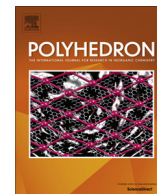




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Copper oxide surfaces modified by alkylphosphonic acids with terminal pyridyl-based ligands as a platform for supported catalysis

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ABSTRACT

Self-assembled monolayer (SAM) films of phosphonates have been successfully formed via reaction of 11-hydroxyundecylphosphonic acid or 4,4'-di(methylenephosphonic acid)-2,2'-bipyridine with the oxide layer of copper via the Tethering by Aggregation and Growth (TBAG) deposition method. The hydroxyl-terminated SAM was further modified with isonicotinic acid or 4,4'-dicarboxy-2,2'-bipyridine through a Steglich esterification reaction. These three surfaces derivatized with pyridyl-based ligands are potential platforms for supported catalysis. As a proof of concept, $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ was bound to the surfaces through the pyridyl-based ligands to yield tethered analogs of the known carbon dioxide reduction catalyst, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$. Surface modification reactions were confirmed through specular reflectance infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Characteristic core binding energies were observed in the XPS analyses for phosphorus (P 2p), nitrogen (N 1s), and ruthenium (Ru 3p and Ru 3d), verifying the presence of the various surface functionalizations. IR and XPS data indicate that the phosphonate binding to the copper surface is tridentate in nature.

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1. Introduction

Copper has appeal due to its high thermal and electrical conductivity and its use as a structural metal. However, a major disadvantage to the use of copper is its susceptibility to corrosion, particularly in devices that rely on the integrity of the interconnecting material such as microelectronics. One approach to protect against copper surface corrosion has been the use of self-assembled monolayers (SAMs). SAMs have been demonstrated to be a powerful and versatile means of modifying the surface properties of not only copper [1–31] but also other metals such as gold [32–37], steel [38,39], iron [40–43], titanium [44–62], aluminum [63–65], and zinc [66–68]. As is evident from the literature, surfaces modified with SAMs have applications in a wide array of areas such as sensing, biocompatibility, corrosion resistance, lithography, and catalysis.

The main approach for the modification of copper surfaces with SAMs has been the use of alkanethiols or alkaneselenols [1–25]. Often implemented on the coinage metals, alkanethiols are known to self-assemble to form ordered monolayers [32]. The thiol or selenol head group chemisorbs to the metal surface, which, in the case of copper, results in complete or almost complete

reduction of the native oxide layer dependent upon the conditions for monolayer formation [1–7]. Previous studies have indicated that thiolate monolayers on gold are subject to oxidative instability, which may limit their useful lifetime in catalytic applications [69–71].

A relatively unexplored approach, the use of alkylphosphonic acids, takes advantage of the native oxide layer on copper to modify the surface. Phosphonic acids have been shown to form robust phosphonate SAMs on a wide range of metal oxide surfaces through the formation of covalent Metal–O–P bonds [31,42,64,72]. These monolayers are mechanically strong and chemically resistant to hydrolysis and oxidation [49,50,73]. The bonding mode has been reported as being monodentate, bidentate, or tridentate depending upon the metal used [29,30,43–45,57,74,75]. For a comprehensive review of the current research involving modification of metal oxide surfaces with phosphonic acids and esters see [76].

First mentioned by Folkers in 1995 [26], the use of alkylphosphonate monolayers on copper has received little research attention in the intervening years. When copper was included among the engineering metal surfaces surveyed by Van Alsten, it was found that monolayers formed on copper with bisphosphonates were less dense and less ordered than those seen with alkanethiols [27]. An under-potentially deposited copper layer on gold allowed for the formation of alkylphosphonate monolayers on those surfaces [28]. More recent work has shown that variously

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terminated phosphonate monolayers can be formed on copper oxide surfaces, such as with perfluoro [29] and pyrrolyl [30] ω -functional groups for applications in non-wetting surfaces and in formation of electroactive polymer films, respectively. Analysis of XPS spectra of copper surfaces before and after deposition of octadecylphosphonic acid indicates that the formation of the phosphonate monolayer is caused by a condensation reaction between the phosphonic acid head groups and the surface hydroxyl species (Cu–OH) present in the native oxide layer [31]. Employing the Tethering by Aggregation and Growth (TBAG) deposition method developed by Schwartz et al. [55–62] may be a way to form comprehensive monolayers on the copper oxide surface without the need to further oxidize the surfaces via hydrogen peroxide, as employed by Refs. [29,30].

