Supporting information

Pick up, Move and Release of Nanoparticles Utilizing Co-

non-solvency of PNIPAM

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Material and methods

Materials

N-Isopropylacrylamide (NIPAM, Aldrich, 97%) was recrystallized twice in toluene/hexane mixture (50% v/v). Copper (I) bromide (CuBr, Aldrich, 98%) was washed by acetic acid three times, and dried overnight. (3-aminopropyl)triethoxysilane (APTES), 2-bromo-2-methylpropionyl bromide (BiBB, 98%), triethylamine (TEA, \geq 99%), copper (II) bromide (\geq 99%), *N*,*N*,*N'*,*N'*,*P*-pentamethyldiethylenetriamine (PMDETA) (98%), were purchased from Sigma-Aldrich and used as received without any purification. The solvents used in the experiments, such as methanol (absolute), tetrahydrofuran (THF), toluene, hexane and sulfuric acid (95-97%), were bought from Biosolve. Hydrogen peroxide and ethanol were purchased from Merck, and were used as received. Silicon nanoparticles ($D = 80 \pm 15$ nm) were bought from Aldrich with 40 wt.% suspension in water. MilliQ water was made from a MilliQ Advantage A 10 purification system (Millipore, Billerica, Ma, USA). The preparation of the PNIPAM brushes is the same as reported in the reference¹ and according to a well-established recipe.² First, vapor deposition was utilized to attach the APTES molecules to a piranha washed silicon surface. Next, a one-step reaction between amine group

and BiBB was performed to link the initiator to the silane. The PNIPAM brushes were grafted from the surface using surface initiated atom transfer radical polymerization (SI-ATRP).³ For a movie showing the sample preparation procedure, see Ref JoVE.⁴

Colloidal probe preparation

The preparation of the colloidal probes is based on a regularly employed technique.⁵ Polystyrene (PS) spheres (Duke Standards 4205A, Thermo Scientific, diameter 5 µm) and SiO₂ spheres (Cospheric, SiO₂MS-1.8, diameter 7.75 µm) were diluted in water and drop-coated on a freshly cleaved mica surface, and dried with nitrogen. Individual colloids were lifted up from the substrate by a tungsten wire (World Precision Instruments, Inc.) controlled by a home-made micromanipulator under an optical microscope. The tungsten wire was chemically etched in 1 M KOH water solution (30V, platinum electrode) until the end-diameter was of about 10-15 µm in order to transfer individual colloids only. Next, the tungsten wire was cleaned in ethanol and dried under nitrogen (inducing wire-colloid capillary adhesion). The spheres were then fastened using a UV-cured glue (Optical Adhesive 81, Norland Products, Inc.) to an AFM cantilever (TL-CONT-50, Nanosensors) and photocured using high intensity UV lamp (Hamamatsu LC8, type 02A) for 3 minutes under air. The quality of the prepared colloidal probes was monitored by high-resolution scanning electron microscopy (SEM) imaging (see Figure S1). The gold colloid probes (6 µm diameter, CP-CONT-Au-C, sQube, NanoAndMore, Germany) were used directly and some of them were used to graft PMMA from the surface using SI-ATRP⁴ yielding a PMMA dry brush thickness of 236 nm.

Brush Characterization

The PNIPAM brushes were characterized by Fourier transform infrared spectroscopy (FTIR, Bruker Vertex 70v spectrometer), and the characteristic groups of PNIPAM are amide I and II appeared at 1632 and 1530 cm⁻¹ respectively (see Figure S2), which gave the evidence of PNIPAM brushes grafting on the substrates. The brushes of reference samples were degrafted from the surface in *p*-toluene sulfonic acid aqueous solution at 80 °C.⁶ Then the molar mass was determined to be $M_n = 1 \times 10^5$ g/mol by using gel

