



Attachment of nanoparticles to the AFM tips for direct measurements of interaction between a single nanoparticle and surfaces

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Abstract

Here we report a universal method of attachment/functionalization of tips for atomic force microscope (AFM) with nanoparticles. The particles of interest are glued to the AFM tip with epoxy. While the gluing of micron size particles with epoxy has been known, attachment of nanoparticles was a problem. The suggested method can be used for attachment of virtually any solid nanoparticles. Approximately every other tip prepared with this method has a single nanoparticle terminated apex. We demonstrate the force measurements between a single ~50 nm ceria nanoparticle and flat silica surface in aqueous media of different acidity (pH 4–9). Comparing forces measured with larger ceria particles (~500 nm), we show that the interaction with nanoparticles is qualitatively different from the interaction with larger particles.

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1. Introduction

It is generally believed that interaction with nanoparticles can differ from interaction of large micron sized particles. Fluctuation in counterion cloud, heterogeneity in charge distribution at the area of particle–surface contact, different catalytic activity, all these can result in noticeable deviation the nanoparticle interactions when compared with micron size particles. From a calculation point of view, the use of the popular Derjaguin approximation is no longer valid when the tip surface distance is larger than the particle radius. Moreover, many nanoparticles are not necessarily spherical. This makes it hard to calculate/predict such type of interaction. In the present work, we consider Nanophase ceria that are rather cubical than spherical particles. Such particles are broadly used in modern semiconductor industry in the process of chemical mechanical planarization (CMP). Therefore, it is of great interest to measure

interaction with single nanoparticles directly. Atomic force microscopy (AFM) is the technique that allows measuring interactions between various surfaces and a sharp stylus, tip. In principle, one can consider the AFM tip, having nanoscale radius of curvature, as an effective “nanoparticle” [1–4]. However, the number of materials used to make the AFM tips is limited to silicon (which is in ambient conditions oxidized to silica) and silicon nitride (which is also oxidized [3]). These tips can be coated with various metals and diamond (commercially available from the AFM tips suppliers). Even then, it is still an assumption that such AFM tips can mimic nanoparticles. Direct measurements of forces involving such particles can therefore be very useful from both fundamental and practical points of view.

Direct attachment, gluing of spherical multi-micron size particles to the AFM cantilevers was demonstrated first in 1991 [5], and has been broadly used to study to molecular forces and mechanics of biological cells [6–8]. Chemical functionalization of AFM tips with various molecules has demonstrated its great importance for studying molecular interactions, force spectroscopy, detection, etc. Using wet chemistry procedures, researchers manage to attach cells and bacteria to the AFM can-

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tilevers. Recently colloidal spherical gold nanoparticles have been attached/grown on the AFM tip with the help of a wet chemistry approach [9]. It is worth mentioning an “inverted” approach to study forces between nanoparticles and surfaces [10,11]. The surface was mimicked by a large spherical particle attached to the AFM cantilever whereas the nanoparticles were deposited on a flat substrate.

Here we report a rather simple method of attachment/functionalization of AFM tips with nanoparticles. The particles of interest are glued to the AFM tip with epoxy. It may look similar to gluing of spherical multi-micron size particles to tipless AFM cantilevers. However, that method cannot be directly extended to nano-sized particles because of the following two reasons: (1) to attach a single particle to the cantilever, it has to be visible under optical microscope. This is not the case for nano-sized particles. (2) The smaller the particle, the easier for epoxy to engulf it. Because the layer of epoxy deposited on the cantilever is at least several cubic microns, it is quite tricky to avoid coating of the particles with the epoxy.

