Applied Surface Science 456 (2018) 25–36

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Synthesis and surface characterization of self-assembled monolayers of thiazoles incorporating hydrocarbon and fluorocarbon chains on copper substrates

Shujun Chen[a,b,c], Bin Xiang[a,*], Siyi Chen[b], Xuefeng Zou[a], Yang Zhou[a], Jian Hou[c,*]

[a] College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, PR China
[b] College of Materials and Chemical Engineering, Sichuan University of Science & Engineering, Sichuan, Zigong 643000, PR China
[c] State Key Laboratory for Marine Corrosion and Protection, Luoyang Ship Material Research Institute (LSMRI), Qingdao 266101, PR China

ARTICLE INFO

Keywords:
Self-assembled monolayers (SAMs)
Semi-fluorinated
XPS
ATR-IR
Rigid-flexible combination

ABSTRACT

A series of novel thiazoles incorporated with hydrocarbon and fluorocarbon chains using to form self-assembled monolayers (SAMs) on copper substrates were prepared. The SAMs were investigated by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and contact angle measurements, and the results support that these thiazoles are successfully adsorbed on the substrates, forming hydrophobic films. The anti-corrosion effect of the SAMs was determined by weight loss experiments, scanning electron microscopy and electrochemical methods. It is revealed that the protection ability of the SAMs is detected by the thiazoles concentration, immersion time and fluorocarbon chain length. Quantum chemical calculations were employed to correlate the adsorption mechanism with the structure of the thiazoles molecules.

1. Introduction

Copper is one of the oldest and most widely used metal in various applications due to its physical and chemical properties, such as excellent thermal conductivity and perfect mechanical stability [1,2]. However, the corrosion of copper is a usual and expensive industrial problem. This damage frequently occurs in the atmosphere, oil or aqueous solutions with high aggressive ionic concentration, particularly in the presence of chlorine [3], which will destroy the properties and appearance of copper. Therefore, the prevention of copper corrosion in applications is a great significance subject worthy of intensive investigation.

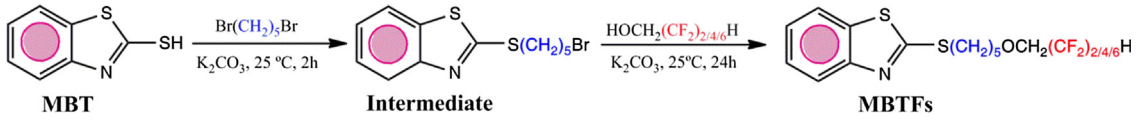
Generally, with regard to the inhibition of copper corrosion, one of the effective methods is spontaneous adsorption inhibitor on the copper surface [4], namely self-assembled monolayers (SAMs) technique, which acts as an insulating layer to isolate the substrate from the aggressive environment. This way has a lot of advantages, such as simply, fast and practical usable. Some organic compounds containing nitrogen, phosphorus and sulfur atoms, such as alkanethiols [2], schiff bases [5], triazoles [6] and thiazoles [7], have been often used as adsorptive corrosion inhibitors to form SAMs on copper surfaces to protect copper against corrosion. However, corrosive species (for example oxygen, ions and water) could permeate the membrane with a certain probability, resulting in the ineluctable corrosion of the metallic substrate [8,9]. Thus, when designing a protective film, the surface wettability plays an important factor. In general, the hydrophobic film supplies a high corrosion resistance for the metal base in aqueous solutions [10]. Recently, Liu et al. prepared a hydrophobic film on copper surfaces using a long alkyl acid, improving the anticorrosion performance of copper in seawater [11]. Meanwhile, Wang et al. also studied this hydrophobic film against copper corrosion under atmospheric environment [10].

As well known, fluorocarbon chain shows low surface energy, which is often employed to improve the hydrophobicity of film [12]. Meanwhile, the fluorinated SAMs surpass their hydrocarbon analogues in some characteristics, such as chemical and biological inertness, thermal stability, and oleo- and hydrophobicity analogues in key characteristics [13,14]. However, the strong rigidity of fluorocarbon chain leads to disordered and metastable SAM phases [15,16]. Thus, semi-fluorinated hydrocarbon inhibitors were used to avoid this defect [17–19]. Despite these advances, there are still some open questions that the semi-fluorinated molecules are difficult to preparation and extremely expensive, which severely restrict their application in practice. Thus, there is a hypothesis that a series of novel inhibitors incorporating hydrocarbon and fluorocarbon chains are prepared through a simple chemical reaction.

