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Chlorine adlayer-templated growth of a hybrid inorganic–organic layered structure on Au(111)

I.I. Rzeźnicka^{a,*}, H. Horino^{b,1}, K. Yagyu^c, T. Suzuki^c, S. Kajimoto^a, H. Fukumura^a

^a Department of Chemistry, Graduate School of Science, Tohoku University, Japan

^b Graduate School of Environmental Studies, Tohoku University, Japan

^c Department of Electronics Engineering and Computer Science, Fukuoka University, Japan

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ABSTRACT

Growth of a hybrid inorganic–organic layered structure on the Au(111) surface using a one-step solution growth is reported. The hybrid structure is consist of 4,4'-bipyridine [4,4'-BiPyH₂]²⁺ cations, Cl anions and Au adatoms, provided from substrate by means of the adsorbate-induced surface phase transition of a surface reconstruction. Its surface and bulk structures were characterized by scanning tunneling microscopy (STM), secondary ion mass spectrometry (SIMS), and Raman spectroscopy. STM results reveal growth of the first [4,4'-BiPyH₂]²⁺ layer on top of the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ chlorine overlayer formed on the Au(111) surface. These two layers are found to provide a platform for a following three-dimensional growth facilitated by hydrogen bonding, aurophilic and π – π stacking interactions.

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1. Introduction

Supramolecular assembly of novel metal–organic nanostructures at surfaces is a topic of intense research motivated by potential application of such hybrid layers in photovoltaics, sensing, molecular electronics and optoelectronics. Although there are many examples showing formation of highly-organized two-dimensional metal–organic frameworks (MOFs), they have mainly been grown on well-defined metal surfaces and under ultra-high vacuum conditions [1–3]. Liquid phase solvothermal layer-by-layer growth of MOFs on a copper surface modified by self-assembled monolayer (SAM) was demonstrated by Wöll and co-workers [4]. Using this approach, MOFs were grown on SAM by sequential immersion of the substrate into first a solution that contains a metal precursor and then second a solution containing an organic ligand.

Adsorption of inorganic anions on well-defined metal surfaces is known to yield adlayers with various ordered structures [5–7]. In these adlayers anions can form a chemisorbed layer or a metal-anion surface compound [8]. The latter is likely to form when the adsorption of an anion leads to ejection of adatoms from a metal surface, inducing

a phase transition of a surface reconstruction. The Au(111) surface has so-called herringbone reconstruction characterized by a compression of atoms in the topmost surface layer where an addition of one Au atom per 22 surface atoms in the bulk-terminated surface layer along the [1 $\bar{1}0$] direction leads to partial compensation of the tensile stress [9]. In the presence of strongly interacting adsorbates, the reconstruction can be lifted by ejection of these extra atoms, providing on average 0.7 Au adatoms per square nanometer of the surface [9]. In addition, step edges and surface defects might supply additional adatoms required for formation of surface compounds. Recently, gold adatoms have been found as one of key structural components guiding self-assembly of organosulfur compounds on the Au(111) surface [9].

Adsorption of chlorine on gold surfaces has been in research focus in recent years due to the emergent field of Au catalysis, where gold and chlorine are frequently encountered. Various experimental techniques, including scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and X-ray photoelectron spectroscopy (XPS) have been used for further understanding of the nature of chlorine adsorption on the Au(111) surface. Chlorine adsorption has been found to be a dynamic process, involving multiple stages at different coverages. Gao et al. reported lifting of the herringbone reconstruction after dosing small amounts of Cl₂ gas at room temperature [8]. At coverages of <0.33 ML, a $p(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer structure has commonly been observed [8,10], while at higher coverages, adatoms were found to be removed from the surface leading to a honeycomb gold–chloride

* Corresponding author.

E-mail address: irzeznicka@m.tains.tohoku.ac.jp (I.I. Rzeźnicka).

¹ Current address: Office of Society-Academia Collaboration for Innovation (SACI), Kyoto University, Japan.

superstructure with six dimers present in each hexagonal unit [8]. Density functional theory (DFT) calculations reveal that incorporation of gold atoms into the adsorbate layer is energetically favorable at coverages above 0.33 ML and binding of Cl^- on both, the top, and the side of the adatom is stronger than that of chlorine overlayer on the Au(111)-(1 × 1) surface [8]. Both the chemisorbed chlorine overlayer and Au-chloride superstructures may serve as templates for the supramolecular assembly of inorganic–organic layered structures.

4,4'-Bipyridine (BiPy) is an important organic ligand. It is known to form various one- to three-dimensional (3D) supramolecular networks with several transition metal ions such as Cu(I), Ag(I), Cd(II), Zn(II), Co(II), and Ni(II) [11]. The very high dimensionality of these networks is due to a delicate interplay between three organizing forces: metal coordination, hydrogen bonding and π - π stacking interactions. At present, there have been no reports on the formation of supramolecular 4,4'-BiPy networks with Au. The use of gold ions, in particular Au(I), offers another, so-called aurophilic interaction, which can facilitate the formation of supramolecular structures [12]. Aurophilic interactions have bonding energies of ~30 kJ/mol, which are comparable to the hydrogen bonding energies [13]. Together with the hydrogen bonding, these interactions can lead to unique supramolecular structures with interesting physical properties. Indeed the $[4,4'\text{-BiPyH}_2]^{2+}$ cation is known to generate ordered solid-state architectures through hydrogen bond interactions with $[\text{MX}_4]^{2-}$ anions [14].