In this work, we explore the possibility of using alkylphosphonate monolayers on the native oxide layer of bulk copper surfaces as a platform for tethering a transition metal-based complex. Transition metal complexes have been immobilized on solid supports such as polymers and inorganic solids [76–78]. These systems have a diverse range of applications from sensing and molecular recognition to luminescence, photocatalysis, and electrocatalysis [76]. Functionalizing a surface with a transition metal catalyst should have the advantage of decreasing the time and cost needed for catalyst recovery and increasing the efficiency of the catalyst through the direct application of an electrochemical potential, particularly if the surface can function as an electrode and an electrocatalyst is bound [33,79,80].

Ruthenium polypyridyl complexes have attracted much attention since the late 1970s due to their potential use in photochemistry and luminescence, dye-sensitized solar cells, sensors, electrochemical activation, and catalysis. For comprehensive reviews of the literature regarding ruthenium polypyridyl complexes see [81,82]. In particular, [Ru(tpy)(bpy)(OH₂)²⁺ (tpy = 2,2';6',2''-terpyridine; bpy = 2,2'-bipyridine) complexes and related compounds have been targeted as efficient water oxidation catalysts due to the photochemical properties of the bipyridine ligand with recent research showing that only one metal center is necessary for oxygen production [83–96]. In an alternate application, [Ru(bpy)(CO)₂Cl₂] complexes and related compounds have been reported in the electroreduction of carbon dioxide [97–105]. In this work, an analog of the reported electrocatalytically active complex [Ru(bpy)(CO)₂Cl₂] has been bound to the oxide layer of bulk copper through three synthetic pathways given in Schemes 1 and 2 that result in phosphonate monolayers of varying alkyl chain lengths and monodentate or bidentate ligation of the electrocatalyst. We report herein on the synthesis and characterization of these derivatized surfaces.

2. Experimental

2.1. Materials

Acetyl chloride (99+%), 11-bromo-1-undecanol (97%), isonicotinic acid (99%), 4-dimethylaminopyridine (99%), N,N'-dicyclohexylcarbodiimide (99%), triethylamine (99%), trimethylsilyl bromide (99%), carbon tetrachloride (reagent grade), selenium (IV) oxide (99.8%), and N-bromosuccinimide (99%) were obtained from Acros Organics. Sodium bicarbonate (certified ACS) and anhydrous sodium sulfate (certified ACS) were obtained from Fisher Scientific. Triethyl phosphite (97%) was obtained from MP Biomedicals, Inc. Tricarbonyldichlororuthenium(II) dimer and azobis(isobutyronitrile) (98%) were obtained from Sigma–Aldrich. 4,4'-dimethyl-2,2'-bipyridine (97%) was obtained from Astatech. The copper surface was obtained as a 300 mm × 300 mm × 1 mm sheet from Fisher Scientific. Methanol (certified ACS), 1,2-dichloroethane (certified ACS), 1,4-dioxane (certified ACS), acetone (certified ACS), concentrated nitric acid (ACS grade), and hexane (HPLC

grade) were obtained from Fisher Scientific. Hydrochloric acid (ACS grade) was obtained from Fisher Scientific and diluted to 6 M prior to use. Ethanol (200 proof, ACS grade) was obtained from Pharmco-Aaper. Chloroform-D with 0.3 v/v% tetramethylsilane (TMS) and methanol-D, both with 99.8%-atom D incorporation, were obtained from Acros Organics. Dichloromethane (HPLC grade), tetrahydrofuran (HPLC grade without preservatives), and acetonitrile (HPLC grade) were obtained from Fisher Scientific and dried and purified using an MBraun SPS Compact solvent purification system prior to use. All reagents were used as received unless otherwise noted.

