

SUPPORTING INFORMATION

Electrochemical Characterization of CuSCN Hole-Extracting Thin Films for Perovskite Photovoltaics

Ladislav Kavan^{1,2*}, Zuzana Vlčková Živcová¹, Pavel Hubík³, Neha Arora², M. Ibrahim Dar²
Shaik M. Zakeeruddin² and Michael Grätzel²

¹J. Heyrovsky Institute of Physical Chemistry, v.v.i., Czech Academy of Sciences, Dolejskova 3, CZ-18223 Prague 8, Czech Republic

²Laboratory of Photonics and Interfaces, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

³Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10, 162 00 Prague 6, Czech Republic

* E-mail: kavan@jh-inst.cas.cz

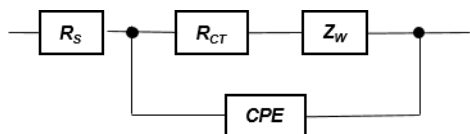


Figure S1: Equivalent circuit used for fitting of impedance spectra.

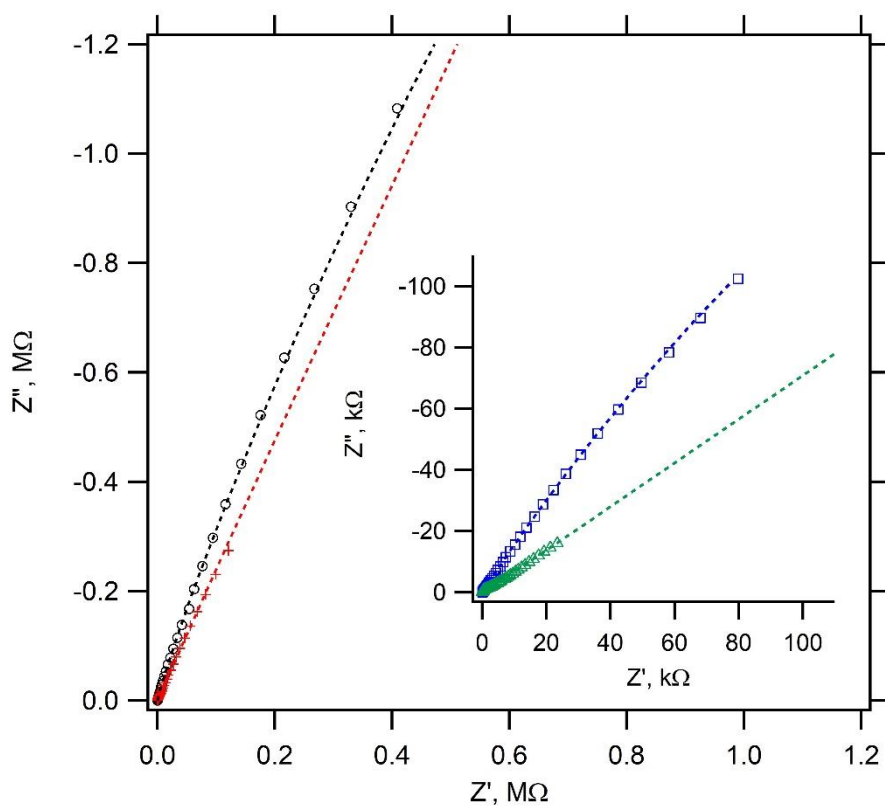


Figure S2: Sample Nyquist plots from electrochemical impedance spectra of CuSCN@GC. The applied potentials (in V vs. Ag/AgCl) were: -0.1 (black points), 0.1 (red crosses), 0.2 (blue squares), 0.3 (green triangles). Dashed lines are fits to the equivalent circuit shown in Figure S1. Electrode area 0.03 cm^2 ; electrolyte solution 0.5 M KCl saturated with CuSCN, pH 6.

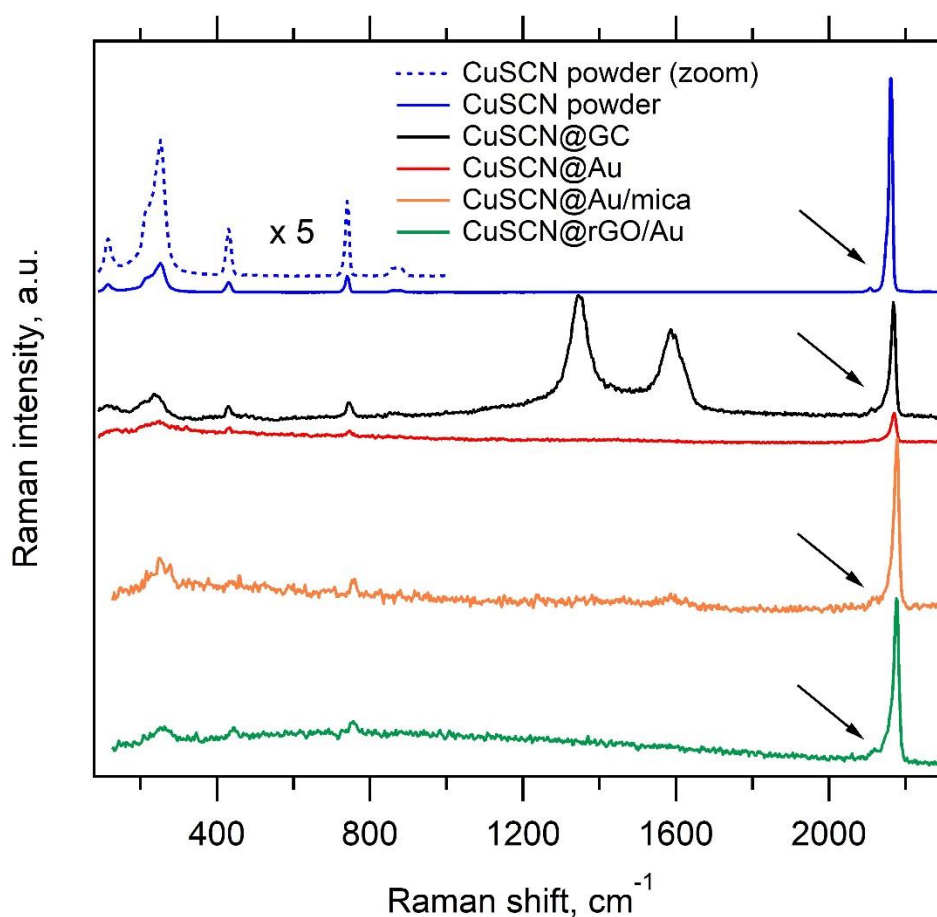


Figure S3: Raman spectra of CuSCN powder and thin films. Blue curve shows the reference spectrum of blank CuSCN powder (spectrum zoomed by a factor of 5 in the intensity scale is plotted by dashed line). The remaining spectra are for thin films deposited by spin-coating from Et₂S solution on glassy carbon, gold and rGO, respectively. Excitation wavelength 532 nm. The main Raman peaks are located at 115, 220, 252, 431, 741 and 2162 cm⁻¹. The small peak at 2110 cm⁻¹ is labeled by arrow. Their tentative assignment is as follows ¹: 220 cm⁻¹ (Cu-S stretching), 252 cm⁻¹ (Cu-N stretching), 431 cm⁻¹ (SCN bending), 741 cm⁻¹ (Cu-S stretching), 2110 cm⁻¹ (C≡N stretching in Cu-NCS) and 2162 cm⁻¹ (C≡N stretching in Cu-SCN). The peaks originating from the GC substrate are at 1350 cm⁻¹ (D-band) and 1588 cm⁻¹ (G-band). Spectra are offset for clarity.

Table S1. Transport properties of a typical CuSCN 60 nm film prepared on high-resistivity glass substrate. The logarithmic mean value of the published mobility data ²⁻⁴ ($\sim 0.01 \text{ cm}^2/\text{Vs}$) was used in the calculation of the values in the rightmost column. Possible variations of the mobility with environment are not considered in making these rough estimates.

environment	conductivity (Scm^{-1})	hole concentration, $N_A \text{ (cm}^{-3}\text{)}$	
		from the measured Hall voltage	from the measured conductivity and literature mobility
air	3.3×10^{-5}	$> 5 \times 10^{14}$	$\sim 2 \times 10^{16}$
vacuum	2.4×10^{-4}	$> 1 \times 10^{15}$	$\sim 1.5 \times 10^{17}$

