X-ray photoelectron spectroscopy study of the interaction of N-heterocyclic carbenes with polycrystalline copper surfaces

By

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Abstract

The interaction of organic molecules with metal surfaces to form self-assembled monolayers (SAMs) has been extensively investigated. The formation of SAM on metal surfaces has potential applications in microelectronics, chemical sensing and metal protection in which the SAM quality and stability play critical roles. Thiols are the most widely used in SAM technology. However, the metal-thiolate bond is rapidly oxidized under ambient conditions. Therefore, new ligands were investigated to replace thiols, namely N-heterocyclic carbenes (NHCs). NHCs are well known as ligands for transition metal complexes. Consequently, they are strong candidates for SAM formation on transition metal surfaces. So far, NHCs have been applied to gold surfaces, which produced films with remarkable stability. However, less is understood about the interaction of NHCs with other transition metals. One particularly interesting transition metal is copper, which has significant applications in electronics, heat transfer, etc. Copper is cheaper than gold, but it is easily oxidized and corroded in different media, thus finding a method of preventing this oxidation is very important. Here, we present a study of NHC interactions with clean and oxidized copper surfaces at different temperatures. Detailed X-ray photoelectron spectroscopy (XPS) experiments have been carried out, using both a standard XP spectrometer at fixed X-ray energy, and experiments at variable photoelectron energies carried out at the Canadian Light Source synchrotron. The result shows that exposing the oxidized copper surface to the NHC solution led to a complete removal or reduction of the oxide layer from the surface, followed by a SAM formation on the reduced surface. Evidence from mass spectrometry shows copper and oxygen complexes in the solution, which proves the ability of the NHCs to interact with the oxide layer and remove it from the surface. Further experiments carried out at varying temperature and NHC exposure times have
revealed further details on the mechanism of carbene reaction with the surface. These results show promise in gaining a more fulsome understanding of the dynamics of NHC interactions with Cu, with a view to designing surfaces that are passivated towards oxidation.
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List of Abbreviations and symbols

AFM                        Atomic force microscope
ANHC                    Addressable N-heterocyclic carbene
ARXPS                  Angle-resolved X-ray photoelectron spectroscopy
CHA                      Concentric hemispherical analyzer
CMA                       Cylindrical mirror analyzer
E_B                     Binding energy
E_K                     Kinetic energy
E_{pass}               Pass energy
ESCA              Electron spectroscopy for chemical analysis
F                         Limiting coverage
\Delta f                Frequency change
FWHM                   Full width at half maximum
GC- MS               Gas chromatography-mass spectrometry
HAS                        Hemispherical analyzer
h_v                   Photon of energy
IMFP                    Inelastic mean free path
j                          Total angular momentum quantum number
\lambda_e                Inelastic mean free path
k_a                    Adsorption rate constants
k_d                    Desorption rate constants
k_{obs}                   Observed rate constants
k                         Rate constant
k_t                      Rearrangement rate constants
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>( l )</td>
<td>Orbit angular momentum quantum number</td>
</tr>
<tr>
<td>( \Delta m )</td>
<td>Mass change</td>
</tr>
<tr>
<td>NHCs</td>
<td>N-heterocyclic carbenes</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz crystal microbalance</td>
</tr>
<tr>
<td>QCM-D</td>
<td>Quartz crystal microbalance with dissipation</td>
</tr>
<tr>
<td>RFA</td>
<td>Retarding field analyzer</td>
</tr>
<tr>
<td>( s )</td>
<td>Spin angular momentum quantum number</td>
</tr>
<tr>
<td>SAMs</td>
<td>Self-assembled monolayers</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface plasmon resonance</td>
</tr>
<tr>
<td>( \theta )</td>
<td>Surface coverage</td>
</tr>
<tr>
<td>SR-XPS</td>
<td>Synchrotron-based X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td>TDS</td>
<td>Thermal desorption spectrometry</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultrahigh vacuum</td>
</tr>
<tr>
<td>( \phi )</td>
<td>Work function</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray-photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Overview

Metals and metal oxides have extraordinary properties, which make them an essential component in numerous applications. They are some of the most attractive materials for various industry and research fields, including nanotechnology, which is the study and application of materials with a size range of 1-100 nm.\(^1\) The use of nanotechnology has grown and developed rapidly in the field of physics, chemistry, bioscience, medicine, and drug industries. The creation of the nanostructures has two approaches: top-down and bottom-up nanofabrication.\(^2\) The top-down approach requires using externally-controlled devices to create the nanostructures, while in the bottom-up approach, the atoms or molecules spontaneously arrange themselves to form the nanostructures based on the concept of self-assembly. Self-assembly is defined as the process in which small components, such as molecules or particles spontaneously form an organized structure.\(^3\) The bottom-up method is the most attractive and widely applied technique because it is a simple and inexpensive technique, and forms well-defined nanostructures with fewer defects compared to the top-down approach.\(^4\)

1.2 Self-assembled monolayers (SAMs)

The mechanism of SAM deposition can be described as the spontaneous formation of ordered molecular assembly by chemisorption of the molecule onto a substrate. The adsorbed molecule can directly attach to the substrate surface forming a single, one molecule thick, closely packed layer, which is defined as a monolayer. The adsorbed molecule, which is the simplest building block of the system, typically consists of three parts: the head group, the alkyl group, and the terminal functional group\(^5\) (Fig.1.1). The head group operates as a
linker, attaching the molecule to the substrate by a strong bond. The packing density of the monolayer depends on alkyl groups, which interact with each other by van der Waals forces. The terminal functional group can be functionalized to attach biomolecules and other functional nanostructures.\textsuperscript{5,6}

\textbf{Figure 1.1:} Schematic representation of SAM preparation and structure
1.3 Self-assembled monolayer (SAM) on metals

SAM formation on metals, semiconductors, and metal oxides have held significant attention for many years as it is the ideal approach to form an organic thin film with a thickness of 1-3 nm \(^1\) on metal surfaces. The formation of a high quality and well-defined monolayer depends on several factors. First, the smoothness and the cleanliness of the metal surface itself can have a major effect on the resulting SAM quality. For this reason, it is essential to remove any organic contamination from the metal surface as the first step for SAM preparation. In addition to the metal surface, the affinity of the headgroup for the substrate plays a major role in the SAM formation. The most common headgroups are thiols, silanes, and phosphonates as they react readily with many different metals.\(^1\) Of the metals, transition metals such as Au,\(^7\) Ag,\(^7\) Cu,\(^7,8\) Pt,\(^9\) Pd,\(^10\) Ni,\(^11\) and Fe\(^5\) have been widely used and studied as substrates for SAM formation.

1.4 Self-assembled monolayer (SAM) on gold

Gold is considered as an ideal substrate due to its the excellent electrical conductivity and high chemical inertness. Further, it has high resistance to harsh chemicals and low susceptibility to oxidation. It has a strong affinity to organosulfur compounds, especially thiols.\(^12,13\) SAMs of thiol on gold, in which sulfur is the headgroup, have been extensively studied\(^14–18\) and considered as an ideal model of SAM, as they result in a highly ordered molecular assembly, and are easily prepared.

Nuzzo and Allara both first reported the preparation and characterization of self-assembled monolayers (SAMs) of alkanethiolates on gold in the 1980’s.\(^14\) They showed the formation of an ordered, oriented monolayer of di-n-alkyl disulfides on gold surface. SAMs
of thiol and its derivatives on gold have been extensively investigated\cite{7,15,16,19,20} since the initial Nuzzo and Allara report was published.

The adsorption of thiol on gold substrates can be carried out from either the vapor or the liquid phase; however, the simplest and most common way is the adsorption from the liquid phase. The initial step is to prepare a thiol solution by dissolving a thiol compound in an appropriate organic solvent. The most common type of solvents used for thiol SAM formation is alcohols, such as methanol and ethanol. Then, the gold substrate is immersed into the thiol solution for an adequate time, which is typically from 2 – 24 hours to form an ordered and densely packed monolayer. The initial step towards the formation of the monolayer includes the deprotonation process, in which the hydrogen is eliminated from the thiol compound to form the thiolate. After deprotonation, metallic Au is oxidized to Au$^+$. The general mechanism for this process is:\textsuperscript{6,21}

\begin{equation}
RS-H + Au_n^0 \rightarrow RS-Au^+. Au_n^0 + \frac{1}{2} H_2(g)
\end{equation}

The formation of thiol SAM on gold generally includes two phases. In the first phase, the thiol molecules adsorb rapidly on the gold surface in a lying-down orientation. The disordered molecules cover 80-90\% of the gold surface in this step.\textsuperscript{15,21} The surface coverage increases in the second phase due to the organization of the disordered molecules and transition from lying-down orientation to a standing-up phase.\textsuperscript{22}

The structure of the thiol monolayer on bulk gold has been determined to be in a \((\sqrt{3} \times \sqrt{3})R30^\circ\) arrangement.\textsuperscript{15} The sulfur atom, which has an sp$^3$ configuration, is bonded to three gold atoms with intermolecular spacing (S-S) of \(~5\) Å.\textsuperscript{19,23–25} Two types of
interactions are involved in the thiol film formation on gold. The interaction of the sulfur atom, which is the headgroup, with the gold surface creates a bond with an estimated energy of 126 kJ mol\(^{-1}\). In addition, inter-chain interactions (van der Waals) play an essential role in organizing and stabilizing the monolayer.\(^{25}\)

**1.4.1 The kinetics of thiol adsorption on gold**

Studying the kinetics of thiol adsorption on gold is fundamental to understand the thiol-gold system. Numerous techniques have been employed to study the kinetics, such as contact angle, ellipsometry, quartz crystal microbalance (QCM), and surface plasmon resonance (SPR). For example, Bain studied the kinetics of thiol adsorption on gold by using ellipsometry and the contact angle.\(^{15}\) Based on this work, the adsorption process occurs in two steps (Fig.1.2). The initial step took only a few seconds or minutes and the molecules adsorb rapidly and randomly on the gold surface. The estimated coverage in this step was 80-90\%. The fast-initial step was followed by a slow step, which took hours, or sometimes days, depending on reaction conditions. In this step, the surface coverage was increased due to the organization of the molecules on the gold surface.\(^{15}\) The study implied that the thiol could displace organic contaminants on the gold surface, which affects the initial step. Bain's observations have attracted many researchers to reinvestigate this topic; however, most of them agreed with Bain and reached a consistent result.\(^{16–18}\)
Various models have been developed and applied to study the kinetics of thiol SAM formation on gold. Table 1.1 shows some of the most common models used to fit the measured data. The Langmuir model (Model 1) is the most widely used to describe the adsorption of alkanethiols on gold.\textsuperscript{16–18} For example, the Blanchard group detected the adsorption process of thiol on gold by the QCM and fit the data with the Langmuir model.\textsuperscript{16,17} The study was conducted over a wide range of concentrations. They reported that the SAM of thiol on gold reached an equilibrium, which involved adsorption/desorption processes. The steady state was achieved in less than 1 min. The rate of the adsorption was found to be concentration dependent, but not for high concentrations of thiol.\textsuperscript{22} The Blanchard group expanded their study to investigate the effect of temperature on the kinetics and to calculate thermodynamic parameters. The experiment was conducted between 288 – 303 K and the results indicate no linear relationship between the rate of adsorption and the

\textbf{Figure 1.2:} Schematic diagram of the adsorption process of thiols on gold.
temperature. However, the adsorption process is more spontaneous when the temperature is lower. Based on this, they concluded that the adsorption of thiol on the gold surface is not a diffusion-limited reaction.  

Table 1.1: The most common fitting models used to study the kinetics of thiol adsorption on gold.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
</tr>
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<tbody>
<tr>
<td>(1) Langmuir Model</td>
<td>$\theta (t) = [1 - \exp(-kt)]$</td>
</tr>
<tr>
<td></td>
<td>where $\theta$: is the surface coverage.</td>
</tr>
<tr>
<td></td>
<td>$k$: is the rate constant.</td>
</tr>
<tr>
<td>(2) The Rearrange-Limited Langmuir Model</td>
<td>$\theta (t) = F_1[1 - \exp(-k_{obs,1}t)] + F_2[1 - \exp(-k_{obs,2}t)]$</td>
</tr>
<tr>
<td></td>
<td>where $\theta$: is the surface coverage.</td>
</tr>
<tr>
<td></td>
<td>$F_1$ and $F_2$: are the limiting coverage.</td>
</tr>
<tr>
<td></td>
<td>$k_{obs,1}$ and $k_{obs,2}$: are the observed rate constants.</td>
</tr>
<tr>
<td>(3) An empirical three step model</td>
<td>$\theta (t) = a[1 - \exp(-k_{obs,1}t)] + b[1 - \exp(-k_{obs,2}t)] + c[1 - \exp(-k_{obs,3}t)]$</td>
</tr>
<tr>
<td></td>
<td>where $\theta$: is the surface coverage.</td>
</tr>
<tr>
<td></td>
<td>$a$, $b$, and $c$: are the pre-exponential factors.</td>
</tr>
<tr>
<td></td>
<td>$k_{obs,1}$, $k_{obs,2}$ and $k_{obs,3}$: are the observed rate constants.</td>
</tr>
</tbody>
</table>

Kai Hu and co-workers tracked the SAM formation of thiol on gold by using atomic force microscopy (AFM). The experiment was started by adjusting the AFM tip with a negatively charged silica sphere. A charged thiol (HSC\textsubscript{10}COO\textsuperscript{-}) was used for this experiment. The idea of following the adsorption steps was based on measuring the force between the AFM tip, which was modified with a negatively charged silica sphere, and the
gold surface, as a function of the thiol adsorption time.\textsuperscript{18} The Langmuir model was applied to the collected data and the results were consistent with a two-step adsorption process.

In contrast to the Langmuir model which described the rate of the initial step, the rearrange-limited Langmuir model (Model 2) can also describe the two-step adsorption process of thiol on gold. This model has frequently been used by several groups to explain the growth of the thiol film on gold.\textsuperscript{20,26–28} For example, DeBono \textit{et al.} employed the SPR techniques to investigate the adsorption.\textsuperscript{26} The study included the effect of the chain length, and the injection system (static and dynamic) of the thiol on the adsorption rate. The measurements revealed that the thiol adsorbed rapidly in the first step with 80\% coverage for the long chain and 50\% coverage for the short chain. They also found that the fast step was followed by a slow rearrangement step, that the injection system has an impact on the adsorption rate, and that a dynamic system accelerates the adsorption process compared to the static system.\textsuperscript{26}

Damos and co-workers also confirmed the two-step adsorption of thiol on gold by using SPR techniques and they further developed the rearrange-limited Langmuir model.\textsuperscript{20} They assumed that many molecules adsorbed on the surface during the initial step. Then, excess thiol molecules desorbed from the surface while the rearrangement process for the adsorbed molecules took place to form the SAM on the surface.\textsuperscript{20} Therefore, in addition to the adsorption rate, they defined the desorption and the rearrangement rate and overall provided more detailed information about the thiol adsorption process.

Based on this work, Jiang \textit{et al.} further showed that the adsorption of thiol (thiophene dendron thiols) occurred in three steps (Model 3).\textsuperscript{29} The initial fast adsorption/desorption
step is followed by two slow steps in which the short and long rearrangement process are
took place as follows: 29

\[ A - SH + Au \xrightarrow{k_a} \frac{A-S}{Au} \xrightarrow{k_d} \frac{k_r}{Au} A-S-Au \] (1.2a)

\[ \frac{A-S}{Au} \xrightarrow{k_r} A-S-Au \] (1.2b)

\[ A-S-Au \xrightarrow{k_t} A^{*-S}-Au \] (1.2c)

where:

\( A-SH \) represents the thiol.

\( \frac{A-S}{Au} \) represents the initially adsorbed species.

\( A-S-Au \) is the preliminary reorganized species.

\( A^{*-S}-Au \) is the final reorganized species.

\( k_a \) and \( k_d \) are the adsorption and desorption rate constants.

\( k_r \) and \( k_t \) are the rearrangement rate constants.

### 1.5 Copper as a substrate for SAMs

Copper is one of the most important transition metals and the main component of many
alloys. It has a very high thermal and electrical conductivity.\textsuperscript{30} Also, copper is inexpensive
compared to other metals having comparable properties. Due to its remarkable properties,
copper is a highly attractive material for various applications (Fig. 1.3), which involve heat
exchange and electrical conductivity. However, it is rapidly oxidized upon exposure to air
or in a humid environment and forms layers of copper oxides and copper hydroxides. Another serious problem is corrosion; copper is easily corroded in aqueous media. The oxide layers and the corrosion products, which form on the copper surface, have an impact on its properties and therefore limit its applications.

