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SHOP NOTES

These are "how to do it" papers. They should be written and illustrated so that the reader may easily follow whatever instruction or advice is being given.

Portable ultrahigh-vacuum sample storage system for polarization-dependent total-reflection fluorescence x-ray absorption fine structure spectroscopy

Yoshihide Watanabe,[a] Yusaku F. Nishimura, and Ryo Suzuki
Toyota Central R&D Labs., Inc., Yokomichi 41-1, Nagakute, Aichi 480-1192, Japan

Hiromitsu Uehara
Catalysis Research Center, Hokkaido University, Kita 21-10, Sapporo, Hokkaido 001-0021, Japan

Tomoyuki Nimura
AVC Co., Ltd., Inada 1450-6, Hitachinaka, Ibaraki 312-0061, Japan

Atsushi Beniya and Noritake Isomura
Toyota Central R&D Labs., Inc., Yokomichi 41-1, Nagakute, Aichi 480-1192, Japan

Kiyotaka Asakura and Satoru Takakusagi
Catalysis Research Center, Hokkaido University, Kita 21-10, Sapporo, Hokkaido 001-0021, Japan

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A portable ultrahigh-vacuum sample storage system was designed and built to investigate the detailed geometric structures of mass-selected metal clusters on oxide substrates by polarization-dependent total-reflection fluorescence x-ray absorption fine structure spectroscopy (PTRF-XAFS). This ultrahigh-vacuum (UHV) sample storage system provides the handover of samples between two different sample manipulating systems. The sample storage system is adaptable for public transportation, facilitating experiments using air-sensitive samples in synchrotron radiation or other quantum beam facilities. The samples were transferred by the developed portable UHV transfer system via a public transportation at a distance over 400 km. The performance of the transfer system was demonstrated by a successful PTRF-XAFS study of Pt_4 clusters deposited on a TiO_2(110) surface. © *2015 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4936344]

I. INTRODUCTION

Typically, studies of supported metal nanoclusters by x-ray absorption fine structure spectroscopy (XAFS) are carried out on samples prepared by the evaporation or deposition of sputtered metal on a substrate, which results in a distribution of nanocluster sizes. Several groups have performed XAFS measurements combined with polarization-dependent, total-reflection, and fluorescence techniques to enhance the weak intensities that result from the low concentration of supported metal nanoclusters.[1–5]

We planned to investigate the surface-deposited mass-selected clusters using the polarization-dependent total-reflection fluorescence x-ray absorption fine structure spectroscopy (PTRF-XAFS) to highlight cluster–substrate interactions and size-dependence, which are expected to influence the catalytic properties of the mass-selected clusters. Such clusters, which may comprise several atoms to tens of atoms, have been studied after deposition on a surface,[6–10] and have been reported as very active catalysts.[11,12] The complexity of combining the mass-selected cluster deposition system with XAFS measurements is that the samples must be transferred without exposure to atmosphere. It is difficult to combine XAFS measurement chamber with a mass-selected cluster deposition system, because of their limitation in mounted space and machine (beam) time. We tried to perform the PTRF-XAFS experiments, as previously described:[1] the samples were transferred over a distance from the mass-selected cluster deposition equipment[13] via an ultrahigh-vacuum (UHV) sample storage system.

Several UHV transfer systems have been developed and reported.[14–17] Their design of transfer system and chamber featured for their usage and function. There are several transfer systems reported, and some of them are commercially available. Crider *et al.* reported in 1976 that they developed a satellite vacuum system for a LEED-AES system with the sample transfer capability.[15] Fleisch *et al.* reported in 1978 that they developed a right angle and end-on type transfer with magnetic drive rods.[17] Clausing *et al.* in 1979 reported the sample transfer for plasma–wall interaction research in fusion energy.[14] Firpo *et al.* reported in 2005 that they

