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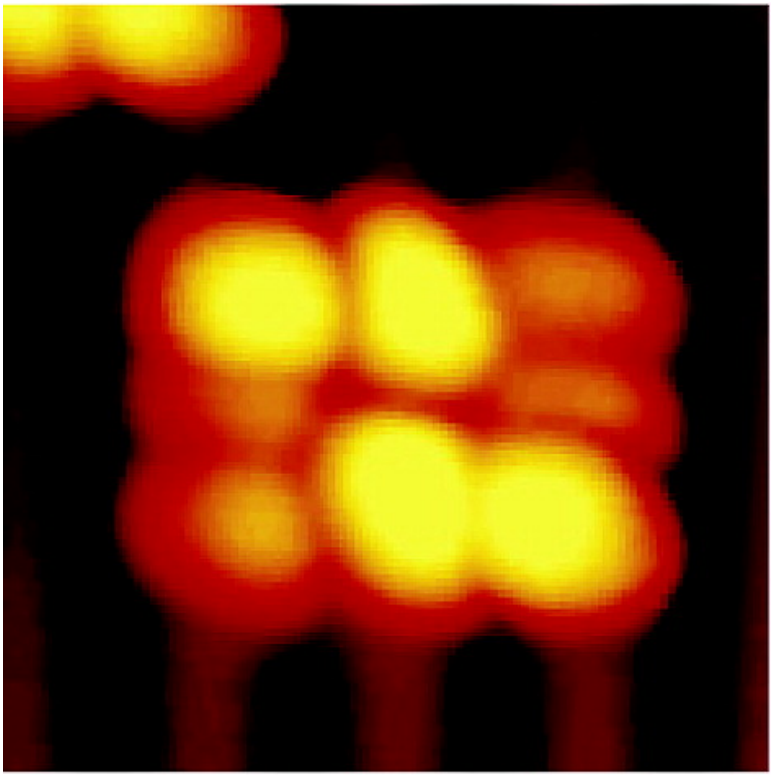
J. Am. Chem. Soc., **2003**, 125 (48), 14680-14681• DOI: 10.1021/ja0377403 • Publication Date (Web): 08 November 2003



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Published on Web 11/08/2003

Self-Assembly of Monodispersed, Chiral Nanoclusters of Cysteine on the Au(110)-(1 × 2) Surface

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The synthesis of small, functional objects in large numbers will be of essential importance for future nanotechnology. A test case is provided by small clusters that, in general, may exhibit special properties linked to their size, making the synthesis of clusters with a narrow size distribution highly desired. Clusters formed by nucleation and growth of metal or semiconductor atoms vapor-deposited onto solid surfaces typically show a size dispersion (full width at half-maximum of the size distribution curve) of more than half the average cluster size[1−3] (more narrow size distributions have been realized in a few cases of "magic clusters",[4] exhibiting geometric or electronic shell closing, or by exploiting strain in the substrate[5] or cluster[6]). In contrast to agglomeration of individual atoms, molecular self-assembly, i.e, the spontaneous formation of structurally well-defined aggregates from preexisting molecular building blocks,[7,8] may allow a more selective assembly process by utilizing specific intermolecular interactions. In a sense, the ultimate example is provided by the biological world, where protein synthesis can be viewed as the formation of nanostructures of highly controlled sizes based on (a coded) assembly of amino acids. The self-assembly of organic molecules on solid surfaces has recently been studied extensively, not least because such systems can be investigated directly at molecular or submolecular resolution by scanning tunneling microscopy (STM).[9] While the primary focus has been on extended, two-dimensional, molecular overlayers,[10] some studies have addressed the agglomeration of molecules into nanostructures of specific shapes,[11−15] such as wires or clusters, providing clues to self-assembly strategies which may pave the way for a controlled synthesis of functional nanostructures.

Here we report the synthesis of surface-bound molecular nanoclusters displaying a remarkable monodispersity. The clusters self-assemble from the naturally occurring amino acid cysteine[16,17] (a thiol) upon its vapor deposition onto the (110) surface of a gold single crystal under ultra-clean vacuum conditions.

