Electronic Supplementary Information

for

Underpotentially-deposited silver substrates reverse odd-even interfacial properties of CF_3-terminated SAMs

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Cyclic Voltammograms

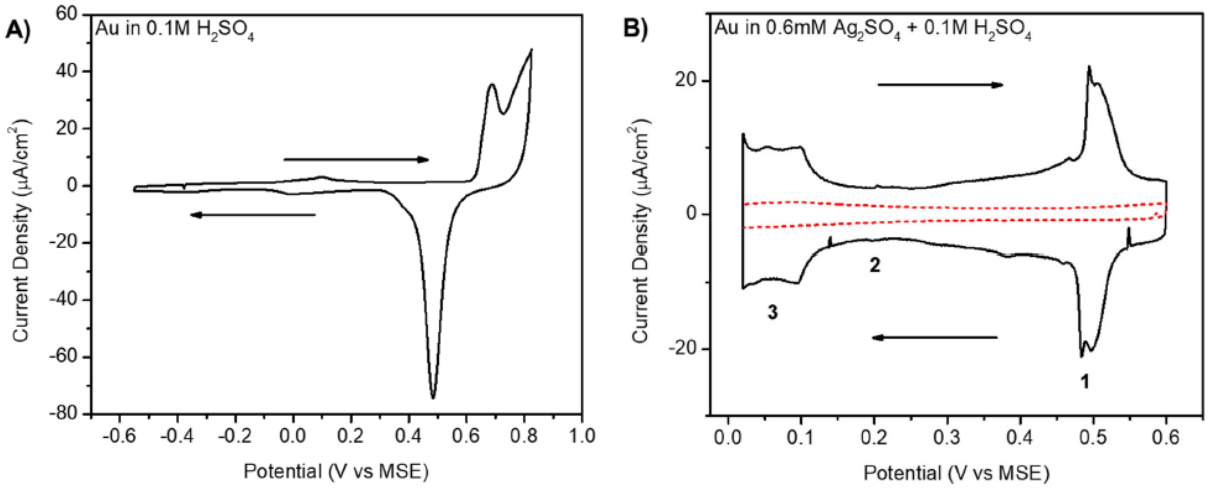

Figure S1. Representative cyclic voltammograms for A) bare gold and B) silver on gold in sulfuric acid electrolyte, at a scan rate of 15 mV s^{-1}. The arrows denote the direction of the scan. The red dashed line represents the Au CV in pure H_2SO_4 in the potential region shown. Regions 1–3 in Figure B) denote the different layers of Ag deposited onto the gold.[1] Regions 1 (0.25–0.55 V vs MSE) and 2 (0.15–0.25 V vs MSE) correspond to the deposition of the first full monolayer of Ag onto the Au slide and region 3 (~0.1 V vs MSE) begins the bulk deposition of metal.[1]

Stripping voltammetry was used to determine the coverage, in monolayers, of silver deposited onto the polycrystalline gold slides.[2] It performed by starting with a potential slightly negative of the UPD peak at 0.15 V vs MSE and oxidizing the electrode along the range shown in Figure S1 B) until the CVs stopped changing. Representative cyclic voltammograms for the bare Au, Au in Ag solution, and UPD Ag stripping are shown in Figure S2. The initial positive sweep of the Ag oxidation in the stripping voltammogram was analyzed to determine the UPD Ag coverage on the Au slides. The stripping voltammograms were first normalized to the corresponding bare Au double layer current shown in Figure S2. The Ag stripping peak was then integrated, and the area was divided by the scan rate and the geometric surface area of the slide to determine the Ag charge density. The charge density was then divided by the literature value of 222 μC/cm^2 for the charge density of a full monolayer of Ag on Au (111), which corresponds to $\phi_{UPD} = 0.8$.[3,4] This value was chosen because it corresponds to an epitaxial layer of Ag on Au and because the evaporated gold used in this study is considered to be mostly (111) in character.[2]

