CHAP Enhances Versatility in Colloidal Probe Fabrication

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Abstract

A colloidal probe, comprising a colloidal particle attached to an atomic force microscope cantilever, is employed to measure directly interaction forces between the particle and a surface. It is possible to change or even destroy a particle while attaching it to a cantilever, thus limiting the types of systems to which the colloidal probe technique may be applied. Here we present the Controlled Heating and Alignment Platform (CHAP) for fabricating colloidal probes without altering the original characteristics of the attached particle. The CHAP applies heat directly to the atomic force microscope chip to rapidly and precisely control cantilever temperature. This minimizes particle heating and enables control over the viscosity of thermoplastic adhesive, to prevent it from contaminating the particle surface. 3D-printed components made the CHAP compatible with standard optical microscopes and streamlined the fabrication process while increasing the platform's versatility. Using the CHAP with a thermoplastic wax adhesive, colloidal probes were fabricated using polystyrene and silica particles between 0.7 and 40 μm in diameter. We characterized the properties and interactions of the adhesive and particles, as well as the properties of the completed probes, to demonstrate the retention of particle features throughout fabrication. Pull-off tests with CHAP's probes measured adhesive force values in the expected ranges and demonstrated that particles were firmly attached to the cantilevers.

Introduction

In 1991 Ducker *et al* introduced the colloidal probe, in conjunction with atomic force microscopy (AFM), as an approach to directly measure forces in colloidal systems[1]. Prior to the advent of this technique, experiments on colloidal interactions had been limited to macroscopic substrates or indirect observations[1,2]. Probe fabrication capability is often a limiting factor for colloidal probe studies because

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existing methods can only manufacture probes from a limited set of materials. Here we address some challenges associated with fabricating colloidal probes and present the Controlled Heating and Alignment Platform (CHAP) to build probes that retain the original surface chemistry and geometry of the probe particle.

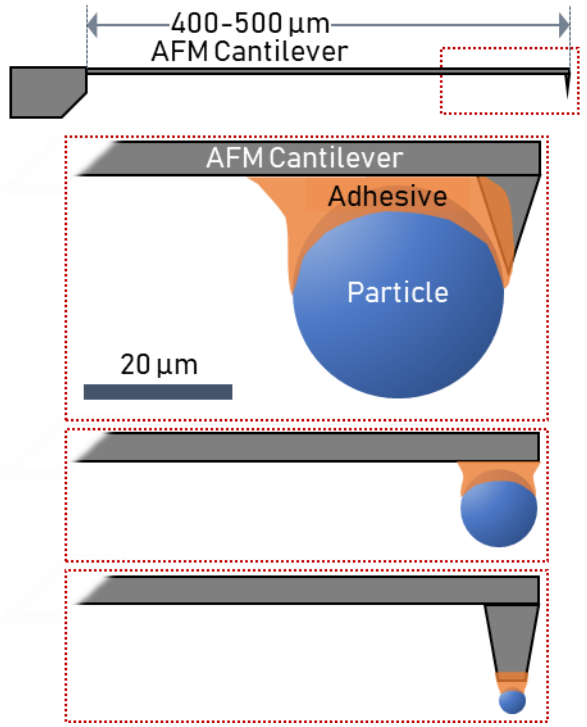

Figure 1: Colloidal Probe Designs. Tipped cantilevers are acceptable if particle diameter > tip length (10-20um). Tipless cantilevers are viable if particle size and placement prevents the cantilever from interacting with substrate during operation. Plateau tips work when particle diameter < plateau diameter.

Reviews of the methods used to manufacture colloidal probes are available in the literature[3–5]. The goal of any method is to affix a particle to the end of a cantilever. The attachment strategy depends on the size and chemical composition of the particle, the adhesive used, the methods for delivering materials to the cantilever, and the geometry of the cantilever (**Fig. 1**). Typical adhesives are thermoplastic resins, *i.e.*, Shell Epikote 1004, or polymerizable glues, *e.g.*, Norland Optical Adhesive (NOA)[4,5]. These require a curing or melting step using heat, chemicals or ultraviolet radiation (UV). Particles may be melted or sintered directly to the cantilever without any adhesive[5]. Heating is typically carried out in a heating oven or a heating stage, or by direct ohmic heating of the substrates bearing the particles and adhesives[5–7].

