

## Size-dependent interactions of silica nanoparticles with a flat silica surface



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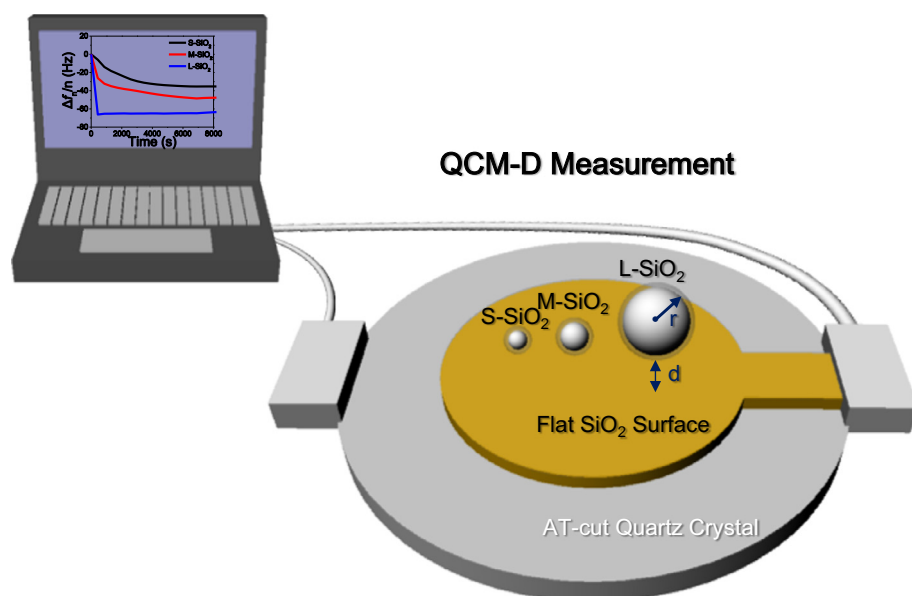
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### GRAPHICAL ABSTRACT



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### ABSTRACT

We have investigated the surface chemistry of SiO<sub>2</sub> nanoparticles (NPs) with different sizes and their corresponding interactions with a flat substrate of surface curvature  $\sim 0$ . As the size of the NPs increases, the SiO<sub>2</sub> surface is increasingly covered with H-bonded silanol groups, thereby increasing the  $\zeta$ -potential and shifting the isoelectric point higher in pH. Interactions between the SiO<sub>2</sub> NPs and the flat SiO<sub>2</sub> surface were analyzed *in situ* using quartz crystal microbalance with dissipation (QCM-D) method, and the results were interpreted based on an extended Derjaguin–Landau–Verwey–Overbeek theory. At very low ionic strength (1 mM NaCl), there was no particle adsorption onto the surface due to the highly repulsive energy barriers to this interaction. On the other hand, QCM-D results showed that the significant adsorption of SiO<sub>2</sub> NPs onto a flat SiO<sub>2</sub> surface occurred under conditions of high ionic strength (100 mM NaCl). Interestingly, the adsorption behaviors of three different-sized SiO<sub>2</sub> NPs on the surface

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QCM-D  
XDLVO

varied considerably with size. SiO<sub>2</sub> NPs with small size have high adsorption affinity with the flat SiO<sub>2</sub> surface due to an extremely low energy barrier for the interactions, whereas relatively large SiO<sub>2</sub> NPs have very weak adsorption affinity with the flat surface due to the repulsive energy barrier formed by the increase in the electrostatic and hydration repulsion energy.

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## 1. Introduction

Metal oxide nanoparticles (NPs) have been extensively investigated in a wide range of fields including the biological [1,2], pharmaceutical [3], environmental fields [4,5], and industrial applications [6–8]. It is well known that the structural [9], electrical [10], catalytic [11,12], and magnetic properties [13] of NPs are highly size-dependent. Interestingly, surface charge properties have been observed to vary with NPs size due to NPs' high surface area and curvature effect [14–16].

Surface charge plays a key role in a variety of NPs' interactions (e.g., molecule adsorption, desorption, etc.). Recently, many researchers have investigated the size dependence of NPs' surface charge properties on their interactions with ions [17], biomolecules [18], and surfactants [19]. Ridley et al. experimentally and theoretically investigated the adsorption of Sr<sup>2+</sup> onto different-sized NPs [17]. Emami et al. studied the effect of NP size upon interactions between biomolecules and NPs [18].

Among the various metal oxides, silica (SiO<sub>2</sub>) is one of the most actively studied NP materials in various fields of research ranging from fundamental research to practical application [20–22]. There are different types of silanol groups (e.g., isolated, geminal, and vicinal) that affect the surface charge. Isolated silanol groups on the surface of smaller SiO<sub>2</sub> NPs are far apart from each group by the NPs' high surface curvature, and thus resulting in little interaction between them [23]. The surface curvature decreases with increasing the radius of NPs, leading to strong hydrogen bonding (H-bonding) between silanol groups through bridging water molecules [23]. The isolated and vicinal (H-bonded) silanol groups have pK<sub>a</sub> values of 4.5 and 8.5, respectively [24,25]. The variation in the surface silanol structures among the different-sized SiO<sub>2</sub> NPs leads to differences in their surface charge properties.