**Figure 1.3:** Some of the major applications of copper.\textsuperscript{31–33}

### 1.5.1 Copper oxides and hydroxide

In addition to its zero-valent state, Cu also commonly exists in Cu\textsuperscript{1+}, and Cu\textsuperscript{2+} valence states. For example, copper in cuprous or cuprite oxide (Cu\textsubscript{2}O) has an oxidation state +1 and therefore exists with a full 3\textit{d} shell (3\textit{d}\textsuperscript{10}). It has a cubic structure (Fig.1.4a) in which each Cu atom is coordinated with two O atoms.\textsuperscript{34,35} An oxygen-rich environment is the most
important factor that contributes to the chemisorption of the oxygen on the copper surface to produce a layer of cuprite oxide. Cuprite oxide is formed at the first stage of copper oxidation, at low temperature and pressure, so it is known as the primary oxide for copper.\textsuperscript{36} Cuprite oxide is a p-type semiconductor with a direct band gap of 2.02 - 2.17 eV,\textsuperscript{36} therefore, it is widely used as a solar absorber in photovoltaic cells.\textsuperscript{37}

Cupric oxide (CuO), with a Cu oxidation state of +2, has an incomplete 3\textit{d} shell (3\textit{d}^9). Cupric oxide has a monoclinic structure (Fig.1.4b) in which each copper atom is four-fold coordinated by O atoms while each oxygen atom coordinates to a copper atom with a distorted tetrahedron geometry.\textsuperscript{36,38} Cupric oxide is also a p-type semiconductor with a direct band gap of 1.2 – 1.9 eV,\textsuperscript{36} and therefore it has many applications, such as diodes, cathodes in lithium batteries, catalysis, field emission devices, and gas sensors.\textsuperscript{39}

Copper also readily exists as copper hydroxide (Cu(OH)\textsubscript{2}), which has an orthorhombic pyramidal structure (Fig.1.4c).\textsuperscript{40} It has a +2 oxidation state with an incomplete 3\textit{d} shell similar to cupric oxide. Copper hydroxide is known to be a metastable phase of copper, in which it can spontaneously decompose into cupric oxide and water.
Figure 1.4: The structure of: (a) Cu\(_2\)O. (b) CuO. (c) Cu(OH)\(_2\).\(^{41,42}\)
1.5.2 Copper oxidation at ambient conditions

Copper is a highly reactive metal and can oxidize spontaneously under many conditions. Platzman and co-workers have investigated the oxidation process of copper exposed to ambient air. X-ray-photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and spectroscopic ellipsometry were employed to study the oxidation process. Their results showed the formation of oxide layers on the copper surface once exposed to air and an increase in the layer thickness as a function of time. This study illustrates that the oxidation process of copper has three main stages:

(a) **The formation of Cu$_2$O:** when the copper is placed in an oxygen-rich environment, oxygen immediately adsorbs onto the surface to form a Cu$_2$O layer.

The formation of the Cu$_2$O layer is a result of electron transfer through the metal/oxide interface which can be described by the following equation:

$$4Cu^+ (m) + O_2(g) \rightarrow 2Cu_2O(s) \quad (1.3)$$

(b) **The formation of Cu(OH)$_2$:** an overlayer of Cu(OH)$_2$ is formed as a result of the interaction of the copper ions with hydroxyl group (OH$^-$) present in the surroundings (see Eq. 1.4).

$$Cu^+ (m) + 2OH^-(aq) \rightarrow Cu(OH)_2(s) \quad (1.4)$$

(c) **Transformation of Cu(OH)$_2$ to CuO:** at room temperature, and in a wet environment, the metastable Cu(OH)$_2$ transforms rapidly to a stable layer of CuO by the following reaction$^{34,43}$:

$$Cu(OH)_2(s) + 2OH^-(aq) \rightarrow Cu(OH)_4^{2-}(aq) \rightarrow CuO(s) + 2OH^-(aq) + H_2O \quad (1.5)$$
1.6 Self-assembled monolayer (SAM) on copper

In order to prevent the rapid oxidation and subsequent formation of oxides and/or hydroxides, many different types of SAMs have been investigated in order to protect the copper surface. For example, phosphines, amines, carbonyls, cyanides, and thiols have been used to functionalize and protect copper. Of these, SAMs of thiols are the most common approach used, as thiols have been shown to form a relatively stable layer that can prevent the oxidative process. The preparation of SAM of thiol on copper is similar to the preparation for gold as the SAM can be prepared from the vapor or the aqueous phase; however, adsorption from solution is the most common approach. In this method, a copper substrate is simply immersed in a thiol solution, which is prepared by dissolving the thiol in an appropriate solvent, for a sufficient period of time. The effect of thiol concentration and time have been explored at length, but one recurring challenge is the reproducibility of forming a high-quality thiol SAM on copper due to the high reactivity of copper towards oxygen.

1.6.1 SAM of thiol on clean copper

Laibinis et al. first explored the adsorption of thiol from solution onto copper surfaces in 1991. This initial report revealed the formation of densely packed and oriented SAMs of alkanethiols on copper. Chemical vapor deposition was used to prepare copper substrates to minimize the formation of oxide. Characterization of the copper surface using XPS showed the existence of the thiolate adsorbed on the surface, which indicated film formation. However, the O 1s spectrum revealed a significant amount of Cu$_2$O on the surface after thiol deposition. They described the adsorption by the following equations:
RSH + Cu\(^0\) \rightarrow RSCu\(^1\) + \frac{1}{2} H_2 \quad (1.6)

RSH + Cu\(^1\) \rightarrow RSCu\(^1\) + H^+ \quad (1.7)

The adsorption of thiol on the copper surface generates a non-metallic copper surface as Equations 1.6 and 1.7 illustrate. In addition to chemical composition, the structure and orientation of the thiol SAM itself was also explored in this study. The infrared spectroscopy showed that the alkyl chains are all in a trans conformation at an angle of 12° from the surface normal.\(^7\)

Similarly, Sung and coworkers investigated the adsorption of thiol onto polycrystalline copper surfaces, which were determined to be almost free of oxygen before deposition.\(^49\) The results were similar to what has been reported by Laibinis. In addition to the aliphatic thiol, an aromatic thiol SAM on copper was also explored.\(^50\) It was shown that benzenethiol can form an organized SAM with high surface coverage on the polycrystalline copper surface.

A study of the adsorption process of n-dodecanethiol on copper surfaces was conducted by Dilimon using electrochemical impedance spectroscopy.\(^51\) The results revealed that the formation of thiol layer on a copper surface occurs in two steps, as in the case of gold. In the first step, the thiol molecules are adsorbed rapidly on the copper surface within 10s leading to a film with 90% coverage. The first step is followed by a slow step of further adsorption and consolidation in order to form an organized layer on the copper surface.\(^51\)
1.6.2 SAM of thiol on oxidized copper

In contrast to pristine oxide free copper, the effect of thiol SAMs on the oxidized copper surface has been investigated.\textsuperscript{52–55} In these works, copper surfaces have purposefully been oxidized using various methods, such as exposing the pure copper to hydrogen peroxide, in which the thickness of the oxide layer depends on the oxidation method. These oxidized copper surfaces are then exposed to the thiol solutions for various periods of time, and then typically characterized with XPS to show the thiol effect and structure on both oxidized and clean surfaces. In most studies, XPS showed that the SAM structures on both clean and oxidized copper are similar in quality, which means that the oxide layer didn’t prevent the SAM formation. The studies explained this result by the ability of thiol to remove CuO from the surface and then form SAM on the reduced copper surface.

Sung \textit{et al.} have proposed the mechanism for the redox reaction of thiol on the oxidized copper surface based on gas chromatography-mass spectrometry (GC-MS) results.\textsuperscript{52} They imply that the oxide layer is reduced while the thiol is oxidized to disulfide by the following reactions:

\begin{equation}
2\text{RSH} + \text{CuO} \rightarrow (\text{RS})_2 + \text{Cu} + \text{H}_2\text{O} \quad (1.8)
\end{equation}

or

\begin{equation}
2\text{RSH} + 2\text{CuO} \rightarrow (\text{RS})_2 + \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad (1.9)
\end{equation}

In the presence of excess thiol, the Cu(I) thiolate complex is generated as following:

\begin{equation}
\text{RSH} + \text{Cu} \rightarrow \text{Cu}^{1}\text{SR} + \frac{1}{2} \text{H}_2 \quad (1.10)
\end{equation}

or

\begin{equation}
2\text{RSH} + \text{Cu}_2\text{O} \rightarrow 2\text{Cu}^{1}\text{SR} + \text{H}_2\text{O} \quad (1.11)
\end{equation}
Calderon took into account the deprotonation of thiol to generate the thiolate anion, which reacts with Cu$_2$O as in the following reactions:

$$\text{Cu}_2\text{O} + 2\text{RSH} \rightarrow 2\text{CuSR} + \text{H}_2\text{O} \quad (1.12)$$

$$\text{Cu}_2\text{O} + 2\text{RS}^- + \text{H}_2\text{O} \rightarrow 2\text{CuSR} + 2\text{OH}^- \quad (1.13)$$

The water molecule from solution is contributing to the oxide reduction process by protonating the oxygen atom of Cu$_2$O.

Based on the above reactions, the thiol concentration has a significant impact in reducing the oxide on the copper surface. Fonder has also reported the role of n-dodecanethiol concentration as an important parameter in reducing the oxide layer from the copper surface. The report found that thiol concentration improved the efficiency of removing the oxide layer.

### 1.6.3 Solvent effect on SAM of thiol on copper

Although, both copper and gold readily react with thiols, copper is a much more reactive metal, and can even interact with the solvent during SAM formation. Therefore, the solvent type is an essential factor during this process and can have a significant influence on the quality of the SAM formed. Most importantly, it has been found that using common alcohol solvents, such as ethanol and methanol, form thiol SAMs with low quality on copper due to their interaction with the copper surface. The influence of the type of solvent on thiol SAM formation on clean and oxidized copper surfaces, was studied by Zhang. The study demonstrated that using high polarity solvents has a significant role on the formation of a highly ordered and densely packed SAM on clean and oxidized copper surfaces.
1.6.4 The stability of thiol SAM on copper

The structure of the film formed on the metal surface can subsequently determine the chemical and physical properties of the surface, and thus define the practical applications. Further, the stability of SAMs is an essential factor for their application. For an easily oxidized metal like copper, the stability of the SAM in ambient conditions is critical. For example, a significant change in the film structure of thiol on copper has been observed after one week of air exposure, where the adsorbed thiolate species oxidized to sulfonate. The oxidation rate was found to be dependent on the thiol chain length; as the thiol chain length increases the oxidation rate decreases, which is likely an effect of the extra stability of the SAM afforded by the interchain stabilization.

Thermal desorption spectrometry (TDS) was employed to study the thermal stability of decanethiol and benzenethiol on clean and oxidized copper surfaces. The results revealed a decomposition of thiol films at 373 and 423K for decanethiol and benzenethiol on clean copper surfaces, respectively. The decomposition mechanism involved two steps, the oxidation of the head group to sulfonate, and then the desorption of the alkyl chain or phenyl depending on the thiol type. Decanethiol on the oxidized copper surface exhibited a higher stability than on the clean surface; it decomposed at a slightly higher temperature due to the presence of the Cu$_2$O, which reduced the interaction between the alkyl chain and the copper surface during the decomposition process. Other groups have also reported the decomposition of thiol SAMs, which occurred between 300-400 K with sulfur remaining on the surface, and subsequently generates a copper sulfide layer.
1.7 Introduction to N-heterocyclic carbenes (NHCs)

1.7.1 Carbenes

Carbenes are molecules that contain a neutral divalent carbon atom with six electrons in its valence shell.\textsuperscript{63,64} Carbenes are highly reactive species, with very short lifetimes, which make the carbenes typically difficult to be isolated. The first isolation of a free carbene was in 1991 reported by Arduengo \textit{et al.}, and they succeeded in preparing stable ‘bottleable’ crystalline N-heterocyclic carbene.\textsuperscript{64,65} Carbenes can be classified into two groups: singlet carbenes and triplet carbenes (Fig.1.5). For the singlet carbene, the lone pair of electrons occupies the sp\textsuperscript{2} orbital leaving the p orbital empty while no vacant orbital remains for the triplet carbene, in which each electron occupies different orbital with parallel spin.\textsuperscript{63,66} The lone pair, which occupies the sp\textsuperscript{2} orbital, stabilizes the carbene; therefore, the singlet carbene is more stable than the triplet.

![Singlet carbene diagram](image1.png)

![Triplet carbene diagram](image2.png)

**Figure 1.5:** The carbene states: singlet and triplet electronic structure.

1.7.2 N-heterocyclic carbenes (NHCs)

The Wanzlick - Arduengo carbenes, which are commonly known as N-heterocyclic carbenes (NHCs), are carbene species that contains at least one nitrogen atom within the ring structure.\textsuperscript{67} N-heterocyclic carbenes can be used to coordinate to many different
transition metals and p-block elements, and therefore have many uses as organocatalysts.\textsuperscript{68} The most significant application for NHCs is as ligands for transition metals.

**The electronic structure**

NHCs can provide remarkable stability to transition metals due to their unique electronic structure. The carbene carbon atom has sp\(^2\)- hybridization (Fig. 1.6), while the adjacent nitrogen atoms have \(\sigma\)-electron withdrawing and \(\pi\)-electron donating effects, which stabilize the sp\(^2\) carbon lone pair electrons. These lone pair electrons can subsequently participate in strong \(\sigma\) bonding to various transition metals.\textsuperscript{68,69} Overall, NHCs are electron–rich, strong neutral \(\sigma\)-donors, and weak \(\pi\)-acceptors.

![Figure 1.6: The electronic structure of NHCs: stabilization via \(\sigma\)-electron withdrawing and \(\pi\)-electron donating effects of nitrogen atoms.](image)

**The reactivity of the NHCs**

Although NHCs are remarkably stable while bound to a material, they are highly reactive in their unbound state. NHCs are strongly basic; consequently, they can act as ligands in transition metal chemistry and also as reducing agents.\textsuperscript{70} NHCs are sensitive to oxygen and moisture (Scheme 1.1), so they require an inert gas atmosphere.\textsuperscript{65,71,72} However,
NHCs are well known and widely used as ligands for transition metal complexes. NHCs form a strong bond once coordinate to a metal center.

**Scheme 1.1:** The reactivity of NHCs.

**The NHC-metal bond**

NHC-metal complex plays a significant role in the field of oxidation catalysis and cross-coupling reactions. Both the steric and electronic structure of NHCs contribute to NHC-metal complex strength and stability. NHCs are strongly bonded to the metal centers forming a highly stable complex with little tendency of dissociation (Scheme 1.2). This has a significant effect on the complex lifetime.

**Scheme 1.2:** The NHC-metal complexation.
The formation of NHC-metal complex depends on the electronic structure of both the NHC and the metal. The NHC-metal bond involves three types of orbital interaction: σ-donation, π- donation, and π- backdonation, which is illustrated in Figure 1.7. The average length of the NHC-metal bond is 2.00 Å. For example, the average length of Ag-NHC is 2.095 Å.

**Figure 1.7:** Representation of the orbital interactions between NHC and a transition metal (TM).
1.7.3 Functionalizing metal surfaces with NHCs.

In 2013, Johnson and co-workers published a study of functionalizing gold surfaces with a functional “addressable” N-heterocyclic carbene (ANHC). A quartz crystal microbalance with dissipation (QCM-D) was used to study the binding of ANHC to gold surfaces and to obtain the average mass density of the monolayer. The results indicated the formation of an ANHC monolayer on the gold surface with coverage less than the estimated value. Unfortunately, the study didn’t reveal any information about monolayer stability.

Crudden, Horton, et al. studied the adsorption of N-heterocyclic carbenes (NHCs) on gold surfaces to form robust and stable self-assembled monolayers, but the preparation method required an inert atmosphere. The monolayer formation on gold was examined by XPS and scanning tunneling microscopy (STM). The stability of the NHC film on gold was investigated in detail and showed high stability in air, water, and at elevated temperatures. Also, the results revealed a remarkable stability for the NHC film over a wide range of pH and boiling solvents, including coordinating solvents, such as THF. Moreover, 80% of the film remained stable after exposing it to 1% H₂O₂ for 24h. Most importantly, it was shown that thiol SAMs did not survive any of these conditions. Therefore, the thermal, chemical and electrochemical stability of NHC films on gold makes them an excellent alternative for thiols in several applications.

Finally, Crudden, Horton et al. also developed a new type of NHC, a bench-stable NHC precursor based on a hydrogen carbonate salt. The NHC precursor demonstrated NHC formation on gold surfaces from both solution and vapor phases under ambient conditions giving carbon dioxide and water as byproducts. The resulting films of the bench-stable NHC on gold were as electrochemically stable as the NHC film on gold, which was...
reported in the initial report. The thermal stability of the monolayers was tested by the temperature programmed desorption (TPD), which revealed that the degradation temperature of the NHC from the gold surface is 605 K. This result was used to determine the NHC-Au bond strength, which is found to be 158 ± 10 kJ mol⁻¹.

Recently, the formation of SAMs of NHCs on copper surface was investigated by Larrea et al., in which three different molecules of NHCs (benzimidazolium bicarbonates with dimethyl, diethyl, and diisopropyl substituents) were vapor deposited onto clean Cu(111) surface. The resulting SAMs were examined by STM, high-resolution electron energy loss spectroscopy (HREELS), and temperature programmed desorption (TPD). The result revealed the role of N,N substituents in determining the adsorption geometry of NHC on Cu surface. HREELS spectra give strong evidence for the adsorption of NHCs on Cu surface. In addition, HREELS result showed that benzimidazolium bicarbonates with dimethyl and diethyl substituents are aligned parallel to Cu surface while the bulkier NHC (benzimidazolium bicarbonates with diisopropyl substituents) bind perpendicular to the Cu surface. Furthermore, STM result showed a highly-ordered SAM of benzimidazolium bicarbonates with dimethyl substituents by forming (NHC)₂Cu complex on Cu surface. The thermal stability of the NHCs SAMs on Cu was examined by TPD, which showed a remarkable stability up to 570K.

