SURFACE MODIFIED ELECTRODES AND THEIR REACTIVITY

by

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To my family

献给我的家人

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Surface Modified Electrodes and Their Reactivity

Abstract

by

JUN WU

Various aspects of the adsorption of Cd^{2+} on self assembled monolayers (SAM) of 4-heptadecylpyridine (HDpy) and 7-tridecyl-4-methyl-1,10-bipyridine (TMbipy) supported on an octadecylsilane (ODS)-modified Ge prism have been examined both *ex situ* and *in situ* using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). Analysis of spectra acquired *ex situ* for HDpy/ODS/Ge and TMbipy/ODS/Ge before and after exposure to Cd^{2+} , yielded values for the fraction of uncoordinated pyridine, $\theta(py_{un})$, and uncoordinated bipy, $\theta(bipy_{un})$ of ca. 0.5 and ca. 0.1, respectively. The adsorption isotherm was obtained for HDpy/ODS/Ge in contact with Cd^{2+} -containing solutions in the range 10 nM < $[Cd^{2+}] < 0.1$ mM.

The affinity of Cd^{2+} toward commercial carboxyl-terminated iron oxide beads (C-TIOB) and synthesized undecanoic acid (UA)-SAM functionalized hematite nanoparticles were investigated using anodic stripping voltammetry (ASV) as a function of both pH and $[Cd^{2+}]$ in the μ M range. Adsorption data collected as a function of $[Cd^{2+}]$ and pH revealed a marked increase in the binding constant of Cd^{2+} for carboxylate ions upon attachment to the solid support, over values predicted from standard solution phase equilibria. The number density of carboxylic/carboxylate groups on the surface of

synthesized UA- SAM functionalized hematite nanoparticles, which was determined by titration, was consistent with a closed-packed monolayer.

Tetrahedral amorphous carbon containing nitrogen (taC:N) films have been deposited on semiconductor (SC) electrodes (n-GaAs, n-CdS, n-CdSe) using an ion-filtered cathodic vacuum arc (FCVA) carbon source under high vacuum. The electrochemical properties of the specimens denoted as taC:N|SC were studied in dark and under illumination. Whereas the particular bare SC electrodes were found to undergo corrosion under illumination in neutral solutions, the corresponding taC:N|SC counterparts did show protection, albeit limited, against surface degradation. Depending on the specific SC, the taC:N|SC junctions were found to be rectifying or ohmic. The photocurrent and the photovoltage of taC:N|n-GaAs were proportional to the intensity and to the logarithm of the intensity of illumination, respectively. The deposition conditions were found to influence markedly the properties of the resulting taC:N|SC films. Unfortunately, none of the taC:N|n-GaAs specimens examined showed protection against photocorrosion in alkaline solution.

Introduction

The binding of metal ions in solution to macromolecules and solid surfaces are of pivotal interest to a variety of disciplines ranging from biology to geology. Such interactions involve functional groups, as proteins, or surface sites, as in metal oxides and oxyhydroxides, particularly of iron and aluminum. This thesis examines certain aspects of the interactions of Cd2+ with molecules immobilized on surfaces. The molecules studied bear chemical groups with strong affinity for metal ions. Chapter 1 of this dissertation describes experiments involving self-assembled monolayers (SAM) that incorporated pyridine and bipyridine terminal groups and were supported on the surface of an IR transparent attenuated total reflection (ATR) element. This arrangement made it possible to determine the extent of adsorption by monitoring changes in the vibrational features of the terminal groups using ATR Fourier transform infrared spectroscopy (ATR-FTIR). In direct analogy with the behavior found for a variety of aqueous pyridine (py) and bipyridine (bipy) metal-ion complexes, Cd2+ bonding to either SAM led to shifts toward higher energies in the skeletal vibrational modes of the ligands in the region 1650 to 1400 cm-1. Adsorption isotherms were determined from a statistical analysis of the spectral data collected over the range 10 nM < [Cd2+] < 0.1 mM. For the most concentrated solution, the fraction of uncoordinated py, $\theta(py_{un})$, and uncoordinated bipy, θ (bipy_{un}) was ca. 0.5 and ca. 0.1, respectively.

Chapters 2 and 3, examine Cd2+ adsorption on commercial carboxyl-terminated iron oxide magnetic beads (C-TIOB, Sigma) a few microns in diameter, and suspended in aqueous solutions. Correlations between the concentration of Cd2+ in solution, the extent

of the interactions between the metal ion and the functional groups, and the pH were determined using anodic stripping voltammetry (ASV). Advantage was taken of the superparamagnetic character of C-TIOB to confine and/or remove the beads to assess the influence of dispersed C-TIOB on the amount of Cd2+ detected by ASV for [Cd2+] in the μ M range. Adsorption data collected as a function of [Cd2+] and pH revealed a marked increase in the binding constant of Cd2+ for carboxylate ions attached to the solid support, over values predicted from standard solution phase equilibria data. A similar approach was implemented for measurements involving adsorption of Cd2+ on superparamagnetic maghemite particles coated by us with 11-undecanoic acid SAM bearing carboxyl terminal groups covalently-bound through siloxane groups (see Chapter 3). The surface density of the carboxyl groups in this case was determined by direct titration of suspensions in aqueous solutions, yielding results consistent with the formation of a closed-packed monolayer. Based on the analysis of the ASV, the affinity of Cd2+ ions in aqueous solutions toward the SAM was comparable with that found for the commercial C-TIOB particles.

Also examined in this dissertation (Chapter 4) were the photoelectochemical properties of semiconductor (SC) electrodes (n-GaAs, n-CdS, n-CdSe) coated with tetrahedral amorphous carbon containing nitrogen (taC:N) films that were deposited under high vacuum using an ion-filtered cathodic vacuum arc (FCVA) carbon source. Photoelectrochemical data collected in ferro/ferricyanide neutral solutions under illumination indicated that the taC:N film protected the underlying SC against photocorrosion, at least for short times. Depending on the SC used, the taC:N|SC junctions were found to be rectifying or ohmic. In the case of taC:N|n-GaAs, the

photocurrent and the photovoltage of were proportional to the intensity and to the logarithm of the intensity of illumination, P (mW/cm2), respectively. The lack of long-term stability was attributed to the presence of pinholes or defects in the taC:N films.

Chapter 1. Binding of Cd²⁺ to Self-Assembled Bilayers Bearing Pyridine Terminal Groups: ATR-FTIR Spectroscopic Studies *

* This chapter is largely based on the paper by: Burshtain, D.; Wu, J.; Melman, A.; Mandler, D.; Scherson, D. A. Langmuir **2004**, 20, 4498-4502.

1.1 ABSTRACT

Various aspects of the adsorption of Cd^{2+} on self assembled monolayers (SAM) of 4-heptadecylpyridine (HDpy) and 7-tridecyl-4-methyl-1,10-bipyridine (TMbipy) supported on an octadecylsilane (ODS)-modified Ge prism have been examined both ex situ (dry) and in situ (in the presence of aqueous solutions) using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). In direct analogy with the behavior found for a variety of genuine pyridine (py) and bipyridine (bipy) metal-ion complexes, Cd²⁺ binding to both SAM led to shifts in the skeletal vibrational modes of the corresponding uncoordinated ligands in the region 1650 to 1400 cm⁻¹, toward higher energies. Analysis of spectra acquired ex situ for HDpy/ODS/Ge and TMbipy/ODS/Ge before and after exposure to 0.1 mM [Cd²⁺], yielded values for the fraction of uncoordinated py, $\theta(py_{un})$, and uncoordinated bipy, $\theta(bipy_{un})$ of ca. 0.5 and ca. 0.1, The features attributed to py_{un} groups for spectra collected for respectively. HDpy/ODS/Ge in situ and ex situ were found to be virtually identical, making it possible to isolate by graphical means the most prominent band of py_{co} centered at ca. 1615 cm⁻¹ for HDpy/ODS/Ge collected in situ. The resulting bands for pure pyco and pyun in situ were then used to deconvolute spectra recorded in situ for HPpy/ODS/Ge in contact with Cd^{2+} -containing solutions in the range 10 nM < $[Cd^{2+}]$ < 0.1 mM, from which information regarding the adsorption isotherm was obtained.

1.2 INTRODUCTION

Functionalized self-assembled monolayers (SAM) have received considerable attention in recent years as versatile interfacial systems for sensing and other analytical applications.¹⁻⁴ Attention in our laboratories has been focused on SAM bearing terminal groups capable of binding simple cations in solution (including hydronium) using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) as a highly sensitive and rather specific probe of such interactions.^{5,6} Much success was achieved with this technique for determining in situ and quantitatively acid-base properties of carboxyl-terminated alkane chain SAM supported on Ge,⁵ as well as for monitoring various aspects of Cd^{2+} (and few other metal ions) adsorption on the same type of layers.⁶ This contribution represents an extension of our previous work to include SAM incorporating pyridine (py) and bipyridine (bipy) terminal functionalities. Interest in these specific species has been prompted by enhancements in the rates of heterogeneous electron transfer between electrodes and large solution-phase species of biological significance, particularly cytochrome c,^{7,8} opening new prospects for the development of electrochemically-based biosensors. As will be shown in this work, the well documented shifts in the skeletal vibrational modes of both py and bipy induced by coordination to metal ions found for fully characterized complexes,^{9,10} could be easily detected in situ for both types of SAM by ATR-FTIR. Furthermore, statistical analysis of the *in situ* spectra in the case of py terminated layers made it possible to construct plots of the fraction of both coordinated and uncoordinated py groups, i.e. $\theta(py_{co})$ and $\theta(py_{un})$, respectively, as a function of $[Cd^{2+}]$.

1.3 EXPERIMENTAL SECTION

Attenuated total reflection (ATR) Fourier transform infrared (FTIR) measurements were performed with an IBM IR-98 FTIR spectrometer (Bruker 113v) equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector, using as the ATR element a Ge prism (11 reflections) mounted in an ATR-FTIR liquid cell described elsewhere.¹¹ Prior to cell assembly, the prism was polished with 0.05 μm alumina powder, followed by ultrasonication and thorough rinsing with pure water. As specified below, 4-heptadecylpyridine (HDpy) and 7-tridecyl-4-methyl-1,10-bipyridine (TMbipy) were synthesized following general routes,¹² using commercial chemicals of the highest available purity.

Synthesis (*The chemicals HDpy and TMbipy were synthesized by Dr. Doron Burshtain in the Hebrew University of Jerusalem, Israel.*)

a. 4-heptadecylpyridine (HDpy).

To a solution of diisopropylamine (1.4 mL, 9.9 mmol) in dry THF (5 mL) under nitrogen at 0°C was added butyllithium (3.3 mL of 2.5 M solution in hexanes, 8.25 mmol). The reaction mixture was stirred for 5 min at 0°C, and a solution of 4-picoline (0.9 ml, 9.25 mmol) in dry THF (20 mL) was added through a syringe pump over a period of 1.5 h. After stirring for an additional 1.5 h at 0°C, a solution of 1-bromohexadecane (2.8 mL, 3.27 mmol) was added drop wise to the mixture, stirred once again for 1.5 h at 0°C, and, subsequently, quenched with an ice-water bath. Once the volume was reduced to ca. 5 mL volume, the material subsequently extracted with ethyl acetate, dried with sodium sulfate, evaporated, and the residue then purified by flash chromatography using 30% ethyl acetate/40-60 petroleum ether mixture as eluent to yield the title compound (2.2g, 6.9 mmol). ¹H NMR (CDCl₃, 300 MHz) = 0.87(t, 3H, t)

J=6.6Hz), 1.61(br. quintet, 2H, *J*=7.2Hz), 2.58(t, 2H, *J*=7.5Hz), 7.08(d, 2H, *J*=6.0Hz), 8.46(d, 2H, *J*=6.0Hz). The microanalysis yielded C, 82.81; H, 12.70, N, 4.58%, in good agreement with theoretical values for HDPY, i.e. C, 83.21; H, 12.38; N, 4.41%.

b. 7-tridecyl-4-methyl-1,10-bipyridine (TMbipy).