2.2. Characterization techniques

Infrared spectroscopy was conducted using a PerkinElmer Spectrum RX1 Fourier Transform Infrared Spectrometer. Spectra of solid compounds were taken as the bulk solid using a Pike MIRacle Attenuated Total Reflectance accessory. IR of modified surfaces was conducted using a Fixed-Angle Specular Reflectance accessory versus a blank copper coupon background. All surface IR spectra were averaged over 256 scans at 4 cm⁻¹ resolution.

NMR spectra were recorded on a 300 MHz/52 MM Bruker spectrometer or a 60 MHz Varian spectrometer in deuterated solvents using TMS as an internal standard.

X-ray photoelectron spectroscopy was conducted using a Kratos Axis Ultra X-ray photoelectron spectrometer. Survey scan analyses were conducted with an analysis area of 300 × 700 microns and a pass energy of 160 eV, while high-resolution analyses were of the same sample size were conducted with a pass energy of 20 eV.

2.3. Synthesis of 11-hydroxyundecylphosphonic acid (1)

11-Hydroxyundecylphosphonic acid was synthesized via a Michaelis–Arbuzov reaction on the bromo functional group of 11-bromo-1-undecanol following protection of the hydroxyl group with acetyl chloride. The procedure outlined below is modified from those previously reported in the literature [106,107]. NMR peak assignments of products follow those in the literature [106,107].

Acetyl chloride (1.4 mL, 0.020 mol) was added dropwise to a solution of 11-bromo-1-undecanol (5.06 g, 0.0201 mol) and triethylamine (2.8 mL, 0.020 mol) in dry dichloromethane (10 mL) and stirred at 0 °C under nitrogen for 3 h. The solution was washed with saturated sodium bicarbonate solution (30 mL) and deionized water (2 × 25 mL). The organic layer was isolated, dried over sodium sulfate, and the solvent was removed by rotary evaporation. Yield: 3.79 g, 66%. ¹H NMR (CDCl₃/TMS, 300 MHz): δ /ppm = 4.05 (t, 2H, CH₂O), 3.41 (t, 2H, CH₂Br), 2.05 (s, 3H, CH₃), 1.85 (m, 2H, *CH₂CH₂O), 1.62 (m, 2H, *CH₂CH₂Br), 1.42–1.28 (m, 14H, CH₂).

11-Bromoundecylacetate (3.79 g, 0.0129 mol) was refluxed in a three molar excess of triethyl phosphite (7.5 mL, 0.044 mol) at 150 °C under nitrogen for 5 h. Excess triethyl phosphite was removed via short path vacuum distillation to give a golden yellow, oily product. Yield: 4.22 g, 93%. ¹H NMR (CDCl₃/TMS, 300 MHz): δ /ppm = 4.05 (m, 6H, CH₂O), 2.05 (s, 3H, CH₃), 1.5–1.75 (m, 4H, CH₂, CH₂P), 1.1–1.5 (m, 22H, CH₂, CH₃).

A solution of diethyl(11-acetoxyundecyl)phosphonate (4.22 g, 0.0120 mol) and trimethylsilyl bromide (TMSBr, 6.6 mL, 0.050 mol) in dry acetonitrile was stirred under nitrogen at room temperature for 24 h. Methanol was then added in excess, and the solution was stirred under nitrogen at room temperature for 24 h [108,109]. The resulting solution was treated with 6 M HCl to yield a white, crystalline solid (1), recovered by vacuum filtration. Yield: 2.62 g, 87%. ¹H NMR (CD₃OD/TMS, 300 MHz): δ /ppm = 4.93 (s, 3H, OH), 3.50 (m, 2H, *CH₂OH), 1.2–1.8 (m, 20H, CH₂, CH₂P).

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