

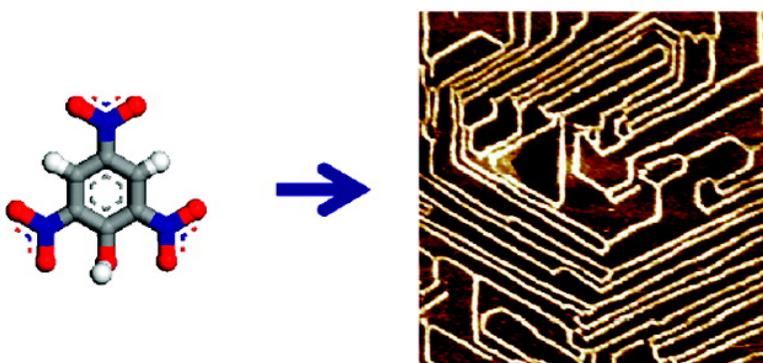
Article

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Oriented Organic Islands and One-Dimensional Chains on a Au(111) Surface Fabricated by Electrodeposition: An STM Study

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Abstract: Organic islands and oriented one-dimensional (1D) chains are fabricated on a Au(111) surface by electrodeposition. The cyclic voltammograms (CVs) of Au(111) in solutions containing nitrobenzene and picric acid show an electrochemical reaction in a negative potential region, which results in irreversible reductive deposition. The deposition process is monitored by in situ electrochemical scanning tunneling microscopy (ECSTM). At the double layer potential region, for example, nitrobenzene molecules form a well-defined adlayer in a ($\sqrt{3} \times \sqrt{3}$) structure. With potential shifting negative to the reductive region, nitrobenzene is reduced to hydroxyaminobenzene. Organic islands were formed first and then aggregated into ordered 1D chains. The formation of these organic islands and 1D chains is completely potential-dependent. Intriguingly, the so-prepared islands and 1D chains are well-oriented along the reconstructed lines of the underlying Au(111) substrate and stable under ambient conditions even if the sample was removed from electrolyte solution. The results reported here provide a simple and effective method to fabricate oriented organic nanodots and nanowires on a solid surface by an electrochemical technique.

Introduction

Controlled and patterned fabrication with organic molecules on a solid surface is a challenge in nanotechnology and materials science.^{1–3} Fabricating nanometer-scale elements such as dots, wires, films, and desirable patterns is an important issue and a prerequisite in micro/nanoelectronics and manufacturing nanodevice.^{4–7} With the development of organic solids, functional organic molecules were demonstrated to be promising candidates in solar cells, organic field-effect transistors (OFETs), information storage, etc.^{8–10} The most common techniques for preparing organic films and patterns include physical vapor deposition, dip-pen, spin-coating, STM or UV-light-induced polymerization, and microfabrication.^{11–17} For example, by pulsing iodine-

coated Au(111), polythiophene has been directly visualized.^{18,19} A well-ordered array of organic molecular chains on a Cu(110) surface by controlled oxidation succeeded under UHV.²⁰ On the other hand, electrochemistry plays an important role in surface pattern fabrication and nanotechnology.^{21,22} Underpotential deposition produces submonolayer formation of metallic atoms.²³ Layer by layer deposition can be achieved by controlling electrode potential.²⁴ Furthermore, Kolb et al. successfully fabricated well-defined patterns on various substrates by electrodepositing atoms from the STM tip.²⁵ Yau et al. reported an electrochemical polymerization of aniline on Au(111).²⁶ These

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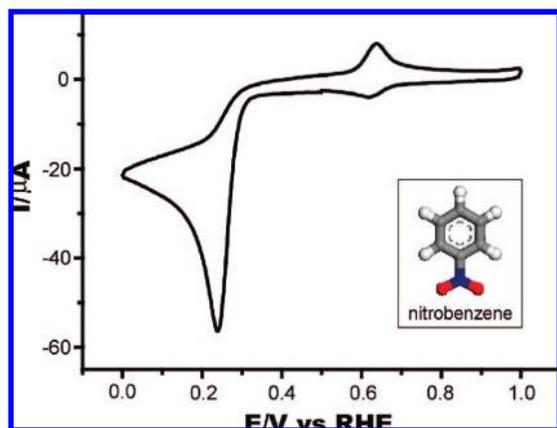


Figure 1. The cyclic voltammogram of a Au(111) electrode in 0.1 M HClO₄ + 0.1 mM nitrobenzene. The potential scan rate was 50 mV s⁻¹. The inset is the chemical structure of nitrobenzene.

works are very important in fabricating surface patterns. However, fabricating oriented, stable, and controlled organic dots, wires, and patterns is still of interest in nanotechnology and the development of electronic devices.

