Electronic Supplementary Information (ESI)

Microcontact Printing Graphene Oxide Nanosheet for Fabricating Patterned Polymer Brushes

Peng Xiao[a], Jincui Gu[a], Jing Chen[a], Jiawei Zhang*[a], Rubo Xing[b], Yanchun Han[b], Jun Fu[a], Wenqin Wang[c], Tao Chen*[a]

[a]*Division of Polymer and Composite Materials, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Science, Ningbo 315201,China. Email: tao.chen@nimte.ac.cn*
[b] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022,China.*
[c]*Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211,China.*

Experimental

Materials: Reagent grade chemicals were used as received from Sinopharm Chemical Reagent. Toluene, ethyl acetate, ethanol and deionized water were used as rinsing solvents. Styrene (99%) was obtained from Alfa Aesar China (Tianjin) Co., Ltd, which was purified by neutral Al_2O_3 column chromatography and dried with a 0.4nm molecular sieve at room temperature for 3 days. PDMS stamps with strip and grid structures were fabricated from Sylgard 184 (the ratio between component A and B was 1:10) on a silicon master. Silicon wafers and glasses were cleaned in a mixture of H_2O_2/H_2SO_4(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!).

Preparation of Graphene Oxide Aqueous Solution: Graphene oxide (GO) sheets were synthesized by a modified Hummers' method (W. S. Hummers and R. E. Offeman, *J. Am.Chem.Soc.*1958, **80**, 1339-1339) and exfoliation of graphite oxide was achieved by a strong ultrasonication method. The obtained brown dispersion was

then washed and centrifuged to remove any unexfoliated graphite oxide. The final GO nanosheets with diameter less than 2μm, which were used for GO patterning.

Microcontact printing: The PDMS stamp was inked by exposing the stamp features to an ethanol solution of graphene oxide for 3 min and drying with nitrogen, before being brought into contact with substrates surface for 1 min to fabricate the patterned SAMs on silicon and glass substrates.

Self-initiated photografting and photopolymerization (SIPGP): The patterned 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 substrate surface was submerged in ~2mL of distilled and degassed bulk monomer and irradiated with an UV fluorescent lamp with a spectral distribution between 300 and 400 nm (intensity maximum at λ = 365 nm with a total power of ~240mW/cm^2) for required time (PS and PDMAEMA for 1h). All the polymerization experiments were carried out under inert N_2 atmosphere. Following SIPGP, the functionalized films were exhaustively rinsed with different solvents (toluene, ethyl acetate, and ethanol for styrene) followed by ultrasonication for several minutes in order to remove any physisorbed polymer. The contrast experiments were carried out by putting GO spin-coating on glass or silicon inside a glove box in the absence of monomers under inert N_2 atmosphere.

Freestanding patterned films Fabrication: Freestanding polymer brushes grafted micro-patterned GO films were fabricated by immersing the silicon wafer in KOH solution (1 M) overnight, and transferred from the silicon substrate onto another silicon surface.

Characterizations: Atomic force microscopy (AFM) images were taken by a multimode AFM (Being Nano-Instruments, Ltd) operating in the contact and/or tapping mode using silicon cantilevers (spring constant: 0.15Nm^{-1}, resonant

frequency: 12KHz for cantilever of contact mode, spring constant: 3~40 Nm^{-1}, resonant frequency: 75~300 KHz for cantilever of tapping mode). 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, Data physics) used a charge-coupled device (CCD) camera and an image analysis processor. The water (Milli-Q) droplet volume was 3μL, 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. Fourier Transform infrared (FTIR) Spectroscopy (Nicolet 6700, Thermo scientific, USA): The spectra were measured with a spectrometer. Absorbance spectra were collected using a spectral resolution of 4 cm^{-1}at room temperature over a frequency range of 4000-500 cm^{-1}. The background spectra were recorded on corresponding KBr. 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 with a frequency range of 3200-1000 cm^{-1}. The volume resistance of GO, rGO and PS-GO on glass or SiO_2/Si surfaces were measured on NAPSON CRES-BOX Semi-automatic four-point probe sheet resistance/resistivity measurement system. For each sample, 6 different points were measured and averaged. The optical micrographs were obtained by a Laser Scan Confocal Microscope (ZEISS LSM 700) with digital CCD camera.

