Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information:

Brushing up from "Anywhere" under Sunlight: A Universal Surface-Initiated Polymerization from Polydopamine-Coated Surfaces†

Wenbo Sheng,‡[b] Bin Li,‡[ac] Xiaolong Wang[a], Bin Dai,[b] Bo Yu*[a], Xin Jia*[b] and Feng Zhou*[a]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, 730000, Lanzhou, China. E-mail: yubo@licp.cas.cn; zhouf@licp.cas.cn
[b] Key Laboratory of Chemical Materials of Xinjiang Uygur Autonomous Region, School of Chemistry and Chemical Engineering, Shihezi University, 832003, Shihezi, China. E-mail: jiaxin@shzu.edu.cn
[c] University of Chinese Academy of Sciences, 100049, Beijing, China.

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‡ These authors contribute equally to this work.

Contents:

1. Materials

Methacrylic acid sodium (MAA-Na, 95%), N-isopropylacrylamide (NIPAm, 99%), and styrene (99%) were purchased from J&K Chemical Ltd. 3-Sulfopropyl methacrylate potassium salt (SPMA, 95%, TCI), 2-(methacryloyloxy)ethyltrimethylammonium chloride (METAC, 80% in water, TCI). Polydimethysiloxane (PDMS, Sylgard 184, Dow corning). Dopamine and acridine orange base were obtained from Aldrich. Gold surfaces (100 nm Au deposited onto 5-7 nm Cr) were prepared by electron beam deposition on silicon wafers.

2. Surface characterization

The absorption spectra were measured in a UV-2600 UV-vis spectrophotometer (SHIMADZU). The infrared spectra were obtained on a Nicolet (iS10) infrared spectrometer equipped with a smart attenuated total reflection (ATR) accessory. Contact angle measurements were performed using a DSA100 optical contact angle (CA) meter (Kruss Company, Germany). Optical and fluorescent images were taken with a fluorescence microscope (Olympus BX51). Atomic force microscopy (AFM) measurements were performed on an Agilent Technologies 5500 AFM under ambient conditions, the surface morphology, roughness and film thickness were obtained in tapping mode using a commercial pyramidal Si tip.

3. Methods

3.1 Polydopamine coating

Dopamine (2 mg/mL) was dissolved in 10 mM Tris-HCl (pH 8.5), and substrates were dipped into the solution. The dopamine solution was then irradiated with a 36-watt ultraviolet radiation lamp, the color of the solution changed to dark brown due to the UV-assisted self-polymerization of dopamine. After that, the polydopamine coated surfaces were rinsed with ultrapure water and dried by N_2. The thickness of the PDA films were determined using a L116E ellipsometer (Gaertner, USA) followed published procedures.[1]

3.2 Patterning of PDA

A photomask was placed on top of the gold wafer and a dopamine solution (2 mg/mL, pH 8.5) was pipetted onto the photomask to form a thin layer in contact with the substrate. The wafer was placed ca. 10 cm below the UV light, and was then irradiated for 3 hours, the substrate was washed with water and ethanol and then allowed to dry.

3.3 Typical procedures for the surface-initiated radical polymerization

To a quartz vial, PDA functionalized substrate was immersed in a solution containing monomer or monomer/solvent mixture at room temperature and degassed by passing a continuous stream of dry N_2 through the solution while being stirred (30 min), the vial was tightly sealed and subsequently placed ca. 10 cm below the light source (simulated sunlight with a 300 W xenon lamp coupled with an AM 1.5G filter (Beijing Perfectlight Technology Co. Lt, PLS-SXE300UV) and was irradiated for a certain of time, the temperature was kept at 20 °C during the polymerization, then the polymer coated substrate was washed by ultrasonification in water and ethanol, respectively, and allowed to dry with a stream of N_2. The film thicknesses were measured by an ellipsometer.

3.4 Surface patterning through photografting

Method I: To a polydopamine uniformly functionalized gold surface, a photomask was fixed on the top of the PDA coated substrate, then the monomer solution was pipetted onto the mask, the wafer was placed ca. 10 cm below the sunlight source and was then irradiated for a certain of time, washed and yielded polymer patterned surface.

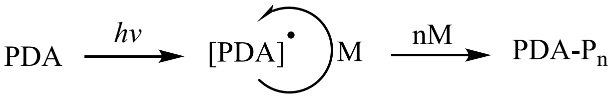
Method II: To a clean gold surface, a photomask was fixed on the substrate, and the dopamine solution (2 mg/mL, pH 8.5) was pipetted onto the mask for the generation of PDA patterns, the wafer was washed and dried for further polymer growth. The PDA patterned gold surface was covered with monomer solution and was placed ca.

