



# Water structure at the interfaces between a zwitterionic self-assembled monolayer/liquid water evaluated by sum-frequency generation spectroscopy

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## ABSTRACT

A silane coupling agent having a zwitterionic end group was covalently bound to a semi-cylindrical fused silica prism for sum-frequency generation (SFG) analyses and to a flat glass for estimating biological affinity. It was found that total intensity of the O–H stretching region (3000–3600 cm<sup>-1</sup>) of the SFG spectrum derived from water in contact with a zwitterionic SAM-modified surface was smaller than that of SFG spectra derived from water in contact with a positively or negatively charged SAM-modified surface and a bare silica prism. These results indicated that water molecules in the vicinity of the zwitterionic SAM-modified surface are not strongly oriented in comparison with those of lopsidedly charged SAMs and bare silica. Moreover, the zwitterionic SAM surface suppressed non-specific adsorption of bovine serum albumin in contrast to the significant adsorption to lopsidedly charged SAMs and the bare cover glass. On the other hand, fibroblasts gradually adhered to the SAM surfaces and extended regardless of the electrical charge of the SAM, though the number of cells that adhered to the zwitterionic SAM was the smallest. The results strongly suggested that the charge neutralization of a solid material surface is very important for anti-biofouling properties.

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## 1. Introduction

Silane coupling agents having trichloro-, trimethoxy- or triethoxy-silane at the end group form a “self-assembled monolayer” (SAM) on the surface of a glass and an oxidized silicone [1–3]. Moreover, it is well known that molecules possessing thiols or disulfides also form a SAM on metal or semiconductor surfaces through chemisorptive bonds such as Au–S and Ag–S bonds [4,5]. Modification of the material surface with various kinds of SAMs having a functional soft moiety has been extensively examined in order to increase the usefulness of solid materials as biosensors for enzymes, lectins and DNAs [6–8].

Construction of surfaces that suppress non-specific binding of biomolecules is important for designing biomedical materials.

For example, a surface composed of polymer films derived from a zwitterionic monomer such as 2-methacryloyloxyethyl phosphorylcholine (phosphobetaine, MPC) [9,10], 3-sulfo-*N,N*-dimethyl-*N*-(3-methacrylamidopropyl) propanaminium inner salt (sulfopropylbetaine, SPB) [11,12] or 1-carboxy-*N,N*-dimethyl-*N*-(2-methacryloyloxyethyl) methanaminium inner salt (caboxymethylbetaine, CMB) [13–16] and a water-insoluble comonomer such as *n*-butyl methacrylate (BMA) showed high biocompatibility (suppression of non-specific adsorption of proteins and adhesion of cells). Furthermore, it has been found that zwitterionic polymer brushes [17–21] and poly(ethylene glycol) (PEG)-modified solid surfaces [22–26] have excellent biocompatible properties because of the steric stabilization effect of flexible graft chains.

By using Raman and infrared spectroscopies, it was previously found that the hydrogen-bonded network structure of water in the vicinity of zwitterionic polymers and PEG is not greatly deranged [13–15,27–29], whereas, polyelectrolytes perturbed the network structure of vicinal water [30]. Moreover, using the sum frequency generation (SFG) technique, which can detect molecules without centro-symmetry at interfaces [31–33], we found that

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water molecules around brushes and thin films composed of a charge-neutralized polymer hardly received strong orientation in comparison with those around lopsidedly charged polymer surfaces [34–36]. Based on these findings, it has been suggested that small perturbation of the water structure at interfaces between polymer materials and liquid water is one of the important factors for expression of excellent biocompatibility.

In the present study, the silanol surface of a cover glass and a semi-cylindrical silica prism was modified with a silane coupling reagent possessing the zwitterionic end group. It was previously reported that there was little aggregation of silica nanoparticles modified with a zwitterionic SAM in an aqueous solution containing proteins such as lysozyme [37]. It was also found that a gold surface modified with a zwitterionic SAM suppressed non-specific adsorption of proteins [38]. From these findings, it was assumed that the surface modified with a zwitterionic SAM possesses the same potential as that of zwitterionic and amphoteric polymers.

As mentioned above, we have been interested in the role of interfacial water on anti-biofouling properties (biocompatibility) of solid materials, and we have proposed that materials inert to the structure of interfacial water are biocompatible [34–36]. To confirm the validity of this hypothesis, the water at the interface between a zwitterionic SAM-modified surface and liquid water was investigated by SFG analysis. It was found that the charge neutralization of solid surfaces does not generally induce a strong orientation of interfacial water and is decisive for expression of the anti-biofouling property.