In this paper, we report an electrochemical deposition of organic molecules on Au(111). Nitrobenzene and picric acid are molecules containing nitro groups. These molecules are well studied in antiterrorism and environmental protection.^{27,28} The cyclic voltammograms (CVs) of Au(111) in solutions containing nitrobenzene and picric acid show an electrochemical reaction at a negative potential region, which results in irreversible reductive deposition. The nitro groups will be gradually reduced into hydroxyamino and amine dependent on applied electrode potentials.²⁸ Taking this advantage, we have successfully deposited oriented organic islands and 1D chains on Au(111). The formation of these oriented organic islands and chains were intensively investigated by in situ electrochemical STM. The process was clearly observed during deposition. It is found that although a well-defined nitrobenzene adlayer in a ($\sqrt{3} \times \sqrt{3}$) symmetry was observed at a double layer region, hydroxyaminobenzene molecules aggregated into islands at a reductive potential. With the time release and potential change, the islands form well-oriented one-dimensional organic chains. The width of the chains is on a nanometer scale. This process is totally potential-dependent similar to the process of metallic atom deposition. Intriguingly, the organic chains are well-oriented along the reconstructed line of a Au(111) substrate and form regular patterns. The resulting chains are stable under ambient conditions even if the sample was removed from electrolyte solution. The results demonstrate that electrodeposition would be a simple and effective method to fabricate oriented organic nanodots and nanowires on a solid surface.

Results and Discussion

1. Deposition in Nitrobenzene Solution. Figure 1 is a cyclic voltammogram of a Au(111) electrode obtained in a solution of 0.1 M HClO₄ + 0.1 mM nitrobenzene. In this experiment, the first scan was made in a negative direction from 500 mV

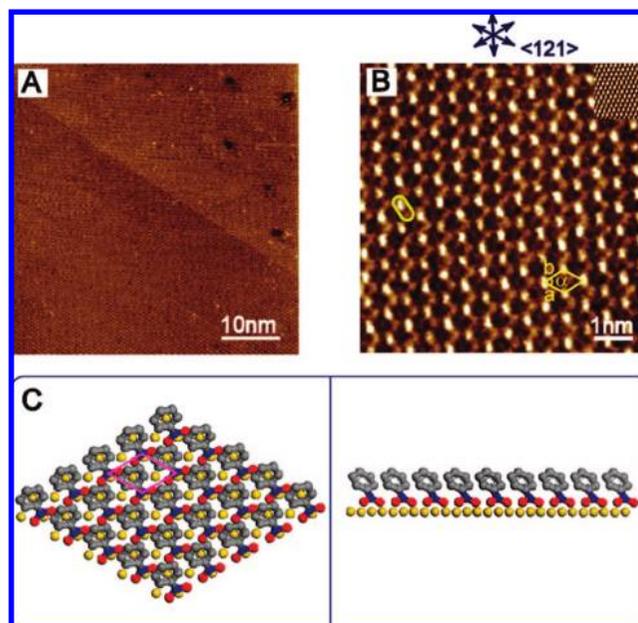


Figure 2. (A) Large scale and (B) high resolution STM images recorded on nitrobenzene adlayer at 550 mV in 0.1 M HClO₄ + 0.1 mM nitrobenzene. The imaging condition is $E_{\text{bias}} = -186$ mV and $I_{\text{tip}} = 3.2$ nA. The inset in B is an atomic resolution STM image of the underlying Au(111) substrate (4 nm \times 4 nm). (C) Proposed structural model for the ordered adlayer with top view (left) and side view (right).

vs RHE (reversible hydrogen electrode in 0.1 M HClO₄). In the CV an irreversible cathodic peak at 240 mV can be seen, which is ascribed to the reduction of the nitro functional group to a hydroxyamino group with a four-electron transfer.^{29,30} The paired asymmetric peaks near 650 mV in the CV are due to the oxidation/reduction of the hydroxyamino/nitroso group. After the electrochemical measurement, the structural change with the reductive electrodeposition of nitrobenzene on a Au(111) surface is investigated by in situ electrochemical STM. The structure and structural transition of nitrobenzene adlayer were clearly observed.

