Exploring Corrosion Resistance of Self-Assembled Monolayer Thin Films on Mild Steel Substrates

V.Sribharathy[1]*, S. John Mary.[2] Susai Rajendran[3]

[1.] *Department of chemistry, Anna Adarsh college for women,Chennai,-600040*

[2.] *Department of Chemistry, Loyola College, Chennai 600 034, India.*

[3.]*St Antony's College of Arts and Sciences for Women, Tha-maraipadi , Dindigul – 624 005, Tamilnadu, India*

**Corresponding author: bharathyvijayagopal1985@mail.com*

Abstract

Well-ordered Self Assembled Monolayers (SAMS) using adipic acid (AA) were formed on the oxide of iron carbon steel surface by immersion method. This leads to ordered, robust monolayer bound to the surface in a tetradentate manner. Monolayer formation takes place when carbon steel is immersed in an aqueous solution containing 60 ppm of Cl^- and 150 ppm of adipic acid for 5 minutes, and rinsing the physisorbed molecules in distilled water and heating in a hot air oven. The adipic acid monolayer 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 monolayer 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 monolayer adsorbed on metal surfaces can reduce electrochemical activity on the surface, often the first step in corrosion.

Keywords: *Self-assembled films; iron oxide surface; polarization study; electrochemical impedance spectroscopy; AFM; FTIR; corrosion.*

1. Introduction

Nanometer-sized particles are attracting considerable attention because of their unique properties,including optical, electrical, electrochemical, photo electrochemical and magnetic properties [1-3]. SAMs are ordered molecular assemblies formed by the adsorption of an active surfactant on a solid surface. The most elegant method for SAM formation consists of dissolving molecules in a solution and exposing an appropriate metal or substrate to this solution. Noble metals, such as gold and silver are hot spots of the research because they can be easily prepared and exist steadily.

Moreover, these nano-particles can be manipulated as desired. Much research efforts have been focused on transforming self-assembled (SA) nanoparticles into ordered structures [4]. Specific structures can provide controlled fabrication of nanometer-sized building blocks with distinctive and useful properties [5]. Polymer-stabilized nanoparticles are usually self-assembled into two-dimensional arrays on the substrate [6]. Yiwei Tan et al. [7] had reported the self-organization of wire-pattern arrays of Ag nanoparticles. Byeong-Hyeok Sohn et al. [5] had demonstrated a directed self-assembly of two different kinds of nanoparticles on a block copolymer micellar template using gold and iron oxide. The self-assembling process has been investigated to improve the corrosion inhibition of metals because self-assembled substances are able to react spontaneously on the metal surface and form compact and stable films [8]. These films can protect metal from corrosion successfully. Iron is a widely used metal with extensive industrial applications and the study of its corrosion inhibition has attracted much attention [9, 10]. The first work to use self-assembled films on iron for corrosion protection was self-assembled alkane thiols [11]. But the application of thiol-compounds is limited due to their toxicity. The SAMs are excellent systems for a more fundamental understanding of phenomena affected by competing intermolecular, molecular-substrates and molecule-solvent interactions like ordering and growth, wetting, adhesion, lubrication, and corrosion [12-31].

In the present work, SAMs of oxide / carbon steel surface using adipic acid (AA) were formed on carbon steel surface by immersion coating (immersing metal surface in an aqueous solution containing 60 ppm of Cl^-,

in the absence and presence of 150 ppm of adipic acid). The modified samples were characterized by Fourier Transorm Infrared (FTIR) spectroscopy and Atomic force Microscopy (AFM). The formation, uniformity, ordering and bonding of the monolayer 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.

2. Experimental Section

2.1. Development of Self Assembled Monolayer

Very pure adipic acid of analytical reagent grade was used in the present study. 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^3 were polished to a mirror finish and degreased with trichloroethylene and stored in on oven at 100°C for more than 1 h.

The cleaned substrates were placed in the oven for 24 h. They were then immersed in an aqueous solution containing 60 ppm Cl^- in the absence and presence of 150 ppm of adipic acid for 5 min and placed in an oven at 100°C for at least 1 h.