1.8 Thesis motivation

The primary motivation of this thesis is to investigate the interaction of N-heterocyclic carbenes with copper surfaces to see if similar stable films can be achieved for a much more reactive metal than gold. The goal is to generate and develop functional copper surfaces to utilize in various applications where a pure copper surface is desired, as opposed to the
traditional copper oxides or hydroxides. A secondary goal of this work is to study the effect of removing existing oxides and hydroxides from copper, and the subsequent protection of the copper surface from further oxidation.

1.9 Outline of the thesis

This dissertation is composed of seven chapters. Chapter 2 provides a comprehensive review and description of XPS as a powerful technique for surface analysis. XPS is extensively used in this thesis to characterize metal surfaces.

Chapter 3 investigates the adsorption of N-heterocyclic carbenes on copper surfaces at room temperature. The study was conducted on clean and oxidized copper surfaces, which exposed to two types of NHC, “free” and bicarbonate (salt type). XPS was employed to study the structure of copper surfaces.

Chapter 4 is an extension of the work in chapter 3. In this chapter, synchrotron radiation-based X-ray photoelectron spectroscopy (SR-XPS) was employed to provide a more detailed examination of the layered structure and chemical composition of the copper surfaces resulting from NHC adsorption at room temperature.

Chapter 5 investigates the influence of the temperature on the interaction of NHC with copper surfaces using a combination of standard XPS and synchrotron radiation-based X-ray photoelectron spectroscopy (SR-XPS).

Chapter 6 addresses the experimental results for the adsorption kinetics of N-heterocyclic carbenes on gold surfaces. SAM formation of NHC on copper is investigated
in chapters 3, 4, and 5; however, defining the surface reaction mechanisms is fundamental and towards that end, it is important to understand the kinetics of adsorption on metal surfaces. In this study, a gold surface was used because of its lower reactivity towards oxygen compared to copper. The study was conducted by using XPS and QCM-D techniques.

Chapter 7 presents the general conclusions of this thesis and a brief description of the future work.
1.10 References


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(64) Diez-González, S. N-heterocyclic carbenes: from laboratory curiosities to efficient synthetic tools; RSC Pub.: Cambridge, 2011.


2.1 History

In 1887, Hertz discovered the photoemission phenomenon, which describes the effect of electron emission from a surface when X-rays interact with that surface. The process of an X-ray striking a surface to produce an electron is called the photoelectric effect (Fig. 2.1). The photoelectric effect generally remained without explanation until 1905, when Einstein explained and documented the theory of the photoelectric effect.\textsuperscript{1} Einstein’s explanation was the basis for the later development of one of the most powerful techniques in surface science, which is now known as X-ray photoelectron spectroscopy (XPS).

\textbf{Figure 2.1:} The photoelectric effect, light strikes a metal surface causing electron to be ejected from the metal.
2.2 The concept and principle of XPS

2.2.1 The photoemission process

XPS is a surface sensitive technique, which can be employed to measure surface composition and to investigate the electronic structure of a sample (molecules and surfaces). As this technique provides chemical analysis, it is also known as electron spectroscopy for chemical analysis (ESCA).\textsuperscript{1} Based on the photoelectric effect, the sample is irradiated with a photon of energy \((h\nu)\), which is absorbed by an electron with a binding energy \((E_B)\). The electron is subsequently excited and ejected from the surface with a kinetic energy \((E_K)\) of:\textsuperscript{2,3}

\[
E_K = h\nu - E_B - \phi
\]  

(2.1)

where \(\phi\) is the work function of the spectrometer. The photoemission process is illustrated in Figure 2.2.

\[\text{Figure 2.2: A schematic diagram of the photoemission process, where } E_F \text{ is the Fermi energy.}\]
The photoemission process can be explained by a three-step model (Fig. 2.3). The first step is the photoexcitation where the element absorbs the photon, and excitation of the electron takes place to create a photoelectron. The second step is the travel of the photoelectron from the bulk to the sample surface. The emission of the photoelectron takes place in the final step, in which the photoelectron escapes into the vacuum.

**Figure 2.3:** A schematic diagram of the three-step model.

### 2.2.2 The Auger process

Figure 2.4 demonstrates the Auger process. The process involves three electrons. When a photon of energy \( (hv) \) strikes an atom, an electron from the core- level is ejected as in Figure 2.2. The ejection of the electron creates a core hole and an electron from a higher-level falls to fill the vacancy. This will produce an excited state ion with excess energy. The emission of
another electron takes place to remove the excess energy, this electron is called an Auger electron.\textsuperscript{3,5}

\textbf{Figure 2.4:} A schematic diagram of the Auger process.

\textbf{2.3 Instrumentation}

Figure 2.5 shows a schematic diagram of the basic components of the XPS. The main parts are: vacuum system, X-ray source, and the electron energy analyzer.\textsuperscript{2,3,6,7} Each part will be briefly described in the following sections.
2.3.1 Vacuum system

To conduct an experiment with the XPS, ultrahigh vacuum (UHV) is required. The XPS technique is very sensitive to surface contamination, so UHV is needed to prevent the adsorption of contaminants and maintain clean sample surfaces. To achieve these conditions a typical pressure is $10^{-9} - 10^{-11}$ torr is necessary.\footnote{3}
2.3.2 X-ray source

A source is needed to generate X-rays, which interact with the material being investigated. The interaction produces photoelectrons, which are subsequently analyzed. The X-ray sources should be able to provide high energy and small linewidth (< 1 eV) and can be either X-ray tubes (laboratory sources) or synchrotron radiation (SR).\(^9\)

X-ray tubes consist of an anode and a cathode system (Fig. 2.6). An anode with high potential (5-15 kV) is typically employed. Table 2.1 lists potential materials that can be used as an anode in the X-ray tubes.\(^2,3\) However, Al K\(\alpha\) and Mg K\(\alpha\) are the most common X-ray sources used in the XPS.

![Figure 2.6: A schematic diagram of an X-ray tube. The heated filament (cathode) provides electrons towards the anode then x-ray photons are released.](image)
Table 2.1: Energies and linewidth of the X-ray candidate materials.

<table>
<thead>
<tr>
<th>X-ray source</th>
<th>Energy (eV)</th>
<th>Linewidth (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y Mζ</td>
<td>132.3</td>
<td>0.47</td>
</tr>
<tr>
<td>Zr Mζ</td>
<td>151.4</td>
<td>0.77</td>
</tr>
<tr>
<td>Nb Mζ</td>
<td>171.4</td>
<td>1.21</td>
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<td>Na Kα</td>
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<tr>
<td>Mg Kα</td>
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<td>0.70</td>
</tr>
<tr>
<td>Al Kα</td>
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<td>0.85</td>
</tr>
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<td>Ti Kα</td>
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</tr>
<tr>
<td>Cu Kα</td>
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<td>1.50</td>
</tr>
<tr>
<td>Ag Lα</td>
<td>2984.4</td>
<td>2.6</td>
</tr>
</tbody>
</table>

The cathode of the X-ray tube is a heated filament at ground potential. Tungsten filaments are the most commonly used cathodes. However, lanthanum hexaboride (LaB₆) is beginning to replace tungsten in newer XPS systems, in which X-ray monochromators are used.⁷,¹⁰,¹¹

On the other hand, synchrotron radiation (SR) is electromagnetic radiation emitted by a charged particle (electron) moving in a curved path or orbit at velocities close to the speed of light under magnetic field control.¹²,¹³ In this system, three types of magnetic elements are employed to generate the synchrotron radiation: bending magnets, wigglers, and undulators. The charged particles reach the target energy in the booster (Fig. 2.7) then transferred to the storage ring where they circulate for hours. A typical synchrotron storage ring can hold current from 100 to 1000 mA where the energy range is < 1GeV to 3 GeV. The beam lifetime, which depends on the stored current, is approximately from 4 -12 h.¹² Synchrotron radiation has high
intensity, a broad smooth spectrum, is linearly polarized in the horizontal plane, and has a short pulse time structure.\textsuperscript{14,15}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{synchrotron_diagram}
\caption{A schematic diagram of the synchrotron.}
\end{figure}

\subsection{2.3.3 Electron analyzer}

An electron analyzer is designed with either magnetic or electric fields. The reflected electrons enter the analyzer through a collecting lens with specific energy called the pass energy ($E_{\text{pass}}$), then the electron analyzer disperses the emitted photoelectrons and sorts them based on their kinetic energy. The resolution is directly dependent on the kinetic energy of photoelectrons as well as the intensity of the spectra. Three types of electron analyzers are common for XPS:
the retarding field analyzer (RFA); the concentric hemispherical analyzer (CHA) or hemispherical analyzer (HSA); and the cylindrical mirror analyzer (CMA). The CHA is the most common analyzer for XPS due to its high sensitivity and resolution, which are significant factors in determining the elemental identity and chemical state.\textsuperscript{3,6}

2.4 The X-ray photoelectron spectrum

2.4.1 Spin-Orbit splitting

The XPS spectrum of the elements is either singlet or doublet. A doublet peak is due to spin-orbit coupling, which correlated to the angular momentum quantum number. The total angular momentum quantum number is $j = l \pm s$ (where $l$ is the orbit angular momentum quantum number, and $s$ is the spin angular momentum quantum number). When $l = 0$, a singlet XPS peak is observed. If $l > 0$ (Table 2.2) a doublet peak is detected with different binding energy. The area ratio for the peaks is shown in Table 2.2.\textsuperscript{3}

<table>
<thead>
<tr>
<th>Subshell</th>
<th>$l$ values</th>
<th>$j$ Values</th>
<th>Area ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0</td>
<td>1/2</td>
<td>-</td>
</tr>
<tr>
<td>p</td>
<td>1</td>
<td>1/2, 3/2</td>
<td>1:2</td>
</tr>
<tr>
<td>d</td>
<td>2</td>
<td>3/2, 5/2</td>
<td>2:3</td>
</tr>
<tr>
<td>f</td>
<td>3</td>
<td>5/2, 7/2</td>
<td>3:4</td>
</tr>
</tbody>
</table>

Table 2.2: Spin-orbit splitting parameters
2.4.2 Chemical shift in the XPS spectrum.

The change in the chemical state of the atom can be detected in the XPS as a change in the binding energy, as well as the peak width and shape. The shift in the binding energy is due to different chemical environments of the atom and so it is called the chemical shift.\textsuperscript{2,7} The direction of the shift, which can be positive or negative, correlates to the change in the valence electron density of the atom. If the atom accepts some charge (negative), the binding energy will decrease and shift to the lower value. Contrary to this, the binding will increase and shift to higher value if the atom donates charge (positive). This can explain the shift for metal oxides, where a shift to higher binding energy is observed.\textsuperscript{2,6}

The electronegativity of the ligand has a contribution to the change of the atom’s initial state energy; ligands with high electronegativity lead to a positive shift in the binding energy.\textsuperscript{16} Another factor is ligand polarizability, which has an impact on the final state relaxation energy of the metal atom. During the photoemission process, the creation of the core hole on the central atom has a polarizing effect on the ligand. Hence, polarization of the ligand has an influence on determining the binding energy shift.\textsuperscript{16}

Another type of shift in binding energy is observed for solid materials. The coordination number of atoms on the surface is different from the bulk.\textsuperscript{1} As a result, the surface atoms exhibit a shift in the binding energy compared to bulk atoms. The detection of the shift in binding energy at the surface can be achieved by employing a radiation source with a high-energy resolution, such as synchrotron radiation. Synchrotron radiation has an energy range in which a short escape depth of the ejected electron is achieved to get a high surface sensitivity.\textsuperscript{1}
2.4.3 Shake-up satellites

Shake-up satellite peaks are observed when valence electrons are excited to a higher unfilled level as a result of a change in nuclear charge. As a consequence, the kinetic energy of the ejected photoelectron is reduced, and a satellite structure (shake-up) appears a few eV higher (binding energy) than the main peak of the element.\textsuperscript{3,7} A satellite structure (shake-up) can be detected for first-row transition metals\textsuperscript{15,17} where it is used to identify and differentiate the oxidation states of the metal.

2.4.4 Auger series (lines)

There are four main Auger series which can be observed in the XPS. The series are KLL, LMM, MNN, and NOO. The energy level for the Auger series is represented by letters K, L, M, N…etc. (Table 2.3).\textsuperscript{3} The Auger transitions for the elements based on the atomic number is presented in Table 2.4.\textsuperscript{3} The Auger process involves three electrons as described previously, so the notation of the Auger transition includes three letters. The first letter represents the shell which has a vacancy created by removing the core electron. The second letter is for the shell where the relaxation electron falls to fill the hole at the core level. The third letter represents the shell where the second hole is created by ejecting the Auger electron.\textsuperscript{3}
Table 2.3: The energy level notation for XPS and Auger.

<table>
<thead>
<tr>
<th>Notation</th>
<th>XPS</th>
<th>Auger</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s(_{1/2})</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>2s(_{1/2})</td>
<td>L(_1)</td>
<td></td>
</tr>
<tr>
<td>2p(_{1/2})</td>
<td>L(_2)</td>
<td></td>
</tr>
<tr>
<td>2p(_{3/2})</td>
<td>L(_3)</td>
<td></td>
</tr>
<tr>
<td>3s(_{1/2})</td>
<td>M(_1)</td>
<td></td>
</tr>
<tr>
<td>3p(_{1/2})</td>
<td>M(_2)</td>
<td></td>
</tr>
<tr>
<td>3p(_{3/2})</td>
<td>M(_3)</td>
<td></td>
</tr>
<tr>
<td>3d(_{3/2})</td>
<td>M(_4)</td>
<td></td>
</tr>
<tr>
<td>3d(_{5/2})</td>
<td>M(_5)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4: The observable Auger transitions for the elements.

<table>
<thead>
<tr>
<th>Atomic number (Z)</th>
<th>Auger transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 &lt; Z &lt; 14</td>
<td>KLL</td>
</tr>
<tr>
<td>14 ≤ Z &lt; 40</td>
<td>LMM</td>
</tr>
<tr>
<td>40 ≤ Z &lt; 82</td>
<td>MNN</td>
</tr>
<tr>
<td>82 ≤ Z</td>
<td>NOO</td>
</tr>
</tbody>
</table>
The kinetic energy of the Auger electron doesn’t depend on the X-ray source. So, the energy of the Auger electron (E_{ABC}) can be calculated by Equation 2.2:\textsuperscript{3,6}

\[ E_{ABC} = E_A - E_B - E_C - \phi \] (2.2)

where \( E_A \), \( E_B \), and \( E_C \) are the binding energies of the electrons in levels A, B, and C which are involved in the Auger process. \( \phi \) is the work function.

The qualitative and quantitative analysis of Auger spectra provides chemical information about the sample being studied. It is considered as a “chemical fingerprint” tool that can be used for the identification of the element and its oxidation states. Also, electronic structure details, such as hybridization, electron delocalization, and screening effects can be obtained from Auger spectra.\textsuperscript{14,18}

2.5 Angle-resolved X-ray photoelectron spectroscopy (AR-XPS)

Angle-resolved X-ray photoelectron spectroscopy (AR-XPS) is a powerful technique which can be employed to differentiate between the XPS signals of the surface and the bulk for the studied specimen. It is considered a non-destructive depth profile technique that is used to study the chemical composition of the sample layer.\textsuperscript{6} Figure 2.8 shows a diagram for the angle resolved method.
In a typical XPS experiment, the photoelectron is detected at a take-off angle (the angle between the path of the ejected photoelectron and the surface plane) of $90^\circ$ to the surface.$^{3,7}$ Under these conditions, the XPS signal is for the bulk since it is sensitive to the bulk more than the surface (Fig. 2.9 (a)). In AR-XPS, the emission angle is changed by changing the tilt of the sample from $0^\circ$ to $< 90^\circ$. By changing the emission angle ($\theta$) the escape depth of photoelectrons is changed:$^3$

$$\text{Depth} = \lambda_e \cos \theta \quad (2.5)$$

where $\lambda_e$ is the inelastic mean free path for electrons in the sample.
The XPS signal for the surface layer (0 -10 nm) is detected at high emission angle (grazing angles) (Fig. 2.9 (b)).\textsuperscript{3} AR-XPS is a widely used technique due to its advantages; it is mostly used to study self-assembled monolayers on substrates.
2.6 References

(8) X-Ray Photoelectron Spectroscopy (XPS)

Chapter 3

The interaction of N-heterocyclic carbenes with Cu surfaces at room temperature

3.1 Introduction

Copper is a transition metal that has interesting properties such as high thermal and electrical conductivity, high resistance to electromigration, and excellent workability.\textsuperscript{1,2} In addition, copper is inexpensive compared to other metals, such as gold. Therefore, copper is a good alternative to gold and silver and an essential component in many applications particularly in the electronics industry, in transportation, in machinery and for building construction.\textsuperscript{3} One of most attractive properties of copper is its conductivity; however, copper susceptibility to corrosion and oxidation has significant impacts on its conduction efficiency. These limitations have been approached by employing protective surface coatings, such as polymers, and noble plating materials.\textsuperscript{4,5} One of the most common coating approach is to apply self-assembled monolayers (SAMs) of various molecules onto copper, whereupon the metallic state of copper is protected to prevent transformation to higher oxidation states.