[a]Electronic mail: e0827@mosk.tytlabs.co.jp

developed a transfer system pumped by a high performance getter pump, and it reached under 3×10^{-9} Pa without battery. This makes it possible to transport with air freight.[16]

Here, we report a newly developed portable UHV transfer system for the samples' transfer between the two separated UHV systems with a different mechanism of sample manipulation. The samples were prepared at Toyota Central R&D Labs., Inc. (Nagakute, Japan). The PTRF-XAFS measurements were performed at the Photon Factory at the Institute of Materials Structure Science (KEK-IMSS-PF, Tsukuba, Japan). The samples were transferred by the developed portable UHV transfer system via a public transportation at a distance over 400 km.

II. SYSTEM LAYOUT AND DESIGN

We have designed a portable UHV samples storage system to transfer samples between the cluster deposition chamber and the PTRF-XAFS measurement chamber under UHV conditions. The requirements for the portable UHV sample storage system are as follows: (1) the sample holder capable of receiving the flag style sample plate (Omicron type) manipulated via the dual shaft wobblestick with the straight pincer grip (Ferrovac GmbH) in our cluster deposition chamber; (2) the sample holder with a keyhole and a locked mechanism by a magnetic transfer rod with a key type grip; (3) a portable UHV sample storage system should be bakable, transferable, and stowable in a travel suitcase; (4) maintaining a secure holding of the samples during a public transportation; (5) at least three sample holders should be stored; and (6) the sample holder transferable through mini UHV gate valve DN40.

Figure 1 shows a schematic drawing of the developed portable UHV samples storage system: (a) docked with the PTRF-XAFS measurement chamber and (b) docked with the junction chamber connected with the mass-selected cluster deposition chamber.

The developed transfer system consists of the portable UHV sample storage system chamber with a battery-powered ion pump (blue) and the junction chamber with a turbomolecular pump system and a long-stroke magnetic transfer rod with a gate valve (yellow). This UHV sample storage system provides the handover of samples between the two different sample manipulating systems.

A. Portable sample storage system chamber

Figure 2(a) shows a schematic drawing of the portable UHV sample storage system chamber. This comprises the small chamber with a viewing port, the light weight magnetic transfer rod with the sample holder stacker, a battery-powered ion pump, and a mini UHV gate valve. The atmosphere of the sample chamber is kept under an UHV of 10^{-7} Pa by the action of the battery-powered ion pump (Varian VacIon Plus20 27 l/s). The vacuum conditions in the sample chamber are guaranteed to last at least 72 h when the ion pump is powered only by the battery. The components of the system are described below.