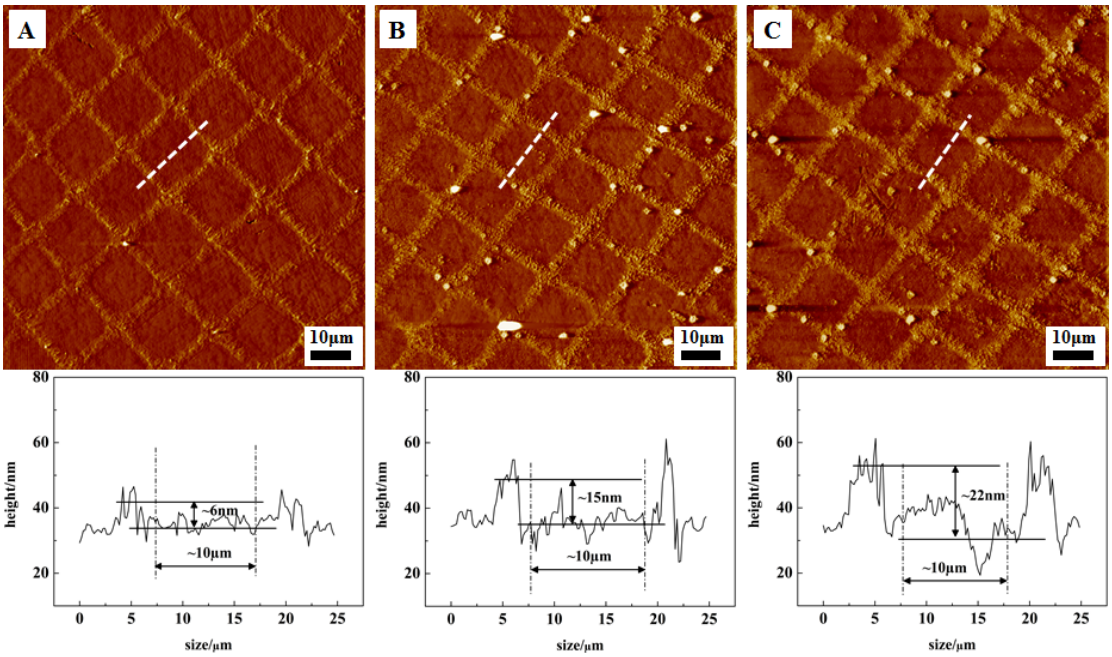

Figure S1. Tapping-mode AFM height images (90μm×90μm) and section analysis of GO patterns of different ink concentrations for different thickness of GO A) 6±2 nm, B) 15±2 nm, B) 22±3 nm.

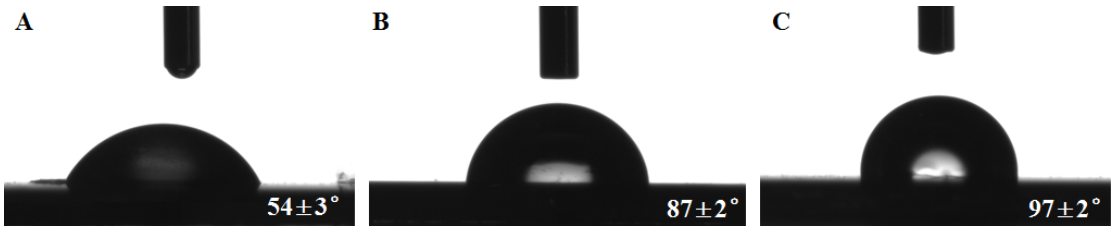

Figure S2. Static water contact angle measurements for (A) Original graphene oxide (GO) film on silicon wafer treated by fresh piranha solution. (B) Polystyrene brushes grafted from GO amplified by SIPGP. (C) Reduced graphene oxide (rGO) film by UV reduction.