To this end, in this study, a series of inhibitors coupling

* Corresponding authors.
E-mail addresses: xiangbin@cqu.edu.cn (B. Xiang), houjian@sunrui.net (J. Hou).

https://doi.org/10.1016/j.apsusc.2018.06.082
Received 24 September 2017; Received in revised form 24 May 2018; Accepted 9 June 2018
Available online 15 June 2018
0169-4332/



MBTF$_2$, n=2, 2-((5-(2,2,3,3-tetrafluoropropoxy)pentyl)thio)benzo[d]thiazole;

MBTF$_4$, n=4, 2-((5-((2,2,3,3,4,4,5,5-octafluoropentyl)oxy)pentyl)thio)benzo[d]thiazole;

MBTF$_6$, n=6, 2-((5-((2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy)pentyl)thio)benzo[d]th.

Scheme 1. The structures and the preparation routes of related molecules, **MBTF$_2$**, n = 2, 2-((5-(2,2,3,3-tetrafluoropropoxy)pentyl)thio)benzo[d]thiazole; **MBTF$_4$**, n = 4, 2-((5-((2,2,3,3,4,4,5,5-octafluoropentyl)oxy)pentyl)thio)benzo[d]thiazole; **MBTF$_6$**, n = 6, 2-((5-((2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy)pentyl)thio)benzo[d]th.

hydrocarbon and fluorocarbon chains have been successfully synthesized and used to form protective SAMs on copper. The self-assembled film was characterized by ATR-IR, XPS and contact angle tests. Meanwhile, the optimum conditions for the formation of the film, such as assembly time and temperature, were researched using electrochemistry test technique. Besides, the relation between molecular structure and adsorption mechanism was theoretically investigated by quantum chemical calculations.

2. Experimental

2.1. Materials

All the chemicals, unless otherwise stated, are analytical grade and purchased from Acros Corporation and Aldrich Corporation. The self-assembled molecules (MBTFs) used in this article were prepared in our laboratory. The synthesis routes are shown in Scheme 1. The detail experimental procedures are given in supplementary information. The novel compounds were characterized by NMR and IR. Furthermore, their purity (> 95%) was detected by high performance liquid chromatography.

Intermediate, ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86–7.85 (d, 1H, J = 6 Hz, Ar–H), 7.74–7.73 (d, 1H, J = 6 Hz, Ar–H), 7.41–7.38 (t, 1H, J = 18 Hz, Ar–H), 7.28–7.25 (t, 1H, J = 18 Hz, Ar–H), 3.42–3.39 (t, 2H, J = 18 Hz, $-CH_2-$), 3.35–3.33 (t, 2H, J = 12 Hz, $-CH_2-$), 1.93–1.88 (m, 2H, $-CH_2-$), 1.87–1.82 (m, 2H, $-CH_2-$), 1.64–1.59 (m, 2H, $-CH_2-$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.86, 153.26, 135.36, 126.01, 124.17, 121.45, 120.93, 33.39, 33.16, 32.11, 28.44, 27.25; IR (KBr pellet): 567.8, 642.1, 705.4, 726.7, 753.8, 992.4, 1017.1, 1076.8, 1126.2, 1240.5, 1309.2, 1425.1, 1456.3, 2857.2, 2934.7, 3058.8, 3060.2.

MBTF$_2$, ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86–7.85 (d, 1H, J = 6 Hz, Ar–H), 7.75–7.73 (d, 1H, J = 12 Hz, Ar–H), 7.41–7.39 (t, 1H, J = 12 Hz, Ar–H), 7.29–7.27 (t, 1H, J = 12 Hz, Ar–H), 5.99–5.81 (m, 1H, $-CF_2H$), 3.80–3.76 (t, 2H, J = 24 Hz, $-OCH_2CF_2-$), 3.56–3.54 (t, 2H, J = 12 Hz, $-CH_2-$), 3.36–3.33 (t, 2H, J = 18 Hz, $-CH_2-$), 1.87–1.82 (m, 2H, $-CH_2-$), 1.67–1.62 (m, 2H, $-CH_2-$), 1.56–1.51 (m, 2H, $-CH_2-$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.98, 153.28, 135.15, 125.99, 124.14, 121.42, 120.90, 115.03, 110.79, 109.14, 107.49, 72.38, 67.88, 33.29, 28.95, 28.83, 25.01; ^{19}C NMR (200 MHz, $CDCl_3$) δ (ppm): −125.47, 140.01; IR (KBr pellet): 727.9, 758.5, 832.8, 996.7, 1019.5, 1113.4, 1204.3, 1232.4, 1275.3, 1311.7, 1428.5, 1460.9, 2865.7, 2940.1, 3065.5.

