

Electronic Supplementary Information (ESI)

A microcontact printing induced supramolecular self-assembled photoactive surface for patterning polymer brushes

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Experimental

Materials. Styrene and DMAEMA were both purified by neutral Al₂O₃ column and dried with a 0.4-nm molecular sieve at room temperature for 3 days. PDMS stamps with grid structures and no pattern structures were both fabricated from Sylgard 184 (the ratio between component A and B was 1:10) on a silicon master and smooth side of optical disk. CVD graphene was rinsed thoroughly with anhydrous ethanol, dried in a stream of nitrogen before use. Silicon wafers were cleaned in a mixture of H₂O₂/H₂SO₄(1:3,v/v) at 80°C (“piranha solution”) for 2h and washed thoroughly with Milli-Q-grade water. (Caution: Piranha solution reacts violently with organic matter!).

Microcontact printing: The PDMS stamp was inked by exposing the stamp features to an ethanol solution of 1-pyrenemethylamine (1mM) for 3 min and drying with nitrogen, before being brought into contact with silicon substrate/ graphene for 30s to fabricate the patterned active surface on silicon substrates. Unpatterned SAMs are fabricated by inked flat stamp using the same ink solution and contact time.

Self-initiated photografting and photopolymerization(SIPGP): The patterned and unpatterned polymer brushes were synthesized following a literature procedure (I. Amin, M. Steenackers, N. Zhang, A. Beyer, X. H. Zhang, T. Pirzer, T. Hugel, R. Jordan and A.

Golzhauser, *Small*, 2010, **6**, 1623-1630). The patterned substrates was submerged in ~2mL of distilled and degassed bulk monomer and irradiated with an UV lamp with a spectral distribution between 300 and 400 nm distribution between 300 and 400 nm (intensity maximum at $\lambda = 350$ nm with a total power of ~ 9 mW/cm²) for 8h. Following SIPGP, the functionalized films were exhaustively rinsed with different solvents (toluene, ethyl acetate, and ethanol for styrene, ethanol for DMAEMA) following ultrasonicated for several minutes in order to remove any physisorbed polymer.

Characterizations. Atomic force microscopy (AFM) images were taken by a multimode AFM (Being Nano-Instruments, Ltd) operating in the tapping mode using silicon cantilevers (spring constant: 3~40 Nm⁻¹, resonant frequency: 75~300 KHz). Static water contact angles were measured at room temperature using the sessile drop method and image analysis of the drop profile. The instrument (OCA-20, Dataphysics) used a charge-coupled device (CCD) camera and an image analysis processor. The water (Milli-Q) droplet volume was 3 μ L, and the contact angle was measured after the drop was stable on the sample. For each sample, the reported value is the average of the results obtained on three droplets.

Attenuated total Reflectance Fourier transform infrared (ATR-FTIR) Spectroscopy (Cary 610, Agilent Technologies, Australia): The spectra were measured with a spectrometer. Absorbance spectra were collected using a spectral resolution of 4 cm⁻¹. The background spectra were recorded on corresponding silicon substrate. The ATR-FTIR spectrum of silicon-based patterned PS brush displays the characteristic stretching vibrational of CH- at around $\nu = 3026$ (cm⁻¹), C-C at $\nu = 1449, 1492, \text{ and } 1599$ (cm⁻¹) and the methylene groups of the polymer backbone with a maximum around $\nu = 2919$ (cm⁻¹). The spectrum of the PDMAEMA shows the characteristic stretching vibrational of CH- at $\nu = 2948, 2823, 2771$ (cm⁻¹), C=O at $\nu = 1727$ (cm⁻¹) (**Figure 3D**).

X-ray Photoelectron spectrum (XPS) (AXIS ULTRA DLD, Kratos Analytical Ltd., Manchester, UK) measurements were carried out at pressures between 10⁻⁹ and 10⁻⁸ mbar. All peaks are referenced to the signature of the C 1s peak for carbon at 284.8 eV, The XPS system was equipped with a monochromatic Al K α source. The Raman scattering measurements were performed at room temperature on a Raman system

(inVia-reflex, Renishaw) with confocal microscopy. The solid-state diode laser (532 nm) was used as an excitation source.