The FTIR spectrum of the original GO film showed a rich collection of stretching vibrational of O-H at a wide band ν =3000-3700(cm^{-1}), C-OH at ν = 1384 (cm^{-1}), C=O at ν =1736(cm^{-1}), aromatic C=C at ν = 1627 (cm^{-1}) and C-O vibration of epoxide groups at aroundν =1165 (cm^{-1}) (Figure S3B-a).The spectrum of PS shows the

characteristic stretching vibrational modes of the phenyl group peaks at CH- at aroundν =3026(cm^{-1}), C-Cbetweenν =1449, 1492, and1599(cm^{-1}) and the methylene groups of the polymer backbonewith a maximum aroundν=2919 (cm^{-1}) (Figure S3B-c).The spectrum of the PDMAEMA shows the characteristic stretchingvibrational of CH- at ν=2948, 2823, 2771(cm^{-1}), C=O at ν = 1727 (cm^{-1}) (Figure S2B).

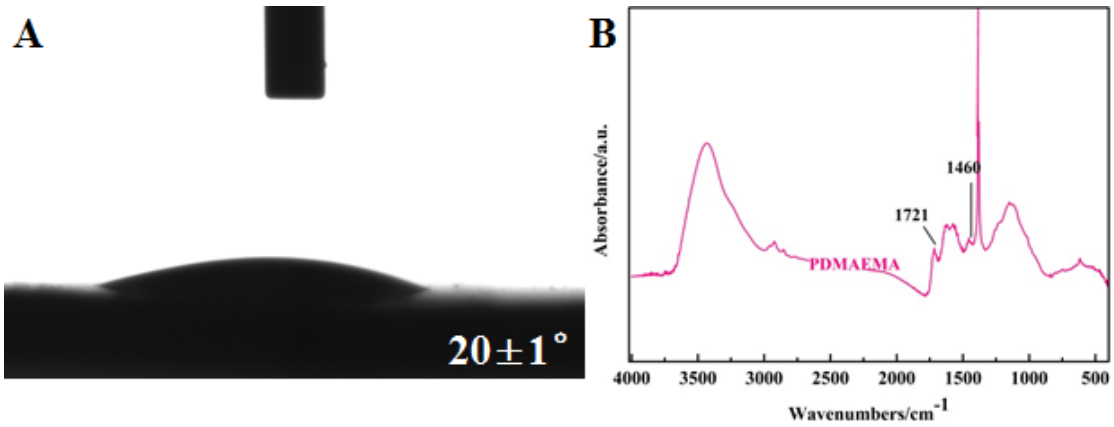

Figure S3. A) Static water contact angle measurements for PDMAEMA grafted from micro-patterned GO surface. B) FTIR spectrum of PDMAEMA brush microstructures grafted from GO on silicon surface.