Figure 2A is a typical large-scale STM image recorded on Au(111) in a solution of 0.1 M HClO₄ + 0.1 mM nitrobenzene at 550 mV. It is clear that the atomically flat terrace is now covered by a well-ordered nitrobenzene adlayer. The molecules form regular molecular rows. The internal molecular structure, orientation, and packing mode are revealed by a high resolution STM image shown in Figure 2B. In order to determine the molecular orientation in the nitrobenzene adlayer in the experiment, the lattice of Au(111) substrate was also imaged by changing bias potential as shown in the inset of Figure 2B. By comparison with the underlying lattice, it is concluded that the molecular rows are parallel to the direction of the underlying Au(111) substrate. On the basis of the adlayer symmetry, a unit cell is outlined. The parameters of the unit cell are measured to be $a = b = 0.52 \pm 0.05$ nm. The crossing angle of molecular rows is $\alpha = 60 \pm 2^\circ$. Therefore, a ($\sqrt{3} \times \sqrt{3}$) structure can be decided for the ordered nitrobenzene adlayer. It is noted from the chemical structure and molecular size that there is not enough space to accommodate nitrobenzene molecules in the as-proposed ($\sqrt{3} \times \sqrt{3}$) unit cell in a flat-lying orientation. A careful observation reveals that each molecule in the STM image can be recognized as a set of two spots, as indicated by a yellow

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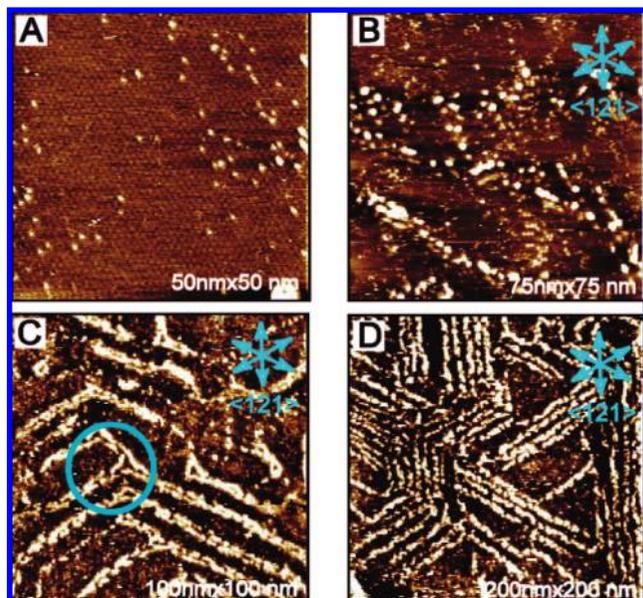


Figure 3. (A–C) STM images recorded on nitrobenzene adlayer at 300, 220, and 200 mV, respectively. The imaging condition in A: $E_{\text{bias}} = -186$ mV, $I_{\text{tip}} = 2.4$ nA; B: $E_{\text{bias}} = -61$ mV, $I_{\text{tip}} = 3.5$ nA; C: $E_{\text{bias}} = -97$ mV, $I_{\text{tip}} = 4.5$ nA. (D) STM image obtained by holding the potential at 200 mV for 4 h. Imaging condition is $E_{\text{bias}} = -97$ mV and $I_{\text{tip}} = 4.7$ nA.

circle. In addition, one spot is usually brighter than another in a single molecule. Therefore, it is reasonable to conclude that nitrobenzene molecules in the adlayer take a tilted orientation on a Au(111) surface. In this adsorption configuration, the nitrobenzene molecules bind on Au(111) with their nitro groups, while the phenyl rings tilt on the surface, resulting in the difference contrast in the STM image. The bright spot in the STM image corresponds to the phenyl group and the dark spot to the nitro group. Based on the above analysis, a tentative structural model with top and side views for the ordered nitrobenzene adlayer is proposed in Figure 2C.

