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Oligomerization of Proline Catalyzed by Ni on a Au(111) Surface

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ABSTRACT: The reaction of (S)-proline with two-dimensional Ni nanoclusters on Au(111) results in the formation of ordered structures constructed from two distinct types of nickel proline complex. Scanning tunnelling microscopy and density functional theory are combined to analyze the supramolecular arrangements produced as a function of annealing temperature. Octahedral Ni(pro)₃ complexes are the fundamental building blocks of multiple phases identified by the formation of hexagonal pores of 1 nm diameter. Coexisting with the hexagonal porous phases is a *honeycomb* phase constructed from Ni(pro)₂ complexes. In contrast to the thermal stability of the hexagonal porous phases, the *honeycomb* phase transforms on heating to a *mesh* phase which is concluded to be constructed from pro-pro dipeptide species coordinated to Ni ions. At even higher temperature, more extensive oligomerization occurs to produce an ordered *rose* phase whose structure is consistent with the formation of oligoproline species.

INTRODUCTION

Naturally occurring α -amino acids are key building blocks in the formation of peptides and proteins. With the exception of glycine, all α -amino acids are chiral and can exist in two mirror equivalent enantiomeric forms. In nature, α -amino acids exist almost exclusively in the L enantiomeric form, despite the fact that the L and D forms are energetically equivalent. As a consequence of this biomolecular homochirality, living organisms on Earth can respond in dramatically different ways to two enantiomers of a chiral molecule. As a result, many pharmaceutical and agrochemical compounds are required to be produced as single enantiomers. The development of enantioselective heterogeneous catalysts that can be applied in the pharmaceutical industry has long been an important goal. One of the most successful methods for the fabrication of such catalysts has been the adsorption of simple chiral molecules onto metal surfaces: for example, cinchona alkaloids on platinum¹ and α -hydroxy acids or α -amino acids on nickel.² A large number of surface science studies have been devoted to understanding the interaction of small chiral biological molecules with metal surfaces³⁻⁴ and the interaction of pro-chiral catalytic reagents with chirally modified surfaces.⁵⁻¹⁵ In addition, the interaction of amino acids with solid surfaces is important in the formation of peptides and proteins. 'Salt-induced peptide formation' is proposed as a possible mechanism for the formation of small biopolymers and involves metal amino acid salts as intermediates in the polymerization of amino acids.¹⁶

We previously reported the adsorption of (*S*)-proline on Au(111)¹⁷ and Ni/Au(111).¹⁸ (*S*)-Proline was found to adsorb weakly on Au(111) as a mixture of zwitterionic, anionic and neutral species. Ordered structures were observed in low-temperature scanning tunnelling microscopy (STM) images.¹⁷ The periodicity of the molecular features was consistent with intermolecular distances in the solid state crystalline form of proline. When Ni is deposited in submonolayer quantities onto Au(111), 2-D Ni clusters nucleate into the elbows of the ($\sqrt{3}\times 22$)

herringbone reconstruction.¹⁹ The adsorption of (*S*)-proline results in the removal of Ni from these clusters and the formation of Ni(pro)₃ clusters which form porous 2-D islands and 1-D chains in low-temperature STM images.¹⁸ X-ray photoelectron spectroscopy (XPS) measurements revealed that the adsorption of proline caused significant oxidation of Ni and the formation of proline species.¹⁸ This information combined with DFT calculations and the three-fold appearance of the clusters in the porous islands led to the conclusion that the Ni(pro)₃ clusters contained a Ni ion in an octahedral environment with the (*S*)-proline ligands adopting the Λ -*fac* geometry whereby the three N atoms are on the same side of the central Ni ion and the three O atoms of the carboxylate functionalities are on the opposite side. Such clusters were concluded to bind to the Au(111) surface via the three carboxylate groups contained in each cluster.¹⁸

In this study, STM is used to identify ordered supramolecular architectures which we conclude are constructed from Ni(pro)₃ and Ni(pro)₂ bioinorganic clusters. While the Ni(pro)₃ phases are relatively thermally stable, the phase containing Ni(pro)₂ clusters transforms, on annealing, into two further ordered phases. DFT calculations support the conclusion that the first phase produced contains dipeptide species. We conclude that the higher temperature phase is constructed from oligomers of proline with ordering being facilitated by interactions between the oligomeric species and Ni ions.

EXPERIMENTAL SECTION

STM experiments were performed at 300 K using an Omicron variable temperature STM under ultra-high vacuum (UHV) conditions with a base pressure of 1×10^{-10} mbar. STM measurements were carried out in constant current mode using an electrochemically etched W tip. A Au(111) single crystal was cleaned by cycles of argon ion sputtering (0.8 kV) and annealing (873 K)

until the characteristic ($\sqrt{3} \times 22$) herringbone reconstruction of the gold surface²⁰ was observed and large terraces formed. STM images have not been corrected for thermal drift.

Ni deposition was achieved by passing a current directly through a high purity Ni filament and the Ni deposition rate was calibrated via STM by monitoring the size of the 2-D Ni clusters that nucleate into elbows of the herringbone reconstruction.¹⁹ Typically, the Ni deposition rate was $\sim 0.04 \text{ MLmin}^{-1}$.

