# FEDSM-ICNMM2010-30851

## SOLID/WATER INTERFACE OF FUNCTIONALIZED SILICA SURFACES STUDIED BY DYNAMIC FORCE MEASUREMENTS

Yan Wu

Department of Chemistry and Engineering Physics, University of Wisconsin-Platteville Platteville, Wisconsin, USA M. Basar Karacor Department of Mechanical Engineering, The Ohio State University Columbus, Ohio, USA

Shaurya Prakash

Department of Mechanical Engineering, The Ohio State University Columbus, Ohio, USA

#### Mark A. Shannon

Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign Urbana, Illinois, USA

## ABSTRACT

In this study, silica surfaces were chemically modified yielding dissimilar surfaces with -Br, -NH<sub>2</sub>, and -CH<sub>3</sub> functional group terminations. The dynamic response of an oscillating micro-cantilever with a gold-coated tip interacting with the functionalized silica surfaces was studied in electrolyte solutions with pH ranging from 4 to 9. The amplitude and phase of the cantilever oscillation were monitored and used to calculate the effective stiffness of the AFM cantilever, which relates to the double layer interactions and the hydrodynamic damping at the solid/water interface. The data for the dynamic response of the AFM over silica surfaces as a function of chemical functionalization and electrolyte pH show that the effective stiffness has distinctive dependence on the surface charge of functionalized silica surfaces. The hydrodynamic damping also correlates strongly with the relative hydrophobicity of the surface, suggesting a dependence on interfacial characteristics including effective slip lengths. It is hoped that the experimental data reported here will provide insights for development of more theoretical models explaining the underlying mechanisms.

**Keywords**: atomic force microscopy, dynamic response, double layer interactions, hydrodynamic damping, surface functionalizaton

## INTRODUCTION

In microfluidic and nanofluidic devices and systems, surface properties of the channel of the walls are critical for

determining electrokinetic transport due to the high surfacearea-to-volume (SA/V) ratios. There is an increasing interest in controlling and systematically engineering the surface properties of the channels by chemically changing only the confined surfaces through chemical functionalization [1-5]. In this study, we investigated the small amplitude dynamic responses of a micro-cantilever to silica surfaces with dissimilar functional moieties in aqueous electrolyte solutions. The oscillation amplitude of the cantilever in our experiments is kept small (around 2nm or less) compared to the Debye length (9.6 nm for 1 mM NaCl). Silica surfaces were chemically modified yielding surfaces with -Br, -NH<sub>2</sub>, and -CH<sub>3</sub> functional group terminations, respectively, according to a 'click' functionalization scheme as described previously [6]. Native fused silica surfaces with silanol (-OH) terminated groups were used as a reference surface for comparison to functionalized surfaces. The effect of distance-dependent damping and double layer interaction can be decoupled based on a previously developed model [7]. The model utilizes the amplitude and the phase of the cantilever oscillation to calculate the effective interaction stiffness and damping coefficient, which relate to the electric double layer interactions and also to distance-dependent hydrodynamics at the solid/water interface. The purpose of this study is to evaluate the dependence of the dynamic response of a micro-cantilever on the chemical functionalization of sample surfaces at the material/water interfaces.

## **EXPERIMENTAL METHODS**

11-Bromoundecyltrichorosilane (BUTS; Gelest, Inc.. Morrisville, PA) was solution deposited in a 1% v/v anhydrous cyclohexane (Sigma-Aldrich, MO) by soaking the samples for two hours. After the soaking, the samples were rinsed with excess cyclohexane followed by methanol. The samples were dried in an N2 stream and were then chemically modified according to a previously developed 'click' functionalization methodology[6], yielding surfaces with -Br, -NH<sub>2</sub>, and -CH<sub>3</sub> functional group terminations, respectively. Surface characterization is done by contact angle (CA) measurements (Rame-Hart Model 250-00) measured as the advancing angle of a sessile drop of Millipore (18 M $\Omega$ ) water, and X-ray photoelectron spectroscopy (XPS) (PHI Model 5600) to verify the chemical composition of the adherent surface layers.

Aqueous sodium chloride solutions (1 mM) were freshly prepared from reagent grade chemicals (Sigma-Aldrich). The electrolyte concentration was chosen so that the characteristic length of the double layer interaction (Debye length) is around 10 nm and will remain relatively the same when the electrolyte solution is titrated with NaOH and HCl from pH 3 to 9. The pH of the resulting NaCl solutions was confirmed via a digital pH meter (Accumet, Fisher Scientific). The solution pH levels were recorded before and after each measurement and the mean values were reported in the results.

The AFM force measurements were carried out on an Asylum Research (Santa Barbara, CA) MFP3D atomic force microscope with a closed fluid cell to accommodate the Gold coated silicon nitride probes (Biolever, samples. Olympus) with a rectangular cantilever (nominal spring constant of 0.03 N/m) were used. The probe has a pyramid shaped tip with a typical tip height of 7  $\mu$ m and tip radius of 30 nm. The thermal spectrum of the cantilever in liquids was measured as a guide to pick the drive frequency at the resonance frequency (around 11 kHz) of the cantilever for acoustic excitation. The amplitude of cantilever oscillation was tuned to be ~ 5 nm when the tip is about  $6 \,\mu\text{m}$  away from the sample surface and the Q factor of the resonance curve was recorded. For each of the dynamic force curves, the amplitude signal and the phase signal were measured as a function of the piezo-actuator displacement.