After the STM images of the ordered nitrobenzene adlayer were recorded at 550 mV, the electrode potential was negatively shifted at an increment of 10 mV. Figure 3A–C shows the typical STM images acquired on a Au(111) surface at different potentials. It is observed from Figure 3A that bright islands appear on the ordered nitrobenzene adlayer at 300 mV, where the nitro group reduction is initiated and results in the formation of hydroxyamino group, consistent with the results in CV measurement in Figure 1. Several molecular defects are also observed in this image. When the electrode potential is shifted to 220 mV, the density of the islands is clearly increased and the islands locally form a continuous short chain as shown in Figure 3B. Further shifting potential to 200 mV results in the formation of a well-oriented 1D molecular chain shown in Figure 3C. A careful inspection found that the chain consists of two subchains, as the part marked by a blue circle in Figure 3C. The average width of the chain is measured to be about 4 nm. The chains are found to be composed of molecular islands. From this observation, it is reasonable to conclude that the oriented chains are formed by an accordant aggregation of islands with the potential shifting. By comparison of the chain orientation and underlying Au(111) substrate, it is found that the so-formed chains preferentially align along the direction of the underlying Au(111) lattice and lie in the reconstructed herringbone lines of the Au(111) surface.

The previous results have demonstrated a strong selectivity in the adsorption sites of the adsorbate such as surface defect, step edge,^{31,32} and reconstructed herringbone line.^{33–36} The adsorption at these sites will decrease the total energy of a system between adsorbate and adsorbed substrate and thus form a stable adlayer. In the present study, when the reductive electrodeposition at a negative potential region is happening, the nitrobenzene molecules will be reduced into hydroxyaminobenzene with a structural transition from the previous ($\sqrt{3} \times \sqrt{3}$) structure. For structural formation and transition, it is known that the interactions between adsorbates and adsorbate/substrate play dominant roles. Compared with the interaction between nitrobenzene and the Au(111) substrate, the interaction between hydroxyaminobenzene and Au(111) is weak because of the nitro group reduction to hydroxide. Benzene as well as the phenyl ring has a weak interaction with the Au(111) substrate. Benzene has a high mobility on Au(111) so that there is no ordered adlayer formed at room temperature, in contrast to the ordered structure of benzene on Pt(111), Rh(111), and Cu(111).^{37–39} In the present research, it is believed that the hydroxyaminobenzene molecules adsorb but diffuse on a Au(111) surface. The diffusion produces an adlayer without long-range ordering as shown in Figure 3. However, the reconstructed herringbone lines on a Au(111) surface acts as a barrier and template. Owing to the position selectivity, the diffused molecules cease at the herringbone region, which thus results in a stable hydroxyaminobenzene adlayer. Because of the random diffusion and congregation, the molecular islands are formed first. Through island aggregation, the 1D organic chain is finally induced along the surface herringbone template. Figure 3D is a typical STM image obtained after holding the potential at 200 mV for 4 h. It can be seen from the image that the density and continuity of the linear chains have increased.

It is interesting to note that at the initial stage of the reductive deposition, the coexistence of short-range ordered molecular clusters, dispersed islands, and discontinuous chains can be observed. Figure 4A is a typical STM image demonstrating the coexistence. The image was acquired at 220 mV. The yellow and red arrows indicate a molecular cluster and dispersed island, respectively. The structural details of the clusters and the dispersed islands are revealed by a high resolution STM image in Figure 4B. Individual molecules are clearly seen in the image. Each molecule can be recognized as a set of three bright spots forming a triangle. From the results of electrochemical measurement, the molecules at this potential should be hydroxyaminobenzene. A careful observation found that the molecular orientation is different among these molecules and without long-range ordering. The ordered adlayer can only correspond locally in the upper left region of the image. In this region, the

