



Full Length Article

Sulfur amino acids and alanine on pyrite (100) by X-ray photoemission spectroscopy: Surface or molecular role?



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ABSTRACT

This paper describes the first successful adsorption of the cysteine, cystine, methionine and alanine amino acids on the pyrite (100) surface under ultra-high vacuum conditions with crucial chemical adsorption parameters driving the process. We have demonstrated by X-ray photoemission spectroscopy (XPS) that the surface pretreatment annealing process on pyrite surfaces is a critical parameter driving surface reactivity. The presence of enriched monosulfide species on the pyrite (100) surface favours the amino acid NH_2 chemical form, whereas a longer annealing surface pretreatment of over 3 h repairs the sulfur vacancies in the pyrite, enriching disulfide species on the pyrite surface, which promotes NH_3^+ adsorption due to the sulfur vacancies in the pyrite being replaced by sulfur atom dimers (S_2^{2-}) on the surface. Furthermore, even if the surface chemistry (monosulfide or disulfide species enrichment) is the main factor promoting a partial conversion from NH_2 to NH_3^+ species, the unique chemical structure of each amino acid provides a particular fingerprint in the process.

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1. Introduction

Understanding the adsorption, interaction and reactivity of organic molecules on surfaces is one of the most promising approaches for developing many scientific and technological applications [1–15]. The detailed study of molecule–substrate interactions is essential for elucidating the mechanisms in the formation of molecular structures, developing strategies to functionalize surfaces and developing organic–inorganic platforms for new devices [3,16–19]. Biomolecule adsorption studies have focused on adsorption on metallic surfaces, such as silver, gold, copper, and stainless steel [12,14,15,20–24]. In addition, minerals can provide different surface properties to modify biomolecule–surface processes; among such minerals is pyrite.

Iron pyrite (FeS_2) is one of the most common minerals on earth with important applications in a wide range of technological and geochemical processes. Understanding cleaning and treatment promoting surface ordering [25,26] and the reactivity of the surface of this mineral is fundamental because many chemical, geochemical and biological reactions occur at pyrite surfaces [27–29]. Pyrite is also a semiconducting mineral, and the presence of crystalline defects, such as steps, kinks, dislocations, impurities or vacancies,

may alter the reactivity of semiconducting materials and modify their electronic properties [30]. The crystal structure of pyrite is NaCl-type cubic and comprises Fe^{2+} at the cation site and S_2^{2-} dimers at the anion site aligned along the cube diagonal direction $\langle 111 \rangle$. The (100) monocrystalline face, used in our experiments, is the most stable pyrite plane [31].

In addition, pyrite is a key surface in the context of the origin of life and prebiotic chemistry [32]. A possible alternative to the prebiotic soup theory was proposed by Wächtershäuser, who advocates that the first reactions for amino acid formation did not occur in a bulk solution in the oceans, but rather on mineral surfaces (such as pyrite); due to the surface catalytic properties, amino acids can adsorb, concentrate and react [33]. Therefore, amino acid adsorption is a promising method to study pyrite surface properties and the chemical impact of the surface on the adsorbed molecules.

Furthermore, our current objective is to shed more light on how the presence of a sulfur atom in the molecular structure dictates molecular adsorption and pyrite surface reactivity properties. In our experiments, we attempt to prove how the surface annealing pretreatment process can modify the properties of pyrite and, consequently, the chemical adsorption form of different amino acids adsorbed on it. In a simple model, an amino acid, represented in the neutral-form by $(\text{NH}_2\text{-R-COOH})$, can adsorb on a surface in anionic ($\text{NH}_2\text{-R-COO}^-$), cationic ($\text{NH}_3^+\text{-R-COOH}$), zwitterionic ($\text{NH}_3^+\text{-R-COO}^-$) or in the unmodified neutral form. Although zwitterionic and anionic forms have been the most frequently reported,

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[34] there is no *a priori* rule to decide whether a particular amino acid should deprotonate or not in contact with a specific surface. The main aim of our studies is to investigate how the molecular adsorption chemical form could be driven by the pyrite surface chemistry.

In our previous work, we reported remarkable differences with respect to cystine molecular adsorption on the pyrite (100) surface (non-ordered) and a crystallographically ordered pyrite (100) surface induced by longer annealing pretreatment conditions [35]. The presence of an ordered structure on the surface, as indicated by the LEED pattern, favors the cystine NH_3^+ chemical form, whereas the absence of the surface ordering promotes cystine NH_2 adsorption due to the sulfur-deficient surface. Therefore, the annealing surface pretreatment process could be crucial to determining the mineral reactivity.

Pyrite is a highly reactive surface and contains two crucial types of surface functional groups that drive molecular chemistry on the surface depending on the surrounding conditions [36]. Molecular adsorption under anoxic conditions was observed to be more favourable, and the presence of oxygen induced a partially blocked molecular adsorption [36].

Pyrite surface preparation was performed under ultra-high vacuum (UHV) conditions. The use of an ultra-high vacuum system is a prerequisite for conducting these experiments as it allows the accurate control of the molecular dosing conditions, UHV clean environment and sample temperature to the desired experimental conditions. Our equipment has been specifically developed to make feasible *in situ* molecular dosing and *in situ* physico-chemical characterization of the sample by X-ray photoemission spectroscopy (XPS) and low energy electron diffraction (LEED).

