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A novel colloid probe preparation method based on chemical etching technique*

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Abstract: Several fundamental problems in hydrophobic force measurements using atomic force microscope (AFM) are discussed in this paper. A novel method for colloid probe preparation based on chemical etching technology is proposed, which is specially fit for the unique demands of hydrophobic force measurements by AFM. The features of three different approaches for determining spring constants of rectangular cantilevers, including geometric dimension, Cleveland and Sader methods are compared. The influences of the sizes of the colloids on the measurements of the hydrophobic force curves are investigated. Our experimental results showed that by selecting colloid probe with proper spring constant and tip size, the hydrophobic force and the complete hydrophobic interaction force curve can be measured by using AFM.

Key words: Hydrophobic force, Atomic force microscope (AFM), Colloid probe, Chemical etching
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INTRODUCTION

Hydrophobic force is the unusually strong and long-range attractive force exhibited between hydrophobic surfaces in water (Israelachvili and Pashley, 1982), which is among the most important nonspecific interactions in biological systems and plays a central role in many surface phenomena. Although many studies were carried out over the past 20 years, the nature of the hydrophobic force is still not clear, no single theory can account for all observed experimental behavior, even the experimental data on similar systems is often contradictory (Ishida *et al.*, 2002; Meyer *et al.*, 2005). Accurate measurement of interaction forces between different surfaces is important for a variety of natural phenomena and industrial processes. The emergence of the atomic force microscope (AFM) enables researchers to directly measure the interaction force between a sharp tip and a flat surface both in air and in water. But the measured force cannot be compared with theory, because the geometries of the tip are not regular or even too small to be known. After Ducker *et al.*(1991) used colloid probe technology to successfully measure the interaction forces between a colloid sphere and a flat surface in aqueous solutions, the measured forces could be theoretically analyzed and compared with theory for the first time. The measurement of hydrophobic force by AFM is somewhat difficult, since the cantilever might stick to the flat surface during the measurement due to the large adhesion forces if a small spring constant cantilever was used. Rabinovich and Yoon (1994) solved this problem by using a stiffer rectangular silicon cantilever with a spring constant of 30~120 N/m.

However, there are some sticky troubles in preparation of the colloid probes (Ducker *et al.*, 1991; Rabinovich and Yoon, 1994). In the traditional colloid probe preparation processes, a silica glass bead is used as the colloid particle and mounted near the apex of the cantilever using an extremely small amount of epoxy resin by means of a micromanipulator. Due to

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the small size of the glass beads, normally in diameters of 7~30 μm, the adhesion process should be carefully controlled to make the glass bead just adhered to the right position on the cantilever without large tolerance to avoid possible errors in the following surface force measurement. It is a really hard job, and the success rate of the preparation is mainly dependent on the experiences of the operator. Another sticky business is the chemical modification of the colloid particles. To measure the hydrophobic force, both the originally hydrophilic glass bead and the flat sample surfaces, normally the silicon wafer chip used as the substrate, should be modified to be hydrophobic by molecular self-assembly technology, typically the OTS SAM (octadecyltrichlorosilane self-assembled monolayer). But, for a single glass bead with a diameter about 30 μm, the pre-cleaning treatments, chemical modification as well as the final cleaning procedures after the modification reaction are also arduous work. The hydrophobicity and quality of the hydrophobic SAM on the modified small bead surface cannot be guaranteed, and the quality flaws of the SAMs could finally spoil the accurate measurement of the surface forces.

Here, we propose a novel method for colloid probe preparation based on the chemical etching technology, which potentially overcomes the shortcomings in the traditional processes and contributes greatly to the improvement of the surface force measurements by AFM. By using the chemical etched colloid probe, we measured the hydrophobic interactions by AFM. Our results showed that the hydrophobic force and the complete interaction force curve could be measured by using AFM. The calibration of the spring constants of the cantilevers is also a very important factor for surface force measurement. Three different calibration approaches, including the geometric dimension, Cleveland and Sader methods, were experimentally compared, the features of the three methods are discussed in this paper.

