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Exploring the Thiol (-SH)/Metal Interface

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Abstract

L-cysteine is one of the promising amino-acid that has drawn an immense interest in bio-electronics applications. Through multiple functional groups, it acts as a linker between proteins of biomolecules and metal electrodes of inorganic metals. Hence the interaction between metal and L-cysteine considered to be an area that a greater understanding is required. Photoelectron spectroscopic methods have been successfully used to resolve electronic configurations at these interfaces. When using these spectroscopic methods, it starts with thin films at around 1 - 2 angstroms and then reaching bulky layers so that the change of interaction is revealed through photoelectron kinetic energy. In many cases single crystals and in some cases poly-crystals of metals. Here we review metal-cysteine interaction through the thiol (-SH) and noble metal bond in brief.

Keywords: Cysteine; thiol bond; photoelectron spectroscopy.

1. Introduction

(Willner and Kartz reviewed advances and the scientific progress in electrically contacted, layered enzyme electrodes, and discussed the future applications of the systems in various bioelectronic devices, for example, amperometric biosensors, sensoric arrays, logic gates, and optical memories [1]. Further Umeron and Eduok reviewed the applications of carbohydrate biopolymer derivatives for inhibition of metal corrosion [2]. Nikolei and coworkers have published on biosensors application to detect food toxicants, environmental pollutants and clinical interest compounds using lipid films [3]. With all above mentioned applications and possibilities it is important to study the interaction of biomolecules with metals. Among the main four biomolecules (carbohydrates, protein, lipids, and nucleic acids) many efforts have been made to develop biosensors with accompanying proteins [4,7].

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Hence, proteins attract an immense interest among the scientists. Cysteine is one of the twenty amino acids that make up the majority of proteins. It performs admirably in the field of bioelectronics as a linker between proteins or biomolecules in the biological world and metal electrodes in the inorganic world. The charge carrier injection properties of such biological systems are dominated by the interface electronic structures between amino acids like L-cysteine and metals. Hence the study of interface electronic structure is quite interesting.[8], [9] L-cysteine has many functional groups, including a carboxylic group [-COOH], an amino group [-NH2], and a thiol group [-SH]. The thiol or thiolate groups are said to have a high affinity for noble metals. It is the only proteinogenic amino acid containing a thiol group So proteins containing cysteine and its bonding to the metals surface such as Gold, Silver, Copper, and Palladium etc. is an interesting topic to discuss. Usually, these kinds of molecules are attached to the metal surfaces using either chemisorption (similar to thiolate-metal bonding) or physisorption (similar to the bonding to metal surfaces by the amino and carboxyl functional groups). The cysteine thiol group is also a nucleophile and may undergo addition and substitution processes. L-bonding Cysteine's strengths are typically strong due to the interaction of the -SH group with the other functional groups. However, it is dependent on the characteristics of the metallic partner. [10,11]

2. Methods of analysing cysteine-metal bond

The unique feature of bonding with metals shown by L-cysteine, usually studied by photoelectron spectroscopic (PES) methods. Generally, work function, secondary electron cut-off, highest occupied molecular orbital (HOMO) onset, charge injection barrier, ionization energy and interface states are estimated by these methods. These PES methods are classified depending on the source of ionization energy as ultraviolet photoelectron spectroscopy and X-ray photoelectron spectroscopy (otherwise known as Electron Spectroscopy for Chemical Analysis (ESCA)).

2.1. X-ray photoelectron spectroscopy (XPS)

The principle of XPS (or we should say PES) is based on the photoelectric effect, which states that surface electrons of a solid can be pushed off by electromagnetic radiation (photoelectrons). The first person to observe the photoelectric effect is considered as Heinrich Hertz (in 1887) which led Albert Einstein to present the photoelectric law that was awarded with the Nobel prize in 1921.

$$E_k = h\nu - E_I$$

Where E_k is the kinetic energy of electrons, h is the Plank's constant, ν is the photon frequency, and E_I is the ionization energy The photoionization process where a photoelectron emits follows s three step model.