To a solution of diisopropylamine (1.4 mL, 9.9 mmol) in dry THF (5 mL) under nitrogen at 0°C was added butyllithium (3.8 ml of 2.5 M solution in hexanes, 9.5 mmol). The reaction mixture was stirred for 5 min at 0°C and a solution of 4,4-dimethyl-2,2bipyridine (1.0 g, 5.4 mmol) in dry THF (20 mL) then added via a syringe pump over a period of 1.5 h. After stirring for an additional 1.5 h at 0°C, a solution of 1bromododecane (1.3 mL, 5.4 mmol) was then added drop wise, and stirred once again for an additional 1.5 h at 0°C, followed by quenching with an ice-water mixture and final evaporation to ca. 5 mL volume. The product was then washed with ethyl acetate and subsequently extracted with 30 mL 10% HCl/H₂O (w/w). The solid salt obtained was washed several times with ether and then mixed with a sodium bicarbonate solution to remove excess water from the solid prior to final extraction with ethanoic acid (Et-OAc). The organic solution was dried with sodium sulfate and the Et-OAc then evaporated to provide the title compound (0.8g, 2.26 mmol). ¹H NMR (CDCl₃, 300 MHz): 0.87(t, 3H, J=7.0 Hz), 1.25(m, 10H), 1.68(br. quintet, 2H, J=7.6Hz), 2.44(s, 3H), 2.68(t, 2H, J=8.1 Hz), 7.13(dd, 2H, J=1.6, 5 Hz), 8.22(br.s, 2H), 8.54(dd, J=3.5, 5.0 Hz). The microanalysis results yielded C, 80.77; H, 10.42; N, 7.79% in agreement with the theoretical values for TMP, i.e. C, 81.76; H, 10.29; N, 7.95%.

Assembly and Characterization of Self-Assembled Monolayers (SAM) and Bilayers (SAB)

ODS/Ge SAM - As described in detail elsewhere,⁵ the assembly of the octadecylsilane (ODS) SAM on Ge was performed by injecting a 4 mM solution of octadecyltrichlorosilane (OTS, Aldrich, 95%) in benzene (Aldrich, 99%) into the custommade liquid cell fixed in the cavity of the FTIR spectrometer.¹¹ The spectrum was monitored over time until no further changes were observed indicating that the monolayer assembly was completed. The cell was then emptied, rinsed several times with neat benzene to remove solution-phase OTS, and finally flushed with nitrogen gas until no features attributable to benzene could be detected in the ATR-FTIR spectrum. At this stage, the spectrum of this dry ODS/Ge SAM was recorded and stored in the computer for further analyses.

HDpy/ODS/Ge and TMbipy/ODS/Ge SAB – In stark contrast with the results obtained earlier for SAB incorporating carboxyl-terminated groups,^{5,6} no changes in the spectrum of dry, freshly-prepared ODS/Ge SAM could be discerned following exposure to homogeneous ethanolic 4 mM solutions of either HDpy or TMbipy and subsequent drying, indicating that under such conditions neither material shows affinity for the ODS/Ge surface. However, signals consistent with the formation 4-HDpy and TMbipy layers could be clearly identified upon injecting the materials into the cell as 4 mM micellar solutions in 50% ethanol/water (v/v). Analogous procedures have been reported by Plant and coworkers for the spreading of hybrid bilayer membranes.¹³ After steady conditions were achieved, the cell was rinsed with ultrapure water dried under a nitrogen flow, and the spectrum of the dry HDpy (or MTbipy)/OTS/Ge SAB recorded.

Cd²⁺ Adsorption on HDpy (or MTbipy)/ODS/Ge SAB - The interactions of Cd²⁺ with the terminal pyridine (py) or bipyridine (bipy) moieties in HDpy, and MTbipy/ODS/Ge

SAB, respectively, were investigated *in-situ* by injecting into the ATR cell aqueous solutions of Cd(ClO₄)₂ (Alfa) in 0.1 M NaClO₄ (Aldrich, 99%), in the range 10^{-8} - 10^{-4} M, in sequence, starting at the most dilute extreme, i.e. 10 nM. For each [Cd²⁺], sufficient time was allowed to elapse for the spectral signals to achieve steady state values. The ATR-FTIR spectrum of neat, aqueous 0.1M NaClO₄ in contact with the SAB was also recorded and used as a reference spectrum in subsequent quantitative analyses. Once the entire series had been completed, i.e. data for the solution with the highest [Cd²⁺] (= 0.1 mM) had been recorded, the cell was dried under N₂ flow without further rinsing and the spectrum of the dry Cd²⁺/SAB/Ge recorded.

1.4 RESULTS AND DISCUSSION

In agreement with previous studies,^{5,6} the *ex situ* spectrum of ODS/Ge SAM dried from a benzene solution, using the spectrum of the dry, pristine Ge prism as a reference (see curve a, Fig. 1-1), displayed methylene stretching bands, $v_a(C-H)$ at ~2919 and $v_s(C-H)$ H) at ~2850 cm⁻¹, characteristic of a well-ordered, close-packed alkane chain monolayer,¹⁴⁻¹⁶ with no detectable contributions from other species.

1.4.1 HDpy/ODS/Ge

The dried spectrum of ODS/Ge following contact with a micellar solution of HDpy in 50%(v/v) water/ethanol, using the spectrum of the dry ODS/Ge as a reference, showed clear features ascribed to ring skeletal bands of the py functionality¹⁷ in the range 1650 to 1400 cm⁻¹ (see curve b, Fig. 1-1), consistent with adsorption of HDpy on the ODS/Ge substrate. It is noteworthy that the frequencies of $v_a(C-H)$ and $v_s(C-H)$, remained virtually unchanged, providing evidence that the two layers in the SAB are close-packed. However, the integrated intensities of these bands are more than three times

larger than those found for the corresponding features for ODS/Ge. The most likely explanation for this effect may be found in an increase in the tilt angle of HDpy compared to ODS, and/or of ODS in HDpy/ODS/Ge, induced by the presence of the HDpy overlayer. Although the formation of an HDpy multilayer on ODS/Ge (assuming the tilt angle for HDpy is the same as that for ODS in ODS/Ge) would also lead to such an increase, it is doubtful that multilayers would survive the thorough washing with water before the spectrum was acquired.

a. Cd²⁺ Adsorption on HDpy/ODS/Ge SAB

Evidence for Cd^{2+} binding to the py moeity in HDpy in the SAB was obtained from a series of *in situ* spectra recorded following exposure of HDpy/ODS/Ge to aqueous solutions of $Cd(ClO_4)_2$ in 0.1 M NaClO₄ for $[Cd^{2+}]$ in the range 10 nM to 0.1 mM. These experiments were performed in sequence for increasing $[Cd^{2+}]$. As shown in Fig. 1-2, the resulting spectra, using the spectrum of HDpy/ODS/Ge in a (Cd²⁺-free) 0.1 M NaClO₄ solution recorded in situ (wet) as a reference, were characterized by a series of bipolar bands in the region $1650 - 1400 \text{ cm}^{-1}$, which became more intense as $[Cd^{2+}]$ was increased. In this representation, negative-, and positive-pointing peaks reflect a decrease in uncoordinated py, pyun, and an increase in coordinated py, pyco, respectively, induced by Cd²⁺ exposure. The observed shifts in the py bands toward higher energies are consistent with the behavior found in the IR spectra of py in poly(4-vinyl pyridine) coordinated to Zn^{2+} (from 1597 to 1617 cm⁻¹),¹⁸ and also in the grazing incidence reflection IR spectrum of LB films bearing more complex terminal py groups exposed to Cu²⁺ and Cd²⁺ solutions.¹⁹ In fact, the position of the peaks, as well as the magnitudes of the shift for Cd^{2+} coordination (from 1600 to 1618 cm⁻¹) are in good agreement with

those found in this work. Further, albeit indirect, evidence for Cd^{2+} coordination was provided by the large increase in the intensity of the perchlorate features at ca. 1100 cm⁻¹, for higher $[Cd^{2+}]$ associated with perchlorate,²⁰ which acts as the main counter ion to preserve electroneutrality.¹⁹

More subtle effects were also noticed in the $v_a(C-H)$ and $v_s(C-H)$ region. In particular, for very low $[Cd^{2+}]$, the positive-pointing component of the bipolar feature occurred at higher energy, indicative of a slight disorder of the layer. As the $[Cd^{2+}]$ increased, however, precisely the opposite polarity was observed, consistent not only with a reordering of the layer, but also with a slight increase in its tilt angle. Similar effects have been reported in earlier work in our laboratory involving carboxylterminated SAB,⁶ and also by Caminati et al.,²¹ who reported a shift of the $-CH_2$ vibrations due to the change in the environment and in the steric constraint of the aliphatic chain induced by the interaction of nickel-pyridine in Langmuir-Blodgett films.

Once the *in situ* spectrum of the HDpy/ODS/Ge layer exposed to $[Cd^{2+}] = 10^{-4}$ M had been recorded, the cell was emptied and the supported SAB dried by flowing N₂ gas. The spectrum of this dry layer using the spectrum of dry ODS/Ge as a reference is shown in curve b, upper panel Fig. 1-3. The spectrum of the dry HDpy/ODS/Ge layer before exposure to Cd²⁺ solution, using the same reference spectrum, is shown in curve a in this same figure. In harmony with the data recorded *in situ*, the difference between the two upper panel spectra (see lower panel, Fig. 1-3) displayed a set of bands in the py region shifted toward higher energies. Estimates of the extent of Cd²⁺-coordinated py can be made first by assuming that curve b consists of contributions due to both py_{un} (ca. 1600 cm⁻¹) and py_{co} groups (ca. 1615 cm⁻¹), as clearly evidenced by the data shown in the

insert, and then by subtracting from that same curve the contributions due to py_{un} , in curve a, Fig. 1-3. Since the functional form of the feature associated with the pure py_{co} is not known *a priori*, the fraction of py_{un} was determined by simply subtracting from curve b, increasing contributions due to py_{un} using a graphical approach. Since the peaks occur at different energies and their widths are relatively small, this procedure proved very reliable, as under-, or over-subtraction led to noticeable positive or negative shoulders on the sloping low energy end of the high energy feature, i.e. py_{un} , respectively (see Fig. 1-4). Within the uncertainties of this approach, the fraction of py_{un} sites, $\theta(py_{un})$, as measured *ex situ*, was estimated to be about one-half.