The sample was then exposed to (S)-proline (SigmaAldrich, $\geq 99.5\%$) via sublimation from a solid doser in the same manner as has been previously reported.¹⁷

Computational Details: All calculations used the PBE functional²¹ with Grimme's 3-center dispersion correction and Becke-Johnson damping.²²⁻²³ Molecular calculations were carried out using the ORCA program²⁴ and the Ahlrichs def2-TZVP basis set²⁵ without f-functions. Periodic calculations used the VASP software²⁶⁻²⁸ with PAW pseudopotentials²⁹⁻³¹ and a plane-wave basis set with an energy cut-off of 400 eV. In calculations that explicitly treated the (111) gold surface, this was approximated by a slab consisting of three layers of atoms, with the two lower layers frozen at the bulk geometry, and a 15 Å vacuum slab to accommodate the adsorbate and prevent interactions between adjacent slabs. In the calculation of the energies for the pairs of Ni(pro)₃ clusters, without explicit treatment of the adsorbent, the effect of the surface was described by forcing some atoms to remain in the same plane. For the various arrangements of Ni(pro)₃ clusters, the outermost three oxygen atoms of each cluster were chosen.

Simulated STM images were created with the p4vasp program³², using the Tersoff-Hamann approximation.³³

RESULTS AND DISCUSSION

Phases Constructed from Λ -fac Ni(pro)₃ Clusters. Our earlier low temperature STM study focussed on the low coverage regime, identifying the formation of small islands of Λ -fac Ni(pro)₃ species. The room temperature STM study reported here focuses on high proline coverages and reveals that the assembly of Λ -fac Ni(pro)₃ species resulted in the formation of a number of distinct ordered phases under a wide range of preparation conditions. For Ni coverages from ~ 0.1 ML up to >1 ML, ordered structures constructed from Λ -fac Ni(pro)₃ species were observed on Au regions of the surface, usually after an annealing treatment in the 400-430 K range, though there were cases where these species were observed without the requirement for annealing pointing to the fact that the formation of Ni(pro)₃ clusters can occur even at 300 K. The fact that ordered phases were not routinely observed prior to annealing may be due to the need to desorb unreacted proline. The packing density of Ni(pro)₃ clusters was found to depend on the availability of Ni atoms on the Au(111) surface. When imaging at room temperature, there was a threshold Ni coverage of slightly less than 0.1 ML below which no ordered phases were observed. In this case, the only evidence for (S)-proline adsorption was the disappearance of Ni clusters. The lack of ordered phases under these conditions can be attributed to the high mobility of Λ -fac Ni(pro)₃ species at 300 K. This is an important observation as it leads to the following conclusion: the coverage of Ni(pro)₃ species is limited by the initial coverage of Ni and ordered phases can only be observed in room temperature STM experiments if the Au(111) surface is saturated with Ni(pro)₃ species.

Figure 1: (a) STM image ($14.1 \text{ nm} \times 14.1 \text{ nm}$, 0.08 nA , $+1.3 \text{ V}$) of the hexagonal HP phase formed by a saturation exposure of (S)-proline at 300 K on a 0.15 ML Ni/Au(111) surface followed by annealing the surface to 430 K . (b) Schematic model of the hexagonal HP phase (c) STM image ($15.4 \text{ nm} \times 15.4 \text{ nm}$, 0.06 nA , $+1.6 \text{ V}$) of the rectangular HP structure formed by a saturation exposure at 300 K of (S)-proline on a $>1.0 \text{ ML}$ Ni/Au(111) surface followed by annealing the surface to 410 K . (d) Schematic model of the rectangular HP phase (e) STM image ($17.4 \text{ nm} \times 17.4 \text{ nm}$, 0.23 nA , -1.03 V) of the $(5 -1 | 8 13)$ structure formed by a saturation exposure at 300 K of (S)-proline on a 0.35 ML Ni/Au(111) surface followed by

annealing the surface to 440 K. (f) STM image (18.0 nm × 18.0 nm, 0.53 nA, -1.3 V) of the poreless structure formed by a saturation exposure at 300 K of (S)-proline on a 0.35 ML Ni/Au(111) surface followed by annealing the surface to 430 K. Each scale bar represents a distance of 2 nm.

In our earlier low temperature STM study,¹⁸ we reported that a common motif adopted by the Λ -*fac* Ni(pro)₃ clusters involved the formation of hexagonal pores (diameter ~1 nm) surrounded by six Ni(pro)₃ clusters arranged in a hexagonal arrangement. When imaged at 300 K, this motif was observed in a number of ordered phases. The simplest of these phases is shown in the STM image in Figure 1a whereby a hexagonal unit cell is observed consistent with a commensurate (5 -1 | 1 6) structure. This corresponds to a local Ni coverage of 2/31 ML (0.065 ML) and a local (S)-proline coverage of 6/31 ML (0.194 ML). The dimensions of the unit cell are 16.1 Å × 16.1 Å with an angle of 120° between the unit cell vectors. Each unit cell contains two Λ -*fac* Ni(pro)₃ clusters rotated by 180° with respect to each other. If each cluster is thought of as an equilateral triangle, the two clusters are arranged in a side to side orientation slightly offset from each other. Each Λ -*fac* Ni(pro)₃ cluster is surrounded by three clusters of the opposite orientation resulting in the formation of the (5 -1 | 1 6) structure. Reflection domains of this structure were never observed suggesting the formation of chiral domains from the chiral bioinorganic building blocks. We shall refer to this hexagonal unit cell containing hexagonal pores as the *hexagonal HP* phase. Figure 1b shows a model for the *hexagonal HP* phase. This was produced by constraining the clusters to the unit cell derived from experiment. The optimization was carried out in the absence of the Au surface with the clusters being restricted to a plane by fixing the height of the outermost O atoms of the clusters.