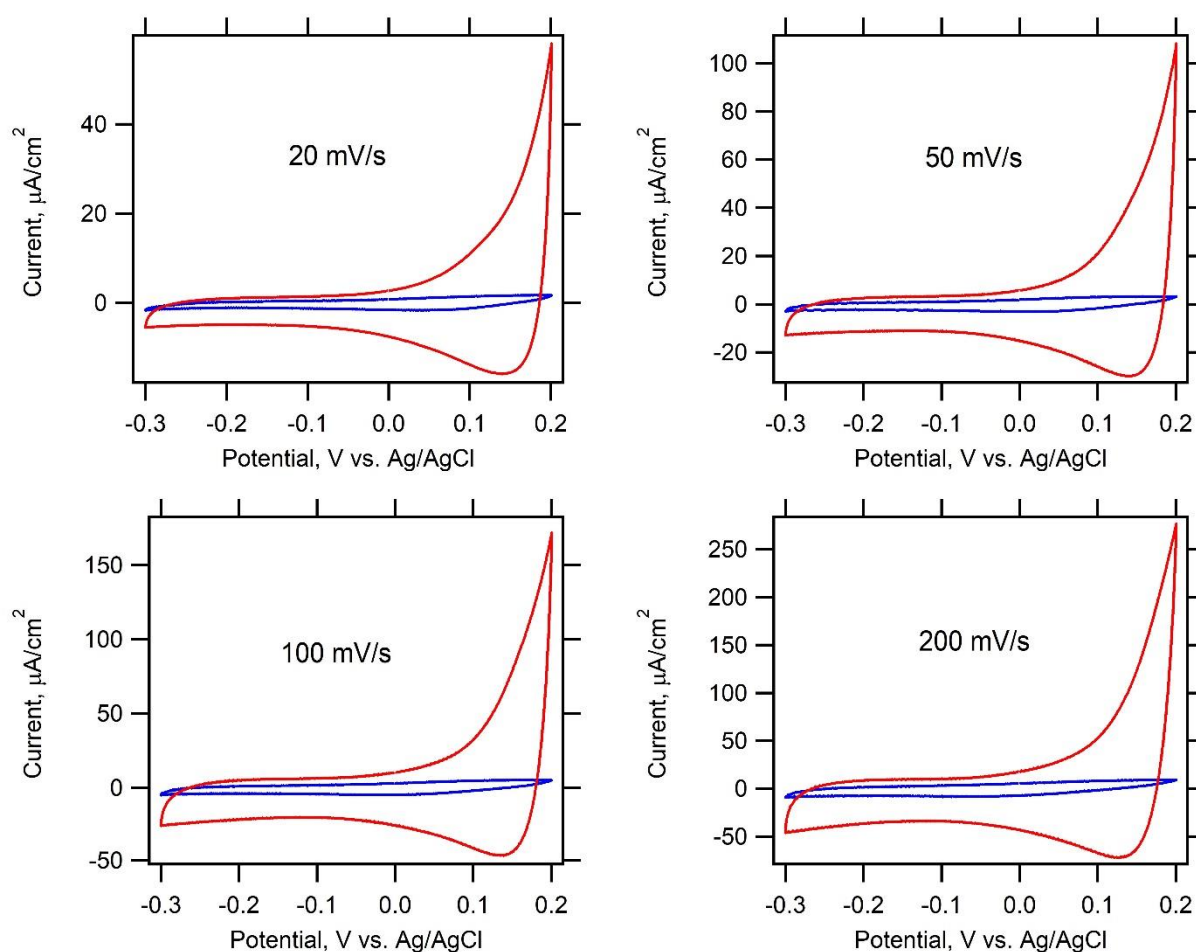


Figure S4: Cyclic voltammogram of a thin film of CuSCN (red curves) deposited on a FTO substrate. Blue curves are reference voltammograms of blank substrate material. Scan rates are annotated in the corresponding plots. Electrolyte solution 0.5 M KCl saturated with CuSCN, pH 6.

Table S2. Electrochemical parameters of the studied electrode materials in aqueous electrolyte solution (0.5 M KCl saturated with CuSCN, pH 6).

Electrode	C_H (from CV) ^b [$\mu\text{F}/\text{cm}^2$]	C_H (from EIS) ^b [$\mu\text{F}/\text{cm}^2$]	E_{FB} [V vs. Ag/AgCl]	N_D or N_A [cm^{-3}] ^c
FTO	30	40	-0.42	$4 \cdot 10^{20}$
CuSCN@FTO	130	25	0.12	$5 \cdot 10^{20}$
Au	45	60	-	-
CuSCN@Au	160	30	0.08	$5 \cdot 10^{20}$
GC	20	20	-	-
CuSCN@GC	100	25	-0.02	$1 \cdot 10^{20}$
rGO	30	20	-	-
CuSCN@rGO	120	25	0.00	$2 \cdot 10^{20}$

^a Helmholtz capacitance from cyclic voltammetry (CV) determined from Eq. 4 (main text).

^b Helmholtz capacitance from electrochemical impedance spectra (EIS). For semiconducting electrodes, the C_H values were estimated at potentials near the flatband potential (Eq. 5 in the main text).

^c Concentrations of majority charge carriers determined from Mott-Schottky plots (N_D for n-semiconductor, i.e. FTO or N_A for p-semiconductor, i.e. CuSCN).

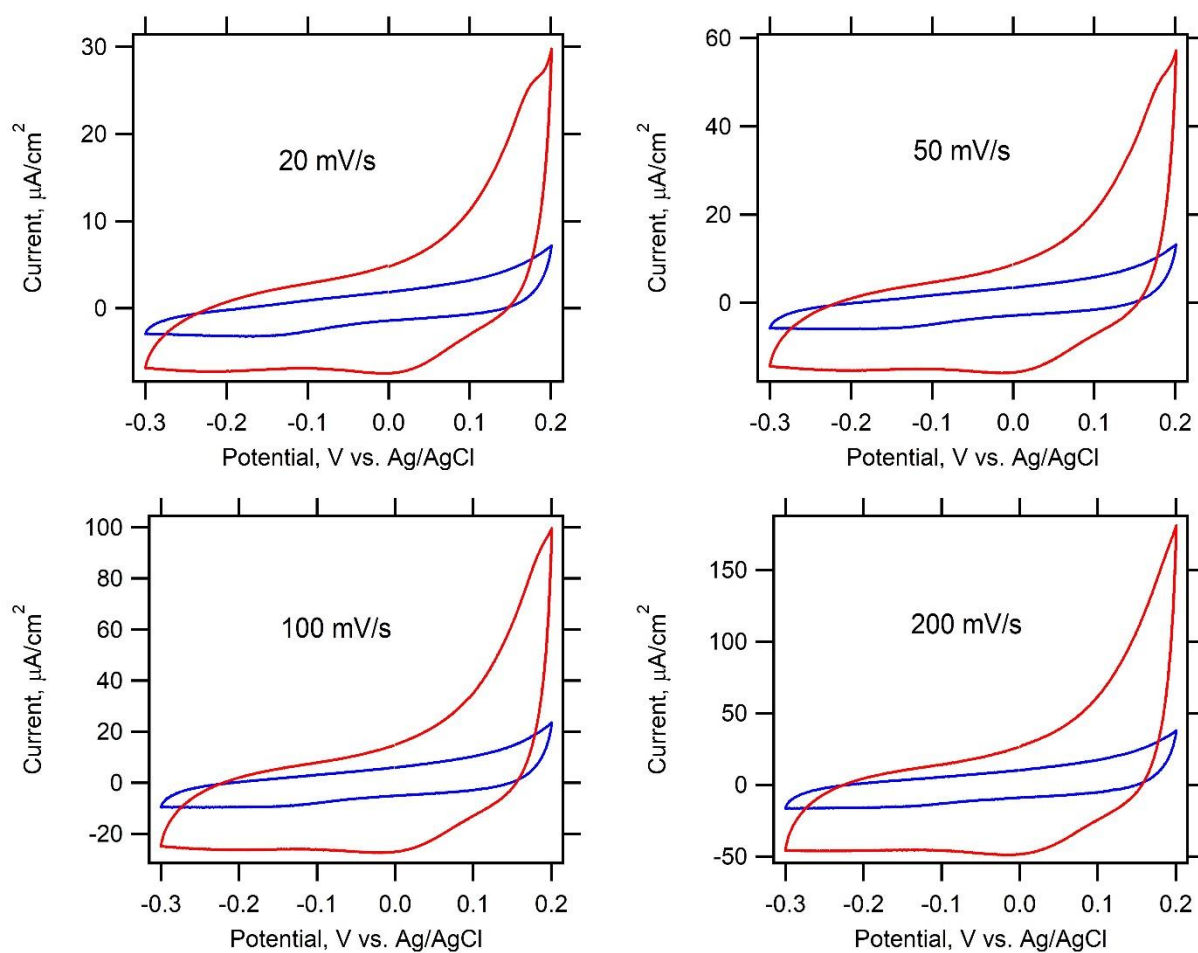


Figure S5: Cyclic voltammogram of a thin film of CuSCN (red curves) deposited on an Au substrate. Blue curves are reference voltammograms of blank substrate material. Scan rates are annotated in the corresponding plots. Electrolyte solution 0.5 M KCl saturated with CuSCN, pH 6.