2.2. Characterization of the Monolayer

The substrates were studied using a Perkin Elmer 1600 FTIR spectrophotometer. FTIR spectrophotometer was used to analyze the nature of interaction between the molecules of adipic acid (AA) and the substrate and the alkyl chain ordering the νCH_2 peaks as the reference. The film was removed carefully, mixed with KBr and made into pellets and FTIR spectra were recorded.

The carbon steel specimen immersed in blank and in the inhibitor solution for a period of 5 mins was removed, rinsed with double distilled water, dried and subjected to the surface examination. Atomic force microscopy (Veecoinnova model) was used to observe the samples' surface in tapping mode, using cantilever with linear tips. The scanning area in the images was 5 μm x 5 μm and the scan rate was 0.6 mm.

Polarization studies were carried out in a CH–Electrochemical workstation with impedance, model 660 A. It was provided with an IR compensation facility. A three electrode cell assembly was used. The working electrode used was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and platinum was used as the counter electrode. From polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (b_c and b_a) and linear polarization resistance (LPR) were calculated. During the polarization study, the scan rate (v/s) was 0.01; hold time at E_f (s) was zero and quiet time (s) was 2.

The instrument used for polarization study was used to record electrochemical impedance spectra (EIS) also. The cell setup was also the same. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms at various frequencies. Value of charge transfer resistance (Rt), double layer capacitance (Cdl) and impedance, log (Z/ohm) were derived from Nyquist and Bode plots. Electrochemical impedance spectra were recorded with initial E (v) = 0; High frequency (Hz = 1 x 105); Low frequency (Hz = 1); Amplitude (v) = 0.005 and Quiet Time (s) = 2.

3.Results

3.1. FTIR Spectra

A simple procedure of immersing mild steel into an aqueous solution containing 60 ppm of 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 ion present in the medium with iron. There is also the 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 characterized by FTIR spectra to determine alkyl chain conformation and head group-substrate bonding. Position of the CH_2 stretching in the infrared spectrum can be used to determine the ordering of the alkyl chain within a film [32].

For disordered chains, the frequency of the CH_2 stretching is close to that of a liquid alkane (νCH_2asym ~ 2924 cm^{-1}) due to the presence of a gauche conformation in the alkyl chains [33]. For well-ordered alkyl chains, the frequency is shifted to lower wavenumbers and is close to that of a crystalline alkyl (νCH_2asym ~ 2914 – 2918 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 CH_2asym and CH_2sym appear at 2810 and 2724 cm^{-1}. The FTIR spectrum of iron oxide

film formed on a metal surface after immersion in 60 ppm Cl^- is shown in Fig 1c. The peaks due to iron oxide appear at γFeOOH = 1045, 1632 cm^{-1}; αFeOOH = 602 cm^{-1}. The peaks due to Fe_3O_4 are absent.

The position of the peaks corresponding to ν_{CH2}asym and ν_{CH2}sym after immersion in an aqueous solution containing 60 ppm of Cl^- and 150 ppm of adipic acid for 5 minutes and after rinsing in distilled water to remove any physisorbed material or multilayers were 2811cm^{-1} and 2808 cm^{-1}, respectively (Fig 1b). This indicates that the film is stable, well ordered and strongly bound to the surface. The IR spectra further indicate that the organic molecules are bound to the surface in a tetradentate manner as determined from the shifting of ν_C=O and νOH stretching of the two carboxyl groups of adipic acid specifically the ν C = O has shifted from 1725 to 1595 cm^{-1} and ν_{OH} has shifted from 3412 to 3423 cm^{-1}. Similar bidentate interaction has been reported for alkyl phosphonic acid on nickel oxide surface and other organic molecules on other oxides.

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 a uniform monolayer [33].