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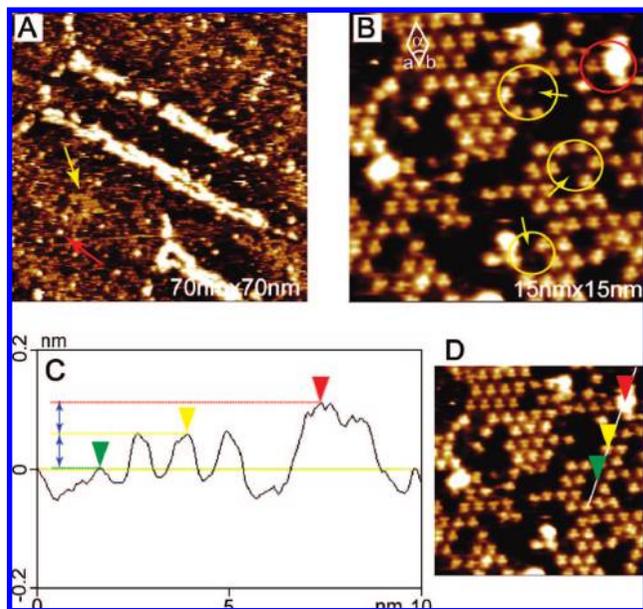


Figure 4. Large scale (A) and high resolution (B) STM images acquired at 220 mV. The imaging condition for B is $E_{\text{bias}} = -93$ mV and $I_{\text{tip}} = 3.2$ nA. The yellow circles and arrows indicate the dark region. Red circles indicate an island. (C) A topographic profile for the indicated line in Figure D. (D) STM image showing the position for cross-sectional profile measurement.

molecular rows align along the underlying lattice and the molecules take the same orientation on a Au(111) surface. A unit cell is outlined. The parameters of the unit cell are measured to be $a = b = 1.0 \pm 0.1$ nm. The crossing angle α is $60 \pm 2^\circ$. Therefore, a (3×3) structure can be determined, different from $(\sqrt{3} \times \sqrt{3})$ structure at 550 mV. As indicated above, from electrochemical results, the nitrobenzene molecule should be reduced to hydroxyaminobenzene at this potential. From the molecular image and intermolecular distance, the hydroxyaminobenzene molecules in the (3×3) structure take a flat-lying orientation on a Au(111) surface. Furthermore, molecular defects are also visible in the STM image such as the dark region indicated by yellow circles and arrows in Figure 4B. A bright molecular island is also indicated by a red circle in this image. To understand the corrugation height difference, a cross-sectional profile along island, molecule, and defect was measured as shown in Figure 4C. The red, yellow, and green arrows indicate the three different structures of island, individual molecule, and dark area in the defect region. It can be seen from the cross-sectional profile that there is a sequence corrugation height difference of ca. 0.06 nm between dark region (green arrow) and individual molecule (yellow arrow) and island (red arrow). The results demonstrate a continuous multilayer of the hydroxyaminobenzene molecules on Au(111) at the initial deposition. However, with the sustaining deposition, molecular diffusion and aggregation result in the formation of organic chains. No ordered molecular ordering could be observed on the chain surface because of random aggregation. On the basis of the above analysis, it is clear that the islands and chains can be electrodeposited by controlling potential. The hydroxyaminobenzene molecules accumulate, forming islands and chains. From the chemical structure of the hydroxyaminobenzene molecule, intermolecular reaction, such as hydrogen bonding between molecules and π - π stacking between different layers, could be responsible for the formation of islands and chains. The well-oriented chains are consistently observed at a reductive

potential region even if the potential was scanned to 100 mV. Furthermore, the well-oriented 1D chains are stable on Au(111) not only in solution under potential control but also under ambient conditions even after being removed from solution without potential control, as shown in Figure S1 of Supporting Information. A schematic illustration for the potential dependent deposition process is shown in Figure 5. With the electrode potential shifting negatively, the adlayer with long-range ordered structure at the double layer region is transferred to islands and oriented 1D organic chains.

2. Deposition in Picric Acid Solution. To understand the role of the nitro group in organic island and 1D chain formation, the reductive deposition of picric acid has been also investigated. Figure 6 shows the CV of Au(111) in a solution of 0.1 M HClO_4 + 0.1 mM picric acid. On the basis of the result reported previously,²⁸ three irreversible negative peaks at 370, 320, and 250 mV are ascribed to the sequential reduction of three nitro groups to hydroxyamino groups, which are finally reduced into amine groups. The peak at 930 mV is due to the oxidation of the amine group. As an indirect indication, this peak can only be observed in the second cycle of the CV. If the CV is scanned positively from 500 mV, the oxidative peak was not observed at the first cycle (see Figure S2 in Supporting Information).