Adsorption of 4,4'-BiPy on transition metal surfaces has been a topic of several studies [15–17]. On the Au(111) surface, it has been reported that no ordered layers were found with adsorption from neutral solutions [18,19]. However, ordered layers were found with adsorption from acidic solutions, or under an electrochemical control [15,20]. Their STM images showed a formation of extended, one-dimensional molecular chains. Futamata et al. proposed that in halide-containing solutions, $[4,4'\text{-BiPyH}_2]^{2+}$ adsorbs on the Au(111) in the proximity of the chloride ions (at the second layer) through a Coulomb interaction with Cl^- [21]. Any nanoscale molecular image to prove this scenario has so far not been reported.

Here, we report a chlorine adlayer-templated growth of a hybrid inorganic–organic layered structure on the Au(111) surface using a one-step solution growth. This hybrid structure consists of 4,4'-bipyridine $[4,4'\text{-BiPyH}_2]^{2+}$ cations, Cl anions and Au adatoms, provided from the gold substrate by means of the adsorbate-induced surface phase transition of the surface reconstruction. Its surface and bulk structures were characterized by scanning tunneling microscopy (STM), secondary ion mass spectrometry (SIMS), and Raman spectroscopy. STM results showed the growth of the ordered layer on top of the well-defined chlorine overlayer. These two layers provide a platform for a following three-dimensional growth, facilitated by hydrogen bonding, aurophilic, and π - π stacking interactions.

2. Materials and methods

2.1. Materials

4,4'-Dipyridyl (98%) was purchased from Aldrich and used without further purification. Hydrochloric acid (37%) and ethanol (99.5%) were purchased from Wako-Pure Chemicals, Japan.

2.2. Sample preparation

Slides of thin film of Au deposited on mica (SPI Supplies/Structure Probe, Inc., USA) were used as substrates. Prior to immersion into a 4,4'-dipyridyl (4,4'-BiPy) solution slides were flame annealed in a butane flame in order to form (111) terraces. The annealed substrates were immediately immersed into a 1 mM ethanolic solution of 4,4'-BiPy and acidified with 0.1 M HCl to pH 3. At this pH, 4,4'-BiPy is mostly diprotonated according to the acid dissociation constants which are $\text{p}K_1 = 3.5$ and $\text{p}K_2 = 4.9$ [22].

2.3. Scanning tunneling microscopy

The nanoscope IIIA scanning tunneling microscope (STM), Digital Instruments, operating at ambient conditions, was used for overlayer imaging. The scanner calibration was periodically checked using the atomic lattice of HOPG and a clean Au(111) surface. Tips were made of mechanically cut Pt/Ir wire or an electrochemically etched Au wire ($\phi = 0.3$ mm). STM images were acquired at room temperature in a constant height or a constant current mode with a tunneling current of 0.7 nA and sample bias of 200 mV.

2.4. Raman spectroscopy

Raman spectra of the surface-grown crystals were acquired using a confocal Raman spectrometer (Jobin Yvon, Horiba HR 800 Lab Ram) equipped with a Peltier-cooled Synapse CCD camera detector. The excitation source was a 633-nm He–Ne laser with an output of 0.8 mW at the sample. The same objective lens (100 × M Plan N Olympus objective with NA 0.9) was used to deliver an excitation laser beam as well as to collect the backscattered light from the sample. Spectra were collected in the 80–3400 cm^{-1} range with a 100 μm spectrometer slit width and a 600 grooves/mm grating. All spectra were recorded under linear polarization conditions. A silicon peak at 520.7 cm^{-1} was used to calibrate the Raman system. A Kaiser super notch filter was used for rejection of the Rayleigh light. It reaches >90% transmission at ~80–100 cm^{-1} and has only 1–2% transmitted signal fluctuations in the range from 80 to 130 cm^{-1} .

Raman spectra for thin overlayers were acquired using a homebuilt scanning tunneling microscope based tip-enhanced Raman setup (STM-TERS), described elsewhere, and equipped with a new notch filter from Ondax Inc. [19].

2.5. Secondary ion mass spectrometry (SIMS)

SIMS data were collected using a commercial TOF.SIMS⁵ (Ion-TOF GmbH) instrument equipped with a 25 kV pulsed Bi_3^{++} primary ion gun. The analyzed area corresponded to a square size of 300 $\mu\text{m} \times 300 \mu\text{m}$. The primary ion current used was ca. 0.2 pA. The spectra were collected with ion densities below 1.8×10^{10} ions cm^{-2} assuring data collection under the static regime.

3. Results and discussion

Fig. 1(a) shows a large area STM image of the Au surface obtained after the immersion of Au/mica film into the 4,4'-BiPy solution (adjusted with 0.1 M HCl to pH = 3) for two days at room temperature. As shown in a zoomed image in Fig. 1(b) a periodic overlayer structure was found on flat terraces of the Au(111) face. The overlayer consists of bright stripes having a width of ~7.5 Å. The stripes are separated by a region of dark contrast having a width of ~3 Å, as indicated in Fig. 1(b). The depth of dark vacancies (DV) present in the overlayer is in the range of 1.3–1.5 Å. The overlayer was observed to grow along the crystallographic directions of the underlying Au(111) surface as shown in Fig. 1(c). A similar overlayer structure was observed by Wang et al. and has been proposed to originate from flat-lying molecules [20]. In this work further insights into overlayer formation were obtained. By careful alternation of the tunneling conditions and scanning speed, another structure that originated from the underlying layer was detected, overlapped with the striped structure described above, as shown in Fig. 1(d) (notice the transition at the bottom of the image). In this underlying layer, individual atoms, arranged into a rectangular lattice with a unit cell of $a = 5$ Å, could be resolved, as shown in Fig. 1(e) and (f). This atomic arrangement is assigned to the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, which has been observed upon adsorption of 0.33 ML of Cl_2 on the Au(111) surface at room

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