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Interfacial Characterizations and Analytical Applications of Chemically-modified Surfaces

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DEDICATION

This dissertation is dedicated to my family, whose love and support helped me through the difficult times, my husband Xiaobing Xie, my parents Zhengli Wang and Chunmei Nie, and my brother Jianping Wang.

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GENERAL INTRODUCTION

Introduction

During the past decade, important advances have been made towards intelligent design and fabrication of chemically modified surfaces for a variety of applications, including electrocatalysis, corrosion, lubrication, environmental monitoring, chemical sensors, and biotechnology.[1-4] The utility of the surface modification in chemical analysis is of particular interest because of the critical role of liquid- and gas-solid interfaces in a host of transduction mechanisms that rely on the specificity and extent of the interactions between an analyte and the surface. Novel strategies and methodologies have been developed to achieve the desired surface architecture on various surfaces including polymer coatings and monolayer assemblies. These developments have created enormous opportunities in many cross-disciplinary fields such as material science, analytical chemistry and physical chemistry, aiming at both advancements in fundamental understanding and technological applications of interfacial phenomena. Central to these efforts are the ability to tailor the surface architecture in ways that will optimize the rates and selectivities of chemical processes occurring at the interfaces, and the ability to examine interfacial reactions at levels that will allow nanoscale or molecular structures to be rationally probed. For the latter ability, while the use of scanning probe microscopies (SPM) has proved valuable due to their capabilities in characterizing the microscopic structure of surfaces with a high spatial resolution, relatively little efforts have been given to study the microscopic interfacial reactivities in situ. The creation of these abilities constitutes one of the major challenges to analytical chemists. To meet the challenge, the goal of this work is to explore several new strategies and approaches to the surface modification and the microscopic characterization of interfaces in the areas mainly targeting sensor technologies that are of interest to environmental control or monitoring, and SPM techniques that can monitor interfacial chemical reactions in real time.

As a starting point, the following sections will review the latest developments in the above activities with focus on specific areas. First, a literature review of the development of optical pH sensors is provided. Second, the development of scanning force microscopy (SFM) is described with emphasis on the instrumentation and modes of operation. Finally, a review of a variety of methods for the elimination of chloride interference in chemical oxygen demand (COD) determination is presented.

Optical Sensors. Chemical sensors are probes used to determine the concentration of an analyte through chemical interaction with an immobilized reagent. If this interaction between the analyte and the reagent causes a change in the optical properties of the reagent phase which is measured through the optical fiber, they become fiber-optical chemical sensors. Development, characterization, and application of optical chemical sensors for pH, metal ions, gases, and biological materials have in recent years become an area of rapidly increasing research activity.[5-14] Chemical sensors involving the immobilization of colorimetric reagents at optical fibers have been developed for applications in biomedical[14] and environmental analyses,[15] as well as in process analytical chemistry.[12]

The large number of optical pH sensors developed is, in part, a result of the availability of acid-base indicators on which to base the sensor design, and, in part, due to the importance of pH determinations. Compared with the electrochemical sensors, the main advantages that the optical pH sensors offer include the lack of necessity of reference electrodes, minimal susceptibility to electrical interference, internal calibration, and most importantly, capability for remote sensing through fiber optics.[16] Most of the optical sensors developed for pH measurement are based on absorbance[17-28] or fluorescence[13, 29-38] measurements in the UV-visible region via an indicator immobilized on a support material. However, measurements based on changes in reflectance,[39-45] fluorescence lifetime,[46, 47] evanescent wave absorption[48-50] and infrared spectroscopy[51] have also been developed. Sensors for pH have employed acid-base indicators that have been immobilized at a variety of polymeric materials,[19-22, 30, 38, 40-43, 51-53] ion-exchange resins,[33, 39, 54] and porous[32, 37, 55] or "sintered" glasses.[31] Diverse techniques have been utilized to immobilize the acid-base indicators, which include adsorption of the chromophore on polymeric supports[56-58] or directly on the fiber;[19] covalent bond to the fiber[59] or to a fixed support;[60] entrapment in polymeric structures;[61, 62] and sol-gel procedure.[50, 63] Most optical pH sensors developed suffer from some disadvantages compared with the electrochemical sensors, such as limited dynamic range, poor long-term stability, and slow response. In Chapter 1, the development of a new pH sensing film with a large pH dynamic range, fast response, and improved long-term stability based on the covalent immobilization of fluoresceinamine at cellulose acetate thin film.