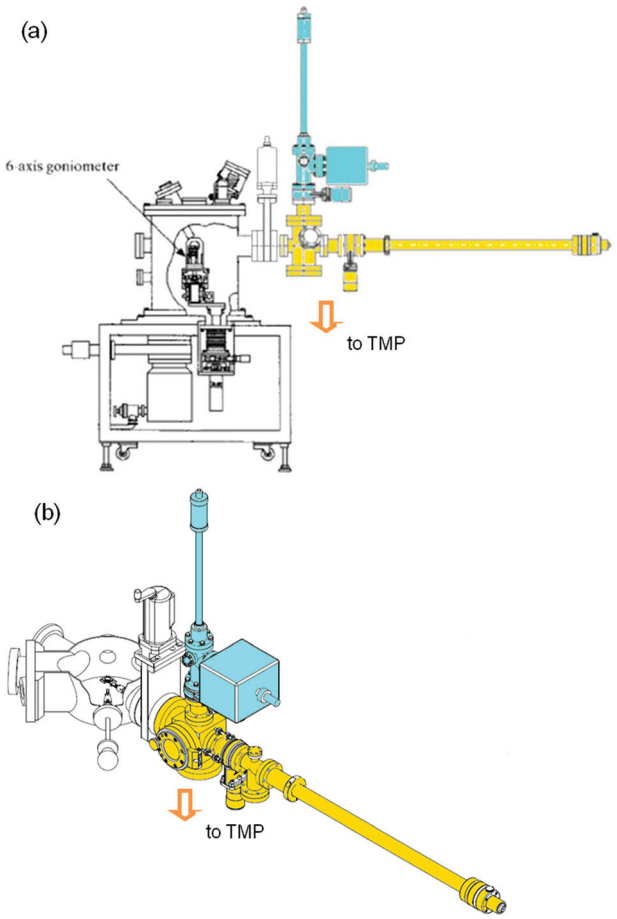

FIG. 1. (Color) Schematic drawings of the portable UHV sample storage systems: (a) docked with the PTRF-XAFS measurement chamber via the junction chamber and (b) docked with the junction chamber of the cluster source chamber via another junction chamber. In each figure, blue indicates portable UHV sample storage system, and yellow indicates junction chamber.

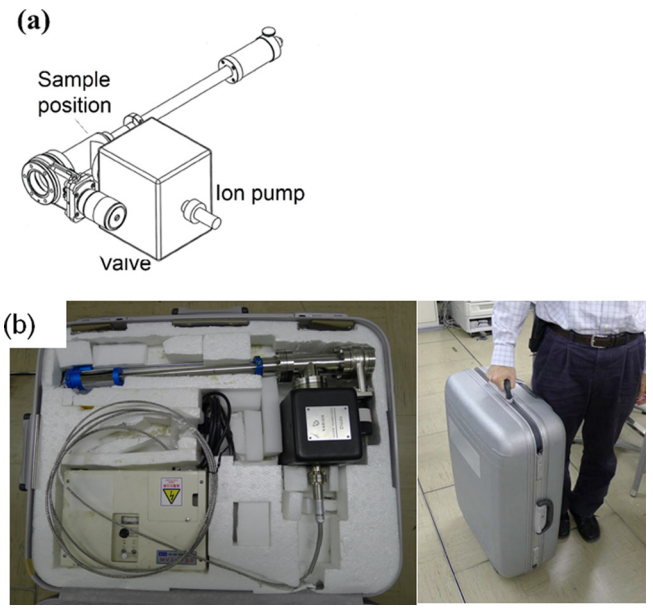

FIG. 2. (Color online) Portable UHV sample storage system: (a) schematic drawing of portable UHV sample storage system and (b) picture of the system placed in its suitcase.

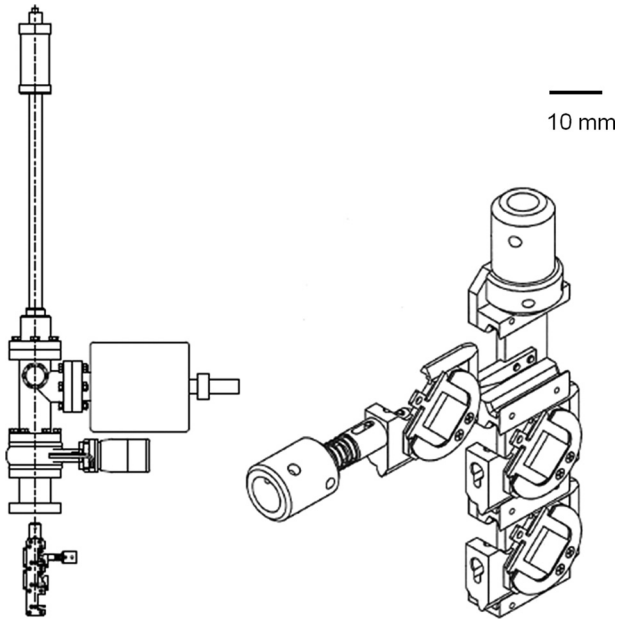

FIG. 3. Perspective stereographic drawings of the newly designed sample plate holder with a sample on an Omicron-type plate.