The main ideas on the suggested here method are in (1) gluing not a single nanoparticle but a large amount of nano-sized particles at once, (2) gluing not to the cantilever but to a standard Si_3N_4 pyramidal tip, (3) depositing nanoparticles to the epoxy coated tip not immediately, but after the epoxy being semi-rigidified, becoming viscous enough to avoid engulfing the particles before complete curing. The suggested method can be used for attachment of virtually any solid nanoparticles. Almost any other tip prepared in this method has a single outstanding particle at the apex. This allows one measuring forces between that single outstanding particle and various surfaces. To demonstrate the method, we attached ceria ~ 50 nm nanoparticles and measured forces between single nanoparticles and flat silica surface. By choosing non-spherical particles of ceria, we are trying to solve experimentally a challenging problem of studying their interaction with various surfaces. This problem, being of a large applied interest, cannot be solved theoretically as yet.

2. Experimental

2.1. Materials, methods, and instruments

NanoTek[®] ceria particles (~ 50 nm) by Nanophase Technologies Corp. were used in this work. Larger ceria particles (0.5–1 μm) are Opaline (Rhodia Electronics & Catalysis). Araldite 10-min two component epoxy resin was used to glue the particles to the AFM tip. Silica surface was prepared by CMP polishing (by Rohm and Haas EM, Inc.) of silica coated (multi-micron thickness) silicon 6' wafers up to subnanometer surface roughness. Interaction between the tip and pad surfaces was measured in an aqueous 10 mM solution of KOH and HNO_3 of various pH, ranging from 4 to 9. While changing pH, the equilibration with new environment was reached within several minutes. A Dimension 3100 Nanoscope AFM (DI/Veeco, CA) was used in this work. The AFM operated in the force/force–volume modes while measuring the forces (16 \times 16 \times 512 pixels mode). Standard silicon nitride inte-

grated pyramidal tips (Veeco/DI probes) fixed on a cantilever with the spring constant $k \sim 0.14$ N/m (it was determined before gluing the particles by resonance method using built-in option in the AFM software) were used for attaching ceria particles. Other cantilevers of different stiffness and geometry can be used in the same way to attach particles. The AFM software v.5.12r4 was employed. Averaging of collected force data was done with the help of MAnalysis v.2.01 software (by Dr. Gorbunov, Valdimir Tsukruk's Laboratory). Sensitivity of the AFM photodetector was determined assuming no deformations of the tip and sample in the compliance (contact) region of the force curve. The forces were measured starting from neutral pH, then going too higher pH 9, returning to neutral pH, going to lower pH 4, and returning to neutral pH again to check any possible deterioration of the tip, the change of tip geometry.

Ceria particles were glued to the AFM tip by using either built-in micromanipulator of Dimension Nanoscope AFM or stand along Micromanipulator 6000 (Micromanipulator Inc.) Two magnetically attached mechanical transducers (micromanipulators, 1 μm resolution) were utilized with Micromanipulator 6000. Either metallic (platinum) wire or glass fibers were used as the manipulating tips of the transducers. Glass fibers were obtained by pulling glass borosilicate pipette tips over propane flame.

2.2. Attachment of nanoparticles to the AFM tip

The main idea is in using small amount of epoxy glue spread over a standard Si_3N_4 pyramidal tip. (Epoxy should be resistive to the medium in which the AFM probe will be used.) After putting epoxy on the tip (as described below), the glue must be semi-cured (~ 5 min for 10-min epoxy, room temperature) before putting nanoparticles onto the tip. This prevents a possible leakage of the glue and engulfing the nanoparticles by the glue. Specific details of the method are described below for the use of each of these micromanipulators.

2.2.1. Using built-in micromanipulator of Dimension 3100 Nanoscope AFM

Both components of epoxy glue were mixed on small plastic dish. Small drop of the mix was spread on one part of a glass slide with the help of a plastic ribbon. Dry ceria powder was placed on the other part of the same slide. Spreading epoxy over glass slide was very important here. After that, one can find some epoxy droplets of several microns in size. Using AFM built-in video system, the AFM tip was put in contact with such a small droplet of epoxy. This allowed placing only a little amount of epoxy in the tip apex. Comparing the size of the epoxy droplet on the slide before and after the touching with the AFM tip, one can estimate the amount of epoxy deposited onto the tip. The amount of deposited epoxy should not be more than a few cubic microns. After waiting for epoxy to cure a bit (total ~ 5 min for this 10 min epoxy), the tip was put in contact with the ceria powder. After keeping the tip in the ceria for 1–2 min, the tip was disengaged and stored for further processing. The rest of the processing is common for both methods, and is described later on.