Interpreting colloidal probe measurements requires knowledge of the particle properties. This includes bulk characteristics, *i.e.*, modulus, and surface properties, *i.e.*, chemistry and topography. One concern when manufacturing colloidal probes is that changes to the particle may be introduced in the process. Chemical, heat or radiation exposure may alter the particle bulk or surface, while adhesives may contaminate or completely cover the particle surface. UV-polymerizable liquid glues like NOA avoid concerns due to heat but are more likely to contaminate a particle surface before hardening.

Colloidal probes can be classified as either ‘model’ or ‘native’, depending on the fate of the original particle. Model probes are created by modifying the particle surface after it has been attached

to the cantilever (*e.g.*, plasma cleaning followed by chemical modification)[8–10]. Model probes allow control over probe geometry and chemistry, but not characterization of the original particle. To characterize the original particle, particle morphology and chemistry must be conserved to create a 'native' colloidal probe. This requires particle materials to possess a melting temperature (T_m) or a glass transition temperature (T_g) above that needed for the adhesive[7]. For example, Epikote 1004 resin melts at ~100° C, which limits the use of polymers like poly(methyl methacrylate (PMMA), poly(vinyl chloride) (PVC), poly(acrylonitrile butadiene styrene) (ABS) and polystyrene (PS)[3]. To date, studies using native colloidal probes have been restricted to the limited range of materials compatible with current fabrication methods.

In this article we describe a platform for manufacturing colloidal probes while preserving the features of the original particle, including its native surface. This is achieved by controllably heating the AFM chip and minimizing exposure of the particle to heat and molten adhesive. The CHAP can create native probes from a wider range of materials than existing fabrication methods, including polymers with $T_g \leq 100°$ C, enabling direct AFM characterization of previously inaccessible colloidal systems. 3D-printed components provide independent control of an AFM chip and modified coverslips within the confined geometries of high-magnification microscope objectives. This method can be used with a wide range of particles and minimizes the potential for changes to the particle surface chemistry or geometry from exposure to heat, chemicals, radiation, or external forces. Colloidal probes with PS and silica microspheres were fabricated and used to demonstrate force mapping and pull-off measurements.

Design Considerations

The CHAP was designed for versatility, precision and ease of use. 4-axis control (X, Y, Z, tilt) of both an AFM chip and a glass coverslip allows alignment with particles as small as 1 μm. Materials to be aligned with the AFM cantilever are coated onto glass coverslips, which slot into the alignment system and can be interchanged as needed. The CHAP attaches to a standard optical microscope (OM) and is compatible with objective working distances as short as 0.31 mm. The possibility of changing the particle is minimized by the design of the heating mechanism and choice of adhesive.

