

Tailoring Phthalocyanine Metalation Reaction by Quantum Size Effect

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Considerable progress has been made in developing a novel catalyst by modifying the surface composition and structure in recent years.^{1,2} Alternatively, one can tailor surface chemistry by exploiting the quantum size effect (QSE) in nanostructured systems. For example, in a metal ultrathin film grown on a semiconductor substrate, the electrons are strongly confined by the semiconductor band gap and vacuum barrier. Due to this quantum confinement, the electronic structure of the film is thickness-dependent. As a result, its surface reactivity could be tuned by the film thickness with atomic-layer precision.^{3–6} Thickness variation of only one atomic layer was shown to lead to a change of factor 3 in surface oxidation of Pb films.⁵ However, what was observed in these studies is actually a surface property manifestation of the quantum films themselves. Whether a chemical reaction can indeed be modulated by QSE remains unexplored.

In this Communication, we report on the direct evidence for a QSE-modulated chemical reaction by studying the metalation of phthalocyanine (H₂Pc) (Figure 1a) with Fe atoms on Pb(111) films. The metalation reaction has previously been investigated on Ag(111),⁷ but the substrate effect for catalyzing the reaction is not well understood. By directly imaging the reactants (H₂Pc molecules and Fe atoms) and iron phthalocyanine (FePc) products on Pb mesa by scanning tunneling microscopy (STM), we could precisely measure the amount of FePc products when the thickness varies one atomic layer by one atomic layer. The situation allows us to establish a direct relation between QSE and surface reaction with atomic-layer precision.

Our experiments were conducted in a Unisoku ultrahigh vacuum low temperature STM system where a molecular beam epitaxy chamber is installed for *in situ* sample preparation. The base pressure of our system is 5.0×10^{-11} Torr. The wedge-shaped Pb(111) mesas (Figure 1b) with various thicknesses were grown on Si(111) substrate, and the detail of growth was described elsewhere.^{5,6} The unique geometry with a flat-top (111) surface and consecutive thickness of the Pb mesa enables us to study the thickness-dependent behavior under identical experimental conditions. H₂Pc and FePc molecules (Alfa Aesar) were first outgassed by heating to 540 K for 48 h in vacuum. During deposition, the temperature of the Knudsen cell was 510 K for H₂Pc and 500 K for FePc, respectively. High purity Fe (99.999%) atoms were dosed from a PBN Knudsen cell at a constant flux rate of approximately 0.00025 ML/s. Here 1 ML is defined as the atom density of the Pb(111) surface, 9.43×10^{14} atoms/cm². The STM measurements were carried out at 80 K with a constant current of 0.1 nA using a polycrystalline PtIr tip. All STM topographic images were processed by WSxM software.⁸