2.2.2. Using Micromanipulator 6000 station

Using this station, one can process several cantilevers with one batch of epoxy at once. It is restricted only by the time of epoxy curing. In principle one can use more slowly curing epoxy. For example, we also successfully used 30 min epoxy. To process several cantilevers at the same time, one can align the cantilevers with the tips looking up on a glass slide. A drop of premixed epoxy and ceria powder should be placed nearby on the same glass slide. Epoxy is deposited to the AFM tips with the help of one manipulator by using a glass or metallic fiber/needle. It is worth noting the benefit of using glass fibers for manipulating. As glass is transparent, it is relatively easy to see the cantilever/tip through the fiber, which is beneficial while positioning the fiber above the cantilever. The fiber is slightly dipped in an epoxy drop. Then it is important to touch glass slide surface with the tip nearby to control the amount of epoxy transferred from the fiber. If needed glass side can be touched several times until a regular size small droplet remains on the glass surface. After that the manipulator fiber with epoxy is used to transfer the epoxy to the AFM tips. Having waited for epoxy to semi-cure as described above, one should use the second manipulator with a glass fiber to transfer ceria to the epoxy coated AFM tips. To do that the glass manipulator fiber is first dipped into ceria particles. Under normal humidity conditions, adhesion forces (mostly capillary force due to water adsorbed layers) should be enough to pick up agglomerates of ceria particles. If normal humidity is not feasible to have, one can still use the tip of the first manipulator with some semi-rigidified epoxy. However, the risk of having ceria contaminated with epoxy increases. The ceria agglomerates are then placed onto the AFM tips. This can be controlled with optical system of micromanipulator system (200 \times magnification is sufficient to do it). The chips with cantilevers are dismantled from the glass slide, and processed further. The below description is common for both manipulators.

The cantilevers with ceria particles attached with either of the above methods are placed in incubator at ca. 80 °C for 24 h to completely cure epoxy. After that each cantilever is put in ultrapure Milli-Q water and ultrasonicated for 10–30 s to get rid of not strongly enough attached particles.

2.3. Characterization of the attached particles

To be sure that we prepared a single nanoparticle terminated tip, we need to check the following: (1) If the AFM probe obtained is terminated with a single particle. (2) This is indeed ceria particle, not just outstanding apex of the original AFM tip, or not epoxy leaked out (so the outstanding particle could be coated with the epoxy). To test if we are dealing with a single particle, we imaged the attached particles by using inverse grid (TG01, by NT-MDT/MicroMash Inc.) which consists of vertical sharp silicon tips. This technique produces inverted image of the AFM tip. It should be noted that this method is less invasive comparing to electron microscopy, which can alter the surface with electron beam and may require some conductive coating. To be sure that we are dealing with ceria particles, but not epoxy that can be leaked out between ceria particles, or original apex

coated with epoxy, or just exposed silicon nitride apex of the original AFM tip, we recorded the pH dependence of adhesion between the obtained tips and flat silica surface.

3. Results and discussion

Comparing using both manipulators, we can note that the AFM manipulator gives ease and more control, whereas the use of Micromanipulator 6000 station allows making larger quantity of the tips. While it is not feasible to position each nanoparticle precisely with a manipulator using the described method, the pyramidal tip geometry helps to have virtually every other tip made in these methods to have a single outstanding nanoparticles located at the tip apex. Fig. 1 shows inversed image of the AFM tip with the attached ceria particles obtained as described in the previous section. An SEM image of the same tip is also shown (to get a reasonable SEM image, the tip was coated with gold). Looking at the cross-sections, one can find how many particles are at the apex. Comparing to the size of individual particle (\sim 50 nm), it is clear that the AFM tip shown in Fig. 1 has only a single terminal particle. It should not be unexpected to see non-circular cross-section because Nanophase ceria comprises of non-spherical particles. Definitely in the case of non-spherical particles, each tip then represents only a particular orientation of the nanoparticle with respect to the surface. Studying the interactions involving such particles, one can investigate dependence of the forces on the particle orientation by doing series of experiments with different tips. While such study is beyond the scope of the present paper, we did the measurements using several ceria tips as described below.