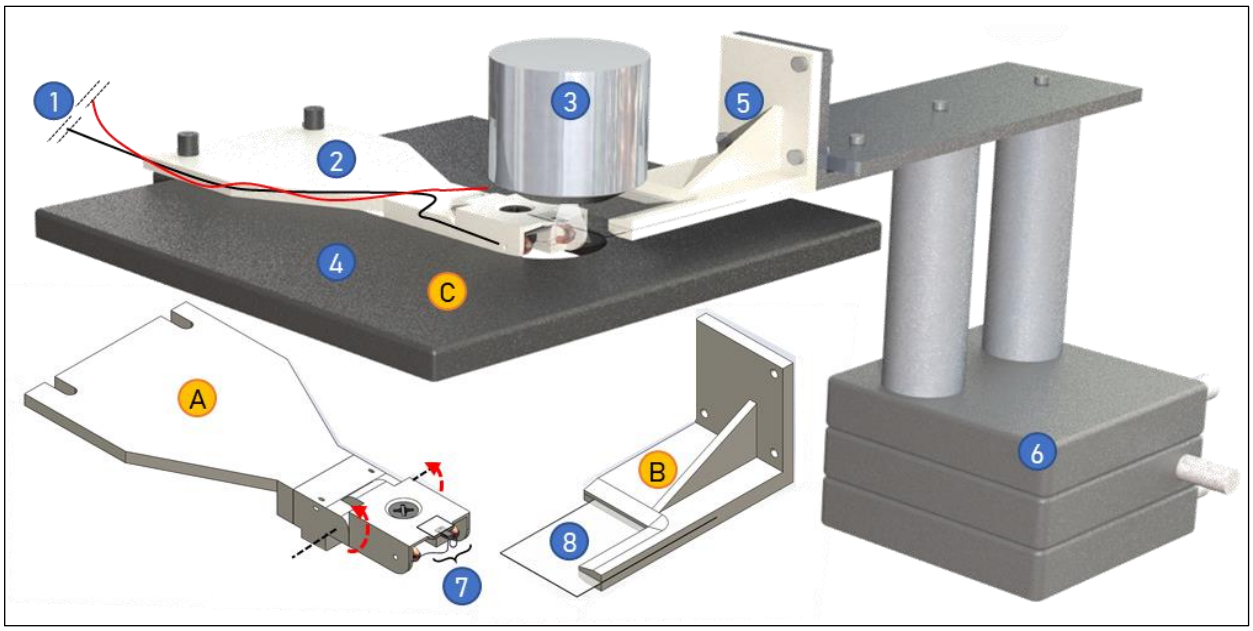

Figure 2: CHAP components. A: Probe Mount; B: Material Mount; C: CHAP aligned with microscope (only stage and objective shown). 1) Power supply. 2) Probe Mount. 3) Microscope objective. 4) Microscope stage. 5)Material Mount. 6) CHAP translation stage. 7) AFM chip and heating element. 8) Glass coverslip.

Design Description

The CHAP consists of two parts, the *Probe Mount* and the *Material Mount* (**Fig. 2**). The Probe Mount was built around the 3D-printed plastic chassis labeled **(A)** in **Fig. 2**. A ProJet 3500 HDMax printer produced 3D-printed components out of proprietary polyurethanes. The flat body was mounted onto an Olympus BX-60 microscope stage via slots in the back. The hinged head attached to the body with a set of pegs. A cross section of the head with fittings is shown in **Fig. 3**. A 0.17 mm thick glass sheet was bonded with epoxy on the top of the head, covering the rectangular slot in the front to create a groove that fit an AFM chip. The chip was held from below by a Teflon™ tongue. A steel tongue supported the Teflon™. Wires connected a Tenma DC power supply to a copper pin at each end of the heating element. The current output of the power supply controlled the temperature of the heating element, comprising a 0.12 mm diameter Chromel™ wire that passed over the Teflon™ tongue to ensure good contact with the AFM chip. The Teflon™ tongue was raised to clamp a chip in place using the clamping screw and nut. A hinge allowed the front of the head to tilt up to 90°. When the head is horizontal, the 0.17 mm thick glass sheet is the only part of the mount above the AFM chip. This makes the Probe Mount compatible with short working distance objectives. Safety precautions included a shroud to cover exposed conductors on the head and grounding the microscope body to the power supply.

