

Solution Phase Post-modification of Trimesic Acid Network on Au(111) with Zn²⁺ Ions

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ESI-1. Experimental Details

As for Au(111) single crystals we employed Au single crystal beads obtained by melting a gold wire (99.999%, Aldrich, diameter: 0.5 mm) under a hydrogen/oxygen flame. A gold wire was cleaned with aqua regia before melting to a bead, and the bead underwent several times cleaning and re-melting processes without growing to develop distinctive facets of (111) and (100). For STM measurements, the bead crystals were used as obtained. For electrochemical studies, the bead crystals were modified: one of the (111) facets on a bead single crystal was identified with laser reflection pattern, and the bead was cut and polished to the perpendicular direction of the identified (111) facet starting from emery papers to 0.25 μm alumina paste. Finally, the round single crystal bead became a hemisphere whose face is mirror-like Au(111) of ~ 2 mm in diameter. Before any experiment, clean and ordered Au(111) surfaces were routinely prepared by annealing in a hydrogen/air flame followed by quenching in water.

The adsorption of TMA was carried out by dipping clean and ordered Au(111) crystals into a solution of 1 mM TMA (95%, Aldrich) in 0.1 M HClO_4 (Suprapur, Aldrich) solution for 60 min.¹ Modification of the TMA monolayer with Zn^{2+} ions was performed by dipping the Au(111) crystal with a pristine TMA layer to a solution of 1 mM Zn acetate (99.99%, Merck) in 0.1 M HClO_4 solution.

In STM experiments with a home-made STM cell for liquid environments, a single crystal Au bead was positioned so that the (111) facet is pointed toward a W tip coated with polyethylene. The employed STM instrument was Nanoscope IIIa (Digital instruments Inc., Santa Barbara, CA, USA). The existence of a TMA layer was confirmed by imaging in the TMA solution. Then, the TMA solution was replaced with the solution containing Zn^{2+} ions, followed by approaching the STM tip to the Au(111) surface. The imaging was performed in

constant current mode, and the normal bias voltage and set current were around -100 mV and 1 nA, respectively. The calibration of the employed scanners was carried out using HOPG and iodine adsorbed on Au(111)^{2,3} at an atomic level. Also, the corrugation line of reconstructed Au(111) with TMA served as an internal standard. On the other hand, sizes of STM features in images, including distances between them, were estimated statistically using at least three images obtained with independent replica experiments and at least 10 features in each image. Potential control during STM imaging was carried out, when needed, using a three electrode system as describe below.

In voltammetric experiments, a conventional three electrode system was employed. Specifically, the reference electrode was a home-made Ag/AgCl electrode with 1.0 M NaCl solution, and the counter electrode was a Pt wire. The working electrode was a hemispherical Au bead, whose (111) face was exclusively exposed to solution by maintaining meniscus position. The potentials reported in this work are the values as measured against the employed reference electrode. The supporting electrolyte was 0.1 M phosphate buffer solution (99.7% Aldrich) of pH 4.4.

1. J. Kim, C. K. Rhee, H.-J. Koo, E. E. Kasapbasi, M.-H. Whangbo, *J. Phys. Chem. C.*, 2013, **117**, 22636.
2. W. Haiss, J. K. Sass, X. Gao, M. J Weaver, *Surf. Sci. Lett.*, 1992, **274**, L593.
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ESI-2. Contoured nanoporous network of anionic TMA on Au(111).

Fig. 1(a) shows an STM micrograph of a TMA adlayer formed in 0.1 M HClO₄ solution of 1 mM TMA. Our previous work¹ has revealed that the TMA adlayer imaged as in Fig. 1(a) was a nanoporous anionic network of $(5\sqrt{3} \times 5\sqrt{3})R30^\circ$. In the inset of Fig. 1(a), there are two hexagons whose side lengths are 0.83 ± 0.02 nm: six bar features point out from the corners of the red hexagon, while three bar features reside on the sides of the green hexagon. A primary motif of the pristine TMA network (the red hexagon) is a crown-like TMA hexamer (see below), interconnecting to other six hexamers via hydrogen bonds between the carboxylic acids as shown in Fig. 1(b), so that the green hexagons are produced. Note that the green hexagons are drawn intentionally smaller than the red ones for clarity in Fig. 1(b), although their actual sizes are equal.

