



# Corrosion inhibitive property of self assembled Nano Films formed by Adipic Acid molecules on carbon steel surface

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## ABSTRACT

Well-ordered SAMs using adipic acid were formed on the oxide of iron carbon steel surface by immersion method. This leads to ordered, robust monolayers bound to the surface in a tetradentate manner. Monolayer formation takes place when carbon steel is immersed in an aqueous solution containing 60ppm of  $\text{Cl}^-$  and 100ppm of adipic acid for 5 minutes, and rinsing the physisorbed molecules in distilled water and heating in a hot air oven. The adipic acid monolayers on iron oxide steel carbon can withstand rinsing with water, concentrated acid and base exposure. Additionally, these monolayers are stable over the course of at least one week. The formations of monolayers were confirmed by AFM study and FTIR spectra. The SAMs were tested by polarization and EIS electrochemical analysis. The results of this study show that adipic acid monolayers adsorbed on metal surface can reduce electrochemical activity on the surface, often the first step in corrosion.

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## Introduction

Nanometer-sized particles are attracting considerable attention because of their unique properties, including optical, electrical, electrochemical, photo-electrochemical and magnetic properties<sup>[1-3]</sup>. Noble metals, such as gold and silver, are hot spots of the research because they can be easily prepared and exist steadily. Moreover, we can manipulate these nanoparticles according to our will. Much effort has been done in exploring self-assembled (SA) nanoparticles into ordered structures<sup>[4]</sup>. Specific structures can provide controlled fabrication of nanometer-sized building blocks with distinctive and useful properties<sup>[5]</sup>. Polymer-stabilized nanoparticles are usually self-assembled into two-dimensional arrays on the substrate<sup>[6]</sup>. Yiwei Tan et al.<sup>[7]</sup> had reported the self-organization of wire-pattern arrays of Ag nanoparticles. Byeong-Hyeok Sohn<sup>[5]</sup> had demonstrated a directed self-assembly of two different kinds of nanoparticles on a block copolymer micellar template. These two particles are gold and iron oxide. The self-assembling process has been investigated to improve corrosion inhibition of metals because self-assembled substances are able to react spontaneously on the metal surface and form compact and stable films<sup>[8]</sup>. These films can protect metal from corrosion successfully. Iron is a widely used metal with extensive industrial application and the study of its corrosion inhibition has attracted much attention<sup>[9,10]</sup>. The first work to use self-assembled films on iron for corrosion protection was self-assembling alkanethiols<sup>[11]</sup>. But the application of thiol-compounds is limited due to their toxicity<sup>[12]</sup>. Ilona Felhosi et al.<sup>[12]</sup> studied the formation of self-assembled films of alkane

monophosphonic acids on iron surface and explained its mechanism of corrosion protection.

In the present work, SAMs of adipic acid (AA) were formed on carbon steel surface by immersion coating (immersing metal surface in an aqueous solution containing 60ppm of  $\text{Cl}^-$ , in the absence and presence of 100ppm of adipic acid). The modified samples were characterized by FTIR, and atomic force microscopy (AFM). The formation, uniformity, ordering and bonding of the monolayers accomplished by immersion method have been evaluated. Furthermore, the electrochemical properties of the unmodified and modified carbon steel surfaces were characterized by polarization study and electrochemical impedance spectroscopy (EIS) analysis to test the ability of the monolayer to reduce the corrosion of the surface.

## Experimental Section

### Material

Very pure adipic acid of analytical reagent grade was used in the present study.

### Preparation of the substrates

Carbon steel substrates (Composition : wt % : 0.026% S, 0.06% P, 0.4% Mn, 0.1% C and the rest Fe) of dimensions 1 x 1 x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and stored in oven at 100°C for 1 h or more.

### Formation of monolayers

#### Immersion deposition monolayers

The cleaned substrates were placed in the oven for 24 h. They were then immersed in an aqueous solution containing 60ppm  $\text{Cl}^-$  in the absence and presence of 100ppm of adipic acid for 5 mts and placed in an oven at 100°C for at least 1 h.

### Characterization of the monolayers

The substrates were studied using a Perkin Elmer 1600 FTIR spectrophotometer. The film was removed carefully, mixed with KBr and made into pellets. FTIR spectra were recorded.