In general, self-assembled monolayers (SAMs) are widely used and have many applications such as microfabrication and metal protection systems.\textsuperscript{6−9} For the formation of high-quality SAMs, the balance between intermolecular and molecule-surface interactions is of fundamental importance.\textsuperscript{10,11} Further, the choice of the molecule and substrate must be considered such as the affinity of the molecule to the substrate. So far, the most extensively studied SAM system is based on alkylthiols on gold\textsuperscript{12−15}, mostly because of sulfur’s high
affinity towards gold and the fact that gold is relatively stable. Thus, this system provides excellent fundamental understanding of SAM deposition, but has fewer industrial applications. On the other hand, thiols also have an affinity to other, more commonly used transition metals such as silver, copper, etc. Indeed, the fundamental interaction between thiols and copper have been studied extensively, but the reproducibility of the resulting SAMs is still a major challenge, because of the high susceptibility of copper to oxidation during the adsorption process. The formation of thiol SAMs on copper often leads to the formation of copper (I) thiolate. This has been confirmed by XPS; which has observed thiolate species in S 2p spectra at 162.4 eV, while corresponding Auger spectra revealed a Cu$^{1+}$ state at 916.5 eV.

More recently, N-heterocyclic carbenes (NHCs) have been reported to form SAMs on gold surfaces, and the resulting SAMs were found to exhibit remarkable stability under a variety of experimental conditions. Interestingly, NHCs are a class of molecule that forms complexes with many different transition metals, and thus could potentially be used for deposition on copper. Towards this end, the vapor deposition of NHC on a Cu single crystal was reported by Larrea et al. They presented the formation of NHC SAMs on a Cu (111) surface with stability up to 570K as shown by using temperature programmed desorption (TPD). They also demonstrated the effect of substituents at the N, N-positions of the NHC on the binding mode with the Cu (111) surface. The results show that bulky NHC molecules bind perpendicular to the Cu surface, whereas small NHCs bind parallel to the surface. This study points out the fundamentals of forming NHC SAMs on the copper surface. However, the technical feasibility of vapor phase deposition is still a challenge as it requires specialized equipment, gas flows, and an elevated temperature, which is not suitable.
for heat sensitive substrates. Thus, a facile, simple, and more economical method would be highly useful in manufacturing applications.

In addition to surface protection, another practical challenge is removing oxides from copper surfaces, i.e., etching. Etching is a process in which chemical action is used to remove surface layers of the metal. In the case of copper, a thick film of oxidation and corrosion products is formed on the surface, which hinders electrical conductivity. Therefore, etching is used to remove oxide layers from the copper surface generating an intact metallic surface. Different etching techniques have been employed; however, some processes etch both copper and copper oxides, which produces a rough surface. One common etching method is the use of concentrated nitric acid. This method removes oxide from the surface; however, washing off excess nitric acid from the surface can reoxidize the surface. For example, when using water, Cu(OH)$_2$ can be formed thereby negating the etching process somewhat. Nitric acid reacts vigorously with metals, which can cause significant structural damage to the surface, as it reacts with bare copper as well. In addition, the safety of using nitric acid is a consideration since it reacts violently with many other materials.

Towards this end, thiols have been shown to etch copper surfaces. The etching process has been explained by a redox reaction, in which the oxide layer is reduced upon oxidation of thiol to disulfide. The disulfide species was detected by gas chromatography-mass spectrometry (GC-MS) while XPS confirmed the reduction of Cu$^{2+}$ to Cu$^{1+}$ and the formation of a copper (I) thiolate complex. In addition to the formation of a nonmetallic state of copper, traces of oxidized species such as sulfonate were detected on the surface. Also, the thiol etching approach was founded to be less efficient on bulk copper (foil) than
electroplated copper. Therefore, an alternative technique that combines etching of the surface and protecting the surface from further oxidation is highly desirable.

Here, a facile wet-chemical SAM method is described to form a NHC nanostructured film on copper surfaces, to help design a more metallic copper system for use in various applications. Further, we present a novel method for etching CuO as well as Cu by NHCs. This method is an excellent alternative to etching by thiols since by-products, such as sulfonate and sulfide are not formed on the surface. In the current study, we first examine the chemical mechanism of NHC formation for both free carbene and hydrogen carbonate salt carbene, and second, the possibility of surface etching by both types of NHCs. Combined, using NHCs as both an etching promoter as well as the final surface protecting SAM is proposed. Conditions which provide both aspects were systematically studied using element specific X-ray photoelectron spectroscopy.
3.2 Materials and Methods

For this study we prepared six Cu substrates: Clean copper (Cu\textsubscript{clean}), oxidized copper (Cu\textsubscript{ox}), Cu\textsubscript{clean}-HCO\textsubscript{3}_{iPr}, Cu\textsubscript{clean}-free\_iPr, Cu\textsubscript{ox}-HCO\textsubscript{3}_{iPr}, and Cu\textsubscript{ox}-free\_iPr. Cu\textsubscript{clean} was prepared by immersing 1 cm\textsuperscript{2} copper foil (Goodfellow, purity 99.99\%, thickness 1mm) in acetic acid (J.T. Baker Chemical Company, purity 99.7\%) at 50\textdegree C for 10 min.\textsuperscript{31} The substrates were then dried under nitrogen gas. Cu\textsubscript{ox} substrates were prepared by immersion of the Cu\textsubscript{clean} in a hydrogen peroxide (Fisher Scientific, 31\%) solution at 50\textdegree C for 1 min. Cu\textsubscript{clean}-HCO\textsubscript{3}_{iPr}, and Cu\textsubscript{clean}-free\_iPr were prepared by immersing Cu\textsubscript{clean} in a 10 mM solution of [a] 1,3-Diisopropylbenzimidazolium hydrogen carbonate (HCO\textsubscript{3}_{iPr}) (see ref.14) and [b] 1,3-Dihydro-1,3-bisisopropyl-2H-benzimidazol-2-ylidene (free\_iPr) (see ref.15) dissolved in 1,2-Dichloroethane (Sigma-Aldrich, 99.8\%) respectively for 24h at room temperature. Cu\textsubscript{ox}-HCO\textsubscript{3}_{iPr}, and Cu\textsubscript{ox}-free\_iPr were prepared by immersing Cu\textsubscript{ox} in a10 mM solution of [a] 1,3-Diisopropylbenzimidazolium hydrogen carbonate (HCO\textsubscript{3}_{iPr}) and [b] 1,3-Dihydro-1,3-bisisopropyl-2H-benzimidazol-2-ylidene (free\_iPr) dissolved in 1,2-Dichloroethane for 48h at room temperature. All substrates were then rinsed with anhydrous 1,2-Dichloroethane and dried under an argon gas stream. Some of the immersion solutions were extracted after the NHC deposition occurred on the copper samples and were submitted for mass spectrometry analysis. All analyses were performed using Thermo scientific LTQ orbitrap velos pro mass spectrometer.
XPS measurements were performed using a Thermo Microlab 310F ultrahigh vacuum (UHV) surface analysis instrument using Al Kα X-rays (1486.6 eV) or Mg Kα (1253.4 eV) at 15 kV anode potential and 20 mA emission current with a surface/detector take off angle of 75°. Survey spectra were collected, along with high-resolution element scans dependent on the sample. In all cases, the C1s peak at 284.8 eV was used as a reference to calibrate the high-resolution spectra. Spectra were subjected to a Shirley baseline and fitted by using mixed Gaussian-Lorentzian functions. Cu₂O (Sigma-Aldrich), CuO (Sigma-Aldrich), and Cu(OH)₂ (Sigma-Aldrich) were used as standard materials.

3.3 Results and Discussion

The high-resolution spectra of Cu 2p exhibit two peaks with a splitting of approximately 19.9 eV, which is consistent with the standard separation value of Cu 2p₃/₂ and Cu 2p₁/₂. However, in this study we focused on the Cu 2p₃/₂ peak to analyze the Cu 2p. Figure 3.1 shows the Cu 2p₃/₂ spectra for the commercial Cu₂O, CuO, and Cu(OH)₂ samples in addition to the copper substrates reference (Cu_clean and Cu_ox) and the Cu samples modified with NHC.
Figure 3.1. The fitted XPS spectra of Cu 2p\textsubscript{3/2} for commercial Cu\textsubscript{2}O, CuO, Cu(OH)\textsubscript{2}, Cu\textsubscript{ox}, Cu\textsubscript{clean}, and Cu samples modified with NHC.
First, the Cu 2p region for the samples containing Cu\(^{2+}\) species (Cu\(_{\text{ox}}\), CuO, and Cu(OH)\(_2\)) is completely different than for other samples. The Cu 2p\(_{3/2}\) spectra of the Cu\(^{2+}\) samples exhibit a broad peak centered at \(\sim 1\) eV higher in binding energy than the other samples. In addition, the samples with Cu\(^{2+}\) display satellites peaks, which are characteristic of Cu\(^{2+}\) species, originating from the excitation of the valence (3d) electrons to higher unfilled levels.\(^{33}\) The Cu 2p\(_{3/2}\) for the Cu\(_{\text{ox}}\) peak is resolved to two peaks at 933.5 and 934.6 eV (see Table 3.1) which are consistent with CuO and Cu(OH)\(_2\) respectively.\(^{34,35}\) In contrast, satellite peaks are not observed in Cu\(_{\text{clean}}\) and all Cu-NHC samples, which indicates the absence of the Cu\(^{2+}\) species in those samples. Also, the spectra of Cu\(_{\text{clean}}\) and all Cu-NHC samples display similarly sharp peaks centered around 932.6 eV which is attributed to metallic Cu.\(^{34}\) A summary of the peaks positions obtained from this work and data from literature is shown in Table 3.1.

The Cu 2p\(_{3/2}\) spectra reveal sharp peaks at 932.4 eV and 932.6 eV for Cu\(_{\text{clean-free_iPr}}\) and Cu\(_{\text{clean-HCO}_3\text{iPr}}\) respectively, which correspond to either metallic copper Cu\(_0\) or Cu\(^{1+}\), as these cannot be distinguished from Cu 2p XPS. However, no signal for Cu\(^{2+}\) was observed for the NHC modified copper substrates. Interestingly, there is a slight shift in the binding energy for Cu\(_{\text{clean-free_iPr}}\) compared to Cu\(_{\text{clean-HCO}_3\text{iPr}}\), which may potentially associate with the difference in the deposition mechanism of both types of NHC molecules.
### Table 3.1: A summary of the peak positions (Cu 2p, Cu(LMM), and O 1s) obtained from this work and data from the literature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>BE (eV)</th>
<th>KE (eV)</th>
<th>BE (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu (2p)</td>
<td>Cu (LMM)</td>
<td>O (1s)</td>
<td></td>
</tr>
<tr>
<td>Cu (metallic)</td>
<td>932.5</td>
<td>918.8</td>
<td>-</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>932.6</td>
<td>918.8</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>932.7</td>
<td>918.6</td>
<td>-</td>
<td>35</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>932.5</td>
<td>917.2</td>
<td>530.1</td>
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<td></td>
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<td>916.5</td>
<td>530.4</td>
<td>35</td>
</tr>
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<td>932.5</td>
<td>916.7</td>
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<td>CuO</td>
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<td>918.0</td>
<td>529.6</td>
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<tr>
<td></td>
<td>933.6</td>
<td>917.8</td>
<td>529.6</td>
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<td>933.5</td>
<td>917.9</td>
<td>529.7</td>
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</tr>
<tr>
<td>Cu(OH)$_2$</td>
<td>934.6</td>
<td>916.5</td>
<td>531.2</td>
<td>34</td>
</tr>
<tr>
<td></td>
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<td>934.6</td>
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</tr>
<tr>
<td>Cu$_{\text{clean}}$</td>
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<td>(a) 918.8</td>
<td>532.2</td>
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<tr>
<td></td>
<td>(b) 916.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$_{\text{ox}}$</td>
<td>(a) 933.5</td>
<td>917.8</td>
<td>(a) 529.7</td>
<td>This work</td>
</tr>
<tr>
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<td>(b) 934.6</td>
<td></td>
<td>(b) 531.4</td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{\text{clean}}$ - free$</em>\text{iPr}$</td>
<td>932.4</td>
<td>(a) 916.9</td>
<td>(a) 530.0</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>(b) 918.8</td>
<td></td>
<td>(b) 531.6</td>
<td></td>
</tr>
<tr>
<td>Cu$_{\text{clean}}$ - HCO$<em>3$$</em>\text{iPr}$</td>
<td>932.6</td>
<td>(a) 916.9</td>
<td>(a) 530.2</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>(b) 918.8</td>
<td></td>
<td>(b) 532.3</td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{\text{ox}}$ - free$</em>\text{iPr}$</td>
<td>932.4</td>
<td>(a) 916.8</td>
<td>(a) 530.1</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>(b) 918.8</td>
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<td>(b) 531.8</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(c) 534.6</td>
<td></td>
</tr>
<tr>
<td>Cu$_{\text{ox}}$ - HCO$<em>3$$</em>\text{iPr}$</td>
<td>932.5</td>
<td>(a) 916.9</td>
<td>(a) 530.2</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>(b) 918.8</td>
<td></td>
<td>(b) 532.1</td>
<td></td>
</tr>
</tbody>
</table>
Although the eventual NHC on the surface has been determined to be the same as in the previous work,\textsuperscript{22} the mechanisms by which the NHCs are deposited are completely different. Scheme 3.1 illustrates the deposition mechanism of both types of NHC molecules on copper. The free\textsubscript{--}iPr deposits directly on the copper surface after deprotonation by a strong base (e.g., KtBuO), while the deposition mechanism of HCO\textsubscript{3}--iPr involves two steps. The first step is the deprotonation of NHC by the HCO\textsubscript{3}-- internal base to generate free NHC in solution in addition to CO\textsubscript{2} and H\textsubscript{2}O as by-products. This is followed by the deposition of the NHC on the Cu surface. Hence, the difference in the deposition mechanism for both types of NHC has a potential effect on the kinetics of NHC adsorption. Based on this concept, free NHC has a relatively faster rate of adsorption than NHC salt which adsorbed in two steps, not to mention the by-products CO\textsubscript{2} and H\textsubscript{2}O which may slow down the adsorption process. This distinction in the adsorption kinetics may lead to a difference in the surface density (coverage), thus the amount of electrons donated from both types of NHC (a and b) are not equal, which explains the slight variation in the Cu 2p\textsubscript{3/2} binding energy for Cu-NHC samples.

![Scheme 3.1](image)

**Scheme 3.1:** The deposition mechanism of both types of NHC molecules on Cu surface.
Most interestingly, the samples which were oxidized prior to reacting with NHC look almost identical to the Cu\textsubscript{clean} sample, as well as the Cu\textsubscript{clean}-NHC samples. The treatment of Cu\textsubscript{ox} surface with NHC solution shifts Cu 2p \textsubscript{3/2} peak ~1eV to lower binding energy, while the satellite peaks completely disappear (see Fig. 3.1), thereby indicating that there is no Cu\textsuperscript{2+} in the Cu\textsubscript{ox}-NHC samples.

Studying the Cu 2p region by standard XPS typically does not provide enough information to discriminate between Cu\textsuperscript{0} and Cu\textsuperscript{1+} since both lie in the same range of binding energy. Technically, Cu\textsuperscript{1+} has lower binding energy than Cu\textsuperscript{0} but the difference is too small (~ 0.4 eV) to distinguish in the Cu 2p region.\textsuperscript{36} However, the Cu \textsubscript{LMM} region is more sensitive to the copper oxidation states than the Cu 2p\textsubscript{3/2} \textsuperscript{37,38} and, therefore; the Cu \textsubscript{LMM} Auger spectra were acquired to obtain more information. Figure 3.2 displays the collected Cu \textsubscript{LMM} Auger spectra. Notably, the Cu \textsubscript{LMM} Auger region comprises many components within the spectrum, which, although not completely resolved, can be qualitatively compared to determine the oxidation state of the Cu for each sample. First, the Cu \textsubscript{clean} spectrum shows a major peak at 918.8 eV which is characteristic of metallic copper (Cu\textsuperscript{0}) as shown in Table 3.1.\textsuperscript{34,39} On the other hand, the oxidized reference Cu\textsubscript{ox} show a negative shift in this major peak of around 1 eV.

For the Cu\textsubscript{clean} modified with NHCs, the spectra show the same metallic copper peak at 918.8 eV; however, we note that an additional weak signal was observed at 916.9 eV which corresponds to Cu\textsuperscript{1+}. Importantly, no signal for Cu\textsuperscript{2+} (typically at 917.8 eV) was detected for any of the Cu\textsubscript{clean}-NHC samples. A dramatic change was observed for the Cu\textsubscript{ox} treated with NHC; the peak at 917.8 eV disappeared entirely after exposing the Cu\textsubscript{ox} to the NHC solution. New peaks showed up at 918.8 eV and 916.9 eV which correspond to
metallic copper Cu\textsuperscript{0} and Cu\textsuperscript{1+} respectively. However, the spectra for the two types of NHC modified Cu\textsubscript{ox} surface are not symmetrical. The spectrum for the free type of NHC (free\_iPr) modifying Cu\textsubscript{ox} reveals a high Cu\textsuperscript{1+} on the surface compared to the that of salt type (HCO\textsubscript{3}\_iPr) when is used. Notably, no peak for Cu\textsuperscript{2+} appeared on the surface of either sample. The implication from this is that the interaction of NHC with the Cu surface, whether it is clean or has an oxide layer, leads to a metallic surface. In contrast, thiol interaction with copper typically generates a large amount of Cu\textsuperscript{1+} on the surface, as evidenced by previous studies showing Auger peaks at 916.5 eV\textsuperscript{20,28} Based on this alone, NHCs can lead to a more metallic surface of copper and thus may enable many different types of applications where metallic copper is needed, e.g., microelectronics.
Figure 3.2: The XPS spectra of Cu LMM Auger spectra for Cu$_2$O, CuO, Cu(OH)$_2$, Cu$_{ox}$, and Cu$_{clean}$, and Cu samples modified with NHC. Vertical dash lines illustrate kinetic energy for Cu, Cu$_2$O, CuO, and Cu(OH)$_2$ in the Cu LMM Auger region.
Figure 3.3 shows the metallic Cu percentage, extracted from the Cu LMM Auger spectra. The Cu$_{\text{clean}}$ and Cu$_{\text{ox}}$ surfaces exhibit similar content of metallic Cu after exposure to the salt type of the NHC (HCO$_3$-iPr), while the Cu$_{\text{ox}}$ treated with free-iPr displays less metallic Cu$^0$ and more Cu$^{1+}$ species than the other substrates. However, this result does not solely represent the Cu state on the surface. Notably, the escape depth of the Cu Auger electron is approximately 15 Å,\textsuperscript{40} and therefore, several layers of the surface and bulk are incorporated into this information. Accordingly, the electronic structure of the surface is not clearly identified; therefore, a more surface sensitive XPS technique would be very informative to distinguish the surface from the bulk states of copper in this regard.