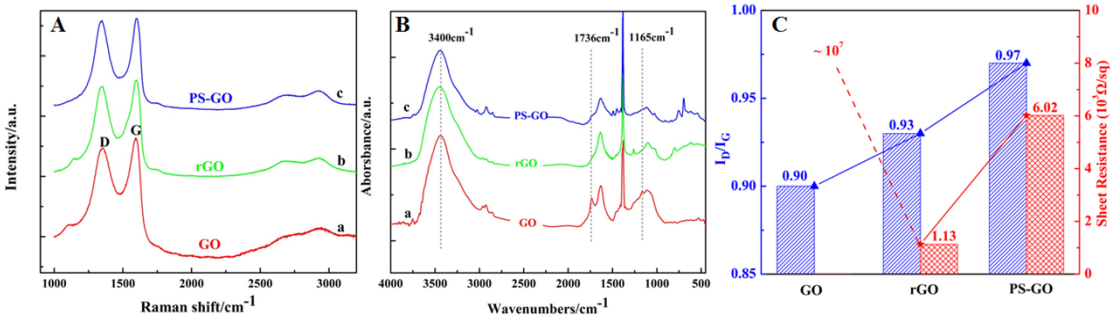

Figure S4. A) Raman spectra of a) original GO film on glass, b) rGO film on glass by UV reductionand c) PS grafted GO film on glass by SIPGP. B) FTIR spectra of a) GO. b) rGO and c) PS-GO for 1 h UV irradiation. The sharp peaks in 1384cm^{-1} derived from the characteristic peak of additional KBr. C) Sheet Resistance properties of rGO and PS-GO homogenous films(column of grid patterns); The intensity ratios of D and G bands for GO, rGO and PS-rGO at the same irradiation time (column of line patterns).

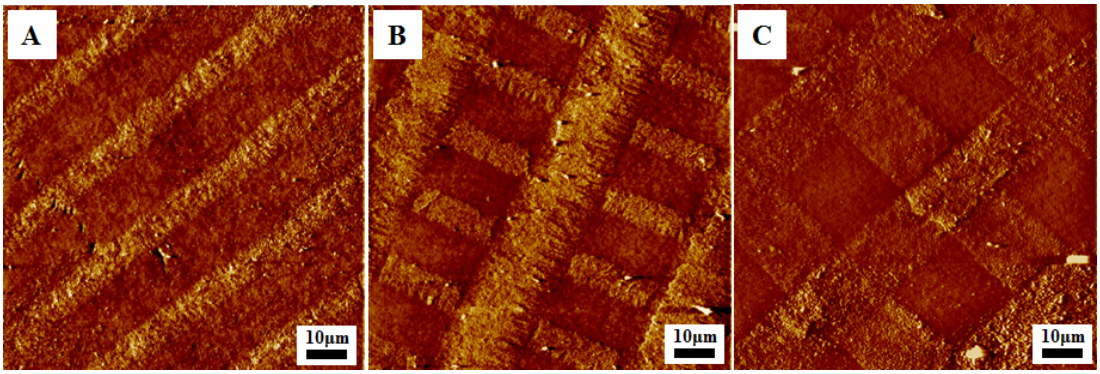

Figure S5. Tapping mode of AFM height images (90µm×90µm) of patterned GO: A) 20µm line pattern, B) 10µm lines×20µm lines pattern and C) 20µm lines×20µm lines pattern.

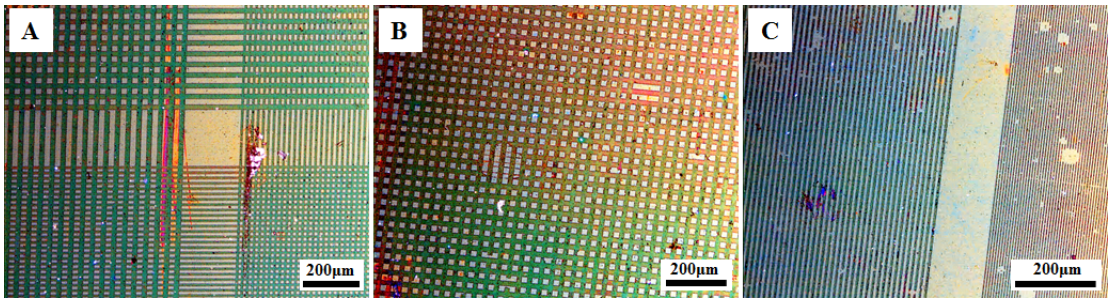

Figure S6. Optical images for PS brushes grafted micropatterned GO: A) Hierarchical patterns, B) 20µm lines×20µm lines patterns, C) 10µm lines and 5µm lines patterns.