### Atomic force microscopy

Atomic force microscopy (Veeco innova model) was used to observe the samples' surface in tapping mode, using cantilever with linear tips. The scanning area in the images was  $5 \mu\text{m} \times 5 \mu\text{m}$  and the scan rate was 0.6 HZ / second.

### Potentiodynamic Polarization Study

Polarization studies were carried out in a CHI – Electrochemical work station with impedance, model 660 A.

### Electrochemical Impedance Spectroscopy (EIS) measurements

The instrument used for polarization study was used to record electrochemical impedance spectra also. The cell set up was also the same.

### Results

#### Immersion deposition method

#### FTIR Spectra

A simple procedure of immersing mild steel into an aqueous solution containing 60 ppm of  $\text{Cl}^-$  and 100 ppm of adipic acid for 5 minutes led to spontaneous film formation on the iron oxide surface, produced by the interaction of chloride iron present in the medium with iron. There is also possibility of formation of iron-adipic acid film, in the absence of iron oxide, if there is less corrosion or no corrosion of carbon steel. The samples were characterised by FTIR spectra to determine alkyl chain conformation and head group-substrate bonding [16, 13]. Position of the  $\text{CH}_2$  stretching in the infrared spectrum can be used to determine the ordering of the alkyl chain within a film [15, 17-19].

For disordered chains, the frequency of the  $\text{CH}_2$  stretching is close to that of a liquid alkane ( $\nu \text{CH}_2 \text{ asym} \sim 2924 \text{ cm}^{-1}$ ) due to the presence of a gauche conformation in the alkyl chains [18, 20]. For well-ordered alkyl chains the frequency is shifted to lower wave numbers and is close to that of a crystalline alkyl ( $\nu \text{CH}_2 \text{ asym} \sim 2914 - 2918 \text{ cm}^{-1}$ ) which is considered to have a high degree of order, with all-trans conformation throughout the alkyl chain. The FTIR spectrum of pure adipic acid (AA) is shown in Fig 1a. The peaks due to  $\nu \text{CH}_2 \text{ asym}$  and  $\nu \text{CH}_2 \text{ sym}$  appear at 2810 and  $2724 \text{ cm}^{-1}$ . The FTIR spectrum of iron oxide film formed on metal surface after immersion in 60ppm  $\text{Cl}^-$  is shown in Fig 1b. The peaks due to iron oxide appear at  $\gamma \text{FeOOH} = 1045, 1632 \text{ cm}^{-1}$ ;  $\alpha \text{FeOOH} = 602 \text{ cm}^{-1}$ . The peaks due to  $\text{Fe}_3\text{O}_4$  are absent. [20a].

The position of the peaks corresponding to  $\nu \text{CH}_2 \text{ asym}$  and  $\nu \text{CH}_2 \text{ sym}$  after immersion in an aqueous solution containing 60ppm of  $\text{Cl}^-$  and 100ppm of adipic acid for 5 minutes and after rinsing in distilled water to remove any physisorbed material or multi layers, were  $2811 \text{ cm}^{-1}$  and  $2808 \text{ cm}^{-1}$ , respectively (Fig 1c). This indicates that the film is stable, well ordered and strongly bound to the surface.

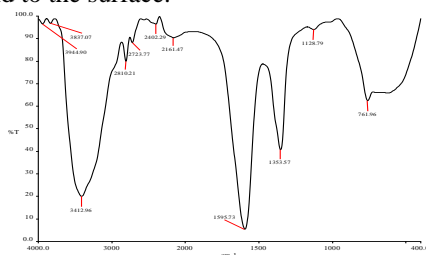


Fig 1 a) Pure adipic acid

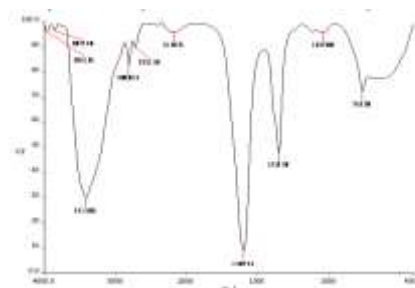


Fig 1 b) Adipic acid +  $\text{Cl}^-$  60ppm

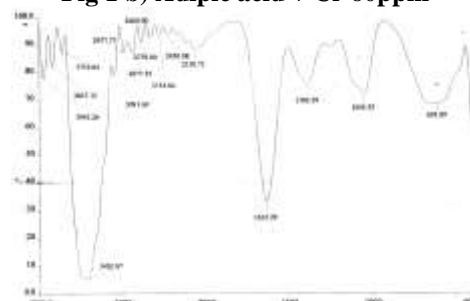


Fig 1 c) iron oxides formed on metal surface after immersion in solution containing 60ppm of  $\text{Cl}^-$