We focused our efforts on the spectroscopic characterization of amino acid adsorption on pyrite surfaces from different preparation treatment conditions, which drive the molecular adsorption process in different ways. In our case, the selected amino acids used in this study are sulfur amino acids with additional reactive sulfur groups in their structures as follows: cystine (disulfide bridge S-S), cysteine (thiol -SH) and methionine (thiolate -S-R), and an exception, alanine, without sulfur in its structure (see Fig. 1). Alanine will help us to make a comparison study of the sulfur atom influence during molecular adsorption on pyrite surfaces from different pretreatment annealing surface conditions. In all experiments, amino acids were successfully adsorbed on the surface, showing interesting results as a function of the pretreatment surface conditions and demonstrating that the nature of the surface is critical in driving the molecular chemical form adsorbed even for the many amino acids, which have different chemical structures.

In the present work, by combining the adsorption of different amino acids on pyrite surfaces and XPS spectroscopic characterization, we define a general rule dictated by pyrite surface reactivity that can be applied to several amino acid adsorptions, even with different chemical structures.

2. Experimental

The natural pyrite (100) single crystal provided by the Surface Preparation Laboratory was mounted in a multi-technique (XPS, UPS, LEED and STM) ultra-high vacuum (UHV) chamber. The pyrite (100) sample was cleaned by repeated cycles of Ar^+ ion sputtering during 10 min at 700 keV and annealing at 593 K. In addition, surface treatment procedures differing in the annealing period were conducted (10 min, 5 h and 10 h). The surface order was confirmed by the presence of (1×1) LEED pattern for 5 and 10 h of annealing (absence of LEED pattern for 10 min annealing), and surface cleanliness was monitored using XPS in all cases (10 min, 5 h and 10 h of annealing). The pre-treatment pyrite surface process previous

to the molecular adsorption has been described in detail in previous work from our group [35], furthermore a summary figure of this surface process which has been characterized by a correlation study between XPS and LEED results is included in the supporting information (see Fig. S1).

The pyrite sample was never heated beyond 600 K to avoid thermal decomposition making the disappearance of the LEED pattern irreversible. No sample degradation was observed during the experiments reported in this manuscript.

L-Cystine, L-cysteine, L-methionine and L-alanine (purity $\geq 98\%$) powders purchased from Sigma-Aldrich were used without further purification. A lab-built molecular doser was employed to sublime the molecules in UHV conditions. The doser contained a tantalum envelope holding the chemical, with a thermocouple facing the sample material. The tantalum envelope was heated by direct current. A K-type thermocouple was attached to the bag on the outside near the chemical to probe its temperature. Before sublimation, each amino acid was outgassed and then heated to the sublimation temperature and exposed to the pyrite crystal; during the sublimation, the main chamber pressure typically rose to 1×10^{-9} mbar. The thickness of the organic layer has been calculated from the Fe $2p_{3/2}$ peak intensities on a clean pyrite(100) sample and pyrite(100) after molecular exposure, assuming that the attenuation length obeys the equation given by Whitesides et al. [37]. The average coverage for our studies, including different amino acids, is in the range of 0.3–0.5 monolayers ($<1\text{ML}$), which confirm that most of the molecules measured are in direct contact with the surface.

X-ray photoelectron spectroscopy analysis of the samples was performed in an ultra-high vacuum chamber equipped with a hemispherical electron analyser using an Al $K\alpha$ X-ray source (1486.6 eV) with an aperture of $7\text{ mm} \times 20\text{ mm}$. The base pressure in the chamber was 3×10^{-10} mbar, and the experiments were performed at room temperature. The XPS peak decomposition of different components was shaped, after background subtraction, as a convolution of Lorentzian and Gaussian curves and analysed using the XPS Fitt software.

3. Results

3.1. Sulfur amino acid adsorption on the pyrite (100) surface

The interaction of sulfur amino acid compounds with pyrite is studied here by evaluating the relevance of the different sulfur functional groups (-SH, S-S, -SR) driving the molecular interaction on the pyrite surface under the same selected conditions. This strategy is designed to evaluate how different sulfur functional groups drive molecular interaction with the sulfur and iron surface groups of the pyrite surface.

The presence of specific molecular functional groups may dictate chemical bonding to a particular surface group instead of molecule-molecule interaction, due to the high affinity with iron or sulfur atoms from the pyrite surface. First, we studied the adsorption of cysteine, an amino acid with a thiol group (-SH) as part of its structure, followed by methionine with an (-SR) and finally a comparison study with cystine with an (S-S) disulfide group as part of its structure, (previously reported from our group). These studies were performed under ultra-high vacuum conditions on the pyrite (100) surface to avoid any contaminants on the surface *via* the complete absence of oxygen and carbon (as described above).

Amino acids provide two different functional groups, carboxylic acid (COOH) and amino (NH_2) groups, either or both of which could potentially be involved in bonding to the mineral surface. The side chain of the amino acid can also play an important role; as an example, for a sulfur-containing amino acid such as cysteine, the strong

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