\textbf{Figure 3.3:} The metallic Cu percentage for: Cu$_{\text{ox}}$, Cu$_{\text{clean}}$, and substrates treated with NHC solution.
O 1s XPS can also be used to distinguish various surface compounds of copper. The main oxygen species which are typically present on the metal surfaces are: lattice oxygen, surface oxygen, subsurface oxygen, and adsorbed oxygen species,\textsuperscript{41–44} and all have characteristic binding energies as shown in Figure 3.4.

\textbf{Figure 3.4:} The binding energy range for O 1s XPS spectrum.

Lattice oxygen is characteristic of metal oxides (O\textsuperscript{2−} ions). Surface oxygen is assigned to OH\textsuperscript{−} and (O\textsubscript{2})\textsuperscript{2−} ions, while subsurface oxygen (oxygen present in the bulk near the surface) refers to oxygen vacancies or defect oxide ((O\textsuperscript{−} ions) oxygen with low coordination number). The last species is adsorbed oxygen, which is characteristic of adsorbed water \textsuperscript{45}, oxidized carbon functional groups \textsuperscript{46,47}, and surface contamination \textsuperscript{48,49}.
Figure 3.5 shows the acquired O 1s spectra for the reference materials and Cu substrates. The O peak for CuO has the lowest binding energy at 529.7 eV, while the Cu$_2$O and Cu(OH)$_2$ peaks are exhibited at 530.5 and 531.1 eV respectively. The O 1s spectrum for Cu$_\text{clean}$ reveals a weak signal at 532.2 eV, which is a weakly adsorbed O species attributed to surface contamination. There is no signal for CuO in the O 1s region for Cu$_\text{clean}$ or any of the Cu-NHC samples. In contrast, two peaks were observed in the O 1s region for Cu$_\text{ox}$ (see Table 3.1) at 529.7 and 531.4 eV, which correspond to CuO and Cu(OH)$_2$ (see Table 3.1).

The Cu$_\text{clean}$-NHC samples exhibit two O components at 530 ± 0.2 eV and 532 ± 0.5 eV. The former peaks are ascribed to the lattice oxygen (Cu$_2$O), and adsorbed water or O in C-O group respectively. On the other hand, exposing Cu$_\text{ox}$ to both types of NHCs removes entirely the preexisting O species (CuO and Cu(OH)$_2$) from the surface while new O components appear. The Cu$_\text{clean}$ and Cu$_\text{ox}$ treated with HCO$_3$-_iPr exhibit similar O components. On the other hand, Cu$_\text{ox}$ exposed to free-_iPr shows three O species at 530.1, 531.8 and 534.6 eV which can be assigned to Cu$_2$O, subsurface oxygen, and oxygen from organic contaminants or adsorbed water, respectively.
**Figure 3.5**: The fitted XPS spectra of O 1s for Cu$_2$O, CuO, Cu(OH)$_2$, Cu$_{\text{ox}}$, Cu$_{\text{clean}}$, and Cu samples modified with NHC. Vertical dash lines illustrate O binding energy for Cu$_2$O, CuO, and Cu(OH)$_2$. 
The corresponding high-resolution spectra of C 1s and N 1s are shown in Figure 3.6. A single C peak was detected for Cu\text{clean}, which is consistent with previous observations for copper cleaned with acetic acid.\textsuperscript{31} Moreover, there is no signal for C at higher binding energy, which implies no reaction between acetic acid and the Cu surface. Cu\text{clean} surface also displays no signal in the N 1s region. The analysis of the C 1s and N 1s peaks for Cu\text{ox} surface shows different components for C and N, which demonstrate the surface contaminants. The C 1s spectrum shows a peak at 288.4 eV, which is similar to what has been reported by Vasquez \textit{et al.} for CuO.\textsuperscript{54}
Figure 3.6: The fitted XPS spectra of (a) C 1s and (b) N 1s for the Cu samples.
Intense C and N signals were detected for Cu clean modified with NHCs. The C 1s is resolved to two components at 284.8 and 286.1 ± 0.3 eV, which correspond to sp² and sp³ C respectively.⁵⁵,⁵⁶ N 1s spectra display component at 400.0 ± 0.2 eV, which is similar to what has been observed for NHC on Au.²¹,²² The Cu_{ox} treated with both NHCs show drastic changes for C 1s and N 1s spectra, which includes an increase in the intensity of the C 1s and N 1s peaks. The C peak at 288.4 eV was completely disappeared after exposing the surface to the NHC solution, while the N 1s spectrum has increased in intensity and shifted (~0.5 eV) to higher binding energy (400.0 ± 0.4 eV). However, a trace of N contamination remains on the Cu_{ox} surface treated with free_iPr. Therefore, the presence of C and N indicates the adsorption and the formation of NHC layer on copper surfaces. Also, the results show that NHC plays a significant role in reducing the Cu surface and removing surface contaminants.

Table 3.2 shows C: N peak area ratio for Cu samples, which were exposed to NHC. The peak areas were normalized by using the atomic sensitivity factors. The stoichiometric C: N ratio in the NHC molecules should be 13:2. However, the Cu-NHC samples are showing a much higher C: N ratio, which may be a result of pre-existing C contamination on the surface. In addition, transferring the samples into the XPS chamber may introduce surface contaminants, which could eventually increase the C: N ratio. Moreover, the high content of C may indicate the decomposition of some of the NHC molecules on the surface.
For further investigation, the solutions into which the substrates were immersed were subjected to mass spectrometric analysis. Figure 3.7 shows one of the high-resolution electrospray ionization mass spectra of the immersion solution. Two major species of NHC-O and NHC-Cu were detected (see Table 3.3), which provides strong evidence for traces of Cu and O in solution after deposition.
**Figure 3.7:** High-resolution electrospray ionization mass spectrum of the immersion solution (NHC solution in which Cu sample was immersed in).

**Table 3.3:** Compounds elucidated by mass spectrometry and their molecular weights

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Compound 1" /></td>
<td>218.15</td>
</tr>
<tr>
<td><img src="image" alt="Compound 2" /></td>
<td>467.27</td>
</tr>
</tbody>
</table>
NHC is well known as a ligand for transition metal complexes including NHC-Cu.\textsuperscript{57} NHC-Cu complexes can undergo rapid oxidation (Eq. 3.1) upon exposure to air, \textsuperscript{58} which may explain the presence of NHC-O complex.

\begin{equation}
\begin{array}{c}
\text{[} \text{NHC-Cu} \text{]} \\
\text{[} \text{NHC-Cu} \text{]} + \text{O}_2 \\
\text{[} \text{NHC-Cu} \text{]} \rightarrow 2 \text{[} \text{NHC-O} \text{]}
\end{array}
\end{equation}

Furthermore, NHC itself can also react with O to form the NHC-O (Eq. 3.2) complex, which was also detected by mass spectrometry in this work (Table 3.3).\textsuperscript{58}

\begin{equation}
\begin{array}{c}
\text{[} \text{NHC} \text{]} + [\text{O}] \\
\text{[} \text{NHC} \text{]} \rightarrow \text{[} \text{NHC-O} \text{]}
\end{array}
\end{equation}

Given that the deposition of NHC from HCO$_3$ salt generates H$_2$O and CO$_2$, there is also the likelihood of oxidation of excess NHC. But in general, the presented XPS analysis and mass spectrometry provide clear evidence for the etching effect of NHC towards both clean and oxidized copper.
Based on the results in this chapter, there are two proposed mechanisms for how the NHC binds to Cu surfaces, which is illustrated in Figure 3.8. One of the proposed mechanisms is that NHC can bind directly to the Cu surface and directly form a Cu-C bond. The other proposed mechanism is the binding of NHC to the surface oxide, which leads to a Cu-O-C linkage. The metal-O-C linkage was reported for Fe, Cu, Ag, and Zr, in which an O 1s peak was observed between 531.7 eV and 532.8 eV, which is in the same range as the results for Cu-NHC samples.

![Figure 3.8: The schematic for the binding mechanism of NHC onto the Cu surfaces.](image)
3.4 Conclusion

A comprehensive study of NHC interactions with Cu surfaces was introduced. The study was performed at room temperature by exposing clean and oxidized Cu surfaces to the free and salt type NHC. Detailed characterization of Cu surfaces was demonstrated by XPS. The presented XPS spectra show a similarity in the chemical structure for both Cu\textsubscript{clean} and Cu\textsubscript{ox} after exposing the samples to the NHC solution. In addition, the results indicate the ability of the NHC to remove the CuO and the organic contaminants (C and N) from the surface and reduces surface oxides. However, the salt type NHC exhibited significant etching of the Cu surfaces compared to the free type. Mass spectrometry provided strong evidence for the NHC effectiveness in etching Cu surfaces, in which traces of NHC-O and NHC-Cu were found in the immersion solution. Overall, we have demonstrated here a facile approach for the SAM formation of NHCs on copper surfaces, which can be a promising platform for many further applications, which required more metallic copper surfaces.
3.5 References


Chapter 4

A depth profiling study of copper surfaces treated with of N-heterocyclic carbenes at room temperature

4.1 Introduction

X-ray Photoelectron Spectroscopy (XPS) depth profiling is a powerful technique to study the composition from bulk up to the outmost surface of a sample. Depth profiling investigations can be conducted by various techniques; however, non-destructive depth profiling can be achieved by angle-resolved X-ray photoelectron spectroscopy (AR-XPS). AR-XPS is based on changing sample tilt angle to control the electron escape depth. For AR-XPS, a standard X-ray source is commonly employed in this technique, but the drawback is that the higher angles (which provide more surface sensitivity), lead to lower electron counts released from the surface, and hence the quality of the spectra obtained suffers dramatically.

The use of synchrotron radiation XPS (SR-XPS) can also give non-destructive depth profiling information. SR-XPS has some unique features over the standard XPS. SR-XPS has a tunable photon energy, a high resolution, a high photon flux, a smaller spot size, and a high-energy light, which covers a wide range of wavelengths.\(^1\)\(^-\)\(^3\) Because of these aspects, the surface sensitivity of SR-XPS is provided by changing the energy of the incoming photons, which changes the inelastic mean free path (IMFP) of electrons escaping from the material. The IMFP, \(\lambda\) is the distance an electron will travel before it undergoes an inelastic collision as it travels through the material, \(i.e\)

\[
I_s = I_0 e^{-d/\lambda} \quad (4.1)
\]
where $I_s$ is the intensity of electrons from the XPS line of a particular element without being scattered, and $I_0$ is the flux of electrons originating at depth $d$. The relationship to electron kinetic energy may be found experimentally using the “universal curve” shown in Figure 4.1. By modulating the energy of the incoming photons, information regarding the first few Ångstroms of the material to hundreds of Ångstroms within the material can be probed.

![Figure 4.1: Universal curve of photoelectron mean free path as a function of photoelectron energy.](image)

In the previous chapter, we showed that NHCs have a strong ability to interact with Cu surfaces by removing oxide layers and forming a robust film on the surface. Standard XPS was employed to study Cu surfaces and determine their chemical structure. In this chapter, we employ synchrotron-based X-ray photoelectron spectroscopy (SR-XPS) to study in more detail the chemical composition of the nanostructured film of NHC on Cu surface as a function of depth.
4.2 Materials and Methods

For this study we prepared six Cu substrates: Clean copper (Cu_{clean}), oxidized copper (Cu_{ox}), Cu_{clean}-HCO_3\_iPr, Cu_{clean}-free\_iPr, Cu_{ox}-HCO_3\_iPr, and Cu_{ox}-free\_iPr. Cu_{clean} was prepared by immersing 1 cm² copper foil (Goodfellow, purity 99.99%, thickness 1mm) in acetic acid (J.T. Baker Chemical Company, purity 99.7%) at 50°C for 10 min. The substrates were then dried under nitrogen gas. Cu_{ox} substrates were prepared by immersion of the Cu_{clean} in a hydrogen peroxide (Fisher Scientific, 31%) solution at 50°C for 1 min. Cu_{clean}-HCO_3\_iPr and Cu_{clean}-free\_iPr were prepared by immersing Cu_{clean} in a 10 mM solution of 1,3-Diisopropylbenzimidazolium hydrogen carbonate (HCO_3\_iPr) (see ref.14) and 1,3-Dihydro-1,3-bisisopropyl-2H-benzimidazol-2-ylidene (free\_iPr) (see ref.15) dissolved in 1,2-Dichloroethane (Sigma-Aldrich, 99.8%) respectively for 24h at room temperature. Cu_{ox}-HCO_3\_iPr and Cu_{ox}-free\_iPr were prepared by immersing Cu_{ox} in a 10 mM solution of 1,3-Diisopropylbenzimidazolium hydrogen carbonate (HCO_3\_iPr) and 1,3-Dihydro-1,3-bisisopropyl-2H-benzimidazol-2-ylidene (free\_iPr) dissolved in 1,2-Dichloroethane for 48h at room temperature. All substrates were then rinsed with anhydrous 1,2-Dichloroethane and dried under an argon gas stream.

Synchrotron-based X-ray photoelectron spectroscopy was conducted on the variable line spacing plane grating monochromator (VLS PGM) beamline at the Canadian Light Source (CLS), located at the University of Saskatchewan in Saskatoon. The beam-line covers a photon energy range between 5.5 and 250 eV with a photon energy resolution of (E/ΔE >10,000) The XPS spectra were measured using photon energies of 230, 205, and 180 eV where we observed 3p peaks for Cu (binding energy of Cu 75 eV). We also obtained the valence band region (0-30 eV) and for N 2s (binding energy observed at 31 eV)
4.3 Results and Discussion

Typically, 2p spectrum of Cu is studied with regular XPS; however, a beamline configured to perform XPS in the Cu 2p binding energy range is not available at CLS. Cu 3p is not routinely studied with regular XPS as it has a relatively low excitation cross section, compared to Cu 2p. For pure metallic copper, the 3p doublet spectrum is present in a 2:1 intensity ratio (3p\(^{3/2}\) and 3p\(^{1/2}\)) with a splitting of 2.4 eV. Based on this, the deconvolution of the collected Cu 3p spectra was carried out by constraining the peaks to have relative peak intensities of 2:1 with equivalent full width at half maximum (FWHM) values and a doublet separation of 2.4 eV for each chemical state. Fig.4.2 shows example spectral fit for Cu\(_{ox}\) at photon energies of 230, 205, and 180 eV. At 230 eV, the Cu 3p spectrum displays two pairs of peaks: each pair represents Cu 3p\(^{3/2}\) and 3p\(^{1/2}\). A major peak at 76.2 eV represents a bulk like state, which corresponds to CuO (see Table 4.1). Another component appears at higher binding energy (78.2 eV), signifying a surface state. The bulk state constitutes about 92% of the total signal and the surface state is 8%. Bulk to surface intensity is varying with electron photon energy, which controls the electron escape depth. At the more surface sensitive (180 eV), bulk intensity decreases to 70% while surface state increases to 30%.
Figure 4.2: High resolution XPS spectra of Cu 3p at 230, 205, and 180 eV photon energy for Cu$_{\text{ox}}$. Fitting shows two pairs of peaks, each pair represents a chemical state, red and green lines represent bulk state while blue and pink lines represent surface state. A change in the peaks’ position and intensity is observed as a function of photon energy.
Table 4.1: A summary of the binding energy range of Cu 3p\(^{3/2}\) for various Cu compounds.