MBTF$_4$, ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86–7.84 (d, 1H, J = 12 Hz, Ar–H), 7.75–7.73 (d, 1H, J = 12 Hz, Ar–H), 7.41–7.39 (t, 1H, J = 12 Hz, Ar–H), 7.29–7.26 (t, 1H, J = 18 Hz, Ar–H), 6.14–5.95 (m, 1H, $-CF_2H$), 3.92–3.87 (t, 2H, J = 30 Hz, $-OCH_2CF_2-$), 3.60–3.58 (t, 2H, J = 12 Hz, $-CH_2-$), 3.36–3.33 (t, 2H, J = 12 Hz, $-CH_2-$), 1.87–1.82 (m, 2H, $-CH_2-$), 1.69–1.64 (m, 2H, $-CH_2-$), 1.58–1.53 (m, 2H, $-CH_2-$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.04, 153.28, 135.14, 125.98, 124.13, 121.42, 120.89, 72.81, 67.74, 67.57, 67.41, 33.30, 28.92, 24.99; ^{19}C NMR (200 MHz, $CDCl_3$) δ (ppm): −119.90, −125.85, −130.51, −137.41; IR (KBr pellet): 727.5, 757.1, 809.6, 899.6, 976.7, 995.1, 1019.1, 1075.7, 1130.5, 1173.2, 1241.6, 1428.6, 1460.8, 2868.8, 2941.9, 3066.2.

MBTF$_6$, ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.86–7.84 (d, 1H, J = 12 Hz, Ar–H), 7.75–7.73 (d, 1H, J = 12 Hz, Ar–H), 7.41–7.38 (t, 1H, J = 18 Hz, Ar–H), 7.29–7.26 (t, 1H, J = 18 Hz, Ar–H), 6.13–5.94 (m, 1H, $-CF_2H$), 3.93–3.88 (t, 2H, J = 30 Hz, $-OCH_2CF_2-$), 3.61–3.59 (t, 2H, J = 12 Hz, $-CH_2-$), 3.36–3.33 (t, 2H, J = 12 Hz, $-CH_2-$), 1.87–1.82 (m, 2H, $-CH_2-$), 1.69–1.64 (m, 2H, $-CH_2-$), 1.58–1.53 (m, 2H, $-CH_2-$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.04, 153.29, 135.15, 125.97, 124.11, 121.42, 120.88, 72.86, 67.82, 33.30, 28.93, 24.99; ^{19}C NMR (200 MHz, $CDCl_3$) δ (ppm): −119.66, −122.30, −123.55, −129.61, −137.09; IR (KBr pellet): 727.3, 756.2, 798.1, 833.3, 856.9, 996.1, 1020.3, 1079.2, 1141.1, 1199.9, 1308.8, 1428.3, 1460.3, 2867.0, 2935.1, 3065.1.

2.2. Preparation of MBTFs monolayer on copper

These novel MBTFs were dissolved in ethyl acetate in designed concentrations. Copper specimens (purity > 99.5%) were employed and their surfaces were elaborately abraded with a series of emery papers (grading 800, 1200, 1500, and 2000) to get a smooth face. Then, the specimens were rinsed by ultra-pure water and degreased using ethanol sonication bath for 10 min, and dried at room temperature. The copper specimens were then immersed for various desired time in various concentrations of MBTFs solutions at 298 K. For the attenuated total reflection Fourier–transform infrared spectrometry (ATR-IR), X-ray photoelectron spectroscopy (XPS), contact angle, weight loss and SEM analysis, the assembly time and concentration of MBTFs were 24 h and 10 mM, respectively. Finally, the modified copper electrodes were thoroughly rinsed with ethanol and ultrapure water and dried under a stream of nitrogen.

2.3. MBTFs SAMs characterization

ATR-IR and XPS were used to investigate the composition and structural organization of the film formed on the copper surfaces. The ATR-IR measurements were performed by a Perkin Elmer Spectrum 100 in the attenuated total reflectance mode with a diamond crystal, using 16 scans per spectrum and a resolution of 4 cm^{-1} and a spectral range of 500–4000 cm^{-1}. The XPS analyses were conducted on a PHI 5700 spectrometer with Al Ka X-ray radiation (hυ = 1486.6 eV). Contact angles (CA) on the Cu/SAM surface were carried out using an OCA-20 contact angle meter under ambient atmospheric conditions. The reported CA was an average value for 5 times tests on different spots and the average deviation was within 3°. The morphology of the copper surfaces before and after corrosion in 3 wt% NaCl solutions was measured by field emission scanning electron microscope (FE-SEM, JEOL-