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FULL PAPER

Manipulating the Motion of Gold Aggregates Using Stimulus-Responsive Patterned Polymer Brushes as a Motor

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An important goal and major challenge of material science and nanotechnology is building nanomotors for manipulating the motion of nanoparticles (NPs). Here, it is demonstrated that patterned, stimulus-responsive polymer brush microstructures can be used as motor arrays to manipulate the movement of gold NP aggregates in response to external stimuli that induce a conformational change in the brushes as the driving force. The motion of NP aggregates in the out-of-plane direction is achieved with displacements ranging from nanometers to sub-micrometers. These patterned polymer-brush microstructures can find applications as efficient motor arrays and nanosensors, and benefit the design of more complex nanodevices.

1. Introduction

Nature provides fascinating biological systems that are able to transform chemical energy into mechanical motion using complex yet highly efficient protein motors, driven by adenosine triphosphate (ATP). Examples are myosin moving on actin filaments, and kinesin and dynein using microtubules as tracks.[1] An important goal and major challenge of materials science and engineering is building nanomotors or engines to manipulate the motion of nanoparticles (NPs). Atomic force microscopy (AFM) provides the possibility to manipulate atoms, macromolecules, and single colloidal particles on a surface using a cantilever tip.[2] However, AFM generally can not be used to manipulate ensembles of NPs in parallel. Inspired by Nature, the incorporation of ATP synthase into working devices to construct nanomotors was exploited to harness the unique properties of motor proteins. This enabled the development of hybrid organic–inorganic devices capable of using ATP as a driving force.[1a,b,3] However, motor proteins or hybrid systems can only function in buffered solution within a narrow temperature range and require constant delivery of chemical fuel. These shortcomings have motivated the development of polymeric nanomotors that can manipulate NPs under different environmental conditions, with displacements that span the range from the molecular to the sub-micrometer length scale.

Stimulus responsive polymers (SRPs) in their structural diversity ranging from single polymer chains,[4] polymer gels,[5] to surface grafted polymer brushes,[6] offer exciting means to transform changes in their chemical environment into mechanical energy.[7] End-grafting SRPs to a substrate provides a means to incorporate these polymers into devices, such as microcantilever systems, and enables the transformation of conformational changes into directed motion and actuation. Although a number of papers have dealt with the organization of NPs in or on the top of polymer brushes,[2c,8] only a few showed the use of polymer brushes to move the NPs.[2c,8f–k] Moving NPs by polymer brushes typically relies on switching a polymer brush from an extended to a collapsed conformation (or inversely, from a collapsed to an extended conformation) by changing the solvent quality, i.e., causing a phase transition.[8g–k] Santer and Rühe[2c] harnessed the solvent induced, selective phase transition in mixed polymer brushes to move weakly adsorbed silica NPs on top of brushes in the horizontal direction. This directed motion was used to irreversibly move isolated NPs across the brush surface to form larger aggregates. Likewise, Han et al.[8f] demonstrated that CdS NPs that were chemically bound to a block copolymer brushes, could be moved reversibly in the lateral direction on the basis of the phase separation occurring within the block copolymer brush. Although these pioneering inquiries have accelerated the development of synthetic polymer nano-motors, they have not yet harnessed the possibilities afforded by surface patterning and controlling the shape of polymer brushes to manipulate the motion of NPs. Complex polymer brush structures are, however, accessible through electron (e)-beam chemical lithography (EBCL),[9] e-beam induced carbon deposition (EBCD)[10] and microcontact printing (μCP).[11]

Here, we demonstrate the use of patterned, stimulus-responsive, "egg-cup" shaped polymer brush microstructures as motor arrays to manipulate the movement of gold NP aggregates. The motion of NP aggregate normal to the substrate surface was achieved