The IR spectra further indicate that the organic molecules are bound to the surface in a tetradentate manner as determined from the shifting of  $\nu \text{C} = \text{O}$  and  $\nu - \text{OH}$  stretching of the two carboxyl groups of adipic acid specifically the  $\nu \text{C} = \text{O}$  has shifted from  $1715$  to  $1597 \text{ cm}^{-1}$  and  $\nu \text{OH}$  has shifted from  $3417$  to  $3413 \text{ cm}^{-1}$ . Similar bidentate interaction has been reported for alkyl phosphonic acid on nickel oxide surface [21] and other organic molecules on other oxides [16, 14, 13].

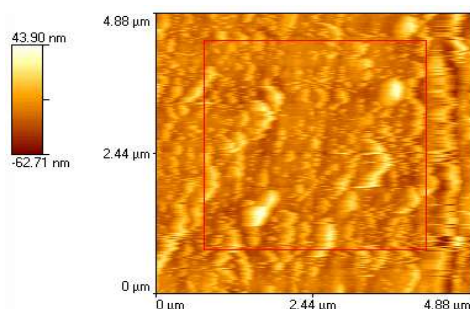
While FTIR spectroscopy can be used to characterize alkyl chain ordering and binding of the molecules to the surface, it cannot determine film thickness and integrity. Therefore, AFM imaging was used to examine the monolayer at nanometer resolution and to verify that the deposition method produces uniform monolayer.

#### AFM imaging

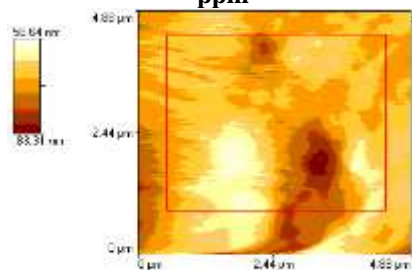
The comparison of the root mean square (rms) roughness of the unmodified substrate to the modified samples is an indicator of the film uniformity. The rms roughness parameter is a measure of the deviations in the surface from the mean plane within the sampling area [22].

Modified surfaces with an rms roughness similar to the control surface are considered to be films of monolayer thickness that follow the contour of the surface, while modified surfaces that have much larger rms roughness than the control are multilayer or non-uniform films [23, 24].

The iron oxide control samples had an average rms roughness of 12.06 nm (Fig 2a). The control sample of iron oxide is rough in comparison to model surfaces such as gold and silicon [25, 26]. Modified samples formed by the immersion method (immersed in 60 ppm of  $\text{Cl}^-$ ) had an rms roughness of 11.51 nm (Fig 2b). The rms roughness of the substrate did not change very much after the adsorption of adipic acid molecules suggesting uniform deposition of the organic molecules on the surface without aggregate or micelle formation. Therefore it is concluded that within the scope of the analysis, the film formed is a single layer of molecules that follows the contour of the underlying substrate.



**Fig2 AFM to photography images of films formed on carbon steel surface after immersed in various test solutions. a )  $\text{Cl}^-$  ppm**



**Fig 2b)  $\text{Cl}^-$  60ppm + Adipic acid 100ppm**

The rms roughness values of the films (SAMs) formed on metal surface after immersion in various test solutions are given in Table 1.

**Table 1: The rms roughness values of the films (SAMs) formed on iron oxide / metal surface immersed in various test solutions.**

Test solution	rms roughness of the films (SAMs), nm
$\text{Cl}^-$ 60ppm	12.0558
$\text{Cl}^-$ 60ppm + AA 100ppm	11.5167

The rms roughness 12.0558 nm is due to oxides of iron, confirmed by FTIR spectrum Fig 1b which are formed when carbon steel is immersed in 60ppm  $\text{Cl}^-$  environment. When 100ppm of adipic acid (AA) is added the rms value decreases to 11.5167 nm. This indicates that the protective film (SAMs) is formed on the metal surface itself, and not on the iron oxide surface. Had it formed on the iron oxide surface the rms value would have been greater than 12.0558. So it is concluded that SAMs are formed not on the iron oxide surface but on the metal itself, even before the corrosion process starts, leading to the formation of iron oxide.