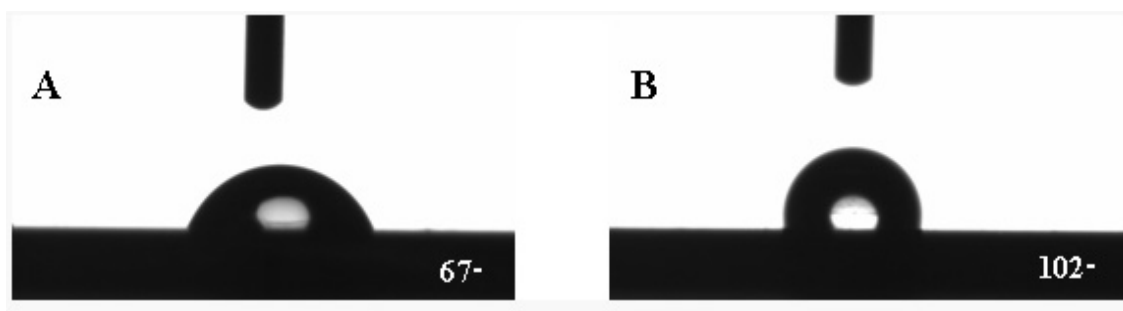


Figure S1. Static water contact angle measurements for (A) homogenous Py-CH₂NH₂ on silicon surface, (B) homogenous PS brushes grafted from photo active surface on silicon surface.

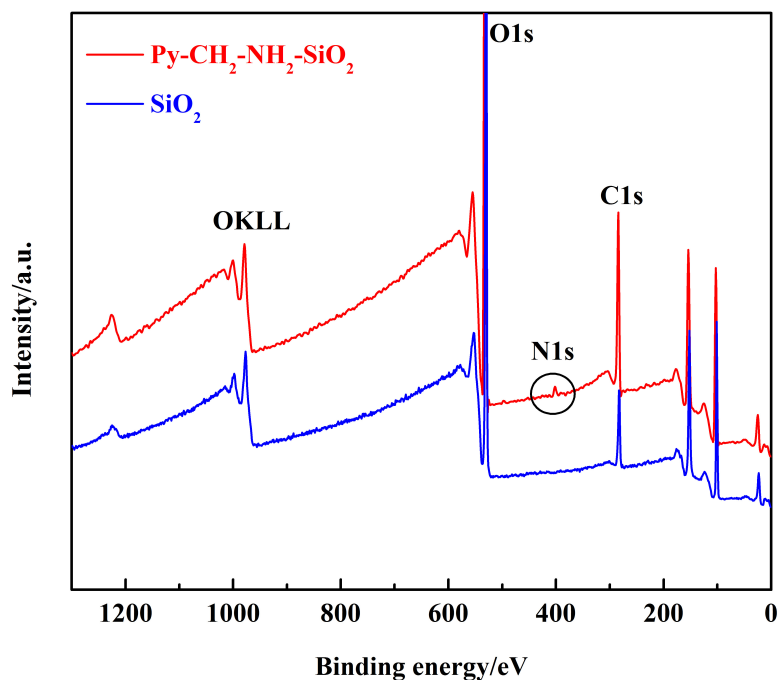


Figure S2. XPS survey scans of SiO₂ surface and Py-CH₂NH₂ modified SiO₂ surface. The minor N peak and strong C peak of substrate surface significantly indicate the successful modification of Py-CH₂NH₂ on SiO₂ surface. Although the pure SiO₂ surface also shows the weak C peak, the little carbon impurity absorbed on the sample is the main reason.

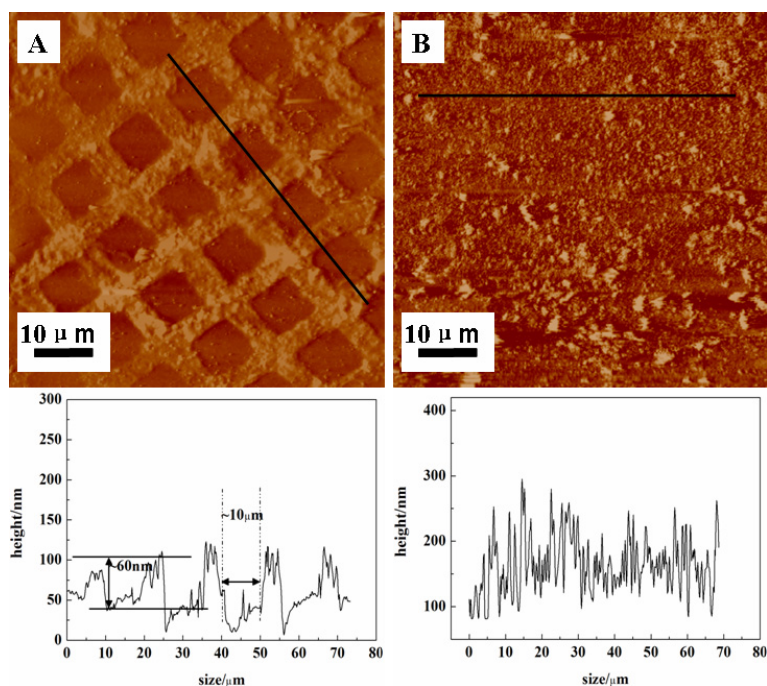


Figure S3. Tapping mode AFM height images ($80\ \mu\text{m}\times 80\ \mu\text{m}$) of A) patterned PDMAEMA brush grafted from SAMs and B) homogenous PS brush grafted from homogenous SAMs on silicon surface.