Quantitative analysis of the data collected *in situ* requires for the *in situ* spectra of the pure py_{un} and pure py_{co} to be known. Evidence for a close similarity between data obtained *ex situ* and *in situ* in the py region, prior to Cd^{2+} exposure, was obtained by subtracting the spectrum of dry HDpy/ODS/Ge from that of the same layer in the presence of 0.1 M NaClO₄. As shown in Fig. 1-5, such spectrum displayed no features other than those ascribed to the solvent in the region $1400 - 1650 \text{ cm}^{-1}$. This implies that the spectrum of py_{un} remains invariant in the presence of the electrolyte. It is significant that differences were indeed observed in the C-H stretching region (see expanded bipolar features in Fig. 1-5), which are consistent with an increase in the degree of disorder upon exposure of the SAB to the electrolyte solution. On this basis, it becomes then possible to extract from the *in situ* spectrum of HDPY/ODS/Ge in contact with 0.1 mM Cd(ClO₄)₂ the feature belonging to the pure py_{co} . To this end, a graphical approach similar to that described above for *ex situ* py_{co} was utilized to yield curve d, Fig. 1-6. Also shown in this figure are the *in situ* spectrum of HDPY/ODS/Ge in contact with $[Cd^{2+}] = 0.1 \text{ mM}$

solution (curve a), the *ex situ* = *in situ* spectrum of pure py_{un} (curve b) and the spectral contribution of pure py_{co} (ca. 0.5 of total py) to the *in situ* spectrum in curve a in this figure (curve c).

b. Adsorption Isotherm – The analysis to be presented in this section relies on a statistical deconvolution of the bipolar feature in the region 1580 to 1635 cm⁻¹ in Fig. 1-2, in terms of the pure py_{un} and py_{co} species shown in curves b and d in Fig. 1-6. Curves a and b are experimental results and curves c and d were determined from the deconvolution. Before this procedure was attempted, the contributions due to the pure electrolyte (0.1M NaClO₄) were subtracted from all the *in situ* spectra in Fig 1-2. Illustrations of the statistical fits are given in Fig. 1-7, where the components of the bipolar spectra are given in solid lines, and the fits to the experimental points are given in dotted lines. Shown in the upper panel, Fig. 1-8 are the calculated fractions of pyun and py_{co} , $\theta(py_{un})$ and $\theta(py_{co})$, as a function of $[Cd^{2+}]$. As clearly indicated, the two sets of results were found to be consistent, as the sums of the calculated fractions (see squares in this figure) were very close to one. Unfortunately, it is not possible to infer from these results the mode of coordination of Cd^{2+} to py, e.g. mono-, bi-, or tridentate. Such information can, in principle, be obtained by measuring in situ [Cd2+] before and after contact of the solution with the SAB; however, such experiments were not pursued in this study.

1.4.2 MTbipy/ODS/Ge

Characteristic features of bipyridine (bipy) in the range 1650 to 1400 cm⁻¹ were found for the spectrum of dry MTbipy/ODS/Ge using that of dry ODS/Ge as a reference (see curve a, Fig. 1-9). A similar spectral behavior to that found for HDpy/ODS/Ge (see previous section) was found in the spectrum of MTbipy/ODS/Ge recorded in situ upon exposure to Cd²⁺ solutions of increasing concentration (see Fig. 1-10), i.e. a shift in the skeletal modes of bipy toward higher energies, consistent with the binding of Cd^{2+} to the bipy terminal functionalities. In this case, however, Cd²⁺ binding led to a monotonic increase in the disorder of the SAB, as evidenced by the shift of the $v_a(C-H)$ and $v_s(C-H)$ features with exactly the opposite polarity as that observed for HDpy/ODS/Ge at high $[Cd^{2+}]$ (see Fig. 1-2). Additional support for this view was provided by the positivepointing character of the water bands (broad peak at ~3300 and 1650cm⁻¹), which suggests a much deeper penetration of the solvent into the self-assembled layer. Shown in curve b, upper panel Fig. 1-9 is the ex situ spectrum of MTbipy/ODS/Ge following exposure to a solution $[Cd^{2+}] = 10^{-4}$ M, and subsequent drying, using dry ODS/Ge as a reference. The corresponding difference spectrum is given in the lower panel in this figure. Based on the method described in the previous section, the amount of bipy_{co} was estimated to be about 90% (see Fig. 1-11). This should not be surprising in view of the better chelating properties of bipy compared to py.^{22,23} Unfortunately, no sufficient data could be collected to construct the adsorption isotherm.

1.5 CONCLUSIONS

Changes in the vibrational (skeletal) modes of pyridine (py) and bipyridine (bipy) terminal groups of HDpy/ODS/Ge amd MTbipy/ODS/Ge self assembled bilayers following exposure to solutions containing Cd²⁺ were monitored by attenuated total reflection infrared spectroscopy (ATR-FTIR). The resulting spectra displayed a new set of bands at slightly higher energy consistent with the binding of the metal ion to the py and bipy moieties. Statistical analysis of the spectral data for HDpy/ODS/Ge recorded *in*

situ for $[Cd^{2+}]$ in the range $10^{-8} - 10^{-4}$ M made it possible to construct independent plots of the fractions of uncoordinated, $\theta(py_{un})$, and coordinated, $\theta(py_{co})$, py sites in the film. Analysis of spectra acquired *ex situ* for HDpy/ODS/Ge and TMbipy/ODS/Ge before and after exposure to 0.1 mM $[Cd^{2+}]$, yielded values for $\theta(py_{un})$ and $\theta(bipy_{un})$ of ca. 0.5 and ca. 0.1, respectively.

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Fig. 1-1 ATR-FTIR spectra of ODS/Ge dried from benzene (curve a) and of HDpy/ODS/Ge dried from 50% ethanol/water (v/v) solution (curve b) using the spectrum of the bare, dry Ge ATR crystal as a reference.



Fig. 1-2 Series of *in situ* ATR-FTIR spectra of HDpy/ODS/Ge exposed to aqueous solutions of $Cd(ClO_4)_2$ in 0.1 M NaClO₄ at the specified values of $[Cd^{2+}]$ using the spectrum of the same interface in a $(Cd^{2+}-free)$ 0.1 M NaClO₄ as a reference. These experiments were performed in sequence for increasing $[Cd^{2+}]$. The broad negative-pointing bands at 3200 and 1600 cm⁻¹ are due to water.



Fig. 1-3 ATR-FTIR spectra of dry HDpy/ODS/Ge before (curve a) and after exposure to 0.1 M Cd^{2+} solution (curve b) using dry ODS/Ge as a reference. The region around 1600 cm-1 is shown in expanded form in the insert. Shown in the lower panel in this figure is the difference between these two curves.


Fig. 1-4 Graphical method for determining the amount of uncoordinated py in dry HDpy/ODS/Ge after exposure to 0.1 M Cd²⁺ solution. Curves a and b represent the spectra recorded before and after Cd²⁺ exposure in the dry states. The set of curves in solid grey lines correspond to curve b - x(curve a) for values of x of 0.47, 0.50, 0.53, 0.55, 0.58, 0.60 and 0.63. The best value of x is estimated to be 0.5 (see text for details).



Fig. 1-5 Spectrum of HDpy/ODS/Ge *in situ* (in 0.1 M NaClO₄ (aq)) using HDpy/ODS/Ge *ex situ* as a reference. Shown in the insert is the expanded region comprising the most prominent peak of py to illustrate the invariant character of the py functionalities in the two environments.



Fig. 1-6 Graphical method for determining the spectrum of the pure py_{co} group in HDpy/ODS/Ge *in situ*. Curve a. *In situ* spectrum of HDpy/ODS/Ge in contact with $[Cd^{2+}] = 0.1$ mM solution. Curve b. *Ex situ* (= *in situ*, see text for details) spectrum of pure py_{un} . Curve c. Spectral contribution of pure py_{co} (ca. 0.5 of total py) to the *in situ* spectrum in curve a in this figure. Curve d. *In situ* spectrum of pure py_{co} .



Fig. 1-7 Illustrations of the statistical fits of the electrolyte-subtracted bipolar feature in the *in situ* spectrum of HDpy/ODS/Ge in the presence of $[Cd^{2+}]$ at the specified values in the panels, in the region 1580 to 1635 cm⁻¹ in terms of the pure py_{un} and py_{co} (see curves b and d, Fig. 6, respectively). The best fits to the experimental points are shown by the solid lines.



Fig. 1-8 Plots of $\theta(py_{un})$ (open circles) and $\theta(py_{co})$ (solid circles), determined from the data collected *in situ* shown in Fig. 1-7 as a function of $[Cd^{2+}]$. The squares in this figure represent the values of $\theta(py_{un}) + \theta(py_{co})$.



Fig. 1-9 ATR-FTIR spectra of dry MTbipy/ODS/Ge before (curve a) and after exposure to a 0.1 M Cd^{2+} solution (curve b) using dry ODS/Ge as a reference. Shown in the lower panel in this figure is the difference between these two curves.



Fig. 1-10 Series of *in situ* ATR-FTIR spectra of MTbipy/ODS/Ge exposed to aqueous solutions of $Cd(ClO_4)_2$ in 0.1 M NaClO₄ at the specified values of $[Cd^{2+}]$ using the spectrum of the same interface in a $(Cd^{2+}-free)$ 0.1 M NaClO₄ as a reference. See caption Fig.1-2 for other details.



Fig. 1-11 Graphical method for determining the amount of uncoordinated bipy in dry MTbipy/ODS/Ge after exposure to a 0.1 M Cd^{2+} solution. Curves a and b represent the spectra recorded before and after Cd^{2+} exposure in the dry states. The set of curves in solid grey lines correspond to curve b – x(curve a) for values of x of 0.05, 0.1, 0.2, 0.3. The best value of x was estimated to be 0.1 (see text for details).

Chapter 2. Cadmium Ion Adsorption on Carboxyl-Terminated Iron Oxide Beads *

* This chapter is largely based on the paper by: Wu, J.; Sun, J.; Stefan, L. C.; Scherson, D. A. Journal of Physical Chemistry B **2004**, 108, 12276-12279.

2.1 ABSTRACT

The affinity of Cd^{2+} toward carboxyl-terminated iron oxide beads (C-TIOB, Sigma) suspended in aqueous solutions was investigated using anodic stripping voltammetry (ASV) as a function of both pH and $[Cd^{2+}]$ in the μ M range. Advantage was taken of the superparamagnetic character of C-TIOB to confine and/or remove the beads *within* the enclosed vessel, using an external magnet, and thus assess the influence of dispersed C-TIOB on the amount of Cd^{2+} detected by ASV. Within experimental error, the difference between ASV data recorded before and after adding and then confining the particles by magnetic means, which provides a measure of the amount of Cd^{2+} adsorbed on C-TIOB, was found to yield results comparable to those of identical measurements with fully dispersed C-TIOB. Adsorption data collected as a function of $[Cd^{2+}]$ and pH revealed a marked increase in the binding constant of Cd^{2+} for carboxylate ions upon attachment to the solid support, over values predicted strictly from standard solution phase equilibria.