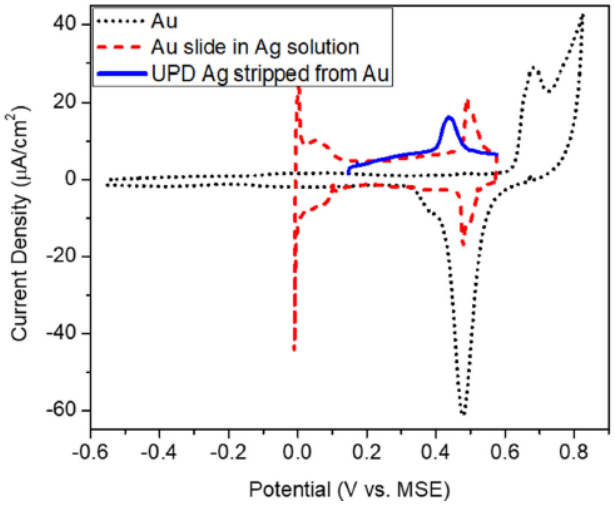

Figure S2. Overlapped voltammograms: Au in H_2SO_4 (black dot), Au in Ag solution (red dash), and the first scan of Ag stripped from Au (blue solid line).

The UPD Ag coverage obtained by calculation was 0.46 ± 0.03. The coverage determined from voltammetry falls short of the ϕ_{UPD} = 0.8 value for a full monolayer of silver on gold. Part of this discrepancy could be due to the calculation for the surface area of the gold slide; since the surface roughness before and after the voltammetry was unknown, no correction factor could be applied to account for it, yielding a smaller value for the coverage. Similar results were obtained in a study by Jennings et. al., where coverage of the Ag UPD layer was 0.41 ± 0.05 and thus, noted that coverages determined by coulometric measurements can underestimate surface coverage,[2] Coverage calculated using XPS binding energies were still lower than 0.81 in value. However, monolayer coverage was assumed.[2]

XPS Spectra

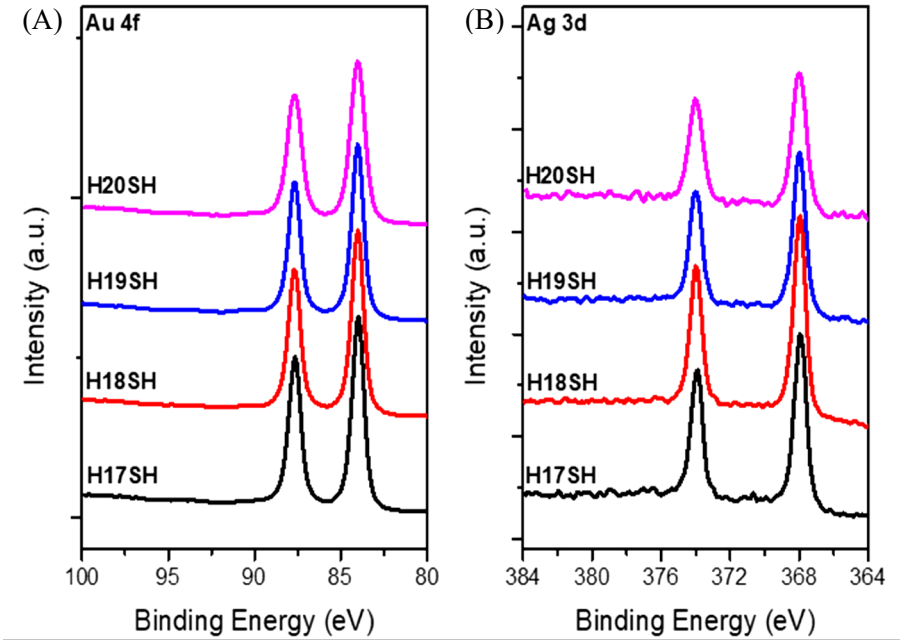

Figure S3. XPS spectra for the (A) Au 4f and (B) Ag 3d region for the HnSH SAMs on UPD Ag substrates

Table S1. XPS Peak Positions for the HnSH SAMs on Au and UPD Ag

Adsorbate/ Metal	Peak Position (eV)					
	Ag $3d_{5/2}$	Ag $3d_{3/2}$	C 1s (CH_2/ CH_3)	C 1s (CF_2)	F 1s	S 2p
H17SH/Au	-	-	284.9	-	-	162.0
H18SH/Au	-	-	285.0	-	-	162.0
H19SH/Au	-	-	285.0	-	-	162.0
H20SH/Au	-	-	285.0	-	-	162.
H17SH/UPD Ag	368.0	374.0	285.1	-	-	161.9
H18SH/UPD Ag	367.9	374.0	285.2	-	-	161.8
H19SH/UPD Ag	367.9	373.9	285.3	-	-	161.9
H20SH/UPD Ag	367.9	374.0	285.3	-	-	161.8

The "-" indicate that no peak intensities were observed at these binding energies.