Scanning Force Microscopy. Scanning probe microscopies are quickly becoming routine methods in many laboratories. The ability to probe the microscopic and nanoscopic structure of surfaces in a variety of ambient conditions with a low-maintenance instrument that sits on a benchtop has contributed to the popularity of these technologies. Scanning tunneling microscopy (STM), invented in 1982, was the first technique capable of directly imaging surface atoms in real space.[64] The success of STM for achieving atomically resolved images of surfaces triggered the development of a variety of other scanning probe microscopes. Among these, and the most popular, is the scanning force microscopy (SFM), invented in 1986 by Gerd Binnig, Calvin Quate and Christoph Gerber.[65] Whereas STM functions by scanning a sharp metal tip over the surface of a conducting or semiconducting sample, an SFM does not require a tip or a sample to be conductive. Therefore, virtually all materials can be imaged using variations of SFM.

Instead of using a tunneling current to sense the proximity of the scanning tip to the surface, force microscopies take advantage of the variety of short- and long-range forces between two masses (e.g., van der Waals, magnetic, and electrostatic forces). Force microscopes image a sample by scanning a probe mounted on a cantilever across a sample surface and then detecting the changes in the forces between the tip and the surface by measuring the deflections of the cantilever. However, unlike STM there are a number of different methods for detecting the deflection of the cantilever, such as tunneling,[65] capacitance,[66] interferometry,[67] optical beam deflection,[68] and others. Optical beam deflection is the simplest and most widely used of these force detection methods. Figure 1 shows a SFM design equipped with an optical beam deflection system. A laser beam is reflected off of the backside of the cantilever into a position-sensitive diode detector. By using a photodiode composed of four independent parts, the vertical deflection of the cantilever in