10 cm below the sunlight source and was irradiated for a certain of time, washed and yielded patterned polymer coated surface.

3.5 Binary pattern formation

To prepare binary polymeric surface (i.e., surface containing two different polymer s), we used a photomask to grow the first polymer (PNIPAm) from the PDA covered substrate, polymerization only occured in regions where the PDA is present, resulting in patterned polymers. Then, PNIPAm patterned gold surface was submerged in the aqueous SPMA solution to grow the second polymer (PSPMA), in this case, polymerization only occurred in the blank PDA regions to form binary polymers.

4. Supporting graphs and tables



$$\text{PDA} \xrightarrow{hv} [\text{PDA}]^{\bullet}\ \text{M} \xrightarrow{\text{nM}} \text{PDA-P}_n$$

Scheme S1. A simple proposed mechanism photoinduced radical polymerization on the PDA surface.[2-4]

Fig. S1 Setup for UV assisted deposition of polydopamine.

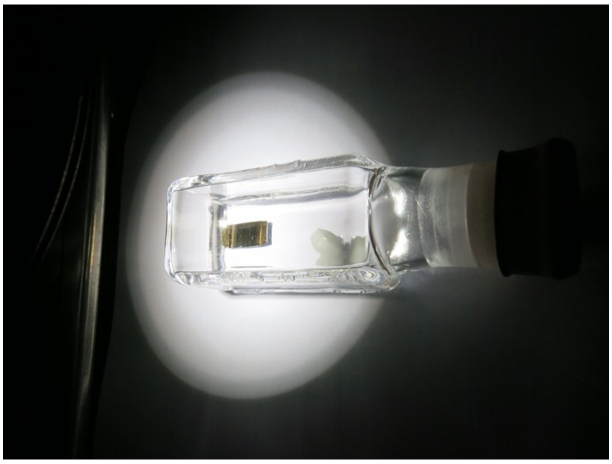


Fig. S2 Surface-initiated polymerization setup.

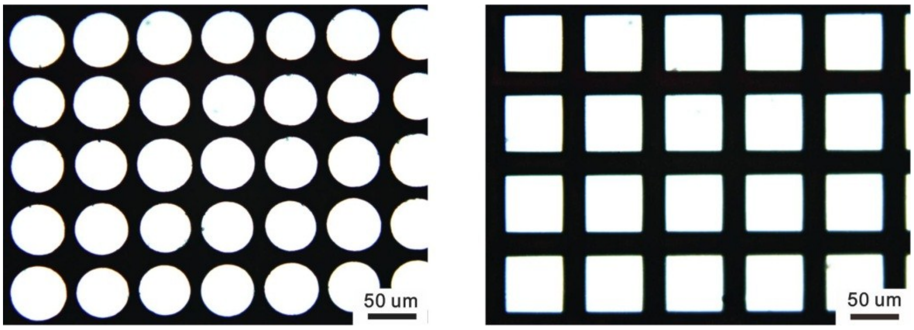
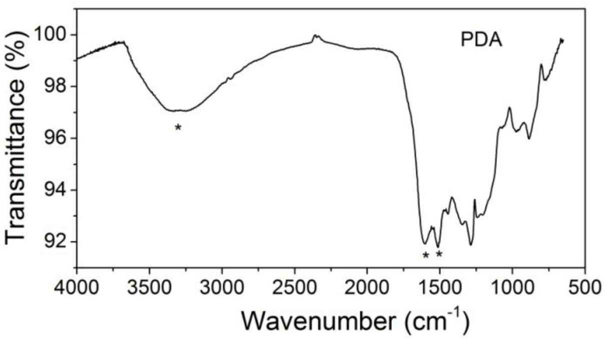
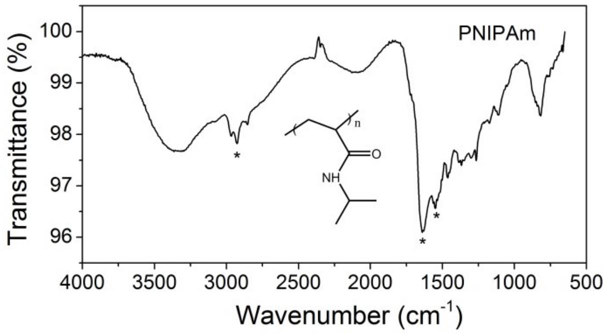


Fig. S3 Optical microscopy images of two types of photomasks used in this experiment.