The experiments were performed in an ultrahigh vacuum system equipped with the home-built, variable temperature Aarhus STM.[18] The Au(110) crystal was cleaned by repeated cycles of sputtering by 1.5 keV Ar^+ ions and annealing at 800 K, resulting in an atomically clean surface exhibiting the well-known (1 × 2) missing-row reconstruction with every second close-packed gold row in the topmost layer removed.[17,19] Cysteine molecules ($HS-CH_2-CH(NH_2)-COOH$, Aldrich 97%, outgassed to remove volatile contaminants) were vapor-deposited in situ onto the gold surface from a heated glass crucible. STM imaging was performed at different substrate temperatures between 120 and 270 K.

When deposited on Au(110)-(1 × 2) at a substrate temperature of 120 K, cysteine is found to form irregular agglomerates as seen in the STM image of Figure 1a. However, when this adsorption system is slightly annealed, the molecules re-organize and self-assemble into identical, well-defined nanoclusters as demonstrated in the STM image of Figure 1b. A close-up of the resulting

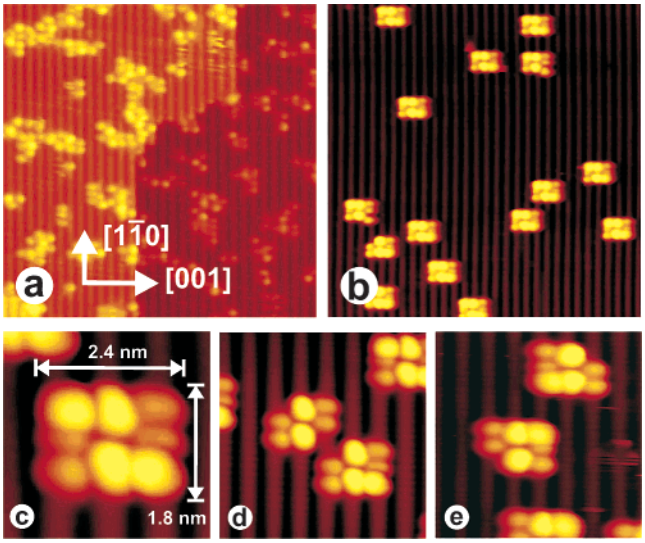

Figure 1. STM images of cysteine on Au(110)-(1 × 2). The missing-row reconstruction results in the close-packed gold rows along the [1−10] direction seen running vertically in all the images. (a) Irregular cysteine agglomerates formed after deposition at 120 K (24.5 × 24.5 nm^2). (b) L-Cysteine nanoclusters formed after annealing to 270 K (24.5 × 24.5 nm^2). (c) Close-up of an L-cysteine nanocluster (3.2 × 3.2 nm^2). (d) Imperfect nanoclusters formed from L-cysteine lacking upper left or lower right corner units (6.5 × 6.5 nm^2). (e) Imperfect nanoclusters formed from D-cysteine, related by mirror symmetry to the L-cysteine clusters of (d) (6.5 × 6.5 nm^2). All STM images were acquired in the constant-current mode with a sample bias of −1.2 V compared to the tip and with a tunneling current of ∼0.1 nA.

nanoclusters is shown in Figure 1c. The lateral extent of the cluster is 2.4 and 1.8 nm in the [001] and [1−10] directions, respectively. The cluster consists of a central part composed of two subunits centered on a close-packed gold row, surrounded by three smaller subunits on each side on top of neighboring close-packed rows. The upper left and lower right corner units appear higher than the other four side units. Compared to the height of the gold atoms in the topmost atomic row, the maxima of the center, the high corner, and the side units of the cysteine clusters have apparent heights of 0.23, 0.19, and 0.15 nm, respectively, as deduced from constant-current STM topographs. Some clusters lack one or both of the high corner units (see Figure 1d), but no other imperfections are observed. The size of the self-assembled cysteine clusters is thus extremely monodispersed: Out of several hundred clusters observed after annealing to an optimum temperature of 270 K, 71% are complete, 26% lack one, and 3% lack both corner units. (At higher annealing temperatures, the clusters dissolve and other adsorption structures form.)