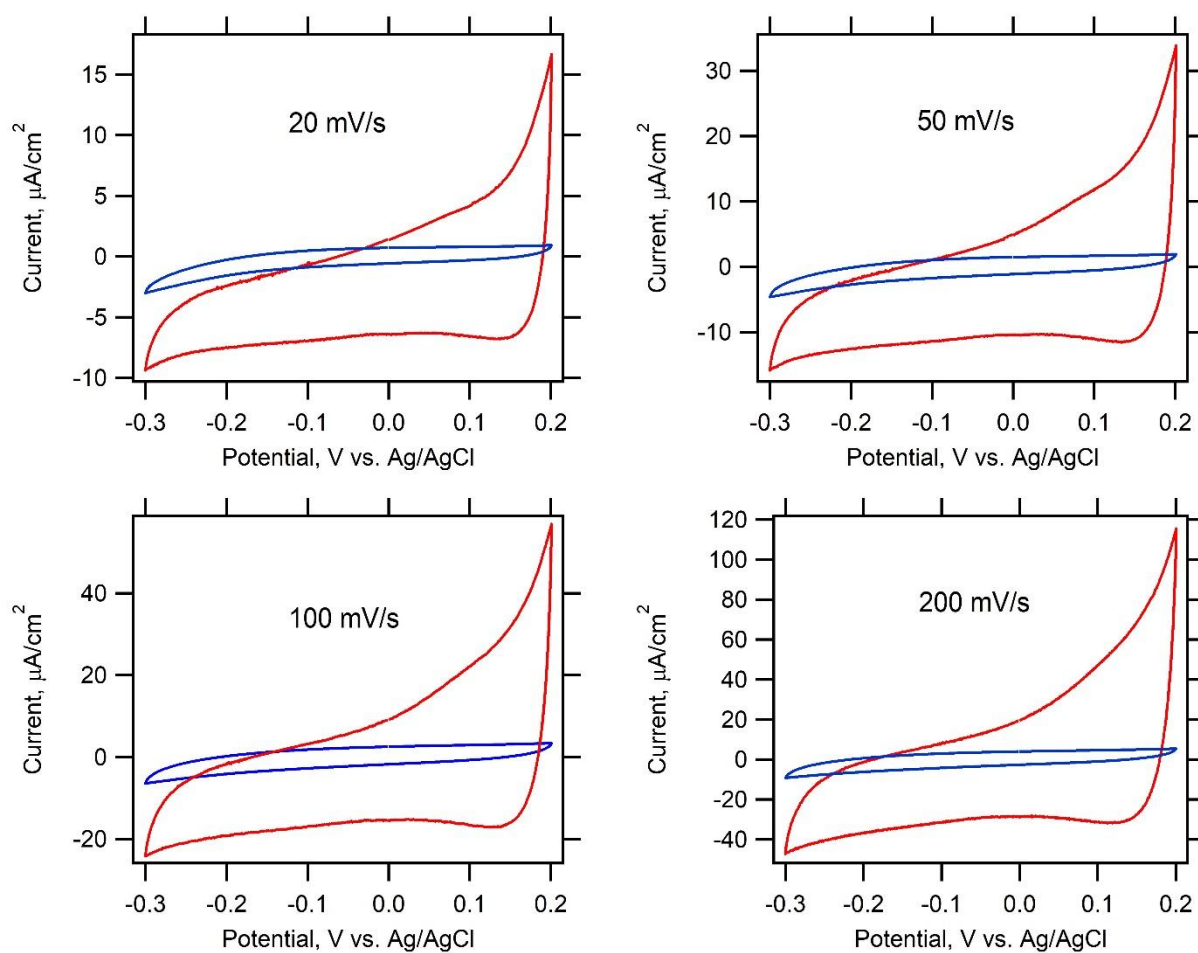


Figure S6: Cyclic voltammogram of a thin film of CuSCN (red curves) deposited on a glass-like carbon substrate. Blue curves are reference voltammograms of blank substrate material. Scan rates are annotated in the corresponding plots. Electrolyte solution 0.5 M KCl saturated with CuSCN, pH 6.

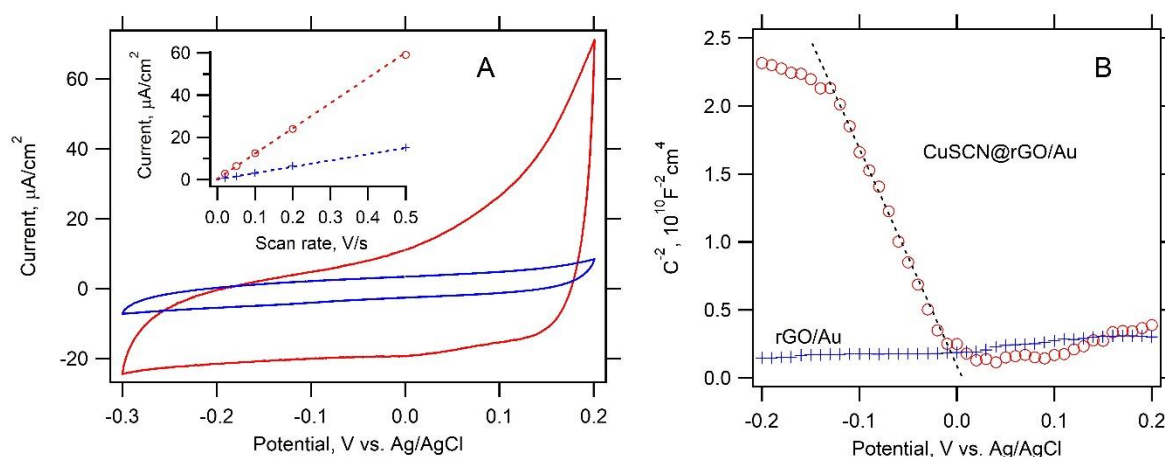


Figure S7: [A] Cyclic voltammogram of a thin film of CuSCN (red curve) deposited on reduced graphene oxide (rGO) at Au substrate. Blue curve is a reference voltammogram of blank rGO. Scan rate 0.1 V/s. Inset shows the voltammetric current detected at -0.1 V vs. Ag/AgCl at various scan rates for CuSCN film (red open-points markers) and reference blank rGO (blue crosses markers). [B] Mott-Schottky plot from electrochemical impedance of a thin film of CuSCN on rGO (red curve). Blue curve is a reference plot of blank rGO. Electrolyte solution 0.5 M KCl saturated with CuSCN, pH 6 in all cases.

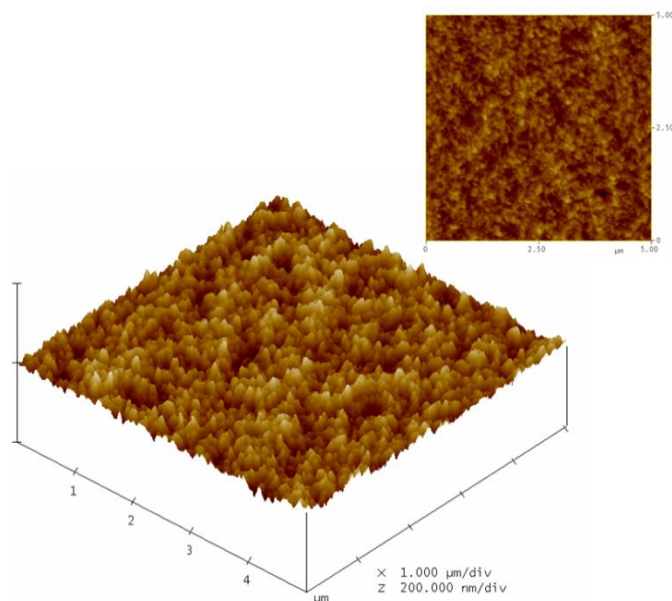
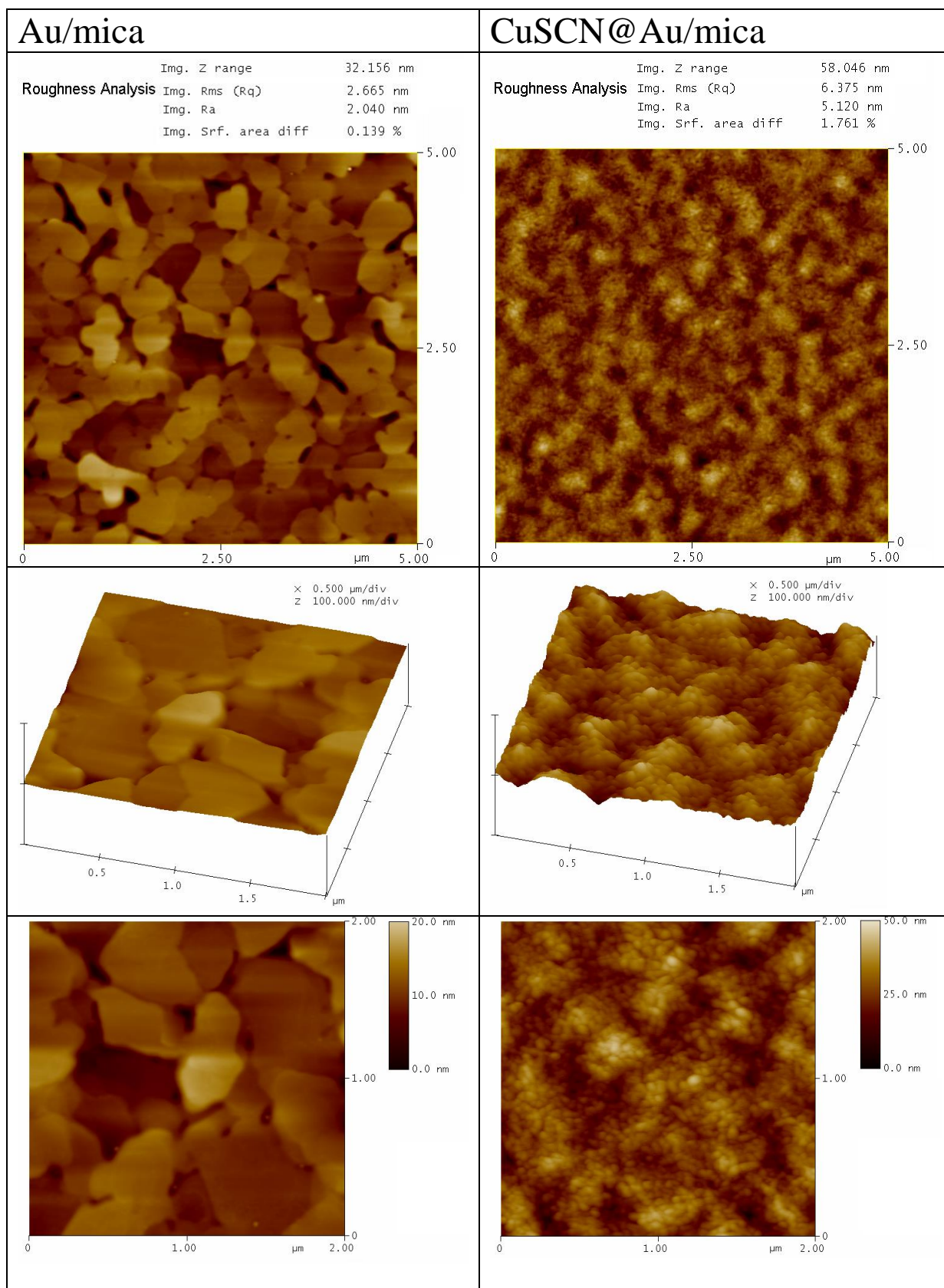