2.2 INTRODUCTION

The binding of metal ions in solution to macromolecules and solid surfaces are of pivotal interest to a variety of disciplines ranging from biology to geology.¹⁻³ Such interactions involve, by and large, functional groups, as in the case of proteins,^{1,4,5} or specific surface sites, as in metal oxides and oxyhydroxides, particularly of iron and aluminum.^{6,7} Attention has been focused in our laboratory on the implementation of attenuated total reflection-Fourier transform infrared (ATR-FTIR) for the spectroscopic detection of metal-ion binding to self-assembled monolayers (SAM) incorporating alkane chains bearing carboxylic/carboxylate^{8,9} or pyridyl terminal groups.¹⁰ For those studies, SAM were formed spontaneously on the surface of a second alkane chain SAM exposing methyl terminal moieties at one end and covalently linked to the surface of a Ge internal reflection element (IRE) through siloxane groups at the other.^{8,9} Much of the effort has centered on the interactions of Cd^{2+} with such biomimetic analogues of cell membranes motivated in part by the adverse effects of this highly toxic metal ion on the nervous system, lungs, testis, pancreas and placenta in humans. Increases in the concentration of Cd²⁺ in the body have been traced primarily to cigarette smoking, ingestion of contaminated food, especially fish and grain and cereal products, and also occupational hazards, such as those derived from battery, metal coating and alloy industries.¹

The degree of environmental toxicity of Cd^{2+} and that of other heavy metal ions as well, is controlled by the thermodynamics and kinetics of adsorption on soil components, especially humic and fulvic acids, and hematite. In fact, the use of phosphatic fertilizers, and the settling of air borne industrial pollution have led to alarming increases in the amount of Cd^{2+} in certain agricultural land areas.³ Among the research strategies being pursued to assess the degree of contamination are direct measurements on actual soil using *ex situ* ICP-AE for Cd-content determination.²

This paper examines the affinity of Cd^{2+} for commercially available carboxylterminated iron oxide beads (C-TIOB, Sigma) in aqueous electrolytes as a function of pH and $[Cd^{2+}]$. These particles can be regarded as model systems for certain kinds of soil, and their systematic study could provide much needed insight into the underlying physicochemical bases that govern adsorption and release of metal ions from such complex particulate media. The concentration of solution phase Cd^{2+} was measured using anodic stripping voltammetry (ASV) and the amount of adsorbed Cd²⁺ was calculated from the difference between ASV data collected before and after placing the particles in contact with the solution. Measurements were performed both as a function of $[Cd^{2+}]$ in the μ M range at constant pH (= 7), and of pH at constant [Cd²⁺] (= 25 μ M). The effect of dispersed particles on the ASV data was explored by taking advantage of the superparamagnetic character of C-TIOB, which allowed for the particles to be manipulated within the enclosed vessel, including confinement and removal, using an external magnet. Such unique magnetic properties have been ingeniously exploited by the groups of Willner, Vandegrift and Heineman for electrocatalytic and immunoassay applications.¹¹⁻¹⁴

2.3 EXPERIMENTAL SECTION

The concentration of Cd^{2+} both in the absence and in the presence of suspended or magnetically confined C-TIOB in the solution was measured by ASV using a glassy carbon (GC) rotating disk electrode (RDE, Pine Instruments, disk area: 0.164 cm²) controlled by a Pine RDE 3 rotator. Potential control was achieved with a Potentiostat/ Galvanostat (RDE3, Pine Instruments). Unless otherwise specified, all measurements were performed in 50 mL of N₂-purged, 10 mM 4-morpholinepropane sulfonic acid (MOPS, Fisher, 98%) buffer, in 0.1M NaClO₄ (Aldrich, 99%) aqueous solutions prepared with ultrapure water (Millipore) containing Cd(ClO₄)₂ (Alfa, 99%) at a specified concentration. The solution pH, as measured with a Chemcadet pH meter, was adjusted by adding NaOH or HClO₄ at concentrations of 0.1 N for pH 4-6, and 1 N for pH 6-8. All values of [Cd²⁺] reported herein were corrected for changes in the volume (less than ca. 5%) induced by such additions.

The metal deposition step was performed at a constant rotation rate, $\omega = 2500$ rpm, for 60 s, with the RDE polarized at -1.0 V vs SCE, a potential negative enough for Cd²⁺ deposition to proceed under strict diffusion limited control. The rotation was then interrupted, and the potential immediately scanned at 5 mV/s in the positive direction up to 0.0 V vs SCE to strip the Cd metal deposits. Measurements of this type over a much wider [Cd²⁺] range were used to construct a calibration curve in the form of average deposition current, i_{ave}, i.e. integrated charge under the stripping peak divided by the total deposition time, i.e. 60 s, vs [Cd²⁺], yielding linear plots over the range 1 μ M - 0.6 mM (see open circles in Fig. 2-1).

Experiments involving Cd^{2+} adsorption were carried out by pipetting 1 mL of a C-TIOB suspension (Sigma, 240 µmol –COOH/g C-TIOB, 20 mg/mL in an aqueous suspension) under ultrasonic agitation. On this basis, this volume of suspension contains ca. 20 mg of particles which bear the equivalent of ca. 4.8 µmol –COOH. This aliquot was then placed in a cuvette and washed three times with pure water, using magnetic confinement (see below) and dispersion cycles, and then added as a wet powder to 50 mL of the buffer solution.

The extent of Cd^{2+} adsorption on C-TIOB (see below) as a function of $[Cd^{2+}]$ in the μ M range was determined at a single fixed pH (= 7) for a prescribed weight of particles in the solution, i.e. 20 mg, by adding small aliquots of Cd(ClO₄)₂ solutions, either 0.1M or 0.01M, so as not to affect the volume significantly. No changes in the ASV were found in measurements recorded in sequence in the same solution affording strong evidence that steady state adsorption is achieved very quickly.

The amount of Cd^{2+} adsorbed on the magnetic particles, $Q_{Cd^{2+}}$ in µmol Cd^{2+}/g C-TIOB was calculated from:

$$Q_{Cd^{2+}} = V([Cd^{2+}]_{in} - [Cd^{2+}]_{fin})$$

where V is the volume of the solution, and $[Cd^{2+}]_{in}$ and $[Cd^{2+}]_{fin}$ represent the concentration of Cd^{2+} in the media, determined from the i_{ave} ASV values, using the calibration curves in Fig. 2-1, before and after addition of C-TIOB to the medium, respectively.

Similar experiments were also carried out at a single $[Cd^{2+}]_{in}$ (= 25 µM) as a function of pH, both in ascending (pH 4 to 8.4) and descending order (pH 8.4 to 4).

2.4 ANALYTICAL CONSIDERATIONS

Several factors can complicate the interpretation of ASV data recorded in the presence of C-TIOB in the solution under the conditions employed in this work:

i. Hydrodynamic flow distortions induced by the dispersed particles during the metal deposition step.

- ii. Incorporation of particles into the metal deposits
- iii. Changes in the effective concentration of Cd²⁺ within the diffusion boundary layer of the RDE induced by dynamic equilibrium between Cd²⁺ adsorbed on the surface of the particles and in the solution phase, as thoroughly discussed in a more general context by van Leeuwen and coworkers.¹⁵⁻¹⁷

A series of experiments were designed to examine the extent to which these effects could affect the quantitative character of the data by taking advantage of the superparamagnetic properties of C-TIOB. First, ASV curves were recorded in 25 μ M [Cd²⁺] in 10 mM MOPS/0.1M NaClO₄ buffered (pH =7) solutions, both in the presence of 10 mg C-TIOB, and following their removal by filtration using a syringe-type arrangement (Disposable syringe filter, 0.45 μ m Gelman Sciences). As evidenced by the results obtained, the ASV curves (not shown in this work) were virtually superimposable, yielding integrated values differing by no more than ca. 3 %. The values of Q_{Cd²⁺} calculated from these data before (\mathbf{O}) and after (\mathbf{A}) filtration at ca. [Cd²⁺]_{fin} = 18.3 μ M are shown in Fig. 2-2. A discussion of error propagation will follow later in this section.

A variant of the experiment above was devised in which an external permanent magnet (NdFeB, Edmund Industrial Optics) was used to confine the particles <u>in</u> the solution and a new ASV recorded. The results obtained for 5 and 50 μ M Cd²⁺ solutions for 20 mg C-TIOB dispersed (D) and subsequently magnetically confined *in* the solution (MCi) are shown in the form of histograms in Panels A and B in Fig. 2-3, as either i_{ave} (left ordinate) or i_{ave} normalized by the value recorded before adding particles to the solution shown as bar F in this figure (see right ordinate). The confined particles were then removed from the solution by displacing the magnet along the walls of the vessel

and new ASV data collected and analyzed yielding the value displayed as MCo in the histogram. The overall procedure was then reversed by first bringing the confined particles into the solution (rMCi) and finally allowing them to redispersed by removing the magnet altogether (rD). As indicated in Fig. 2-3, i_{ave} was larger when the particles were dispersed in (see D and rD, in Fig. 2-3) than when removed magnetically from the solution (see MCo in the same figure). The average values of $Q_{Cd^{2+}}$ in the presence of particles (see \bigcirc in Fig. 2-2), based on D and rD in Fig. 2-3, were larger than those obtained from measurements in which the C-TIOB were confined outside the solution (see \square in Fig. 2-2) by 1.3% and 6.1% for $[Cd^{2+}]_{in} = 5$ and 50µM, respectively.

The relative error in
$$\frac{Q_{Cd^{2+}}}{V} = \alpha \frac{\sqrt{[Cd^{2+}]_{in}^2 + [Cd^{2+}]_{fin}^2}}{[Cd^{2+}]_{in} - [Cd^{2+}]_{fin}}$$
 increases with Cd^{2+}

concentration, where α is the (fixed) relative error in the concentration measurement. Assuming $\alpha = 5\%$, the relative error in $\frac{Q_{Cd^{2+}}}{V}$ for $[Cd^{2+}]_{in} = 50\mu M$ is 18.8% and thus much larger than that caused by the larger i_{ave} in the presence of the particles in the solution, i.e. 6.1 %, as discussed above.

In summary, ASV affords a versatile in situ means of determining reliable values of the extent of Cd^{2+} adsorption on dispersed C-TIOB. As will be shown in the next section, this method can be conveniently used to establish correlations between the amount of Cd^{2+} adsorbed on C-TIOB and $[Cd^{2+}]_{fin}$, elucidating the various factors that govern the interactions between the metal ion and the functionalized nanoparticles, including adsorption isotherms and the effect of pH.

2.5 RESULTS AND DISCUSSION

2.5.1 Effects of [Cd^{2^+}] - Shown in Fig. 2-1 is a log-log plot of i_{ave} as a function of $[Cd^{2^+}]_{in}$ up to 0.1 mM before (open circles) and after (solid circles) dispersing 20 mg C-TIOB in the solution, where • and • represent data obtained in two independent runs. As indicated, i_{ave} decreased upon addition of particles to the solution in the entire range of $[Cd^{2^+}]$ examined. This behavior is consistent with Cd^{2^+} adsorption on carboxylic groups on C-TIOB, and in line with that observations made on flat surfaces^{8,18} and other particulate media reported elsewhere.^{19,20} These results can be displayed in a more useful form in terms of $Q_{Cd^{2^-}}$ in µmol Cd^{2^+}/g C-TIOB (see left ordinate, Fig. 2-2), or alternatively in terms of mole ratio of adsorbed Cd^{2^+} to surface carboxylate/carboxylic groups (see right ordinate in the same figure) as a function of $[Cd^{2^+}]_{fin}$ for $[Cd^{2^+}]_{in}$ up to 70 µM (see • and • in this figure). At higher concentration, the error becomes very large (>20%) and therefore no data are given. It is interesting to note that the values on the right ordinate in Fig. 2-2 are still below 0.5, which corresponds formally to full electroneutrality, i.e. 1 Cd^{2^+} per 2 (–COO⁻).

In additional experiments, adsorbed Cd^{2+} on C-TIOB in equilibrium with $[Cd^{2+}]_{fin}$ either 0.48 or 30.1 μ M (see \bigcirc in Fig. 2-2) was confined <u>in</u> the solution with the external magnet and the liquid removed with a syringe. Subsequently, fresh buffer *without* Cd^{2+} was added to the vessel and ASV was recorded within several hours, while the particles were kept magnetically confined <u>in</u> the solution. As evidenced from the data (not shown here), the amount of Cd^{2+} detected even for the more concentrated solution was very small. However, upon removing the magnet to allow full particle dispersion, the resulting ASV yielded values of $[Cd^{2+}]_{fin}$ of 0.34 and 14 μ M (see \blacksquare in Fig. 2-2), respectively. As shown in the figure, these new points lie very close to the original adsorption curve; hence, to a good degree of approximation, and, within the concentration range examined, the adsorption process is reversible, and, therefore, that the data represents the adsorption isotherm. Unfortunately, the data appears too limited and the errors involved in the high concentration region are too large to warrant further analysis of the functional form of the adsorption isotherm. Other methods capable of measuring directly the amount of adsorbed metal would be required to provide more reliable values over a more extended concentration range.