permeation chromatography (GPC) in THF. The grafting density is around 0.25 chains per nm², which we estimated from swelling ratio (we used the swelling ratios in Ref⁷ as a reference). The molecular weight is rather high for ATRP, but is nevertheless commonly achieved with PNIPAM: similar molecular weights have been obtained in Ref⁷. ⁸. AFM measurements were carried out on a Multimode 8 AFM with a NanoScope V controller, a JV vertical engage scanner and a liquid cell (Bruker, Santa Barbara, CA). Soft colloid probes were employed to measure the swelling ratio and adhesion force at various ethanol-water compositions (typically k = 0.3 N/m ± 0.03). We gently scratched off the brushes using Teflon tweezers, and the dry height was determined by measuring the relative height between bare silicon and brush surface. In various composition of ethanol-water mixture, a low force (1.5 nN) was applied to measure the swellen height, which was normalized by the dry thickness to give the swelling ratio. All the measurements were done on at least 3 different positions of the samples. The determined swelling ratio varied by 20% between experiments and the position of the solubility minimum varied by 5%. The PNIPAM surface with attached silicon nanoparticles was scanned by AFM in tapping mode. Silica cantilevers (NanoWorld) with a resonance frequency of 320 kHz and a spring constant of 42 N/m were used for this.

AFM Adhesion Force Measurements

To obtain the adhesion forces, we first approached the AFM cantilever towards the PNIPAM until a maximum repulsive force of 60 nN was reached. The force was measured upon retraction of the cantilever from the PNIPAM brush at a velocity of 0.8-1 µm/s, where the adhesion force was defined as the minimum force before the colloid and the brush loose contact. The typical ramp curves in different solvent compositions are shown in Figure S3. Each datapoint is obtained by averaging over at least 30 force-distance curves captured on three different positions on the same sample, where we found the same forces within 10%. Experiments were also repeated on 3 different samples that were prepared in the same batch. For all these samples we found qualitatively the same results (30% deviations in different samples).

Particle transfer measurements

To test the efficiency of particle transfer, we dispersed silicon particles (D = 80 nm) in ethanol-water (v/v = 3/7) solution. Subsequently, a 1x1 cm² PNIPAM brush (dry height = 150 nm) substrate was kept in the mixture for 20 seconds. Next, the substrate was soaked in ethanol-water (v/v = 3/7) solution without particles for 1 minute to remove the weakly attached particles. After gently drying the sample with a nitrogen stream, the surface morphology was imaged by AFM in tapping mode. The release of particles was achieved by sonication of the sample in water or ethanol for 2 minutes in an ultrasonic cleaner (Branson 2510DTH). Next, the wafer was dried and tested by AFM measurements. The number of particles was counted using ImageJ. First define a resolution to recognize all the particles in the image, and then collect the particle numbers automatically by the software.



Figure S1. SEM image of typical PS and silica colloid cantilevers, the diameter is around 5 and 7.75 μm respectively.



Figure S2. FTIR spectrum of PNIPAM brushes.



Figure S3. Typical ramp curve at various ethanol volume fraction in water (0, 10, 20, 40, 60, 100%). The approach and retract velocity is 0.8 μ m/s, and the ramp size is 2 μ m. The scale bar equals 60 nN.



Figure S4. The adhesion force between PNIPAM brush and a colloid (gold, PS, PMMA) in various compositions of ethanol-water mixtures. The adhesion force is obtained from the force separation curves measured for a retraction velocity of $0.8 \mu m/s$ after the colloid has been pushed into the brush with a normal force of 60 nN. The solid line is guide for the eye.



Figure S5. AFM imaging of PNIPAM surface (a), soaking in silicon particles water solution (b), after sonication for 2 minutes (c), particle height (d). The dry PNIPAM brush is 150 nm, and the scale bar is 400 nm.



Figure S6. AFM imaging of silicon surface (a), soaking in silicon particles aqueous solution with 30% ethanol volume fraction (b), after sonication for 2 minutes (c), particle height (d). The dry PNIPAM brush is 150 nm, and the scale bar is 400 nm.



Figure S7. Statistic of silicon particles by PNIPAM brush, PNIPAM surface (a), soaked in silicon aqueous solution for 20 seconds (b), after sonication in ethanol for 2 minutes (c), PNIPAM surface before soaking (d), soaked in silicon aqueous solution with 30% ethanol for 20 seconds (e), after sonication in ethanol for 2 minutes (f), silicon surface (g), soaked in silicon aqueous solution with 30% ethanol for 20 seconds (h), after sonication in ethanol for 2 minutes (i). The dry PNIPAM brush is 150 nm, and the scale bar is 1 μ m.



Figure S8. Cycles of numbers of picking up silicon particles using PNIPAM brush at 30% volume fraction of ethanol and release with sonication in ethanol for 2 minutes.



Figure S9. The relative dry height change of PNIPAM brush after sonicating in ethanol for 2 minutes for 4 cycles.

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