<table>
<thead>
<tr>
<th>Cu 3p(^{3/2})</th>
<th>Binding energy range /(eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>74.9 – 75.2</td>
<td>7–9</td>
</tr>
<tr>
<td>Cu(_2)O</td>
<td>75.0 – 75.2</td>
<td>9,10</td>
</tr>
<tr>
<td>CuO</td>
<td>76.2 – 76.8</td>
<td>9,10</td>
</tr>
<tr>
<td>Cu(OH)(_2)</td>
<td>77.0</td>
<td>9,10</td>
</tr>
</tbody>
</table>

For this study, Cu references (Cu\(_\text{clean}\) and Cu\(_\text{ox}\)) were exposed to both types of NHC (free and HCO\(_3^-\)) for 24h (Cu\(_\text{clean}\)) and 48h (Cu\(_\text{ox}\)) at room temperature. Having introduced a few spectra in detail, we can summarize the spectral data (Cu 3p\(^{3/2}\) at photon energy of 180 eV)) in graph form (Fig. 4.3) to compare it with binding energy range of Cu 3p\(^{3/2}\) for various Cu compounds from literature. Exposing Cu\(_\text{clean}\) and Cu\(_\text{ox}\) to both types of NHC displays a similarity in the bulk state around 75.2 ± 0.2 eV, which can be assigned to metallic Cu or Cu\(_2\)O since both lie in the same range of binding energy. However, Cu-NHC samples are showing distinct surface state. Cu\(_\text{clean}\)-NHC samples show surface states at lower binding energy similar to Cu\(_\text{clean}\) (reference), while the surface states are observed at higher binding energy for Cu\(_\text{ox}\)-NHC samples like Cu\(_\text{ox}\) (reference). These results indicate that the interaction of NHC with Cu surfaces forms a metallic surface on Cu\(_\text{clean}\) while it partially removes CuO from Cu\(_\text{ox}\) surface, which can be attributed to several factors, such as oxide thickness and efficiency of NHC.
Figure 4.3: Spectral data of Cu 3p\(3/2\) for Cu samples at photon energy of 180 eV compared to data of various Cu compounds from literature.

Cu valence band spectra (3d) were collected in this study, which observed in the binding energy range of 1-30 eV. Figure 4.4 shows the high-resolution Cu 3d spectra for Cu and CuO introduced by Jiang.\(^{11}\) Cu is showing a sharp peak around 3.5 eV in the valence band region where CuO exhibits a broad peak in addition to satellite peaks spread over binding energies of 8-18 eV. Those peaks are due to the \(d^8\) final states, which are resulting from Cu being bonded with oxygen.\(^{11,12}\) Figure 4.5 a shows similar trend for Cu references (Cu\(_{\text{clean}}\) and Cu\(_{\text{ox}}\)). Moreover, O 2p signal is overlap with Cu 3d and can be observed between 5.5 to 7 eV.\(^{12}\)
Figure 4.4: High-resolution Cu 3d spectra (valence region) for Cu and CuO obtained by Jiang.¹¹
Figure 4.5: High-resolution Cu 3d spectra (valence region) for (a) Cu references and Cu-NHC samples from this work. (b) CuO collected by Steiner. 12 Zoom-in of the valence band region (8-22 eV) for (c) Cu references and Cu-NHC samples from this work. (d) CuO collected by Steiner. 12
Cu 3d spectra for Cu\text{clean} samples modified with NHC show no signal for O 2p (Fig. 4.5 a) in addition to the absence of satellite peaks in the higher binding energy region (see Fig. 4.5 c). In contrast, Cu 3d spectra for Cu\text{ox} samples exposed to NHC exhibit O 2p signal in addition to satellite peaks in the binding energy region of 8-18 eV. This is an indication for the existence of O bonded to Cu surface. These results are consistent with the results from Cu 3p spectra, which demonstrate the partial removal of CuO from Cu\text{ox} samples that exposed to NHC.

4.4 Conclusion

A study of NHC interaction with a Cu surface at room temperature using SR-XPS is presented. At room temperature, NHCs are able to interact directly with clean copper surfaces, which leads to the formation of NHC film on the metallic surface within 24h. On the other hand, the interaction of the oxidized copper surfaces with NHCs resulting in a partial removal of the oxide layer due to some factors related to the samples’ preparation. This study is explored again during the second trip to CLS and will be presented in detail in the next chapter.
4.5 References


Chapter 5

The interaction of N-heterocyclic carbenes with Cu surfaces at elevated temperatures

5.1 Introduction

SAMs on metal surfaces have been widely employed in many applications, such as microelectronics and metal protection. However, there are various technical obstacles related to the deposition process of SAMs, which can often limit their applications. For example, the time required during SAM formation at room temperature is commonly 24 hours, which has a major impact on the manufacturing process of these functionalized surfaces. Therefore, optimizing SAM formation on various materials has remained an ongoing challenge. For example, several factors have been investigated to optimize the formation of SAMs, such as concentration, solvent type, and temperature, in order to minimize the treatment time, increase surface coverage, and improve the overall quality of the SAM.

Temperature plays an important role in SAM formation as it affects both kinetics and thermodynamics of the SAMs formation process. Temperature is a prominent parameter to control SAM formation, although, it is the least studied, and only a few examples were found in the literature. In addition most of the studies have been conducted on gold since it is considered as an ideal substrate for SAM formation because of its excellent conductivity and low chemical inertness. For example, the effect of temperature on the SAM structure of thiol on the gold surface was investigated by using scanning tunneling microscopy (STM). This study pointed out the effect of temperature on the domain size and number of
vacancy islands at the surface. It was found that the adsorption of thiol on the gold surfaces at higher temperatures formed a well-ordered SAM with a large domain size and reduced the density of vacancy islands on the surface. Korolkov and co-workers reported the effect of temperature on the structure of thiol SAM on gold surface and on the immersion time. Evidence from STM showed the formation of a densely packed layer of thiol with no defects within 1 second at 393K. Moreover, no trace was detected for oxidized thiol species from XPS.

The temperature effect on SAM formation on copper is rarely addressed, mainly because of the susceptibility of copper to oxidation and corrosion, which increases at elevated temperatures. A single study conducted by Kwok et al presented the effect of temperature on the SAM formation of thiol on copper. They employed electrochemical impedance spectroscopy (ELS), cyclic voltammetry (CV), and linear scan voltammetry (LSV) for sample characterization. The main observation from this study was that increasing temperature increased thiol surface coverage on the copper surface.

In chapter 3, it was demonstrated that NHC can remove oxide layers from copper surfaces and forms a robust SAM within 48h at room temperature. However, this amount of time is one of the major obstacles in many applications, which requires a rapid SAM formation, such as microcontact printing for electronic device manufacturing. Here, we investigated the effect of the immersion temperature as a function of time on the CuO removal rate as well as SAM formation on Cu surfaces. XPS was used to characterize Cu surfaces, and in addition, a high-resolution synchrotron-based XPS was employed to more closely examine the interfacial structure of Cu.
5.2 Materials and Methods

For this study we prepared four Cu substrates: Clean copper (Cu\textsubscript{clean}), oxidized copper (Cu\textsubscript{ox}), Cu\textsubscript{clean}- HCO\textsubscript{3} iPr and Cu\textsubscript{ox}- HCO\textsubscript{3} iPr. Clean copper (Cu\textsubscript{clean}) was prepared by immersing the copper substrates (Goodfellow, purity 99.99%, thickness 1mm) in glacial acetic acid (J.T. Baker Chemical Company, purity 99.7%) at 40\textdegree C for 10 min. Note that for the standard-XPS characterization, Cu substrates were hand-polished with 3000 grit paper for 5 min then sonicated in acetone for 5 min before the cleaning process with acetic acid. The substrates were then dried under nitrogen gas. Oxidized copper (Cu\textsubscript{ox}) substrates were prepared by immersion of the Cu\textsubscript{clean} in a hydrogen peroxide solution (Fisher Scientific, 31%) at room temperature for 1 min. Cu substrates were then immersed in a 10 mM solution of 1,3-Diisopropylbenzimidazolium hydrogen carbonate (HCO\textsubscript{3} iPr) dissolved in 1,2-Dichloroethane (Sigma-Aldrich, 99.8%) for 15 min, 4h, and 8h at 80\textdegree C while being stirred, while room temperature samples were immersed for 8h, 24h for Cu\textsubscript{clean}, and 8h, 72h for Cu\textsubscript{ox}. All substrates were then rinsed with anhydrous 1,2-Dichloroethane and dried under an argon gas stream.

XPS measurements were performed using the Kratos Nova AXIS spectrometer (ultrahigh vacuum, 10\textsuperscript{-10} Torr) equipped with an Al X-ray source. The XPS data were collected using AlK\alpha radiation at 1486.69 eV (150 W, 15 kV). Survey spectra were collected, along with high-resolution element scans dependent on the sample. In all cases, C1s peak at 284.8 eV was used as a reference to calibrate the high-resolution spectra. Synchrotron-based X-ray photoelectron spectroscopy was conducted on the variable line spacing plane grating monochromator (VLS PGM) beamline at the Canadian Light Source (CLS), located at the University of Saskatchewan in Saskatoon. The beam-line covers a photon energy range between 5.5 and 250 eV with a photon energy resolution of \((E/\Delta E)\).
The XPS spectra were measured at photon energies of both 230 and 180 eV, where we can observe 3p peaks for Cu. The deconvolution of Cu 3p spectra was previously illustrated in chapter 4. We also obtained N 2s (binding energy observed at 31 eV). All spectra were subjected to a Shirley baseline and fitted by using mixed Gaussian-Lorentzian functions.

5.3 Results and Discussion

5.3.1 Standard X-ray photoelectron spectroscopy (XPS) characterization

The Cu surfaces, Cu\textsubscript{clean} and Cu\textsubscript{ox} samples were exposed to the NHC solution at a temperature of 80°C for 15 minutes and 2 hours, respectively. Figure 5.1 shows the Cu 2p region for the Cu samples. The Cu 2p\textsubscript{3/2} peaks of reference samples (see Table 5.1) are consistent with metallic Cu for Cu\textsubscript{clean}, and a combination of CuO and Cu(OH)\textsubscript{2} for Cu\textsubscript{ox}\textsuperscript{10,11}. The Cu 2p\textsubscript{3/2} peaks of Cu-NHC samples exhibit sharp peaks centered around 932.3 eV, which is attributed to either Cu\textsuperscript{0} or Cu\textsuperscript{1+} since they cannot be distinguished by the standard XPS. Notably, there are no characteristic peaks of Cu\textsuperscript{2+} in the Cu 2p region for Cu-NHC samples, including the Cu\textsubscript{ox} surface treated with NHC. This result indicates the complete removal of CuO from the surface. In addition, Cu 2p \textsubscript{3/2} spectra demonstrates similarity in the peaks’ shape and position for both the Cu\textsubscript{clean} and Cu\textsubscript{ox} surfaces modified with NHCs. A slight shift in the binding energy of Cu 2p\textsubscript{3/2} peaks (~ 0.3 eV) for Cu-NHC samples can be attributed to the adsorbate-induced effect (strong \(\sigma\) donation from NHC ligand).\textsuperscript{12}
Figure 5.1: The XPS spectra of Cu 2p$_{3/2}$ for Cu$_{ox}$, Cu$_{clean}$, and Cu samples modified with NHCs at 80°C.
Table 5.1: A summary of the peaks’ analysis of Cu 2p$_{3/2}$, O 1s, C1s, and N1s obtained through exposure of Cu to NHC at 80°C.

<table>
<thead>
<tr>
<th>Cu surface</th>
<th>Conditions</th>
<th>Element</th>
<th>BE (eV)</th>
<th>FWHM</th>
<th>%Area</th>
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</thead>
<tbody>
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<td>ref</td>
<td>Cu 2p$_{3/2}$</td>
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<td>0.9</td>
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<tr>
<td></td>
<td></td>
<td>O (1s)</td>
<td>532.2</td>
<td>2.6</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C (1s)</td>
<td>284.8</td>
<td>1.5</td>
<td>100</td>
</tr>
<tr>
<td>(2) ox</td>
<td>ref</td>
<td>Cu 2p$_{3/2}$</td>
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<td>1.8</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O (1s)</td>
<td>529.6</td>
<td>1.3</td>
<td>43</td>
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<tr>
<td></td>
<td></td>
<td>C (1s)</td>
<td>284.8</td>
<td>1.2</td>
<td>66</td>
</tr>
<tr>
<td>(3) clean</td>
<td>15 min/80°C</td>
<td>Cu 2p$_{3/2}$</td>
<td>932.3</td>
<td>0.9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O (1s)</td>
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<td>0.9</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C (1s)</td>
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<td>1.1</td>
<td>51</td>
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<tr>
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<td></td>
<td>N (1s)</td>
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<td>1.1</td>
<td>78</td>
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<tr>
<td>(4) ox</td>
<td>2h/80°C</td>
<td>Cu 2p$_{3/2}$</td>
<td>932.2</td>
<td>0.9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O (1s)</td>
<td>530.0</td>
<td>1.1</td>
<td>36</td>
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<tr>
<td></td>
<td></td>
<td>C (1s)</td>
<td>284.8</td>
<td>1.3</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N (1s)</td>
<td>400.2</td>
<td>1.2</td>
<td>71</td>
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</table>
Figure 5.2 displays Cu LMM Auger spectra. The spectrum of Cu_{clean} surface shows a high-intensity peak at 918.7 eV, which is a characteristic of metallic copper (Cu^0).\textsuperscript{10} In contrast, the Cu_{ox} spectrum shows a peak at 917.9 eV, which indicates the presence of Cu^{2+} species on the surface.\textsuperscript{11} Auger spectra for Cu substrates modified with NHCs show a major peak at 918.7 eV, consistent with Cu^0, in addition to a relatively weak signal at 916.8 eV, corresponding with Cu^{1+}.\textsuperscript{11} Importantly, there is no signal at 917.9 eV, which has entirely disappeared in the Cu_{ox} sample after treatment with NHC and indicates the absence of Cu^{2+} species in Cu-NHC samples. These results illustrate the ability of NHCs to interact with Cu surfaces, irrespective of the surface type (clean or oxidized), and therefore the formation of a metallic Cu surface. However, as a result of the reaction, there appear to be residual Cu oxides present, either in the form of Cu^{1+} as Cu_2O or as Cu(OH)\textsubscript{2}. As indicated in Fig. 5.2, these two states lie close together in the Auger spectrum and are hard to distinguish. In order to do so, we review the O 1s spectra.
Figure 5.2: XPS spectra of Cu LMM Auger spectra for Cu$_{ox}$, Cu$_{clean}$, and Cu samples modified with NHC at 80°C. Vertical dash lines illustrate kinetics energy for Cu, Cu$_2$O, CuO, and Cu(OH)$_2$ in the Cu LMM Auger region.

O 1s spectra for Cu substrates are shown in Figure 5.3. Cu$_{clean}$ exhibits a weak signal at 532.2 eV, consistent with weakly adsorbed O species as associated with surface contamination.$^{13-15}$ On the other hand, the O signal at 529.6 eV for Cu$_{ox}$ confirms the presence of a CuO layer on the surface.$^{10,11}$ Further, this type of O signal was not present in
Cu\textsubscript{clean} and all Cu-NHC samples. The O 1s spectra of Cu-NHC samples show peaks at 530 ± 0.1 eV and 532.0± 0.2 eV, which are assigned to the lattice oxygen (Cu\textsubscript{2}O), and surface contamination or oxidized carbon functional groups\textsuperscript{10,16,17} which may result from the decomposition of some NHCs molecules on the surface. Furthermore, after the NHC treatment, the Cu\textsubscript{ox} sample exhibits a third species of O at 531.2 eV, which may correspond to surface hydroxyl (OH\textsuperscript{-}).\textsuperscript{18}

**Figure 5.3:** XPS spectra of O 1s spectra for Cu\textsubscript{ox}, Cu\textsubscript{clean}, and Cu samples modified with NHC at 80°C. Vertical dash lines illustrate O binding energy for Cu\textsubscript{2}O, CuO, and Cu(OH)\textsubscript{2}. 

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Figures 5.4 and 5.5 present C 1s and N 1s spectra. A single C peak was detected for \( \text{Cu}_{\text{clean}} \), which represents the C contamination on the surface. In contrast, \( \text{Cu}_{\text{ox}} \) shows a higher composition of C, in particular at 288.4 eV, which is assigned to a carbonate species, as reported previously for CuO.\(^{19}\) Notably, there are no significant peaks for N in any of the reference samples (\( \text{Cu}_{\text{clean}} \) and \( \text{Cu}_{\text{ox}} \)).

\[
\begin{align*}
\text{Cu}_{\text{clean}} & \quad -\text{HCO}_3\_\text{iPr} \\
\text{Cu}_{\text{ox}} & \quad -\text{HCO}_3\_\text{iPr} \\
\text{Cu}_{\text{clean}} & \quad \text{Cu}_{\text{ox}}
\end{align*}
\]

\[\text{Binding Energy (eV)}\]

**Figure 5.4:** XPS spectra of C 1s spectra for \( \text{Cu}_{\text{ox}} \), \( \text{Cu}_{\text{clean}} \), and Cu samples modified with NHC at 80°C.
Figure 5.5: The fitted XPS spectra of N 1s spectra for Cu$_{\text{ox}}$, Cu$_{\text{clean}}$, and Cu samples modified with NHC at 80°C.
Cu-NHC samples demonstrate two major C species at 284.8 eV and 285.8± 0.1 eV, which are associated with sp² and sp³ C, respectively.²⁰,²¹ An additional C peak appears at 288.3 eV after exposing Cu₉ox to NHC; this peak can be assigned to the oxidized NHC molecules on the surface. Cu-NHC samples also display a high intensity of N signal compared to reference samples (Cu_{clean} and Cu₉ox). Two N components are exhibited around 400.2 eV and 401.7 eV for Cu-NHC samples. A major peak around 400.2 eV is attributed to N in NHC molecule.²²,²³ The small contribution from the peak around 401.7 eV is assigned to the quaternary N functional groups,²⁴–²⁶ which are produced as a result of the interaction between nitrogen’s lone pair and Cu surface, or due to the opening of imidazole ring, which forms different N species, such as protonated amine.²⁷–²⁹ Overall, N XPS results provide strong evidence for the presence of NHC molecules on Cu surfaces.