1. Molecule absorbs the photon – energy of the photon is transferred to the electrons of the molecule and then become photoexcited.
2. Excited electron travel to the surface of the molecule – on the way the excited electron may or may not collide with other particles and in the case of a collision electron will transfer part of its energy to the particle.
3. Detection of the excited electron that escapes from the molecule surface in to the vacuum.

XPS operates with high energy X-ray sources (1000-1500 eV) hence are capable of probing core electrons of a molecule.

2.2. Ultraviolet photoelectron spectroscopy (UPS)

The method operates the same principle as X-ray photoelectron spectroscopy (XPS), inducing photoelectric effect through ionization of molecules by radiation with energies of 10s of eVs. Compatible sources are helium, argon and neon gas discharge lamps. (Though He I (21.2 eV) and He II (40.8 eV) are frequently used). Due to the lower energy range core level emissions are inaccessible in most cases of UPS. Hence, spectral details of valance band is the limit for UPS, where electronic work function and valance band details are the two measurements can be drawn. The shorter inelastic mean free path enables greater surface sensitivity for UPS than XPS. (i.e. information depth is within 3 mean free path lengths (λ) Even though there are different setups for UPS and XPS experiments, synchrotron radiation can provide both UPS and XPS energy ranges.

2.3. Synchrotron radiation (SR)

In principle SR is produced by forcing relativistic charged particles to move along curved trajectories by using arrays of magnets called bending magnets. Then either undulators or wigglers (insertion devices) are used to trace sinusoidal transverse path along with forward motion, which generates electromagnetic radiation. SR provides a wide spectral range from infrared to hard X-rays. A modern synchrotron consists of a linac (linear accelerator), a booster ring, a storage ring, and beamlines [12]. Linac generates the initial beam for storage by accelerating electrons with electric fields, booster ring accelerates electrons to relativistic speeds, inside the storage ring bending magnets enables the circular (more of a polygonal) path, the radiation generated by insertion devices together with bending magnets provide the source for beamlines where the users will test samples.

Work function, SECO (work function Φ (precisely - electron work function) is a measure of the minimum energy required to remove an electron from a solid surface. Surface cleanliness and crystal plane determines the work function of metals.), (HOMO) onset, charge injection barrier, ionization energy (electron binding energy) and interface states are few parameters that can be drawn from such PES experiments. [8]

Table 1: Work function values of crystal surfaces found in literature (all values are in eV) [13]

Surface	Cu	Au	Ag	Pd
100	4.474	5.004	4.210	5.133
110	4.195	4.929	4.059	4.628
111	4.711	5.160	4.345	5.207
Polycrystalline	-	-	-	5.1±0.1[14]

Apart from the PES methods, scanning tunnelling microscopy [15], [16], Fourier transformation infrared spectroscopy, voltammetry [17] like methods have been used as aiding procedures to study the adsorption of l-cysteine on metals.

2.4. Noble metals

Also called precious metals, this group consists of ten elements. There are 6 platinum group metals, and 4 other precious metals. In current review, focus is on copper, silver, gold and palladium. These metals are scarce in nature, and chemically neutral. Their relatively a lesser number of applications in other areas apart from medical and electronic equipment can be attributed to the expensiveness of these materials as well [18].

3. The Newns-Anderson Model

In 1935 Gurney proposed a simple formalism for the calculation of “reasonable properties” of adsorbates on surfaces using a jellium model. He made an assumption that, an orbital of the adsorbate was interacting with a band of levels in metal, which enabled to derive “reasonable results” regarding the adsorbate surface binding. However, this approach couldn’t calculate quantitatively. Later in 1969 Newns showed that the Gurney’s model appeared from a formalism made by Anderson in 1961, which was developed for defects in solids. He proposed that those calculations can be analytically used for the adsorption on jellium surfaces. This was eventually identified as the Newns-Anderson Model. The highlighting point of the model is that it enables the derivation of the density of states (DOS) of the adsorbate. [19,21] Masel (1996) stated that the, Newns-Anderson model is used to interpret the UPS data. As we discussed in UPS a photon (UV region) releases electrons on surfaces and number of electrons that are removed from the surface is measured as a function of energy. Based on that the approximation that, the number electrons left the surface at any initial energy is proportional to the DOS at the particular energy can be proposed. Hence UPS can be used to calculate the DOS of adsorbates to a certain extent. He presented; DOS calculated from Newns-Anderson model for two regular cases to understand the bonding nature.