The *hexagonal HP* phase was generally a minority phase. Two other phases exhibiting the characteristic hexagonal pores were observed far more frequently. Figure 1c shows an STM image of the most common phase observed. In this case, the surface preparation involved a saturation exposure of (S)-proline at 300 K on a ~ 1.0 ML Ni/Au(111) surface. Under these conditions, the surface is not completely covered by Ni, significant second layer growth of Ni is observed on the 2-D Ni clusters and areas of clean Au are observed between the Ni clusters. It is on these bare Au regions that the ordered phases are observed. The surface has been annealed after (S)-proline exposure to 410 K. The trimeric features produce an ordered structure giving a unit cell consistent with a commensurate (5×8) structure. One of the unit cell vectors is identical to that observed in the *hexagonal HP* structure (Figure 1b). The longer unit cell vector has a length of $26.4 \text{ \AA}$ and there is an angle of 80° between the two vectors. We shall refer to this phase as the *rectangular HP* phase. The corners of the unit cell consist of hexagonal pores of diameter ~ 1 nm and each unit cell contains four Λ -*fac* Ni(pro) $_3$ clusters. The local coverage of Ni in the *rectangular HP* phase is $4/58$ ML (0.069 ML) and the local coverage of (S)-proline is $12/58$ ML (0.207 ML). The *rectangular HP* phase has a slightly higher density than the *hexagonal HP* phase. The *hexagonal HP* phase can be described by a hexagonal pore surrounded by a hexagonal arrangement of six Λ -*fac* Ni(pro) $_3$ clusters. Each Λ -*fac* Ni(pro) $_3$ cluster is shared by three hexagons. Each pore in the *rectangular HP* phase is similarly surrounded by three pairs of Λ -*fac* Ni(pro) $_3$ clusters. Two pairs are shared with adjacent hexagons along the shorter unit cell dimension. The remaining two clusters in each hexagon which are on opposite sides of the pore are paired with equivalent clusters in adjacent hexagons along the long dimension of the unit cell. This pairing consists more of a point to point interaction. The optimised arrangement is shown in Figure 1d.

An additional ordered domain that is commonly observed when imaging at 300 K is shown in Figure 1e. As with the *hexagonal* and *rectangular HP* phases, one unit cell vector corresponds to the (5 -1) surface direction. The longer unit cell dimension is 32.8 Å and there is an angle of ~91° between the unit cell vectors. In matrix notation, this structure can be described by (5 -1 | 8 13) and contains six Λ -*fac* Ni(pro)₃ clusters per unit cell giving a local Ni coverage of 6/73 ML (0.082 ML) and a local (S)-proline coverage of 18/73 ML (0.247 ML). Within each unit cell, there are three pairs of Λ -*fac* Ni(pro)₃ clusters. There is a straightforward relationship between this and the *rectangular HP* phase. Essentially an additional row of Λ -*fac* Ni(pro)₃ cluster pairs is accommodated parallel to the shorter unit cell vector. Figure 1f shows a room temperature STM image following a saturation exposure of a ~0.4 ML Ni/Au(111) surface to (S)-proline at 300 K and a subsequent annealing treatment to 430 K. Ni clusters remain visible on the surface. In the regions of Au surface between the Ni clusters, the surface is covered in a tightly packed arrangement of features exhibiting approximately 3-fold symmetry which we assign to Λ -*fac* Ni(pro)₃ clusters. The observed structure is consistent with a commensurate unit cell described in matrix notation as (4 1|3 6) containing two Λ -*fac* Ni(pro)₃ clusters per unit cell. The local coverage of Ni in these ordered islands corresponds to 2/21 ML (0.095 ML) and the local coverage of (S)-proline is 6/21 ML (0.286 ML). Within a unit cell, the two triangular features are inverted with respect to each other.

Figure 2: (a) STM image (100 nm $\times$ 100 nm, 0.08 nA, -1.10 V) following a saturation exposure at 300 K of (S)-proline on a 0.2 ML Ni/Au(111) surface followed by annealing the sample to 430 K. The alignment of pores is shown to be dependent on the underlying herringbone reconstruction. The boundaries between adjacent domains of the reconstruction are identified by the green lines. The scale bar represents a distance of 10 nm. (b) Schematic diagram showing the relationship between the preferred alignment direction of the pores and the soliton boundaries of the herringbone reconstruction (shown as pairs of parallel black lines).

Both the (5 -1 | 8 10) and (5 -1 | 8 13) phases should exhibit three rotationally equivalent domains on an fcc (111) surface. Indeed all three rotational domains can be observed in different scanning areas of the sample. However, the particular rotational domain observed is strongly influenced by the herringbone reconstruction of the Au(111) surface. The atomic structure of the reconstructed Au(111) surface differs from a bulk terminated surface by the inclusion of an extra Au atom for every 22 subsurface Au atoms along a direction perpendicular to the soliton boundaries of the reconstruction.²⁰ Instead of the surface being 3-fold symmetric on an atomic scale, the one-dimensional compression leads to