2.5.2 Effect of Solution pH –A series of experiments were performed with $[Cd^{2+}]_{in} = 25$ μ M in 10 mM MOPS in 0.1M NaClO₄ (Aldrich, 99%) buffer solutions, both in the absence and presence of 20 mg of C-TIOB in the media, to determine changes in $[Cd^{2+}]$ (or, equivalently, in the amount of Cd^{2+} uptake) as a function of pH. As shown in solid squares in Fig. 2-4, the values of $[Cd^{2+}]$ derived from i_{ave} in the range 4 < pH < 8.5, in the absence of C-TIOB, normalized by the average of the six data points, $[Cd^{2+}]_{ave}$, were found to be fairly independent of pH. Corresponding values for $[Cd^{2+}]_{fin}$ determined in the presence of dispersed C-TIOB normalized by $[Cd^{2+}]_{ave}$ (open and solid circles in Fig. 2-4) were much lower, i.e. > 20% over the entire pH region, consistent with the binding of Cd^{2+} to the particles. As indicated, the normalized $[Cd^{2+}]$ data collected first in descending (filled circles) starting at pH 8.3, and then in ascending (see open circles) pH, yielded in this case a plateau for 4.1 < pH < ca. 5.5, followed by a steady decrease as the pH increased. Also noteworthy is the fact that the values observed were fairly independent on whether the pH was increased or decreased. However, excursions to much lower pH values, e.g. 3, led to a loss of adsorption efficiency (not shown in this figure), probably caused by the onset of dissolution of hematite (and thus of surfactant) into the media.

This overall behavior can be rationalized, at least, qualitatively based on solution phase equilibria, by assuming pK_a (for the surface carboxylic acid) of ca. 8, and a metalcarboxylate complexation constant pK = 5 (see solid line in Fig. 2-5). Both these values are ca. 3 units higher than those reported for free carboxylic monoacids, and also for the Cd²⁺ acetate complex in solution phase.²¹ Such an upward shift in pK_a has been well documented for alkane-type SAM bearing carboxylic groups (and other surfaces as well),^{9,22} and attributed, at least in part, to the increased proton affinity of the ensemble of closely packed negatively charged carboxylate groups.^{22,23} Based on these considerations, the same effect would be expected to occur for metal ion binding, as evidenced by the much lower value of the complexation constant of Cd²⁺ with acetate (logK = 1.61 and 1.07) compared to oxalate (logK = 3.71).²¹

The composition of the solutions that could best simulate the results obtained for the metal surface adsorption on C-TIOB was determined by solving the appropriate set of non-linear algebraic equations that describe the various equilibria and mass balance conditions using Mathematica. Four equations were required for Cd^{2+} complexation at different pH. Best fits to the experimentally observed surface complexation were obtained by adjusting the acidity constant, K_a and the complexation constant of Cdcarboxylate, K_{ML}, *or* the formality of the corresponding carboxylic acid, i.e.

$$M + L \leftrightarrow ML, \quad K_{ML} \qquad (1)$$
$$HL \leftrightarrow H + L, \quad K_a \qquad (2)$$

$$F(M) = [M] + [ML]$$
(3)
$$F(L) = [L] + [ML] + [HL]$$
(4)

where the charges of the various species have been omitted for clarity.

In this case, Eq.(1) above must be replaced by a two-step complexation for Cd acetate, which were assumed to be the same as those reported in the literature .

The results of the simulation, shown in Fig. 2-4, point to extraordinary enhancements in the affinity of carboxylate for Cd^{2+} (and numerous other metal ions as well) induced by surface immobilization at the high coverage levels involved in C-TIOB. This effect is best illustrated by calculating the extent of complexation in homogeneous solutions containing carboxylate/carboxylic groups at the same equivalent concentration as that used in the experiments, i.e. 20 mg C-TIOB x 240 nmol COOH/COO⁻ per mg, or 4.8 x 10⁻⁶ mol/0.05 L = 96 μ F (microformal), and the same concentration of cadmium, i.e. 25 μ F.

Based on the above simulation, hardly any Cd^{2+} (< 0.5%) will be complexed by carboxylate for solutions 4 < pH < 9. In fact, in order to promote binding to the level found for the carboxyl-bearing particles, the concentration of COOH/COO⁻ groups in the solution would have to be raised by at least 3 orders of magnitude (see dotted line in Fig. 2-4).

One possible explanation for the lower (normalized) $[Cd^{2+}]_{fin}$ measured in the plateau region (blank circles), i.e. ca. 20%, compared to solutions devoid of particles (see solid squares in Fig. 2-4), may be found in the presence of specific sites on the surface displaying high affinity for Cd^{2+} , which become saturated in the entire pH region examined for $[Cd^{2+}]$ at which these experiments were performed. Some evidence in

support of this view has been provided by Scoles et al. who studied Cd^{2+} adsorption on SAM bearing carboxylic terminal groups supported on Au,²⁰ where adsorption of the metal ion was either found to be irreversible, or showed large hysteresis when the pH value was decreased. In fact, in their studies, the presence of adsorbed Cd^{2+} on SAM could be verified from *ex situ* X-ray measurements of films removed from the solution and could only be eliminated by washing with a 0.01 M solution of HNO₃.

2.6 CONCLUSIONS

The most salient aspects of the work herein described may be summarized as follows:

- 1. Confinement of carboxylic/carboxylate groups at rather high coverages, i.e. ca. 0.1 nmol/cm², to surfaces of the type examined in this work, promotes the reversible binding of solution phase Cd^{2+} in aqueous electrolytes. This phenomenon is conceptually analogous to the upward shift in pK_a for carboxyl terminated surfaces, compared to those found in solution phase, and thus consistent with an increase in the *effective* metalligand complexation constant for the heterogeneous system.
- 2. Within the limitations specified above, *in situ* ASV may be regarded as being sensitive only to solution phase species, and, thus, offers a number of advantages over alternate *ex situ* techniques reported in the literature.

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Fig. 2-1 Log-log plots of i_{ave} as a function of $[Cd^{2+}]$ in recorded in the absence (\circ) and presence (\bullet , \bullet) of 20 mg C-TIOB particles in 0.1M NaClO₄ in 10 mM MOPS buffer solutions at pH = 7 (see text for details). The symbols \bullet and \bullet represent data obtained in two independent runs.



Fig. 2-2 Plots of Q_{Cd}^{2+} as a function of $[Cd^{2+}]_{fin}$ in 0.1M NaClO₄ in 10 mM MOPS buffer solutions at pH = 7 in the presence of 20 mg C-TIOB. Also shown in this figure are the data in the form of the mole ratio of adsorbed Cd^{2+} to surface carboxylic groups (see right ordinate). The symbols • and • represent data obtained in two independent runs as indicated in Fig. 2-1, and the lines through them are simple best fits (using splines) to these sets. Other symbols are explained in the text.



Fig. 2-3 Histograms of i_{ave} for 5 µM (Panel A) and 50 µM (Panel B) Cd²⁺ in 0.1M NaClO₄ in 10 mM MOPS buffer solutions at pH = 7 before (F) and after adding 20 mg C-TIOB into the solution, for the particles dispersed (D), magnetically confined in the solution (MCi), removed from the solution, by displacing the magnet along the walls of the vessel (MCo), reintroduced into the solution (rMCi) and finally redispersed by removing the magnet (rD). The right ordinate represents the same data normalized by i_{ave} before adding 20 mg C-TIOB particles into the solution (F).



Fig. 2-4 Plots of normalized $[Cd^{2+}]_{fin}$ in solution as a function of pH for 25 μ M Cd(ClO₄)₂ in 0.1M NaClO₄/10 mM MOPS solutions in the absence (solid squares) and the presence of 20 mg C-TIOB recorded for decreasing (solid circles) starting at pH 8.3 and subsequently for increasing pH (open circles). The solid line in this figure was obtained from a simulation involving solution phase species (no particles) containing 96 μ F (micro formal) of a carboxylic acid with pK_a = 8.00, and a metal-carboxylate binding constant of 10⁵. The dotted line in this figure represents the results of yet another simulation for a solution containing the same amount of Cd²⁺ and a concentration of acetate of ca. 96 mF (see text for details).

Chapter 3 Metal-Ion Adsorption on Carboxyl-Bearing Self-Assembled Monolayers

Covalently Bound to Magnetic Nanoparticles *

* This chapter is largely based on the paper by: Hai, B.; Wu, J.; Chen, X. F.; Protasiewicz, J. D.; Scherson, D. A. Langmuir **2005**, 21, 3104-3105.

3.1 ABSTRACT

Hematite nanoparticles have been functionalized with a self-assembled monolayer of undecanoic acid (UA) by covalent attachment via siloxane groups. The number density of carboxylic/carboxylate groups on the surface was determined by titration yielding values on the order of 10^{14} UA molecules/cm² and thus consistent with a closed-packed monolayer. The ability of these functionalized particles to adsorb Cd²⁺ in the ppm range was demonstrated using *in situ* anodic stripping voltammetry.

3.2 INTRODUCTION

Self-assembled monolayers (SAM) supported on solid substrates continue to attract much interest in such diverse areas as biosensors, paint technology, magnetic fluids, metal recovery, and pollution abatement.¹⁻⁷ Attention has been focused in recent years on the preparation and characterization of SAM bearing a growing variety of functional groups on particles of characteristic dimensions in the sub-µm range.^{3,8,9} In addition to large surface to volume ratios, materials in a highly divided form have been shown to exhibit unique optical and magnetic properties.^{6,10} In particular, nanoparticles of well-known paramagnetic substances display superparamagnetism, i.e. turn magnetic only when placed in an external magnetic field. This effect has opened new prospects for the development of novel separation and confinement strategies, as illustrated by the work of the groups of Willner^{11,12} and Vandegrift^{13,14} in the areas of magneto-switchable electrocatalysis and magnetically-assisted separations, respectively.

This paper describes procedures for the preparation and characterization of welldefined, 11-undecanoic acid SAM bearing carboxyl (external) terminal groups, covalently-bound through siloxane groups to commercial superparamagnetic maghemite particles. The synthetic approach relies on the hydrolysis of chlorosilane functionalized species on the partially hydroxylated oxide surface, leading to the formation of a polymeric network of siloxane chains bound to the underlying substrate. The same strategy was introduced by Sukenik and coworkers for the functionalization of both flat and highly curved surfaces.^{3,15,16} Evidence for the closed-packed nature of the SAM examined in this work was obtained by direct titration of suspensions in aqueous solutions, following the methods reported by Winnik and coworkers for carboxylfunctionalized polymeric spheres.¹⁷ Furthermore, quantitative information regarding the affinity of these SAM for Cd^{2+} ions in aqueous solutions was obtained from anodic stripping voltammetry as an analytical tool for *in situ*, i.e. in the presence of dispersed particles, detection of solution phase Cd^{2+} .

3.3 EXPERIMENTAL SECTION

3.3.1 Synthesis of 11-(Trichlorosilyl) undecanoyl chloride (TUC) (*This synthesis was done by Bin Hai in our group.*)

Our procedure is largely adapted from that reported earlier,¹⁵ but, for convenience, details are given here. In a N₂-filled glovebag, 5 mL HSiCl₃ (49.5mmol, Aldrich, 99%), 0.87 mL (4.06 mmol) 10-undecenoyl chloride (98%, Acros Organics), 0.1 mL 4% H₂PtCl₆·6H₂O (\geq 37.5% as Pt, Aldrich) in isopropanol (99.9% Aldrich) solution, and a magnetic stirring bar were placed in sequence into a 30 mL pressure tube. The tube was then sealed, transferred into a 60-65 °C oil bath, and heated for 16 hours. After the reaction was complete, as signaled by the disappearance of the olefinic protons of the starting material in the ¹H-NMR spectrum of reaction aliquots, the contents of the tube were transferred into a 15 mL round-bottom flask in a N₂-filled glovebag. The remaining HSiCl₃ was removed under vacuum at room temperature and the title product isolated by Kugelrohr distillation at 145-155°C and 1 mm Hg. Yield: 0.3377 g (25%). NMR and IR spectroscopic data for the pure TUC product were in accord with corresponding data reported previously.