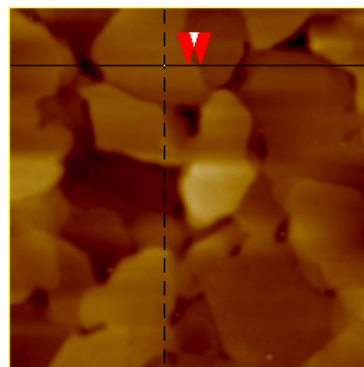
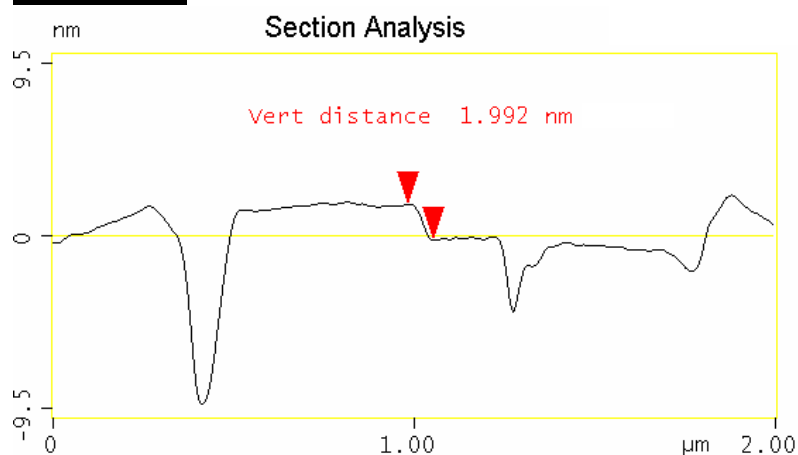
Figure S8: Tapping mode AFM topography/height images 2D (top) and 3D (bottom) of CuSCN@GC electrode.

A



B

Au/mica



CuSCN@Au/mica

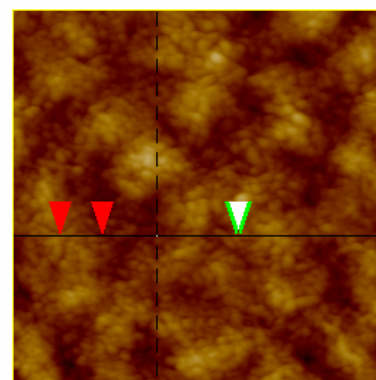
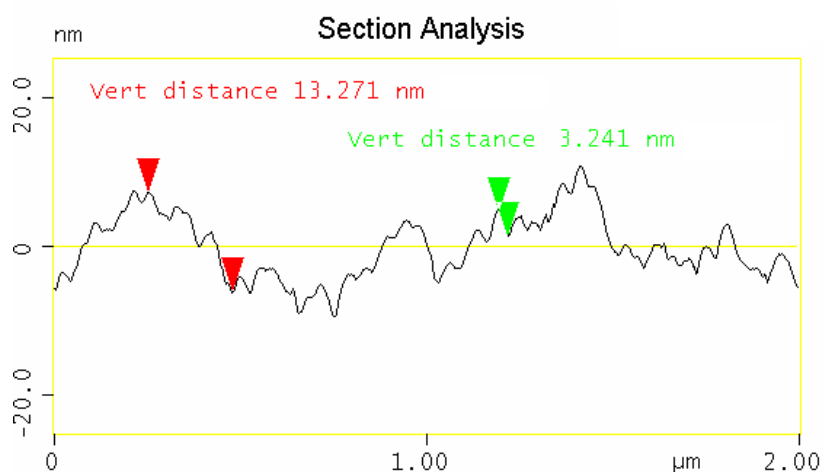


Figure S9 [Part A; Right column] Taping mode AFM topography/height images of CuSCN@Au. The substrate was atomically flat Au(111) deposited at mica (purchased from Agilent Technologies). The CuSCN film was deposited by dynamic spin-coating (5000 rpm) as detailed in the main text. [Part A, Left column] The AFM images of blank Au substrates.

[Part B; Bottom chart] Section analysis of the AFM image of CuSCN@Au sample which is shown in the part A. The substrate is atomically flat Au(111) deposited at mica (Part B, Top chart).

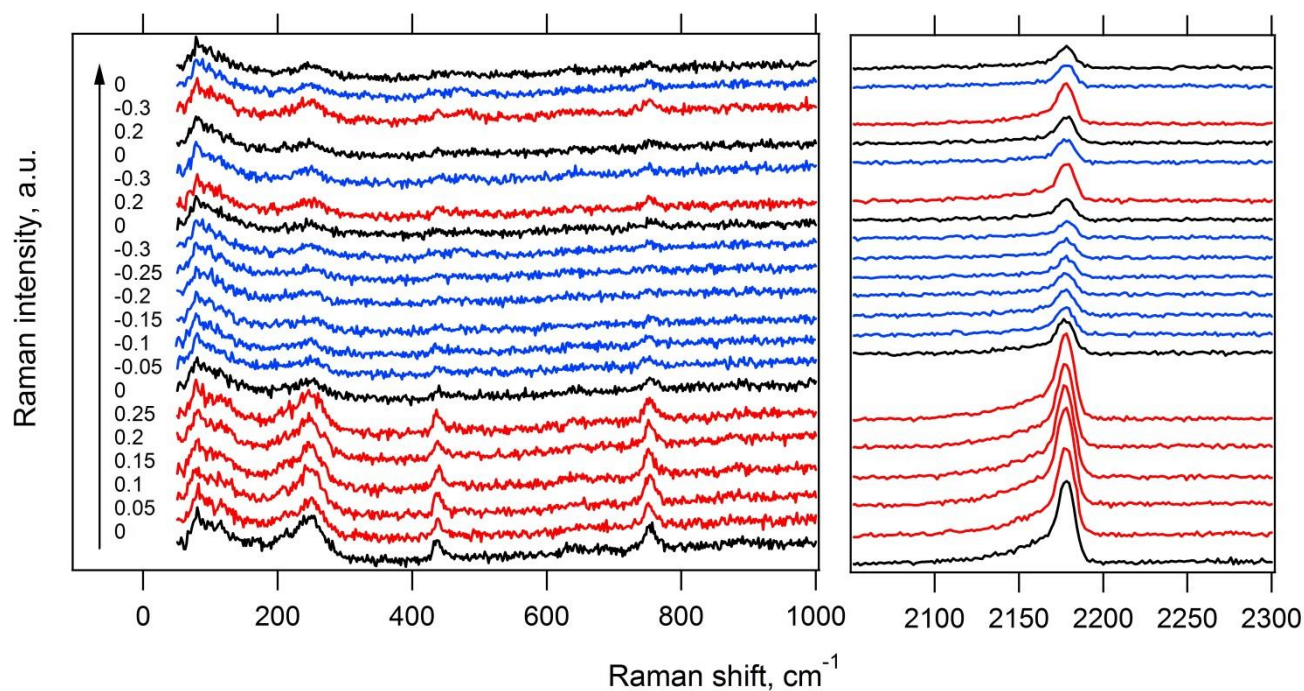


Figure S10: *In-situ* Raman spectroelectrochemistry of a thin film of CuSCN deposited on Au substrate. The applied potential (in V vs. Ag/AgCl) is shown on the left-side chart. The measurement sequence follows the arrow, i.e. the first spectrum was acquired at 0 V (bottom black line) and the last spectrum was acquired again at 0 V (top black line). The positive/negative potentials are visualized by red/blue curves, respectively. Electrolyte solution: 0.5 M KCl saturated with CuSCN, pH 6. Spectra are offset for clarity, but the intensity scale is identical in each chart.