1. a metal with a broad band
2. a metal with a narrow band similar to the d-band in a metal

The adsorbate has a series of sharp energy levels. When the adsorbate interacts with the metal surface, those sharp energy levels are split into two bands, i.e. bonding and antibonding bands. Now consider the surface has a narrow distribution of states, then the two bands will be separated, and can be bonded via normal molecular orbitals. But the usual situation on a metal or semiconductor surface is different. The bonding and antibonding bands are wide and, hence they overlap. This produces a mixed band centred near the original energy levels of the adsorbate [22].

4. Research efforts to understand the thiol-metal bonding

4.1. Theoretical works

N. B. Luque and E. Santos developed a combining density functional theory with a quantum mechanical model under the ab-initio studies of Ag-S bond formation during the adsorption of L-cysteine on Ag (111). By examining the projected densities of states onto the various molecules’ atoms and doing charge density difference calculations as the zwitterion radical gets closer to the surface, researchers have looked at how the adsorbate and silver bond form. It is possible to identify the bond’s polar nature. By fitting the density of states, it has been possible to calculate the coupling constants between the sulfur orbitals and the d and sp bands for the first time. Analysis is done on how the sp bands contribute to the stability of the sulfur–silver link. They suggest that due to d bands are too far below the Fermi level, copper, gold, and silver do not make suitable hydrogen adsorption catalysts. The coin metals, on the other hand, are fantastic in adsorbing thiols. Due to the sulfur atom's greater distance from the surface than hydrogen at equilibrium, interactions with the sp bands serve to maintain its binding to the surface [23].

Laarson and co-workers used density functional theory methods to study the interactions of two thiolsmethanethiol and benzenethiolwith Au13. They found local distortion of the gold cluster upon bonding to a thiol group. Consequently, this resulted in modification of electronic structure of the complex [24]. Wang et.al used densityfunctional theory calculations to study the existence, the magnitude, and the nature of silver-sulfur bond dipole at surface. They claimed that it is important to study this nature of SAMs of functionalized thiols that are used in organic opto-electronic devices with better charge carrier dynamics [25]. Tielens and Santose provided period DFT calculations within a model for chemical bond breaking to study the bonding of propanethiol molecules on a Au (111) surface. They proposed a two-step mechanism for the Au-S bond formation. They found bonding and anti-bonding electronic states of thiol bond, and the process of bond breaking has been analysed. However, they proposed that during this bon breaking the C-S bond is not affected while strong AgH bond is formed [26]. Gottschalck and Hammer studied adsorption of sulfur, mercapto (HS-), and methylthiolate (CH3S–) on Au (111) using DFT calculations. They reported strong bonds with the gold surface through S-end. Also, they mentioned that mercapto and methylthiolate adsorbed in bridge or bridgelike sites while sulfur adsorbed in fcc sites [27]. Another interesting work by Yang et. at is reported in 2002, where they studied adsorption of a sulfur atom and a sulfur molecule on the Pt (111) through first-principles full-potential linearized augmented plane-wave (FLAPW) and pseudopotential calculations. They varied the sulfer coverage and found ou that, S 2p core levels shift to higher binding energy with the increase of S coverage [28].

4.2. Experimental Works

Ogawa et. al. pointed out the importance of studying the sulfer containing L-form aminoacids (methionine and cysteine), based on the fact that noble metals are not completely anti-corrosive. They used UPS to study the interaction between dental alloys (composed of Ag, Au, Pt, Pd, and Cu) and L-cysteine. They reported that, there is a new peak appears at around 2 eV for all dental alloys, suggested this was due to the bonding of S, 3sp orbitals with dental alloys surface forming the metal sulfur bond [29].

Renzi in his publication in 2009, presented the electronic properties of thiolate/metal interface. He investigated the work function change, molecular level alignment and interfacial state formation of different interfaces, namely methylthiolate/Au(111) and dimethyldisulfide/Au(111). Additionally, he studied the cysteine/Au (111) system where, the interface formed by molecules with large intrinsic dipole moment [30].