Table S2. XPS Peak Positions for the F1HmSH SAMs on Au and UPD Ag

Adsorbate/ Metal	Peak Position (eV)					
	Ag $3d_{5/2}$	Ag $3d_{3/2}$	C 1s (CH_2/ CH_3)	C 1s (CF_2)	F 1s	S 2p
F1H16SH/Au	-	-	284.8	292.6	688.3	162.0
FH17SH/Au	-	-	284.8	292.7	688.4	162.0
FH18SH/Au	-	-	248.9	292.6	688.3	162.0
FH19SH/Au	-	-	284.8	292.8	688.3	161.9
F1H16SH/UPD Ag	367.9	373.9	285.1	292.9	688.6	161.8
F1H17SH/UPD Ag	367.9	373.9	285.1	292.9	688.5	161.8
F1H18SH/UPD Ag	368.0	374.0	285.1	293.0	688.6	161.9
F1H19SH/UPD Ag	367.9	374.0	285.1	293.0	688.5	161.8

The "-" indicate that no peak intensities were observed at these binding energies.

Table S3. Surface Tension Values of the Contacting Liquids Used in the Study

Liquid	γ_{LV} (mN/m)	Liquid	γ_{LV} (mN/m)
H_2O	72.8	**NB**	43.8
GL	65.2	**BNP**	44.6
FA	57.3	**DC (cis)**	31.7
DMSO	43.5	**DC (trans)**	29.4
DMF	34.4	**HD**	27.1
ACN	28.7	**FDC**	19.2

Table S4. Advancing Contact Angles (°) of the Polar Liquids on HnSH and F1HmSH SAMs on Au and UPD Ag Surfaces

Adsorbate	H_2O	GL	FA	DMSO	DMF	ACN	NB	BNP
H17SH/Au	118	97	95	79	71	65	70	64
H18SH/Au	117	101	98	83	74	68	73	70
H19SH/Au	117	98	95	80	72	65	69	65
H20SH/Au	119	101	99	84	74	69	72	70
H17SH/UPD Ag	120	102	98	82	74	65	74	68
H18SH/UPD Ag	117	98	92	79	72	63	69	65
H19SH/UPD Ag	119	103	98	83	75	68	73	69
H20SH/UPD Ag	118	98	95	80	72	63	70	65
F1H16SH/Au	113	101	93	74	63	55	69	75
F1H17SH/Au	113	99	89	70	60	51	66	72
F1H18SH/Au	114	102	95	75	67	57	71	78
F1H19SH/Au	114	98	92	71	63	53	67	75
F1H16SH/UPD Ag	112	101	93	69	59	50	67	73
F1H17SH/UPD Ag	115	104	98	75	65	56	70	78
F1H18SH/UPD Ag	113	100	92	70	62	52	66	76
F1H19SH/UPD Ag	116	105	97	76	67	57	71	80

Table S5. Advancing Contact Angles (°) of the Nonpolar and Weakly Polar Liquids on HnSH SAMs and F1HmSH SAMs on Au and UPD Ag Surfaces

Adsorbate	BNP	DC	HD	FDC
H17SH/Au	64	51	45	37
H18SH/Au	70	56	49	41
H19SH/Au	65	51	44	38
H20SH/Au	70	55	49	42
H17SH/UPD Ag	68	56	48	40
H18SH/UPD Ag	65	51	44	37
H19SH/UPD Ag	69	56	50	43
H20SH/UPD Ag	65	52	45	38
F1H16SH/Au	75	65	61	26
F1H17SH/Au	72	64	59	22
F1H18SH/Au	78	68	63	30
F1H19SH/Au	75	66	60	25
F1H16SH/UPD Ag	73	67	60	22
F1H17SH/UPD Ag	78	70	63	30
F1H18SH/UPD Ag	76	67	62	25
F1H19SH/UPD Ag	80	70	65	30

References

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