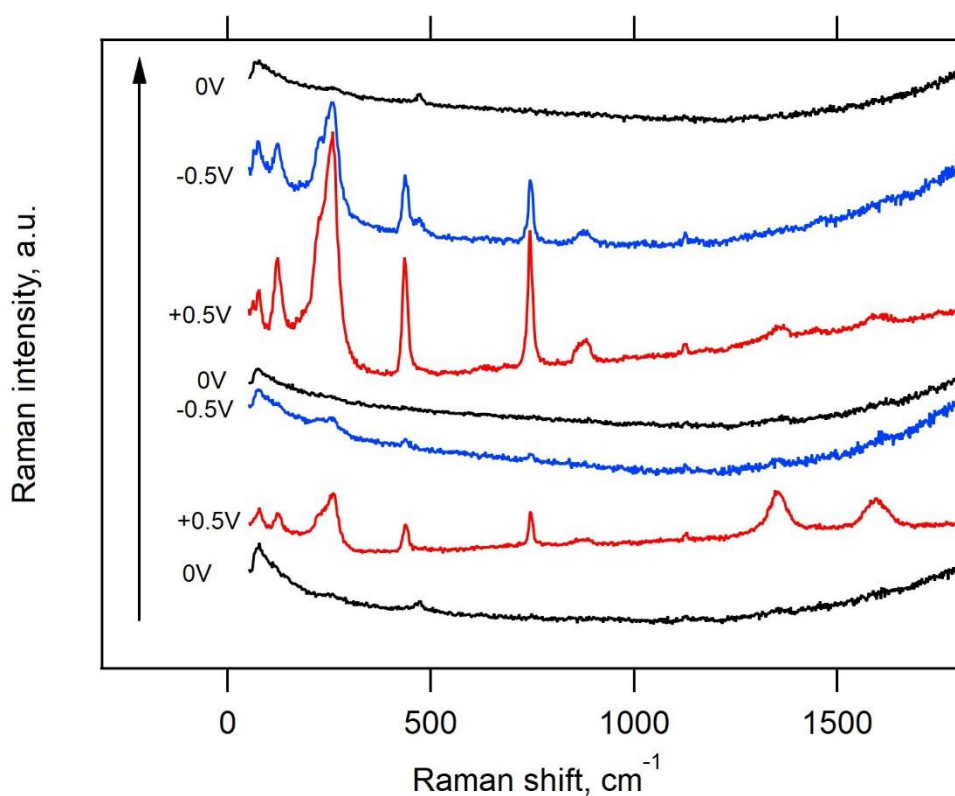


Figure S11: In-situ Raman spectroelectrochemistry of a thin film of CuSCN deposited on GC substrate. The applied potential (in V vs. Ag/AgCl) is shown on the left-side chart. The measurement sequence follows the arrow, i.e. the first spectrum was acquired at 0 V (bottom black line). This starting spectrum was actually acquired on a previously used film (tested between -0.3V to 0.25 V) which is shown in the main text (Fig. 5, top line). The last spectrum in Fig. S11 was measured again at 0 V (top black line). The positive/negative potentials are visualized by red/blue curves, respectively. Electrolyte solution 0.5 M KCl saturated with CuSCN, pH 6. Spectra are offset for clarity, but the intensity scale is identical. It is interesting to note that the „anodic Raman enhancement“ at 0.5 V exhibits some hysteresis, i.e. the Raman signal persists even in the subsequently measured spectrum at -0.5 V, and disappears only in the next spectrum at 0 V. Furthermore, the intensity enhancement progresses when the anodic treatment at 0.5 V was repeated in the next run of spectral acquisition.

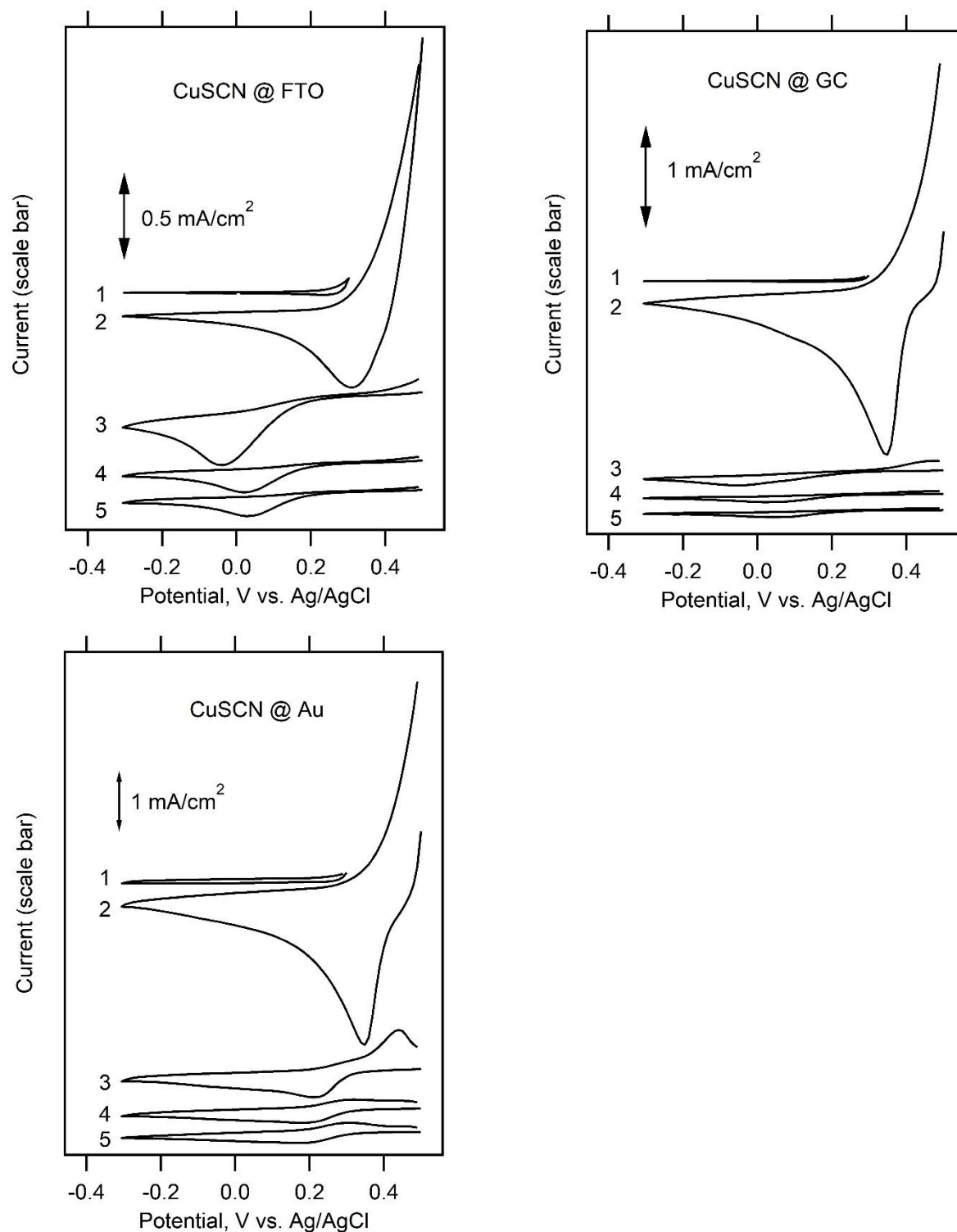


Figure S12: Cyclic voltammograms of CuSCN films on FTO substrate (left upper chart), glass-like carbon (right upper chart) and Au substrate (bottom chart). Scan rate 0.1 V/s. Electrolyte solution 0.5 M KCl saturated with CuSCN, pH 6. On all charts, the voltammogram 1 is for the initial scan of a fresh electrode within vertex potentials 0.3 V and -0.3 V. The voltammograms 2-5 are subsequent scans measured after 100 s of arresting the potential at 0.5 V and then cycled from 0.5 V to -0.3 V and back.

