

Supporting Information

Multicomponent Patterning of Indium Tin Oxide

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All reagents and solvents were purchased from Sigma-Aldrich and used as supplied unless otherwise stated. Ethanol, isopropanol and deionized water were filtered through a 0.2 μm filter before use. SEM images were recorded on the FEI XL30 SEM-FEG microscope detecting secondary electrons at 15 mm working distance. XPS spectra were recorded on the Kratos Axis Ultra XPS spectrometer equipped with a mono-Al X-ray source. ITO substrates ($\sim 1\text{ cm} \times 1\text{ cm}$) were manufactured by coating silicon wafers with 2000Å ITO using an RF dielectric sputter system (Kurt Lesker PVD 75). Chemically modified ITO substrates were analyzed for surface roughness using tapping mode atomic force microscopy on the Veeco D3100 using TESP silicon nitride probes with a 42 N/m spring constant.

Si/SiO₂ master fabrication

NR9-1500PY (Futurrex) was spun on a clean silicon chip at 3000 rpm for 40 sec. The resulting substrate was baked on a digital hot plate at 155°C for 2 min to produce 180nm of the resist on Si. Photolithography (Karl Suss MA6/BA6) was performed using a photomask (Photo Sciences, Inc.) bearing 16 μm hexagons with an exposure time of 11.5 sec. After UV exposure, the substrate was baked on a digital hot plate at 105°C for 70 sec, developed in RD6 (Futurrex) for 11 sec and immediately rinsed with water. The dried substrate was baked in an oven at 110 °C for 5 min and descumed in oxygen plasma for 1 min at 100 watts and 6×10^{-1} mbar O₂ pressure (Emitech K-1050X plasma asher). The oxide layer was etched away through the opening in photoresist using reactive ion etching (Trion

Technology Phantom II) for 22 min using CF_4 and O_2 . Any remaining oxide was removed using buffered oxide etch (BOE). The negative resist was removed with nanostrip (55 °C, 2 min) producing a patterned silicon/ SiO_2 master.

SAMs formation

NHS-terminated SAM formation. ITO surfaces were rinsed briefly with water, ethanol and isopropanol and dried under a stream of filtered argon. They were subsequently cleaned in a plasma oxidizer (Emitech K-1050X, 5 min, 100 W) to remove any organic contaminants. Vapor phase silanization was accomplished using a protocol similar to that published by Riener et al Octyl-terminated surfaces were made by placing ITO substrates in a glass bottle under high vacuum containing 2 mL vials of octylpropyltrimethoxysilanes (30 μL) and triethylamine (10 μL). After 16 hours the surfaces were removed and rinsed thoroughly with dichloromethane and ethanol and dried under a filtered stream of argon. Amino-terminated surfaces were formed by placing ITO substrates in a glass bottle containing 2 mL vials of aminopropyltrimethoxysilanes (30 μL) and triethylamine (10 μL). After 2 hours, the surfaces were removed and rinsed with dichloromethane and ethanol and dried under argon. The octyl-functionalized surface was subsequently covered with $\sim 50 \mu\text{L}$ of a 0.1 M solution of 2,5-dioxopyrrolidin-1-yl 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzoate in CCl_4 and reacted under UV light ($\lambda=254 \text{ nm}$) for 1.5 hours at room temperature¹. After the reaction, the NHS-functionalized surface was thoroughly washed with dichloromethane and isopropanol, dried under a stream of argon and used immediately.

Carbene-terminated SAM Formation. ITO surfaces were rinsed briefly with water, ethanol and isopropanol and dried under a stream of filtered argon. They were subsequently cleaned in a plasma oxidizer (Emitech K-1050X, 5 min, 100 W) to remove any organic contaminants. Amino-terminated surfaces were formed by placing ITO substrates in a glass bottle containing 2 mL vials of aminopropyltrimethoxysilanes (30 μL) and triethylamine (10 μL). After 2 hours, the surfaces were removed and rinsed with dichloromethane and ethanol and dried under argon. The amino-functionalized surface was subsequently immersed in a 10 mM solution of 2,5-dioxopyrrolidin-1-yl 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzoate in CCl_4 for 2 hours in the dark. After the reaction, the carbene terminated surface was thoroughly rinsed with dichloromethane and isopropanol, dried under a stream of argon, and reacted immediately with a 7 mM solution of C60 in benzene under UV light ($\lambda=254 \text{ nm}$) for 1 hour. The C60 modified ITO substrate was rinsed with dichloromethane and ethanol and dried under argon.

Preparation of Catalytic Stamps

Acidic polyurethane-acrylate stamps. Sulfonic acid modified and inactive stamps were prepared according a previously published protocol.¹

Preparation of Reactive Stamps

Polyurethane-acrylate stamps. Patterned and flat PUA stamps lacking the sulfonic acid moiety were prepared according to a previously published protocol.¹ The PUA stamps were inked in either a 2 mM solution of azido-dPEG3amine (Quanta Biodesign, OH) in anhydrous dichloromethane or a 7 mM solution of C60 in benzene for 2 minutes at room temperature and dried under argon.

Stamping protocol

For both catalytic and reactive printing applications, the appropriate polyurethane-acrylate stamp was placed on the top of the modified ITO substrate at room temperature for 2 min with no external load. After the reaction, the stamp and the substrate were separated. The substrate was rinsed with ethanol and dried with filtered argon. The stamp was rinsed with ethanol and dried with filtered argon, and kept at room temperature before the next application. To successfully pattern C60, the stamp/surface system was exposed to UV light ($\lambda=254$ nm) for 2 minutes.

References

1. Shestopalov, A. A.; Morris, C. J.; Vogen, B. N.; Hoertz, A.; Clark, R. L.; Toone, E. J., Soft-lithographic approach to functionalization and nanopatterning oxide-free silicon. *Langmuir* **2011**, 27 (10), 6478-85.