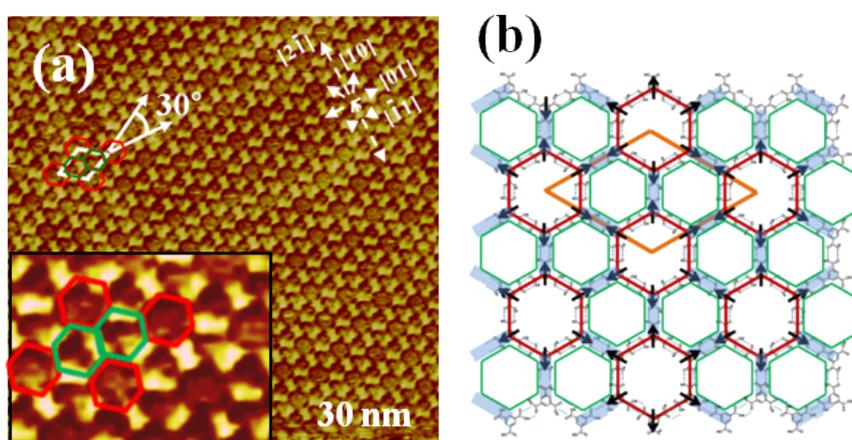


Fig. 1. The TMA network on Au(111): (a) an STM image with an inset of a zoomed-in image, and (b) its schematic of a $(5\sqrt{3} \times 5\sqrt{3})$ structure. In (b), the green hexagons are drawn intentionally smaller than the red ones for clarity, although their actual sizes are equal.

The crown-like TMA hexamer as in Fig. 2 represents the red hexagon in Fig. 1(b), which is a primary motif of the network. Specifically, the TMAs in a hexamer are anchored to the Au(111) surface by anionic interaction of carboxylates (whose oxygen atoms are denoted in blue), and are swiveled to form intermolecular hydrogen bonds between the

anchoring carboxylates and the carboxylic acids (whose oxygen atoms are denoted in red). One crown-like hexamer interconnects to other six hexamers via hydrogen bonds between the carboxylic acids, so that the green hexagons are produced. Therefore, the resulting TMA adlayer is a contoured network of the crown-like hexamers consisting of anionic TMAs. More details about the TMA network are described in ref 1.

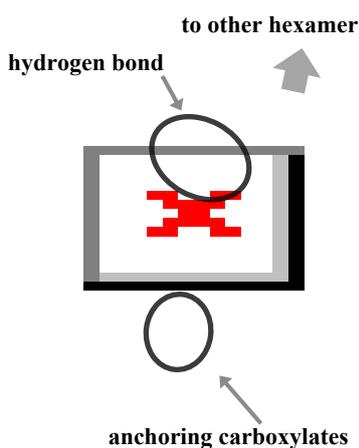


Fig. 2. A model for the crown-like primary TMA hexamer of contoured anionic TMA network of a $(5\sqrt{3} \times 5\sqrt{3})$ structure on Au(111). The colors of the balls correspond to the following atoms: gray (carbon), blue (oxygen in anchoring carboxylate), red (oxygen in hydrogen bonding carboxylic acid), and white (hydrogen in carboxylic acid).

1. J. Kim, C. K. Rhee, H.-J. Koo, E. E. Kasapbasi, M.-H. Whangbo, *J. Phys. Chem. C.*, 2013, **117**, 22636.

ESI-3. Estimation of Zn²⁺ ion coverage in the modified TMA network

Table 1 summarizes structural parameters of the TMA networks unit cells before and after modification with Zn²⁺ ions. In the ($5\sqrt{3} \times 5\sqrt{3}$) unit cell of pristine TMA network, there are 24 TMA molecules on 75 Au atoms. After modification, there are 24 TMA molecules on 300 Au atoms in the ($10\sqrt{3} \times 10\sqrt{3}$) unit cell because the unit cell size is doubled. If one chevron consisting of three TMA molecules accommodates two Zn²⁺ ions, there would be 16 Zn²⁺ ions in the ($10\sqrt{3} \times 10\sqrt{3}$) unit cell, equivalent to the coverage of 0.053. Here, coverage is defined as a number of Zn²⁺ ions to that of Au atoms within a unit cell. On the other hand, if each TMA molecule shares three hydrogen bonds with other three adjacent TMA molecules as in the case of flat-lying TMA network of (6×6) on Au(111)¹, and if each hydrogen bond accommodate one Zn²⁺ ion, then the number of hydrogen bonds confined to a TMA molecule in the ($10\sqrt{3} \times 10\sqrt{3}$) structure is 3/2, leading to 3/2 Zn²⁺ ions per a TMA. In this particular case, the coverage of Zn²⁺ ion will be 0.120.

Table 1. Structural parameters of the TMA networks unit cells before and after modification with Zn²⁺ ions.

network	unit cell	numbers of chemical species within unit cells			coverage [*]
		TMA	Zn ²⁺	Au	
pristine TMA	($5\sqrt{3} \times 5\sqrt{3}$)R30°	6	-	75	-
modified TMA with Zn ²⁺ ion	($10\sqrt{3} \times 10\sqrt{3}$)R30°	24	16	300	0.053
	($10\sqrt{3} \times 10\sqrt{3}$)R30°†	24	36†	300	0.120†

*Coverage is defined as a number of Zn²⁺ ions to that of Au atoms within a unit cell.