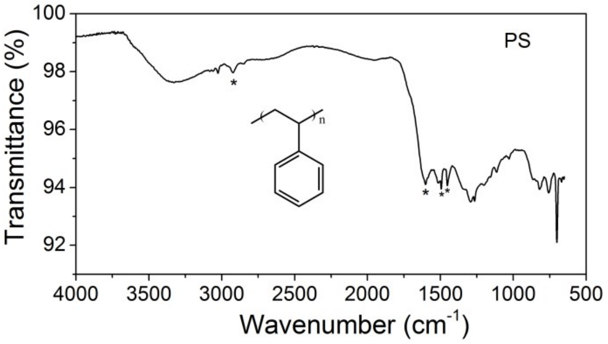
Fig. S4 Patterning of PDA using a photomask.



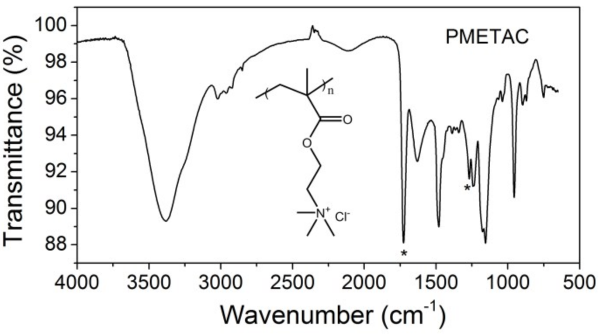
PDA: Peaks at 1515 and 1600 cm^{-1}, an absorption band between 3200-3500 cm^{-1} (stretching vibration of catechol -OH groups) appeared, supporting the presence of PDA on the gold substrate.



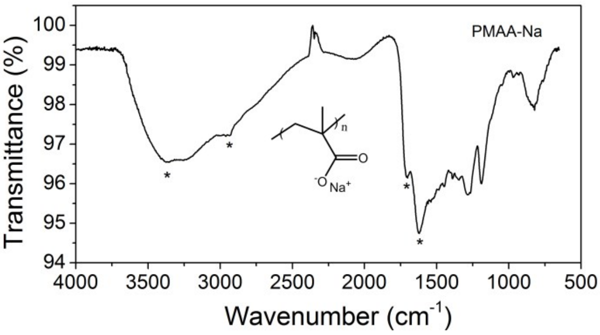
PNIPAm: Peaks of the C-H groups (2900-3000 cm^{-1}), and the two characteristic peaks at 1640 cm^{-1} (amide stretch) and 1550 cm^{-1} (N-H stretch) indicate the success grafting of PNIPAm.



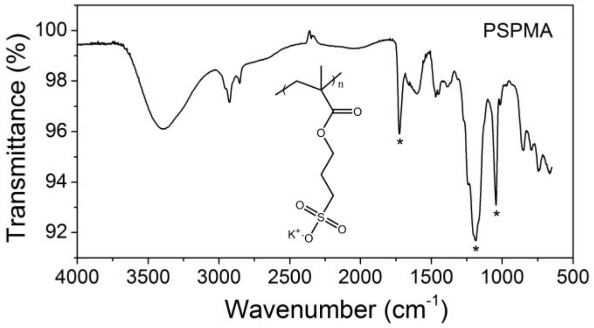
PS: The absorption between 2800 cm^{-1} and 3000 cm^{-1} are the asymmetric and symmetric stretching vibrations of -CH_2. The bands at 1601 cm^{-1}, 1493 cm^{-1}, 1452 cm^{-1} can be assigned to the vibration of the benzene ring.



PMETAC: The peaks at 1720 cm^{-1} (C=O stretching) and 1265 cm^{-1} (C-N stretching) demonstrated the successful grafting of the PMETAC.



PMAA-Na: The strong absorption peak at 1620 cm^{-1} and 1700 cm^{-1} should belong to the absorption of carboxylic groups, the appearance of peak between 3200-3500 cm^{-1} indicates the presence of -OH. The absorption peaks in the region 2800-3000 cm^{-1} correspond to the -CH_2 and -CH_3 groups.



PSPMA: The spectra show the stretching of carbonyl groups at 1730 cm^{-1}, asymmetric sulfonate stretch around 1200 cm^{-1}, symmetric sulfonate stretching around 1045 cm^{-1}, and the stretching of C-O in the ester at 1245 cm^{-1}.

Fig. S5 ATR-IR spectra of PDA, PNIPAm, PS, PMETAC, PMAA-Na and PSPMA modified gold surfaces.

