DIRECT ASSEMBLY OF A HYDROGEL NANO-TIP ONTO SILICON MICROCANTILEVERS FOR WEAR STUDY AND FACILE REGENERATION OF SOFT ATOMIC FORCE MICROSCOPE PROBES

Seokbeom Kim[1], Yeowon Yoon[1], and Jungchul Lee[1]
[1]Sogang University, Seoul, SOUTH KOREA

ABSTRACT

Recently, hydrogel nano-probes have been proven to be exclusively useful for high-speed and less damage atomic force microscope (AFM) imaging on soft or biological matters. However, from the classical tribology standpoint of view, soft and compliant natures of hydrogel nano-probes seem incompatible with long-term reliable imaging. Here, we report counter-intuitive results showing the hydrogel AFM tip better-suited for repeated non-contact amplitude modulation (AM) mode AFM imaging compared to the silicon tip. In addition, we show that the hydrogel tip attachment could be repeated multiple times after the removal of the worn or deformed tip.

INTRODUCTION

Polymeric cantilevers [1, 2] have drawn continuous attention due to their intrinsic low elastic moduli and ease of manufacturing. Recently, hydrogel (PEGDA) AFM cantilevers have shown unique capabilities including geometry, property, and functionality tuning by compressible replica molding, combination of materials selection and mold design, and encapsulation of functional nanomaterials [3]. In addition, the aforementioned study has reported that hydrogel tip materials may exhibit wear-resistant characteristics with the aid of their viscoelastic nature [3-5]. The hydrogel materials are consisted of cross-linked polymer chain as covalent bond. The cross-linking universally and powerfully reduces wear but leaves nanoscale homogeneity intact [6-9]. However, the prolonged life of PEGDA tip in comparison with silicon tip was only observed during short term dynamic-mode imaging at relatively high scan rates (>25 Hz) and such an optimistic observation might be due to the lower resonance frequency of the PEGDA cantilever than that of the silicon cantilever. To make sure the promising wear-resistance of the hydrogel tip, we need to compare wear behaviors of a pair of AFM cantilevers that exhibit the same geometry, dimension, and mechanical properties but different tip materials, i.e., one with silicon and the other with hydrogel.

In this paper, we propose a direct hydrogel tip assembly onto a tipless silicon cantilever and use the hydrogel tip attached (hydrogel-silicon hybrid) cantilever in comparison with all-silicon AFM cantilevers exhibiting similar spring constant and resonance frequency. With these pairs, wear characteristics are systematically investigated during non-contact AM mode AFM imaging. In addition, we prove that the hydrogel tip attachment could be repeated multiple times.

FABRICATION

To make a fair and reasonable claim, a hydrogel tip is attached to tipless silicon cantilevers and compared with all-silicon AFM cantilevers exhibiting similar spring constant and resonance frequency. To attach the hydrogel tip onto silicon microcantilever, the direct assembly method is used with the setup shown in Figure 1 (a). the setup is consisted of high power UV LED, mechanical stage for manipulating the cantilever, and bi-axially compressible mold mount with motorized stages. The mold