Figure 7A–D show a series of STM images acquired by shifting the electrode potential from 500 to 200 mV. Different from nitrobenzene, picric acid molecules do not form ordered structures on Au(111) at 500 mV. A disordered adlayer is seen in Figure 7A. Aligned bright clusters appear on the surface at 360 mV, indicated by yellow ellipses in Figure 7B. The islands locally form a continuous short chain. Decreasing the potential to 250 mV, islands align one by one along with the preferred direction in Figure 7C. With the island aggregation, 1D organic chains are formed. A well-defined chain pattern like a “circuit line” is seen at 200 mV, as shown in Figure 7D. These oriented chains with a width of ca. 7 nm extend in a large area on a Au(111) surface. A careful observation found that the patterned chains are preferentially along the reconstructed lines of underlying Au(111) (Figure S3 in Supporting Information). The deposition of the organic molecules is totally dependent on electrode potential. Although elucidation of the component detail of the chains is in progress, it is clear that the formation of the organic islands and chains is a function of applied potentials. With the potential shifting negative to 100 mV, well-oriented 1D chains were consistently observed on Au(111).

In summary, the electrodeposition is investigated on Au(111) in 0.1 M HClO_4 solution containing nitrobenzene and picric acid molecules by CV and STM. Both CVs obtained at Au(111) in two solutions show irreversible cathodic reductive peaks. At the double layer potential region, an ordered nitrobenzene adlayer with a $(\sqrt{3} \times \sqrt{3})$ structure was observed on Au(111), while a disordered structure was observed on Au(111) in a picric acid-containing solution. Intriguingly, oriented organic islands and 1D chains with the two molecules can be fabricated on Au(111) by a simple electrochemical reductive deposition. The formation process is clearly seen in in situ STM. It is found that the formation of islands and chains is potential-dependent and the islands and chains are oriented preferentially along the reconstructed lines of the underlying Au(111) surface. Molecular aggregation and diffusion on a Au(111) surface in the reductive deposition is responsible for the formation of the oriented islands and chains. Furthermore, the so-prepared islands and 1D chains are stable in not only electrolyte solution under potential control but also under ambient conditions when Au(111) electrode was

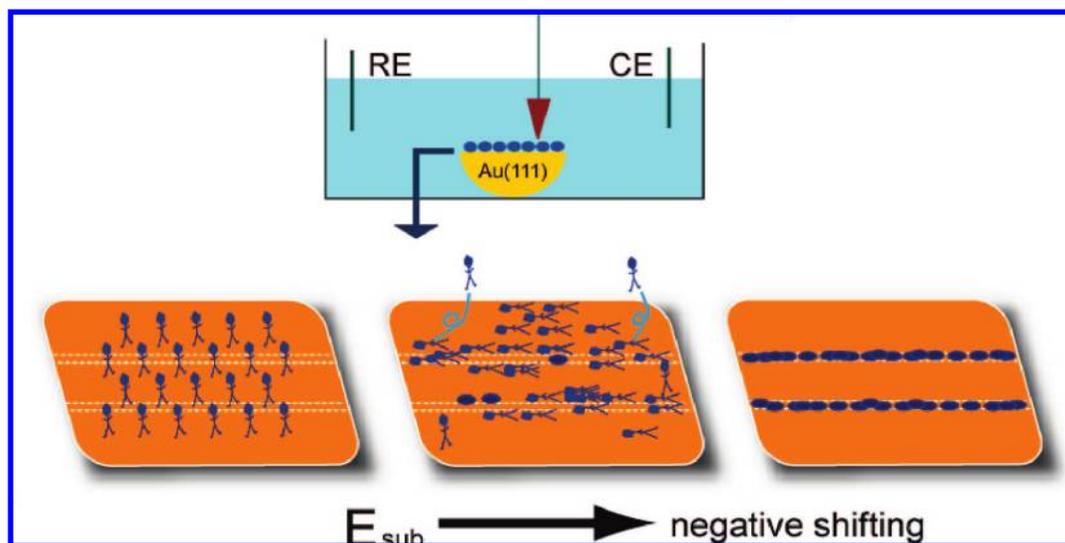


Figure 5. The structural transition of the nitrobenzene adlayer at the potentials from the double layer region (left) to the initial reductive stage (middle) and stable reductive stage (right). The dashed lines show the reconstructed lines of the underlying Au(111) substrate.

