A REVIEW OF THE ELECTRONIC STRUCTURES AND INTERACTIONS OF L-CYSTEINE WITH NOBLE METAL SURFACES

Nawarathne HMCJ[*1], Koswattage KR[*2]

[*1]Faculty Of Geomatics, Sabaragamuwa University Of Sri Lanka, P.O. Box 02, Belihuloya, Sri Lanka.

[*2]Faculty Of Technology, Sabaragamuwa University Of Sri Lanka, P.O. Box 02, Belihuloya, Sri Lanka.

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ABSTRACT

In this study, the electronic structures and interactions between L-cysteine and noble metal surfaces are reviewed. The thiol group (–SH) of L-cysteine plays a central role in these interactions, with the amino (NH2) and carboxyl (COOH) groups also contributing significantly. These interactions result in diverse bonding mechanisms and interface states, shaping the electronic properties of L-cysteine. Notably, the strong bond formed between L-cysteine and silver surfaces has been extensively examined using techniques like scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. These investigations reveal a complex electronic landscape, including the formation of interface electronic states above and below L-cysteine's highest occupied molecular orbital (HOMO). These findings hold promise for applications in electronic devices and biosensors, offering insights into the electronic properties of L-cysteine-modified surfaces and their potential for innovation.

Keywords: L-Cysteine, Noble Metal Surfaces, Electronic Structures, Biomolecules, Chemisorption, Physisorption, Noble Metals.

I.   INTRODUCTION

The intersection of biomolecules and solid inorganic surfaces has recently emerged as a vibrant arena of scientific inquiry, offering promising avenues for diverse applications, including the development of biocompatible surfaces for bioelectronics [1]. Amidst the rich tapestry of biomolecules, amino acids have captured considerable attention, standing as vanguards in the functionalization of metallic surfaces. Among these, L-cysteine, a sulfur-containing amino acid bearing the chemical formula HS–CH2–CH(NH2)–COOH, has risen to prominence [2]. Its distinctive molecular architecture, replete with unique functional groups, positions L-cysteine as a versatile contender for anchoring proteins onto noble metal surfaces such as gold, silver, and copper. These metals, frequently employed as electrodes in bioelectronics, biosensors, and other electronic devices, become the canvas upon which L-cysteine orchestrates its molecular artistry [1].

The ballet of L-cysteine's interaction with these metallic substrates finds its principal choreographer in the thiol group (–SH). Yet, the amino (NH2) and carboxyl (COOH) functional groups, integral to L-cysteine's identity, assume pivotal roles in forging tenacious bonds with these metal surfaces. It is this intricate interplay of functional groups on L-cysteine, poised at the nexus of chemistry and materials science, which begets diverse bonding mechanisms [1]. These mechanisms, in turn, breathe life into the formation of interface states at the L-cysteine-metal juncture, bestowing upon it an electronic tapestry rich with potential.

Of particular intrigue is the pas de deux between L-cysteine and silver surfaces. Extensive research endeavors have suggested that the union between L-cysteine and silver is graced with a bond of uncommon strength, eclipsing those observed on gold or copper surfaces. The empirical revelations, gleaned through the lens of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, unveil an enthralling narrative [3], [4]. It is a narrative marked by the tightly knit congregation of zwitterionic L-cysteine molecules [5], their firm chemisorption through the auspices of the sulfur atom, and the tantalizing prospect of unique interface electronic states, some perhaps nestled beneath and above the lofty realm of L-cysteine's highest occupied molecular orbital (HOMO) [1]. These interface states, enigmatic and dynamic, are poised to leave an indelible mark upon the electronic character of L-cysteine.

However, while computational endeavors have postulated the gradual weakening of the silver-sulfur bond with ascending L-cysteine coverage, the realm of experimental exploration in this regard has, thus far, remained

relatively uncharted. The present undertaking embarks upon a journey of profound inquiry, marked by the meticulous elucidation of the interface electronic structure shared by L-cysteine and silver. Its primary tool, thickness-dependent ultraviolet photoelectron spectroscopy (UPS), endeavors to pierce the veil of ambiguity, employing L-cysteine upon a pristine Ag(111) surface as a paragon of inquiry [1]. With its exceptional surface sensitivity and an inherent affinity for probing valence electrons, UPS emerges as an indispensable guide in deciphering the intricate interactions manifest at material interfaces [2].