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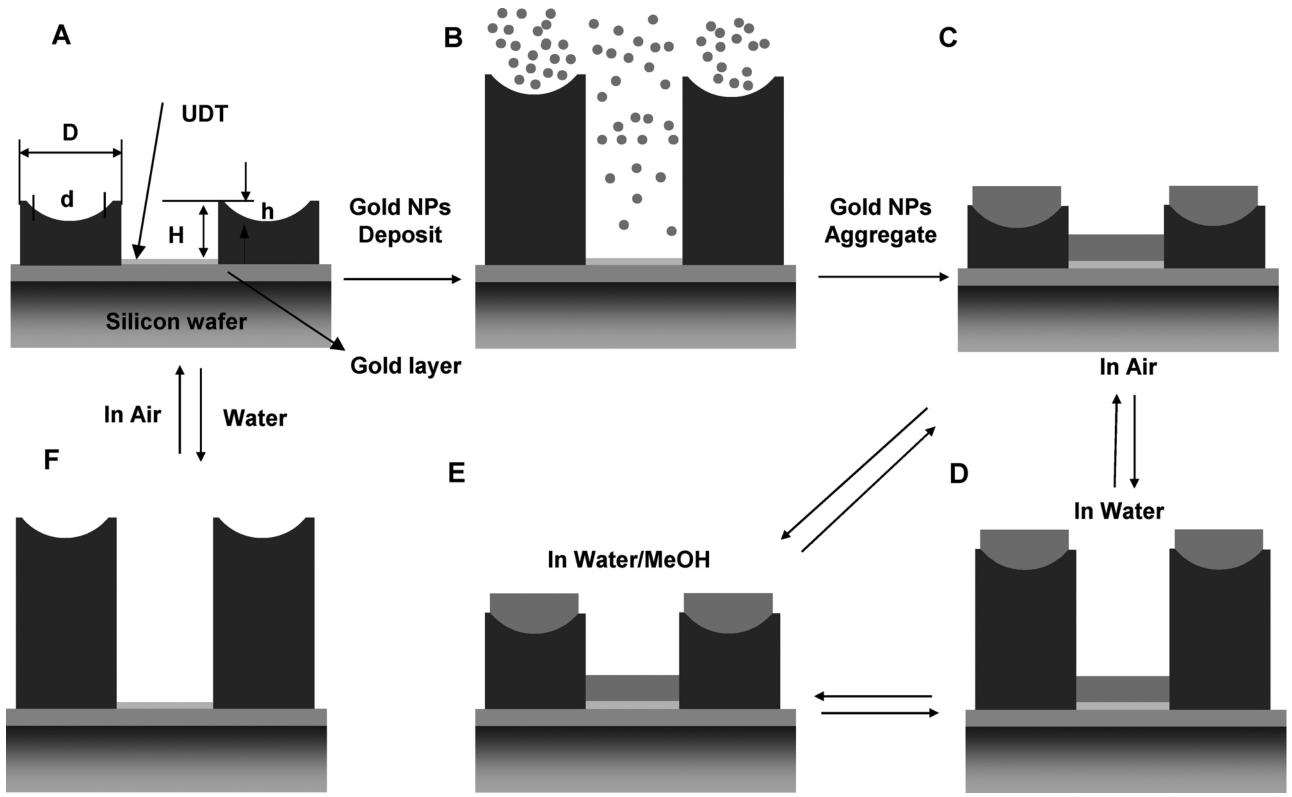

Figure 1. Schematic illustrations showing the displacement of gold NP aggregates by inducing a conformational change of patterned, "egg-cup" shaped, polymer brush microstructures. A) Dimensions of the polymer brush microstructures. B) Deposition and C) nucleation and growth of gold NPs on the brush microstructures. Displacement of gold NP aggregates through triggering a conformational change of brush microstructures by (D) water and (E) water/MeOH. F) Unloaded brush microstructures swell in water more than loaded structures.

with displacements ranging from the nanometer to the submicrometer length scale. We also provided some new insights into the relationship between the solvent-induced conformational change of the polymer brush and the ensuing mechanical work applied by the brush to the gold NP aggregates.

