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A high-temperature *in situ* cell with a large solid angle for fluorescence X-ray absorption fine structure measurement

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We present the design and performance of a high-temperature *in situ* cell with a large solid angle for fluorescence X-ray absorption fine structure (XAFS) spectra. The cell has a large fluorescence XAFS window (116 mm^φ) near the sample in the cell, realizing a large half-cone angle of 56°. We use a small heater (25 × 35 mm²) to heat the sample locally to 873 K. We measured a Pt-SnO₂ thin layer on a Si substrate at reaction conditions having a high activity. *In situ* measurement enables the analysis of the difference XAFS spectra between before and during the reaction to reveal the structure change during the operation. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4914459>]

I. INTRODUCTION

Fluorescence X-ray absorption fine structure (XAFS) is a powerful technique for determining the local structure in a dilute system.^{1,2} When X-ray absorption occurs with the core electron emission as a photoelectron, the created core hole is filled by a transition from the outer shell electrons accompanied with an emission of a fluorescence X-ray. Consequently, if the sample is dilute or in a thin film, the fluorescence X-ray intensity becomes proportional to the absorption coefficient. Because the fluorescence X-ray emission occurs in a 4π sr, the use of a large solid-angle detector, such as a multielement solid state detector (SSD)³ or a Lytle detector,⁴ is desirable. Recently, a crystal monochromator is used to detect fluorescence XAFS which improves the detection limit and an energy resolution.⁵⁻⁹

The strong penetration power of an X-ray allows investigators to perform *in situ* XAFS measurement under reaction conditions to reveal catalytic mechanisms.¹⁰ Numerous *in situ* fluorescence XAFS experiments have been performed on the systems of fuel cell, corrosion, catalyst, and gas sensors.^{5,6,11-29} *In situ* fluorescence XAFS cells require a large fluorescence window at a position sufficiently close to the sample to secure a large solid angle. When the polymer window is used for the *in situ* fluorescence XAFS measurements, it is difficult to realize the large solid angle because the fluorescence window temperature raises easily even if the peripheral region of the window is cooled by water flow owing to low thermal conductivity of polymer window material. Kappen and Grunwaldt *et al.* used a thin quartz tube as an incident and fluorescence X-ray window^{7,8} where the quartz window can be in contact with the sample because the quartz window is a temperature proof material. Another alternative is

to decrease the power supply by decreasing the sample size. High-brilliance synchrotron radiation is now available, and the X-ray can be focused to an area less than a few mm² for the small samples to be used. In this study, we selected this option so that the distance between the window and the heater could be as short as 35 mm. The window temperature reached only 373 K without any cooling, even when the sample was heated to 703 K. The cell used in this study enables us to measure the *in situ* fluorescence XAFS of flat substrate, electrode, large surface area film, and powder samples. In this paper, we measured the fluorescence XAFS spectra of a Pt-SnO₂ thin film on a Si substrate as model sensor catalyst under the working conditions.

II. *IN SITU* CELL

A. Structure of the *in situ* cell

Figure 1 shows a photograph and schematic sketches of the *in situ* cell. To install the cell more easily at any beam line, the cell body was made of aluminum to increase its portability. The cell weight was just 2.4 kg. In addition, local heating of the cell body could be avoided because of Al's high thermal conductivity. The volume of the cell is about 1.3 l in order to keep the volume/sensor area ratio in the same order of the real sensor which was 4 × 10³ cm and 1.3 × 10³ cm for real and model sensors, respectively. The cell body had gas flow ports and an incident X-ray window. We used a 200-μm-thick Kapton (DuPont, USA) for the incidence and fluorescence X-ray windows, which were fixed to the body using an epoxy adhesive. We made a large fluorescence Kapton window with an area of 116 mm^φ.