3.3.2 Preparation of 11-Undecanoic acid-Functionalized Hematite (11-UA-γ-Fe₂O₃)

To a 250 mL flask containing 100 mL heptane, were added 0.2 mmol TUC, followed by 310 mg γ -Fe₂O₃ (99+%, Alfa Aesar) and the mixture subsequently agitated in an

ultrasonic bath for 2h, while circulating water to keep the medium at room temperature. The 11-UC- γ -Fe₂O₃ particles were then spatially confined using a magnet and the heptane solution and excess surfactant were decanted. After two subsequent washings with neat heptane, the particles were dispersed in dilute NaOH (pH = 9-10) three times to afford the carboxyl terminated particles, i.e. 11-UA- γ -Fe₂O₃, by hydrolysis of the acid chloride groups, as free flowing powder.

3.3.3 Determination of 11-UC Coverage

The surface density of carboxylic groups on the 11-UC- γ -Fe₂O₃ particles was determined by titration before and after addition of ca. 20 mg 11-UC- γ -Fe₂O₃ particles to thoroughly and continuously dearated (N₂), well-stirred solutions (magnetic bar) prepared by mixing 8 mL NaOH (9.13 mM) with 50 mL water in a three-neck 100 mL flask. The NaOH concentration was determined using a solution of HCl standardized (9.78 mM) with sodium carbonate (ACS certified, 99.8%). Solutions were purged with N₂ for at least one hour prior to titration with HCl. pH readings were made with a pH electrode (Chemcadet, Model 5984-50) immersed in the solution following addition of HCl aliquots from a regular buret.

3.3.4 Adsorption of Cd²⁺ on 11-UC-γ-Fe₂O₃

The extent of Cd^{2+} adsorption on 11-UC- γ -Fe₂O₃ particles was determined by anodic stripping voltammetry at room temperature using a glassy carbon (GC) rotating disk electrode (RDE, Pine Instruments) in a 100 mL three-neck round bottom flask. The deposition step was performed with the RDE rotating at 2500 rpm for 60 s, at which point the rotation was stopped, and the potential then scanned linearly between -1.0 and 0.0 V vs SCE at a rate of 5 mV/s. Experiments were carried out in thoroughly and continuously purged solutions of 10 mM 4-morpholinepropane sulfonic acid (MOPS, Na salt, 98%, Acros Organics) buffer (pH 7 adjusted with 1 M HClO₄) containing Cd²⁺ in the range 1 μ M \leq [Cd²⁺] \leq 0.8 mM. The latter solutions were prepared by adding appropriate amounts of 10⁻³ M, 10⁻² M or 10⁻¹ M Cd(ClO₄)₂ in 0.1 M NaClO₄ (99%+, Aldrich), first in the absence and then in the presence of 10 – 25 mg 11-UC- γ -Fe₂O₃. The results of these experiments made it possible to calculate the amount of Cd²⁺ adsorbed on 11-UC- γ -Fe₂O₃ as a function of [Cd²⁺] by difference, from which the adsorption isotherm could be constructed.

3.4 RESULTS AND DISCUSSION

Shown in Fig. 3-1, are titration curves of a 9.13 mM NaOH solution obtained in the absence (open circles) and in the presence of 20.4 mg 11-UC- γ -Fe₂O₃ particles (solid circles). The region about the inflection points is given in expanded form in the insert. As clearly indicated in the figure, addition of the superparamagnetic particles yielded two well-defined inflection points (V₁ = 7.64 mL, pH₁ = 7.2, and V₂ = 8.04 mL, pH₂ = 5.08, as determined from quantitative calculations), as opposed to one for the neat NaOH solution (V_o = 7.76 mL, pH = 6.32). On this basis, the volume consumed by titration of the functional groups amounts to V₂ – V₁ = 0.4 mL, from which the total amount of surface carboxylate is estimated to be 9.78 x 0.4 (ca. 3.9 µmol) or ca. 1.9 x 10⁻⁴ mol carboxylate/g 11-UC- γ -Fe₂O₃ particles. In a duplicate experiment involving 15.4 mg 11-UC- γ -Fe₂O₃ the value obtained was 2.1 x 10⁻⁴ mol carboxylate/g UC- γ -Fe₂O₃ particles, i.e. within 10%. Based on the average γ -Fe₂O₃ particle diameter reported by the manufacturer, i.e. 20-30 nm, the surface density of carboxylate groups determined from

our titration measurements, ca. 10^{14} molecules/cm², is of the same order of magnitude as that of closed-packed alkane chains SAM on solid supports reported in the literature.¹⁸

Plots of Q (see left ordinate) vs $[Cd^{2+}]_{fin}$, where Q is the amount of adsorbed Cd^{2+} in mmol per g of 11-UC- γ -Fe₂O₃ over the range, $1 \leq [Cd^{2+}]_{fin} \leq 70 \ \mu$ M, recorded in 10 mM MOPS buffer (pH = 7) containing 20 mg 11-UC- γ -Fe₂O₃ particles are shown in Fig. 3-2, where $[Cd^{2+}]_{fin}$ represent the final concentration of Cd^{2+} in the solution. The open and solid circles in Fig. 3-2 represent data obtained in two separate trials. The same data, but in terms of mole ratio of adsorbed Cd^{2+} /surface carboxylic groups vs $[Cd^{2+}]_{fin}$ are given in the right ordinate in this figure. Based on these results, the last point in this plot is close to 0.5, which corresponds to full charge balance, $1(Cd^{2+})/2(-COOH)$. Unfortunately, the relative error in Q (= V($[Cd^{2+}]_{in} - [Cd^{2+}]_{fin})$), where V is the total volume of the solution and $[Cd^{2+}]_{in}$ represent the initial concentration of Cd^{2+} in the solution, increases with Cd^{2+} concentration. More specifically, the relative error of Q/V is inversely proportional to $([Cd^{2+}]_{in} - [Cd^{2+}]_{fin})$, assuming the relative error in the concentration measurement is fixed, e.g. 5%.

The synthetic approach outlined in this report, while specific to yielding carboxylfunctionalized particles, lends itself to a much greater range of functionality, and, hence, a greater range of applications than the capture of cadmium ions. For example, it has been shown previously that both bromo- and cyano-substituted analogues (11-UBr and 11-UCN) are as readily prepared as 11-U-C(O)Cl.¹⁹ Having in hand these two materials, the functionalities accessible are nearly endless. In particular, amine, polymamine, amide, and phosphine fuctionalities can expand the repertoire of metals ions that could be sequestered. Conversion of 11-UC-Br to more complicated functional groups could render elements of molecular recognition to the nanoparticles. These areas are under current investigation.

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Fig. 3-1 Titration curve of a 9.13 mM NaOH aqueous solution in the presence (solid circles) and in the absence (open circles) of 20 mg of UC- γ -Fe₂O₃ particles (see text) using an HCl solution (standardized with Na₂CO₃) as a titrant. Insert: Expanded region of the titration curve around the inflection points, where the arrows point to the end points.



Fig. 3-2 Plots of Q (see left ordinate) vs $[Cd^{2+}]_{fin}$, where Q is the amount of adsorbed Cd^{2+} in mmol per g of 11-UC- γ -Fe₂O₃ vs $[Cd^{2+}]_{fin}$ for 0.1 M NaClO₄ in 10 mM MOPS buffer solutions at pH = 7 containing 20 mg 11-UC- γ -Fe₂O₃ particles. The right ordinate gives the same information in terms of mole ratio of adsorbed Cd^{2+} /surface carboxylic groups. The open and solid circles represent data collected in two separate trials.

Chapter 4 Photoelectrochemistry of taC:N film Coated Semiconductor Electrodes

4.1 ABSTRACT

Tetrahedral amorphous carbon containing nitrogen (taC:N) films have been deposited on semiconductor (SC) electrodes (n-GaAs, n-CdS, n-CdSe) using an ion-filtered cathodic vacuum arc (FCVA) carbon source under high vacuum. The electrochemical properties of the resulting specimens denoted generically as taC:N|SC were studied in ferro/ferricyanide aqueous solutions in dark and under illumination. Whereas the particular bare SC electrodes were found to undergo corrosion under illumination in neutral solutions, the corresponding taC:N|SC counterparts did show protection, albeit limited, against surface degradation for all SC examined. Depending on the specific SC, the taC:N|SC junctions were found to be rectifying or ohmic. In the case of n-GaAs in neutral $Fe(CN)_6^{4-}$ solution, junctions were initially rectifying and developed photovoltages of several hundred millivolts. Further, the photocurrent and the photovoltage of taC:N|n-GaAs were proportional to the intensity and to the logarithm of the intensity of illumination, P (mW/cm^2), respectively. The deposition conditions, including triggering times, substrate bias and partial pressure of nitrogen in the chamber were found to influence markedly the properties of the resulting taC:N|SC films. The extent of photocorrosion protection under illumination was determined for taC:N|n-GaAs prepared under different deposition conditions by holding the potential at 0.4V vs. Ag/AgCl in 2mM ferrocyanide/1M KCl solution. Unfortunately, none of the taC:N|n-GaAs specimens examined showed protection against photocorrosion in 0.1M NaOH alkaline solution, an effect ascribed to the presence of pinholes or defects in the taC:N films. Until a sufficiently uniform film of taC:N on n-GaAs can be grown to protect the surface against photocorrosion in alkali, a definitive claim for a n-GaAs $|aC:N|Fe(CN_{16}^{-3/-4})|$

photoanode cannot be made. However, the results in neutral solution where the pores are not so readily attacked, are strong evidence for this conclusion.

4.2 INTRODUCTION

The study of the photoelectrochemical properties of semiconductor (SC) electrodes is of great interest to the field of solar energy conversion into electricity, either by direct light to electrical power generation,¹⁻³ or through the medium of photoelectrolysis to useful chemicals, such as hydrogen, that may subsequently be used to power for example a fuel cell.^{4, 5} Two major strategies have been examined toward implementation of these concepts: the coupling of a conventional solar cell to an electrolyzer, or an integrated method using the photovoltaic SC as an electrode immersed in an aqueous electrolyte which participates in an electrochemical reaction.^{4, 6} A severe limitation to any SC photoelectrochemical cell in aqueous electrolytes, either a photovoltaic cell generating electricity or a photosynthetic cell producing a net chemical conversion, is the competing photocorrosion of the SC electrode, which can eventually destroy the SC electrode.⁷⁻¹⁰ In particular, the photocorrosion of n-GaAs involves generation of holes upon illumination to yield a Ga(III) and As(III) containing oxide film in neutral media, which passivates the surface for a short time or to soluble products in alkaline solution without any protection.¹⁰ Metal coatings have been considered as protective layers for GaAs, but films thick enough to prevent substrate exposure have only limited transparency in the visible range.^{11, 12} In some cases, such as n-GaAs/Au, the photojunction is a solid state one and the electrolytic reaction has only a contacting function. GaAs can also be passivated in sulfide/selenide solution forming a spontaneously protective layer thereby avoiding the need of using additional coverage.¹³⁻¹⁵ From a general perspective, a good protective coating for SC electrodes should be light transparent, electrically conductive and chemically inert. Tetrahedral amorphous carbon containing nitrogen films (taC:N) has

emerged as a good candidate meeting all these requirements. This material is a diamondlike, tens of nanometers thick, faintly yellowish film of low absorption over the visible spectrum. It contains a high percentage (80-88%) of sp³ – hybridized carbon sites, offering excellent chemical resistance and a very wide electrochemical window in aqueous electrolytes.^{16, 17} The incorporation of nitrogen into the films to ca. 10 at.% has been found to yield films ca. 30-70 nm thick, with resistivities of ca. 10 Ω cm.^{16, 17} All these properties makes taC:N a possibly ideal SC electrode coating for photoelectrochemical cell applications. The deposition of taC:N as implemented in our laboratories relies on the use of a commercial ion-filtered cathodic vacuum arc (FCVA) carbon source operating under reduced nitrogen pressures in a high vacuum chamber at room temperature. The ability to grow relatively smooth films taC:N at ambient temperature on virtually any substrate make sit particularly advantageous over borondoped diamond films which contrastingly requires high substrate temperature and yield very rough deposits.

