Supporting Information

Diamond Colloidal Probe Force Spectroscopy

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Table of contents

1. AFM and FIB characterization of the diamond colloidal probe ................................................. 2
2. Young’s modulus determination by Hertz and DMT fitting ......................................................... 4
3. Hydrophobic interaction between H-Colloid and HPCD ............................................................ 5
4. SEM characterisation of the used probes ...................................................................................... 6
5. DLVO fitting of the force curves obtained in solution ................................................................. 6
1. **AFM and FIB characterization of the diamond colloidal probe**

Further characterization of the diamond probes is shown in Figure S1. In addition to scanning electron microscopy (SEM), the surface morphology after oxidation was determined by atomic force microscopy (AFM) reverse imaging on a standard silicon AFM tip (Nanoworld, PPP-NCHR, tip radius: < 10 nm) (reverse imaging: a high aspect ratio object is imaged which provides the topography of the scanning probe). The roughness was determined in a region of the AFM image, which does not show artifacts resulting from the strong curvature of the sphere as shown in Figure 1d). A root-mean square (RMS) roughness of 18 nm was obtained, which is close to the RMS roughness of 16 nm obtained for a nanocrystalline diamond (NCD) film grown on a flat substrate using the same growth conditions (see Figure S2). Variations of up to 2 nm are commonly observed for NCD layers with such a thickness. The measured region is close to the hole in the diamond film which is resulting from the placement of the templates onto a substrate. As this region is not facing in the growth direction, this indicates that the diamond growth is homogeneous over the silica sphere. An oxygenated diamond sphere is shown in Figure S1, which shows the expected RMS roughness. This shows that the oxygen plasma treatment did not significantly alter the surface of the diamond film as expected. For hydrogen plasma treatments etch rates are lower and hence there will also be no change in roughness.1

The thickness of the diamond film of approx. 200 nm was confirmed using a focused ion beam (FIB) cross-section as shown in Figure S3. Here, due to the strong ion bombardment and redepositions, a surface damage is observed, which results in smoothening of the diamond film.
Figure S1: Surface morphology characterization of an oxygen-terminated diamond sphere attached to an AFM cantilever by reverse imaging. a) 3d image, b) AFM topography as measured and c) corrected for the strong curvature. The highlighted region in c) was used to determine the RMS roughness (18 nm) of the sphere. d) SEM image of the corresponding diamond sphere on the cantilever.

Figure S2: AFM topography of an NCD layer grown under the same conditions as the diamond spheres (RMS roughness: 16 nm).
Figure S3: SEM image showing a FIB cross-section of an as-grown diamond sphere showing the approx. 200 nm thick diamond film grown on the silica particle. Due to the strong ion bombardment and redepositions, the surface morphology of the diamond film is significantly altered. Milling rates for diamond are rather low and hence these effects are observed especially for small structures.

2. Young’s modulus determination by Hertz and DMT fitting

For determining the elasticity of a substrate with diamond colloidal probes, a polydimethylsiloxane (PDMS) standard sample was used that has a Young’s modulus of $2.5 \pm 0.7$ MPa as defined by the manufacturer. As measurements were conducted in air, the hydrogenated diamond colloid was used to suppress strong capillary forces (Note: measurements with the uncoated silica colloid are not possible using the same conditions).

The used probe with a spring constant of 0.14 N/m is shown in Figure S5 a). Fitting was done with the JPK Data Processing software employing eq. (1) and a radius of 2.7 µm for the sphere (2.5 µm silica particle + 200 nm diamond film). It should be noted that due to the large size of the colloidal particle, varying the radius by 200 nm will also lead to a result that is in the range of the manufacturer specification. The Derjaguin-Muller-Toporov (DMT) model (Eq. (1)) takes the adhesion into account, which facilitates the fitting procedure for the shown measurements as in this case the whole force curve may be fitted. In order to keep noise out of the fit, however, only the contact region including the cantilever snap-in (approx. 8% of the curve) were used.\(^2\)

\[
F - F_{adh} = \frac{4}{3} \frac{E}{1-\nu^2} \sqrt{R \delta^2} \quad (1)
\]

$F$ is the applied force, $F(adh)$ is the adhesion, $\nu$ the Poisson’s ratio, $E$ the Young’s modulus, $R$ the radius of the sphere and $\delta$ the indentation depth.