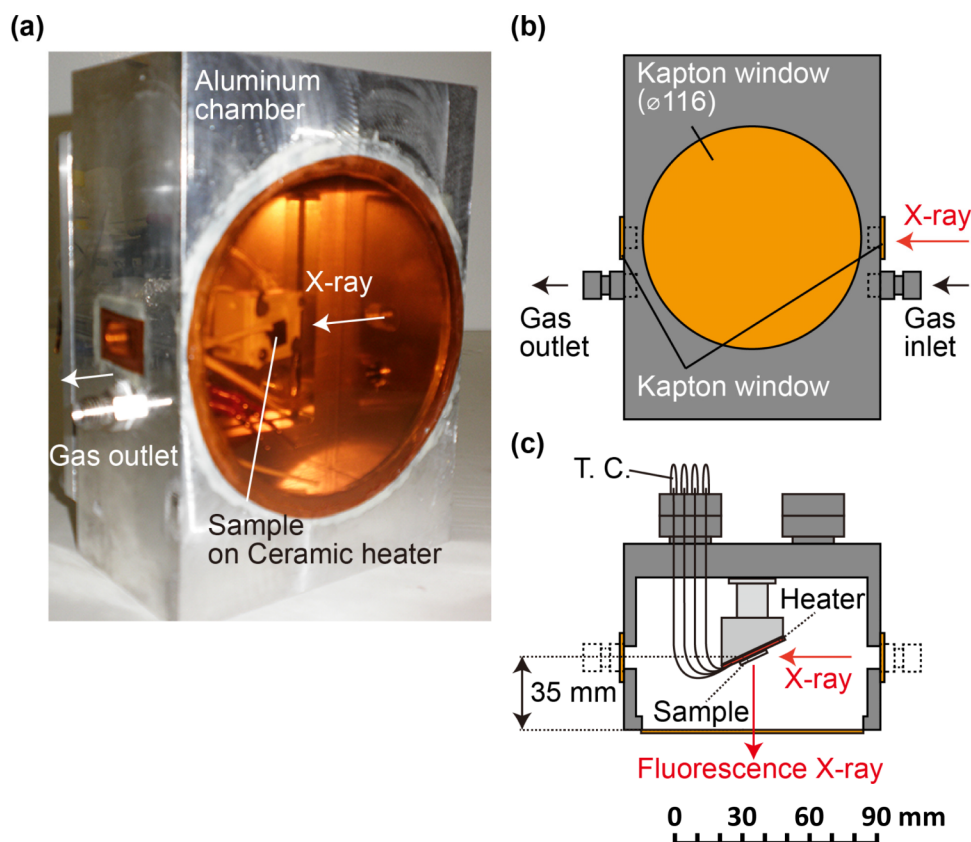


FIG. 1. A photograph and the schematic drawings of the *in situ* cell. It is (a) photograph, (b) top view, (c) side view.

The cell body had a sample stand with electric feed-throughs for heating the sample. The pyrolytic graphite heater was wrapped with pyrolytic boron nitride (pBN) (HTR1001; Adcap Vacuum Technology Corporation, Japan) and was used to heat the sample to 873 K. The heater size was 25 mm ϕ . Temperature was controlled in a proportional–integral–derivative (PID) manner using the temperature controller designed especially by the Sakaguchi Electric Heating Corporation. This temperature controller measured temperature by a chromel–alumel thermocouple attached to the back of the sample. Its temperature sampling time was as short as 25 ms. It controlled the temperature by another chromel–alumel thermocouple attached to the sample holder, as shown in Fig. 2. The heater was fixed to the sample holder. The sample was fixed at two corners with jigs and clinchers to ensure good contact with the heater. The sample holder and jigs were made of Al₂O₃ to reduce heat dissipation. The angle between the X-ray direction and the sample stage was set at 25° as no diffraction from the Si substrate was detected at this angle empirically. The length from the sample to the window was approximately 35 mm. We did not use a water-cooling system. With this configuration, we can guarantee a large half-cone angle of 56°.

B. XAFS measurements

We applied this *in situ* fluorescence XAFS measurement to the characterization of a thin-film catalyst for gas sensor developed on a Si substrate. SnO₂ is a semiconductor whose

electric conductivity changes with the existing gas composition. Pt-doped SnO₂ (Pt-SnO₂) thin film deposited on the SnO₂ sensor film shows a high methane sensitivity with a low power consumption and this opens a new way to realize battery-driven gas sensors.^{30–33} Using the fluorescence XAFS to study the local structure of Pt in this fresh Pt-doped SnO₂ film at room temperature, we found that the Pt took a solid solution structure, being located at the Sn position of the SnO₂ lattice.³⁴ In literatures, a Pt metal cluster is considered to be an active structure in the reaction.^{35,36} In addition, the structures of catalysts during working conditions are often different from