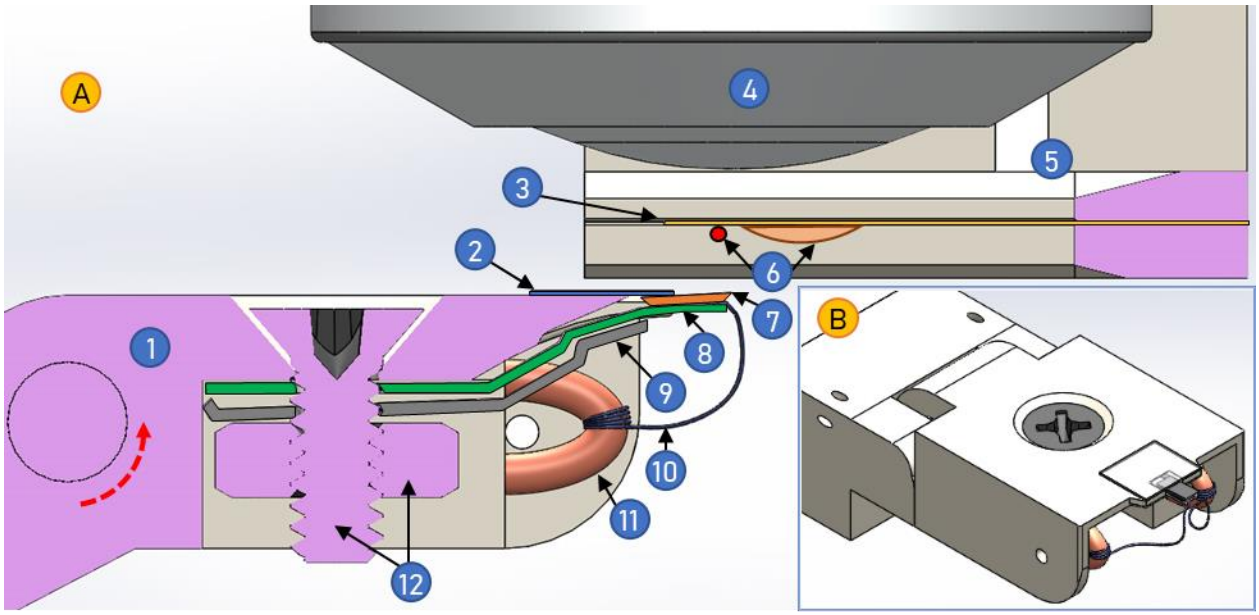

Figure 3: CHAP Detail. A: Cross section of CHAP Probe Mount aligned with Material Mount under microscope; B: Probe Mount head with fittings (wires to power supply not shown). 1) Probe Mount; 2) Glass plate. 3) Glass coverslip. 4) Microscope objective. 5) Material Mount. 6) Particle and adhesive on coverslip. 7) AFM chip. 8) Teflon tongue. 9) Steel tongue. 10) Heating element. 11) Copper pin (connects to power supply). 12) Clamping screw and nut.

The Material Mount, item **(B)** in **Fig. 2**, holds coverslips in a 3D-printed slotted bracket. The slot is tapered, and coverslips are secured only by friction to simplify replacement. The bracket was bolted to a 3-axis translation stage and could be rotated and tilted by adjusting the mounting bolts. The stage was bolted to an aluminum plate, which was clamped onto the table next to the microscope. A coverslip held in the bracket could be manipulated under an OM independent of the OM stage. The thin profile of the setup could be used with short working distance objectives. **Fig. 2** item **(C)** shows the Probe Mount and Material Mount aligned with an OM (only the OM objective and stage are shown).

Any adhesive that spreads on a coverslip can be used with the CHAP. In this work we used Mounting Wax 80 (MW80, Electron Microscopy Sciences) which has a reported flow point of 80°C.

Process Description

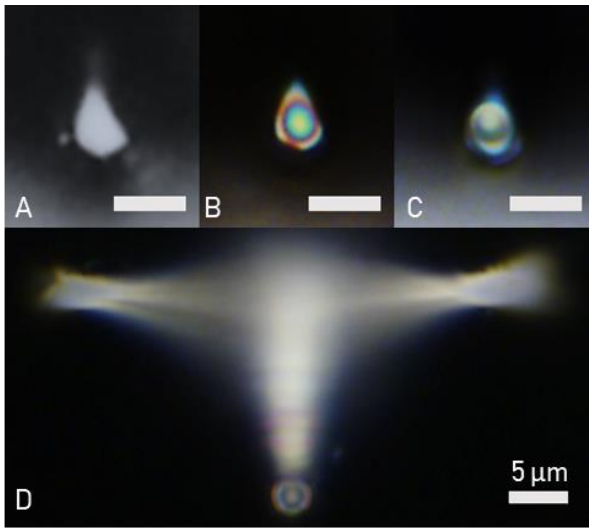

Figure 4: Flattened AFM tips during probe fabrication. Tips A-C point out of the page, tip D points down. A: Bare tip; B: Tip with MW80; C&D: Tip with MW80 and 1.9 µm PS particle. All scale bars 5 µm.

To manufacture a colloidal probe, an AFM chip was loaded in the Probe Mount with the bottom (contact) side of the cantilever facing up. Cantilevers may or may not contain a tip. Tips that have been damaged in other applications can be "given new life" in the CHAP by grinding the end of the damaged tip to create a plateau for attaching particles. The tips shown in **Figs. 4** and **5** were created by flattening sharp tips. MW80 was melted on a hotplate then spread onto a coverslip with a pipette. Another coverslip was coated with particles by dusting with dry particles or by spreading a particle suspension on the coverslip and evaporating the solvent. Putting particles on a separate coverslip minimized their exposure to heat during adhesive transfer to the cantilever, but particles and adhesive could also be applied to the same coverslip. Coverslips with adhesive or particles could be stored and reused indefinitely.

