



Supporting Information

In situ Raman Microdroplet Spectroelectrochemical Investigation of CuSCN Electrodeposited on Different Substrates

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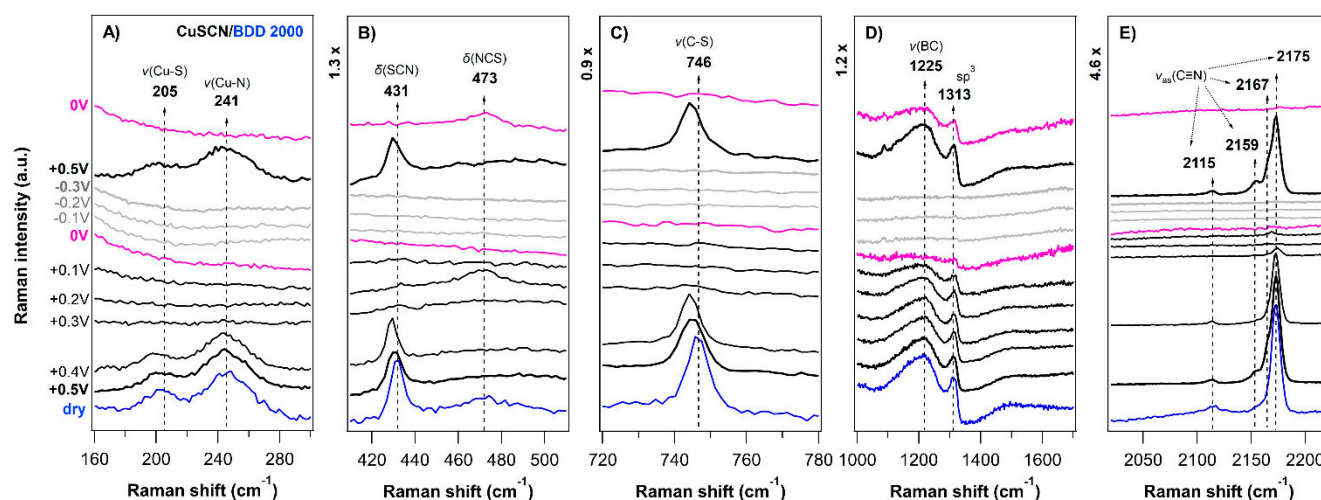


Figure S1. In situ Raman- μ SEC spectra of the CuSCN layer (spectral regions of 160–300, 410–510, 720–780, and 2020–2220 cm^{-1} in charts A, B, C, and E, respectively) electrodeposited on the BDD 2000 substrate (spectral region of 1000–1700 cm^{-1} in chart D) with B/C ratio in the gas phase 2000 ppm as a function of the applied potential (vs. Ag/AgCl; shown on the left-side chart) in 6 M LiCl. The measurement sequence is as follows: the first spectrum was acquired at +0.5 V (bottom thick black trace), and the last spectrum was acquired at 0 V (top thick pink trace). The sequence of negative potentials (from –0.3 V to –0.1 V) is visualized by grey traces and the sequence of positive potentials (from +0.1 V to +0.5 V) is visualized by black traces. The reference (ex situ) Raman spectrum of dry CuSCN layer on BDD 2000 substrate is shown for comparison (blue trace). Spectra are offset for clarity; the intensity scale is identical for all the charts.

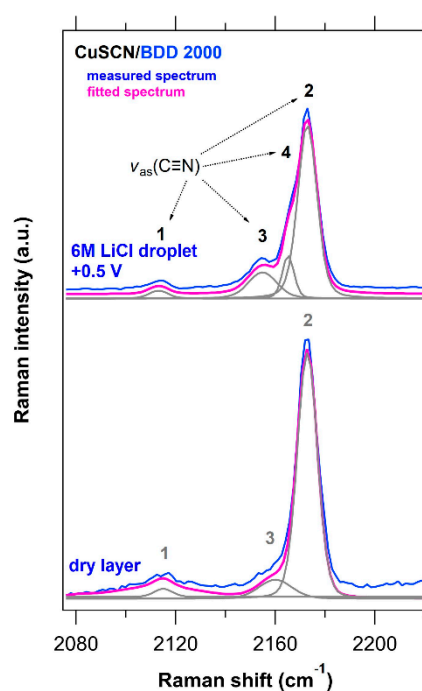


Figure S2. Raman spectra (blue trace) of electrodeposited CuSCN i) dry (ex situ) layer (bottom), and ii) in 6 M LiCl microdroplet (top) at +0.5 V vs. Ag/AgCl potential upon the in situ Raman- μ SEC measurement, on the BDD 2000 substrate in the region of SCN vibrations (2080–2200 cm^{-1}). The pink and gray traces represent the fits and individual peak positions, respectively, using Voigt lineshapes.