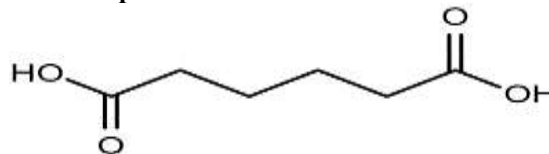
#### Stability of monolayer films

The monolayers formed by deposition method were analyzed for stability. After rinsing in water, the samples were left under atmospheric conditions for one day and analyzed. The monolayer remained ordered and bound to the surface as indicated by the lack of change in the FTIR spectra over one day. Stability to acid and base exposure was tested by rinsing modified substrates 1 M HCl or 1 M NaOH. FTIR spectra taken after these treatments remained unchanged.

Film stability and chain ordering can be dependent on alkyl chain length. In general, stability and order increase as the chain length increases [27, 28-31]. Therefore, a long chain length (> 11 carbons) is commonly used in the formation of SAMs. Substantial disorder is generally found in films formed by short chain molecules, although ordered monolayers of short chain phosphonic acids have been formed on nitinol, titanium and stainless steel oxide [16, 13, 32]. In the present study there are only 6 carbons in the chain. However, the monolayer is found to be stable. Since adipic acid is a dicarboxylic acid tetradentate

bonding is expected, and this leads to the stability of the monolayer. It is obvious from the proposed structure of the monolayers, there is some strain in the  $\text{CH}_2$  chain, as per Baeyer's strain theory.

#### Structure of adipic acid



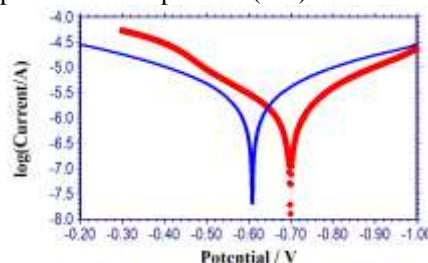
There are even number of (four)  $\text{CH}_2$  groups in adipic acid. Therefore there is strain in the  $\text{CH}_2$  chain. Interestingly, if the number of  $\text{CH}_2$  groups is odd number (1, 3, 5) as in the case of malonic acid, glutaric acid and pimelic acid, more stability is expected, in the SAMs after coordination to the metal surface in a tetradentate fashion. Further research in this line will confirm the proposed concepts.

This will also be reflected in the more corrosion resistance offered by these SAMs, during electrochemical studies such as polarization study and AC impedance spectra.

These conclusions are confirmed by visual observations also. In the blank experiment (60ppm  $\text{Cl}^-$  only) brown film was observed on the metal. In the presence of 100 ppm of AA brown film was absent and thin interference films (VIBGYOR colour) were noticed.

#### Potentiodynamic Polarization Study

The potentiodynamic polarization curves of carbon steel immersed in an aqueous solution containing 60ppm of  $\text{Cl}^-$  in the absence and presence of adipic acid (AA) are shown in Fig 3.



**Fig 3 polarization curves of carbon steel immersed in various test solutions**

a)  $\text{Cl}^-$  60ppm b)  $\text{Cl}^-$  60ppm + Adipic acid 100ppm

The corrosion parameters such as corrosion potential ( $E_{\text{corr}}$ ), Tafel slopes ( $b_c$ ,  $b_a$ ), linear polarization resistance (LPR) and corrosion current ( $I_{\text{corr}}$ ) are given in

Table 2.