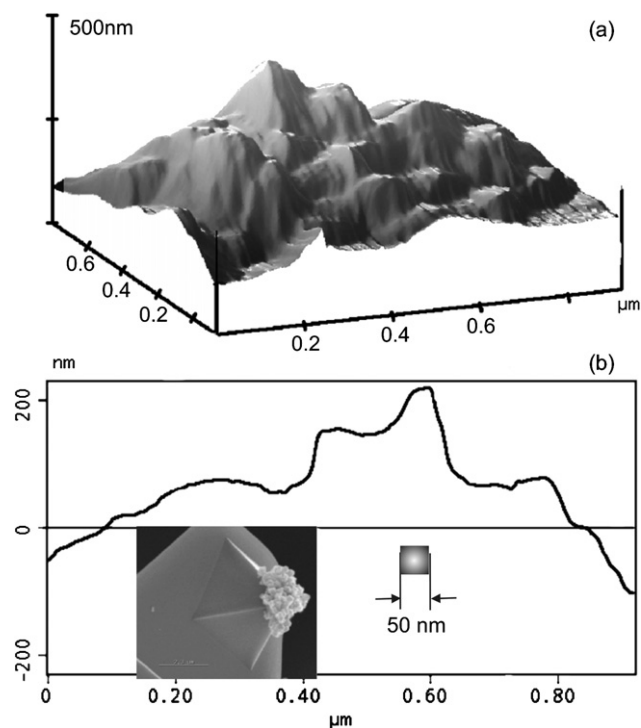


Fig. 1. (a) an AFM image of the tip obtained with the inverted grid and (b) corresponding cross-section (insert is a SEM image of the attached nanoparticles and the AFM tip). A 50 nm “particle” is shown on the cross-section for scale.

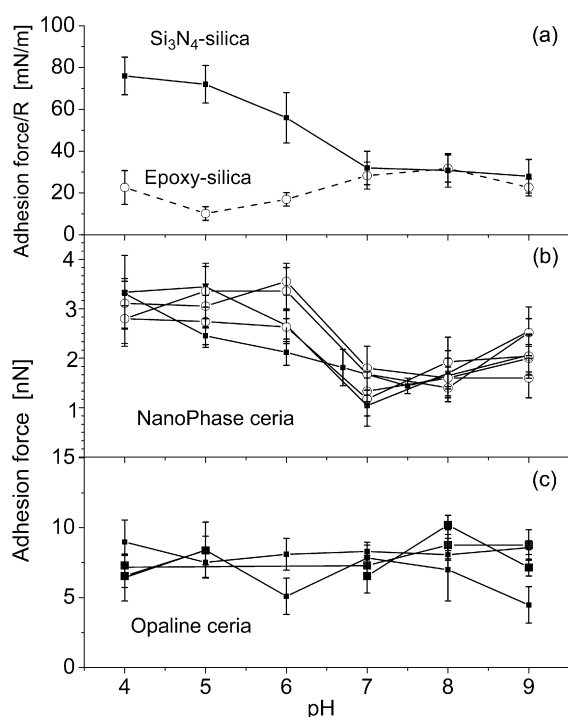


Fig. 2. Forces of adhesion between silica surface and original silicon nitride tips and tips coated with just epoxy (a), and ceria-terminated tips (b, c). Each point is an average of ~ 200 force measurements. The “error bar” of each point is one standard deviation of variability among the force measurements. Forces measured for the Si_3N_4 and epoxy tips are normalized to the effective tip radius.