The nature of the taC:N|SC junction itself will modify the resulting electrolyte redox system results, and it is only known so far that on n-Si, either ohmic or rectifying junctions result under different preparation conditions. No data exist for the semiconductors examined here.

The principal objective of the work presented in this chapter was to develop and implement procedures for the deposition and subsequent characterization of tetrahedrally coordinated amorphous nitrogen-containing carbon films (taC:N) on a few selected semiconductor (SC) substrates. Of particular interest was to examine the factors that

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control whether a taC:N|SC junction is ohmic, i.e. no photoeffects (A), or rectifying (B), i.e. capable of photovoltage effects.

4.3 EXPERIMENTAL SECTION

4.3.1 Preparation of taC:N film

The taC:N films were prepared in a high vacuum chamber under a base pressure in the range of $2x10^{-8}$ to $1x10^{-7}$ torr, using a commercial FCVA carbon ion source (RHK Arc 20) shown schematically in Fig. 4-1. The carbon plasma was produced from the arc spot on a graphite (Alfa, 99.9995%) cathode in 0.125" diameter. A curved magnetic filter was used to eliminate plasma contamination by macro-particles and neutral atoms. The triggering rate was 0.5Hz with the trigger and arc voltage 21KV and 400V, respectively. The nitrogen content of the films could be varied by adjusting the partial pressure of N_2 in the deposition chamber with a leak valve and an ion gauge. Films prepared under different N₂ pressures in the range $5x10^{-5}$ to $2x10^{-2}$ torr were studied in our work. The thickness of the films could be varied by reducing or increasing the number of arcs in the range 500-5000. Typical bias applied to the substrate was -80eV unless specified. Ta, n-GaAs (100) (Silicon doped), n-CdS (1.1 Ω cm) and n-CdSe (1 Ω cm) were used as deposition substrates. Before deposition, all substrates were etched with 1M HCl and washed with water, acetone and isopropanol. Ohmic contacts to the back of the SC were achieved by coating gemanium-gold alloy for GaAs or pasting indium/gallium eutectic for n-CdS and n-CdSe.

4.3.2 Photoelectrochemical testing

The taC:N|SC electrode was sealed under compression in a custom made cell exposing an area of 0.0754cm² to the electrolyte solution. Electrochemical and

photoelectrochemical measurements were performed both in the dark and also under illumination using a He-Ne (632.8nm) or an Ar-ion laser (457-514nm) (Fig 4-2) in 2mM/50mM ferrocyanide or in 1mM ferro/ferricyanide neutral solution (1M KCl) using Ag/AgCl in neutral and SCE in neutral and alkaline solution (0.1M NaOH) as reference electrodes. Photopotentials were determined by measuring the potential of taC:N|SC electrodes under illumination vs a Au foil immersed in the same solution (1mM ferro/ferricyanide in 1M KCl). The stability of taC:N|SC was investigated in 2mM ferrocyanide/1M KCl solution by holding the potential at 0.4V vs. Ag/AgCl and monitoring the current under laser illumination as a function of time. Ideally the current would be limited by ferrocyanide diffusion at these light intensities, but increases as GaAs photocorrosion dominates.

4.3.3 Morphological Characterization of taC:N films

The thickness of taC:N film on quartz following 2500 arcs deposition measured with a Dektak profilometer was ca. 70 nm. The AFM images were obtained using a Nanoscope II AFM system with MikroMasch Ultrasharp tips.

4.4 RESULTS AND DISCUSSION

4.4.1 Electrochemical and Photoelectrochemical Behavior of taC:N junctions involving various substrates.

Evidence for the protective nature of taC:N films was obtained from experiments involving metallic Ta as a substrate, a metal known to form a passivating oxide layer in aqueous solutions over a wide pH range that displays highly insulating properties.¹⁶ Unlike the behavior found for bare Ta in 2mM ferrocyanide/1M KCl and

Ru(NH₃)₆Cl₃/1MKCl aqueous solutions, for which hardly any current could be detected, taC:N|Ta junctions exhibited reversible behavior for the two redox couples akin to that found for genuine metal electrodes without photoeffects, and thereby consistent with that expected for an ohmic junction.

Three different semiconducting substrates were selected for studies of taC:N|SC junctions: n-GaAs (1.4 eV), n-CdSe (1.7 eV) and n-CdS (2.4 eV), where the value in parenthesis is the band gap.^{6, 18} Specimens were illuminated with a He-Ne laser (632.8nm, 1.96eV) for n-GaAs and n-CdSe, and an Ar-ion laser (457-514nm, 2.42-2.7eV) for the larger band gap n-CdS.

Bare SC surfaces

Shown in the upper panels, Fig. 4-3, are cyclic voltammetry curves recorded for the three bare SC materials in 2mM ferrocyanide/1M KCl in the dark and under laser illumination. As clearly evident from these results, the voltammetric curves obtained in the dark are virtually featureless in the anodic current region over the potential range examined for all three n-type SC. This observation is consistent with the fact that n-type SC can only promote reduction, since electrons are the majority carriers. Upon illumination, all specimens displayed a large positive photocurrent and a negative shift of the zero-current potential, or photopotential, due to anodic photocorrosion. The most reasonable reactions associated with this process may be written as follows:^{9, 10, 19}

 $n-GaAs + 6h^+ \rightarrow Ga(III) + As(III)$

 $n-CdS + 2h^+ \rightarrow Cd(II) + S(0)$

 $n-CdSe + 2h^+ \rightarrow Cd(II) + Se(0)$

where h^+ represents the holes from the illuminated light.

Over time, the photocorrosion process appears to reach steady state, as signaled by the rather reproducible response found upon repeated cycling. The highest photopotential was observed for n-CdS. Even in the presence of $[Fe(CN)_6]^{4-}$ in neutral solutions (see below), photocorrosion eventually dominates over the competing oxidation of $[Fe(CN)_6]^{4-}$. As previously shown for n-GaAs in alkaline solutions, essentially all of the absorbed photons are consumed by the corrosion reaction with no evidence for oxidation of $[Fe(CN)_6]^{4-}$. ^{10, 20}

taC:N|SC Junctions

a. Behavior in the dark The electrochemical behavior of taC:N|SC in 2mM ferrocyanide/1M KCl in the dark and under illumination were found to differ for the three SC examined (see lower panels, Fig. 4-3). The currents observed for taC:N|n-GaAs (left panel) and taC:N|n-CdS (middle panel) were found to be flat in the dark, except for only a small cathodic peak attributed to the reduction of some $[Fe(CN)_6]^{3-}$ formed by leakage current during the positive potential going scan. The taC:N|n-CdSe specimen (right panel) displayed a reversible redox wave even in the dark, without evidence for a photopotential. The junctuion shows ohmic behavior like most made with cleaned Si surfaces. Such a lack of a photo-effect was also observed for some taC:N|p-Si sample prepared by the group in Singapore.

b. Behavior under illumination - The taC:N|n-GaAs junctions (left panel) were found to be clearly rectifying, as evidenced by the observed photovoltage and the oxidation peak of $[Fe(CN)_6]^{4-}$. More detailed aspects of the overall photoelectrochemical behavior of this specific junction will be given in the next section. In the case of taC:N|n-CdS, (see middle panel) a photoinduced oxidation wave was seen but no photopotential was detected. This combination is novel to our experience with taC:N films. We do not have a reasonable explanation for this phenomenon at this stage. Finally, taC:N|n-CdSe behaved similarly to most films on clean Si in that its behavior was virtually identical in the dark and also under illumination, no photoeffect. Such properties are characteristics of an ohmic junction and not unlike those found for the genuine ohmic junction to clean metals as found with taC:N|Ta. A comparison of all three junctions under illumination including taC:N|Ta is given in Fig. 4-4. Both taC:N|n-CdS and taC:N|n-CdSe were found to undergo rather rapid photocorrosion under illumination as judged by the increase of the anodic photocurrent (dotted line, middle and right panel B in fig. 4-4) and by visual inspection.

4.4.2 Photocurrent and photopotential of taC:N|n-GaAs

The effects of light intensity on the photocurrent and photopotential were examined in detail using taC:N|n-GaAs specimens. Shown in Fig 4-5 are cyclic voltammograms of taC:N|n-GaAs in a 2mM ferrocyanide/1M KCl solution in the dark and under illumination as a function of light intensity. Also given in this same figure is the cyclic voltammetry of a Pt electrode in the same solution for comparison. A negative potential shift of about 0.2V was seen for the taC:N|n-GaAs vs. Pt. Under high light flux corresponding to current densities above solution diffusion limits, the net peak current densities for Pt and the taC:N coated electrode are similar, as expected for a protected semiconductor. Under very low light intensity (< 0.75mW/cm²), the anodic current was limited by the amount of injected photons and therefore no peak was clearly discerned. As the light intensity was increased to achieve net photon flux above the limiting current,

an oxidation peak was obtained. Above this light intensity (> 8mW/cm²), the redox peak remained unchanged as would be expected for redox diffusion control.

The dependence of the photocurrent on the light intensity is better illustrated by the results obtained in concentrated 50mM ferrocyanide/1M KCl solution (see Fig. 4-6) both in the dark and under illumination as a function of light intensity P (mW/cm²), where the anodic limiting current is always controlled by the flux of injected photons, P. As indicated, the limiting current increases linearly with P, as shown in the insert in this figure. For P > 8 mW/cm², the limiting current reaches a saturation and mass transport of the redox species in solution becomes predominant.

A plot of the open circuit photopotential of taC:N|n-GaAs in 1 mM ferro/ferricyanide/1M KCl vs a gold electrode in the same solution as a function of logP (see Fig. 4-7) yielded a straight line. The photopotential, E_{ph} , follows the expected behavior ⁶

$$E_{ph} = \frac{nKT}{e} \ln \frac{j_{ph} + J_0}{J_0}$$

In this equation, J_o is the dark current, and j_{ph} is the anodic photocurrent. When j_{ph} is much larger than J_0 , the photopotential E_{ph} is proportional to $logj_{ph}$. Since j_{ph} is proportional to P, a plot of E_{ph} vs. logP should be linear. This was in agreement with the experimental results shown in Fig. 4-7.