## 2. Experimental part

### 2.1. Materials

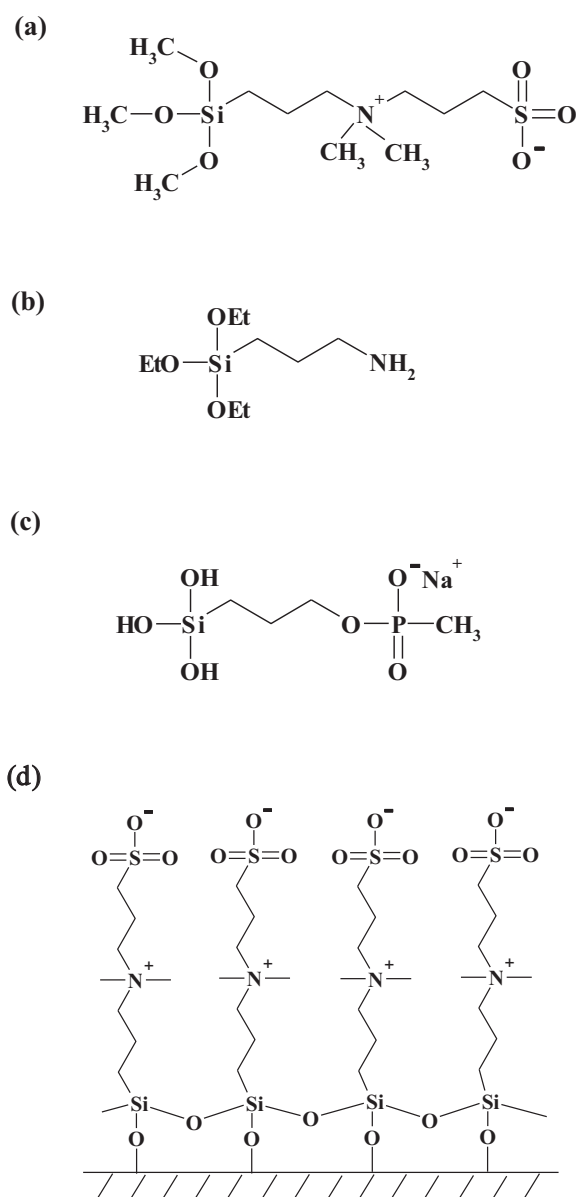
3-Aminopropyltriethoxysilane (APTES), 3-(trihydroxysilyl)propylmethylphosphonate (THPMP) and (*N,N*-dimethyl-3-aminopropyl)trimethoxysilane were obtained from ShinEtsu Chemicals (Tokyo, Japan), Sigma–Aldrich (St. Louis, MO, USA) and Fluorochem Ltd. (Derbyshire, UK), respectively. Other reagents used were commercially available. A fused silica prism with a semi-cylindrical shape (flat face, 25 × 25 mm) was obtained from Daiko, Kyoto, Japan. All aqueous solutions were prepared with ultrapure water (18 MΩ cm, Millipore System).

### 2.2. Preparation of 3-(dimethyl-(3-(trimethoxysilyl)propyl)ammonio)propane-1-sulfonate (SPB-TMS, Scheme 1(a)) [37]

3-(Dimethyl-(3-(trimethoxysilyl)propyl)ammonio)propane-1-sulfonate was prepared by incubation of (*N,N*-dimethyl-3-aminopropyl)trimethoxysilane (8.0 g, 39 mmol) and 1,3-propanesultone (4.7 g, 39 mmol) in dry acetone (40 mL) under an atmosphere of Ar at room temperature for 12 h. The white precipitate was recovered and, after washing with cold dry acetone, was dried *in vacuo* (10.3 g, 80.6% yield). <sup>1</sup>H NMR (D<sub>2</sub>O, 500 MHz) δ: 0.5–0.6 (t, 2H, SiCH<sub>2</sub>), 1.6–1.7 (m, 2H, SiCH<sub>2</sub>CH<sub>2</sub>), 1.9–2.0 (m, 2H, <sup>-</sup>O<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>), 2.4–2.5 (t, 2H, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.9 (s, 6H, N<sup>+</sup>CH<sub>3</sub>), 3.1–3.2 (m, 2H, <sup>-</sup>O<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.2–3.3 (m, 2H, <sup>-</sup>O<sub>3</sub>SCH<sub>2</sub>), 3.4 (s, 9H, OCH<sub>3</sub>).

### 2.3. Preparation of zwitterionic SAM (Scheme 1(d))

An aqueous solution of SPB-TMS (1 wt%) was incubated with a glass or a flat face of a silica prism at 80 °C for 6 h. The surface-modified substrate was rinsed two times with water and once with MeOH and then dried *in vacuo*. For comparison, the substrate was also modified with APTES or THPMP. For modification with APTES, a glass plate and a silica prism were incubated in APTES solution



**Scheme 1.** Chemical structures of (a) SPB-TMS, (b) APTES, and (c) THPMP and (d) schematic of the zwitterionic SAM-modified substrate.

(total concentration, 0.1 M) dissolved in MeOH containing 0.1 mM NaHCO<sub>3</sub> at room temperature for 18 h. The surface-modified glass and silica prism were rinsed two times with 0.1 mM NaHCO<sub>3</sub> in MeOH and once with MeOH and then dried *in vacuo*. The same procedures were adopted for modification of the bare glass and the silica prism with THPMP.

### 2.4. Measurement of contact angles

Static contact angle,  $\theta$ , of a sessile drop of water (5  $\mu$ L) on the SAM-modified glass surface was measured at fifteen points, and the data were averaged (sessile drop method). A contact angle meter (CA-D, Kyowa Interface Science, Tokyo, Japan) was used for the measurements.

### 2.5. $\zeta$ -Potential of the silicon wafer

The  $\zeta$ -potential of the glass surfaces modified with a silane coupling reagent was determined in 10 mM NaCl solution using ELSZ-2

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