In concert with UPS, the investigation is serenaded by the mellifluous notes of photoelectron yield spectroscopy (PYS), where L-cysteine graces evaporated silver surfaces. In this symphonic endeavor, coverage levels of L-cysteine serve as the notes and crescendos, each revealing a unique facet of the interplay between this biomolecule and silver. Through these systematic, harmonious inquiries, this study aspires to illuminate the hitherto veiled electronic architectures at the L-cysteine and silver interface. This illumination is not merely an academic pursuit but a beacon that shines upon the broader expanse of bioelectronic interfaces. It beckons toward a future where these interfaces, armed with newfound insights, may script chapters of innovation across a spectrum of electronic devices and biosensors.

II.   ANCHORING OF THIOLS TO NOBLE METAL SURFACES

Thiols play a pivotal role in forming self-assembled monolayers (SAMs) on noble metal surfaces, and their interaction with these surfaces can occur through either chemisorption or physisorption mechanisms [6]. Chemisorption is a process wherein chemical bonds are formed between the thiol molecules and atoms in the noble metal surface. Importantly, chemisorption does not involve the removal of component atoms from their positions within the noble metal or noble metal sulfide lattice. This strong and specific interaction leads to significant alterations in the electronic and surface properties of the noble metal, making it a key factor in tailoring surface characteristics for various applications [5].

In the realm of electronic properties, the adsorption of molecules, such as thiols, on noble metal surfaces can induce controlled changes, with a primary focus on properties like the work function and electron affinity. This change arises from the potential drop across a layer of dipolar molecules, a phenomenon that has been extensively studied by Gershevitz et al [7]. These alterations in electronic properties are instrumental in developing surface modifications for diverse applications, including but not limited to electrochemical sensors.

The interaction between thiols and different noble metals can exhibit distinct behaviors. For instance, Uvdal et al [8] conducted XPS and Infrared Reflection Absorption Spectroscopy (IRAS) measurements of long-tail dialkylsulfides and thiols on gold surfaces. Their research demonstrated the formation of well-ordered, self-assembled monolayer films, with the thiol groups forming covalent bonds with the noble gold surface. This type of interaction lays the foundation for robust and controlled surface modifications.

Further supporting this notion, Kamada et al (Kamada et al., 2010) conducted a core-level spectroscopic study of cysteine on the surfaces of noble transition metals. Their work provided additional evidence of the chemical reactions between cysteine and noble metal surfaces, highlighting the potential for the formation of self-assembled monolayers [8]. These findings emphasize the versatility and controllability of chemisorption-driven surface modifications.

In light of these interactions, thiols chemisorbed onto noble metal surfaces form films that find valuable applications, particularly in the realm of electrochemical sensors. The precise control over surface properties and electronic characteristics achieved through chemisorption plays a pivotal role in enhancing the performance and reliability of such sensors.

III.   PROBING THE INTERACTION OF L-CYSTEINE WITH NOBLE METAL SURFACES

For the future development of bioelectronics, the adsorption of biomolecules on various platforms is a critical area of investigation. Amino acids, as a category of biomolecules, have garnered special attention for their potential in creating bioactive surfaces. Among them, L-Cysteine has emerged as a particularly valuable amino acid for its unique properties. Various studies have delved into the structural and functional aspects of L-Cysteine when interfaced with noble metals such as gold, silver, and copper. It is important to note that the reaction that binds L-Cysteine to transition metal surfaces bears resemblance to the mechanism responsible for alkanethiols forming self-assembled monolayers [10].

However, understanding the intricacies of the interaction between L-Cysteine and noble metals is paramount for advancing the field of bioelectronics. Much of the existing research has relied on spectroscopic methods to explore these interactions and their outcomes. This review will delve into these spectroscopic methods and their results, shedding light on the electronic structure at the interfaces formed by L-Cysteine and noble metal surfaces.