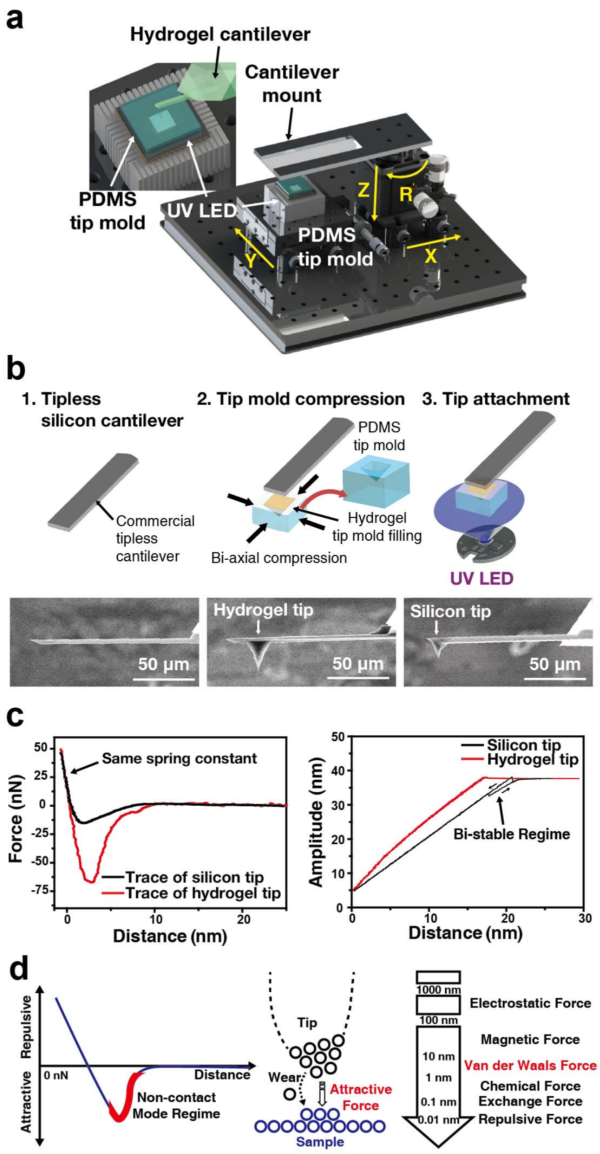

Figure 1: (a) Setup for the direct hydrogel tip assembly onto microcantilevers. (b) Direct hydrogel tip assembly method and SEM images of hydrogel-silicon and all-silicon cantilevers. (c) Force-distance (left) and amplitude-distance (right) curves of hydrogel-silicon and all-silicon cantilevers. (d) Force-distance curve and wear mechanisms in non-contact AM mode regime

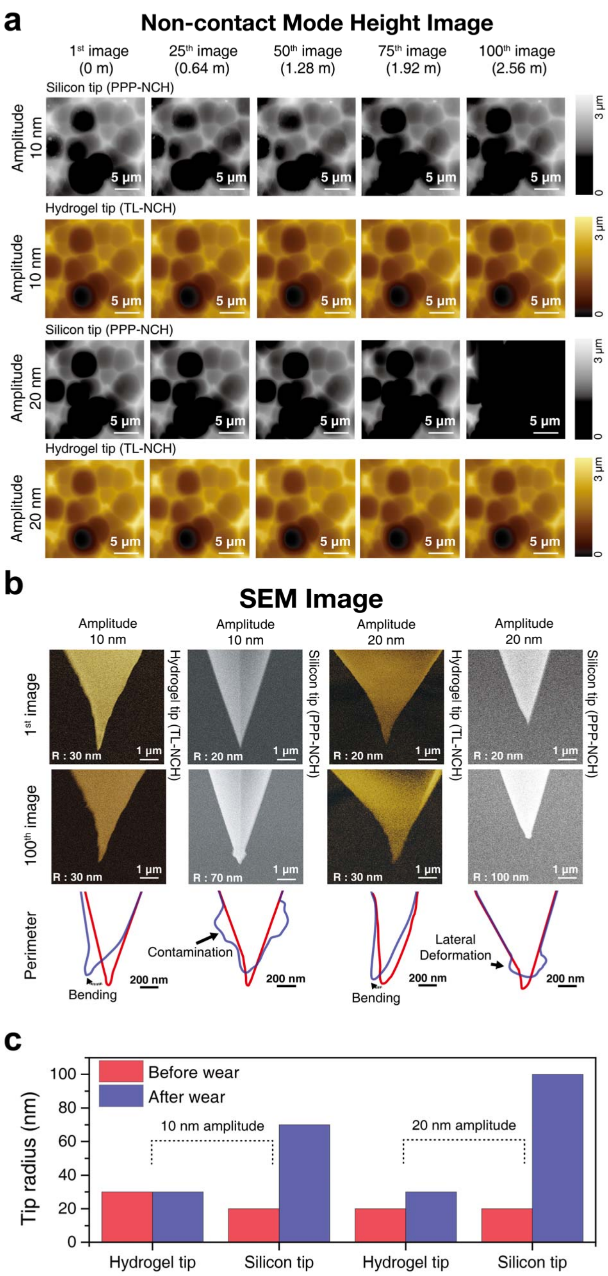

Figure 2: (a) Non-contact AM mode height images for a porous silicon substrate taken with all-silicon cantilevers (black and white) and tipless silicon cantilevers with the hydrogel tip (light and dark yellow) at different free vibration amplitudes. (b) SEM images and tip perimeters of the silicon and hydrogel tips after the 1st and 100th frame imaging (Red and blue lines represent the perimeter around the tip after the 1st and 100th frame of repeated imaging). (c) Sharpness variation of hydrogel and silicon tips before and after the repeated imaging.

is doubly replicated from a negatively etched pyramid shaped silicon mater mold. After mounting on the setup, the mold is filled with the PEGDA pre-polymer (Molecular weight 250 and 1 wt% phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide as a photoinitiator) then bi-axially compressed to enhance the tip sharpness similar to the silicon tip of commercial cantilevers. Once a tipless silicon cantilever is brought close to and makes contact with the PEGDA filled tip mold, UV exposure cures the PEGDA tip which is firmly attached to the cantilever. SEM images show the tipless silicon cantilever before and after the hydrogel tip assembly and all-silicon cantilever (Figure. 1(b) bottom). Figure. 1 (c) shows the hydrogel tip exhibiting the extended attractive regime in the force-distance curve and the hysteresis-free stability in the amplitude-distance curve. Such unique characteristics make the hydrogel tip better-suited for non-contact imaging than the silicon tip. Due to the ambiguous instant of the tip-substrate contact, the non-contact AM mode AFM typically refer to amplitude-modulation dynamic mode imaging in the slightly attractive force regime shown in Figure. 1(d). Therefore, non-contact AM mode imaging tends to minimize tip wear but it is still possible for the tip to interact with the given substrate.