regions of the surface possessing lower symmetry. These regions can be identified by the direction of the soliton boundaries and across the whole surface there exist three region types related to each other by a 120° rotation. Within a given region of the herringbone reconstruction, the $(5 \text{ } -1 | 8 \text{ } 10)$ and $(5 \text{ } -1 | 8 \text{ } 13)$ structures strongly favor one rotational domain. This is demonstrated in Figure 2a, where a clear preference exists for the shorter $(5 \text{ } -1)$ vector of the unit cell to align as close as possible to the close packed direction perpendicular to the soliton boundaries of the herringbone reconstruction. If the $\text{Ni}(\text{pro})_3$ clusters have a preferred adsorption site, the 4% compression of the atomic spacing between Au atoms perpendicular to the soliton boundaries may lead to a compressive stress in the packing of the clusters that can be relieved by increasing the pore density approximately along this surface direction (Figure 2b). The localised lifting of the 3-fold symmetry of the surface by the herringbone reconstruction was shown to influence the preferred growth direction of 1D chains of nickel pyroglutamate on Au(111) by Trant *et al.*^{5, 34}

To examine the preference for the offset observed when two clusters approach each other, DFT calculations were carried out to determine the energetically preferable arrangement of two $\text{Ni}(\text{pro})_3$ clusters in a plane. A 24-image nudged elastic band calculation was carried out, simulating one of the units sliding past the other in a plane, i.e. with the outermost oxygen atoms of both units forced to remain in the same plane, but without explicit treatment of the gold surface. Figure 3a shows the resulting energy profile and the geometric arrangement at the energy minima. Two minima with different horizontal offsets can be observed, separated by a strong repulsive maximum where the outward-facing oxygen atoms come closest to each other. The most stable minimum, by about 0.1 eV, consists of the upper $\text{Ni}(\text{pro})_3$ shifted to the right by about half a unit. The left minimum is higher in energy but allows denser packing, so it may occur at higher coverage.

Figure 3: (a) Energy profile (in eV) of two adjacent Ni(pro)₃ clusters sliding past each other. (b) STM image (50.0 nm × 50.0 nm, 0.06 nA, +1.5 V) of the low density phase formed by a saturation exposure at 300 K of (S)-proline on a submonolayer Ni/Au(111) surface which has been previously annealed to 475 K to induce alloy formation. After (S)-proline exposure the surface was annealed to 340 K (scale bar 10 nm). (c) displays a section of Figure 3(b) zoomed to 11.9 nm × 11.9 nm (scale bar 2 nm).

An experiment was carried out whereby 0.5 ML Ni/Au(111) was annealed to 475 K to induce alloy formation.³⁵ Under these conditions, the surface morphology is retained in the sense that the 2-D clusters are preserved, though extensive intermixing of Ni and Au occurs in the surface layer. Exposure of this bimetallic surface to (S)-proline at 300 K resulted in the highly porous arrangements of Λ -*fac* Ni(pro)₃ clusters displayed in Figure 3b. The zoomed

image of Figure 3c shows that all adjacent Λ -*fac* Ni(pro)₃ clusters were found to arrange with a relative geometry very similar to the most favored configuration shown in Figure 3a. This highly porous structure was only ever observed for the alloyed surface where the supply of Ni available to form Ni(pro)₃ complexes is strongly depleted; thereby limiting the achievable coverage of Ni(pro)₃. The continued presence of the raised 2-D islands presumably provides stabilization for the low density islands which accounts for the fact that these are not observed at 300 K on the unannealed Ni/Au(111) surfaces. At low Ni coverage, the species are too mobile to image; at high Ni coverage, the surface coverage of Ni(pro)₃ species is much higher resulting in the formation of higher density phases.

To summarise, at room temperature, (S)-proline reacts with nickel atoms in the 2-D Ni clusters to form Ni(pro)₃ complexes. These complexes are highly mobile and begin to populate the regions of Au terrace between the Ni clusters. For Ni coverages below ~0.06 ML, the supply of Ni is exhausted before sufficient Ni(pro)₃ complexes are produced to form a saturated monolayer of the various phases exhibiting the ~1 nm hexagonal pores. Under these conditions, the complexes are too mobile to be routinely observed in room temperature STM images. As we previously reported,¹⁸ low temperature STM reveals that Ni(pro)₃ complexes are formed which condense into small islands. As the Ni coverage is increased, the density of the ordered phases increases further such that the appearance of hexagonal pores is lost and the most dense Ni(pro)₃ phase is produced. For Ni coverages above 0.1 ML, sufficient Ni is present to form the most dense (poreless) phase. Once the surface is saturated with Ni(pro)₃ complexes, no further leaching of Ni from the 2-D-clusters can occur. The survival of these clusters is therefore not a result of passivation by (S)-proline adsorbed on the Ni islands, but simply because there is no space for the formation of additional Ni(pro)₃ complexes. Interestingly, if the Ni/Au surface is pre-annealed to induce surface alloy formation, the supply of Ni available to react with (S)-proline drops significantly.

Presumably, we are able to image the low density phase at 300 K as the surface retains the roughness associated with the initial deposition of Ni clusters. This limits the diffusion of $\text{Ni}(\text{pro})_3$ complexes and allows the nucleation of low density islands.

Phases Constructed from $\text{Ni}(\text{pro})_2$ Species

Honeycomb Phase

Figure 4: STM image ($77.3 \text{ nm} \times 77.3 \text{ nm}$, 0.33 nA , $+0.97 \text{ V}$) of a 0.15 ML $\text{Ni}/\text{Au}(111)$ surface exposed to a saturation dose of (S)-proline at 300 K and subsequently annealed to 390 K (scale bar 15 nm). Areas of the honeycomb phase are labelled HC while regions of hexagonal porous phases are labelled HP. Some residual Ni clusters are circled.