Koswattage et al [1] conducted an insightful investigation into the interaction between L-Cysteine and silver surfaces, utilizing UPS. They probed the photon energy-dependent UPS spectra for L-Cysteine films of varying thicknesses, shedding light on the evolving electronic structure as L-Cysteine was deposited. Notably, their results revealed a distinctive phenomenon: as the thickness of the L-Cysteine film increased, the Fermi edge of silver gradually diminished and eventually disappeared at 64 Å. This disappearance was significant because it allowed the spectrum at 64 Å to represent exclusively the electronic structure of L-Cysteine. At approximately 4.8 eV in this spectrum, a feature emerged, attributed to the binding energy of the HOMO of L-Cysteine, with a HOMO cutoff estimated at around 3.2 eV. These findings were consistent with prior research by Koswattage et al [2] and Kamada et al [9] but disagreed with Beerbom et al [11], primarily due to the zwitterionic form of L-Cysteine.

The spectral structure observed around 2.5 eV, positioned between the Fermi level and HOMO of L-Cysteine, was attributed to the interaction of sulfur-originated states of L-Cysteine with the d orbitals of the metal substrates [1]. This interaction was especially pronounced in silver (Ag) surfaces, where it manifested as a single peak [2]. However, in the case of gold (Au) and copper (Cu), this feature was less distinct. Renzi et al [5] proposed an explanation for this interaction using the Anderson-Newns model, which accounts for the coupling of localized atomic orbitals with extended metallic orbitals. In metals characterized by a half-filled broad s-band and completely occupied narrow d bands, such as silver, atomic orbitals of ad atoms undergo modification due to hybridization with these bonds. This results in the formation of bonding and anti-bonding states analogous to molecular orbitals [12], and in the case of L-Cysteine on silver surfaces, the coupling of sulfur 3p orbitals with Ag 4d orbitals led to the observed spectral feature at 2.5 eV. Koswattage et al [1] associated this feature with bonding and anti-bonding states and observed two peak shifts between 4-5 eV and 8-9 eV. These shifts were in line with the observations of Koswattage et al (Koswattage & Ishii, 2020) and Beerbom et al [11], who identified these peaks as HOMO peaks. Koswattage et al [1] proposed that these peak shifts could be attributed to O, C, and N atom-originated states or potentially resulted from the interaction of O 2sp and N 2sp orbitals with metal surfaces.

The spectra obtained by Koswattage et al [1] and Kamada et al [9] exhibited remarkable similarity, leading to the conclusion that the top of the valence band had a distinct origin from other structures. This phenomenon was attributed to sulfur, carbon, nitrogen, and oxygen atoms, with the structure around the top of the valence band primarily linked to sulfur. Kamada et al [9] further asserted that sulfur-originated states played a pivotal role in the electronic properties and functions of cysteine and related proteins.

It is worth noting that the thick film spectra differed significantly from the thin film spectra due to the interaction between silver and L-Cysteine.

These findings underscore the complexity of the L-Cysteine-noble metal interaction and emphasize the role of spectroscopic techniques in unraveling the electronic structures at these crucial interfaces.

IV. EXPERIMENTAL METHODS FOR L-CYSTEINE INTERACTION STUDIES

In various studies investigating the interaction of L-Cysteine with noble metal surfaces, different experimental methods were employed to understand the complex electronic structures and surface interactions. These methods played a crucial role in elucidating the behavior of L-Cysteine on substrates like gold, silicon, and glass.

One of the key techniques used in these studies is XPS, which provides insights into the elemental composition and chemical states of elements on the sample's surface. In XPS, a high-vacuum chamber is utilized to examine a small piece of the material or surface of interest [13]. X-ray photons are directed at the sample, causing the emission of photoelectrons from its surface. These photoelectrons, when measured for their kinetic energies, reveal valuable information about the sample's chemical composition and chemical states [8], [9].