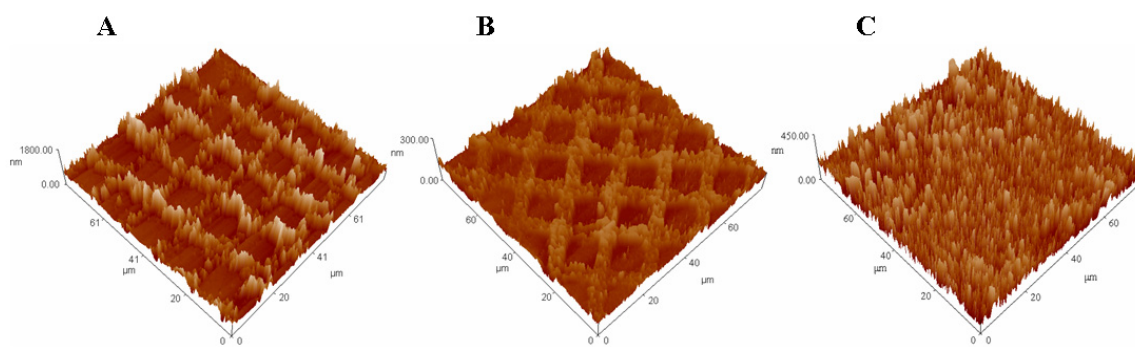


Figure S4. Tapping mode 3D AFM height images ($80\ \mu\text{m}\times 80\ \mu\text{m}$) imaged at room temperature in air of A) Patterned PS brush microstructures. B) Patterned PDMAEMA brush microstructures. C) Homogenous PS brush microstructures on Py-CH₂-NH₂ modified SiO₂ surface.

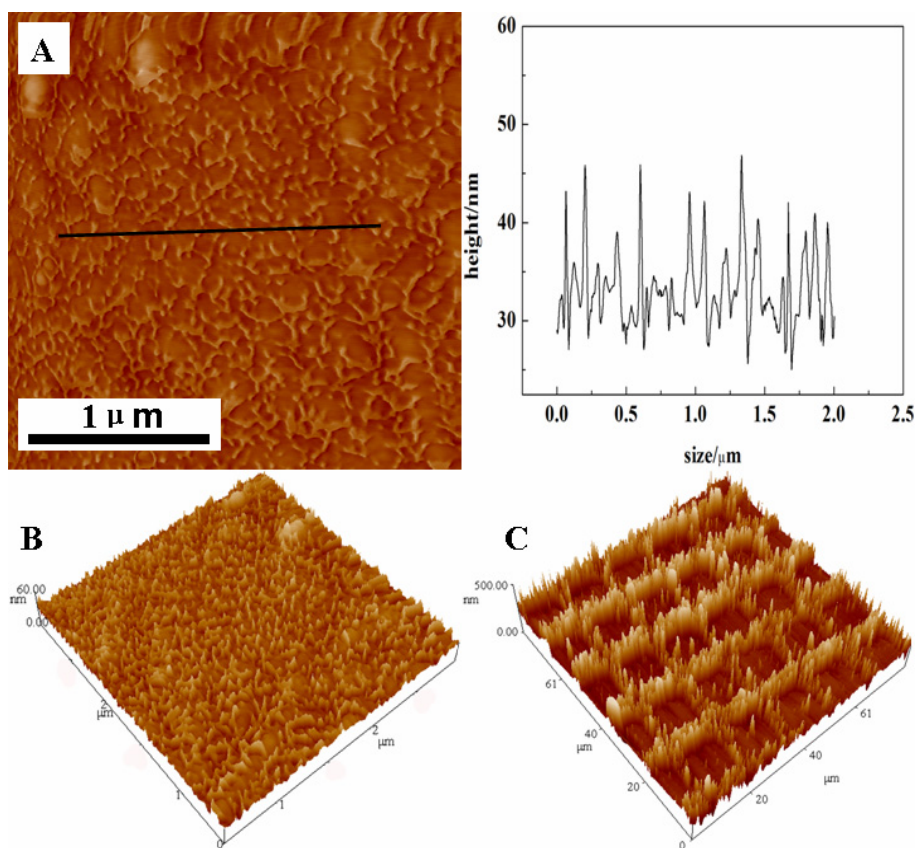


Figure S5. Tapping mode AFM height images imaged at room temperature of A) PS brush microstructures on pristine graphene, which are in the areas between the grid patterns. B) The corresponding 3D image of homogenous PS brush on pristine graphene ($2.5\ \mu\text{m}\times 2.5\ \mu\text{m}$). C) 3D image of PS brush microstructures on patterned graphene ($80\ \mu\text{m}\times 80\ \mu\text{m}$).