A Widely-Applicable Gold Substrate for the Study of Ultrathin Overlayers

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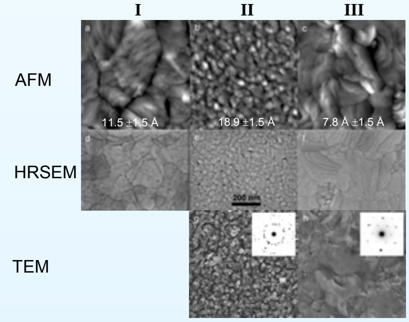
In this work we show that 15-nm-thick gold films evaporated on silanized glass and annealed are semi-transparent, electrically conducting, and morphologically well-defined, showing a smooth, {111} textured surface. Such Au films provide a high-quality, widely-applicable and relatively inexpensive platform for ultrathin overlayers, enabling characterization by a wide spectrum of experimental methods, applied to the same substrate. The exceptional qualities and analytical capabilities of such substrates are demonstrated with several different systems: (i) Cu underpotential deposition (upd); (ii) alkanethiol self-assembly; (iii) formation of gold nanoparticle layers; (iv) binding of the chromophore protoporphyrin IX (PPIX) to a monolayer of 11-mercaptoundecanoic acid (MUA). In the latter case it is shown that the use of Cu^{2+} ions for binding between the carboxylate groups of PPIX and MUA promotes better organization of the porphyrin layer.

Morphology and surface structure of thin, continuous, transparent gold substrates

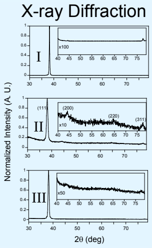
1. a-c: Non-contact AFM (a-c) of gold substrates **I**, **II**, **III**, respectively (z-scale: 50 Å (**I**), 90 Å (**II**), 35 Å(**III**)). Roughness values are shown on bottom of images.

d-f: High-resolution SEM (HRSEM) of gold substrates **I**, **II**, **III**, respectively.

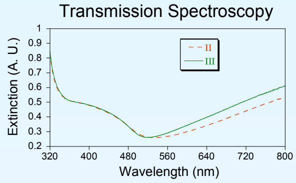
g-h: TEM images and selected-area (80 nm aperture) diffraction patterns (insets) of substrates **II** and **III**, respectively.



2. X-ray diffraction (θ-2θ) shows annealed substrates I and III are more oriented and {111} textured:



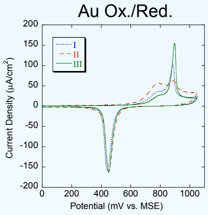
3. Transmission UV-vis spectroscopy of unannealed (II) and annealed (III) substrates shows slight increases in extinction following annealing:



4. Electrochemical characterization.

Left: Cyclic voltammetry of Au substrates I, II, III in 0.1 M H2SO4 showing the Au oxide formation/stripping waves. Scan rate: 0.1 V/s.

Right: Cu underpotential deposition (upd) on Au substrates I, II, III in 1.0 mM CuSO4 + 0.1 M H2SO4. Scan rate: 0.02 V/s.



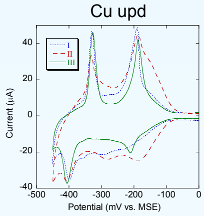
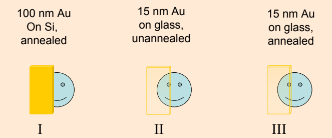


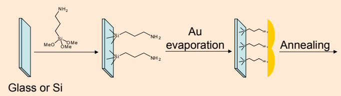
Table: Calculated roughness of substrates I-III

Substrate	Q_{anodic} (µC/cm², ±3.5%)	Roughness (±3.5%)
I	533.3	1.33
II	749.0	1.87
III	558.5	1.39

The Compared Substrates



Substrate Preparation Scheme



Versatility of the transparent gold substrates in characterization of ultrathin overlayers

1. AFM, ellipsometry, contact angles, UV-vis transmission spectroscopy of a single layer of Gold nanoparticles (NPs) on annealed transparent substrates (III)

Transmission UV-vis spectra of:

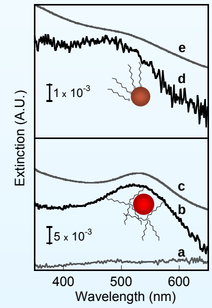
(a) 1,10-decanedithiol SAM,

(b) TOAB-capped NP layer on the SAM in a,

(c) TOAB-capped NP solution in toluene,

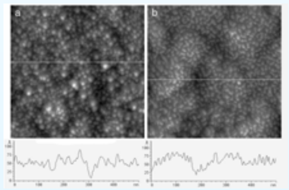
(d) octanethiol-capped NP layer on the SAM in a,

(e) octanethiol-capped NP solution in CHCl3.