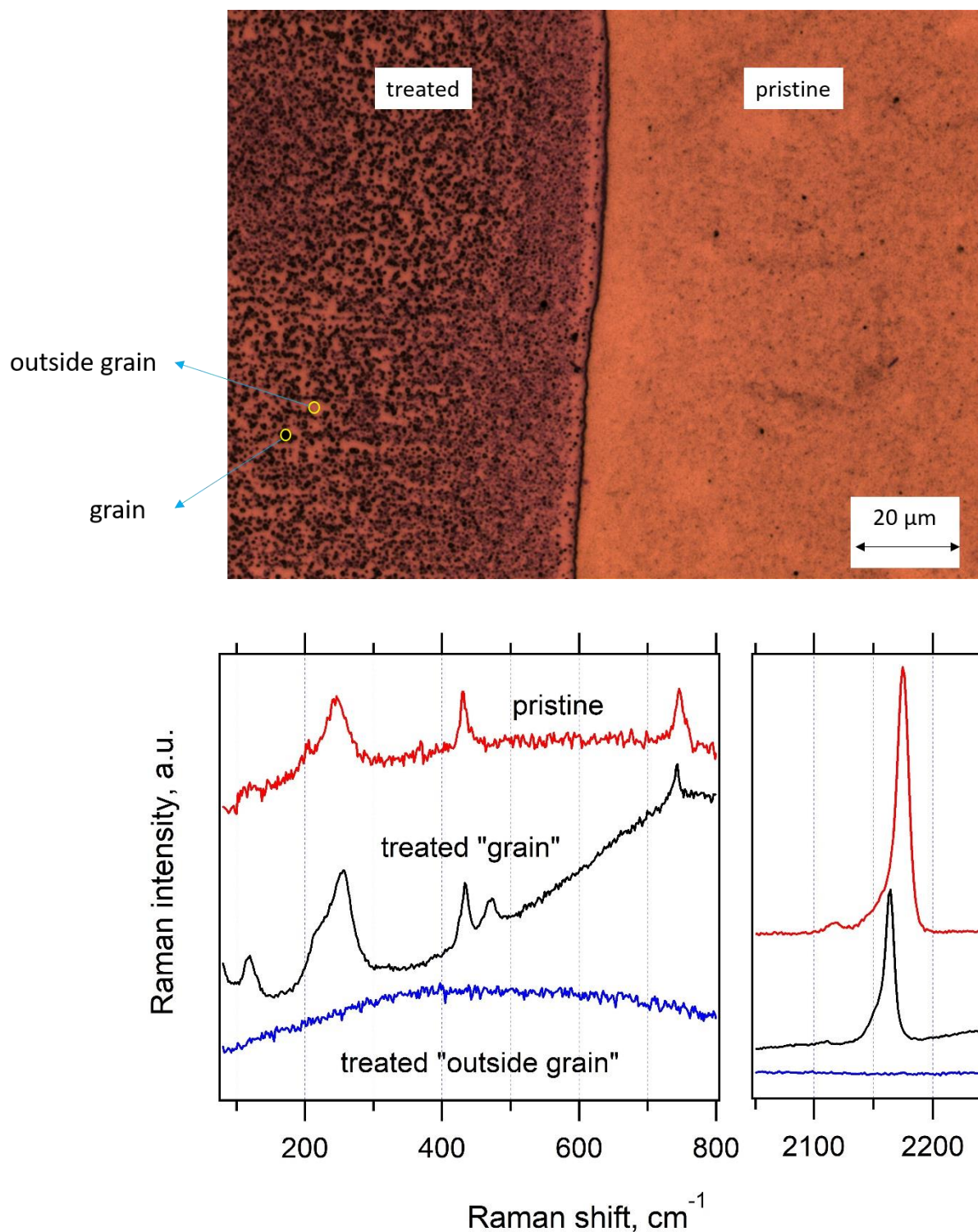


Figure S13: [Upper chart] Microscopic image of the interface of electrochemically treated and untreated CuSCN film on Au-substrate. Treatment in 0.5 M KCl for 100 s at 0.5 V vs. Ag/AgCl and then cycled between 0.5 V and -0.3 V. [Lower chart] Micro-Raman spectrum of pristine (electrochemically untreated) part of the CuSCN film (red line) and two positions in the electrochemically treated part of the film (inside grain: black line; outside grain: blue line). Excitation wavelength 514 nm. The Raman spectrum of the treated sample (grain) exhibits an extra feature at 470 cm^{-1} and a red-shifted (by 10 cm^{-1}) peak of C \equiv N stretching vibration in Cu-SCN.

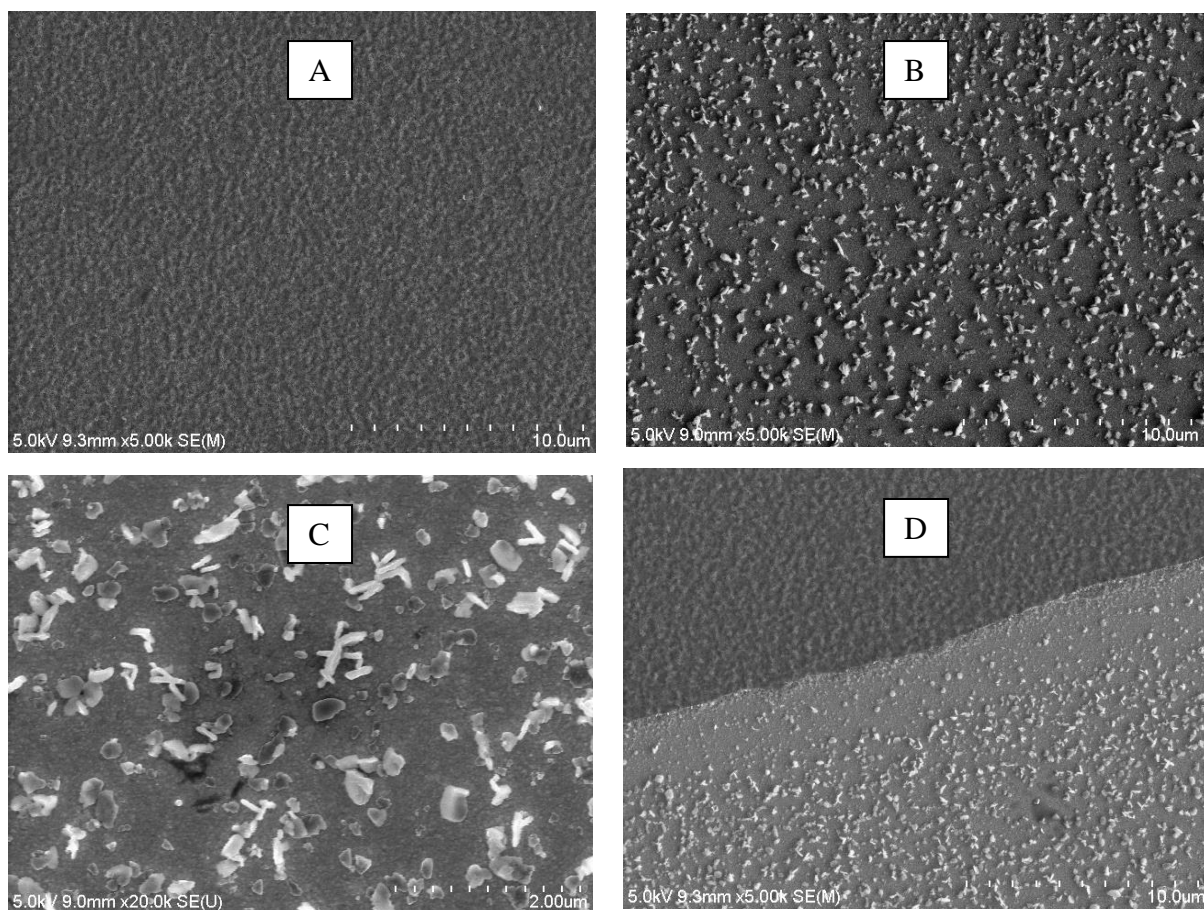


Figure S14: SEM images of CuSCN@Au electrode pristine (A) and electrochemically treated (B-D). Treatment in 0.5 M KCl for 100 s at 0.5 V vs. Ag/AgCl and then cycled between 0.5 V and – 0.3 V. The image in chart [D] shows a border between the treated and untreated parts of the electrode. The electrochemical treatment causes that the originally compact and uniform CuSCN film (A) transforms into sub-micron sized particles of variable shapes (B-D).

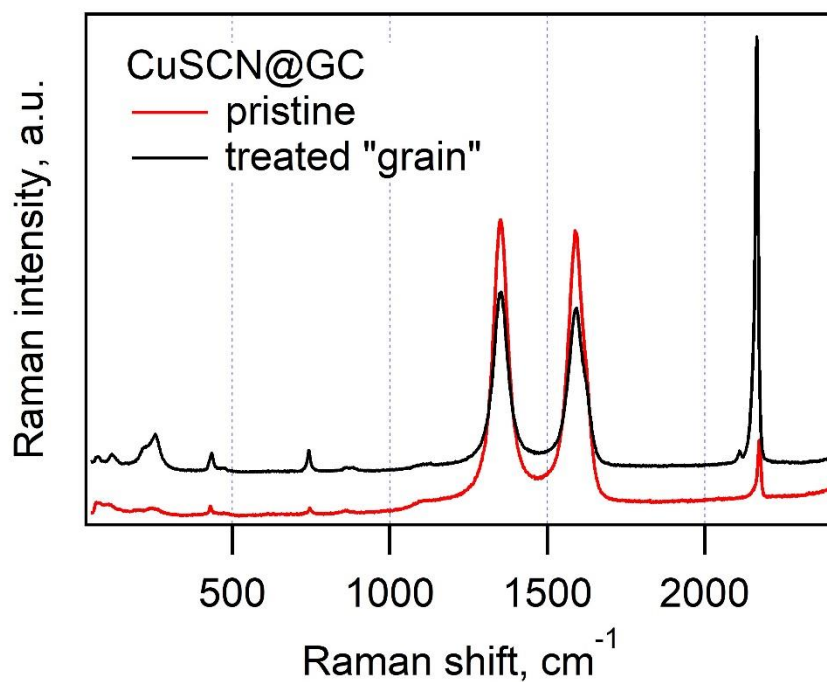


Figure S15: Raman spectra of electrochemically treated and untreated CuSCN film on GC-substrate. Treatment in 0.5 M KCl for 100 s at 0.5 V vs. Ag/AgCl and then cycled between 0.5 V and – 0.3 V. Red curve is for the spectrum of pristine (electrochemically untreated) film. Black line is for the spectrum of electrochemically treated film. Excitation wavelength 514 nm. The Raman spectrum of treated sample (grain) exhibits enhanced Raman features of CuSCN with a red-shifted (by 10 cm^{-1}) peak, which is originally assigned $\text{C}\equiv\text{N}$ stretching vibration in pristine Cu-SCN.

