol-IB (nm)                    16.254
      k:  0.89  LVol-FWHM (nm)               22.723
   Crystal Linear Absorption Coeff. (1/cm)   56.443
   Crystal Density (g/cm^3)                  4.606
   Preferred Orientation Spherical Harmonics
      Order                                  6
      y00                                    1
      y20                                    -0.4302271
      y40                                    0.1047205
      y60                                    0.3839652
      y66p                                   -0.2145924
   Lattice parameters
      a (Å)                                  3.8123319
      c (Å)                                  16.4324289
```

Site	Np	x	y	z	Atom	Occ	Beq
Cu1	4	0.33333	0.66667	0.10860	Cu+1	1	0
Cu2	2	0.66667	0.33333	0.25000	Cu+2	1	0
S1	4	0.00000	0.00000	0.05937	S	1	0
S2	2	0.33333	0.66667	0.25000	S	1	0.4

Digenite ($Cu_{1.8}S$)

```
   Phase name                                  Cu1.8S
   R-Bragg                                     99.992
   Spacegroup                                  Fm-3m
   Scale                                         4.44648e-006
   Cell Mass                                   585.791
   Cell Volume (Å^3)                           174.05413
   Wt% - Rietveld                              62.355
   Double-Voigt|Approach
      Cry size Lorentzian                      283.5
      Cry size Gaussian                        18.2
      k:  1  LVol-IB (nm)                      16.017
      k:  0.89  LVol-FWHM (nm)                 15.635
   Strain
      Strain L                                 0.1274794
      e0                                       0.00028
   Crystal Linear Absorption Coeff. (1/cm)     77.824
   Crystal Density (g/cm^3)                    5.589
   Preferred Orientation Spherical Harmonics
      Order                                    6
      k00                                      1
      k41                                      -0.278672
      k61                                      0.1600219
   Lattice parameters
      a (Å)                                    5.5833490
```

Site	Np	x	y	z	Atom	Occ	Beq
Cu1	8	0.25000	0.25000	0.25000	Cu+1	0.52	0.069
Cu2	32	0.33238	0.33238	0.33238	Cu+1	0.095	0.031
S1	4	0.00000	0.00000	0.00000	S	1	0.009

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