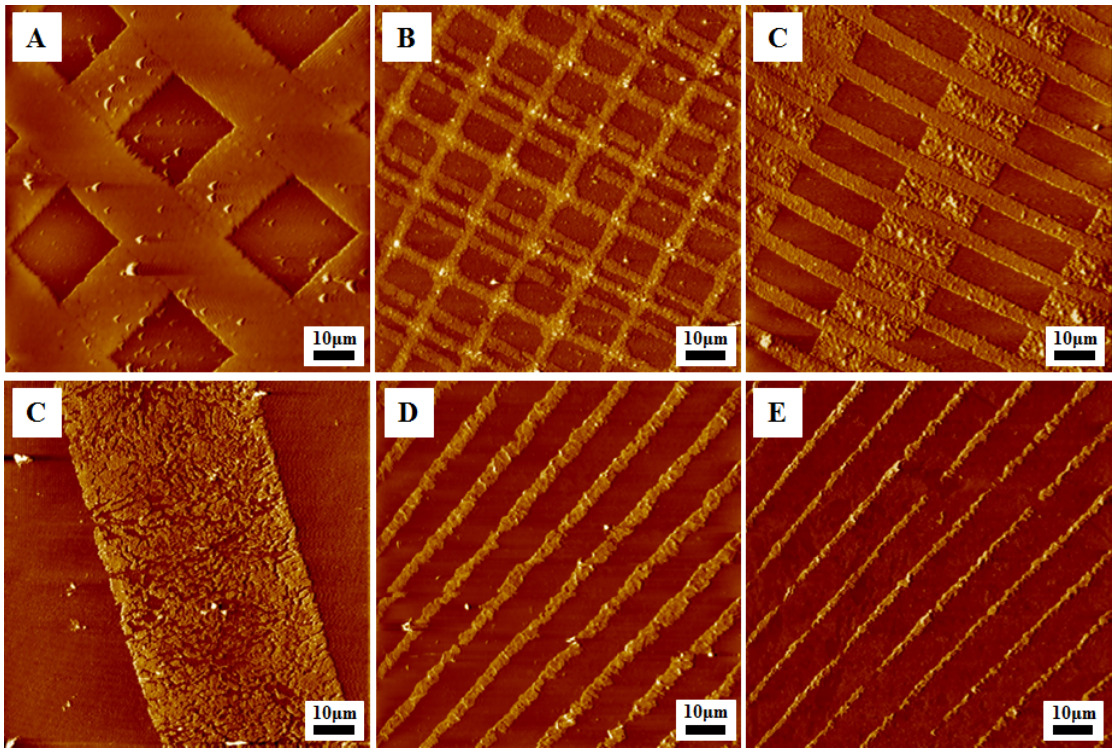

Figure S7. AFM height images of PS brushes grafted micropatterned GO:A) 20μm lines×20μm lines, B) 10μm grids×5μm lines and C) 20μm lines×5μm lines; PDMAEMA brush microstructures: A) 50μm lines, B) 5μm lines and C) 2μm lines grafted from patterned GO surface by SIPGP.