4.4.3 Stability of taC:N|n-GaAs

4.4.3.1 Photocorrosion in alkaline solution

Despite the apparent stability displayed by taC:N|n-GaAs in neutral (1M KCl) solution as evidenced by the reproducible character of the cyclic voltammetry obtained

under illumination at different intensities, the junction did not perform as well in alkaline solutions, a much more aggressive media than neutral pH. As shown in Fig 4-8 the cyclic voltammogram of taC:N/n-GaAs in 2mM K₄Fe(CN)₆/0.1M NaOH in the dark and under irradiation were consistent with corrosion of the junction. The corrosion occurs even in the dark as evidenced by the anodic current and the negative shift of the zero-current potential crossing point relative to that of Pt electrode at the same solution. The most likely explanation for this behavior may be found in the present of pinholes in the structure that expose the underlying semiconductor to the electrolyte solution leading to the formation of soluble species such as GaAs to soluble species, ie. Ga(OH)₄ and AsO₂. In neutral solutions, the less soluble oxide layer is capable of protecting at least momentarily the pinhole areas thereby imparting the specimen higher stability. Nevertheless, the junctions ultimately fail by undercutting. It may thus be concluded, that methods that avoid pin holes, either during preparation or subsequent chemistry, will be required to render viable junctions without photocorrosion. A series of preliminary studies were conducted in order to examine the influence of deposition factors on the properties of the resulting junctions, including film thickness, pressure of N2, bias applied to the substrate, which may be expected to affect the internal stress of the films, and thus the adhesion of the taC:N films to the underlying substrate. The results obtained are given in the section to follow.

4.4.3.2 Effect of preparation conditions on the stability to taC:N|n-GaAs.

a. Nitrogen partial pressure. As is well known the nitrogen content in the films is controlled by the partial pressure of N_2 in the chamber, which in turn affects the sp³/sp² carbon ratio and the internal stress of the film.²¹⁻²³ More specifically, ²² the fraction of sp²

carbon increases with an increase in the N₂ partial pressure, P_N. Studies have indicated first, that for $P_N > 1x10^{-4}$ torr, the ratio of sp^3/sp^2 carbon decreases much faster than for $P_N < 1x10^{-4}$ torr, and, second, that the incorporation of nitrogen in the film results in a decrease of the internal stress of the film, making the film more adhesive.

Samples a through d (see table 4-1) were prepared under a P_N in the range $0 < P_N$ $< 2x10^{-2}$ torr and the stability of the resulting taC:N|n-GaAs junctions compared in 2mM K₄Fe(CN)₆/1M KCl solutions under strong illumination (12mW/cm²) by holding the potential at 0.4 V vs. Ag/AgCl, a value at which photooxidation of solution phase [Fe(CN)₆]⁴⁻ and photocorrosion are found to occur. Whereas samples prepared under $5x10^{-5} < P_N < 1x10^{-3}$ torr (b and d) showed good stability up to about 50 min (Fig 4-9), those involving higher P_N values (c) photocorroded after only a few cyclic voltammogram cycles (results not shown here). This latter behavior was also observed for films prepared with no intentionally added N₂ in the chamber (see Fig. 4-9, sample a).

Sample Name	Arc Times	P _{N2} (torr)	Bias (V)	Stability
а	1250	0	-80	See fig 4-9
b	1250	$5x10^{-4} \sim 1x10^{-3}$	-80	See fig 4-9
с	1250	$3x10^{-3} \sim 2x10^{-2}$	-80	Rapid Corrosion
d	1250	5x10 ⁻⁵ ~1x10 ⁻⁴	-80	See fig 4-9
e	2500	$5x10^{-5} \sim 1x10^{-4}$	-80	See fig 4-9
f	500	$5x10^{-4} \sim 1x10^{-3}$	-80	See fig 4-9
g	5000	$5x10^{-4} \sim 1x10^{-3}$	-80	Rapid Corrosion
h	1250	$5x10^{-4} \sim 1x10^{-3}$	-150	See fig 4-9
i	1250	$5x10^{-4} \sim 1x10^{-3}$	0	Rapid Corrosion

Table 4-1 Preparation conditions of taC:N|n-GaAs samples

b. Film Thickness. The stability of films of different thickness prepared with 500-5000 arcs (sample d-g) were compared in fig 4-9. As mentioned in the Experimental Section, 2500 arcs yielded a taC:N film thickness of ca. 70nm as measured using quartz substrates. Films produced via a larger number of arcs, e.g. 12500, could be easily removed by rubbing. As a means of illustration a film produced with 5000 arcs, the thickness one examined electrochemically (sample g) was found to photocorrode quickly (not shown in fig 4-9). Undoubtedly, poor adhesion causes only short-time protection against photocorrosion. Overall, based on the results shown in the figure, the film that displayed the highest stability among the four examined was d for which the number of arcs was 1250.

c. Substrate bias. Based on reports in the literature, the negative bias applied to the substrate controls the energy of the incident carbon ions, and thus the fraction of sp³ carbon and the internal stress of the film.^{21, 24} As shown in Fig. 4-9, the specimen produced without bias (sample i) corroded quickly, while biased specimens (b and h) showed better protection.

Overall, within the samples we surveyed, the taC:N|n-GaAs film prepared in the range $5 \times 10^{-5} < P_N < 1 \times 10^{-4}$ torr, with a bias = -80V, and 1250 arcs were found to be photoelectrochemically the most stable.

4.4.4 Surface morphology of taC:N films

Insight into the morphology of the taC:N|n-GaAs specimens was gained by imaging using atomic force microscopy. As the thickness of the films increased, specimens displayed higher degree of roughness, as a comparison of the images for the films labeled as d, e and f in Fig. 4-10 indicates. Although rougher and thus thicker films lack stability

a decrease in the film thickness may also leave a higher number of pinholes and thus lead to higher photocorrosion rates. It seems that films prepared via 1250 arcs provide the best compromise between adhesion and coverage, although their overall stability is still limited. Also shown in the figure is an image of a taC:N|n-GaAs junction obtained under higher P_N values which yielded a rougher texture than that obtained under lower P_N . In this case, the stability of this specimen was found to degrade compared to a smoother counterpart.

Additional topographical information was obtained by conventional optical microscopy, which revealed that photocorroded films (see e.g. fig 4-11) are indeed much rougher than pristine specimens. In fact, the damage caused by photocorrosion could also be found by cursory visual inspection.

4.5 CONCLUSIONS

The taC:N|SC showed protection, albeit limited, against photocorrosin in neutral solutions for all SC examined. Depending on the specific SC, the taC:N|SC junctions were found to be rectifying or ohmic. The photocurrent and the photovoltage of taC:N|n-GaAs were proportional to the intensity and to the logarithm of the intensity of illumination, P (mW/cm²), respectively. The deposition conditions, including triggering times, substrate bias and partial pressure of nitrogen in the chamber influence markedly the properties of the resulting taC:N|SC films. Unfortunately, none of the taC:N|n-GaAs specimens examined showed protection against photocorrosion in 0.1M NaOH alkaline solution, an effect ascribed to the presence of pinholes or defects in the taC:N films.

Future work need to be done on the preparation of sufficiently uniform and adhesive film

of taC:N to protect the SC surface against photocorrosion in alkali solution.

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Fig 4-1 Schematic diagram of FCVA used for taC:N deposition in these studies. **H** represents the magnetic field vector generated by the current flowing along a wire coiled around the bellows. (See ref. 16)



Fig 4-2 Schematic diagram of a taC:N/SE photoelectrochemical cell .



Fig 4-3 Cyclic voltammograms of bare SC (Panel A)) and taC:N/SC(Panel B) both in the dark (solid line) and under illumination (dotted line) in 2mM ferrocyanide/1M KCl solution. The intensity of light P=11.7, 0.81, 0.73mW/cm² for n-GaAs, n-CdS and n-CdSe respectively. The taC:N films were deposited on n-GaAs, n-CdS and n-CdSe under a bias of -80V and $5x10^{-5} < P_N < 1x10^{-4}$ torr, 2500 arcs; $5x10^{-4} < P_N < 1x10^{-3}$ torr, 1250 arcs; $5x10^{-3} < P_N < 1x10^{-2}$ torr, 1250 arcs, respectively.



Fig 4-4 Cyclic voltammograms of taC:N/SC (a,n-GaAs; b, n-CdS; c, n-CdSe) under illumination (a, 11.7; b, 0.81; c, 0.73mW/cm²) and taC:N/Ta (d) in 2mM ferrocyanide/1M KCl solution.



Fig. 4-5 cyclic voltammograms of taC:N|n-GaAs in a 2mM ferrocyanide/1M KCl solution in dark (dotted line) and under illumination (solid line) as a function of light intensity ($0.35 < P < 11.7mW/cm^2$). Also given in this same figure is the cyclic voltammogram of a Pt electrode in the same solution (bold solid line) for comparison. Scan rate: 50mV/s. taC:N films were prepared under $P_{N2} = 5x10^{-5} \sim 1x10^{-4}$ torr, bias = - 80V, 2500 arcs.



Fig. 4-6 Cyclic voltammograms of taC:N|n-GaAs in a 50mM ferrocyanide/1M KCl solution in the dark (dotted line) and under illumination (solid line). Scan rate: 10mV/s. Insert is a plot of photocurrent as a function of light intensity P. The taC:N film was prepared under the same conditions as the film in fig 4-5.



Fig. 4-7 Plot of the open circuit photopotential E_{ph} of taC:N|n-GaAs vs a gold electrode in 1 mM [Fe(CN)₆]^{3-/4-}/1M KCl solution as a function of logP.



Fig. 4-8 Cyclic voltammogram of taC:N/n-GaAs in 2mM K_4 Fe(CN)₆/0.1M NaOH in dark(solid line) and light (0.35mW/cm², dotted line). Scan rate: 50mV/s. The taC:N film was prepared under the same conditions as the film in fig 4-5.



Fig 4-9 Current change with time by holding potential at 0.4V for taC:N/n-GaAs samples prepared at different conditions (see table 4-1 for details) in 2mM ferrocyanide/1M KCl under a laser illumination of 12 mW/cm².



Fig 4-10 AFM images of bare n-GaAs and taC:N/n-GaAs samples prepared at different conditions (see table 4-1 for details).



Fig 4-11 Microscopic images on the corroded area (a) and the edge of the corrosion area (b) of photocorroded sample taC:N/n-GaAs (sample e).

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The methods described in this thesis made it possible to determine, with rather high accuracy, adsorption isotherms for Cd^{2+} on functionalized magnetic particles of dimensions in the micron down to the nm range. This approach offers prospect for future application to a wide variety of functional groups and metal ions with relevance to soil remediation and water quality applications. The ability to manipulate particles while dispersed in the liquid media may prove advantageous in the design of reactors for the continuous removal of hazardous metals from aqueous solutions. Collaborations with chemical engineers may prove very useful toward accomplishing such goals. Particularly attractive are schemes in which the particles can be magnetically confined while the pH of the solution is decreased. As shown by the results obtained, such conditions will lead to the release of Cd^{2+} from the binding site, allowing its further capture by, for example, electrodeposition. Also worthy of study is the design and synthesis of functional groups displaying higher affinity than carboxyl- or pyridine-based groups examined in this work. Advances in this area may lead to the development of novel schemes in the areas of magneto-switchable electrocatalysis,²⁶ sensing, and magnetically-assisted separations.

The preliminary results obtained with taC:N as a protective layer for semiconductors used in photoelecrochemical applications, although encouraging, did not, at this early stage, display sufficient long term stability under illumination to offer, at present, the desired degree of protection toward photocorrosion. Much effort will be required to gain a better understanding of the role of the substrate on the growth of taC:N and particularly of the factors that cause pin holes to be formed. Deposition of taC:N films on welldefined surfaces prepared and characterized in ultrahigh vacuum environments are expected to provide much-needed insight that may lead to ways of forming highly coherent, defect-free layers on the substrate. Yet another approach involves the "curing" of defects using species that may block, physically or chemically, the exposed sites. The formation of reliable taC:N junctions would have significant impact in solar energy conversion.

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