2. Results and Discussion

Our strategy for manipulating the motion of gold NP aggregates by patterned, "egg-cup" shaped polymer brushes microstructures is schematically shown in **Figure 1**. These polymer brush arrays consist of poly(*N*-isopropylacrylamide) (PNIPAAM) brushes, synthesized as previously shown by us [detailed information is provided in Figure S1 in the Supporting Information (SI)].[11] Our approach relies on patterning gradients of self-assembled monolayers (SAMs) of thiol initiator on gold surfaces by μCP, making use of a microphase separation that occurs in patterning of certain binary thiol mixtures,[12] to ultimately yield initiator gradient patterns that can be amplified into PNIPAAM brush microstructures by surface initiated atom transfer radical polymerization (SI-ATRP).[13] The resultant PNIPAAM brush microstructures were then used here as containers for the deposition of gold NPs (Figure 1B). Gold NPs were deposited onto the polymer brush patterned sample followed by long-term aging at room temperature to allow for NP nucleation and growth (Figure 1C).[14] As a typical temperature-responsive polymer with a lower critical solution temperature (LCST) of about 32 °C, PNIPAAM adopts an extended conformation when it is in a good solvent, such as pure water at a temperature below the LCST, and adopts a hydrophobically collapsed conformational state above the LCST. For experimental convenience, we opted to perform our experiments isothermally and instead of changing temperature, we induced the phase transition of the PNIPAAM brushes by changing the solvent quality through addition of methanol (MeOH).[6b] We could thus harness the PNIPAAM microstructures as nanomotors to manipulate the motion of gold NP aggregate (Figure 1D and E). We found that brush microstructures that are filled with gold NP aggregate swelled less freely and thus reached a lower swollen height than empty ones under otherwise identical conditions (Figure 1F).

Figure 2A shows typical "egg-cup" shaped, polymer brush microstructures with an outside diameter (*D*) of ~10 μm, an inside diameter (*d*) of ~7 μm, a peripheral height (*H*) of ~400 nm, and an inner height (*h*) of ~120 nm. Genzer et al.[8b] reported that the organization of NPs on a brush layer depends strongly on NP size; for instance, 3.5 nm particles were shown to infiltrate the brush only when the grafting density was sufficiently low, while 16 nm particles remained on top of the brush at every grafting density. We thus chose colloidal gold NPs with a diameter of about 100 nm to ensure that the NPs would stay on the brush surface.

