

Structures of a CO adlayer on a Pt(100) electrode in HClO₄ solution studied by *in situ* STM

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We have obtained the first *in situ* STM atomic images of a CO adlayer on a Pt(100)-(1 × 1) electrode in 0.1 M HClO₄ solution, exhibiting a phase transition from c(6 × 2)-10CO to c(4 × 2)-6CO at $E > 0.3$ V vs. RHE.

The adsorption of CO molecules on a Pt surface is an important topic in various fields such as electrochemistry and surface science.¹ Because Pt anode catalysts (nm-sized Pt supported on carbon black) in a polymer electrolyte fuel cell (PEFC) are seriously poisoned by a trace amount of CO in a reformed fuel,² understanding the phenomenon of CO adsorption on the Pt surface is essential to find a clue for designing a high performance catalyst with CO tolerance. The structures of CO adlayers on a Pt(111) surface, which is the predominant facet exposed by the Pt nanoparticles, have been well characterized by various surface-sensitive techniques.³ In contrast, there are only a few studies on the CO adlayer structure on the well defined Pt(100)-(1 × 1) electrode although Pt(100) is also a very important low-index facet.^{4–7} Markovic *et al.* claimed that the CO adlayer on Pt(100) did not exhibit a long-range ordered structure by using *in situ* surface X-ray scattering (SXS).⁶ In contrast, some ordered structures were observed by *ex situ* low energy electron diffraction (LEED)⁵ and *in situ* STM.⁷ Yoshimi and Ito reported a c(2 × 2)-2CO structure by using *in situ* STM.⁷ However, the CO coverage of 0.5 based on the c(2 × 2)-2CO structure is much smaller than those reported by the other groups,^{4,6} probably because their STM observation was carried out on narrow terraces of Pt(100). Thus, these results reported so far are quite conflicting.

In this paper, we, for the first time, demonstrate clear atomic images of a CO adlayer on a well-defined Pt(100)-(1 × 1) electrode in 0.1 M HClO₄ solution by *in situ* STM techniques. A phase transition from c(6 × 2)-10CO to c(4 × 2)-6CO was found to be triggered by raising the electrode potential. Furthermore, we found an additional CO adlayer structure in the vicinity of steps, which indicates a difference in the electronic properties of the Pt(100) surface between terraces and steps.

A (100) facet formed on a single crystal bead made by melting a Pt wire (4N, Tanaka Kikinokoku, Japan) was used for the *in situ* STM measurements. The single crystal electrode was cooled in a high purity H₂ stream (6N, Sumitomo Seika, Japan) after being annealed in a hydrogen flame, followed by immersing into pure water saturated with H₂. This procedure for preparing the Pt(100) electrode resulted in an atomically flat terrace of (1 × 1) usually extended over 50 nm.⁸ The *in situ* STM apparatus employed was a Nanoscope E (Digital Instruments, USA). The details for the STM

measurement are the same as described in the literature.⁹ The electrolyte solution was prepared from ultrapure grade HClO₄ (Kanto Chemical Co., Japan) and Millipore-Q water. All electrode potentials are reported with respect to the reversible hydrogen electrode (RHE) in the same electrolyte solution. The adsorption of CO was carried out in 0.1 M HClO₄ saturated with 100% CO (4N, Sumitomo Seika, Japan) at 0.1 V for 10 min, followed by removing dissolved CO from the solution by high purity N₂ (4N, Sumitomo Seika Co., Japan). The STM observation was performed in a N₂-filled chamber. After the STM observation, a CO stripping voltammogram was taken to confirm the presence of CO on the electrode.

First, we observed the structure of the CO adlayer on the flat terrace of the Pt(100) electrode. Fig. 1A shows a high-resolution STM image of the Pt(100) electrode at 0.1 V in the 0.1 M HClO₄ solution purged with nitrogen after the CO adsorption. The STM image exhibits an ordered structure completely different from the square (1 × 1) of the Pt(100) substrate. The bright spots in the STM image can be assigned to CO molecules adsorbed on the Pt(100) surface. The CO molecular rows were aligned along the close-packed row, [110], of the Pt(100) substrate. It is noteworthy that the brightness (a measure of height) of the adsorbed CO molecules periodically changes within each molecular row. A rectangular unit cell for the CO adlayer is shown by a solid line in Fig. 1A. The lattice spacings of the unit cell were found to be 1.60 ± 0.07 nm and 0.55 ± 0.03 nm. From these observations, we can propose a c(6 × 2)-10CO structure for the CO adlayer on Pt(100) at 0.1 V as shown in Fig. 1D. The fractional CO coverage, θ_{CO} , based on this model is calculated to be 0.833, which accords well with the value of 0.85 evaluated at *ca.* 0.05 V (−0.25 V vs. SCE) by an electrochemical method.⁴ The periodical height corrugation of the adsorbed CO in the STM image certainly results from the mismatch between the centred lattice layer of the adsorbed CO and the underlying square lattice of the substrate in registry. The brightest, moderate and dark spots in the STM image can be assigned to on-top, near on-top and bridged CO, respectively. The ratio of on-top to bridged CO, derived from Fig. 1D, is 3 : 2 (60% of total CO). This adlayer structure was maintained below 0.2 V in the solution.