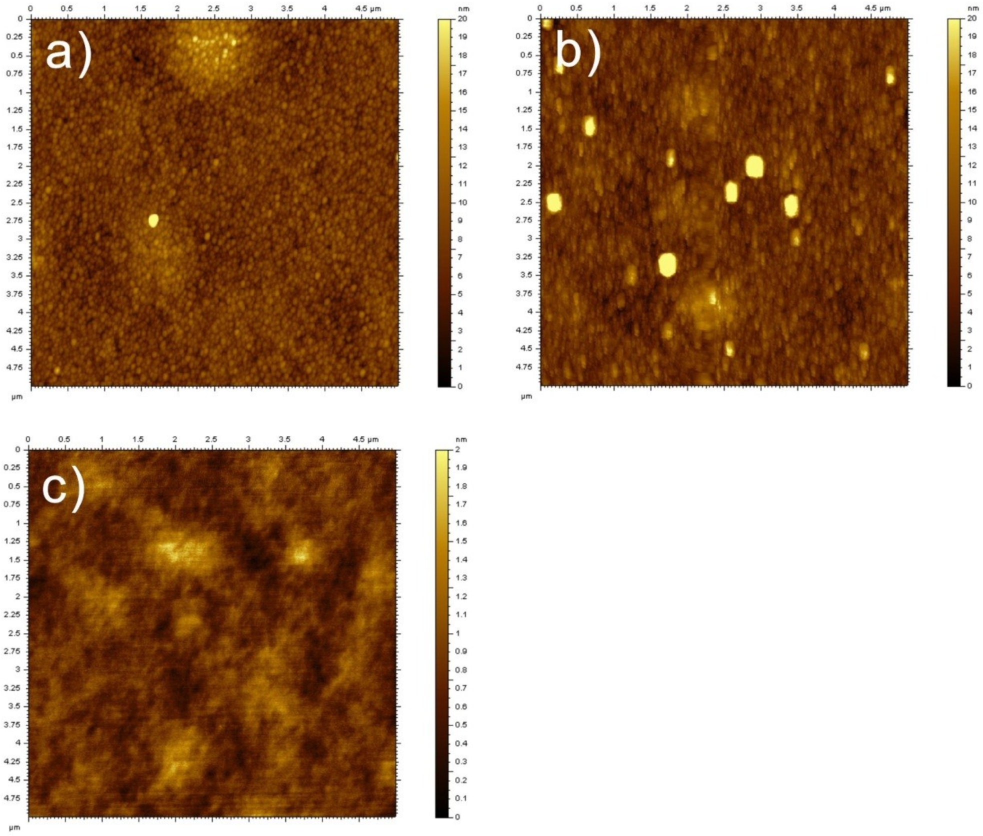


Fig. S6 Roughness analysis of polydopamine and polymer coatings. The root mean square (RMS) roughness of gold, polydopamine (35 nm) coated gold, and PSPMA (87 nm) coated Au was measured by AFM. The RMS roughness was 2.08 nm for bare Au (a), 2.84 nm for polydopamine coated Au (b), and 0.25 nm for PSPMA coated Au surface (c).

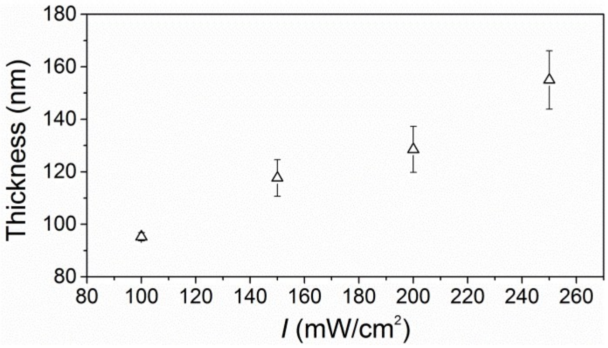


Fig. S7 PMETAC film thickness as a function of optical intensity (*I*) of the simulated sunlight.

Table S1. Contact angle measurements (CAs) of various polydopamine, PSPMA and PS coated substrates (deg).

	Bare	Polydopamine	PSPMA	PS
Al	93 ± 3	50 ± 1	< 10	72 ± 6
Fe	60 ± 3	52 ± 2	< 10	69 ± 2
Ti	26 ± 1	50 ± 1	< 10	78 ± 2
PDMS	89 ± 2	54 ± 6	< 10	77 ± 6
PI	51 ± 1	48 ± 2	< 10	80 ± 7
PTFE	121 ± 5	43 ± 3	< 10	76 ± 2
Mica	15 ± 3	47 ± 7	< 10	70 ± 2

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