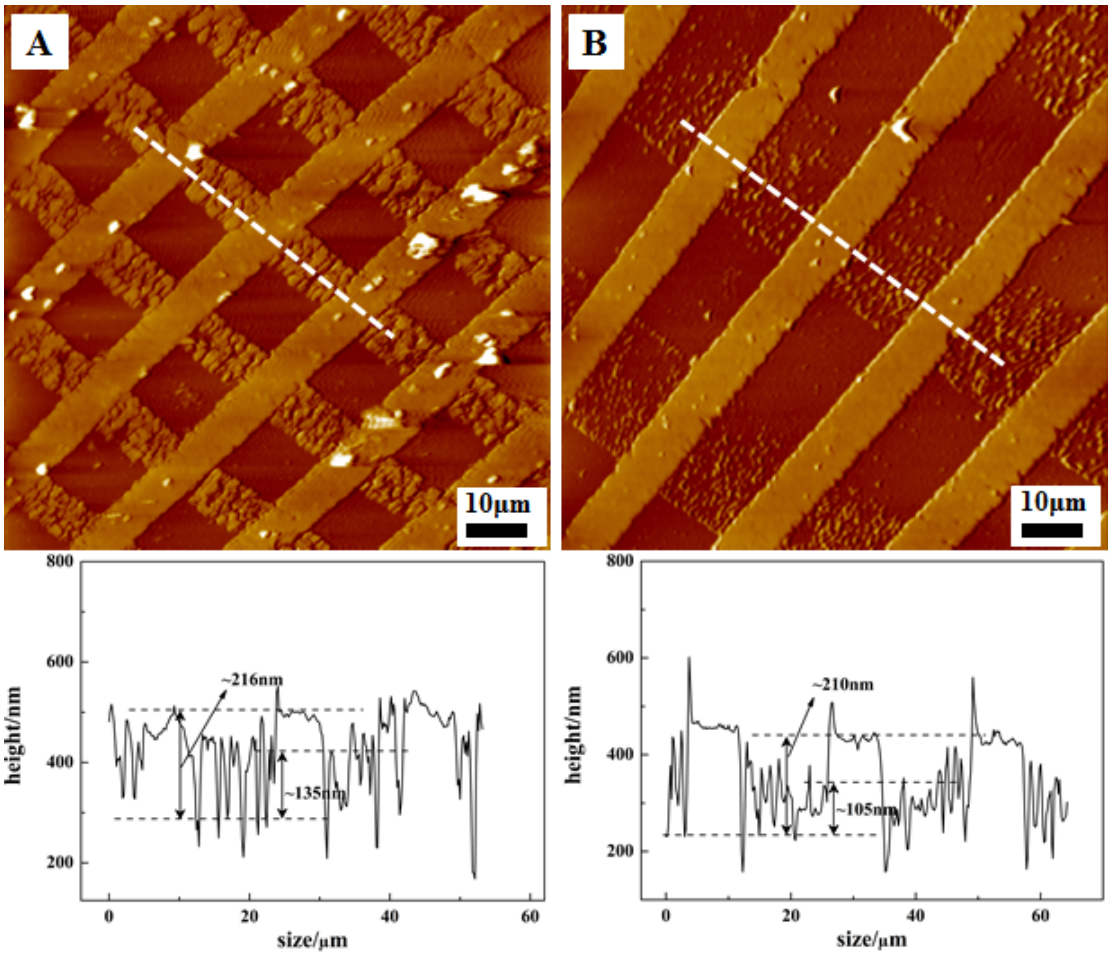

Figure S8. Contact-mode AFM height images (90μm×90μm) and section analysis of PS brush grafted GO microstructures of different ink concentrations (1.5 mg/ mL and 1 mg/ mL for A, 1.5 mg/ mL and 0.2 mg/ mL for B): A) 10 μm lines×10 μm lines and B) 10 μm lines×20 μm lines grafted from patterned GO SAMs on silicon surface by SIPGP.

In order to have more information on freestanding single GO-based polymer brushes pattern, we use atomic force microscope (AFM), which is equipped with optical microscope, to accurately locate the pattern and take a measurement on it. The optical images were all taken under natural light using the equipped optical microscope, as you can see in **Figure 4A**, **Figure S9** and **Figure S11**.

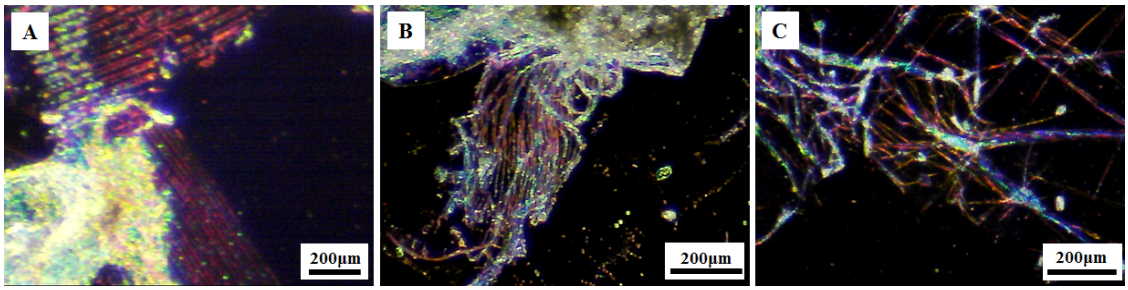

Figure S9. Optical images of freestanding patterned PS brush microstructures transferred onto another silicon wafer: A) 20µm line pattern, B) and C) 5µm line pattern.