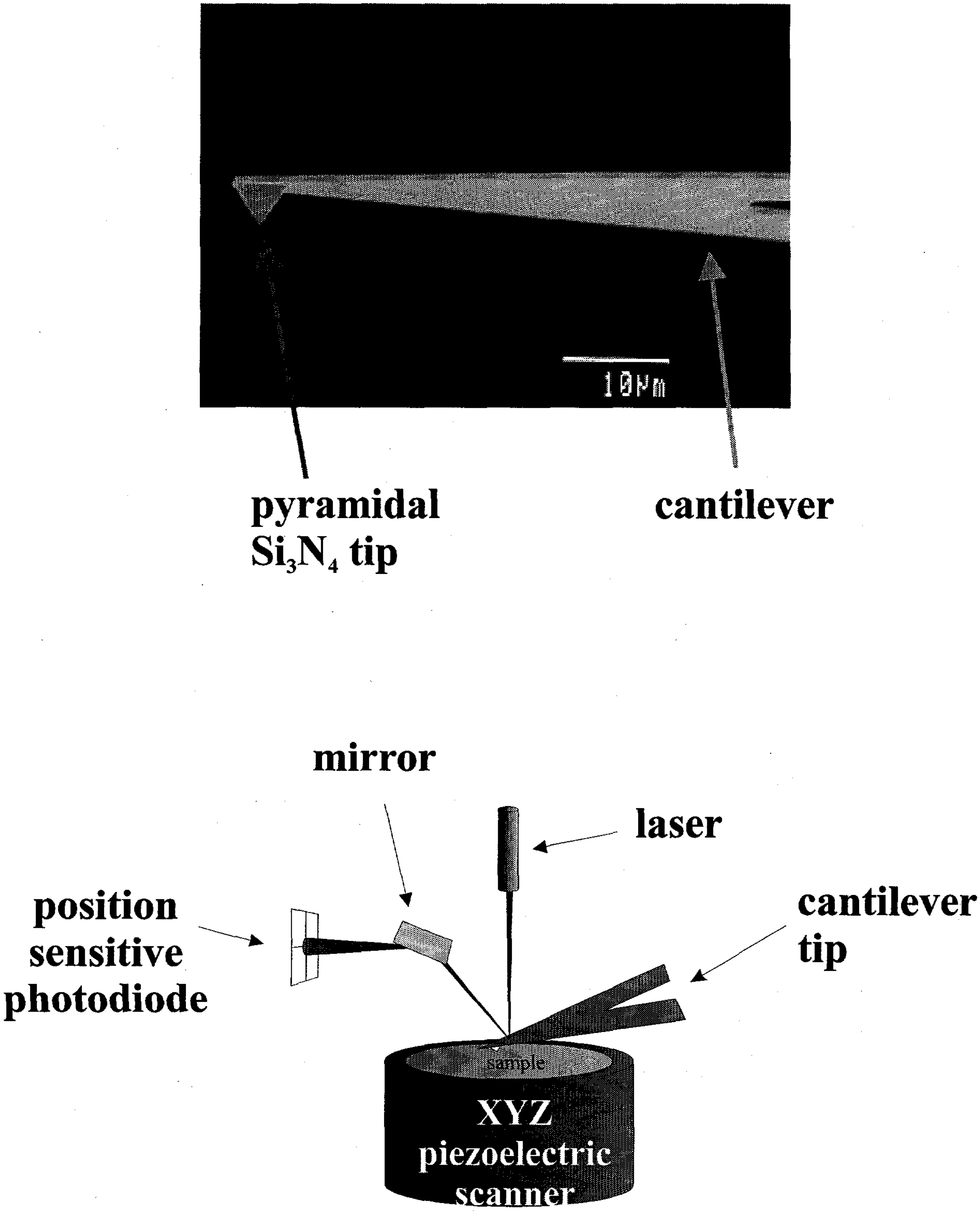

Figure 1. Schematic of the principle components for an optical lever type SFM (Reproduced from (95)).

response to surface topography, as well as its torsional motion due to the frictional force between tip and sample, can be measured simultaneously.

SFM can be operated in various modes. The most elementary mode of SFM operation is the contact mode. With this mode, a cantilevered tip is brought into direct physical contact with a sample. As the tip is rastered across the surface, the deflection of the tip is used to map out the topography. As with all SPM techniques, the use of a feedback loop is optional. In one case, deflection without feedback is plotted as a function of sample position, and in the other case, a feedback loop dynamically adjusts the vertical position of the sample in an effort to keep the deflection constant. Topographical information can be obtained in this way. New modes of SFM have been developed to measure material properties, such as elasticity, adhesion, friction, etc. Elasticity may be determined from one variation of contact mode known as force modulation.[69] The vertical position of the sample is modulated while the tip is in contact with the sample, and the resulting cantilever deflection may be correlated with the elasticity of the tip-sample contact zone. Non-contact mode SFM has also been developed to image soft samples, such as biological materials and soft polymers, which otherwise can be damaged by the larger forces of contact mode operation. A common noncontact SFM technique uses a stiff cantilever held above the sample surface and oscillated at a frequency close to its resonance frequency. When the tip is brought close to the surface, the resonance frequency of the cantilever is modified by the force gradient between the tip and sample. The van der Waals force extends far enough above the sample to influence the tip without the tip actually touching the surface. The change in the oscillation of the cantilever can be measured using most deflection detection methods.

While SFM has proven invaluable in addressing issues related to the nanoscale topography of a wide variety of interfacial materials, we have been focusing on extending the capabilities of SFM to increase the chemical content gained from the imaging process.[70, 71] One of our goals was to take advantage of the nanoscale resolution of SFM to characterize interfacial chemical transformations in situ at the molecular level. The model system we chose to conduct the study results from the spontaneously adsorbed monolayers (SAMs). SAMs have been proposed as model systems for the study of a wide range of surface effects[3] due to their well-defined composition and structure, extraordinary stability both in vacuum and in ambient, and most significantly the high degree of control over the chemical and physical properties of the interface. Of those, the most well studied are formed by the chemisorption of alkyl thiols ($X(CH_2)_nSH$) to gold electrodes.[3] Figure 2 illustrates the idealized structure of an alkyl thiolate monolayer adsorbed on gold. There are effectively three regions to the monolayer film: 1) the adsorbate-substrate interface; 2) the body of the adsorbate; and 3) the adsorbate-environment interface. Among all the characterization techniques for the monolayers, infrared reflection absorption spectroscopy (IRRAS) has proven the most valuable.[72] In our studies, IRRAS was utilized together with SFM to characterize the chemical reactions at the monolayer-solution interface both macroscopically and microscopically. Chapter 2 demonstrates the applicability of SFM for characterizing interfacial chemical reactions at a nanoscale level. Chapter 3 further demonstrates the