One end of the chamber is a mini UHV gate valve DN40, so that the vessel can be connected to various kinds of UHV chambers, including the cluster source chamber and the PTRF-XAFS chamber used in this work.

Figure 2(b) depicts a schematic illustration of the portable UHV sample storage system placed in its dedicated suitcase. The size of the suitcase is $53 \times 70 \times 24$ cm (W × H × L), and the weight of the entire system including a dedicated carrying suitcase is about 23 kg. Hence, the portable UHV storage system is adaptable for conveyance by various modes of transportation. This makes it possible and easier to perform experiments using air-sensitive samples in synchrotron radiation or other quantum beam facilities apart from one's own laboratory.

1. Sample holder storage stacker

Figure 3 shows perspective stereographic drawings of the designed sample holder storage stacker with a sample on an Omicron-type plate. Three sample plate holders may be stacked, stored, and carried once. The stacker, when loaded with the sample plate holders, is designed to pass through a typical DN40 UHV gate valve. The adopted vertically arrayed design enables to minimize the required passing diameter. This compact designed stacker enables a reduction in the size of the portable UHV sample storage system—a significant advantage when it is necessary to move the portable UHV sample storage system via public transportation. In addition, the springs of sample holder storage stacker are effective in locking the sample holders tightly during transport.

2. Sample holder for the PTRF-XAFS measurements

The secure attachment of a sample in the portable UHV sample storage system is a key issue when conveying the transfer system and manipulating the sample into the UHV chambers. For this purpose, we developed a dedicated sample holder and a locking mechanism. Figure 4 shows photographs of the customized sample plate holder, which was designed for use with Omicron-type sample plates. In the photograph, the sample is anchored on a Ta plate welded by Mo strips. After placement, the plate is fixed by a horseshoe-shaped spring, which prevents displacement when conveying the transfer system. For the PTRF-XAFS measurements, it is desirable that the sample is isolated to prevent the incident and emitted x-rays from irradiating a proximate substance, which could emit unexpected x-rays, some of which may be counted by the detector. Hence, the vertical position of the surface of the plate spring was designed to be lower than that of the surface of the sample.

3. Transfer rod

The secure attachment of the sample in the portable UHV sample storage system is critical when manipulating the sample into the UHV chamber. For this purpose, we developed a locking mechanism for the dedicated sample holder. Figure 5 shows photographs of the tip of transfer rod of the junction chamber we developed, which is compatible with UHV chambers used for cluster production and PTRF-XAFS measurement. A key-type tip was mounted on the transfer rod of the junction chamber, as shown in Fig. 5. The tip was

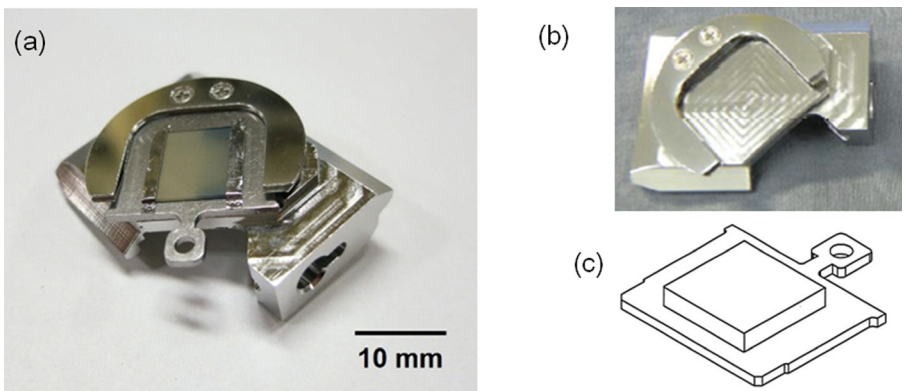

FIG. 4. (Color online) Photographs of the sample holder compatible with the two different UHV chambers: (a) with the Omicron-type sample plate; (b) without the sample plate; and (c) customized Omicron-type sample plate.