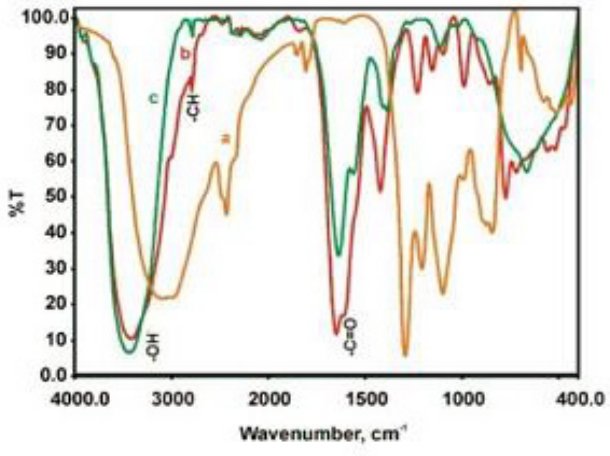


Fig. 1. FTIR spectra (KBr) of films formed on carbon steel surface after immersion in various test solutions (a) pure adipic acid (AA), (b) Adipic acid 150 ppm + Cl^- 60 ppm, (c) iron oxides formed on metal surface after immersion in solution containing 60 ppm of Cl^-.

3.2. 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 [34-36]. 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.

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. Modified samples formed by the immersion method (immersed in 60 ppm of Cl had an rms roughness of 10.59 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. The rms roughness values of the films (SAMs) formed on iron oxide / metal surface after immersion in various test solutions are given in Table 1. 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 60 ppm Cl^- environment. When 100 ppm of adipic acid (AA) is added the rms value decreases to 10.5912 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 nm. 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.

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
Cl^- 60 ppm	12.0558
Cl^- 60 ppm + AA 150 ppm	10.5912

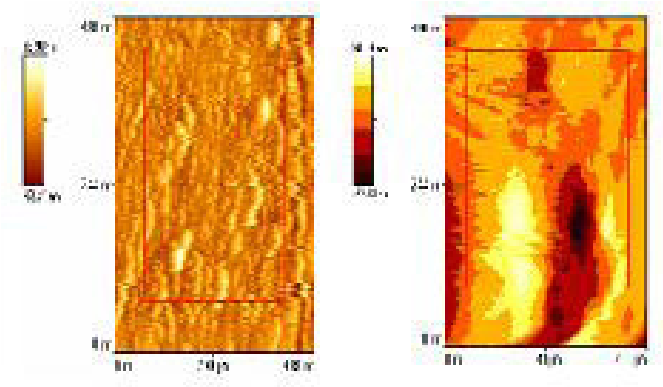


Fig. 2. AFM topography images of films formed on carbon steel surface after immerse on in various test solution (a) Cl^- 60 ppm (b): Cl^- 60 ppm + Adipic acid 150 ppm

3.3. Stability of Monolayer Films

The monolayers formed by the 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 unaltered FTIR spectra over one day. Stability to acid and base exposure was tested by rinsing modified substrates in 1 M HCl. IR 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. 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 [37]. 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 CH_2 chain, as per Baeyer's strain theory. There are even numbers of (four) CH_2 groups in adipic acid. Therefore there is strain in the CH_2 chain. Interestingly, if the number of 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 [38]. 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 (60 ppm Cl^-only) brown film was observed on the metal. In the presence of 150 ppm of AA brown film was absent and thin interference films (VIBGYOR color) were noticed.

3.4. Potentiodynamic Polarization Study

The potentiodynamic polarization curves of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- in the absence and presence of adipic acid (AA) are shown in Fig 3. The corrosion parameters such as corrosion potential (E_{corr}), Tafel slopes (b_c, b_a), linear polarization resistance (LPR) and corrosion current (I_{corr}) are given in Table 2.