WEAR CHARACTERISTICS

The wear characteristics of fabricated hydrogel-silicon (TL-NCH, Nanosensors) hybrid and commercial silicon (PPP-NCHR, Nanosensors) cantilevers are compared in non-contact AM mode imaging using AFM (NX10, Park Systems). The imaging substrate is a porous silicon etched by HNA solution (a mixture of acetic, nitric, and hydrofluoric acids) and the scan area and the number of imaging frame are set to be 25 x 25 μm^2 (cropped to 20 x 20 μm^2 for showing the same area in Figure 2 (a)) and 100, respectively, thus, the cumulative scan distance becomes 2.56 m. Figure. 2 (a) shows non-contact AM mode height images over a same area obtained by the fabricated hydrogel-silicon hybrid and commercial all-silicon cantilevers in different free vibration amplitudes with the 80 % setpoints.

Figure. 2 (b) shows SEM images and perimeters of the tip of hydrogel-silicon hybrid and all-silicon cantilevers before and after repeated non-contact AM mode imaging on the porous silicon substrate at two different free vibration amplitudes (10 nm and 20 nm). The silicon tips exhibit the lateral plastic deformation with appreciable sharpness degradation because the plastic deformation is not necessarily produced equally around the tip. In contrast, the hydrogel tips exhibit the lateral bending with suppressed sharpness change. In addition, the larger free amplitude tends to accelerate the tip wear when the tip material is identical. When the free amplitude is higher (typically more than 10 nm), the system is bi-stable, and jumps between a low-amplitude and high-amplitude mode are inherent to the system because the motion of the lever becomes highly nonlinear. Figure. 2 (c) summarizes the sharpness variation of hydrogel and silicon tips after the repeated imaging.

TIP REGENERATION

Our results clearly confirm the wear-resistance of the PEGDA tip that outlasts the silicon tip due to its material viscoelastic and cross-linking natures. However, the PEGDA tip will also be worn after repeated imaging for extended frames. To address this inevitable issue, we propose a method to regenerate the worn tip. Once the whole cantilever is dipped in a Piranha solution, a mixture of sulfuric acid and hydrogen peroxide, the PEGDA tip is easily removed while the silicon beam remains intact.

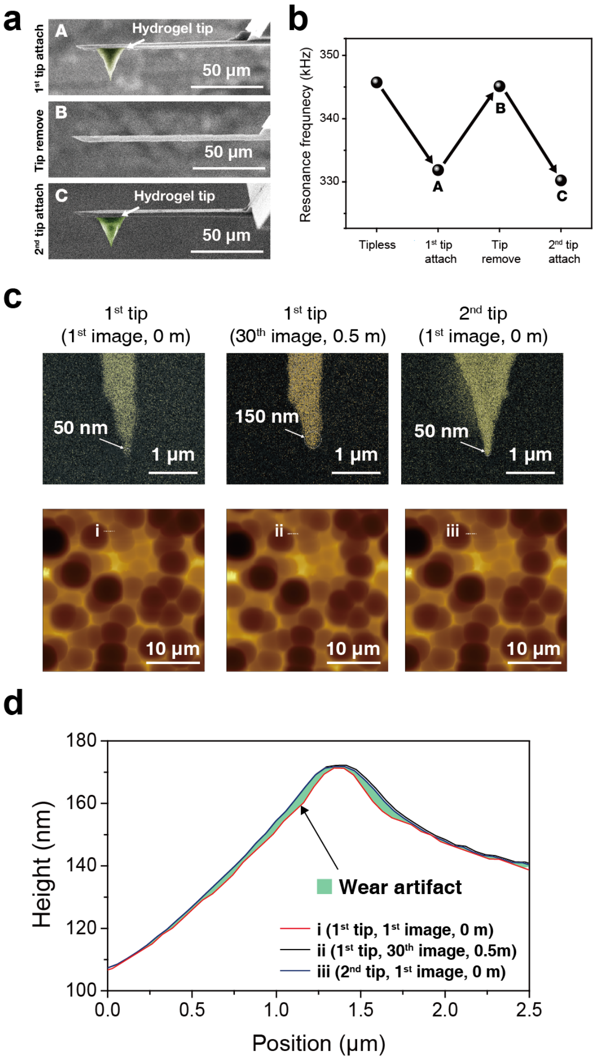

Figure 3: (a) SEM images and (b) resonance frequency of the silicon cantilever with the PEGDA tip taken after the 1st tip attachment (A), the removal of the 1st attached tip (B), and the 2nd tip attachment (C). (c) SEM images (top) of the hydrogel nano-tips and corresponding AFM height images (bottom). (d) Line scans along the dotted lines in (i)~(iii), in (c).