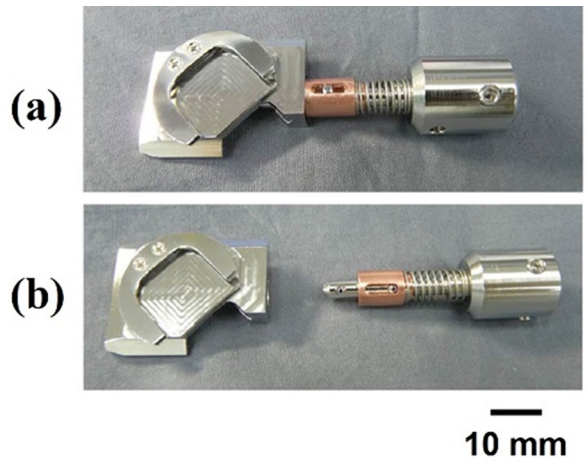

FIG. 5. (Color online) Photographs of the tip of transfer rod in the junction chamber: (a) the tip locked into the sample holder and (b) the tip released from the sample holder, such as after placing the sample on the stage of the UHV chamber.

inserted into the keyhole, and a 90° rotation locked the rod firmly into the sample plate holder. A spring is effective in firmly locking the sample against vibration during transfer. The spring at the end of the transfer rod also enabled the flexible manipulation and easy release of a sample [Fig. 5(b)] during installation on the stage of a UHV chamber.

This key-type tip would be applicable to transport just one sample holder by the function of firmly locking the sample against vibration during transport.

III. SAMPLE TRANSFER TEST AND PTRF-XAFS MEASUREMENTS

This UHV sample storage system provided the handover of samples between the two different sample manipulating systems. The adopted vertically arrayed design enables to minimize the required passing diameter. This compact designed stacker enables a reduction in the size of the portable UHV sample storage system—a significant advantage when it is necessary to move the portable UHV sample storage system via public transportation. Up to three samples can be loaded at the same time in the compact designed sample storage stacker. The samples were transferred by the developed portable UHV transfer system via a public transportation at a distance over 400 km.

A. Sample preparation

The preparation of mass-selected Pt_4 clusters on a $TiO_2(110)$ substrate was carried out in a UHV chamber equipped with a size-selected cluster-ion beam deposition system located at Toyota Central R&D Labs., Inc. (TCRDL, Nagakute, Japan). The details of the deposition system and method are described elsewhere.[13] The mass-selected Pt_4 clusters were then deposited under the soft-landing conditions onto the cleaned $TiO_2(110)$ surface (1×1) anchored on a Omicron-type sample plate. The concentration of Pt_4 clusters was adjusted to 2×10^{14} atoms cm^{-2} based on the Pt cluster ion current.

TABLE I. Pressure data under simulated situations.

Situation	Pressure (Pa)
Static	$<2 \times 10^{-7}$
Flat floor	$<2 \times 10^{-7}$
Tile faced floor	4×10^{-7}
On elevator	$<2 \times 10^{-7}$

B. UHV sample storage system transfer

After cluster deposition, the sample was placed into the customized sample plate holder using a Ferrovac wobble-stick, and then mounted to the sample holder storage stacker in the designed baked-out portable UHV sample storage system chamber.

The portable UHV sample storage system chamber was kept under UHV with a battery-powered ion pump during transport from TCRDL to KEK-IMSS-PF beam line via a public transportation. This portable UHV sample storage system has no pressure gauge. The pressure before and after the transportation was measured by monitoring the current of ion pump. We can infer the pressure during the transport by monitoring the pressure under simulated situation. The pressure was monitored using a cold cathode gauge (Pfiffer IKR261; minimum range is 2×10^{-7} Pa) attached temporally. The estimated pressures under simulated situation were shown in Table I. It would be estimated that the sample was carried under the pressure of below 2×10^{-7} Pa, except a few times with the sudden increase in pressure of almost 4×10^{-7} Pa by unexpected vibration caused from a tile-faced floor. During transportation, there exist a few points of a tile-faced floor at railway stations we should pass through. In Table II, the ion pump current and the estimated pressure were shown before departure and after arrival. There was no difference in the pressure before and after the transport. After arriving at KEK-IMSS-PF, the portable UHV sample storage system chamber was docked with the PTRF-XAFS measurement chamber via the junction chamber. After overnight pumping of the junction chamber, the sample plate holder was successfully mounted on a UHV high-precision six-axis goniometer.[18]