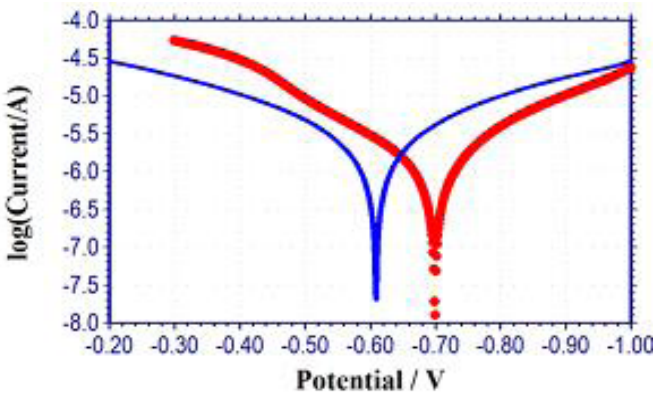


Fig. 3. Polarization curves of carbon steel immersed in various test solutions (a) Cl^- 60 ppm (b) Cl^-60 ppm + Adipic acid 150 ppm

Table 2. : Corrosion parameters of carbon steel immersed in aqueous solution containing 60 ppm of Cl^-

AA ppm	E_{corr} mV vs SCE	b_c mV/ decade	b_a mv/ decade	LPR ohm Cm^2	I_{corr} A / cm^2
0	-609	183	189	23319.1	1.7×10^{-6}
150	-700	163	186	30352	1.205×10^{-6}

Carbon steel electrodes were 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 60 ppm of 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 cm^2 and the corrosion current is 1.735×10^{-6} A/cm^2 (Fig 3a). When 150 ppm of AA is added to the above environment, and allowed to stand for 5 minutes, self-assembled monolayers (SAMs) of AA are formed on the metal surface. Now the LPR value increases from 23319.1 ohm cm^2 to 30352 ohm cm^2 (Fig 3b). The corrosion current decreases from 1.735×10^{-6} A/cm^2 to 1.205×10^{-6}A/cm^2. This reveals that the SAMs formed on the metal surface have corrosion resistant property. The attack of Cl^- ions present in the bulk of the solution, on the metal surface, is prevented by the SAMs of adipic acid.

3.5. *Electrochemical Impedance Spectra*

The electrochemical impedance spectra of carbon steel immersed in various test solutions are shown in Fig 4. The impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) and impedance value, long (Z/ohm), are given in Table 3.

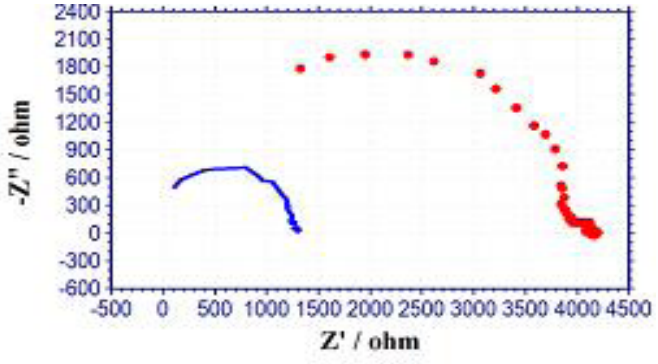


Fig. 4. Electrochemical impedance spectra of carbon steel immersed in various test solution (Nyquist Plots) (a) Cl^- 60 ppm (b) Cl^- 60 ppm + Adipic acid 150 ppm

(When carbon steel is immersed in an aqueous solution containing 60 ppm of Cl^-, and left for 5 minutes, oxides of iron are formed on the metal surface. The R_t value is 1225 ohm cm^2. The C_{dl} value is 4.3162×10^{-9} F /cm^2. The impedance, log (Z/ohm) is 3.60 (Fig 5).)

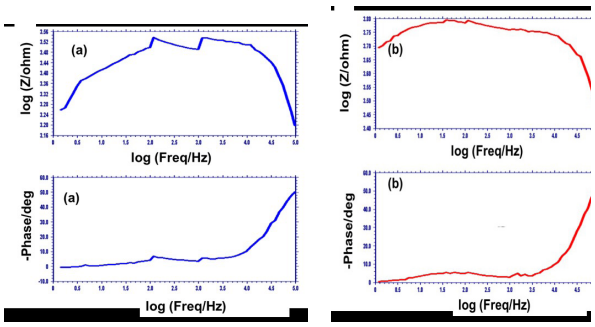


Fig. 5. AC impedance spectra (Bode Plots) of carbon steel immersed in solutions containing (a) Cl^- 60 ppm (b) Cl^- 60 ppm + Adipic acid 150 ppm