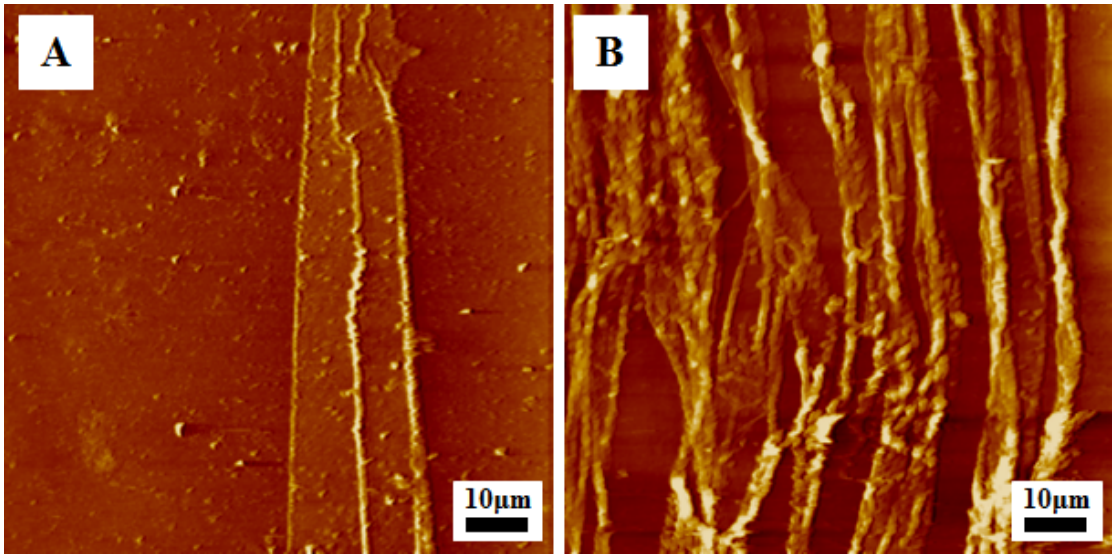

Figure S10. Contact mode of AFM height images (90µm×90µm) imaged at room temperature in air of freestanding PS brushes grafted micropatterned GO:A) 10µm lines and B) 5µm lines that coiled.

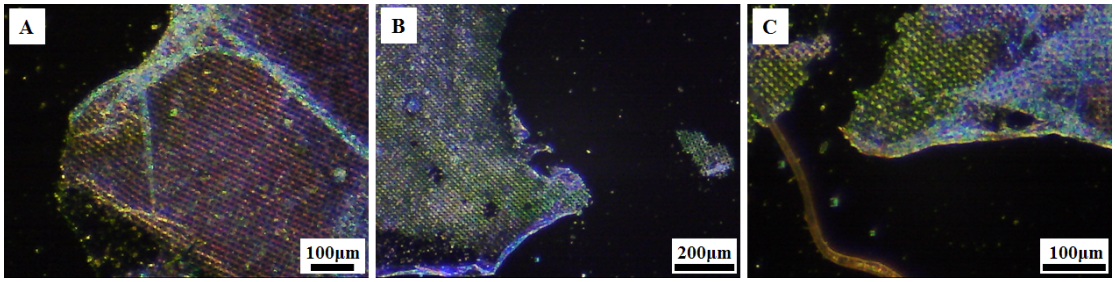

Figure S11. Optical images of freestanding patterned PS brush microstructures transferred onto another silicon wafer: A-C) 10µm grid pattern.