To be sure that we are dealing with ceria terminal particles, the acidity dependence of adhesion between the prepared tips and flat silica surface was recorded by using the force volume modes of scanning. This is shown in Fig. 2. It should be stressed that force volume is the most convenient mode of collecting statistical amount of force data. Each point presented in Fig. 2 is an average of at least 200 force measurements over a surface area of $4 \mu\text{m}^2$. The “error” bars shown in the graphs are indeed variability bars, which represent one standard deviation levels. The actual errors of measurement are negligible comparing to these variability bars. Quite a large variability is probably intrinsic for interaction involving nanoparticles, in particular, due to inhomogeneity of charge distribution on the sample surface at nanoscale.

To check if we have ceria as the terminal particle, we measured the adhesion for the original silicon nitride tips and tips coated with just epoxy for various pH, shown in Fig. 2a. Adhesion between the ceria tips and silica were measured in solutions of the same range of acidities, Fig. 2b. To exclude an unlikely event of “semi-modified” tip, e.g., ceria partially coated with epoxy and so on, we did measurements using several AFM tips with the attached nanoparticles. Furthermore, as we mentioned above, ceria particles are non-spherical. Each new tip may have different particle orientation with respect to the surface. Indeed we see quite a large difference (more than one standard deviation) between forces measured for different tips, Fig. 2b. However, every ceria tip has behavior different from either silicon nitride or epoxy. Relative dependence of the adhesion on pH is rather different for ceria and epoxy, silicon

nitride tips, shown in Figs. 2a and 2b. One can easily see it, for example, looking at the minimum of adhesion. Ceria particles have quite pronounced minimum near neutral pH ~ 7 , while epoxy has it near pH 5 and silicon nitride has no minimum at all. This proves that we are dealing with a single ceria particle at the tip apex. As we mentioned above, it would not be correct to compare absolute values of the forces between different graphs, i.e., Figs. 2a and 2b. Comparing relative force dependence for different pH, it is important to remember that we are dealing with force variability bars, not error-bars. Having two data points with overlapped variability bars does not mean the data are undistinguished.

To compare the behavior of nano-size and micron size particles, we also measured interaction with Opaline ceria particles, Fig. 2c. Compared to the nano-size ceria, Fig. 2b, one can see a noticeable difference, e.g., very weak dependence of the adhesion on pH. To investigate further this difference, we plot long-range forces measured with these particles. Such forces are found in the approach part of the AFM force curves. Fig. 3 shows a typical set of curves for 50 nm (Nanophase) and 500–1000 nm (Opaline) particles. Each force curve is an average over ~ 10 – 20 curves collected over $\sim 4 \mu\text{m}^2$ surface area. Force curves are shifted vertically artificially for better visualization. Deflection of the cantilever down (negative deflection, forces) stands for attraction. One can indeed see the difference in force dependences for these two types of ceria particles. Attraction (deviation of the force curve down from the flat zero level) is stronger for Opaline particles. It starts near roughly 10 nm of tip-sample distance for Opaline whereas near ~ 5 nm for Nanophase ceria. This is a typical difference for bigger particles usually observed due to larger van der Waals attraction. The minimum of adhesion for Nanophase found at pH 7 is well correlated with the maximum of repulsion at that pH, Fig. 3a. Weak dependence of Opaline long-range forces on pH, Fig. 3b, is in agreement with very weak dependence of Opaline adhesion on acidity shown in Fig. 2c.