Phases associated with the Λ -*fac* $\text{Ni}(\text{pro})_3$ clusters were majority phases under all preparation conditions that were investigated. A number of other phases were identified

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3 following different thermal treatments. Whereas the phases constructed from Λ -*fac* Ni(pro)₃
4 clusters were relatively thermally stable, the minority phases underwent significant
5 transformation on heating.
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10 Figure 4 shows the STM image of a phase that was observed most commonly in the
11 vicinity of Ni clusters. The unit cell of this phase is consistent with a commensurate hexagonal
12 unit cell of 16.1 Å x 16.1 Å containing 31 Au atoms. The unit cell dimensions are very similar
13 to the *hexagonal HP* phase. However, one may rule out that the two structures are the same as
14 the two phases were commonly observed in the same STM images, so effects due to tip changes
15 can be eliminated. The size of the features within the unit cell are too small for them to be
16 assigned to the Ni(pro)₃ structure that makes up the majority *hexagonal HP* phase. In addition,
17 the unit cell dimensions are significantly different to those measured for ordered structures
18 formed by (S)-proline on Au(111) at low temperatures, where proline species assembled into
19 ordered arrangements approximating to (2x2) arrays.¹⁷ This phase will be referred to as the
20 *honeycomb* phase and was often observed adjacent to nickel clusters (Figure 4) suggesting that
21 the building blocks of this phase may be nickel rich compared to the Ni(pro)₃ structure perhaps
22 formed by incomplete reaction of nickel with proline. This observation, coupled with the
23 dimensions of the individual features leads to the conclusion that this phase is likely to be made
24 up of Ni(pro)₂ units.
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44 It is difficult to spectroscopically quantify the oxidation state of the Ni species since
45 these phases were minority phases on the surface, but if these structures are truly analogous to
46 those found in the solid state, the central Ni ion is likely to be a Ni(II) species which gives
47 predominantly square planar complexes. Assuming, as is the case in the solid state structures,
48 that each proline species coordinates to the Ni ion via the N and one of the carboxylate O
49 atoms, there are two different possible ways of orientating these prolines in a square planar
50 complex, *cis* (N-Ni bonds adjacent to each other) or *trans* (N-Ni bonds on opposite sides of the
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Ni ion) (Figure 5b). In solid state crystal structures, Ni and Pd have been observed to adopt the trans configuration³⁶⁻³⁷ while the crystal structure of Cu((S)-pro)₂·2H₂O was found to exhibit the cis configuration.³⁸

Figure 5 showing (a) STM image of the *honeycomb* phase (26 nm × 26 nm; 0.33 nA, +0.97 V; scale bar 5.2 nm) (b) gas phase cis and trans Ni(pro)₂ complexes (c) model of trans Ni(pro)₂ complex on surface and (d) simulated STM image

Optimizations Of Adsorbed Ni(Pro)₂ Complexes. Computationally, we found that the trans-Ni(pro)₂ complex is considerably more stable than its cis equivalent. Not only is it more stable in the gas phase (by 0.48 eV), but the oxygen atoms, which are most likely to interact directly with the surface, lie in a plane that can approach the surface without being hindered by the aliphatic rings (see Figure 5b). After geometry optimization of both structures on the surface in the experimentally observed (5 -1 |1 6) unit cell, the energy

difference almost doubles, with the trans-Ni(pro)₂ more stable by 0.83 eV. The optimised model for the adsorbed trans species is shown in Figure 5c.

Figure 5d shows that the simulated STM image for the (5 -1 |1 6) structure constructed from trans Ni(pro)₂ complexes is comparable to the experimental image. We conclude that the *honeycomb* phase is constructed from Ni(pro)₂ complexes in the trans conformation.

Mesh Phase

Figure 6: (a) STM image of 0.15 ML Ni/Au(111) after exposure to a saturation dose of (S)-proline at 300 K followed by an anneal to 400 K (42 nm × 42 nm; 0.6 nA, -1.2 V; scale bar represents 8 nm) (b) zoomed in image of *mesh* phase (6 nm × 6 nm; 0.15 nA, -1.3 V; scale bar

represents 1 nm) (c) optimised model and (d) simulated STM image of the (2 -2| 5 5) structure built from Ni(pro-pro)₂ complexes; (e) optimised model and (f) simulated STM image of the (2 -2| 5 5) structure built from Ni₂(pro-pro)₂ complexes.

The STM image in Figure 6a shows that annealing the sample to 400 K results in the preservation of islands of the various phases constructed from Λ -*fac* Ni(pro)₃ clusters, the disappearance of the *honeycomb* phase and the formation of a new phase which shall be referred to as the *mesh* phase. We conclude that the *honeycomb* phase is replaced by the *mesh* phase upon heating. Figure 6b shows an STM image of the *mesh* phase which is consistent with a commensurate (2 -2| 5 5) rectangular unit cell of 10.0 Å x 14.4 Å containing 20 gold atoms. Each unit cell contains a single feature constructed from three lobes with a central bright feature and lower contrast features at each end.