Another crucial method employed is UPS, designed to probe the electronic structure of materials. By using ultraviolet photons, UPS can eject electrons from the sample's valence band, which are then analyzed for their kinetic energy. The resulting UPS spectrum provides insights into the energy levels of valence electrons and their interactions with adsorbed molecules on the surface [1], [2], [9].

Surface structure investigations were being carried out using Low-Energy Electron Diffraction (LEED), which examines the arrangement of atoms on crystalline surfaces. By directing low-energy electrons at a clean, crystalline surface and analyzing the resulting diffraction pattern, researchers can deduce critical information about the crystal's structure, orientation, and surface quality.

Additionally, STM was employed to visualize and manipulate individual atoms on surfaces. STM involves the precise scanning of a sharp metallic tip in close proximity to the sample surface while maintaining a constant tunneling current. This technique allows scientists to create high-resolution topographic images of the sample's surface, revealing the positions of individual atoms and providing insights into surface structure and defects.

These techniques collectively offer a comprehensive toolkit for probing the interactions of L-Cysteine with noble metal surfaces, shedding light on the fundamental processes occurring at the atomic and molecular levels.

V.   DISCUSSION

In this comprehensive review, an insightful exploration of the intricate electronic structure and interactions between L-cysteine films and noble metal substrates is presented. This analysis draws upon a range of studies employing thickness-dependent UPS spectra, with a focus on understanding the binding energy axis in relation to the Fermi energy position, while also considering findings from previous research.

One significant observation pertains to the evolution of spectral features as the thickness of L-cysteine films varies. Initial comparisons were made with clean Ag(111), revealing the presence of Ag 4d5/2 and Ag 4d3/2 peaks at approximately 4.8 and 6.1 eV, respectively, alongside an estimated work function of 4.5 eV. However, as L-cysteine coverage increases, there is a gradual reduction in the appearance of the Fermi level of Ag(111), culminating in its disappearance at a thickness of 64 Å. This intriguing 64-Å spectrum is considered representative of the electronic structure of L-cysteine, featuring a prominent feature centered around 4.8 eV, attributed to the HOMO [1], [2], [11].

Of particular interest are the findings concerning thinner L-cysteine films, which unveil a spectral feature at approximately 2.5 eV. This feature occupies an intermediate position between the Fermi level and the L-cysteine HOMO, indicating the interaction of a sulfur-originated state within the HOMO with the Ag d orbitals. The observed spectral changes in the d band region are attributed to bonding and antibonding states arising from the coupling of the S 3p orbital with Ag 4d orbitals. Furthermore, intriguing peak shifts, approximately at 5 and 9 eV, are noted, presumably as a consequence of interactions between O 2sp and N 2sp orbitals and the metal surfaces [1], [2].

Critical to the discussion are the insights into work function changes, estimated through the examination of secondary electron cutoff (SECO) shifts. An upward shift of SECO by 0.46 eV towards higher binding energies signifies the presence of an interface dipole between L-cysteine and the Ag(111) surface. Nevertheless, a distinctive trend emerges at low L-cysteine coverage (initiating at 2 Å) as SECO shifts back towards lower binding energies at 16 Å. This intriguing phenomenon suggests a decrease in charge transfer and a concurrent weakening of the interface dipole, likely attributable to the formation of subsequent L-cysteine layers. The estimation of the ionization potential for chemisorbed L-cysteine yields a value of 7.24 eV [1], [2].

Notably, a pertinent observation arises from the spectral changes detected within nominal thickness layers of 8 and 16 Å [1]. These alterations encompass SECO shifting, changes in peak positions, and the disappearance of a distinctive interface state feature. It is posited that these changes can be linked to the formation of second or subsequent layers of L-cysteine, potentially adopting a zwitterionic form [14].

According to Koswattage et al [2] investigation on the interaction between L-Cysteine and silver surfaces using UPS, the appearance of the Fermi edge of silver gradually decreased as the thickness of the film increased with the deposition of L-Cysteine, eventually disappearing at 64 Å. The spectrum at 64 Å was assumed to represent only the electronic structure of L-Cysteine, with a feature centered around 4.8 eV attributed to the binding

energy of the HOMO of L-Cysteine. The HOMO cutoff was estimated to be around 3.2 eV. These values agreed with Kamada et al [9] but disagreed with Beerbom et al [11] due to the zwitterionic form.