Let us discuss the long-range forces shown in Fig. 3. For most of the materials, the change from attraction to repulsion going from lower to higher pH is a typical feature. It is seen in Fig. 3 for both types of ceria particles except for the cases of pH 8 and 9 for Nanophase ceria. If we assumed that the repulsion is due to the electrical double layer forces, such abnormal behavior would mean the increase of surface potential (decrease in magnitude) of ceria with the increase of pH above 7, which is somewhat abnormal phenomenon. Typically van der Waals interaction is considerably less than the electrostatic interaction. Therefore, one can estimate the isoelectric point of ceria from the force curves as the acidity in which the long-range attraction changes to repulsion (because silica is negatively charged above pH 3, see, e.g., [3]). Looking at Fig. 3, one can see that the isoelectric point of Nanophase ceria is \sim pH 6, and \sim pH 8–9 for Opaline ceria. The isoelectric point for Nanophase ceria is in good agreement with what was measured [12] for nanoparticles of ceria in similar ionic environment: pH 6.0 in 10 mM of NaNO_3 . Comparing Opaline ceria, we can refer to US patent #6,238,450 which describes a method of preparation of ceria similar in size to Opaline. In the patent the inventors claim

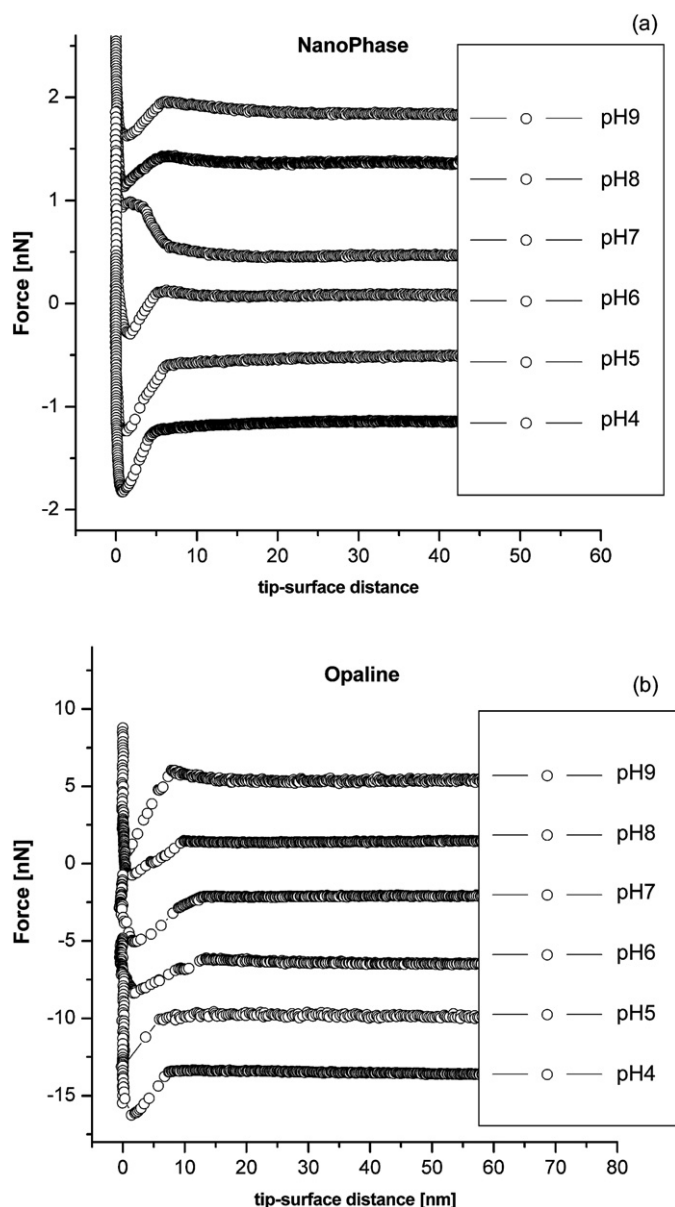
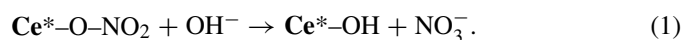


Fig. 3. A representative set of long-range forces of between silica surface and 50 nm (NanoPhase) and 500–1000 nm (Opaline) particles. Each force curve is an average over ~ 10 – 20 curves collected over $\sim 4 \mu\text{m}^2$ surface area. Force curves are shifted vertically artificially for better visualization.