When carbon steel is immersed in an aqueous solution containing 60 ppm of Cl^- and 150 ppm of AA, the R_t value increases from 1225 ohm cm^2 to 2968 ohm cm^2; the C_{dl} value decreases from 4.3162×10^{-9} F/ cm^2 to 1.703×10^{-9} F/cm^2; the impedance value increases from 3.109 to 3.60 (Fig 4d). These results suggest that SAMs formed on the metal surface have corrosion resistanct properties. This results in an increase in R_t value and decrease in C_{dl} value.

Table 3. Impedance parameters of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^-

AA ppm	R_t ohm cm^2	C_{dl} F/cm^2	Impedance log (Z/ohm)
0	1225	4.3161×10^{-9}	3.11
150	2968	1.703×10^{-9}	3.60

4. Discussion

Ordered, complete monolayers of adipic acid were formed on the iron oxide / iron surface. These monolayers were formed using an immersion deposition process. To accomplish monolayer by immersion, a counter action of 150 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 [41-42]. The average surface coverage for adipic acid films on iron surface is found to increase monotonically with solution concentration, 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 . Therefore a higher concentration of the monomer (150 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. For the immersed substrates, increasing the solution concentration leads to the formation of a complete monolayer. When the substrates were heated, the molecules become thermally mobile and therefore more available for nucleation and / or growth [41].

The molecules in the monolayers formed by immersion method were bound to the iron oxide / iron 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 Zirconium. In the present case, adipic acid is bonded to iron oxide/ iron surface in tetradentate manner, since adipic acid is a dicarboxylic acid and coordination can take place through oxygen atoms of carboxyl groups. The cause of the differences in bonding motifs has not been determined but it may be a function of several factors including oxygen-metal-oxygen distance on the surface, hydroxyl content of the native oxide surface and the coordination sites available on the adsorbate molecules.

5. Conclusions

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 60 ppm of Cl^- and 150 ppm 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 monolayer adsorbed on metal surfaces can reduce electrochemical activity on the surface, often the first step in corrosion. Monolayer formation on the iron oxide carbon steel surface is a significant advance in surface modification of iron oxide and can be used as a building block for future applications in corrosion barriers and electronics.

Acknowledgement

The authors are thankful to their management, St. Joseph's Educational and Research Trust, Dindigul and UGC, India for their help and encouragement.

References

[1] Liu, Z. Lin, W. Lin, K.S. Moon, C.P. Wong, Reversible superhydrophobic-superhydrophilic transition of ZnO nanorod/epoxy composite films. ACS Appl. Mater. Interfaces, 4(8) (2012) 3959-64. https://doi.org/10.1021/am300778d.

[2] L. Xiaoling, Z. Junhu, X. Weiqing, J. Huiying, W. Xu, Y. Bai, Z. Bing, L. Bofu, O. Yukihiro, Mercaptoacetic acid-capped silver nanoparticles colloid: formation, morphology, and SERS activity. Langmuir, 19(10) (2003) 4285–4290. https://doi.org/10.1021/la0341815.

[3] N. R. Jana, L. Gearheart, C.J. Murphy, Wet chemical synthesis of high aspect ratio cylindrical gold nanorods. J.Phys. Chem B, 105 (19) (2001) 4065-4067. https://doi.org/10.1021/jp0107964.

[4] H. Zeng, R. Skomski, L. Menon, Y. Liu, S. Bandyopadhyay, D. J. Sellmyer, Structure and magnetic properties of ferromagnetic nanowires in self-assembled arrays, Phys. Rev B, 65(13) (2002), 134426. https://doi.org/10.1103/PhysRevB.65.134426.