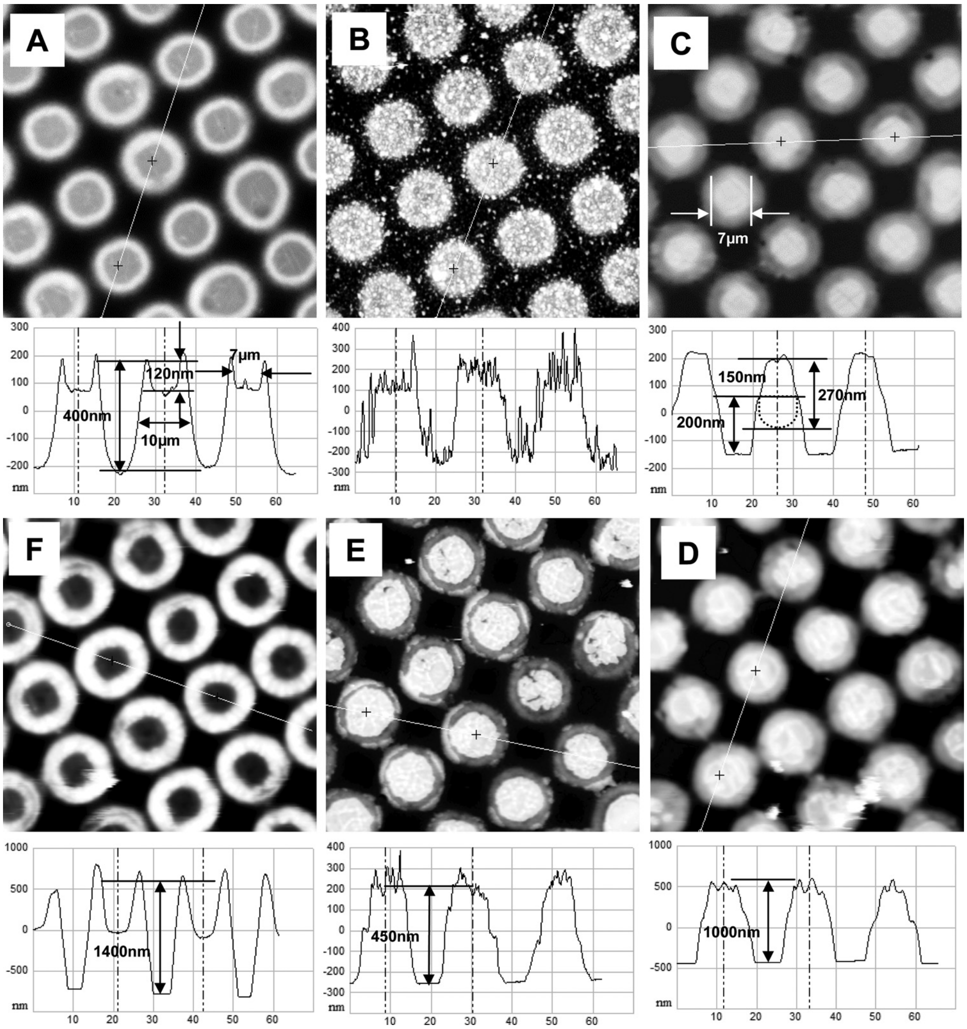

Figure 2. Contact mode AFM height images (60 µm × 60 µm) of: A) "egg-cup" shaped polymer brush microstructures imaged in air; B) one day after deposition of gold NPs; C) after 1 month of nucleation and growth. Height of the NP aggregate loaded brush imaged in (D) good solvent (water) and in (E) poor solvent (methanol:water, 0.1:0.9). F) Height of unloaded polymer brush microstructures imaged in water. The Z scale for all AFM height images is 1200 nm. The PDMS stamp has a circular cylindrical pattern with a feature size of ~10 µm and feature spacing (center-to-center) of ~15 µm. The corresponding 3D images are shown in Figure S2 in SI.

To reduce unspecific NP adsorption, the brush coated substrate was backfilled prior to NP deposition with undecanethiol (UDT) to form a hydrophobic background. For NP deposition, we immersed the brush arrays in previously sonicated (30 min), aqueous solutions (0.05 mg mL^{-1}) of gold NPs for 1 day. Figure 2B shows an AFM image of these brush arrays after drying in a stream of nitrogen and reveals the dispersion of gold NPs across the whole substrate. The substrate was then stored in the aqueous gold NP solution for 1 month under ambient conditions. During this aging process the gold NPs nucleated and grew[14] inside the brush microstructures to form gold NP aggregates with a diameter (d) of ~7 µm and a height (H')of about ~270 nm (Figure 2C). The measured brush height in air of ~200 nm is ~200 nm less than the original height of ~400 nm. This also implies that the gold NPs deposited on the passivated gold substrate grew to a height of ~200 nm, which is ~70 nm less than that of the gold NP aggregates in the polymer "egg-cups." This difference in height growth likely arises from the passivation of the gold substrate background through backfilling with hydrophobic UDT prior to NP deposition.