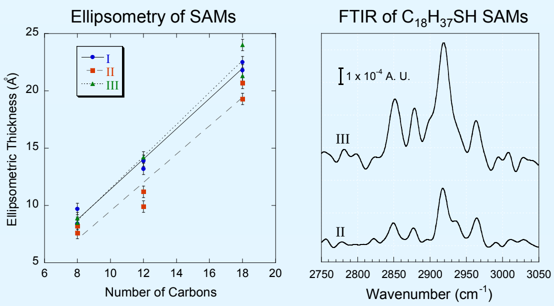
Adsorbate	NPs on dithiol SAM	
	Ellipsometry† -δΔ (deg)	CA (deg) adv(st dev) , rec(st dev)
TOAB-capped NPs	8.1± 0.3	86 (3) , 36 (4)
Octanethiol-capped NPs	3.0± 0.1	105 (2) , 96 (4)

†For the SAM of 1,10-decanedithiol, -dD = 1.1°± 0.1°.



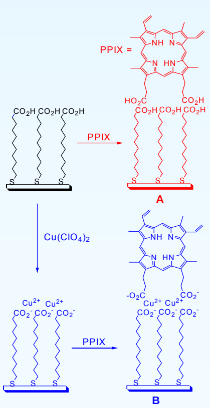
AFM images of monolayers of (a) TOAB-capped and (b) octanethiol-capped NPs bound onto 1,10-decanedithiol SAMs (500x500 nm²).

2. Alkanethiol SAMs characterization by ellipsometry, water contact angles, and RA-FTIR spectroscopy

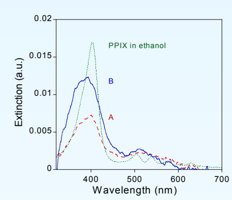


Substrate	Contact angles - adv. (st dev), rec. (st dev) (deg)		
	$C_8H_{17}SH$	$C_{12}H_{25}SH$	$C_{18}H_{37}SH$
I	104.5 (0.2), 105.1 (0.4)	111.8 (1.0), 109.2 (0.1)	106.7 (0.4), 105.0 (1.7)
II	109.7 (1.6), 108.4 (2.4)	111.2 (2.0), 107.0 (2.6)	109.9 (1.0), 107.8 (0.9)
III	103.1 (0.4), 102.1 (0.7)	106.4 (0.9), 104.1 (0.8)	108.8 (1.3), 107.3 (1.0)

3. Protoporphyrin IX (PPIX) binding to free (A) and Cu^{2+}-bound (B) carboxylic acid SAMs, monitored by transmission UV-vis spectroscopy, ellipsometry and contact angles.



- PPIX forms well-packed monolayers on Cu^{2+}-bound carboxylic SAMs than on free carboxylic acid SAMs.



Substrate, Φ (deg)	Atomi…
	Cu
I , 90	1.4
I , 25	1.3
III , 90	2.2
III , 25	2.1

Route (Substrate)	MUA		Cu^{2+}		PPIX	
	Thickness (±1 Å)	CA (deg) adv (st dev), rec (st dev)	Thickness (±1 Å)	CA (deg) adv (st dev), rec (st dev)	Thickness (±1 Å)	CA (deg) adv (st dev), rec (st dev)
A (I)	16.6	18.2 (1.9), -			29.7	50.0 (7.0), 29.8 (2.9)
A (II)	15.4	19.3 (2.8), -			25.1	47.2 (4.9), 22.7 (2.9)
A (III)	16.3	21.7 (2.4), -			30.8	52.9 (4.7), 23.1 (3.0)
B (I)	18.2	31.4 (4.6), -	18.7	35.0 (1.5), 32.0 (4.8)	36.0	76.1 (1.0), 66.2 (3.7)
B (II)	14.5	17.0 (2.5), -	18.4	31.6 (3.6), 25.0 (3.6)	34.1	75.9 (0.9), 72.0 (2.9)
B (III)	17.2	21.0 (1.8), -	19.5	35.4 (2.9), 26.7 (1.9)	34.1	78.6 (0.5), 73.5 (2.0)

Conclusions

- Semi-transparent continuous, 15-nm-thick Au films are stable, morphologically well-defined and highly versatile substrates for the preparation and study of SAMs and other kinds of ultrathin overlayers on Au.
- This enables the use of a wide spectrum of characterization methods, applied to the same substrate, including AFM, XRD, TEM, SEM, XPS, electrochemical methods, CA measurements, ellipsometry, transmission spectroscopy, and RA-FTIR spectroscopy.
- These substrates exhibit a morphology similar to that of thick (≥100 nm) annealed Au films, showing large, flat domains, a strong {111} texture and a low roughness factor.