However, a dramatic change in the adlayer structure was observed by increasing the potential $E > 0.3$ V in the same solution. As shown in Fig. 1B, a typical STM image obtained in the high potential region is quite different from c(6 × 2)-10CO or (1 × 1) of Pt(100). This phase transition was found to be irreversible in the N₂-purged electrolyte solution. A rectangular unit cell for the CO adlayer is shown by the solid line in Fig. 1B. Every CO molecular row in this new structure was aligned along

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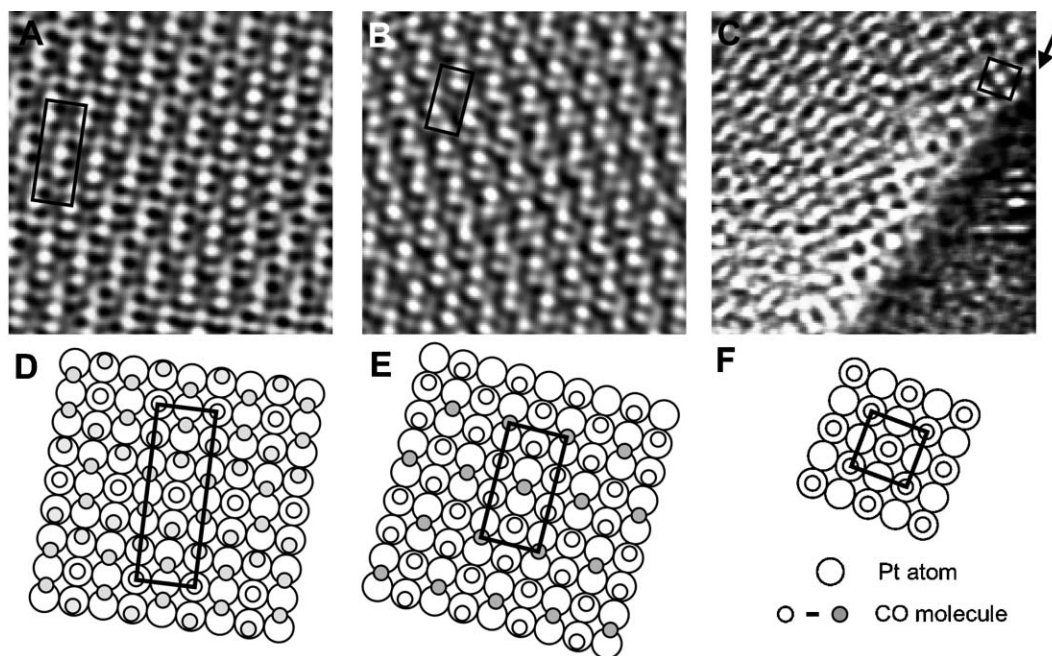


Fig. 1 High-resolution STM images of CO adlayers on a Pt(100) electrode in a 0.1 M HClO₄ solution (A) at 0.1 V and (B) at 0.4 V. (C) A typical STM image of the CO adlayer with a mono-atomic step at 0.35 V. All STM images in the areas of 5 × 5 nm² are filtered. Structural models for (D) c(6 × 2)-10CO, (E) c(4 × 2)-6CO and (F) c(2 × 2)-2CO on a Pt(100) surface.

the [110] direction, similar to the c(6 × 2)-10CO adlayer observed at 0.1 V. The bright and dark spots in the STM image can be assigned to on-top and bridged CO, respectively. The lattice spacings of the new unit cell are 1.06 ± 0.08 nm and 0.57 ± 0.04 nm, which allow us to propose a c(4 × 2)-6CO structure as shown in Fig. 1E. The calculated θ_{CO} was reduced from 0.833 to 0.750 by this phase transition. The same c(4 × 2)-6CO structure was also observed by Rhee *et al.* in their *ex situ* LEED study. However, it is noted that CO was adsorbed at *ca.* 0.05 V in 0.1 M HClO₄ solution, followed by transfer into an ultra high vacuum (UHV) chamber in their work.⁵ As described above, the adlayer structure at such a low potential region is dominantly c(6 × 2)-10CO according to our *in situ* STM. The low θ_{CO} structure obtained in the *ex situ* LEED study can be explained by the partial desorption of CO during the transfer from the electrochemical cell to the UHV chamber. It is also interesting that the ratio of on-top CO in the adlayer (Fig. 1E) was increased to 67% from 60% (in Fig. 1B). This is consistent with the previous result using *in situ* infrared reflection-absorption spectroscopy (IRAS) that the on-top CO was predominant on a Pt(100) electrode in a high potential region.⁴ Thus, at $E = 0.3$ – 0.4 V, θ_{CO} on Pt(100) decreased accompanied by a decrease in the bridged CO probably due to desorption or partial oxidation of CO by increasing the potential. These changes certainly induce the adsorption of water molecules at vacant sites, which subsequently oxidize CO in a higher potential region.

We then focused on the structure of the CO adlayer in the vicinity of a step. At $E > 0.3$ V, an extra structure of the CO adlayer was observed in the vicinity of mono-atomic steps, with the c(4 × 2)-6CO structure on the terraces. Fig. 1C shows a typical STM image of the Pt(100) electrode at 0.35 V with a mono-atomic step indicated by an arrow along the [110] direction. Apparently,

an image different from c(4 × 2)-6CO is seen in the region of 1 nm from the step edge. From the arrangement of bright spots of adsorbed CO in the STM image, this extra structure can be assigned to c(2 × 2)-2CO ($\theta_{\text{CO}} = 0.500$) as shown in Fig. 1F. We assigned these spots to on-top CO, because the height (brightness) of the spots was the same as that of on-top CO in the c(4 × 2)-6CO observed on the terrace. A difference in the electronic properties of the metal surface on terrace and at the step has been reported in theoretical calculations¹⁰ and a high-resolution XPS study.¹¹ The appearance of the c(2 × 2)-2CO structure in the vicinity of the step is the direct evidence of the difference in electronic properties between the adsorption sites, which can trigger the desorption or partial oxidation of CO near the step.

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