The conformational state of stimulus-responsive polymer brushes can be triggered and adjusted through changes in the solvent environment.[7] As one of the simplest SRP systems we used PNIPAAM homo-polymer brushes to move and manipulate gold NP aggregates. In pure water, the overall swollen height of the microstructures is ~1000 nm (Figure 2D). This is significantly larger than the height of ~450 nm in a MeOH/H_2O mixture (0.1:0.9 V/V), in which PNIPAAM adopts a collapsed conformation due to the reduction of its LCST as a result of the co-nonsolvency effect (Figure 2E).[15] The swollen height of the unloaded brush in good solvent is ~1400 nm (Figure 2F). This height difference of ~400 nm suggests that the presence of NP aggregates diminishes brush swelling substantially.

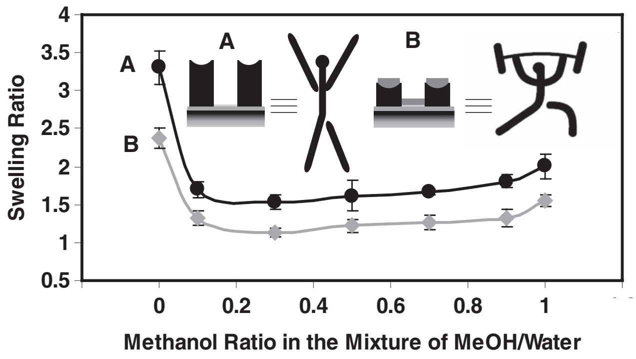

Figure 3. Plot of swelling ratio (defined as ratio of the peripheral height of the "egg-cup" shaped brushes in solvent to the height in air) as a function of methanol volume fraction, and brush loading status (A) unloaded and (B) loaded.

Figure 3 shows that the swelling ratio (defined here as the peripheral height of the "egg-cup" brushes in a particular solvent mixture to the peripheral height in air) of our PNIPAAM brushes can be tuned by changing the relative ratio of methanol and water in the solvent mixture. The observed swelling response of the brushes shown here is consistent with that in previous reports and reflects the fact that end-grafting PNIPAAM to surfaces lowers the LCST compared to that of the free polymer in solution.[6b] Furthermore, Figure 3 also shows that PNIPAAM brushes loaded with NP aggregates swell less than brushes without NP aggregates at all tested MeOH/H_2O ratios; this behavior is illustrated schematically in the inserts of Figure 3 (A and B).

For analytical convenience we simplified the shape of the gold NP aggregates (**Figure 4**A) to that of a sphere segment (with a radius of ~3.5 μm, and a height of ~120 nm, i.e., about equal to the size of the brush "egg-cup") plus a cylinder (with a radius of ~3.5 μm, and a height of 150 nm). When the gold NP aggregates are lifted by the solvent-induced conformational change of the PNIPAAM brushes, the force balance at swelling equilibrium has three major components: i) the gravitational force (F_g), ii) the buoyant force of the solvent (F_s), and iii) the osmotic force of the brushes (F_b), where the latter two balance the gravitational force,

$$F_g = F_s + F_b \tag{1}$$

Thus, $F_b = F_g - F_s = mg - \rho_{solvent}\ V_{solvent}\ g = \rho_{gold} V_{gold}\ g - \rho_{solvent}\ V_{gold}\ g = gV_{gold}\ (\rho_{gold} - \rho_{solvent})$, where m is the mass of gold aggregate, g is the gravitational constant, $V_{solvent}$ is the volume of solvent excluded by the gold aggregate (i.e., equivalent to V_{gold}). For example, upon exposing the brushes to pure water (good solvent), we calculate the value of the force applied by a brush microstructure to a gold NP aggregate to be ~1.5 pN ($g = 9.8$ N kg^{-1}, $\rho_{gold} = 19320$ kg m^{-3}, $\rho_{solvent,\ water} = 1000$ kg m^{-3}, and $V_{gold} = 8.1\ 10^{-18}$ m^3, grey line in Figure 4B), which is of the same order of magnitude as the force developed by Nature's molecular motors, such as kinesin, myosin, or dynein (~1–10 pN).[1a] Considering that a patterned area of 0.5 cm × 0.5 cm has about 1.4×10^5 brush microstructures (Figure 4C), large motor arrays can be fabricated that develop a total force of about 2×10^5 pN (Figure S4 in SI).