In the *honeycomb* phase, there are three Ni ions and six proline species per 31 Au atoms giving a proline coverage of 0.19 ML. The unit cell of the *mesh* phase occupies an area equivalent to 20 Au atoms, so it seems reasonable that each unit cell would contain four proline species (0.20 ML). To conserve nickel, one would expect two Ni ions per unit cell. As will be discussed below, thermal treatment at even higher temperatures produces surface structures that are likely to be formed by an oligomerization process. In aqueous solution, oligomerization of amino acids to form peptides is known to be thermodynamically unfavorable and kinetically hindered.³⁹ However, salt induced peptide formation (SIPF) was introduced in the 1980s as a theory to account for the formation of protein-forming peptides from amino acids. The formation of the peptide linkage was proposed to be catalyzed by divalent metal ions in the form of metal amino-acid complexes. Importantly, anhydrous environments were found to be required to allow SIPF. In the present study, thermal treatment of Ni(pro)₂ complexes was carried out in a UHV environment. Oligomerization of amino acids has been postulated for aspartic acid on Ni(111)⁴⁰ and unequivocally identified on Pd(111).⁴¹

Therefore, we probed the possibility of peptide salts being formed via either of the following surface reactions

Formally, the reaction of two prolinates to form a prolanyl-prolinate dipeptide releases one OH⁻ species. We assume that the formation of one mole of the dipeptide complex therefore releases two moles of OH which would generate an adsorbed O species and H₂O which would desorb into the gas phase.⁴²

We examined a number of possible dipeptide complexes containing one and two Ni ions and identified the most stable of each type. Computationally, we calculated binding energies for these nickel dipeptide complexes from the following equations:

Here, Au₆₀ refers to the Au slab (3 layers of 20 atoms corresponding to the (2 -2 | 5 5) unit cell). (pro-pro)₂ is a gas phase optimised prolanylproline dipeptide molecule.

The difference in energy of the Reactions 1 and 2 was computed; i.e. the change in energy of the following “reaction”:

For the lowest energy Ni_2 and Ni_1 dipeptide complexes, we found that Reaction 3 generates an energy difference of -1.38 eV. Hence we believe the formation of the Ni_1 dipeptide complex is thermodynamically favored. The driving force is the much stronger interaction of O with a Ni adatom on Au than the adsorption energy of O on Au(111).

Figure 6c shows the optimised model and Figure 6d shows the simulated STM image for the most stable Ni_1 complex. The simulated STM image appears quite different to the experimental image (Figure 6b). In the simulated image, the contrast is dominated by the positions of the heterocyclic rings. We conclude that the contrast observed in the STM image is likely dominated by the central Ni ions and the electronegative O and N atoms of the complex.

As a comparison, Figures 6e and 6f show the computationally derived unit cell for the $\text{Ni}_2(\text{pro-pro})_2$ complex and the simulated STM image. In contrast to Figure 6d, the simulated image shows a central bright feature which more closely matches the experimental STM data. The significantly better match between the simulated and real STM images of the $\text{Ni}_2(\text{pro-pro})_2$ complexes suggests that despite the thermodynamic favorability of the formation of the complex containing one Ni ion, we cannot rule out that the formation of $\text{Ni}_2(\text{pro-pro})_2$ complexes is favored kinetically. The discrepancy between simulated and experimental STM images is likely due to the use of the Tersoff-Hamann model in the simulated images. This model approximates the wavefunction of the STM tip as a single s-type function whereas the actual nature of the tip is not known.

Rose Phase

Figure 7: STM image ($22.0 \text{ nm} \times 18.5 \text{ nm}$, 0.29 nA , -1.5 V ; scale bar represents 4 nm) of a $0.15 \text{ ML Ni/Au(111)}$ surface exposed to a saturation coverage of (S)-proline at 300 K and annealed to 435 K (b) Model constructed from hexaproline units – it is proposed that the blue and purple circles correspond to nucleation points where the terminal carboxylate functionality is coordinated to Ni ions. The purple circles identify the corners of the unit cell. Each blue circle lies at the centre of a triangle defined by three adjacent purple circles.

At higher annealing temperatures, while the various phases constructed from Λ -*fac* Ni(pro)_3 clusters persist on the surface, the *mesh* phase largely disappears and is replaced by a new ordered phase which will be referred to as the *rose* phase, shown in Figure 7a. This structure displays a high local order and can be described by a large hexagonal unit cell of dimensions $49.1 \text{ \AA} \times 49.1 \text{ \AA}$ consistent with a $(10\sqrt{3} \times 10\sqrt{3})\text{R}30^\circ$ structure containing 300 Au atoms.

This phase is difficult to model computationally as it has such a large unit cell. The high temperature treatment required to create this phase points to it being generated by further

oligomerization of the dipeptides in the *mesh* phase. Due to the relative inflexibility of the heterocyclic ring in proline, polyproline is well known to adopt relatively rigid structures in biological systems known as PPI and PPII.⁴³⁻⁴⁴ A model which satisfactorily explains the features observed is presented in Figure 7b. The model is constructed of chains of proline oligomers containing six proline units in the PPII form radiating in six directions from a central point. The corners of the unit cell consist of four approximately circular features (shaded in purple in Figure 7b). We propose that these circular features contain Ni species which anchor six hexaprolines via interactions with the carboxylate terminal groups. A second nucleation point exists (marked by the blue circle in Figure 7b) offset from the centre of the unit cell. The six hexaproline species radiating from these nucleation points are rotated by 180° compared to those emerging from the purple circles. In each unit cell, there are twelve hexaproline oligomers giving a total of 72 proline units. The local proline coverage in the *rose* phase is therefore 72/300 or 0.24 ML. This is a slightly higher local coverage than in the *mesh* phase (0.20 ML). This model reproduces the features observed in the STM images including the hexagonal pattern reminiscent of the petals of a rose and the large rectangular pores observed in the image.