5.3.2 Synchrotron-based X-ray photoelectron spectroscopy (SR-XPS) characterization

Similar to the experiments described in chapter 4, SR-XPS was used to characterize Cu surfaces after the exposure to NHC at 80°C and at room temperature. The experiments were carried out at photon energies of 230 eV (bulk sensitive) and 180 eV (surface sensitive), and similarly, we focused on Cu 3p spectrum. Table 5.2 displays a summary of the quantitative analysis of Cu 3p spectra for Cu references, Cu_{clean} and Cu₉ox surfaces, including peak position, percentage area for each chemical state, and area ratio of N to total Cu signal.
Table 5.2: A summary of Cu 3p spectra analysis for Cu\textsubscript{clean} and Cu\textsubscript{ox} surfaces (reference substrates).

<table>
<thead>
<tr>
<th>Cu surface</th>
<th>$hv$ (eV)</th>
<th>3p</th>
<th>BE (eV)</th>
<th>FWHM</th>
<th>%Area</th>
<th>Area of N : Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) clean</td>
<td>230</td>
<td>(3/2)</td>
<td>75.1</td>
<td>2.1</td>
<td>61</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1/2)</td>
<td>77.5</td>
<td>2.1</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>(3/2)</td>
<td>75.1</td>
<td>2.0</td>
<td>56</td>
<td>-</td>
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<td></td>
<td>(1/2)</td>
<td>77.5</td>
<td>2.0</td>
<td>28</td>
<td>-</td>
</tr>
<tr>
<td>(2) ox</td>
<td>230</td>
<td>(3/2)</td>
<td>75.4</td>
<td>2.0</td>
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<td>(1/2)</td>
<td>77.8</td>
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<td></td>
<td>180</td>
<td>(3/2)</td>
<td>75.3</td>
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<td>-</td>
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<td></td>
<td>(1/2)</td>
<td>77.7</td>
<td>1.9</td>
<td>6</td>
<td>-</td>
</tr>
</tbody>
</table>

The deconvolution of Cu 3p spectra reveals two chemical states for each sample, which represent bulk and surface Cu. Further discussion is presented based on Cu 3p\textsuperscript{3/2} peak for each Cu state. First, Cu\textsubscript{clean} exhibits a bulk-like peak with high intensity at 75.1 eV, which is attributed to metallic Cu \cite{30,31} while a surface-like state appears at 73.1 ± 0.3 eV. The shift in the binding energy for the surface relative to the bulk is referred as surface core-level shift (SCLS). \cite{32} The observed shift in the binding energy for the surface relative to the bulk is in good agreement with previously observed surface core-level shifts (SCLS) in Cu 2p region. \cite{33,34} To our knowledge, no published research studies have investigated the SCLS for Cu 3p. Here we observe a large SCLS since the typical magnitude for SCLS is 1 eV or less, \cite{35} which can be attributed to several factors, such as the existence of Cu ad-atoms, in addition to potential oxygen and carbon contamination on the Cu surfaces. For example, a large
SCLS for Al (111) was reported before by Flodstrom et al. as a result of the initial interaction with oxygen. Notably, no significant change in Cu 3p spectrum for Cu$_{\text{clean}}$ was observed when changing photon energy. In contrast, Cu$_{\text{ox}}$ sample exhibits a major peak at 76.0 eV at the 230 eV photon energy, which attributes to CuO. Notably, no N signal was detected on Cu$_{\text{clean}}$ and Cu$_{\text{ox}}$ surfaces.

Figure 5.6 displays an example of Cu 3p spectra for Cu-NHC samples at the 180 eV photon energy and Tables 5.3 and 5.4 present a summary of the characterization results of Cu-NHC samples. Exposing Cu$_{\text{clean}}$ to NHC at room temperature for 8h and 24h displays a metallic Cu peak with high intensity appears at 75.1 ± 0.1 eV for both photon energies. A major SCLS shift of ~ 2 eV to lower binding energy, presumably induced by the NHC, was observed for the surface state. The interaction of NHC with Cu$_{\text{clean}}$ for 8h and 24h has no significant effect on the peak corresponding to the bulk layer composition compared to Cu$_{\text{clean}}$ (ref.), as shown at 230 eV energy. In contrast, NHC had a marked effect on Cu surface layer (at 180 eV). After 8h of exposure, a relatively low intensity N 1s signal is detected while exposing the sample to NHC for 24h results in a strong N signal with, presumably indicating a high coverage of NHC following exposure. In contrast, exposing Cu$_{\text{ox}}$ surface to NHC for 8h reveals a high content of CuO (76.0 eV) at the 230 eV photon energy (bulk energy). This peak has slightly decreased in the intensity and shifted by 0.6 eV to lower binding energy at the more surface sensitive beam energy of 180 eV upon interaction with NHC. The N 1s signal is detected in this case, which implies the interaction between NHC and Cu surface during the 8h. Upon continuing the exposure for up to 72h, the CuO signal has entirely disappeared; furthermore, for 180 eV photon energy the chemical structure of Cu surface is similar to Cu$_{\text{clean}}$ surface, exposed to NHC for 24h. This is consistent with our
previous observation of Cu oxide etching (chapter 3) to yield a clean Cu surface protected with NHC.

Figure 5.6: The high resolution XPS spectra at 180 eV photon energy of Cu 3p (a) Cu$_{\text{clean}}$-NHC (b) Cu$_{\text{ox}}$-NHC after 15 min of exposure at 80°C.
Table 5.3: A summary of Cu 3p spectra analysis for Cu\text{clean}-NHC surfaces at various conditions.

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<th>Cu surface</th>
<th>Conditions</th>
<th>hv (eV)</th>
<th>3p BE</th>
<th>FWHM</th>
<th>%Area</th>
<th>Area of N : Cu</th>
</tr>
</thead>
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<td>8h/RT</td>
<td>230</td>
<td>(3/2) 75.1</td>
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<td>-</td>
</tr>
<tr>
<td></td>
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<td>1.6</td>
<td>5</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(3/2) 77.6</td>
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<td>31</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(1/2) 75.3</td>
<td>1.6</td>
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</tr>
<tr>
<td>(2) clean</td>
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<td>(1/2) 75.0</td>
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</tr>
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<td>(1/2) 75.2</td>
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<tr>
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Table 5.4: A summary of the doublet Cu 3p spectra analysis for Cu<sub>ox</sub>-NHC surfaces at various conditions.

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<th>FWHM</th>
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<th>Area of N : Cu</th>
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<td>16</td>
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<td>(3/2)</td>
<td>77.5</td>
<td>1.9</td>
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<td>(1/2)</td>
<td>76.2</td>
<td>2.4</td>
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<td>(4) ox</td>
<td>4h/80°C</td>
<td>230</td>
<td>(3/2)</td>
<td>75.2</td>
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<td>34</td>
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<td>3.8</td>
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<td>75.0</td>
<td>1.9</td>
<td>53</td>
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<td></td>
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<td>77.4</td>
<td>1.9</td>
<td>27</td>
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<td></td>
<td>(1/2)</td>
<td>75.9</td>
<td>2.0</td>
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<td>(5) ox</td>
<td>8h/80°C</td>
<td>230</td>
<td>(3/2)</td>
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<td></td>
<td></td>
<td>(3/2)</td>
<td>77.4</td>
<td>1.8</td>
<td>12</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(1/2)</td>
<td>77.4</td>
<td>3.3</td>
<td>22</td>
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</tr>
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<td>180</td>
<td>(3/2)</td>
<td>75.1</td>
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<td>0.32</td>
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<td></td>
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<td>(1/2)</td>
<td>73.3</td>
<td>2.1</td>
<td>12</td>
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</tr>
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<td></td>
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<td>(3/2)</td>
<td>77.5</td>
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<td>(1/2)</td>
<td>75.7</td>
<td>2.1</td>
<td>6</td>
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</tr>
</tbody>
</table>
Cu$_{\text{clean}}$ and Cu$_{\text{ox}}$ surfaces were exposed to NHC solutions at 80°C for various times. First, Cu$_{\text{clean}}$ samples exposed to NHC solution for 15 min, 4 h and 8 h (see Table 5.3) show almost identical Cu 3p spectra. For all samples, two different Cu 3p$_{3/2}$ peaks overlapped around 75.0 ± 0.3 eV at the bulk-sensitive energy (230 eV), although they have distinct peak widths (FWHM). This indicates the existence of two different Cu states. This is similar to the 2p spectra of metallic Cu and Cu$_2$O, which demonstrate only a small difference in their binding energies, however, Cu$_2$O has a larger FWHM than metallic Cu.$^{37}$ Therefore, a trace amount of Cu$_2$O is assumed to be present in this sample, which is likely due to higher temperatures used in the synthesis, as the room temperature sample did not elicit any Cu$_2$O formation. Moreover, it is well understood that increasing temperatures can increase the diffusion of oxygen from the bulk to the surface, in particular with copper. Even though the surface was free of oxygen from NHC etching effect, the diffusion of oxygen from the bulk of the material likely played a role in the formation of Cu$_2$O near the surface.

On the other hand, at the more surface sensitive photon energy (180 eV), a significant contribution from the metallic Cu state was observed, likely due to the NHC surface interaction. Similar to previous observations, the surface Cu peak (i.e., 73.2 ± 0.1 eV) appeared at ~ 2 eV lower than the binding energy of the bulk state, which is similar to what was been observed for the Cu$_{\text{clean}}$ reference sample, albeit with a slight increase in the intensity of the metallic surface state for Cu-NHC samples.

Finally, significant amounts of N were observed after exposing the samples to NHC solution for 15 min (see N:Cu ration in Table 5.3), which confirms the presence of NHC molecules on the surface, even within a short time of exposure.
The Cu\textsubscript{ox} samples were also exposed to NHC solution for 15 min, 4 h, and 8 h (see Table 5.4). Interestingly, exposing the Cu\textsubscript{ox} samples to NHC for 15 min has entirely removed CuO, since no signal appeared at 76.0 eV. Moreover, exposing Cu\textsubscript{ox} to NHC for 15 min leads to an increase in the metallic Cu intensity (at the 180 eV photon energy); however, the data in Table 5.4 reveals the absence of N signal in the sample. This result indicates that within 15 min of exposure, NHCs were able to remove CuO and generate a metallic Cu surface, but exposure time was not enough for NHC to deposit to any significant degree on the surface. Exposing Cu\textsubscript{ox} samples to NHC for 4 h and 8 h demonstrated similar distribution of Cu chemical states at both photon energies 230 and 180 eV, which were almost identical to the chemical states in Cu\textsubscript{clean}-NHC samples. Furthermore, the N signal implies the deposition of NHCs film on the surface.

The temperature effect on the adsorption process of NHCs on a Cu surface is illustrated in Table 5.5. In addition to the temperature role in accelerating the adsorption process, it contributes to increasing the surface coverage. Towards this, the N signal for Cu-NHC samples at 80°C increased more than two times compared to the samples at room temperature. The increase in the N signal implies more NHC molecules on the surface and likely a higher surface density.
Table 5.5: A comparison for N:Cu ratio in Cu-NHC samples based on the experiment temperature. The data is for Cu surfaces at 180 eV photon energy and maximum exposure time.

<table>
<thead>
<tr>
<th>Cu surface</th>
<th>Cond.</th>
<th>Area of N:Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) clean</td>
<td>24h/RT</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>8h/80°C</td>
<td>0.24</td>
</tr>
<tr>
<td>(2) ox</td>
<td>72h/RT</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>8h/80°C</td>
<td>0.32</td>
</tr>
</tbody>
</table>

SR-XPS depth profile analysis revealed the layered structure of Cu samples exposure to NHC at room temperature, which is illustrated in Figure 5.7. The layer composition of Cu\textsubscript{clean} after 8h of the exposure to NHC showed a metallic type Cu in all layers; however, the top layer exhibited more contribution of the surface state. It is speculated that the etching process of Cu is taking place on the surface, which causes surface roughness and therefore, an increase in the surface area. Moreover, the low N intensity is an indication of the low surface coverage, which supports the incomplete adsorption process. Cu\textsubscript{clean}, which exposed to NHC for 24h, exhibited bulk and surface states, which were identical in the intensities to the Cu\textsubscript{clean} (ref.), except, the Cu-NHC sample has top layer covered with an ordered film of NHC as a result of the complete adsorption process. Furthermore, the intensity of N signal for the 24h sample has increased to more than double compared to the 8h sample, which indicates a higher NHC surface coverage.
Figure 5.7: Layered structure of the Cu samples exposed to NHC at room temperature obtained from the depth profile analysis.

For $\text{Cu}_{\text{ox}}$, the top layer exhibits a slight decrease in CuO intensity due to etching process by NHC, which took place on the surface but was not completed within 8h of exposure. On the other hand, exposing $\text{Cu}_{\text{ox}}$ to NHC for 72h showed a different layered structure. The bulk-like layer is a combination of a metallic Cu and Cu$_2$O, while the surface layer is mostly metallic. Moreover, the calculated N: Cu ratio (0.10) for this $\text{Cu}_{\text{ox}}$ with 72h NHC exposure was identical to the ratio of $\text{Cu}_{\text{clean}}$ exposed to NHC for 24h, thereby indicating a similar chemical composition of the surface layer for both samples.
Figure 5.8 illustrates layered structure of Cu samples exposure to NHC at 80°C. In general, layer composition of Cu\textsubscript{clean} and Cu\textsubscript{ox} after 8h of the exposure to NHC are identical. Bulk-like layer is a combination of a metallic Cu and Cu\textsubscript{2}O, but surface layer is metallic and highly covered with NHC.

Figure 5.8: Layered structure of the Cu samples exposed to NHC at 80°C obtained from the depth profile analysis.
5.4 Conclusion

A comprehensive study of NHC interaction with Cu surface, at room temperature and at 80°C, is introduced to demonstrate the effects of temperature on the reaction of NHC with Cu surfaces. At room temperature, NHCs are able to interact directly with clean copper surfaces, which results in formation of NHC film on the metallic surface within 24h. On the other hand, the interaction of an oxidized copper surface with NHC to result in a similar surface takes a much longer time than for clean copper. However, the etching process of Cu$_{ox}$ surface by NHC was shown to produce a metallic surface layer, which was identical in the chemical composition to surface layer of clean copper with NHCs. Cu samples were exposed to NHC solutions at 80°C and then characterized by standard XPS as well as SR-XPS. Exposing Cu$_{clean}$ surfaces to NHCs for 15 min was sufficient to form a NHC film on the surface. In contrast, 15 min of exposing Cu$_{ox}$ surfaces to NHCs was not enough for NHC deposition on the surface, but CuO was entirely removed from the surface during this time. Increasing temperature also had a major role in minimizing exposure time by accelerating the adsorption process, in addition to its role in increasing surface coverage. Overall, these findings will have a huge impact on NHC-based SAM applications, as the manufacturing time of these surfaces can be severely reduced by modifying one simple parameter.
5.5 References


Chapter 6

The adsorption kinetics of NHCs on gold surface

6.1 Introduction

Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) (Fig 6.1) is an easy, inexpensive, and extremely sensitive instrument that can be used to detect molecular adsorption at the nanogram scale. It has wide applications in biosensors,\(^1\) drug development,\(^2\) polymers,\(^3\) biomaterials and materials science.\(^4\) The principle of QCM is based on the piezoelectric properties of quartz. QCM sensor is made of quartz crystal coated with metal electrodes on each side connected with a driving oscillator.\(^5\) AT-cut quartz crystal is the most common type, mainly because it shows high performance with excellent temperature stability.\(^6,7\)

![Figure 6.1: The QCM set up.](image-url)
When an AC voltage is applied to the crystal, it begins to oscillate at a specific resonant frequency. The decrease in resonant frequency indicates the adsorption of the molecule on the surface. The theory behind the QCM has been thoroughly explained by Sauerbrey in 1959, but briefly, a linear relationship between the change of the frequency and the mass adsorbed on the surface is demonstrated by Sauerbrey equation:

\[
\Delta m = -\frac{C \Delta f}{n} \quad (6.1)
\]

where \(\Delta m\) and \(\Delta f\) are mass and frequency change, respectively, and \(n\) is the overtone number of the crystal (\(n = 1, 3, 5, 7, 9, 11, 13\)). \(C\) is a constant depending on the physical property of the sensor (\(C = 17.7 \text{ ng/Hz.cm}^2\)).

Our group has previously reported on the successful adsorption of NHCs on metals, in particular, on gold surfaces. Further, the adsorption of NHCs on copper surfaces was demonstrated comprehensively in the previous chapters where temperature of the deposition solution played a significant role in the interaction process, which was believed to be based on the faster kinetics of the reaction. However, the adsorption kinetics of NHC onto any metal have not been explored up to now. Therefore, it is of fundamental importance to understand the kinetics of adsorption on metal surfaces to define the surface reaction mechanisms. Here, an investigation of the kinetics adsorption process of NHCs on gold surfaces by using XPS and QCM-D techniques is introduced.
6.2 Materials and Methods

6.2.1 X-ray Photoelectron Spectroscopy (XPS)

Three different concentrations of [a] 1,3-Dihydro-1,3-bisisopropyl-2H-benzimidazol-2-ylidene in benzene were prepared. Au (111) on mica samples were then immersed in these solutions and XPS measurements were taken at various times of immersion. The NHC preparation and immersion were done inside a glove box in collaboration with the Crudden group. XPS measurements were performed using a Thermo Microlab 310F ultrahigh vacuum (UHV) surface analysis instrument using Al Kα X-rays (1486.6 eV) or Mg Kα (1253.4 eV) at 15 kV anode potential and 20 mA emission current with a surface/detector take off angle of 75°. Survey spectra were collected, along with high-resolution element scans dependent on the sample. In all cases, the Au (4f) at 84 eV was used as a reference to calibrate the high-resolution spectra. Spectra were subjected to a Shirley baseline and fitted by using mixed Gaussian-Lorentzian functions.