EXPERIMENTAL DETAILS

Preparation of the flat hydrophobic sample surfaces

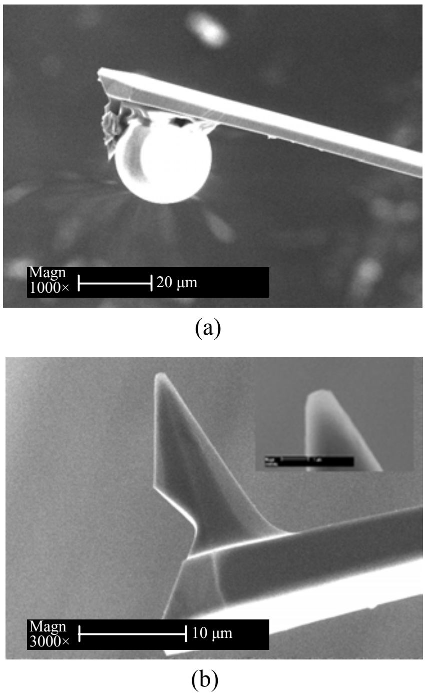
The hydrophobic sample surfaces were prepared by using OTS SAM technology with the experimental details being similar to those of Xu and Higashitani (2000). Silicon (100) plates (1 cm×1 cm) were used as the solid substrates, which were cleaned by sonication in an ultrasonic cleaning tank in acetone, isopropanol (IPA) and distilled water for 5 min, respectively. After each sonication, the substrate plates were rinsed with distilled water, then finally sonicated in superpure de-ionized water (18.23 MΩ·cm) for another 5 min and dried in a stream of nitrogen gas. The well-cleaned silicon plates were immersed into a hot mixture solution composed of concentrated sulfuric acid and hydrogen peroxide (20 ml:10 ml) at 90 °C for 30 min, so that the silicon surface was oxidized to silicon dioxide. After the reaction, the silica plates were rinsed again with super-pure de-ionized water and dried in a stream of nitrogen gas. The well-cleaned and oxidized silica plates were immersed into a freshly prepared 1×10^{-3} mol/L OTS-toluene solution at (18.0±0.1) °C for 30 min, and then withdrawn from the solution as quickly as possible. The modified silica plates were rinsed with toluene, acetone, chloroform and IPA in turn to remove any excess deposit, and dried in a stream of nitrogen gas. The average surface mean roughness of the OTS SAM was (0.23±0.02) nm/(5×5) μm^2 and the contact angle was 107°~110°.

OTS (octadecyltrichlorosilane) was purchased from Acros Organics, USA, and used as received without further treatment. Toluene, chloroform, acetone, IPA, concentrated sulfuric acid and hydrogen peroxide were all of analysis reagent grade.

Colloid probe preparation

Two different preparation methods were used in this experiment. Fig.1a shows the colloid probe prepared by the traditional process. After the modification, the glass bead (diameter of 27 μm, Duke Scientific, USA) was assumed to be coated with an OTS SAM, then adhered to a rectangular cantilever (spring constant of 40.7 N/m, MikroMash Co.) on the position just after the probe tip using a small amount of epoxy resin by means of a micromanipulator (PCS-5000 Series, Burleigh Instrument Inc., USA).

Fig.1b shows the colloid probe made by the chemical etching technique, the cantilever was also from MikroMash Co. with a spring constant of 62.9 N/m. The chemical etching process under the operation of the micromanipulator is clearly shown in Fig.2. This skill is based on the technology of the wet isotropic etching of silicon, which is widely used in the MEMS (micro-electro mechanical systems) fabrication engineering for removal of work damaged surfaces, rounding of sharp anisotropically etched corners, removing of roughness, etc. (Madou, 1997). The etchant used in this experiment was a mixture of HNO_3-HF, which was designed according to the principle in (Schwartz and Robbins, 1976). After the etching, the top of the probe tip became rounded and nearly a hemisphere with diameter of about 1.15 μm (Fig.1b). The reproducibility of the etching process is good. Generally, after about 3~5 min etching, the diameters of the tops of the cantilever tips were about 1~3 μm. The etched cantilever probe was then washed in abundant de-ionized water to remove the residual etchant solution. The chemical modification and the following cleaning procedures for the chemically etched colloid probe were the same as those for flat hydrophobic sample surface.



(a)

(b)

Fig.1 Colloid probes prepared by (a) the traditional process and (b) chemical etching technique

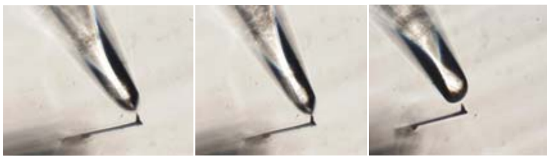


Fig.2 The etching process under the operation of the micromanipulator

Hydrophobic force measurement

A multimode AFM (NanoIIIa, Digital Instrument, USA) was employed to measure the hydrophobic forces. All the measurements were conducted in de-ionized water (18.23 MΩ·cm) by using a liquid cell. Force measurements were conducted at room temperature ((20±2) °C), and always started about 30 min after the injection of the de-ionized water into the liquid cell.