With the AFM chip in place, the Probe Mount was attached to the lowered OM stage by the mounting bolts. The Probe Mount head was typically oriented parallel to the stage or slightly inclined, depending on the cantilever geometry. Tilting the head 90° (perpendicular to the stage) was useful for inspecting the completed probe or checking tip geometry. A coverslip with adhesive was loaded into the Material Mount with the adhesive side down and positioned in the focal plane of the OM using the translation stage. The AFM chip was heated at a constant current (*vide infra*) and the OM stage was raised to bring the hot cantilever tip into contact with the adhesive and then withdrawn. The presence of adhesive on the cantilever could be verified optically due to thin-film interference. **Figs. 4A, 4B,** and **4C** show the ends of flattened-apex AFM tips without adhesive, with adhesive, and with adhesive and a 1.9 µm particle, respectively. Once adhesive was transferred to the tip, the heating element was turned off and the coverslip with adhesive exchanged for one with particles. Small particles (~0.8-2 µm) could be transferred from the coverslip to the cantilever without heating. The cantilever was aligned with a particle on the coverslip and raised to briefly contact the particle. Particles transferred between the glass and cantilever readily, and the transfer could be repeated until a satisfactory alignment of the particle on the cantilever was reached. With the particle in place, the chip was heated a second time at a lower

temperature to soften the wax and fix the particle in place. **Fig. 5** shows probes made with PS particles on flattened-apex tips. Large particles (40 μm) did not transfer spontaneously between the cantilever and coverslip. Hence the particles were transferred by heating the cantilever to soften the adhesive and pressing the cantilever onto the particle. Once the adhesive cooled, the cantilever was retracted, taking the particle with it.

With a thermoplastic adhesive, particle attachment is reversible. By controlling the cantilever temperature, adhesive can be added or removed from the cantilever. It is possible to completely remove the adhesive from the cantilever, or use a coverslip coated with adhesive to remove particulate contaminants from the cantilever.

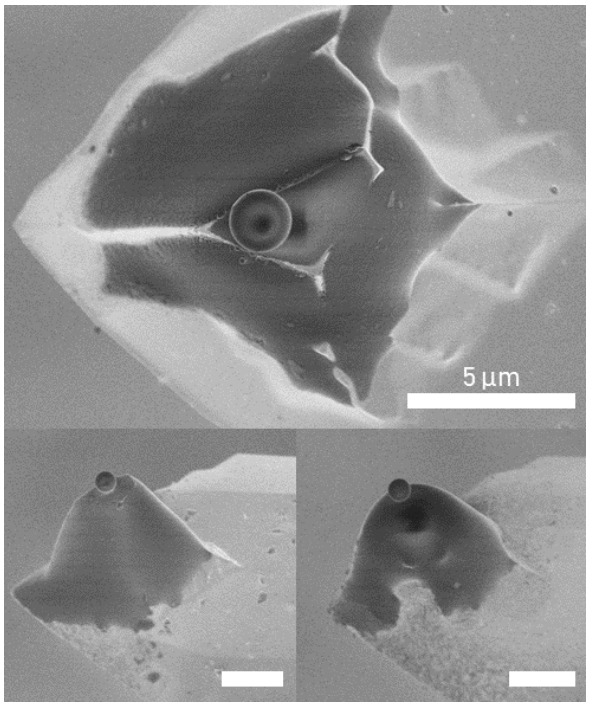

Figure 5: Probes made with flattened AFM tips, MW80 and PS particles. All scale bars 5 μm.

Characterization

The electric current in the heating element controlled the heating of the AFM chip. Cantilever temperature response was monitored using melting point standards such as vanillin (MW 81-83C, Sigma-Aldrich). A crystal of the standard was placed at the end of the cantilever and current was increased until the crystal melted. We noted that the cantilever temperature took up to 5 minutes to stabilize after changes to the current. To determine the minimum heating that would fasten a particle to the cantilever, we transferred a particle to an unheated wax-covered cantilever, heated the cantilever then attempted to dislodge the particle after cooling. The best results were achieved using a pre-heating step to bring the system close to the flow point of the adhesive, followed by a shorter final heating step then immediate cooling to ambient temperatures. For example, with ACS240TS cantilevers, particle attachment does not occur even at long times when heating at 0.540 A. Heating at 0.550 A resulted in attachment but the time to reach the attachment temperature from a cold start varied between tests. Better reproducibility was achieved using a pre-heating step at 0.540 A to bring the adhesive close to the attachment temperature, followed by short final heating at 0.550 A. The length of the second heating step was varied to find the

minimum time that resulted in attachment and found that 30 sec did not but 45 sec did. Each model of cantilever had to be tested to determine the time and current parameters, but the resulting procedure worked with all cantilevers of the same model.