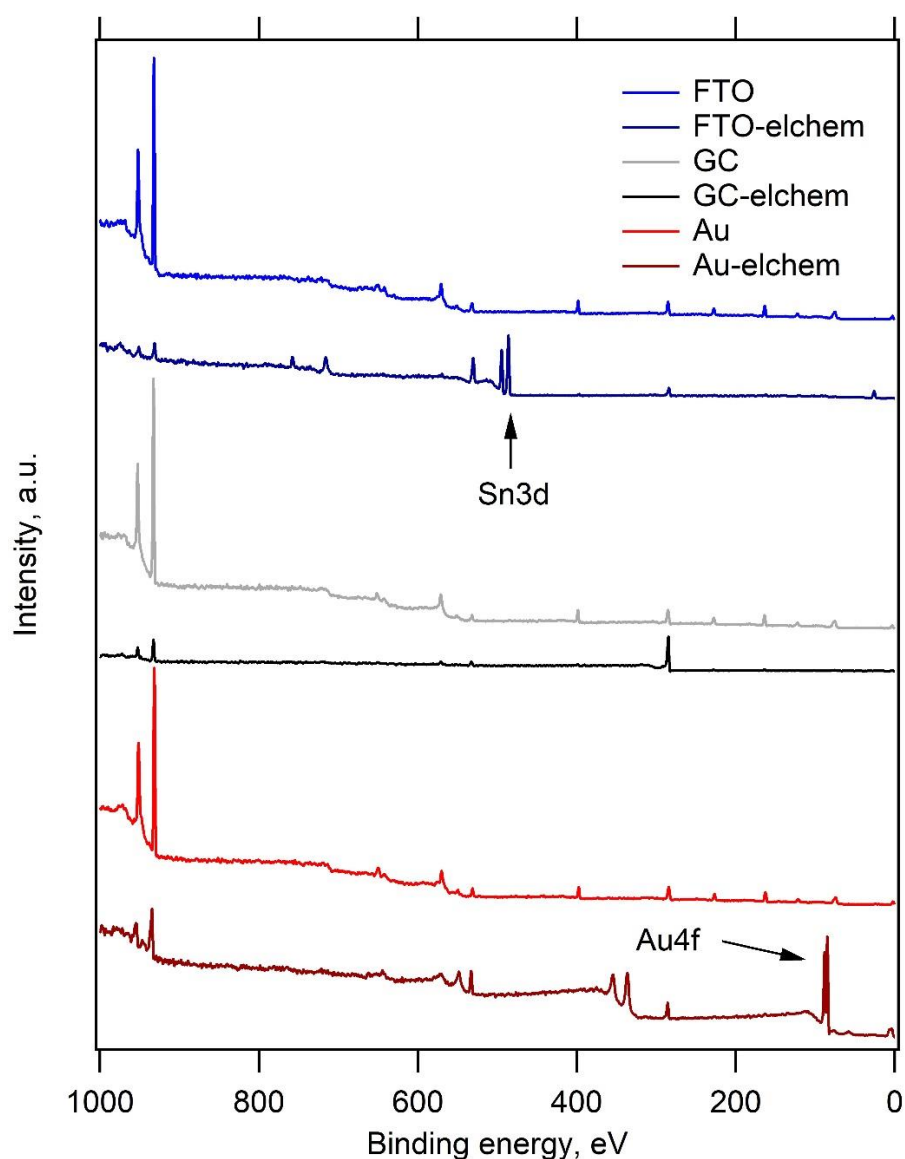


Figure S16: XPS spectra of CuSCN films at various substrates (FTO-top chart; GC-middle chart; Au-bottom chart). The spectra of pristine films and those upon electrochemical treatment are shown. Treatment in 0.5 M KCl for 100 s at 0.5 V vs. Ag/AgCl and then cycled between 0.5 V and – 0.3 V. The photoelectron take-off angle 90°. The treatment causes overall drop of intensity of signals assignable to CuSCN. Furthermore, the signal from a substrate (Sn or Au; which is absent in pristine films) clearly appears upon the treatment. This evidences cracking of the film up to denuding of the bare substrate. (In the case of GC, the uncovered substrate manifests itself by the C1s intensity enhancement only).

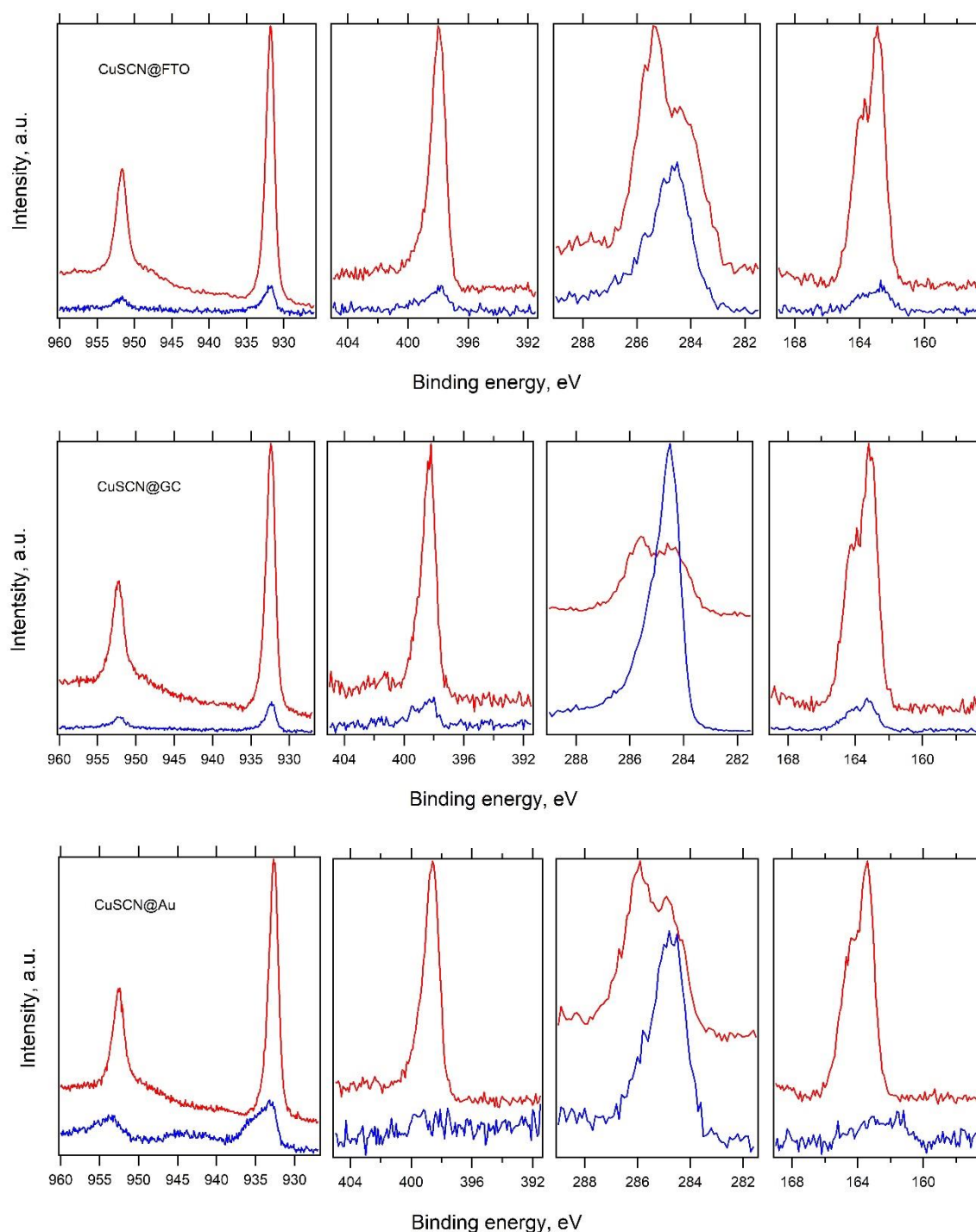


Figure S17: XPS spectra of CuSCN films at various substrates (FTO-top chart; GC-middle chart; Au-bottom chart). The spectra of pristine films (red curves) and those upon electrochemical treatment (blue curves) are shown. Treatment in 0.5 M KCl for 100 s at 0.5 V vs. Ag/AgCl and then cycled between 0.5 V and -0.3 V. The photoelectron take-off angle 90° . The treatment causes overall drop of intensity of signals assignable to CuSCN and disappearance of the C1s signal of $\text{C}\equiv\text{N}$ at ca. 286 eV. The oxidation to Cu(II) manifests itself by shoulders with enhanced binding energies of Cu2p and by the emergence of shake-up satellite which is diagnostic for Cu(II). However, this effect is clearly seen for CuSCN@Au only.

Table S3. Surface analysis by XPS – elemental composition in at%. CuSCN films at various substrates (FTO, GC and Au) were analyzed. Data for pristine films and those after electrochemical treatment are listed. (Treatment in 0.5 M KCl for 100 s at 0.5 V vs. Ag/AgCl and then cycled between 0.5 V and – 0.3 V; labeled ‘*elchem.*’). The analysis was carried out at two take-off angles of photoelectrons, 90° and 9°. The treatment causes overall drop of intensity of signals assignable to CuSCN. Furthermore, the elements marking the substrate clearly appear upon the treatment. This documents massive cracking of the film up to denuding of the bare substrate. (In the case of GC, this is documented solely by the larger surface content of C).