Therefore, the PEGDA tip attachment and removal can be simply repeated multiple times. Figures. 3 (a) and (b) show results of repeated PEGDA tip regeneration for restoration of the tip sharpness by identical SEM images and resonance frequency. Figure. 3 (c) shows SEM and AFM images obtained with accelerated wear conditions and Figure. 3 (d) shows line scans along the white dotted lines in Figure. 3 (c) bottom. There are imaging artifacts resulting from the tip wear that can be simply removed by using the regenerated hydrogel tip. In short, the worn PEGDA tip can be replaced with a new one when imaging artifacts are observed and critical.

CONCLUSION

We report that the hydrogel tip attached to tipless silicon cantilevers exhibits counter-intuitive wear resistance which comes from viscoelastic and cross-linking natures of polymeric materials during non-contact AM mode imaging compared to the silicon tip for the first time. Even though the hydrogel tip is damaged for any reasons, it can be simply removed and regenerated by the direct tip assembly method. Such remarkable characteristics of the hydrogel may enable artifact-free AFM imaging for a variety of biological applications.

ACKNOWLEDGEMENTS

This research was supported by the Commercialization Promotion Agency for R&D Outcomes (COMPA) (2015K000127) and the National Research Foundation of Korea (NRF) funded by the Korea government (MSIP) (NRF-2015K1A3A1A21000288 and NRF-2013R1A1A1076080).

REFERENCES

[1] Genolet, G., Brugger, J., Despont, M., Drechsler, U., Vettiger, P., De Rooij, N. F., Anselmetti, D., “Soft, entirely photoplastic probes for scanning force microscopy”, *Rev. Sci. Instrum.*, vol. 70, pp. 2398-2401, 1999.

[2] Calleja, M., Nordström, M., Álvarez, M., Tamayo, J., Lechuga, L. M., Boisen, A., “Highly sensitive polymer-based cantilever-sensors for DNA detection”, *Ultramicroscopy*, vol. 105, pp. 215-222, 2005.

[3] Lee, J. S., Song, J., Kim, S. O., Kim, S., Lee, W., Jackman, J. A., Lee, J., “Multifunctional hydrogel nano-probes for atomic force microscopy”, *Nat. Commun.*, vol. 7, 11566, 2016.

[4] Adams, J.D., Erickson, B.W., Grossenbacher, J., Brugger, J., Nievergelt, A., Fantner, G.E., “Harnessing the damping properties of materials for high-speed atomic force microscopy”, *Nat. Nanotechnol.*, vol. 23, pp. 147-151, 2015.

[5] Chiappone, A., Fantino, E., Roppolo, I., Lorusso, M., Manfredi, D., Fino, P., Pirri, C.F., Calignano, F., “3D printed PEG-based hybrid nanocomposites obtained by sol–gel technique”, *ACS Appl. Mater. Interfaces*, vol. 8, pp. 5627-5633, 2016.

[6] Berger, R., Cheng, Y., Förch, R., Gotsmann, B., Gutmann, J.S., Pakula, T., Rietzler, U., Schärtl, W., Schmidt, M., Strack, A. Windeln, J., “Nanowear on polymer films of different architecture”, *Langmuir*, vol. 23, pp. 3150-3156, 2007.

[7] Gotsmann, B., Duerig, U.T., Sills, S., Frommer, J., Hawker, C.J., “Controlling nanowear in a polymer by confining segmental relaxation”, *Nano Lett.*, vol. 6, pp. 296-300, 2006.

[8] Altebaeumer, T., Gotsmann, B., Pozidis, H., Knoll, A., Duerig, U., “Nanoscale shape-memory function in highly cross-linked polymers”, *Nano Lett.*, vol.8, pp. 4398-4403, 2008.

[9] Jansen, L., Lantz, M.A., Knoll, A.W., Schirmeisen, A., Gotsmann, B., “Frictional dissipation in a polymer bilayer system”, *Langmuir*, vol. 30, pp. 1557-1565, 2014.

CONTACT

*Jungchul Lee, tel: +82-2-705-7973;
jayclee@sogang.ac.kr