#### **RESULTS AND DISCUSSION**

Figure 1(a) shows a typical set of dynamic force curves using native silica surface in 1mM sodium chloride solution as an example. As shown in Fig.1 (a) the amplitude of the cantilever oscillation is attenuated to around 2 nm due to the hydrodynamic damping when the tip sample distance is reduced from 6  $\mu$ m to 15 nm. Further attenuation of the amplitudes within 15 nm from the sample surface is due to the combined effects of hydrodynamic damping and electric double layer interaction force. The double layer interaction force can be tuned in solutions different pH values. For example, the silica surface is negatively charged at pH4 whereas the gold surface of the tip has positive charge at pH4. When the double layer force is attractive due to opposite charge polarities on silica and gold surfaces in pH4 solution, the phase signal is greater than 90 degree and increases as the tip and sample get closer as shown in Fig.1(b). For pH greater than 4, both the silica surface and the gold surface are negatively charged and the double layer interaction force is repulsive. Both the pH5.5 and the pH8.8 phase curves show that the phase decreases from 90 degree at first as the repulsive force increases with decreasing distance. The pH8.8 curve shows greater change in phase due to a stronger repulsive interaction force. Around 2 to 3 nm from the surface, the pH5.5 and pH8.8 phase curves shown a turn over behavior. The proposed explanation for this turn-over behavior is the highly non-linear interaction force and the effect of higher harmonics of the cantilever vibration dynamics as we discussed in our previous work [7].



**Fig.1** The plots of amplitude (a) and phase (b) vs. tip- sample distance as the tip approaches a native silica surface in 1mM sodium chloride solutions with different pH.

Dynamic force measurements provide a method to decouple the hydrodynamic damping effect with the doublelayer interaction force. As detailed in our previously developed model [7], the effective stiffness (or the force gradient) of the tip-sample interaction,  $k_i$ , and hydrodynamic damping of the AFM cantilever,  $b_s$ , can be expressed in terms of the phase and amplitude signals measured in dynamic force. Figure 2 shows the comparison between the effective interaction stiffness at 3 nm from the functionalized functions surfaces. We chose the 3 nm point because this is the distance when dynamic signals are greatest before turn-over due to higher harmonic vibration modes. Figure 2 shows a common trend of increasing effective stiffness with increasing pH for the functional groups studied with positive  $k_i$  in repulsive interaction and negative  $k_i$  in attractive interaction. Magnitude wise, the repulsive interaction at pH6 and pH9 of -OH and -Br group are stronger than those of -NH2 and -CH3 group. The dependence of the effective interaction stiffness on solution pH and surface functionality indicate that surface charge property of the sample has a direct impact on the dynamic response of the cantilever.



**Fig.2** Comparison of the effective interaction stiffness at 3nm from the surface for native and functionalized silica surfaces.

Figure 3 shows damping coefficient at 3 nm from the sample surfaces for three different pH groups. Since the native silica surfaces do not have added molecules, it is hard to compare the damping coefficient of the native silica surfaces at the same distance with rest the surfaces yet we include the data just for completeness. Figure 3 shows that the hydrodynamic damping of the chemically modified silica surface is affected by two surface properties. First, the surface hydrophobicity, which is indicated by the contact angle, has a strong influence on hydrodynamic damping. In terms of contact angle, the aminated  $(-NH_2)$  surface has the lowest value of 69.5°, followed by -Br surface (83.6°). The  $-CH_3$  terminated surface has the highest the contact angle (106.1°). We observe from Fig. 3 that the higher the surface hydrophobicity, the smaller the damping

coefficient is with the exception of the -NH<sub>3</sub> group terminated surfaces at pH 4 when both the tip and sample have positive charges. The apparent dependence of the hydrodynamic damping on contact angle is attributed to the boundary-slip phenomena. The contact angle dependence of slip length has been reported and verified by many other independent studies with the underlying mechanisms being the subject of continued debate amongst the scientific community. Second, the hydrodynamic damping is also affected by the surface charge density. For each surface studied, with increasing pH (from 4 to 9) the effective surface charge also becomes increasingly negative and it is observed from the data presented in Fig. 3 that the hydrodynamic damping also increases as reflected by the increase in the damping coefficient. It is hypothesized that the boundary slip condition at the solid/water interface is strongly affected by the water structure at the interface. It is well-known that due to the finite size of ions and solvent molecules electrolyte solutions demonstrate considerable structure at charged interfaces [8]. As a consequence, it is not surprising that the structure of the solutions will have some dependence on the surface charge in confined systems.



**Fig.3** Comparison of the damping coefficient at 3nm from the surface for native and functionalized silica surfaces.

In conclusion, the data for the dynamic response of the AFM over silica surfaces as a function of chemical functionalization and electrolyte pH show that the effective stiffness has distinctive dependence on the surface charge of functionalized silica surfaces. The hydrodynamic damping also correlates strongly with the relative hydrophobicity of the surface, suggesting a dependence on interfacial characteristics including effective slip lengths. It is hoped that the experimental data reported here will provide insights for development of more theoretical models explaining the underlying mechanisms.

### ACKNOWLEDGMENTS

This work is supported by the WaterCAMPWS, a Science and Technology Center of Advanced Materials for the Purification of Water with Systems under the National Science Foundation agreement number CTS-0120978. The authors thank the staff and facilities at the Laboratory for Surface Modification at Rutgers University and also express a note of thanks to Prof. Kathryn Uhrich for use of contact angle measurement equipment.

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