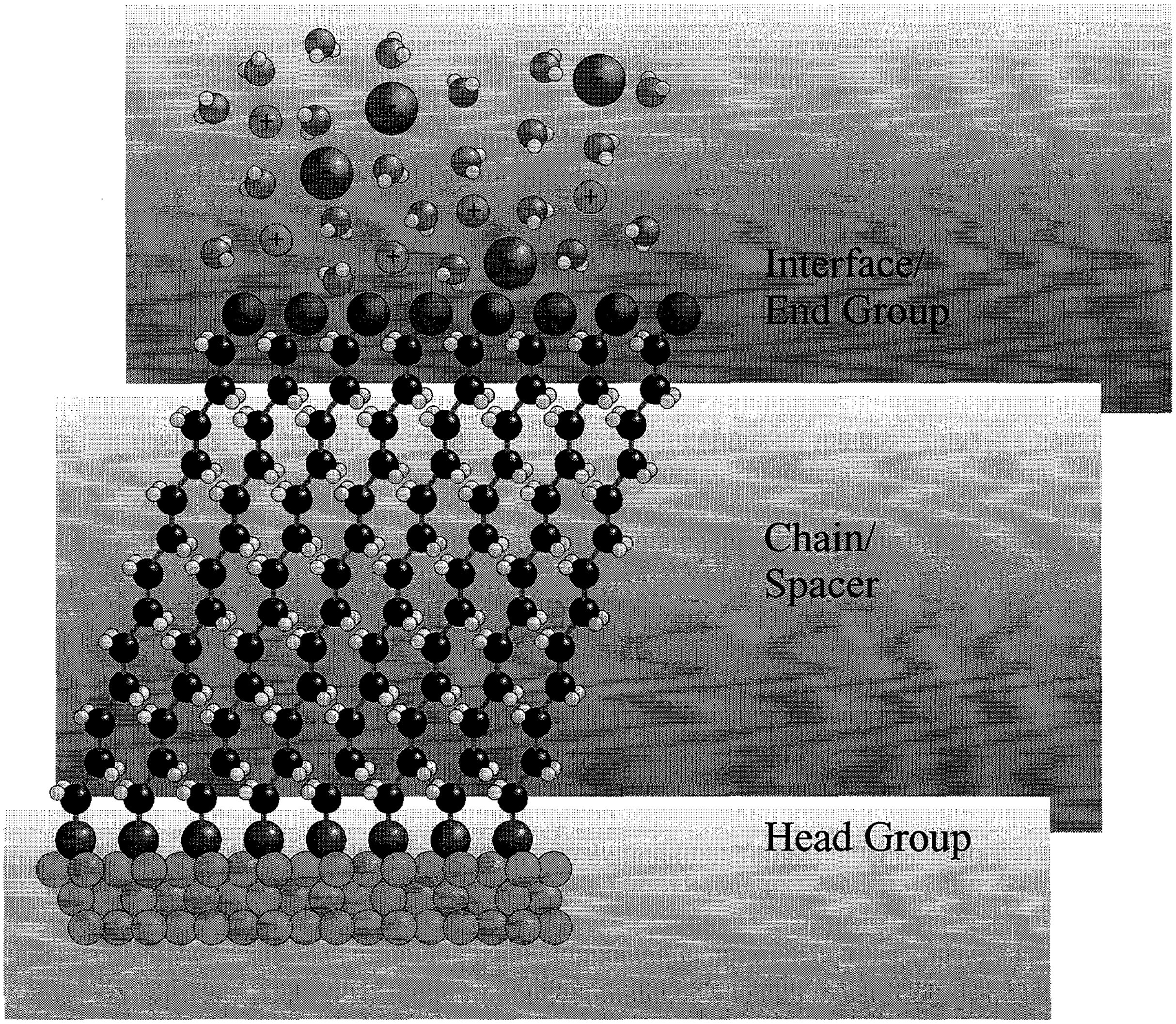

Figure 2. Idealized structure of alkyl thiolate monolayers at Au(111) (Reproduced from (95)).

capability of SFM of modifying surface locally, and the impact of this type of processing to the nanofabrication of surfaces for sensor technology.

Chloride Interference in Chemical Oxygen Demand Determination. Oxygen demand is an important parameter for determining the effect of organic pollutants on receiving water. As microorganisms in the environment consume these materials, oxygen is depleted from the water. This can have adverse effect on fish and plant life. There have been several methods developed to measure this oxygen demand,[73] among which chemical oxygen demand (COD) is widely applied over other methods (e.g., biochemical oxygen demand (BOD) and total organic carbon (TOC)). Acidic dichromate is commonly used for the oxidation of the organic material for a COD determination.[73-92] While not an organic pollutant, chloride ion can be oxidized by acidic dichromate which can result in a positive deviation in a COD determination. In addition, ammonia also gets oxidized in presence of chloride, which is otherwise not oxidized by the acidic dichromate.[93] Thus, the chloride interference in a sample containing ammonia is even more pronounced.