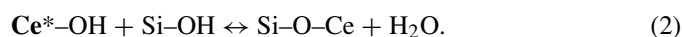
that the surface of ceria particles “maintain a positive ionic surface charge when titrated from a pH of 4 or less to a pH of at least 10.” This implies that isoelectric point of such that ceria is above pH 10. Thus, the estimated isoelectric point of Opaline ceria looks reasonable.

Let us now briefly discuss the observed difference in behavior of adhesion. Due to the lack of quantitative theories describing the interaction with nanoparticles, we restrict our discussion to qualitative speculations. Adhesion comes from both physical and chemical interactions. It is plausible to assume that we are dealing with van der Waals, electrical double layer, and may be some chemical interaction. With a high precision, van der Waals forces are independent of acidity. So the major factors for the adhesion change should come from the electrostatic

and/or chemical interactions. As we mentioned above, comparing Figs. 2 and 3, one can see some correlation between the long-range forces shown in Fig. 3 and the adhesion. However, just electrostatic interaction is clearly not sufficient to explain of features of the adhesion behavior for both types of ceria. For example, weak dependence of Nanophase ceria adhesion for pH 4–6, Fig. 2b is not correlated with the change of long-range forces in Fig. 3a. Fairly negligible change of repulsion in Fig. 3a for pH 8 and 9 is also not correlated well with the noticeable increase of adhesion from pH 8 to 9, Fig. 2b. Chemical modification of ceria surface in presence of nitrate ions has been studied in Refs. [13,14]. Above pH 3 some nitrate ions are strongly (non-electrostatically) bound to ceria “reactive” sites (Ce^*) and gradually released via the exchange reaction,



This could bring some increase of adhesion between such sites and silica surface, which is sufficiently hydrolyzed:



It should be noted that the energy of formation of ceria is less than that of silica. Therefore, it could be a problem of contamination of ceria tips with silica. This was one of the reasons why we check the stability of the results by starting and finishing measurements at Neutral pH. Most of the times the results were stable (only such data are shown in Figs. 2 and 3).

As was noted [14], the number of reactive sites Ce^*-OH on ceria surface increases with the increase of pH. This could explain that the adhesion stays almost the same despite the decrease of attractive electrostatic force, the case of Opaline with pH 4–9 and NanoPhase ceria with pH 4–6. However, there is a competing process. The increase of pH (to the isoelectric point) leads to hydroxylation ($\text{Ce}^*-\text{OH} + \text{OH}^- \rightarrow \text{Ce}-(\text{OH})_2^-$) and deactivation of the reactive sites [14]. So, it would not explain the increase of adhesion for NanoPhase ceria at pH 9.

It should be noted that non-trivial surface chemistry of ceria with respect to different levels of oxidation ($\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$ redox process) has been well known. The valence and defect structure of cerium oxide is dynamic and may change with temperature, pH, presence of other ions, and oxygen concentration [15–17]. Moreover, it has been observed that Raman spectra of cerium nanoparticle are quite different from ceria microparticles [15]. Thus, the observed difference in the force behavior should not be too surprising. However, further speculation about the nature of such difference would be beyond the scope of this work.

4. Conclusion

A new method of making single nanoparticle terminated AFM tips is described. We demonstrated how to use epoxy glue to attach nanoparticles to the AFM tips. Although there is no direct control over each attached nanoparticle, almost every other tip prepared has a single particle terminating the tip. We demonstrated this method with ceria particles of ~ 50 nm. To test such tips and verify that we are dealing with ceria particles, we measured forces between the prepared tips and flat silica surface.

Attaching larger particles of ceria (Opaline), we observed behavior of adhesion and long-range forces that was qualitatively different from nano-size ceria (Nanophase). The nature of such difference was discussed. In principle, the difference of Opaline ceria could be explained not necessarily by its size, but rather the process in which these particles were made. This may result in different amount of defects, impurities, etc.

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