To determine the suitability of MW80 as an adhesive we measured its mechanical properties, characterized its interactions with micron-sized PS microspheres and PS films, and examined completed probes under a scanning electron microscope (SEM). Differential scanning calorimetry (DSC) measurements carried out in a Q20 DSC (TA Instruments) found a T_g of 32°C for MW80 (compared to 49°C for Epikote1004). Mechanical analysis of MW80 samples, carried out with an RSA-G2 Solids Analyzer (TA instruments), showed time independent moduli with an average storage modulus of 1.73 GPa and average loss modulus of 170 MPa at 25°C. This indicated that at room temperature the wax is a rigid solid and would not deform during AFM measurements.

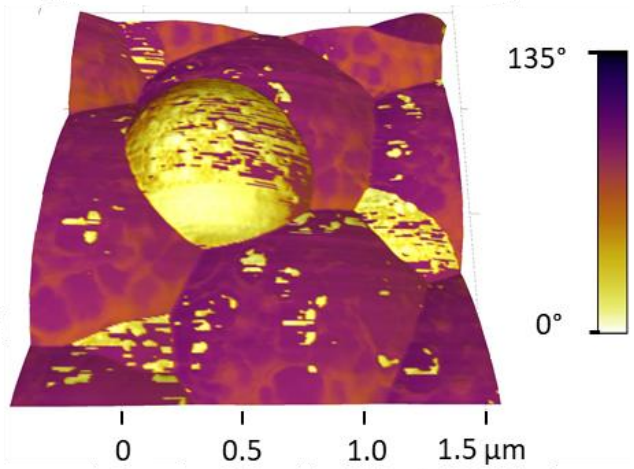

Figure 6: AFM height retrace overlaid with phase retrace showing PS particles (yellow) embedded in MW80 (violet).

Anionic PS microspheres, 0.7-2 µm in diameter, were prepared by soap-free emulsion polymerization and then cleaned by repeated cycles of centrifuging and resuspending in deionized water[11]. MW80 was spin-coated onto glass slides from ethanol. A drop of PS microspheres/water suspension was placed on each film and allowed to dry overnight at room temperature. Once dry, slides were heated on a hotplate at 70-85°C for 1-6 minutes then allowed to cool. Loose particles were removed by ultrasonication in water. Samples were imaged using an MFP-3D AFM (Asylum Research) in AC mode to characterize the wax/particle behavior at different heating conditions. At short heating times, only particle monolayers were visible, or dimpled wax surfaces where particles had been dislodged. At intermediate heating times, wax crept into interstices as particles sank slightly into the wax. At long heating times, particles sank such that some were engulfed in the wax as the wax seeped up between particles. **Fig. 6** displays an AFM phase retrace overlaid on a height retrace and shows PS particles (yellow) mostly engulfed by the wax (violet). A sharp transition at the particle/wax interface is evident in the phase retrace.

Films were prepared by spin-coating PS onto silicon wafers from toluene. Chips of MW80 (3-8 mg each) were melted on the PS surface at 85°C for 2 hours. We measured the contact angle of the wax droplets on PS. The irregular droplet perimeters led to a range of observed contact angles, but in all cases contact angle values were greater than 90°, indicating that liquid MW80 did not readily wet the PS substrate. Colloidal probes made with PS particles were imaged in a Verios SEM to determine the morphology of the particle/wax interface (**Fig. 7**). We did not detect any meniscus between particle and the wax using SEM, although the particle was attached firmly enough to endure thousands of pull-off measurements. The wax appeared to dimple under the particle, even when the particle was pressed with enough force to flatten it. These SEM observations, coupled with high wax/PS contact angles and AFM measurements showing sharp wax-particle interfaces, indicated that MW80 did not creep onto the particle surface during attachment.