[5] B.H. Sohn, J.M. Choi, S.I. Yoo, S.H. Yun, W.C. Zin, J.C. Jung, T. Teranishi, Directed self-assembly of two kinds of nanoparticles utilizing monolayer films of diblock copolymer micelles, J. Am. Chem.Soc, 125(21) (2003)

6368–6369. https://doi.org/10.1021/ja035069w.

[6] T. Teranishi, M. Haga, Y. Shiozawa, M. Miyake, Self-Organization of Au Nanoparticles Protected by 2, 6-Bis (1 '-(8-thiooctyl) benzimidazol-2-yl) pyridine, J. Am. Chem. Soc, 122 (17) (2000) 4237-4238. https://doi.org/10.1021/ja000031u.

[7] L. Feng, S. Li, H. Li, J. Zhai, Y. Song, L. Jiang, D. Zhu, Super-hydrophobic surface of aligned polyacrylonitrile nanofibers, Angew. Chem. Int. Ed, 41(7) (2002) 1221-1223. https://doi org/10.1002/1521-3773(20020402)41:7<1221::AID-ANIE1221>3.0.CO;2-G.

[8] C.T. Wang, S.H. Chen, H.Y. Ma, C.S. Qi, Protection of copper corrosion by carbazole and N-vinylcarbazole self-assembled films in NaCl solution, J. Appl. Electrochem, 33 (2003) 179–186. https://doi.org/10.1023/A:1024097208128.

[9] G.L. Győrik, L. Mészáros, G. Mészáros, B. Lengyel, Some interesting peculiarities in the high frequency part of the impedance diagram obtained in the case of iron dissolution in dilute H_2SO_4 solution, Corros. Sci, 42 (2000) 79-90. https://doi.org/10.1016/S0010-938X(99)00042-6.

[10] K.F. Khaled, N. Hackerman, Investigation of the inhibitive effect of ortho-substituted anilines on corrosion of iron in 1 M HCl solutions, Electrochim. Acta 48 (19) (2003) 2715-2723. https://doi.org/10.1016/S0013-4686(03)00318-9.

[11] N. Katsuhisa , A. Kunitsugu, One- and two-dimensional polymer films ofmodified alkane thiol monolayers for preventing iron from corrosion, Corros. Sci, 41(1) (1999) 57-73. https://doi.org/10.1016/S0010-938X(98)00048-1.

[12] R. Lundy, P. Yadav, N. Prochukhan, E.C. Giraud, T.F. O'Mahony, A. Selkirk, E. Mullen, J. Conway, M. Turner, S. Daniels, P.G. Mani-González, Precise definition of a "monolayer point" in polymer brush films for fabricating highly coherent TiO_2 thin films by vapor-phase infiltration, Langmuir, 36 (41) (2020) 12394-12402. https://doi.org/10.1021/acs.langmuir.0c02512.

[13] D.P. Goronzy, J. Staněk, E. Avery, H. Guo, Z. Bastl, M. Dusek, N.M. Gallup, S. Gun, M. Kucerakova, B.J. Levandowski, J. Machacek, Influence of terminal carboxyl groups on the structure and reactivity of functionalized m-carboranethiolate self-assembled monolayers. Chem. Mater, 32(15) (2020) 6800-6809. https://doi.org/10.1021/acs.chemmater.0c02722.

[14] D.R. James, K.S. Melissa, J.E. Daniel, P. Jean, C.H. Luke, Expanding the scope of surface grafted polymers using electroinitiated polymerization. Langmuir, 36 (26) (2020) 7217-7226. https://doi.org/10.1021/acs langmuir.0c00444.

[15] L. Ross, Y. Pravind, S. Andrew, M. Eleanor, G. Tandra, C. Cian, A.M. Michael, Optimizing polymer brush coverage to develop highly coherent sub-5 nm oxide films by ion inclusion, Chem. Mater, 31(22) (2019), 9338-9345. https://doi.org/10.1021/acs.chemmater.9b02856.