Furthermore, as was shown in Figure 3, a brush loaded with gold NP aggregates swells significantly less than an unloaded brush, under otherwise identical solvent conditions. We thus calculated the compressive, mechanical work applied from a gold NP aggregate to the supporting brush microstructure to be about 300 pN nm. Conversely, this implies that each brush microstructure loaded with a gold NP aggregate needs an additional energy of 300 pN nm to reach the same height (swelling ratio) as an unloaded brush (see details in SI). The calculated mechanical work supplied from an individual brush microstructure motor to lift a gold NP aggregate is plotted in Figure 4B (black line) as a function of the solvent composition. This energy, ranging from ~80 to ~800 pN nm, is on the order of the free energy (~240 pN·nm) released by the hydrolysis of three ATP.[1b]

3. Conclusions

We demonstrated that patterned, stimulus-responsive "egg-cup" shaped polymer brush microstructures can be loaded with nanoparticles and subsequently be used as motor arrays to manipulate the movement of gold NP aggregates. Movement occurs in response to external stimuli that induce a reversible, conformational change in the brushes. The displacements of

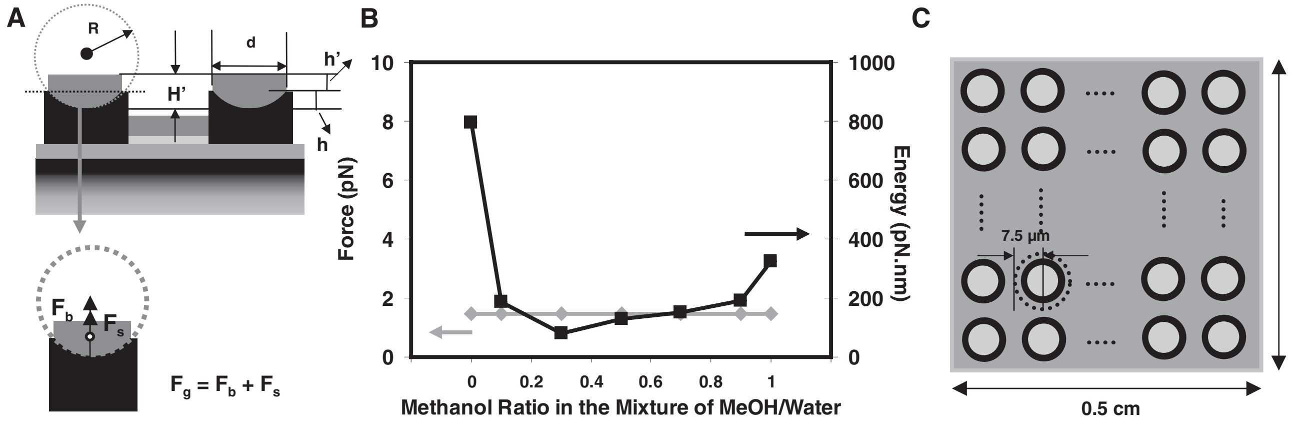

Figure 4. A) Schematic illustrations showing gold NP aggregates and the force balance applied to one aggregate. B) Plot of force (grey line), and mechanical work (black line) exerted by a brush microstructure onto a gold NP aggregate. C) Schematic showing a polymer brush motor array.