The present methods of COD determination mask the effect of chloride ion by addition of a mercury salt[74, 75, 79, 81, 86, 90-92] which reacts with chloride ion to form an unreactive complex. Other attempted approaches to manage the problem of chloride ion interference include the addition of silver salts[82-85] to mask chloride ion, the addition of chromium(III)[87] to reduce the oxidation potential, the determination of the amount of chloride oxidized by iodometric titration with a subsequent correction for the oxidized chloride,[80] and the removal of chloride as hydrochloric acid from an acidified sample solution.[93, 94] However, the effectiveness of these approaches for compensation vary depending on sample matrix.

Furthermore, as environmental regulations are tightening, it has become increasingly important to develop a more environmentally friendly approaches for COD and other chemical analysis. Hence, an efficient and environmentally friendly method of chloride removal in COD determination is clearly needed. Since an electrode can be used as a reagent for oxidation or reduction reaction, and it is also reusable and environmental friendly, we developed an electrochemical approach to the elimination of Cl^- interference in COD analysis and is described in Chapter 4.

Dissertation Organization

Centered on the main theme, four specific topics are presented as four chapters in this dissertation following the general introduction. Chapter 1 describes the development of two immobilization schemes for covalently immobilizing fluoresceinamine at cellulose acetate and its application as a pH sensing film. Chapter 2 investigates the applicability of SFM to following the base-hydrolysis of a dithio-bis(succinimidylundecanoate) monolayer at gold in situ. Chapter 3 studies the mechanism for the accelerated rate of hydrolysis of the dithio-bis(succinimidylundecanoate) monolayer at Au(111) surface. Chapter 4 focuses on the development of an electrochemical approach to the elimination of chloride interference in Chemical Oxygen Demand (COD) analysis of waste water. The procedures, results and conclusions are described in each chapter.

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GENERAL CONCLUSIONS

This dissertation has investigated approaches to chemically modifying metal and polymer surfaces for applications to chemical analysis, and demonstrated SFM's ability to characterize interfacial chemical reactions at nanoscale level for probing the microscopic surface reactivities, which other surface characterization tools cannot do.

Chapter 1 has demonstrated that the pH sensors based on the covalent immobilization of fluoresceinamine at hydrolyzed cellulose acetate film show a rapid response time (< 30 s), a large dynamic range (> 7 pH units), and exceptional long-term stability (several months). The immobilization schemes are both simple and free of organic solvents. Compared with the indirect immobilization scheme, the direct immobilization procedure is simpler, and the large background due to light scattering by the beads is minimized. However, the sensor film prepared through indirect immobilization scheme shows better mechanical strength and gives better long-term stability than the one that was prepared through direct immobilization scheme. An extended pH sensitivity is achieved by co-immobilizing fluoresceinamine and Congo Red at a hydrolyzed cellulosic film.

Chapter 2 and 3 have demonstrated that frictional force imaging can be applied to follow interfacial chemical transformations at microscopic level. The base-hydrolysis of a dithio-bis(succinimidylundecanoate) monolayer chemisorbed on a gold substrate was monitored in situ with scanning force microscopy (SFM). The results indicate that the friction at the microcontact formed between a Si_3N_4 probe tip and a dithio-bis(succinimidylundecanoate)-modified Au(111) substrate increases as the succinimidyl group is replaced by the carboxylate ion. This increase is consistent with an increase in the interfacial surface tension at the microcontact. The correlation between the macroscopic data determined from IRS and the microscopic data determined from the in situ SFM images confirms that the friction change was resulted from the composition change during the hydrolysis. The study also shows the heterogeneity in the reaction rates on different areas of the surface, and the acceleration of the reaction rate by the nano-contact between the tip and surface.

An electrochemical approach to the elimination of Cl^- interference in chemical oxygen demand (COD) analysis was examined in Chapter 4. Both silver-supported reticulated vitreous carbon (RVC) and silver coil electrodes were successfully utilized for removal of Cl^- in controlled and wastewater samples. Chloride ion was removed from samples with initial Cl^- concentrations ranging from 100 to 1000 ppm to levels below 3 ppm, with analysis times of ≤ 15 min, and a COD precision of ≤ ±20%. By coating the surface with a low surface free energy film such as silver sulfide, the probability of particulate entrapment or adsorption on the uncoated electrodes, which attribute to a loss of ~50% COD from sewage wastewater samples, has been reduced to < 10%.

The ability to not only characterize interfaces at atomic scale, but also manipulate atoms and molecules on surfaces with atomic precision will open opportunities for the nanofabrication of materials. For example, the fact that the contact imaging with SFM can accelerate the reaction rate in a localized region creates the possibility of making microscale sensor arrays by creating chemically inhomogeneous patterns of nanometer scale dimensions.

With the advancement of technology, interfacial phenomena will be better understood and play a more important role in a variety of applications.