In the study carried out by Renzi et. al. They adsorped L-cysteine on Au (111) in ultra-high vacuum and analysed by using XPS and high-resolution energy loss spectroscopies (HREELS). They controlled the deposition temperature at 300 K and 330 K (room temperature (RT) and higher than RT). They proposed adsorption at RT forms a heterogeneous first layer with both weakly and strongly bounds molecules are coexisting, while at higher temperature chemisorbed (through Au-S bond) self-assembled homogeneous layer is formed [31]. In 1972, Kennedy and Lever characterized complexes forms by 2-pyridine thiol, 4-pyridine thiol, and 2-methyl-6-pyridine thiol, and some of their oxygen analogues with cobalt (II), nickel (II), zinc (II), cadmium (II), mercury (II), platinum (II), bismuth (III), and tin (IV). They used electronic spectroscopy, magnetism, conductivity, and X-ray powder diffraction, to identify the structures of these complexes. They propose that the metal bonding in all cases is achieve through the sulphur bond, rather than the nitrogen [32].

Laiho et. al. studied the characteristics of self-assembled 1-dodecanethiol monolayers (self-assembly monolayers (SAMs)) on silver and copper surfaces by XPS using SR and conventional Mg-Kα. The claimed that earlier understanding of alkanethiols on silver to be rectified further while A S 2p3/2 component of copper thiolate is observed. Moreover, three more doublets have been observed to be developed during irradiation and attributed to the sulphur chemisorption with copper [33]. Bazylewski and co. introduced, in situ Raman spectroscopy as an effective tool to distinguish between reversible and irreversible thiol modifications in L-cysteine. Where the method is said to be effective tool to study the formation and subsequent breaking of disulfide bonds. They suggest that the reversible formation of the thiol bond from L-cysteine can be satisfied by using excess of reductants like 2carboxyethyl) phosphine. Further they conclude that the findings will be critical to the investigation of cysteine–metal bonding [34].

In 1998, Takao Ishida examined the molecular structures of Organosulfur monolayers comprising alkanethiol, dialkyl disulfide, monosulfide, thiophene, and aromatic thiols on an Au (111) using high-resolution X-ray photoelectron spectroscopy (XPS). Peak fitting showed that these organosulfur had almost the same peaks as those of alkanethiol and dialklyl disulfide monolayers when the S(2p) peaks on the Au surface emerged between 161 and 164 eV.The S(2p) XPS spectra of the monolayer produced from monosulfide with shorter alkyl chains were nearly identical to that of the normal alkanethiol or dialkyl disulfide monolayers. In addition to the strong doublet S(2p) peak seen at 162.0 and 163.3 eV in the S(2p) spectra, another S(2p3/2) peak developed for aromatic derivatized thiol SAMs at about 161 eV. Even at the beginning of monolayer formation or during low-temperature (100 °C) annealing of low molecular density alkanethiol SAMs, the 161 eV peak was seen in the S(2p) XPS spectra of alkanethiol or dialkyl disulfide monolayers. They believe that this 161 eV peak can form both due to the atomic sulfur created by the C-S cleavage and without molecular breakdown [18].

The contact angle measurements, optical ellipsometry, X-ray photoelectron spectroscopy (XPS), reflection absorption infrared spectroscopy (IRRAS), and near edge X-ray absorption fine structure spectroscopic techniques were used to characterize self-assembly monolayer of a series of ω-(4’-methyl-biphenyl-4-yl)-alkanethiols

(CH3-C6H4-C6H4-(CH2)m-SH, m=1-6) formed on polycrystalline gold and silver surfaces. The experimental results demonstrate that there is a strong driving force behind sulfur sp3 and sp hybridization on gold and silver surfaces. The experimental results for gold substrates are inconsistent with the bending capabilities achieved from ab-initio calculations [35].