**Table 2 : Corrosion parameters of carbon steel immersed in aqueous solution containing 60ppm of  $\text{Cl}^-$**

AA ppm	$E_{\text{corr}}$ m V vs SCE	$b_c$ m V / decade	$b_a$ mv / decade	LPR ohm $\text{cm}^2$	$I_{\text{corr}}$ A / $\text{cm}^2$
0	-609	183	189	23319.1	$1.735 \times 10^{-6}$
100	-700	165	188	31352	$1.217 \times 10^{-6}$

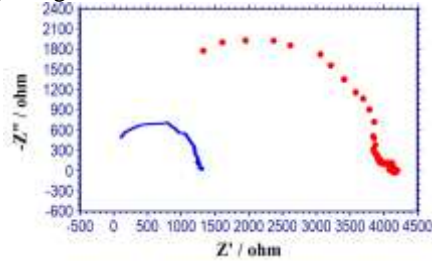
Carbon steel electrode was immersed in various test solutions for 5 minutes to attain the steady state potential. Then polarization curves were recorded. When carbon steel is immersed in an aqueous solution containing 60ppm of  $\text{Cl}^-$ , oxides of iron are formed on the metal surface (FTIR spectra, Fig 1b). The corrosion potential is -609 mV vs SCE. The LPR is 23319.1 ohm  $\text{cm}^2$  and the corrosion current  $1.735 \times 10^{-6}$  A/ $\text{cm}^2$  (Fig 3a). When 50ppm of AA is added to the above environment, and allowed to stand for 5 minutes, self assembling monolayers (SAMs) of AA are formed on the metal surface. Now the LPR value increases from 23319.1 ohm  $\text{cm}^2$  to



31352 ohm cm<sup>2</sup> (Fig 3b). The corrosion current decreases from 1.735x10<sup>-6</sup> A/cm<sup>2</sup> to 1.217x10<sup>-6</sup> A/cm<sup>2</sup>. This reveals that the SAMs formed on the metal surface have corrosion resistance property. The attack of Cl<sup>-</sup> ions, present in the bulk of the solution, on the metal surface, is prevented by the SAMs of adipic acid.

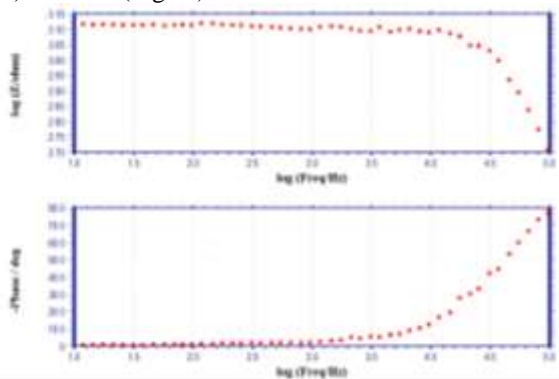
**Electrochemical impedance spectra**

The electrochemical impedance spectra of carbon steel immersed in various test solutions are shown in Fig 4. The equivalent electrical circuit for the model is shown in Fig 5. The impedance parameters such as charge transfer resistance (R<sub>t</sub>), double layer capacitance (C<sub>dl</sub>) and impedance value, log(Z/ohm), are given in Table 3.



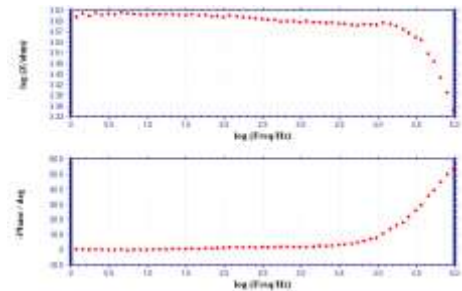
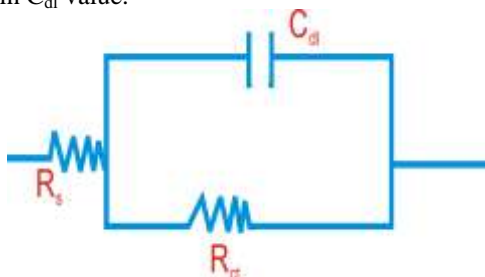
**Fig 4** Electrochemical Impedance spectra of carbon steel immersed in various test solution (Nyquist Plots) a) Cl<sup>-</sup> 60ppm b) Cl<sup>-</sup> 60ppm + Adipic acid 100ppm

When carbon steel is immersed in an aqueous solution containing 60 ppm of Cl<sup>-</sup>, and left for 5mts, oxides of iron are formed on the metal surface. The R<sub>t</sub> value is 1225 ohm cm<sup>2</sup>. The C<sub>dl</sub> value is 4.1632 x 10<sup>-9</sup> F/cm<sup>2</sup>. The impedance, log (Z/ohm) is 3.119 (Fig 4c).