RESULTS AND DISCUSSION

Calibration of the spring constants of the cantilevers

Calibration of the spring constants of AFM cantilevers is very important in surface force measurements by AFM. For an end-loaded cantilevered beam of uniform rectangular cross section, the spring constant, k, could be calculated from the beam's geometric dimensions, theoretically (Stokey, 1989)

$$k=Et^3w/4l^3, \tag{1}$$

where, E is Young's Modulus, t thickness, w width and l length. This is exactly the case of the commercial rectangular silicon cantilevers usually used in the hydrophobic force measurements. Unfortunately, the thickness, t, of the cantilever is seldom uniform due to the limitation of the present micro-fabrication techniques (Fig.3), so that measurement error cannot be avoided. Cleveland *et al.*(1993) considered the variations in the beam's thickness and gave a relatively simple method to determine the spring constants of arbitrarily shaped thin cantilevers, specifically, by measuring the resonant frequency of the beam

$$k=2\pi^3l^3w(\rho^3/E)^{1/2}\nu_o^3, \tag{2}$$

here, ρ is the material density and ν_o the resonant frequency, measurement of which, however, can be strongly influenced by the air damping effects, the gold coating on the cantilevers, and the load position of the added mass. To eliminating these influence factors, Sader *et al.*(1995; 1999) proposed a new method,

$$k=0.1906\rho_f w^2 l Q_f \Gamma_i(\omega_f)\omega_f^2, \qquad (3)$$

where, ρ_f is the air density, Q_f the quality factor in air, $\Gamma_i(\omega_f)$ the imaginary component of the hydrodynamic function, and ω_f the fundamental radial resonant frequency in air. The technology and procedure of the Sader method is relatively much more complex. At present, Sader method is regarded as the standard calibration technique, but the other two methods are still used by some research groups due to its simplicity.

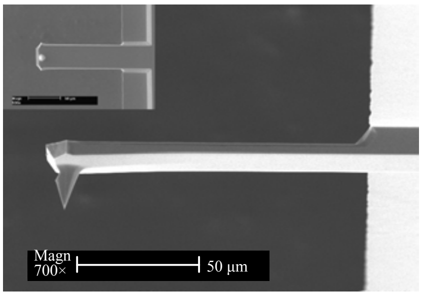


Fig.3 SEM image of a commercial rectangular silicon cantilever from MikroMash Co.

Table 1 compares the three different calibration methods. Two rectangular cantilevers from MikroMash were carefully selected as the test samples (Fig.3). Table 1 shows that compared to the Sader method, the relative errors of the dimension method are at least 8%, while the errors of the Cleveland method are about 3%~5%.

Hydrophobic forces measured by the glass bead probe and the chemical etching probe

Fig.4 shows two typical retracting force curves measured under the same experimental conditions by the glass bead probe shown in Fig.1a and the chemical etching probe in Fig.1b, respectively. It is noted that, for the same OTS SAM surface systems in both cases, the adhesion forces measured by two probes are utterly different (Table 2). What is the real, or much more approaching to the real hydrophobic interaction? We do not know the strict criteria for the hydrophobic interaction up to now, but an obvious criterion is that, at least, the interfacial energy calculated from the measured adhesion force should be consistent with the literature values measured by the early pioneers by means of the traditional or classical methods.

According to JKR theory (Johnson *et al*., 1971), to pull a solid (S) sphere of radius R off a flat solid (S) surface in a liquid (L), the required maximum force, i.e. the adhesion force, F_a, is

$$F_a/R=-3\pi\gamma_{SL}, \qquad (4)$$

where, γ_{SL} is the interfacial energy of the solid (S)-liquid (L) interface. The interfacial energies of typical hydrophobic surface-water interfaces are around 50 mJ/m^2 (Israelachvili, 1992), e.g., for paraffin wax-water interface γ_{SL} is 50 mJ/m^2, for *n*-octane (saturated)-water interface, 51 mJ/m^2, and octadecane ($C_{18}H_{18}$)-water interface, 52 mJ/m^2. Obviously, the hydrophobic interaction measured by the chemical etching probe much more approaches to the real hydrophobic force. What is wrong with the glass bead probe? One of the direct factors arrived at by intuition is the big size of the colloid particle, which could result in a big hydrodynamic resistance during the force measurements in water. But, in the similar experiments by Ishida *et al*.(2001), the hydrodynamic effects was convincingly eliminated completely by means of a static method. However, the adhesion force, as well as the calculated interfacial energy of the OTS SAM in water was still much lower than the typical values (Table 2).