[16]D.L.Elisa,P.Deborah,M.Mauro,P.Daniele,P.Andrea, F.R. Saverio, P.P. Pier, Multifunctional platinum@BSA–rapamycin nanocarriers for the combinatorial therapy of cerebral cavernous malformation, ACS Omega, 3 (11) (2018) 15389-15398. https://doi.org/10.1021/acsomega.8b01653.

[17] H. Yuanyuan, M. Jiani, H. Yu, J. Jing, J. Wei, Effect of end-grafted polymer conformation on protein resistance. Langmuir, 34 (5) (2018), 2073-2080. https://doi.org/10.1021/acs.langmuir.7b03930.

[18] A. Shaheen, J.M. Sturm, R. Ricciardi, J. Huskens, C.J. Lee, F. Bijkerk, Characterization of self-assembled monolayers on a ruthenium surface. Langmuir, 33 (25) (2017) 6419-6426. https://doi.org/10.1021/acs.langmuir.7b01068.

[19] L. Ross, B. Conor, B. Justin, N. Kevin, N.C. Maurice, D. Eric, E. Ryan, Exploring the role of adsorption and surface state on the hydrophobicity of rare earth oxides. ACS. Appl. Mater. Interf, 9 (15) (2017) 13751-13760. https://doi.org/10.1021/acsami.7b01515.

[20] S. Leila, E.F.Z. Victor, P.P. Samuel, J.T. Hastings, J.B. Brad, Relative Contribution of lateral packing density to albumin adsorption on monolayers. Langmuir 32 (32) (2016) 8034-8041. https://doi.org/10.1021/acs.langmuir.6b01885. https://doi.org/10.1021/acs.langmuir.6b01885

[21] A.P. Sergio, J.G. Anthony, L.S. O'Neil, B. Stephen, L. Hong, R.A. Neal, E.P. Jeanne, L.B.

Jean, G. David, R.M. Seth, Phosphonic acids for interfacial engineering of transparent conductive oxides, Chem. Rev, 116 (12) (2016) 7117-7158. https://doi.org/10.1021/acs.chemrev.6b00061.

[22] F. Abraham, E.F. William, S. Frank, N. Gabriele, S. Graham, V.W. Florian, Surface energy and work function control of alox/al surfaces by fluorinated benzylphosphonic acids, ACS Appl. Mater. Interf 8 (18) (2016) 11857-11867. https://doi.org/10.1021/acsami.6b02012.

[23] B. Asif, I. Danish, M.J. Sagar, B. Kathrin, A.H. Tarek, R. Michael, T. Andreas, Z. Michael, Promoting effect of protecting group on the structure and morphology of self-assembled monolayers: terphenylylethanethioactate on Au(111), J. Phys. Chem C, 119(45) (2015) 25352-25363. https://doi.org/10.1021/acs.jpcc.5b06813.

[24] S. Leila, J.B. Brad, Photopatterning of stable, low-density, self-assembled monolayers on gold, Langmuir, 31(9) (2015) 2689-2696. https://doi.org/10.1021/acs.langmuir.5b00001.

[25] K. Youngmin, L. Seungjae, L. Kyungjun, S. Sangdeok, Y.K. Jin, W.L. Hyung, C. Dukhyun, Self-assembled plasmonic nanoparticles on vertically aligned carbon nanotube electrodes via thermal evaporation, ACS. Appl. Mater. Interf, 6 (22) (2014) 20423-20429. https://doi.org/10.1021/am505999e.

[26] T. Melanie, V.N. Marco, K. Stefan, L. Giovanni, C. Christos, P. Luca, G. Angelo, F. Johannes, W. Berthold, M. Paolo, K. Norbert, Surface Modification of ZnO(0001)–Zn with phosphonate-based self-assembled monolayers: binding modes, orientation, and work function, Chem. Mater, 26 (17) (2014) 5042-5050. https://doi.org/10.1021/cm502171m.

[27] K. Volodymyr, P. Georg, Ion adsorption on modified electrodes as determined by direct force measurements under potentiostatic control, J. Phys. Chem C, 118(5) (2014) 2673-2685. https://doi.org/10.1021/jp500425g.