CONCLUSION

Reaction of (S)-proline with Ni at room temperature forms two types of nickel proline cluster. Octahedral Ni(pro)₃ clusters self-assemble to generate a number of ordered arrangements ranging from a low density structure exhibiting large (2 nm) pores through a range of supramolecular assemblies containing 1 nm hexagonal pores to a high density poreless structures. These clusters are stable under annealing treatments up to >430 K. At high Ni:proline ratios, usually in the vicinity of Ni clusters, square planar Ni(pro)₂ clusters are created which assemble into the *honeycomb* phase observed after thermal annealing to

~390 K. Annealing to ~410 K results in the disappearance of the *honeycomb* phase and the formation of the *mesh* phase which we conclude is constructed from clusters containing (pro-pro) dipeptide species and either one or two ionic Ni species. At higher annealing temperature (~430 K), further oligomerization takes place to generate the *rose* phase whose hexagonal unit cell covers an area of 300 Au atoms, contains an unknown number of Ni atoms and, it is proposed, contains 12 pro-pro-pro-pro-pro-proline oligomers. We propose that the carboxylate end of these oligomers coordinates to Ni clusters and is the driving force for the formation of the ordered porous arrangement.

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REFERENCES

1. Mallat, T.; Orglmeister, E.; Baiker, A. Asymmetric Catalysis at Chiral Metal Surfaces. *Chem. Rev.* **2007**, *107*, 4863-4890.
2. Izumi, Y. Modified Raney-Nickel (Mrni) Catalyst - Heterogeneous Enantio-Differentiating (Asymmetric) Catalyst. *Adv. Catal.* **1983**, *32*, 215-271.
3. Raval, R. Chiral Expression from Molecular Assemblies at Metal Surfaces: Insights from Surface Science Techniques. *Chem. Soc. Rev.* **2009**, *38*, 707-721.
4. Costa, D.; Pradier, C. M.; Tielens, F.; Savio, L. Adsorption and Self-Assembly of Bio-Organic Molecules at Model Surfaces: A Route Towards Increased Complexity. *Surf. Sci. Rep.* **2015**, *70*, 449-553.

5. Trant, A. G.; Baddeley, C. J. Chiral Recognition at One-Dimensional Metal-Organic Coordination Networks Initiates the Ordering of Prochiral Catalytic Reagent Methylacetoacetate on Au{111}. *Langmuir* **2011**, *27*, 1788-1795.
6. Wilson, K. E.; Baddeley, C. J. Understanding the Surface Chemistry of Enantioselective Heterogeneous Reactions: Influence of Modification Variables on the Interaction of Methylacetoacetate with (S)-Aspartic Acid Modified Ni{111}. *J. Phys. Chem. C* **2009**, *113*, 10706-10711.
7. Jones, T. E.; Rekasas, A. E.; Baddeley, C. J. Influence of Modification pH and Temperature on the Interaction of Methylacetoacetate with (S)-Glutamic Acid-Modified Ni{111}. *J. Phys. Chem. C* **2007**, *111*, 5500-5505.
8. Jones, T. E.; Baddeley, C. J. Influence of Modification Conditions on the Interaction of Methylacetoacetate with (R,R)-Tartaric Acid-Modified Ni{111}. *J. Phys. Chem. C* **2007**, *111*, 17558-17563.
9. Jones, T. E.; Baddeley, C. J. Investigating the Mechanism of Chiral Surface Reactions: The Interaction of Methylacetoacetate with (S)-Glutamic Acid Modified Ni{111}. *Langmuir* **2006**, *22*, 148-152.
10. Jones, T. E.; Baddeley, C. J. Direct STM Evidence of a Surface Interaction between Chiral Modifier and Pro-Chiral Reagent: Methylacetoacetate on R,R- Tartaric Acid Modified Ni{111}. *Surf. Sci.* **2002**, *519*, 237-249.
11. Demers-Carpentier, V.; Rasmussen, A. M. H.; Goubert, G.; Ferrighi, L.; Dong, Y.; Lemay, J. C.; Masini, F.; Zeng, Y.; Hammer, B.; McBreen, P. H. Stereodirection of an Alpha-Ketoester at Sub-Molecular Sites on Chirally Modified Pt(111): Heterogeneous Asymmetric Catalysis. *J. Am. Chem. Soc.* **2013**, *135*, 9999-10002.
12. Burkholder, L.; Garvey, M.; Weinert, M.; Tysoe, W. T. Structure of Methyl Pyruvate and Alpha-(1-Naphthyl)Ethylamine on Pd(111). *J. Phys. Chem. C* **2011**, *115*, 8790-8797.