Furthermore, Renzi et al [5] suggested that the interaction of a localized atomic orbital with an extended metallic orbital, as observed in the interaction between sulfur-originated state of L-Cysteine's HOMO and the Ag d orbitals, could be explained by the Anderson-Newns model. The coupling of the atomic orbitals with d bands resulted in bonding and antibonding states analogous to bonding and antibonding molecular orbitals [15]. This model provided valuable insights into the observed peak shifts and changes in the d band region, attributing them to bonding and antibonding states [5].

VI.   CONCLUSION

In this comprehensive review, we have delved deeply into the intricate realm of electronic structures and interactions between L-cysteine and noble metal surfaces, with a particular focus on the captivating interplay between L-cysteine and silver (Ag). This exploration draws upon a plethora of studies employing sophisticated spectroscopic techniques, shedding light on the mysterious dance between biomolecules and inorganic substrates.

One of the central observations in this narrative is the evolving spectral landscape as the thickness of L-cysteine films varies. Through comparisons with pristine Ag(111), we unveiled the gradual diminishment and ultimate disappearance of the Fermi level of silver as L-cysteine coverage increased. The emergence of a distinctive spectrum at 64 Å, representing the electronic structure of L-cysteine, cast a spotlight on a feature centered at approximately 4.8 eV, the HOMO of L-cysteine. These findings align with prior research by Koswattage et al [2] and Kamada et al [9], though they stand in contrast to Beerbom et al [11], primarily due to the zwitterionic nature of L-cysteine.

Delving deeper into the spectral intricacies, it can be identified spectral feature at approximately 2.5 eV within thinner L-cysteine films. This feature, positioned between the Fermi level and the L-cysteine HOMO, signifies the interaction of a sulfur-n originated state within the HOMO with the Ag d orbitals. The dynamics in the d band region, along with intriguing peak shifts at approximately 5 and 9 eV, were attributed to interactions between O 2sp and N 2sp orbitals and the metal surfaces, adding layers of complexity to the electronic dialogue between L-cysteine and Ag.

Of paramount significance are the insights into work function changes, elucidated through the examination of SECO shifts. An upward shift of SECO towards higher binding energies—0.46 eV—hinted at the presence of an interface dipole between L-cysteine and the Ag(111) surface. However, a fascinating reversal of this trend occurred at low L-cysteine coverage, reverting SECO to lower binding energies at 16 Å. This intriguing phenomenon points to a decrease in charge transfer and a simultaneous weakening of the interface dipole, likely a consequence of subsequent L-cysteine layers. The estimation of the ionization potential, at 7.24 eV, added a numerical anchor to these dynamic electronic interactions.

Furthermore, a significant observation arises from the spectral changes detected within nominal thickness layers of 8 and 16 Å. These alterations encompass SECO shifting, changes in peak positions, and the disappearance of a distinctive interface state feature—a metamorphosis attributed to the formation of second or subsequent layers of L-cysteine, potentially adopting a zwitterionic form [[16].

In parallel to our exploration, Koswattage et al [1] have undertaken a compelling investigation into the interaction between L-cysteine and silver surfaces, enriching our collective understanding of this intricate interaction. Their findings harmonize with our narrative, painting a consistent picture of electronic structure modifications, bonding states, and work function changes linked to film thickness and molecular interactions.

These revelations underscore the dynamic nature of electronic structures at these interfaces and beckon toward a future where such insights hold the key to innovative strides in the realm of bioelectronics, biosensors, and beyond. As this journey of exploration continues, the tapestry of electronic interactions between biomolecules and noble metal surfaces unfolds with even greater complexity and promise.

VII.   REFERENCES

[1]   K. R. Koswattage and H. Ishii, "Photoemission investigation of interaction between L-cysteine and silver surface," Surface and Interface Analysis, vol. 52, no. 8, pp. 513–517, Aug. 2020, doi: 10.1002/sia.6771.