Although many researchers have investigated the size dependent interactions of SiO<sub>2</sub> NPs, most studies have focused on interactions between several specific molecules and the round shaped surfaces of SiO<sub>2</sub> NPs. To increase the versatile application of spherical SiO<sub>2</sub> NPs, it is essential to understand the interactions between spherical NPs and the surfaces of flat substrates. Especially, the surface curvature of a spherical object can represent a key parameter for understanding its interaction with a substrate of very low surface curvature value,  $\sim 0$ , flat one.

Here, we have investigated the surface chemistry of three different-sized SiO<sub>2</sub> NPs and their respective interactions with a flat SiO<sub>2</sub> surface. The surface density of H-bonded silanol groups increased with increasing SiO<sub>2</sub> NP size, which induced the increases in the  $\zeta$ -potential and the shifts of the isoelectric points toward more basic pH values. To elucidate the size-dependent interaction of SiO<sub>2</sub> NPs with the flat SiO<sub>2</sub> surface, quartz crystal microbalance with dissipation (QCM-D) measurements were performed. QCM-D is a very sensitive technique used to monitor the adsorption of NPs onto surfaces by measuring the accompanying changes in adsorbed mass ( $\Delta m$ , ng/cm<sup>2</sup>) [26,27]. The interactions between the NPs and the surface were evaluated by means of QCM-D under various conditions of ionic strength (1, 10, and 100 mM NaCl). The QCM-D results demonstrated that the particle–surface interaction behaviors strongly depended on the ionic strength. Under conditions of higher ionic strength, attractive interactions were dominated, whereas under low ionic strengths

the interactions were electrostatically repulsive. Particle–surface interaction behaviors showed particle size dependency under fixed conditions of ionic strength because the surface charge of the NPs relied on the particle size. The interaction potential energies between the SiO<sub>2</sub> NPs and the flat SiO<sub>2</sub> surface, calculated based on the extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory, were used to interpret the QCM-D results.

## 2. Experimental section

### 2.1. Synthesis and characterization of SiO<sub>2</sub> NPs

The three different-sized SiO<sub>2</sub> NPs were synthesized by means of hydrolysis of tetraethyl orthosilicate (TEOS, 99.9 + %, Sigma-Aldrich) in an EtOH medium containing water and ammonia as a catalyst [28,29]. The sizes of SiO<sub>2</sub> NPs were controlled by varying the amount of the ammonia catalyst [30]. The particle size increased with increasing amount of ammonia (as described in detail in Table S1 of the Supporting Information). All samples were aged 48 h and then centrifuged for 20 min at 30,000 rpm. The supernatants were decanted and the remaining solids were repeatedly washed with EtOH. Finally, the solids were dried in a convection oven at 110 °C for 24 h, yielding bright white SiO<sub>2</sub> NPs. The shape and size distribution of SiO<sub>2</sub> NPs were measured by means of transmission electron microscopy (TEM, JEM-2100F, JEOL). From the TEM images, the average sizes ( $d_{\text{TEM}}$ ) of the three samples were calculated to be  $8.9 \pm 1.2$ ,  $37.7 \pm 4.8$ , and  $112.5 \pm 1.8$  nm; these samples are respectively denoted hereinafter as S-SiO<sub>2</sub>, M-SiO<sub>2</sub>, and L-SiO<sub>2</sub>. To prepare for surface area analysis, all samples were degassed at 200 °C for 6 h. A seven-point adsorption isotherm was measured over the relative pressure range of 0.03–0.25 using a surface area analyzer (Nova 3200e, Quantachrome) and was then analyzed by means of the Brunauer–Emmett–Teller (BET) method. The surface silanol structures of SiO<sub>2</sub> NPs were studied using a diffuse reflectance infrared Fourier transform spectroscope (DRIFT-FTIR, Nicolet 6700, Thermo Electron) equipped with a HgCdTe detector sensitive to the mid-IR range (4000–400 cm<sup>-1</sup>). The weight loss of SiO<sub>2</sub> NPs was estimated by means of thermogravimetric analysis (TGA, Q-5000 IR, TA Instruments), heating from 40 to 700 °C at a ramp rate of 10 °C/min under a N<sub>2</sub> atmosphere.

### 2.2. $\zeta$ -Potential measurement

The  $\zeta$ -potentials of SiO<sub>2</sub> NPs were measured as a function of pH using a Malvern Zetasizer instrument (NanoZS, Malvern Instrument Ltd.). NPs were suspended in 10 mM NaCl solution to maintain a constant ionic strength. The  $\zeta$ -potentials of the flat SiO<sub>2</sub> films were estimated as a function of pH using a laser zeta potential analyzer (ELS-8000, Otsuka Electronics) equipped with a plate sample cell; polystyrene latex NPs ( $d_{\text{mean}} \sim 200$  nm, Otsuka Electronics) coated with hydroxypropyl cellulose (HPC) were used as mobility-monitoring particles. The  $\zeta$ -potentials were measured at various ionic strengths (1, 10, and 100 mM NaCl).

### 2.3. Quartz crystal microbalance

The quartz crystal microbalance with dissipation (QCM-D, Q-Sense E4, Q-Sense) measurement technique was used to analyze

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