C. PTRF-XAFS measurements

The PTRF-XAFS measurements were performed at BL9A of the Photon Factory at the Institute of Materials Structure Science [KEK-IMSS-PF (2.5 GeV, 400 mA), Tsukuba, Japan] employing a UHV PTRF-XAFS chamber (base pressure: 8×10^{-8} Pa). To reduce undesirable irradiation, the beam size on the sample was regulated with a four quadrant slit $(0.05 \times 0.05$ mm). The total reflection

TABLE II. Pressure data before and after transport.

	Ion pump current (μA)	Estimated pressure (Pa)
Before departure	<1	$<3 \times 10^{-7}$
After arrival	<1	$<3 \times 10^{-7}$

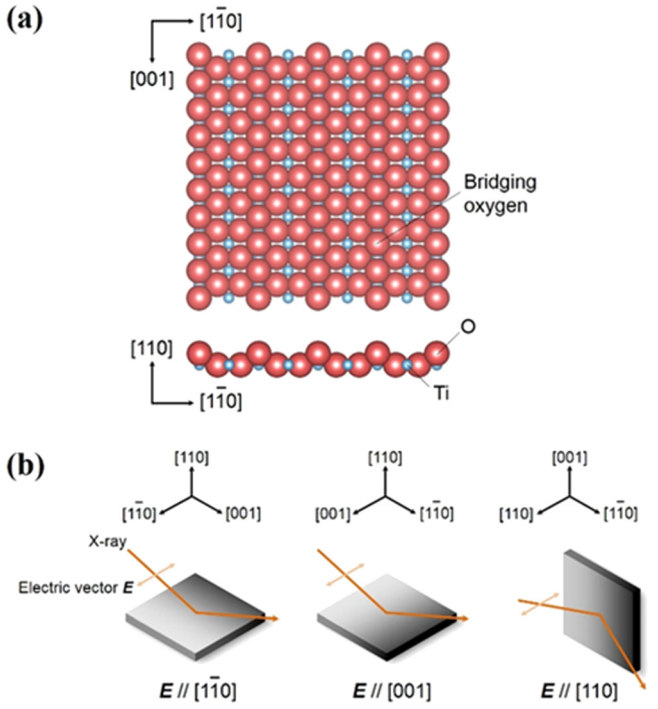

FIG. 6. (Color online) (a) Surface structure of TiO_2(110) (red (large ball): O; blue (small ball): Ti) and (b) orientations for the PTRF-XAFS measurements against the polarization electric vector ***E***.

conditions were adjusted by using a UHV high-precision six-axis goniometer. Taking the anisotropic surface structure of TiO_2(110) into account, as illustrated in Fig. 6(a), the XAFS measurements were implemented under three different orientation conditions relative to the electric vector ***E*** of the incident x-rays [Fig. 6(b)]. The Pt Lα fluorescence was detected by a 19-element Ge solid-state detector (GL0110S, Canberra, USA) at room temperature. A horseshoe-shaped spring for sample holding [Fig. 4(b)] and customized Omicron-type sample plate [Fig. 4(c)] worked well to reduce the unexpected x-ray emission from a sample plate and other materials around a sample, which come from the grazing angle incident x-ray for total reflection. XAFS spectra were successfully measured in all three orientations and without oxidized Pt peak.