13. Bonello, J. M.; Williams, F. J.; Lambert, R. M. Aspects of Enantioselective Heterogeneous Catalysis: Structure and Reactivity of (S)-(-)-1-(1-Naphthyl)Ethylamine on Pt{111}. *J. Am. Chem. Soc.* **2003**, *125*, 2723-2729.
14. Gellman, A. J.; Tysoe, W. T.; Zaera, F. Surface Chemistry for Enantioselective Catalysis. *Catal. Lett.* **2015**, *145*, 220-232.
15. Kyriakou, G.; Beaumont, S. K.; Lambert, R. M. Aspects of Heterogeneous Enantioselective Catalysis by Metals. *Langmuir* **2011**, *27*, 9687-9695.
16. Schwendinger, M. G.; Rode, B. M. Salt-Induced Formation of Mixed Peptides under Possible Prebiotic Conditions. *Inorg. Chim. Acta* **1991**, *186*, 247-251.
17. Seljamae-Green, R. T.; Simpson, G. J.; Grillo, F.; Greenwood, J.; Francis, S. M.; Schaub, R.; Lacovig, P.; Baddeley, C. J. Assembly of a Chiral Amino Acid on an Unreactive Surface: (S)-Proline on Au(111). *Langmuir* **2014**, *30*, 3495-3501.
18. Seljamäe-Green, R. T.; Simpson, G. J.; Grillo, F.; Greenwood, J.; Francis, S. M.; Schaub, R.; Gano, J. E.; Früchtl, H. A.; Lacovig, P.; Baddeley, C. J. Formation of Bioinorganic Complexes by the Corrosive Adsorption of (S)-Proline on Ni/Au(111). *Langmuir* **2015**, *31*, 262-271.
19. Chambliss, D. D.; Wilson, R. J.; Chiang, S. Nucleation of Ordered Ni Island Arrays on Au(111) by Surface- Lattice Dislocations. *Phys. Rev. Lett.* **1991**, *66*, 1721-1724.
20. Barth, J. V.; Brune, H.; Ertl, G.; Behm, R. J. Scanning Tunneling Microscopy Observations on the Reconstructed Au(111) Surface - Atomic-Structure, Long-Range Superstructure, Rotational Domains, and Surface-Defects. *Phys. Rev. B* **1990**, *42*, 9307-9318.
21. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

22. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (Dft-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 15. DOI: 10.1063/1.3382344.
23. Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456-1465.
24. Neese, F. The Orca Program System. *Wiley Interdiscip. Rev.-Comput. Mol. Sci.* **2012**, *2*, 73-78.
25. Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
26. Kresse, G.; Furthmuller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15-50.
27. Kresse, G.; Hafner, J. Ab-Initio Molecular-Dynamics Simulations of the Liquid-Metal Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B* **1994**, *49*, 14251-14269.
28. Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics for Liquid-Metals. *Phys. Rev. B* **1993**, *47*, 558-561.
29. Kresse, G.; Furthmuller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169-11186.
30. Blochl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953-17979.
31. Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758-1775.
32. <http://www.p4vasp.at/>.
33. Tersoff, J.; Hamann, D. R. Theory and Application for the Scanning Tunneling Microscope. *Phys. Rev. Lett.* **1983**, *50*, 1998-2001.

34. Trant, A. G.; Jones, T. E.; Baddeley, C. J. Thermal Treatment of Glutamic Acid-Modified Nickel Nanoclusters on Au{111} Leads to the Formation of One-Dimensional Metal-Organic Coordination Networks. *J. Phys. Chem. C* **2007**, *111*, 10534-10540.
35. Trant, A. G.; Jones, T. E.; Gustafson, J.; Noakes, T. C. Q.; Bailey, P.; Baddeley, C. J. Alloy Formation in the Au{111}/Ni System - an Investigation with Scanning Tunnelling Microscopy and Medium Energy Ion Scattering. *Surf. Sci.* **2009**, *603*, 571-579.
36. Ito, T.; Marumo, F.; Saito, Y. Crystal Structure of Bis-(L-)Prolinato Palladium(II). *Acta Crystallogr. Sect. B-Struct. Crystallogr. Cryst. Chem.* **1971**, *B 27*, 1062-1066.
37. Yukawa, Y.; Igarashi, S.; Yamano, A.; Sato, S. Structure of the Centred Icosahedral Samarium Cluster Formed by Bis(L-Prolinato) Nickel(II) Ligands. *Chem. Commun.* **1997**, 711-712.
38. Mathieson, A. M.; Welsh, H. K. The Crystal Structure of Copper Proline Dihydrate. *Acta Crystallogr.* **1952**, *5*, 599-604.
39. Jakschitz, T. A. E.; Rode, B. M. Chemical Evolution from Simple Inorganic Compounds to Chiral Peptides. *Chem. Soc. Rev.* **2012**, *41*, 5484-5489.
40. Wilson, K. E.; Trant, A. G.; Baddeley, C. J. Interaction of the Pro-Chiral Molecule, Methylacetoacetate, with (S)-Aspartic Acid Modified Ni{111}. *J. Phys. Chem. C* **2012**, *116*, 1092-1098.
41. Mahapatra, M.; Praeger, J.; Tysoe, W. T. Adsorption, Assembly, and Oligomerization of Aspartic Acid on Pd(111). *J. Phys. Chem. C* **2017**, *121*, 13239-13248.
42. Madey, T. E.; Netzer, F. P. The Adsorption of H₂O on Ni(111); Influence of Preadsorbed Oxygen on Azimuthal Ordering. *Surf. Sci.* **1982**, *117*, 549-560.
43. Cowan, P. M.; McGavin, S. Structure of Poly-L-Proline. *Nature* **1955**, *176*, 501-503.
44. Traub, W.; Shmueli, U. Structure of Poly-L-Proline I. *Nature* **1963**, *198*, 1165-1166.

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