†If each TMA molecule shares three hydrogen bonds with other three adjacent TMA molecules, then the number of hydrogen bonds confined to a TMA molecule in the ($10\sqrt{3} \times 10\sqrt{3}$) structure is 3/2. Also if each hydrogen bond accommodate one Zn²⁺ ion, each TMA will have 3/2 Zn²⁺ ions.

ESI-4. Cyclic voltammogram of well-defined Au(111)

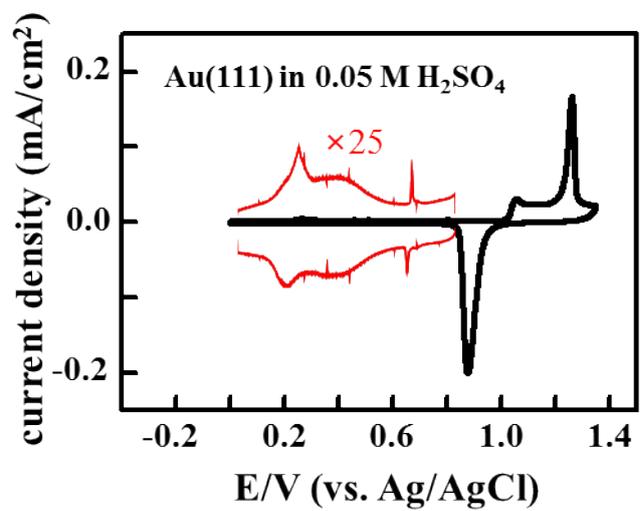


Fig. 3. Cyclic voltammogram of well-defined Au(111) in 0.05 M H₂SO₄ solution. Scan rate: 10 mV/sec

ESI-5. STM images of Au(111) after simultaneous exposure to Zn²⁺ ion and TMA

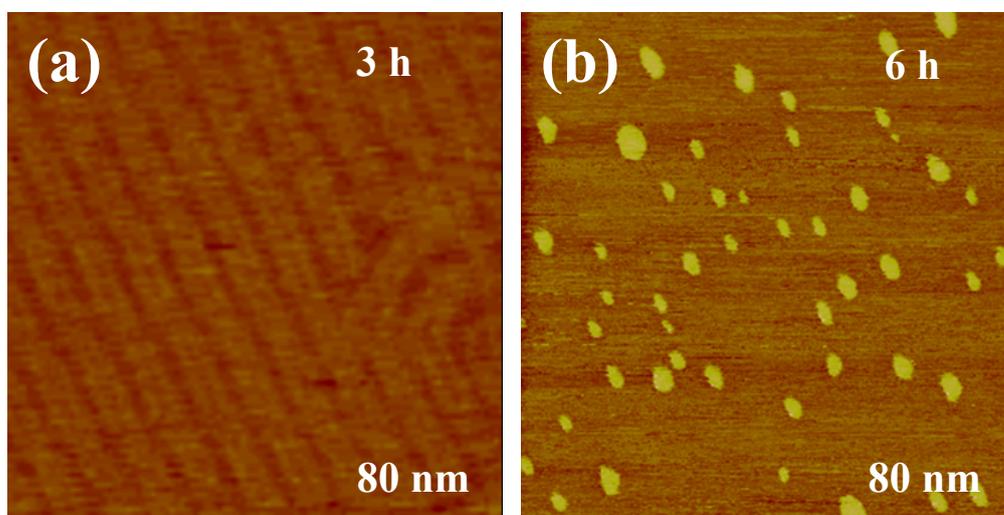


Fig. 4. STM images of Au(111) after contact with a 0.1 M HClO₄ solution containing 1 mM Zn²⁺ ion and 1 mM TMA for (a) 3 hr and (b) 6 hr.

Fig. 4. shows STM images of Au(111) after simultaneous exposure to Zn²⁺ ion and TMA . After 3 hr contact with a 0.1 M HClO₄ solution containing 1 mM Zn²⁺ ion and 1 mM TMA, only the reconstruction lines of clean Au(111) are discernible, indicating that no adsorption of Zn²⁺ ion and TMA took place. After prolonged exposure of 6 hr, however, only Au islands formed by lifting the reconstructed surface of Au(111) are visible. The images do not show any traces of TMA or Zn²⁺ ion, to confirm that Zn²⁺-modified TMA network of chevron pairs was not formed at all. Perhaps, complexes of TMA-Zn²⁺ are formed in solution phase not to adsorb on Au(111) surface. Therefore, it is clear that post-modification of TMA network on Au(111) with Zn²⁺ ion is the only way to produce the Zn²⁺-modified TMA network of $(10\sqrt{3} \times 10\sqrt{3})$ structure on Au(111).