[2]   K. R. Koswattage, H. Kinjo, Y. Nakayama, and H. Ishii, "Interface electronic structures of the L-cysteine on noble metal surfaces studied by ultraviolet photoelectron spectroscopy," in e-Journal of Surface Science and Nanotechnology, The Japan Society of Vacuum and Surface Science, Jul. 2015, pp. 373–379. doi: 10.1380/ejssnt.2015.373.

[3]   M. Honda, Y. Baba, N. Hirao, and T. Sekiguchi, "Observation of Au-S interface of L-Cysteine on gold surface," e-Journal of Surface Science and Nanotechnology, vol. 7, pp. 110–114, Jan. 2009, doi: 10.1380/ejssnt.2009.110.

[4]   M. Honda, Y. Baba, N. Hirao, and T. Sekiguchi, "Metal-molecular interface of sulfur-containing amino acid and thiophene on gold surface," in Journal of Physics: Conference Series, Institute of Physics Publishing, Mar. 2008. doi: 10.1088/1742-6596/100/5/052071.

[5]   V. De Renzi, "Understanding the electronic properties of molecule/metal junctions: The case study of thiols on gold," Surf Sci, vol. 603, no. 10–12, pp. 1518–1525, Jun. 2009, doi: 10.1016/j.susc.2008.10.063.

[6]   C. Vericat et al., "Self-assembled monolayers of thiolates on metals: A review article on sulfur-metal chemistry and surface structures," RSC Advances, vol. 4, no. 53. Royal Society of Chemistry, pp. 27730–27754, 2014. doi: 10.1039/c4ra04659e.

[7]   O. Gershevitz, C. N. Sukenik, J. Ghabboun, and D. Cahen, "Molecular monolayer-mediated control over semiconductor surfaces: Evidence for molecular depolarization of silane monolayers on Si/SiOx," J Am Chem Soc, vol. 125, no. 16, pp. 4730–4731, Apr. 2003, doi: 10.1021/ja029529h.

[8]   K. Uvdal, ~ P Bodo, and B. Liedberg, "L-Cysteine Adsorbed on Gold and Copper: An X-Ray Photoelectron Spectroscopy Study," 1992.

[9]   M. Kamada et al., "Photoelectron spectroscopic study of electronic structures of L-cysteine," J Physical Soc Japan, vol. 79, no. 3, Mar. 2010, doi: 10.1143/JPSJ.79.034709.

[10]   J. A. Syed, S. A. Sardar, S. Yagi, and K. Tanaka, "Electron spectroscopic investigation of ethylmethylsulfide/nickel interface," in Surface and Interface Analysis, Dec. 2003, pp. 1050–1054. doi: 10.1002/sia.1627.

[11]   M. M. Beerbom, R. Gargagliano, and R. Schlaf, "Determination of the electronic structure of self-assembled L-Cysteine/au interfaces using photoemission spectroscopy," Langmuir, vol. 21, no. 8, pp. 3551–3558, Apr. 2005, doi: 10.1021/la040083n.

[12]   "Introduction to the Newns-Anderson model."

[13]   T. C. Taucher and E. Zojer, "X-ray Photoelectron Spectroscopy for Determining Interface Dipoles of Self-Assembled Monolayers," 2020, doi: 10.20944/preprints202007.0406.v1.

[14]   G. Gonella et al., "Ultrahigh vacuum deposition of L-cysteine on Au(110) studied by high-resolution X-ray photoemission: From early stages of adsorption to molecular organization," Journal of Physical Chemistry B, vol. 109, no. 38, pp. 18003–18009, Sep. 2005, doi: 10.1021/jp051549t.

[15]   P. J. Chakravorty and S. B. Khasare, "To Study The Anderson Model With Its Symmetric & Asymmetric Nature," 2016, [Online]. Available: https://www.researchgate.net/publication/301559486

[16]   N. B. Luque, P. Vélez, K. Pötting, and E. Santos, "Ab initio studies of the electronic structure of l-cysteine adsorbed on Ag(111)," Langmuir, vol. 28, no. 21, pp. 8084–8099, May 2012, doi: 10.1021/la301107k.