The cysteine clusters are chiral; they lack a mirror symmetry element due to the different appearance and binding strength of the two corner units. The clusters shown in Figure 1, b−d, are

10.1021/ja0377403 CCC: $25.00

formed by adsorption of enantiomerically pure L-cysteine on an achiral gold surface, and their chirality thus reflects the chirality of the cysteine molecules themselves. Identical, except mirror-imaged, clusters are formed by enantiomerically pure D-cysteine, as displayed in Figure 1e. When the cluster synthesis is performed with the racemic mixture, such that both L- and D-cysteine are present at the surface simultaneously, clusters identical to those obtained from the enantiopure species are formed (not shown). No new structures suggestive of heterochiral clusters were observed. The racemate thus appears to segregate into homochiral clusters, suggesting intermolecular chiral recognition[17] during the self-assembly of the supramolecular cysteine clusters.

Manipulation of the individual cluster along the close-packed [1−10] direction is possible by moving the STM tip over the cluster after bringing the tip into close proximity of the surface ($V_t = 80$ mV, $I_t \approx 0.8$ nA). Manipulation was successful at a substrate temperature of 260 K, but not at 120 K, indicating that the manipulation mechanism is a thermally activated diffusion-type process influenced by the presence of the STM-tip. Attempts to manipulate the clusters along the [001] direction were unsuccessful, reflecting a larger activation barrier for diffusion along this more corrugated direction.

Thiols are known to bind covalently to gold surfaces through a dehydrogenated mercapto (−SH) group.[20] The manipulation experiments provide indirect evidence that this is not the case for the cysteine molecules in the clusters: A covalent S−Au bond is believed to be sufficiently strong that adjacent Au−Au bonds are broken before the S−Au bond itself if a thiol is pulled away from a gold surface.[21] However, the surface exposed by manipulation of a cluster appears unperturbed, suggesting that S−Au bonding has not occurred. This is consistent with the observation that short-chained alkanethiols on Au(111) do not deprotonate until temperatures of 260−290 K are reached[22] (at higher temperatures we indeed find adsorption structures believed to involve covalent cysteinate−gold interaction, see ref 17).

The clusters appear to consist of a single layer of cysteine molecules since (i) the maximum height of the clusters, 0.23 nm, is close to the apparent height of individual cysteine molecules observed in other adsorption structures,[23] and (ii) the height variations over the clusters can, aside from possible STM-imaging effects due to lateral variations in the electronic structure, be accounted for by assuming different molecular adsorption sites on the corrugated missing-row reconstructed surface. The STM images of Figure 1 suggest that the clusters consist of eight cysteine molecules, one for each resolved subunit. This is consistent with the expected footprint of eight cysteine molecules oriented with their backbones approximately parallel to the surface plane.

In summary, the synthesis of highly monodispersed cysteine nanoclusters have been described, providing a prototypical case of molecular self-assembly. At low temperatures, the molecules interact irreversibly to form random aggregates. Thermal excitation allows intermolecular interactions to be overcome, and the ensuing reversibility enables the optimization of the molecular configuration into a local thermodynamic minimum, i.e, the cluster. The intermolecular interactions involved are specific, as evidenced by the lower binding strength of some corner entities and the chiral specificity of the assembly process. The size monodispersity of the clusters is thus not explained by a simple geometric shell-closing effect.[1,4,12] Most likely, the molecular configuration of the cluster is such that it allows all molecular interaction points to be saturated by specific interactions to other molecules within the cluster or to surface atoms, preventing the attachment of additional molecules. The clusters probably consist of a single layer of nondeprotonated cysteine molecules, but the detailed elucidation of their structure, and the corresponding self-assembly mechanism, constitute a challenge for theoretical modeling and/or further experiments.

Acknowledgment. This work was supported by the Danish National Research Foundation and the Danish Natural Science Research Council. Discussions with Bjørk Hammer, Luis Molina, and Kurt Gothelf are gratefully acknowledged.

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(23) See ref 17; the cysteine dimers protrude 0.06 nm above the close-packed gold rows, but since they are resting in 0.144 nm deep vacancy structures in these rows, their total height is ∼0.2 nm.

JA0377403