L-cysteine has been deposited on Au(111) surface from the solution phase and L-cysteine on Au(111) interface has been studied chemically and structurally using scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). An analysis of the interface's chemical composition was obtained using XPS measurements. The formation of a chemical bond between the cysteine thiol group and the gold surface could be able to explained by a peak splitting analysis that is revealed by deconvolution of the Au4f and S2p core level regions. The zwitterionic state of L-cysteine is present, according to the examination of the N1s spectrum. According to the STM structural characterisation carried out in air at room temperature. The L-cysteine overlayer can be seen to create a hexagonal lattice, which occasionally displays a striped modulation [36].

In 2010, R. Rolandi found Perylene diimide derivatives with pendant cysteine residues are strongly susceptible to self-assembly onto [111] Au films due to the presence of thiol functionality, which reveal in combining X-ray photoelectron spectroscopy, atomic force microscopy, and grazing incident broad X-ray scattering synchrotron radiation - techniques. In combining X-ray photoelectron spectroscopy, atomic force microscopy, and grazing incident broad X-ray scattering - synchrotron radiation - techniques hypothesis can be provided by properly correlating the data and performing conformational calculations utilizing meticulous molecular modelling. When perylene derivatives are grafted onto a thermally annealed gold surface, isolated ordered pillars rising up to the substrate plane has been investigated. The adoption of such a surface organization in organic field effect transistors is anticipated since it is anticipated to be favourable to charge mobility [37].

Honda et.al studied Au–S bonds at the L-cysteine modified gold surface using XPS and near-edge x-ray absorption fine structure (NEXAFS) of multi-layer and two-layer L-cysteine surfaces. They reported the formation of a unique chemical bond was found at the sulfur-gold interface. Also, they mentioned "remarkably" large chemical shift of two-layer sample compared with multi-layer sample. They also differentiated this bond to that of indium tin oxide (ITO) and L-cysteine [38]. Beerborm and co-workers, studied the electronic and chemical structure of the interface between the amino acid L-cysteine and Au by means of XPS and UPS. They used dipping method to form L-cyteine layers. They also reported the formation of an interface state 1.5 eV above the HOMO of the L-cysteine [39].

Due to the interest on investigating the thiol-metal bond, we reported a series of thickness dependent UPS analysis of L-cysteine on metal surfaces of Au(111), Ag(111) and Cu(111). We found the presence of a new state between the highest occupied molecular orbital (HOMO) of L-cysteine and the Fermi level of the metals. This can be attributed to the formation of the new state due to an interaction of the d band with HOMO of L-cysteine [8]. As Fisher and colleagues reported, among the above mentioned noble metals , interaction of Ag is said to be stronger than that of Au and Cu. Hence we studied the L-cysteine and Ag(111) interaction by UPS together with photoemission yield spectroscopy (PYS).

From UPS we determined charge injection barrier from the L-cysteine HOMO to the Fermi level of Ag(111), the existence of an interface state, interface dipole, and ionization potential. PYS revealed a change of the work function before and after the deposition sequence of L-cysteine. And we confirmed the suggestions made previously by our results stating that there is a weakening of silver–sulfur bond with increasing coverage of L-cysteine [40]. Similarly we studied synchrotron radiation and ultraviolet photoemission spectroscopy (UPS) data that were focused on the electronic structure at the interfaces of L-cysteine on a Palladium (Pd) surface. And we reported, a sulfur-originated state of L-HOMO cysteine’s interacts with Pd d orbitals to produce thin-film spectra of L-cysteine on Pd surfaces that differ from thick-film spectra of L-cysteine in the valence top region. Additionally, we predicted that the charge transfer between L-cysteine and Pd result in a 0.6-eV SECO shift. The SECO findings support the notion that increased L-cysteine coverage on Pd causes the Pd sulfur bond to weaken [41].

5. Conclusions

In this review paper we have summarized all experimental methods which are dedicated the interaction between L-cystiene. It can be subjected that noble metal d orbitals interact with L-cysteine p orbitals to form interfacial state (an anti-bonding state). These interfacial states can strongly affect the charge transport across the junction. However, increasing the cysteine coverage will weaken the metal-sulfur bond. Therefore, anchoring biomolecules on noble metal surfaces through the L-cysteine– silver may not be effective in bioelectronics applications.

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