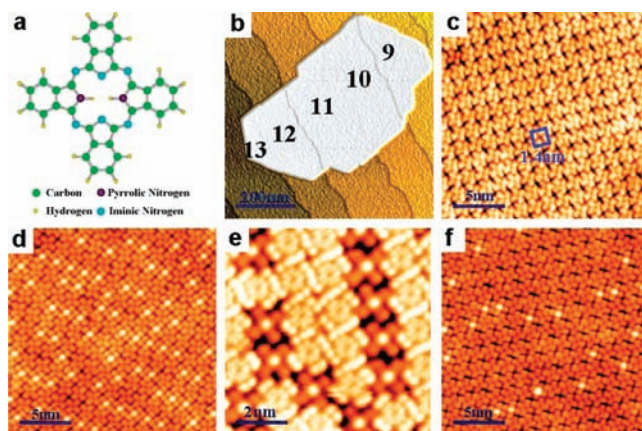


Figure 1. (a) Schematic structure of the H₂Pc molecule. (b) STM image of a typical Pb mesa (white-colored) grown on the Si(111)-7×7 substrate (yellow and dark-yellow colored). The integer numbers dictate the Pb film thickness of the corresponding region in a unit of atomic layer. (c) STM image showing the self-assembled monolayer of H₂Pc on the Pb mesa. The unit cell with a lattice constant of 1.40 ± 0.05 nm is indicated by the blue square. (d) STM image after 0.06 ML Fe deposition onto the H₂Pc monolayer. The molecules with bright center are FePc. (e) High resolution STM image showing the intact molecular orbitals of the H₂Pc molecules. (f) STM image showing the self-assembled monolayer of the mixed FePc (8%) and H₂Pc (92%) molecules, obtained by codepositing H₂Pc and FePc onto the Pb mesa. The tunneling bias (with respect to the sample): (b) 5.0, (c) -0.7, (d) -0.9, (e) 0.7, (f) -1.0 V.

We first carried out an experiment to demonstrate the occurrence of the reaction $\text{H}_2\text{Pc} + \text{Fe} \rightarrow \text{FePc} + \text{H}_2$ on Pb mesas. After deposition of ~ 1.2 ML H₂Pc onto the bare Pb mesas held at room temperature (RT), the self-assembled H₂Pc monolayer was formed, as shown in Figure 1c. Each molecule was imaged as a symmetric cross-like structure with a cavity at the center, in agreement with its structure model depicted in Figure 1a. Further Fe deposition (0.06 ML) on this H₂Pc monolayer at RT lead to the occurrence of bright spots at the center of the molecules, while others remained undisturbed (Figure 1d). Under special tip conditions, possibly terminated by a molecule, the intact molecular orbitals of the H₂Pc molecule could be resolved,⁹ as shown in the high resolution STM image in Figure 1e. The molecules with a bright spot at the center are presumably newly formed FePc molecules in terms of the reaction $\text{H}_2\text{Pc} + \text{Fe} \rightarrow \text{FePc} + \text{H}_2$.⁷ The enhanced contrast at the molecular center is a result of the *d*-orbital contribution of the Fe (II) *d*⁶ system near the Fermi level.¹⁰ To prove the molecule with a bright center to be a FePc molecule, a monolayer mixed with 8% commercial FePc and 92% H₂Pc molecules was prepared on a Pb mesa. The high resolution STM image of the FePc molecules in Figure 1f shows exactly the same structure as that in Figure 1d and 1e. Further deposition of Fe increased the number of molecules with a bright

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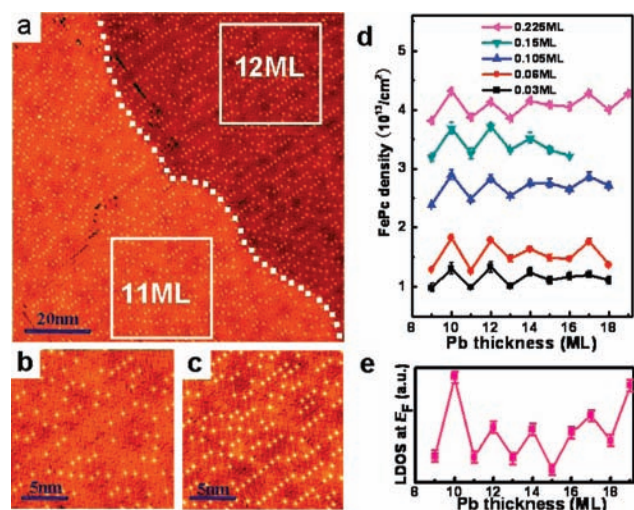


Figure 2. (a) STM image showing different areal density of the FePc products on 11 ML and 12 ML Pb films taken with a sample bias of -2.0 V. The white dotted line indicates the boundary of 11 ML and 12 ML. (b) and (c) Zoom-in STM images from the marked regions in (a) depicting the thickness-dependent metalation. (d) Thickness-dependent FePc density at different Fe coverage. Each data point was obtained by averaging 5–7 extended STM images (size: 50×50 nm², ~ 1300 molecules). (e) Local DOS (E_F) as a function of Pb film thickness measured by using lock-in technique with a bias modulation at 3 kHz. The one-to-one correspondence between the FePc areal density and DOS (E_F) is clearly noted.

center (not shown). Again, in this case we see no difference between the initially deposited FePc molecules and the newly formed FePc molecules. The result suggests that the metalation reaction of H₂Pc molecules through the oxidation of Fe atoms and release of the pyrrolic hydrogen atoms as H₂⁷ occurs on the Pb mesa surface at RT.