Table S1. Fitting parameters of Raman $\nu(\text{C-S})$ position in the CuSCN layers electrodeposited on various substrates (GC, BDD 1000 and 2000 ppm, HOPG, FTO); i) dry (ex situ) layer, and ii) in 6 M LiCl microdroplet at +0.5 V vs. Ag/AgCl potential upon the in situ Raman- μ SEC measurement.

		Peak1	
		Raman shift	FWHM
		(cm^{-1})	
CuSCN/GC	dry layer	746.3	8.2
	+0.5 V μ -droplet	747.7	8.8
CuSCN/BDD	dry layer	745.1	8.2
	+0.5 V μ -droplet	743.8	6.6
CuSCN/BDD2000	dry layer	746.5	6.9
	+0.5 V μ -droplet	744.5	6.9
CuSCN/HOPG	dry layer	746.8	8.5
	+0.5 V μ -droplet	746.8	3.7
CuSCN/FTO	dry layer	745.8	10.8
	+0.5 V μ -droplet	744.3	7.9

Table S2. Fitting parameters of Raman $\nu_{as}(\text{C}\equiv\text{N})$ position in the CuSCN layers electrodeposited on various substrates (GC, BDD 1000 and 2000 ppm, HOPG, FTO); i) dry (ex situ) layer, and ii) in 6 M LiCl droplet at +0.5 V vs. Ag/AgCl potential upon the in situ Raman- μSEC measurement.

		Peak1		Peak2		Peak3		Peak4	
		Raman shift	FWHM	Raman shift	FWHM	Raman shift	FWHM	Raman shift	FWHM
		(cm^{-1})		(cm^{-1})		(cm^{-1})		(cm^{-1})	
CuSCN/GC	dry layer	2114.7	13.4	2174.5	10.6	2158.3	23.9	–	–
	+0.5 V								
	μ -droplet	2116.3	12.5	2176.8	9.2		2169.1/21.2*		
CuSCN/BDD	dry layer	2114.1	10.3	2173.7	9.4		2165.9/23.0*		
	+0.5 V								
	μ -droplet	2111.8	8.2	2172.5	8.6	2158.0	17.5	2165.3	5.1
CuSCN/BDD2000	dry layer	2114.1	35.8	2172.9	9.1	2165.8	25.7	–	–
	+0.5 V								
	μ -droplet	2113.1	9.1	2172.9	9.1	2154.9	13.4	2165.1	5.5
CuSCN/HOPG	dry layer	2115.1	10.6	2174.9	10.3	2159.1	24.4	–	–
	+0.5 V								
	μ -droplet	2115.6	7.5	2174.5	6.5	2159.4	6.4	–	–
CuSCN/FTO	dry layer	2114.5	12.2	2174.6	13.6	2159.2	17.2	2167.1	5.1
	+0.5 V								
	μ -droplet	2111.7	10.5	2175.7	6.7	2156.1	12.3	2166.5	5.6

* due to the low intensity of the shoulder bands, the deconvolution into two peaks (3, 4) was not reliable, and a single peak was used instead

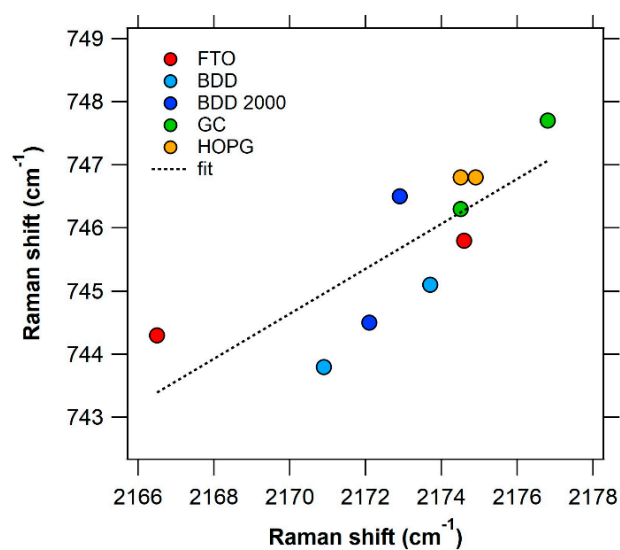


Figure S3. Correlation between the Raman shifts of the C-S stretching vibration at ~745 cm⁻¹ and the C-N stretching vibration at ~2175 cm⁻¹ (fitted as a single Voigt lineshape each). The dotted line represents a least-squares linear fit; the Pearson's correlation coefficient is 0.8.