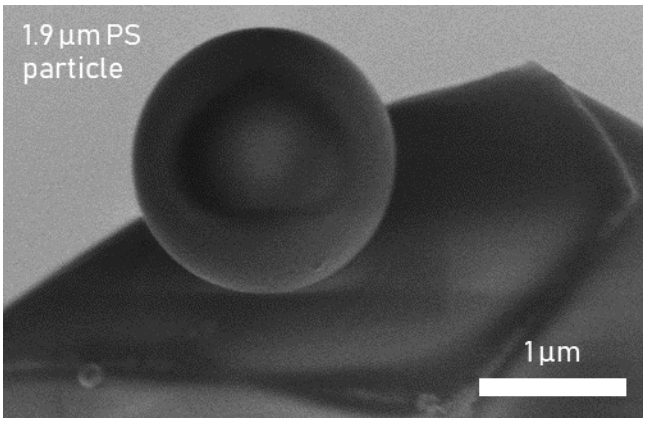

Figure 7: PS particle attached to an MW80-coated plateau tip. No meniscus could be detected.

Probe Testing

To test the performance of colloidal probes fabricated with CHAP, several dozen probes were made using 1 µm silica particles and 1.8 µm PS particles on cantilevers with nominal stiffnesses (K) between 0.2 to 26 N/m. Calibration and force measurements were carried out in an MFP-3D AFM. Measured K values for all cantilevers were in the expected ranges and the K value of a cantilever did not change significantly when different particles were attached. The resonant frequencies of the cantilevers were in the expected range and consistent for different particles on the same cantilever. These consistent calibrations suggest that the performance of a cantilever was

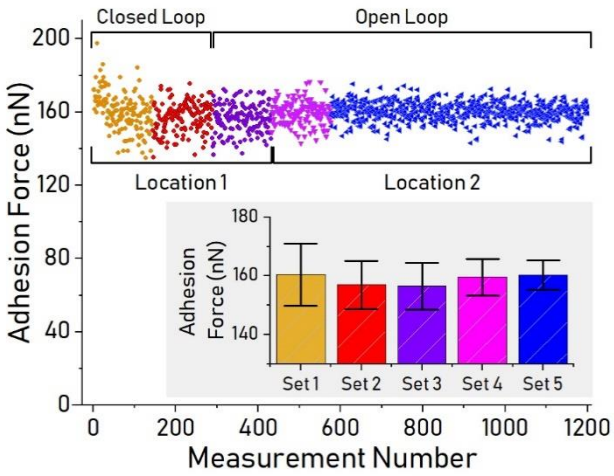

Figure 7: AFM pull-off data for one probe using open/closed control loops at two locations.

insensitive to the adhesive and particles attached, which was unsurprising given the small mass of the particle and small amount of adhesive used.

We collected force maps on surfaces including silica, glass, fluorosilanized silica, PS and Teflon using the PS and silica colloidal probes. Particles remained attached to cantilevers through thousands of pull-off measurements but could be removed with the CHAP. The measured pull-off forces were in the expected range for the materials tested. Probes with silica particles were used to check for hysteresis in pull-off measurements that might result from deformation of the adhesive. No such hysteresis was observed. **Fig. 8** represents a composite of the pull-off forces from force maps on different areas of a PS substrate using a silica particle.

Conclusion

In this paper we presented a novel platform that enables attachment of colloidal particles to AFM cantilevers without altering the native properties of the probe particles. A thermoplastic adhesive was used to secure particles to cantilevers and a novel heating scheme provided faster and more precise control over probe temperature than existing methods. Improved heating control allowed fine tuning of the adhesive's viscosity to protect the particle from contamination by the adhesive. Using MW80 adhesive and operating below 100°C, the CHAP produced native colloidal probes from PS microspheres, a material that is not stable with existing attachment strategies. No cleaning or post-modification of probes is needed, thus further simplifying probe fabrication.

The CHAP expands the range of materials that can survive unchanged through colloidal probe fabrication including polymers with T_g values below 100°C. Thus, direct colloidal probe measurements of important colloidal systems like PS or PMMA can be investigated for the first time. The system was designed for compatibility with common lab equipment (*e.g.*, optical microscope) and simple, robust operation to reduce the barriers to entry for researchers entering the colloidal probe field. For experienced colloidal probe makers, the CHAP offers increased versatility and the potential to simplify and speed up probe fabrication.

Acknowledgement

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