NP aggregates perpendicular to the substrate surface could be tuned from nanometers to sub-micrometers. We investigated the relationship between brush conformational change and the force and mechanical work supplied by the brush to move gold NP aggregates. Our results showed that stimulus-responsive polymer brushes easily develop forces commensurate with those found in Nature for motor proteins. Our results contribute to the development of polymer brush based microstructures that are available in large numbers and could be used in applications ranging from nanomotors[2c,7c] to nanosensors.[8h]

4. Experimental Section

Materials: NIPAAM (99%), copper(I) bromide (CuBr, 99.9%), methanol (MeOH, 99.9%), and undecanethiol (98%) were obtained from Sigma–Aldrich (Milwaukee, WI). Milli-Q (Millipore, Billerica, MA) water (18 MΩcm^{-1}) and methanol were used as polymerization solvents. *N*,*N*,*N*,*N*,*N*-pentamethyldiethylenetriamine (PMDETA) was used as received from Acros Organics (Hampton, NH). Non-functionalized citric acid stabilized gold NPs (~100 nm, 0.05 mg mL^{-1}) was obtained from BBInternational (Cardiff, UK). The thiol initiator ($BrC(CH_3)_2COO(CH_2)_{11}SH$) was synthesized as reported.[13] To immobilize the initiators for surface-initiated polymerization, gold substrates were prepared by thermal evaporation under a vacuum of 4×10^{-7} Torr. For this purpose an adhesion layer of chromium (50 Å) followed by a layer of gold (450 Å) was evaporated onto silicon wafers. Before deposition, silicon wafers were cleaned in a mixture of H_2O_2/H_2SO_4 (1:3, v/v) at 80 °C ("piranha solution") for 10 min and washed thoroughly with Milli-Q-grade water. (Caution: piranha solution reacts violently with organic matter!).

Patterning "Egg-Cup" Shaped Polymer Brush Microstructures:[11] Amplification of patterned gradient SAMs was carried out according to our previously reported procedures.[16] Briefly, the polymerization solution was prepared by adding a solution of NIPAAM monomer to an organometallic catalyst. The organometallic catalyst was formed in a nitrogen atmosphere by adding CuBr (1.8 mg, 0.013 mmol) and PMDETA (14 µL, 0.064 mmol) to MeOH (1.0 mL) as solvent. The mixture was then sonicated for 1 min to facilitate the formation of the CuBr/PMDETA complex. Next, NIPAAM monomer (1.5 g, 17 mmol) dissolved in water (5 mL) was filtered into the catalyst complex solution through a Millipore Millex filter (0.45 µm). The polymerization solution was then transferred into flasks containing the sample substrates with immobilized patterned initiator. The flasks were sealed with rubber septa and kept at room temperature under nitrogen. After the desired reaction time, substrates were removed from the polymerization solution, exhaustively rinsed with DI-water to remove all traces of the polymerization solution, and subsequently dried in a stream of nitrogen. For further details, see the Supporting Information.

Deposition of Gold NPs on "Egg-Cup" Shaped Brush Microstructures: To reduce the concentration of citric acid, gold NPs were transferred from their original suspension (1 mL) into Milli-Q water (2 mL), then centrifuged and after removal of the suspension medium, re-suspended in water; this process was repeated for three cycles.[2d] Prior to deposition, NPs were re-dispersed in water (1 mL) and sonicated for 30 min. NPs were then deposited onto the polymer brush coated substrate by immersing the substrate into the gold NPs suspension under ambient condition for 1 day, or for long term aging (30 days) to induce particle nucleation and growth.[14]

Characterization: The polymer brush patterned substrates were rinsed with Milli-Q-grade water, dried under a stream of nitrogen, and mounted on steel sample disks prior to AFM measurements. AFM topographic images were collected in contact mode using V-shaped silicon nitride cantilevers (Nanoprobe, Bruker, spring constant 0.12 N m^{-1}; tip radius 20–60 nm) using a MultiMode atomic force microscope (Bruker/Digital Instruments, Santa Barbara, CA). Topographic imaging was performed in air, water and water/methanol mixtures. AFM topographic images were obtained under low applied normal forces to minimize compression and lateral damage of the polymer brushes.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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