**Fig 4c)** AC Impedance spectra (Bode plots) of carbon steel immersed in solution containibg 60ppm of Cl<sup>-</sup>

When carbon steel is immersed in an aqueous solution containing 60 ppm of Cl<sup>-</sup> and 100 ppm of AA, the R<sub>t</sub> value increases from 1225 ohm cm<sup>2</sup> to 2968 ohm cm<sup>2</sup>; the C<sub>dl</sub> value decreases from 4.1632 x 10<sup>-9</sup> F/cm<sup>2</sup> to 1.7183 x 10<sup>-9</sup> F/cm<sup>2</sup>; the impedance value increases 3.119 to 3.621(Fig 4d). These results suggest that SAMs formed on the metal surface have corrosion resistance property. This results in increase in R<sub>t</sub> value and decrease in C<sub>dl</sub> value.



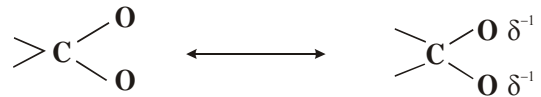
**Fig 4d)** AC Impedance spectra (Bode plots) of carbon steel immersed in solution containibg 60ppm of Cl<sup>-</sup> and 100ppm of adipic acid

Fig 5) Equivalent electrical circuit diagram

R<sub>s</sub> = Solution resistance

R<sub>ct</sub> = Charge transfer resistance

C<sub>dl</sub> = Double layer capacitance



**Fig 6)** Electron density on oxygen atoms of carboxylic group  
**Table 3: Impedance parameters of carbon steel immersed in an aqueous solution containing 60ppm of Cl<sup>-</sup>**

AA ppm	R <sub>t</sub> ohm cm <sup>2</sup>	C <sub>dl</sub> F/cm <sup>2</sup>	Impedance log (Z/ohm)
0	1225	4.1632 x 10 <sup>-9</sup>	3.119
100	2968	1.7183x10 <sup>-9</sup>	3.621

**Discussion**

Ordered, complete monolayers of adipic acid were formed on the metal surface. These monolayers were formed using an immersion deposition process. To accomplish monolayer by immersion, a counteraction of 100 ppm of adipic acid, solution exposure time of 5 minutes and setting temperature of keeping the metal specimens in the oven at 100°C for 1 hr.

The process of monolayer formation using immersion coating has been described as a sequential process of nucleation, growth and coalescence of densely packed two-dimensional islands, finally covering the entire substrate surface or a large fraction of it [33, 34-37]. The average surface coverage for adipic acid films on iron surface is found to increase monotonically with solution concentration, consistent with a quarter surface density of adipic acid molecules. It is proposed that the initial islands are nucleated through the adsorption of individual adipic acid mole from solution [33, 34,35]. Therefore a higher concentration of the monomer (100 ppm) in solution leads to more collisions between monomers and subsequent island nucleation becomes more probable leading to a large number of islands on the surface [34, 38]. For the immersed substrates, increasing the solution concentration leads to the formation of a complete monolayer. When the substrates were heated the tetradentate increased, the molecules become thermally mobile and therefore more available for nucleation and / or growth [39].

The molecules in the monolayers formed by immersion method were bound to the metal surface in a tetradentate manner. This bonding motif was persistent from deposition through solvent, acid and base rinsing and exposure to atmosphere for one day. A bidentate or monodentate bonding motif is seen between phosphonic acids and various metal oxides such as stainless steel 316L and Zircorium [16, 13, 32, 40-43]. In the present case, adipic acid is bonded to metal surface in tetradentate manner, since adipic acid is a dicarboxylic acid and coordination can take place through oxygen atoms of carboxyl groups.

### Summary

Well-ordered SAMs using adipic acid were formed on the oxide of iron carbon steel surface by immersion method. This leads to ordered, robust monolayers bound to the surface in a tetra dentate manner. Monolayer formation takes place when carbon steel is immersed in an aqueous solution containing 60ppm of  $\text{Cl}^-$  and 100ppm of adipic acid for 5 minutes, and rinsing the physisorbed molecules in distilled water and heating in a hot air oven. The adipic acid monolayers on carbon steel can withstand rinsing with water, concentrated acid and base exposure. Additionally, these monolayers are stable over the course of at least one week.

The formations of monolayers were confirmed by AFM study and FTIR spectra. The SAMs were tested by polarization and EIS electrochemical analysis.

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