[28] K. M. Nuruzzaman, Z. Michael, Irradiation promoted exchange reaction with disulfide substituents. J. Phys. Chem C, 117 (28) (2013) 14534-14543. https://doi.org/10.1021/jp4006026.

[29] S.C. Alexander, L.F. Colin, D. Robert, M.D. Dorothy, Structure and orientation of MDBA self-assembled monolayers and their interaction with calcite: a molecular dynamics study, J. Phys. Chem C, 117 (14) (2013) 7148-7153. https://doi.org/10.1021/jp4006235.

[30] W. Hairong, S. Kai, K.G. Avijit, V. Julius, M.S. Peter, J.W.Z. Harold, Dynamics of decanethiol self-assembled monolayers on Au(111) studied by time-resolved scanning tunneling microscopy, Langmuir 29 (7) (2013) 2250-2257. https://doi.org/10.1021/la304902y.

[31] R. Bart, P.P. Sidharam, S. Luc, C.J.M. Van Rijn, J.E. Baio, T. Weidner, Z. Han, Hexadecadienyl monolayers on hydrogen-terminated Si(111): faster monolayer formation and improved surface coverage using the enyne moiety, Langmuir, 28 (16) (2012) 6577-6588. https://doi.org/10.1021/la204770r

[32] A. Raman, M. Dubey, I. Gouzman, E.S. Gawalt, Formation ES of self-assembled monolayers of alkylphosphonic acid on the native oxide surface of SS316L, Langmuir, 22(15) (2006) 6469-6472. https://doi.org/10.1021/la060636p.

[33] E.B. Troughton, C.D. Bain, G.M. Whitesides, R.G. Nuzzo, D.L. Allara, M.D. Porter, Monolayer films prepared by the spontaneous self-assembly of symmetrical and unsymmetrical dialkyl sulfides from solution onto gold substrates: Structure, Langmuir, 4 (1993) 365-385. https://doi.org/10.1021/la00080a021

[34] M.F. Panel, D. Landolt, The influence of gallic acid on the reduction of rust on painted steel surfaces, Corros. Sci, 34 (1993) 1481-1494. https://doi.org/10.1016/0010-938X(93)90243-A.

[35] A.J. Workman, The handbook of organic compounds, three-volume set: NIR, IR, R and uv-vis spectra featuring polymers and surfactants, Academic Press, Elsevier, 2000 34:1481- 1494. 2001.

[36] R. Quinones, E.S. Gawalt, Study of the formation of self-assembled monolayers on nitinol, Langmuir, 23(20) (2007) 10123-10130. https://doi.org/10.1021/la701110p.

[37] A. Faucheux, A.C. Gouget-Laemmel, C. Henry de Villeneuve, R. Boukherroub, F. Ozanam, P. Allongue, J.N. Chazalviel, Well-defined carboxyl-terminated alkyl monolayers grafted onto H− Si (111): packing density from a combined AFM and quantitative IR

study, Langmuir, 22 (2007)153-162. https://doi.org/10.1021/la052145v.

[38] I. Doudevski, W.A. Hayes, D.K. Schwartz, Submonolayer island nucleation and growth kinetics during self-assembled monolayer formation, Phys. Rev. Lett, 81 (1998) 4927. https://doi.org/10.1103/PhysRevLett.81.4927.

[39] D.K. Schwartz, Mechanisms and kinetics of self-assembled monolayer formation, Ann. Rev. Phys. Chem, 52 (1997) 107-137. https://doi.org/10.1146/annurev.physchem.52.1.107.

[40] J.T. Woodward, A. Ulman, D.K. Schwartz, Self-assembled monolayer growth of octadecylphosphonic acid on mica, Langmuir, 12(15) (1996) 3626-3629. https://doi.org/10.1021/la9510689.

[41] J.T. Woodward, I. Doudevski, H.D. Sikes, D.K. Schwartz, J. Phys. chem B, 101(38) (1997), 7535-7541. https://doi.org/10.1021/jp971338r.