To reveal the substrate effect, we then investigated the surface morphology of the Pb surface at different thicknesses after reaction. Figure 2a shows a typical STM image after 0.06 ML Fe deposition on the H₂Pc monolayer at RT. Obviously, the areal density of FePc on 12 ML is greater than that on 11 ML, indicative of the stronger catalytic activity of the 12 ML Pb film. The situation is more clearly seen in the zoom-in images in Figure 2b (11 ML) and 2c (12 ML). Quantitative measurement with five different Fe coverages (0.03, 0.06, 0.105, 0.15, and 0.225 ML) of the reaction products (FePc) is summarized in Figure 2d (see Supporting Information). For each Fe coverage studied, the FePc density always shows an up–down oscillation with a period of 2 ML. Furthermore, below 16 ML, the FePc density on even-layered films is higher, but above 16 ML it turns to odd-layered films. The observed transition thickness 16 ML is the beating point, which can be well-understood under the Sommerfeld–Bohr quantization rule for Pb thin films.^{5,6,11–14} The thickness-dependent reaction activity provides compelling evidence that the Pb substrate does contribute to the metalation reaction. This is further verified by the experiment with the second-layer H₂Pc molecules. In this case, no reaction is observed (not shown), and the metalation occurs predominantly on the first monolayer directly supported by Pb.

In view of the mechanism of such a reaction, one possibility is that the newly formed FePc molecules preferentially adsorb on even-layered Pb films. In this case, a significant position exchange process between the existing H₂Pc molecules and the FePc product molecules has to be involved. It is unlikely because the molecules in the densely packed monolayer must be laterally displaced. To further demonstrate this, we coevaporated H₂Pc and FePc molecules

onto the Pb mesas and measured the density of FePc. The result showed no obvious difference in the FePc density for all Pb film thicknesses studied. The sticking coefficient of Fe atoms is another factor to be considered since the sticking probability and diffusion barrier of Fe on Pb are thickness-dependent. However, this possibility can be excluded by our previous study because the observations are anticorrelated: the stronger metalation here occurs on the thickness of smaller Fe sticking probability.¹⁵ We then consider that the reaction occurs through hybridization interaction between the Pb surface and the adsorbed H₂Pc molecules, which modifies the reaction activation barrier. In terms of the fact that Pb has a much lower electron affinity (0.36 eV) with respect to H₂Pc (~ 2.74 eV),¹⁶ charge transfer from Pb to H₂Pc molecules will occur, which results in partial reduction of the pyrrolic hydrogen cations and thus lowers the reaction activation barrier. Figure 2e shows our measured local density of states at the Fermi level (LDOS(E_F)) as a function of film thickness, revealing a 2-ML oscillation and an odd–even transition at 17 ML.^{5,11–14} One can clearly see that the LDOS(E_F) has a one-to-one correspondence to the density of FePc products (Figure 2d). A higher LDOS (E_F) implies that more electronic states are involved in hybridization, which reduces the barrier more effectively. Consequently, the even-layered films exhibit stronger catalytic activity because of their higher LDOS(E_F). In the thickness regime above 16 ML, the situation is reversed. However, the mechanism holds the same.

In summary, QSE modulated catalytic activity for a chemical reaction is demonstrated for the first time by our STM study of the metalation of the H₂Pc molecules on Pb thin films. We expect that this study opens a path for studying QSE-tuned catalysis.

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Supporting Information Available: Figures S1–S4 and Table S1 show how the quantitative measurement was conducted in Figure 2d. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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