6.2.2 Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) approach.

Various concentrations of [b] 5-(dodecyloxy)-1,3-diisopropyl-1H-benzo[d]imidazol-3-ium hydrogen carbonate were dissolved in dried methanol. QCM-D measurements were then performed using QCM-D E1, from Q-Sense. The 5 MHz AT-cut quartz crystals

![Chemical structures]

[a] 1,3-Dihydro-1,3-bisisopropyl-2H-benzimidazol-2-ylidene
[b] 5-(dodecyloxy)-1,3-diisopropyl-1H-benzo[d]imidazol-3-ium hydrogen carbonate
(diameter of 14 mm and thickness of 100 mm) were used. First, the QCM was flushed with methanol to clean the system, and then the quartz crystals were installed into the flow cells. The system was then rinsed again with methanol at a high flow rate. Finally, the system was dried with nitrogen gas to enable the correct concentrations of NHC solutions to be maintained. The experiment was begun by inserting the sensor and initiating a pump at a rate of 0.1 ml/min. A stable baseline was first achieved by injecting methanol and then the testing solutions were injected. All experiments were carried out at a controlled temperature of 20°C. The data modeling and analysis were carried out with Q-sense Qtools, in which the Sauerbrey model was chosen to convert frequency change to mass change.

### 6.3 Results and Discussion

#### 6.3.1 The adsorption of free NHC on gold surface -XSP study

The kinetics of the free NHC deposition on the gold surface was first studied by XPS. Carbon area for the testing samples was collected at various time of immersion (Fig. 6.2) and normalized by subtracting the peak area of the carbon on the gold reference.

![Figure 6.2: The area of the carbon as a function of the immersion time for gold surfaces.](image-url)
The results may be interpreted using a two steps of adsorption process, in which there is a fast step followed by a slow step; the NHC molecules are rapidly adsorbed on the gold surface then slowly rearrange themselves to form a monolayer. This process can be described by the following mechanism:\textsuperscript{11}

\[ A + Au \overset{k_s}{\underset{k_d}{\rightleftharpoons}} A_i - Au \]  
(6.2a)

\[ A_i - Au \overset{k_t}{\rightarrow} A_r - Au \]  
(6.2b)

where A, Au, A\textsubscript{i}, A\textsubscript{r}, k\textsubscript{s}, k\textsubscript{d}, and k\textsubscript{t} represent the carbene molecule, the adsorption site on gold, the initially adsorbed species, the rearranged species in the monolayer, adsorption rate constant, desorption rate constant, and rearrangement rate constant for the second step of adsorption respectively.

Based on the proposed mechanism (Eq. 6.2 a and b), the rate equations for the adsorption process are:

\[ \frac{d\theta_1}{dt} = k_a C - (k_a C + k_d + k_t)\theta_1 - k_a C\theta_2 \]  
(6.3a)

\[ \frac{d\theta_2}{dt} = k_t \theta_1 \]  
(6.3b)

where \( \theta, \theta_1, \theta_2 \), and C are overall coverage, the coverage in the first step of the adsorption, the coverage for an assembled monolayer, and NHC concentration, respectively.

The integration of Equations 6.3 a and b gives the rearrangement-limited Langmuir model:\textsuperscript{11,12}

\[ \theta = F_1[1 - \exp(-k_{obs,1} t)] + F_2[1 - \exp(-k_{obs,2} t)] \]  
(6.4)

where \( F_1 \) and \( F_2 \) are the limiting coverage in each step.

Equation (6.4) was used to fit the collected data as shown in Figure 6.3.
Figure 6.3: The adsorption of different concentrations of free NHC on gold surface. The black line indicates the curve calculated from the rearrangement-limited Langmuir model (Eq 6.4).

The relationship between $k_{\text{obs,1,2}}$ and $k_a$, $k_d$, $k_t$ can be represented by:

$$k_{\text{obs,1}} + k_{\text{obs,2}} = k_a C + k_d + k_t \quad (6.5a)$$

and

$$k_{\text{obs,1}} \cdot k_{\text{obs,2}} = k_a k_t C \quad (6.5b)$$

Equations (6.5a and 6.5b) were used to calculate $k_a$, $k_d$, and $k_t$. Figure 6.4a shows a plot of $k_{\text{obs,1}} + k_{\text{obs,2}}$ versus $C$ which gave a straight line. The slope equals $k_a$ and the intercept equals $k_d + k_t$. Figure 6.4b shows a plot of $k_{\text{obs,1}} k_{\text{obs,2}}$ versus $C$ which gave a straight line with a slope equal to $k_a k_t$. A summary of the result is illustrated in Table 6.1. Interestingly, the adsorption rate constant $k_a$ for the free NHC is slightly lower than what has been found for thiol (11-mercaptopoundecanoic acid); however, desorption rate constant, $k_d$, is much larger than compared to thiol, indicating a rapid exchange of the NHC molecules. The
relatively low number of data points acquired that the value obtained for $k_t$ had an error that precludes meaningful comparison to the published value for the thiol. As each experiment took over a week to perform using XPS, a more rapid method to determine the rate values was explored using QCM-D.

**Figure 6.4:** Plots of free NHC concentration versus: (a) $k_{\text{obs,1}} + k_{\text{obs,2}}$ (Eq. 6.5a). (b) $k_{\text{obs,1}} k_{\text{obs,2}}$ (Eq. 6.5b) to determine $k_a$, $k_d$, and $k_t$.

**Table 6.1:** The calculated rate constants for the free NHC, hydrogen carbonate salt, and the literature rate constants for thiol.$^{11}$

<table>
<thead>
<tr>
<th>Rate constant</th>
<th>Free NHC (XPS)</th>
<th>Hydrogen carbonate NHC (QCM)</th>
<th>Thiol$^{11}$</th>
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</thead>
<tbody>
<tr>
<td>$k_a$ (L mol$^{-1}$ s$^{-1}$)</td>
<td>$10.8 \pm 2.8$</td>
<td>$9.2 \pm 0.6$</td>
<td>$11.5 \pm 0.2$</td>
</tr>
<tr>
<td>$k_d$ (s$^{-1}$)</td>
<td>$(2.0 \pm 0.2) \times 10^{-2}$</td>
<td>$(2.3 \pm 0.4) \times 10^{-2}$</td>
<td>$(6.0 \pm 1.0) \times 10^{-4}$</td>
</tr>
<tr>
<td>$k_t$ (s$^{-1}$)</td>
<td>$(1.8 \pm 2.0) \times 10^{-4}$</td>
<td>$(5.2 \pm 0.05) \times 10^{-3}$</td>
<td>$(4.5 \pm 0.4) \times 10^{-4}$</td>
</tr>
</tbody>
</table>
6.3.2 The adsorption of hydrogen carbonate NHC on gold surface – QCM-D study

QCM-D technique was employed to study the kinetics of NHC salt deposition on the gold surface. The change in the frequency depends on the adsorbate mass, therefore in this experiment, we used a larger MW NHC molecule compared to the free NHC that we used in the XPS experiment (e.g., 448 g/mol vs 264 g/mol). Figure 6.5 shows the collected result for various concentrations of NHC deposited on the gold.

![Figure 6.5: Mass change as a function of time for various concentrations of NHC salt.](image)

Initially, the mass increased rapidly when NHC molecule is injected and continued to increase at a lower rate compared to the initial rate. This suggests that the adsorption of the NHC salt on the gold substrate also occurs in by two steps. The rearrange-limited Langmuir model (Eq. 6.4) was used to fit the data that obtained from QCM (Fig. 6.6). The rate constants $k_a$, $k_d$, $k_t$ were calculated from Fig. 6.7 and the values are listed in Table 6.1. The resulting values for $k_a$ and $k_d$ are consistent with those obtained using the XPS method, within experimental error. As the adsorption stage is slower for NHC than thiol, and
desorption stage more rapid, it is possible that the deprotonation process to generate the carbene may be contributing to slowing the adsorption rate. The data from this experiment is now of sufficient quality that we can meaningfully compare $k_t$ for NHC and thiol. The significantly higher value for NHC suggests that the rearrangement process of NHC is about 10 times faster than that of thiol adsorption on gold. This is likely due to the wider spacing of NHC on gold since the surface density of 3.5 molecules nm$^{-2}$ was obtained from STM and electrochemistry analysis. Overall, this suggests that despite the slower initial adsorption, NHCs can form a more ordered SAM on gold much more quickly than thiols.

![Figure 6.6: The adsorption of different concentrations of NHC salt on gold. The black line indicates the curve calculated from the rearrange-limited Langmuir model.](image-url)
Figure 6.7: Plots of the NHC salt concentration versus: (a) $k_{obs,1} + k_{obs,2}$ (Eq. 6.5a). (b) $k_{obs,1}k_{obs,2}$ (Eq. 6.5b) to determine $k_a$, $k_d$, and $k_t$.

6.4 Conclusion

In conclusion, the adsorption kinetics of NHC deposition onto gold surfaces was studied by XPS and QCM. In general, the results showed that NHC is adsorbed on the gold surface in two steps. As an initial step, NHC molecules were spontaneously adsorbed onto the gold surface within a few seconds, and the excess molecules were then desorbed from the surface. Then, at a rate slower than the initial step, the rearrangement process took place to form a more ordered monolayer. Overall, this study provides a better understanding of the adsorption mechanism of NHC onto metal surfaces and reveals important distinctive features of NHCs compared to thiol.
6.5 References

Chapter 7

Conclusions and Future Work

7.1 Conclusions

The formation of nanostructures on metal surfaces has become a dominant topic in various research areas. SAMs are a form of nanostructured material and are powerful tools for protection and functionalization of metal surfaces. This thesis has presented a comprehensive study based on the application of NHC SAMs onto polycrystalline copper surfaces.

In chapter 3, a study of NHCs interaction with Cu surfaces at room temperature was presented. The study was conducted by exposing clean and oxidized Cu surfaces to NHCs, which were in “free” and bicarbonate forms. XPS was then employed to study the structure of the copper surfaces. Cu\text{clean} and Cu\text{ox} surfaces were exposed to both types of NHC for 24h and 48h respectively. The results demonstrated a similarity in the chemical structure for both Cu\text{clean} and Cu\text{ox} surfaces after the treatment with NHC. Extensive results from XPS showed that the NHC interaction with copper surfaces leads to the formation of a metallic copper surface. A further novel finding is the ability of the NHC to remove the CuO as well as organic contaminants (C and N) pre-existing from the copper surface. Mass spectrometry was also employed to analyze the NHC solutions, in which the copper samples were immersed in. Traces of NHC complexes were observed and further illustrated the ability of NHCs for removing CuO. However, the form of NHC (\textit{i.e.}, “free” vs. bicarbonate salt) significantly affected the etching process where the salt NHCs exhibited significantly more etching of the Cu surfaces compared to the “free” type.
Chapter 4 is an extension of the work in chapter 3 in order to gain a better understanding of the multilayered structure at the surface of the copper after interaction with NHC. Synchrotron-based X-ray photoelectron spectroscopy (SR-XPS) was used, which allowed a non-destructive, energy dependent, depth-profile of the surface. The surface interaction of Cu with NHC at room temperature was investigated. The results revealed the formation of NHC film on the metallic surface within 24h as a result of the direct interaction of NHCs with clean copper surfaces. On the other hand, results of the interaction of NHCs with oxidized copper surfaces were unsatisfactory; the oxide layer was partially removed from the surface. Therefore, this study was explored again in this thesis.

In chapter 5, a similar methodology was used to investigate the effects of temperature on the interaction of NHC with Cu surfaces. Regardless of the Cu surface type, the interaction with NHC leads to a metallic Cu surface. NHC directly interacted with the Cu\textsubscript{clean} surfaces at room temperature; however, an immersion for 24h was required for the complete adsorption. On the other hand, the interaction of Cu\textsubscript{ox} surface with NHC much longer because of the oxide layer, although this layer was mostly removed from the surface as the first step of the interaction process, followed by the formation of NHC SAM. Cu samples were also exposed to NHC solutions at 80°C for various times. Standard XPS and SR-XPS were employed to characterize the Cu surfaces. The results revealed important aspects of the interaction process. Exposing to Cu samples to NHC for 15 min was sufficient to form NHC film on Cu\textsubscript{clean} surface but not Cu\textsubscript{ox}. However, CuO was entirely removed from Cu\textsubscript{ox} surface during the exposure to NHC for 15 min. The result demonstrated the major role of temperature in accelerating the adsorption process and therefore, minimizing the exposure time and increasing surface coverage.
Overall, a facile wet-chemical method towards the formation of NHC nanostructured films on copper surfaces was developed. The findings will provide useful information from a fundamental standpoint, but will also find much significance for industrial applications, which require the protection of metallic copper surfaces. For example, this work will have a huge impact on microelectronics applications, where metallic copper is highly desired, yet difficult to maintain.

Finally, chapter 6 presented a study of the adsorption kinetics of NHC on gold surfaces. The study was comprehensively conducted by using XPS and QCM. Notably, the QCM adsorption the data were fitted with the rearrangement-limited Langmuir model, similar to thiol adsorption on gold. The results revealed that NHC is adsorbed on the gold surface in two steps. In the initial step, the NHC molecules were spontaneously adsorbed on the gold surface. Then, a fast rearrangement process, took place to form the monolayer. Compared to thiol, NHC rearrangement process is much faster, which denotes the higher reactivity of NHC and potentially indicates the greater versatility of NHC type ligands for SAM technologies.

7.2 Future work

7.2.1 Exploring the effect of NHC concentration

In chapter 5, we demonstrated the role of temperature in the interaction rate of NHC with Cu surfaces. Another important parameter, which directly affects the kinetics of SAM formation is the concentration of the adsorbate molecule. The concentration of the immersed solution does not only affect the adsorption rate, but also the SAM structure. Increasing the concentration may increase surface density and reduce the immersion time that is required
to achieve a fully covered surface. Therefore, using a similar methodology to study of the effect of NHC the concentration would be worthwhile. For example, this study could be conducted at room temperature by preparing series of NHC solutions that have wide range of concentrations. Furthermore, it is worth studying the effect of both temperature and concentration at the same time would be worthwhile to determine the most optimal conditions for deposition. Different techniques could be used to study the effect of NHC concentration, such as XPS and STM.

7.2.2 Further exploration of etching-adsorption mechanism

The interaction of NHC with Cu\textsubscript{ox} surface at elevated temperatures involved two steps, which was also demonstrated by the results outlined in chapter 5. The first step was the removal of CuO from the surface followed by the adsorption of NHC onto the metallic surface. For this proposed mechanism, each step is determined by specific parameters. Further studying the etching-adsorption mechanism will provide more information that can help in controlling the monolayer growth and optimize the resulting SAM structure. For example, AFM (liquid phase imaging) could be used to track the etching process and analyze the morphology of NHC deposited on Cu.

7.2.3 Study the structure of NHC film

The fundamental aspects of the NHC film formation on copper surfaces was the main focus of this thesis. However, the atomic structure of NHC film on copper has remained unexplored. Studying the atomic structure of NHC SAMs on copper will provide more details to help understand the mechanisms of SAM formation, surface density, and characterize the defects on the surface. For example, using STM to study these surfaces would allow atomic resolution imaging of NHCs on the surfaces, which could provide
details regarding ligand orientation and surface coverage density. Further, AFM and XPS imaging techniques could also be used to examine the NHCs on the copper surfaces and could provide useful information regarding the structure of the NHCs on copper. Furthermore, it would be interesting to conduct this study at both room temperature and elevated temperatures, as well to explore the effect of temperature on SAM structure and surface coverage. Understanding the structures of the SAM is essential for an effective use of NHC SAM technology in any potential application.

### 7.2.4 Explore the electrical conductivity of SAM

SAM technology is extensively used in electronics, in which conduction is one of the major requirements. Therefore, a comprehensive study on the conduction of SAM would be worthwhile especially for industrial application. The electrical properties of SAM can be explored by using several techniques such as conductive atomic force microscopy, scanning probe microscopy, and mechanical break junction. For example, conductive atomic force microscopy can be used to study the electrical properties of NHC film on Cu comparable to pure Cu by measuring the current conduction simultaneously with topography by changing the applied voltage.

### 7.2.5 SAMs of NHC on other metals

NHCs are widely used as ligands for transition metals and in this thesis, the interaction of NHC with Cu surfaces was studied. Furthermore, interaction of NHC with Ni was explored and Figure 7.1 shows the preliminary results. The spectra of Ni\text{clean} and all Ni-NHC samples display similarly in the peaks’ shape and position. Interestingly, Ni\text{clean} surface displays no signal in N 1s region; however, a high intensity of N signal was detected for
Ni\textsubscript{clean} modified with NHC. This is an indication of NHC presence on the surface and therefore, the adsorption and the formation of NHC layer on the nickel surfaces.

The results of Ni-NHC samples are similar to the presented results for Cu in this thesis; however, further study is needed. It would be worthwhile to expand the study, so it would cover other transition metals, such as Pt and Pd, which are both widely used metals in surface chemistry, particularly in catalysis applications.
Figure 7.1: XPS spectra of (a) Ni 2P (b) O 1s (c) C1s (d) N1s for Ni samples modified with NHC.