Table 1 Comparison between three spring constant calibration methods

Cantilever No.	Dimensions			ν_0[a] (kHz)	Sader[b]	Cleveland[c]		Geometric dimension[d]	
	$\bar{l}$ (μm)	$\bar{w}$ (μm)	$\bar{t}$ (μm)		k (N/m)	k (N/m)	Error[e] (%)	k (N/m)	Error[e] (%)
1	130	38	4.20	304.95	56.30	54.25	3.4	60.87	8.1
2	129	39	4.15	314.39	56.80	59.62	4.9	61.68	8.6

[a]The resonant frequency was measured in tapping mode in air by AFM; [b]The spring constants by Sader method were calibrated and offered by MikroMash Co.; [c]Calculated from Eq.(2) with the bulk density of the crystal silicon being 2.9635×10^3 kg/m^3 and the bulk Young's Modulus 1.9×10^{11} N/m; [d]Calculated from Eq.(1); [e]The relative error is defined as $|k_{Sader}-k|/k_{Sader}\times 100\%$

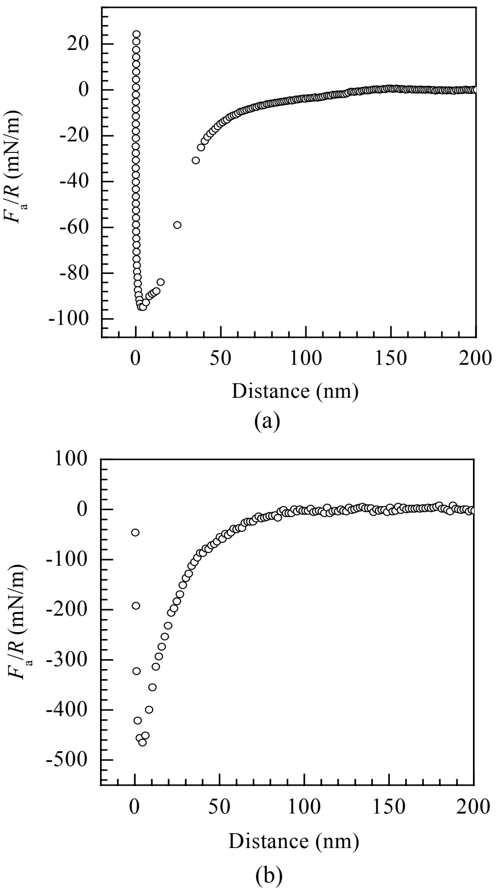


Fig.4 Retracting force curves measured by two different colloid probes (a) By the 27 μm glass bead probe, k=40.7 N/m; (b) By the chemical etching probe with a diameter of 1.15 μm, k=62.9 N/m

Table 2 The adhesion forces and interfacial energies of OTS SAM in water measured by two probes

Probes	Adhesion force F_a/R (mN/m)	Interfacial energy γ_{SL} (mJ/m^2)
Glass bead probe	−94.76	10.6
Chem. etching probe	−465.06	49.4
Ishida *et al.*(2001)	~ −270	~ 28.7

The reasons may be the load position of the colloid particle and its big size. Sader *et al.*(1995) pointed out that the restoring force of the cantilever acting on an attached sphere is a strong function of the sphere position. When the colloid particle load is applied a distance Δl away from the end tip, the spring constant k is related to the end tip spring constant k_E by

$$k=k_E(l/(l-\Delta l))^3. \qquad (5)$$

A glance at the numerous micrographs of colloid probes reveals that in many cases, these spheres are attached at least 10%~15% backward from the cantilever tip since the diameters of the used sphere is at least 7~30 μm. Therefore the real spring constant, as well as the measured forces, should be 30%~60% higher than that predicted by theory, which assumes that the load is at the end tip of the cantilever. Fortunately, our chemical etching probe technology minimizes the risks caused by the particle load position.

CONCLUSION

A novel method for colloid probe preparation based on chemical etching technology was proposed, which is specially fit for the unique demands of the hydrophobic force measurement by using AFM. Our experiments showed that by using the chemical etching probe, accurate measurement of the hydrophobic interaction ensured. Our research also indicated that for the calibration of the spring constants of AFM cantilevers, compared to the Sader method, the relative errors of the dimension method are at least 8%, while the errors of the Cleveland method are about 3%~5%.

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