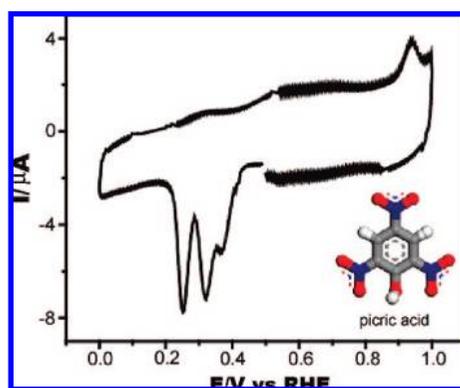


Figure 6. The cyclic voltammogram of a Au(111) electrode in a solution of 0.1 M HClO₄ + 0.1 mM picric acid. The scan rate was 60 mV s⁻¹. The first scan was made in a negative direction from 500 mV.

removed from solution. The results provide an electrochemical method to fabricate and control organic nanopatterns and demonstrate the possibility of constructing oriented organic nanodots and nanowires on a solid surface by electrodepositing organic molecules.

Experimental Section

Nitrobenzene (Sigma-Aldrich) and picric acid (Sigma-Aldrich) were used as received. Electrolyte solution was prepared with ultrapure HClO₄ (Aldrich Chemical Co., 99.999%) and Milli-Q water (Milli-Q, ≥ 18.2 M Ω , TOC < 4 ppb). Molecular models of the nitrobenzene adlayer were built in HyperChem 6.0 and Material Studio 3.0.

Cyclic voltammetry measurements were performed with an EG&G PAR (Princeton Applied Research) Basic Electrochemical System. A reversible hydrogen electrode (RHE) and a platinum wire were used as reference and counter electrodes, respectively. The solutions were deaerated with high purity N₂ before experiments. All electrode potentials were reported with respect to the RHE in 0.1 M HClO₄.

Electrochemical STM experiments were carried out by using a NanoScope E scanning tunneling microscope (Digital Instrument Inc., Santa Barbara, CA). Well-defined Au(111) was prepared by the method described previously.¹⁵ The tunneling tips used were prepared by electrochemical etching of a tungsten wire (0.25 mm in diameter) in 0.6 M KOH. To minimize faradic current, the

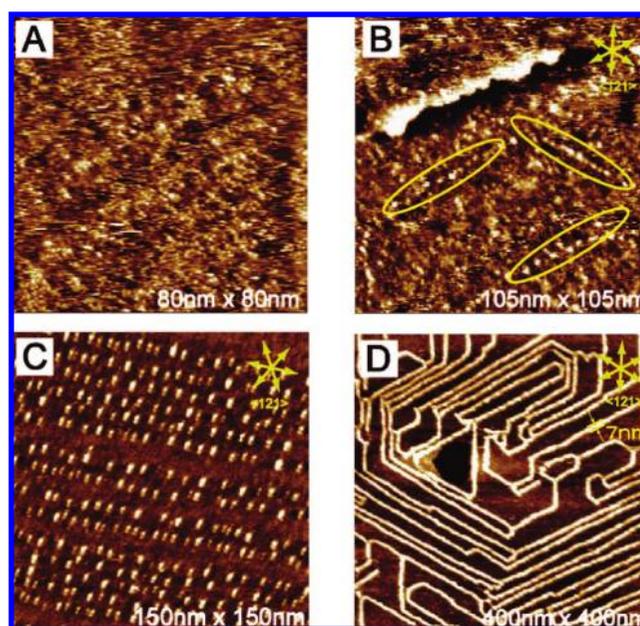


Figure 7. Typical STM images during the deposition of picric acid on Au(111) in 0.1 M HClO₄ at (A) 500 mV, (B) 360 mV, (C) 250 mV, and (D) 200 mV.

sidewalls of the tips were sealed with transparent nail polish. All the STM images were collected in the constant-current mode.

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Supporting Information Available: The STM image showing oriented organic 1D chains under ambient conditions, cyclic voltammograms of Au(111) in 0.1 M HClO₄ solution containing 0.1 mM picric acid made in a positive direction in the first cycle, and the STM image including both organic chains and reconstructed lines. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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