IV. SUMMARY

A portable UHV sample storage system was designed and built to perform PTRF-XAFS studies of mass-selected metal clusters deposited on the substrate. The samples were carried and transferred by the developed portable UHV transfer system via a public transportation at a distance over 400 km. The performance of the transfer system was demonstrated by a successful PTRF-XAFS study of mass-selected Pt_4 clusters deposited on a TiO_2(110) surface.

The system should be applicable for materials' analysis utilizing synchrotron x-ray or particle beams (e.g., neutrons and muons) for other air-sensitive materials after minor remodeling. The adopted key and keyhole sample manipulating system with a 90° rotation lock supported by a coiled spring enables the flexible manipulation and easy release of a sample holder by a coiled spring.

We anticipate that this newly developed, portable UHV sample storage system with a key and keyhole sample manipulating system will find widespread use as a standard system for UHV XAFS measurements, enabling experiments at any light source in the world.

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[1]K. Asakura, W.-J. Chun, M. Shirai, K. Tomishige, and Y. Iwasawa, J. Phys. Chem. B **101**, 5549 (1997).
[2]K. Asakura, S. Takakusagi, H. Ariga, W.-J. Chun, S. Suzuki, Y. Koike, H. Uehara, K. Miyazaki, and Y. Iwasawa, Faraday Discuss. **162**, 165 (2013).
[3]W.-J. Chun, K. Miyazaki, N. Watanabe, Y. Koike, S. Takakusagi, K. Fujikawa, M. Nomura, Y. Iwasawa, and K. Asakura, J. Phys. Chem. C **117**, 252 (2013).
[4]K. Asakura, *Catalysis Book Series*, edited by J. G. Catalano (Royal Society of Chemistry, London, 2012), Vol. 24, p. 281.
[5]S. Takakusagi, H. Nojima, H. Ariga, H. Uehara, K. Miyazaki, W.-J. Chun, Y. Iwasawa, and K. Asakura, Phys. Chem. Chem. Phys. **15**, 14080 (2013).
[6]A. Beniya, N. Isomura, H. Hirata, and Y. Watanabe, Chem. Phys. Lett. **576**, 49 (2013).
[7]A. Beniya, N. Isomura, H. Hirata, and Y. Watanabe, Phys. Chem. Chem. Phys. **16**, 26485 (2014).
[8]U. Heiz, A. Sanchez, S. Abbet, and W.-D. Schneider, J. Am. Chem. Soc. **121**, 3214 (1999).
[9]S. Lee, C. Fan, T. Wu, and S. Anderson, J. Chem. Phys. **123**, 124710 (2005).
[10]S. Vajda *et al.*, Nat. Mater. **8**, 213 (2009).
[11]M. Haruta, Catal. Today **36**, 153 (1997).
[12]Y. Watanabe and N. Isomura, J. Vac. Sci. Technol. A **27**, 1153 (2009).
[13]Y. Watanabe, X. Wu, H. Hirata, and N. Isomura, Catal. Sci. Technol. **1**, 1490 (2011).
[14]R. E. Clausing, L. Heatherly, and L. C. Emerson, J. Vac. Sci. Technol. **16**, 708 (1979).
[15]C. A. Crider, G. Cisneros, P. Mark, and J. D. Levine, J. Vac. Sci. Technol. **13**, 1202 (1976).
[16]G. Firpo, F. Buatier de Mongeot, C. Boragno, and U. Valbusa, Rev. Sci. Instrum. **76**, 026108 (2005).
[17]T. Fleisch, A. T. Shepard, T. Y. Ridley, W. E. Vaughn, N. Winograd, W. E. Baitinger, G. L. Ott, and W. N. Delgass, J. Vac. Sci. Technol. **15**, 1756 (1978).
[18]W.-J. Chun, K. Asakura, and Y. Iwasawa, J. Phys. Chem. B **102**, 9006 (1998).