The results and additional information for the fit is shown in Table S1
Table S1: Results from elasticity fits using the DMT model.

| DMT fit         | Results              |
|-----------------|----------------------|
| Young’s modulus | 2.59 ± 0.06 MPa      |
| Poisson ratio   | 0.5                  |
| Radius          | 2.7 µm               |
| Indentation     | 29.4 nm              |
| Effective radius| 282 nm               |
| Residual RMS    | 1.37 ± 0.03 nN       |
| Fitting region  | 0.1 – 8%             |

3. Hydrophobic interaction between H-Colloid and HPCD

The measurements of the H-colloid on HPCD in air is different to the three other combinations, as here, meniscus forces should be rather low due to the hydrophobicity of both surfaces. Nevertheless, a higher adhesion force is obtained (5.72 nN) in comparison to the O-Colloid on HPCD (2.74 nN). It is known that on hydrophobic surfaces, higher amounts of water can be present than on hydrophilic surfaces. This is explained by the formation of nanodroplets preferably on defect sites, which in total result in a higher volume than a homogeneous water layer. In our study polished PCD has been used, which does not only contain defects but also grain boundaries. Apart from that, the diamond sphere is coated with NCD that has even more grain boundaries as well as sp²-carbon impurities. Both, the substrate and the sphere, are far from perfect and should easily allow nanodroplet formation. Hence, we assume that the increased adhesion force is caused by such nanodroplets and induced by imperfection of the substrate and the colloid surface. Figure S4 shows the adhesion force in dependence of the measurement cycle. Here, a trend towards higher adhesion is observed, which may be assigned to restructuring of the nanodroplets after contact (Note: all measurements were taken on the same spot). In future studies, single crystalline diamond substrates may be used to get a better understanding of this interaction as they provide a more homogeneous surface.

![Figure S4: Measured adhesion force in dependence of the measurement number.](image-url)
4. SEM characterisation of the used probes

![Figure S5: SEM images of the probes used for the force spectroscopic measurements: a) Hydrogen terminated and b) oxygen terminated.](image)

5. DLVO fitting of the force curves obtained in solution

Electrostatic double layer and van der Waals forces should govern the measurements in solution. These forces are described by the DLVO theory (Derjaguin, Landau, Verwey, Overbeek), which is commonly used to explain the stability of colloidal suspensions. With Igor Pro and a fitting procedure by McKee based on an algorithm by Chan et al., we fitted our approach curves to obtain the surface potential and the surface charge density. The fits and the corresponding measured approach curve for the different concentrations are shown in Figure S6. Table S2 summarizes the fit results.

The fitting procedure assumes that for both surfaces, the potential is identical. As both surfaces are oxygen terminated, this approximation is plausible. For the different KCl concentrations the varying Debye length is calculated according to following equation (2):

\[ \kappa^{-1} = \frac{\varepsilon_r \varepsilon_0 k_B T}{2 c N_A z^2 e^2} \]  

(2)

\( c \) is the bulk concentration of the ion, \( N_A \) Avogadro’s constant, \( z \) is the valence of the ion, \( e \) is the elementary charge, \( \varepsilon_0 \) is the permittivity in vacuum, \( \varepsilon_r \) is the relative permittivity of the solvent, \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature.

Surface charge density and surface potential were adjusted to fit the measured data. It is observed that the surface potential is decreasing with increasing KCl concentration. For the surface charge density, the opposite trend is apparent. This may be explained by the ion sensitivity of diamond surfaces as used in ion-sensitive field effect transistors (ISFETS), and is consistent with previous results in our group on detonation nanodiamond, where the KCl concentration strongly influences the surface assembly on silicon substrates.
Figure S6: Approach curves of an oxygen-terminated colloid to an oxygen terminated polycrystalline diamond in different KCl concentrations and corresponding DLVO fits (constant potential and constant charge).

Table S2: Results from DLVO fits of the approach curves obtained in solution for different KCl concentrations

| KCl concentration (M) | Surface potential (mV) | Surface charge density (mC/m²) | Debye length (nm) |
|-----------------------|------------------------|-------------------------------|------------------|
| 10^{-5}               | -145                   | -2.46                         | 96.29            |
| 10^{-4}               | -100                   | -3.20                         | 30.45            |
| 10^{-3}               | -55                    | -4.01                         | 9.63             |
| 10^{-2}               | -48                    | -12.32                        | 3.05             |
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