Substrate	Treatment	Angle	C1s	O1s	N1s	S2p	Cu2p	other
FTO	none	90°	40.8	8.2	16.0	19.4	15.6	-
FTO	none	9°	44.8	9.5	14.8	17.2	13.7	-
FTO	<i>elchem.</i>	90°	39.8	36.5	3.0	4.3	2.9	Sn 13.4
FTO	<i>elchem.</i>	9°	48.1	23.0	9.0	7.2	4.6	Sn 8.1
GC	none	90°	47.7	4.7	14.9	17.5	15.3	-
GC	none	9°	56.5	9.0	10.9	13.6	10.0	-
GC	<i>elchem.</i>	90°	89.8	3.8	2.7	2.0	1.7	-
GC	<i>elchem.</i>	9°	79.8	7.5	7.0	4.0	1.7	-
Au	none	90°	44.1	7.0	14.7	18.1	16.1	-
Au	none	9°	47.6	10.3	13.7	16.5	11.9	-
Au	<i>elchem.</i>	90°	47.1	16.5	0.1	3.2	7.4	Au 25.7
Au	<i>elchem.</i>	9°	81.1	14.7	-	-	1.2	Au 3.0

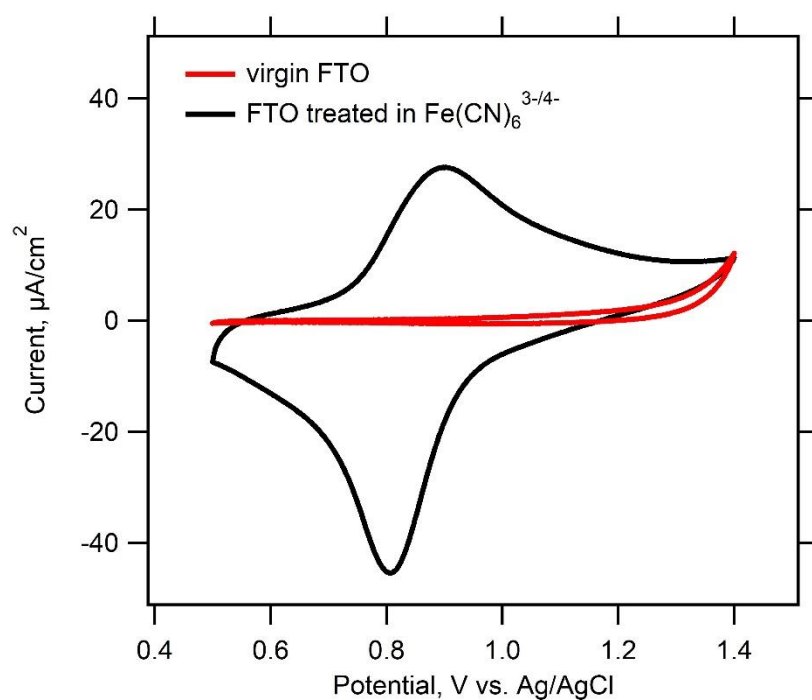


Figure S18: Cyclic voltammogram of a new virgin FTO electrode (red curve) and FTO, which was previously cycled in 0.5 M KCl + 0.5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ + 0.5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ pH 2.5 (black curve). Scan rate 0.2 V/s. The latter voltammogram shows clear signature of the presence of Prussian blue deposit on the FTO surface ^{5,6}.

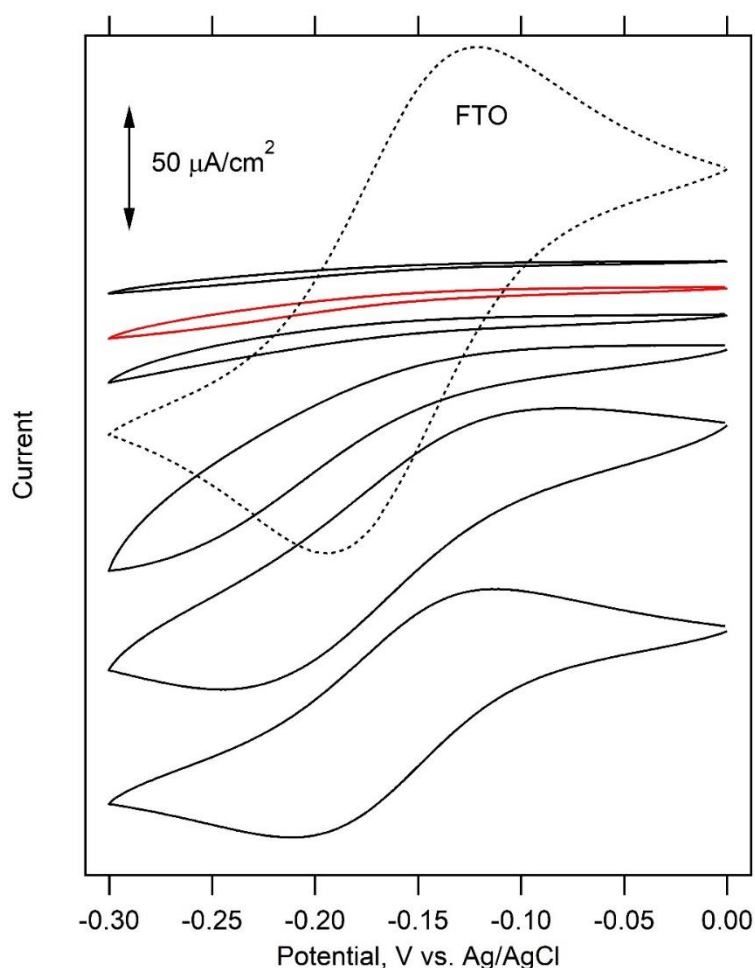


Figure S19: Cyclic voltammogram of 0.5 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ in 0.5 M KCl saturated with CuSCN, pH 6. Scan rate 50 mV/s. Dashed curve is for a blank FTO electrode. The remaining voltammograms (full curves) are for the CuSCN@FTO electrodes. The individual films are distinguished by different conditions of spin-coating, i.e. by rotation rate (low = 1000 rpm or high = 5000 rpm) and by dropping of the CuSCN+Et₂S solution either at static conditions (S, on non-rotating substrate) or at dynamic conditions (D, on rotating substrate). The sequence of experimental conditions is as follows (for top to bottom curves: D-high, D-high, D-low, S-high, S-low, S-low). Though the reproducibility of individual samples is not perfect, the best blocking films (top curves) are regularly fabricated at dynamic spin-coating with high spinning rate. The red curve is a re-plotted voltammogram from the main text.

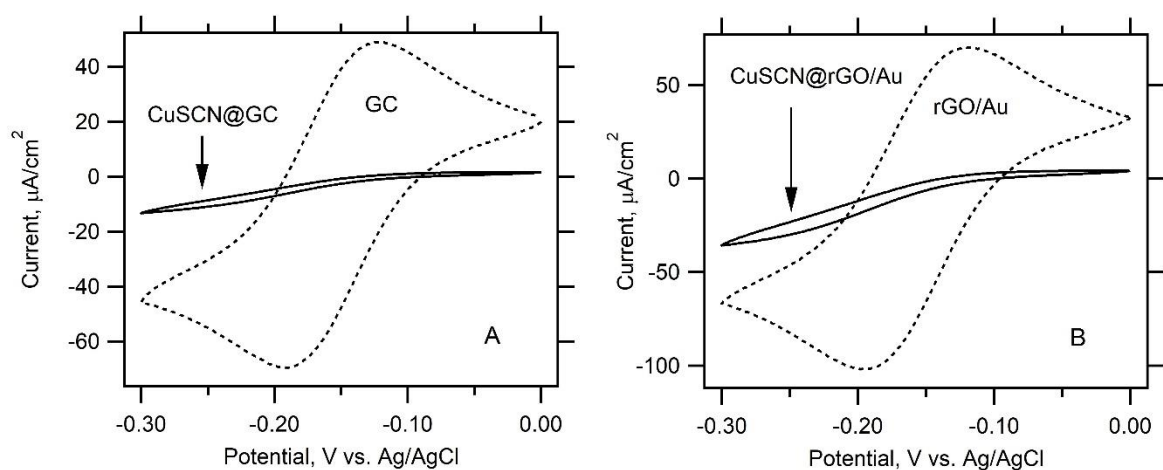


Figure S20: Cyclic voltammogram of 0.5 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ in 0.5 M KCl saturated with CuSCN, pH 6. Scan rate 50 mV/s. [A] CuSCN film deposited on glass-like (GC) electrode, diameter 3 mm. Dashed curve is for a blank (GC) electrode. [B] CuSCN film deposited on reduced graphene oxide (rGO) supported by Au. Dashed curve is for a blank electrode (rGO supported by Au).

Table S4: Photovoltaic parameters of perovskite solar cells based on two different architectures of the hole-extracting system: CuSCN/Au or CuSCN/rGO/Au. Experimental data from Figure 7 in the main text (illumination AM1.5G, area 0.16 cm²). V_{oc} = open circuit voltage, J_{sc} = short circuit photocurrent, FF = fill factor, η = solar conversion efficiency

Hole-extracting system	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	η [%]
CuSCN/Au	1.090	23.4	75.5	19.3
CuSCN-rGO/Au	1.120	23.1	75.8	19.6

References

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