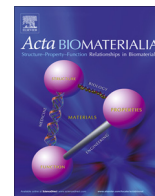




Contents lists available at ScienceDirect

Acta Biomaterialia

journal homepage: www.elsevier.com/locate/actabiomat

Full length article

Molecular level studies on interfacial hydration of zwitterionic and other antifouling polymers in situ [☆]

Chuan Leng ^a, Shuwen Sun ^a, Kexin Zhang ^a, Shaoyi Jiang ^{b,*}, Zhan Chen ^{a,*}^a Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, United States^b Department of Chemical Engineering, University of Washington, Seattle, WA 98195, United States

ARTICLE INFO

Article history:

Received 9 November 2015

Received in revised form 19 January 2016

Accepted 22 February 2016

Available online xxxxx

Keywords:

Antifouling material

Sum frequency generation (SFG) vibrational spectroscopy

Zwitterionic polymer

Hydration

Hydrogen bonding

Biofouling

ABSTRACT

Antifouling polymers have wide applications in biomedical engineering and marine industry. Recently, zwitterionic materials have been reported as promising candidates for antifouling applications, while strong hydration is believed to be the key antifouling mechanism. Zwitterionic materials can be designed with various molecular structures, which affect their hydration and antifouling performance. Although strong hydration has been proposed to occur at the material surfaces, probing the solid material/water interfaces is challenging with traditional analytical techniques. Here in this review, we will review our studies on surface hydration of zwitterionic materials and other antifouling materials by using sum frequency generation (SFG) vibrational spectroscopy, which provides molecular understanding of the water structures at various material surfaces. The materials studied include zwitterionic polymer brushes with different molecular structures, amphiphilic polymers with zwitterionic groups, uncharged hydrophilic polymer brushes, amphiphilic polypeptoids, and widely used antifouling material poly(ethylene glycol). We will compare the differences among zwitterionic materials with various molecular structures as well as the differences between antifouling materials and fouling surfaces of control samples. We will also discuss the effects of pH and biological molecules like proteins on the surface hydration of the zwitterionic materials. Using SFG spectroscopy, we have measured the hydration layers of antifouling materials and found that strong hydrogen bonds are key to the formation of strong hydration layers preventing protein fouling at the polymer interfaces.

Statement of Significance

Antifouling polymers have wide applications in biomedical engineering and marine industry. Recently, zwitterionic materials have been reported as promising candidates for antifouling applications, while strong hydration is believed to be the key antifouling mechanism. However, zwitterionic materials can be designed with various molecular structures, which affect their hydration and antifouling performance. Moreover, although strong hydration has been proposed to occur at the material surfaces, probing the solid material/water interfaces is challenging with traditional analytical techniques. Here in this manuscript, we will review our studies on surface hydration of zwitterionic materials and other antifouling materials by using sum frequency generation (SFG) vibrational spectroscopy, which provides molecular understanding of the water structures at various material surfaces. The materials studied include zwitterionic polymer brushes with different molecular structures, amphiphilic polymers with zwitterionic groups, uncharged hydrophilic polymer brushes, amphiphilic polypeptoids, and widely used antifouling material poly(ethylene glycol). We will compare the differences among zwitterionic materials with various molecular structures as well as the differences between antifouling materials and fouling surfaces of control samples. We will also discuss the effects of pH and biological molecules like proteins on the surface hydration of the zwitterionic materials. All the SFG results indicate that strongly hydrogen-bonded water at the materials' surfaces (strong surface hydration) is closely correlated to the good antifouling properties of the materials. This review will be widely interested by readers of *Acta*

[☆] Part of the Special Issue on Zwitterionic Materials, organized by Professors Shaoyi Jiang, Kazuhiko Ishihara, and Jian Ji.

* Corresponding authors.

E-mail addresses: zhanc@umich.edu (Z. Chen), sjiang@uw.edu (S. Jiang).

Biomaterialia and will impact many different research fields in chemistry, materials, engineering, and beyond.

© 2016 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Polymers are widely used as biomedical materials and marine antifouling coatings [1–4]. For both applications, antifouling property of a polymer is desired. It is generally agreed that if the adsorption amount of molecules (e.g., proteins) on a surface is less than 5 ng/cm², the surface is considered as nonfouling [5]. Extensive research has been performed to design, synthesize, characterize, and apply nonfouling (or antifouling – please notice that nonfouling and antifouling have a similar meaning in this article) polymeric materials [6–8]. Many polymers that exhibit excellent nonfouling properties have been developed and widely used, such as poly (ethylene glycol) (PEG) [9–12], hydrogels [13–15], amphiphilic materials [16–22], and zwitterionic polymers [5,23–26], etc.

For nonfouling materials, whereas different molecular mechanisms have been proposed to interpret their nonfouling performance, it is widely believed that for hydrophilic polymers and some amphiphilic polymers, strong surface hydration is a key contributor to their nonfouling property [27]. A highly hydrated polymer surface can bind water molecules so strongly that other molecules and organisms cannot replace these interfacial water molecules for fouling to occur. Although this interpretation is widely accepted, direct evidence to show the strong interaction between nonfouling polymers and water molecules has rarely been reported. This is because it is challenging to probe the polymer/water interface in situ using traditional surface sensitive analytical techniques. Most of such techniques either require high vacuum to operate (e.g., X-ray spectroscopy, electron microscopy), or do not provide molecular information (e.g., atomic force microscopy).

Recently, sum frequency generation (SFG) vibrational spectroscopy has been developed into a powerful tool to investigate molecular structures of surfaces and buried interfaces, including solid/liquid interfaces in situ in real time [28–30]. In particular, extensive research has been performed to study molecular behavior of water molecules on surfaces and at interfaces [31–33]. Advanced SFG methods such as phase sensitive detection and pump-probe ultrafast SFG as well as simulations of SFG spectra have been used to study detailed structure and fast dynamics of interfacial water molecules [34–37].

In the past years, we have extensively used SFG spectroscopy to study polymer/water interfaces and biological interfaces (e.g., peptides and proteins at solid/liquid interfaces) [38–44]. We revealed different surface structures of polymers in air and water [45–49], and investigated water structures at the polymer/water interfaces [50–52]. The polymers we investigated include antifouling materials such as zwitterionic polymers [50–53], PEGs [50,51,54,55], amphiphilic polymers [53,56,57], and fouling release polymers such as poly(dimethyl siloxane) [58–62]. Herein, we will review our SFG studies on interfacial water structures at various antifouling polymer surfaces. The polymers we examined include zwitterionic polymers (with different negatively charged functional groups, varied distances between positive and negative charges (carbon spacer length), and different side chains), poly(*N*-hydroxyalkyl acrylamide) (PolyHAAAs) (with different lengths of side chains), and polypeptoids (with systematically varied side-chain sequences). These studies provide direct evidence that strong surface hydration is critical to the antifouling property of a polymer material. In addition to the antifouling polymers, some control polymers which show fouling activity were also investigated,

which revealed their weaker surface hydration. Therefore, these studies provide a general and direct correlation between strong surface hydration and good antifouling property.

2. SFG vibrational spectroscopy

SFG vibrational spectroscopy is an intrinsically surface-sensitive and in situ vibrational spectroscopic method [63,64]. An SFG process involves two input photons and one outgoing photon. The outgoing photon has the sum frequency of the input photons (Fig. 1A). Therefore, SFG signal is related to two input optical beams by a second-order nonlinear optical process. Experimentally, visible and infrared (IR) input lasers penetrate a CaF₂ or SiO₂ substrate (window or prism), and overlap spatially and temporally at the polymer surface in air, water, or an aqueous solution (Fig. 1B). The wavelength of the visible beam is 532 nm, where the IR beam is frequency tunable. The reflected SFG signal is collected by a monochromator along with a photomultiplier tube as a function of the wavenumber of the IR beam. All SFG spectra presented in this work were collected using the ssp (*s*-polarized sum frequency output, *s*-polarized visible input, and *p*-polarized IR input) polarization combination.

SFG is surface sensitive because of its selection rule. According to the selection rule, SFG signal intensity is proportional to the square of the second order nonlinear optical susceptibility, $\chi^{(2)}$, of the material under the electric dipole approximation. As a polar third-rank tensor, $\chi^{(2)}$ changes sign under the inversion operation: $\chi^{(2)}(\mathbf{r}) = -\chi^{(2)}(-\mathbf{r})$. For materials with inversion symmetry, $\chi^{(2)}(\mathbf{r}) = \chi^{(2)}(-\mathbf{r})$. The only possible solution for the above two equations is $\chi^{(2)} = 0$. Therefore, for materials with inversion symmetry, no SFG signal can be generated. Most solid polymer systems do have inversion symmetry, because the functional groups in the bulk of these polymeric materials are generally randomly oriented; therefore they would not generate SFG signals. However, because inversion symmetry is broken at the surface/interface, for molecules or functional groups on polymer surfaces or at polymer interfaces, $\chi^{(2)}(\mathbf{r})$ does not equal to $\chi^{(2)}(-\mathbf{r})$. Here, $\chi^{(2)}$ can be non-zero, and SFG signals can be detected from surfaces and interfaces. Due to this selection rule, SFG is intrinsically surface/interface sensitive. The surface/interface sensitivity of SFG is not determined by the penetration depth of the input laser beams into the sample. Even when the input laser beams can penetrate the entire sample, only molecules or functional groups on the surfaces or at the interfaces contribute to the signals due to the SFG selection rule.

As signals detected in other vibrational spectroscopic methods, SFG vibrational peaks can be assigned to different vibrational modes of various functional groups in the molecules. Since SFG is surface/interface sensitive, SFG spectra can be used to determine what types of molecules/functional groups are present on the surface/at the interface according to the peak centers of the vibrational bands in the spectra. The SFG signals detected from water molecules at interfaces usually contain two O–H stretching peaks centered around 3200 cm⁻¹ and 3400 cm⁻¹, generated by strongly hydrogen bonded water and weakly hydrogen bonded water, respectively [65]. SFG intensity is correlated to the ordering of the dipole moments of the interfacial functional groups. Strong SFG signals of water indicate strong ordering of water molecules at the interface. From the water spectra collected from an antifouling material/water interface, we can deduce the hydration strength

Download English Version:

<https://daneshyari.com/en/article/6483277>

Download Persian Version:

<https://daneshyari.com/article/6483277>

[Daneshyari.com](https://daneshyari.com)