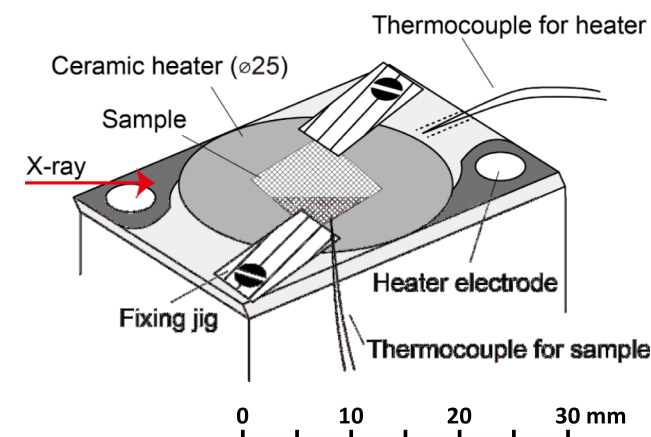


FIG. 2. Sample holder with ceramic heater and thermocouples on the sample stand.

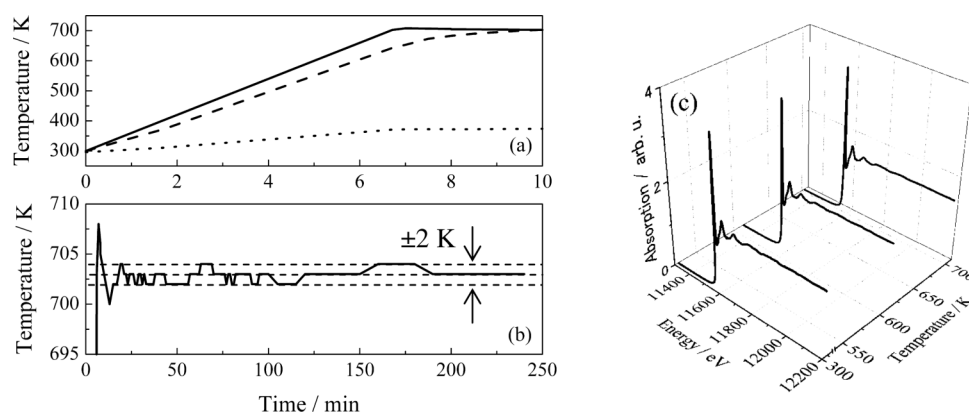


FIG. 3. The heating performance of the cell. (a) The increasing temperature process at the holder (solid line), at the sample (broken line), and at the Kapton window (dotted line). (b) Stability of the temperature for 4 h at the sample position. (c) XAFS spectra at 303, 613, and 703 K under the dry air flow.

those existing before the reactions; thus, there is a possibility that the Pt cluster formed during the reaction conditions plays an important role.^{18,37,38} With this in mind, *in situ* structure analysis is necessary to confirm the actual active structure and reaction mechanism.^{39–46}

Pt L_3 -edge XAFS spectra were measured at an X-ray beam line BL-12C of Photon Factory in Institute for Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF) using a Si(111) monochromator in the fluorescence mode.^{47,48} XAFS measurement was performed in 200 ml/min gas flow. A 19-element SSD was used for the fluorescence detection. XAFS spectra were analyzed with a REX2000 (Version 2.5, Rigaku).^{49–51}

Pt-doped SnO_2 thin layers of 400-nm thickness were prepared on p-type Si substrates covered with native SiO_2 film (600 nm) using a sputter-deposition method, followed by annealing at 803 K. The Pt and SnO_2 contents were controlled according to the loading ratio in the targets. The SnO_2 thin film was formed by sputter-deposition has column structures composed of a few nm particles.⁵² The final Pt concentrations in the films were determined from films dissolved in hydrochloric acid using inductively coupled plasma (ICP) spectroscopy. The Pt loading was estimated to be 10 at. % in the Pt- SnO_2 thin film.³¹ Pt- SnO_2 thin film on a 1 cm^2 Si substrate was loaded in the cell. Judging from the S/N ratio of 10 at. % Pt/ SnO_2 thin film, we can measure $1 \times 10^{17} \text{ cm}^{-2}$.

III. RESULTS AND DISCUSSION

A. Heating performance

Although the sample and sample heater in this study were small, the power of the heater and the heat capacity of the sample were sufficiently large for temperature stability. We actually achieved the stable sample temperature using the temperature controller in a current-control mode with well-tuned PID parameters. Figure 3 shows the heating performance of the *in situ* cell. The temperature was linearly raised to 703 K at the sample position. The sample surface reached this temperature in approximately 3 min, as shown by the dashed line. The temperature overshoot was only 5 K, and the temperature was controlled to within 2 K for a long time. In

the off-line experiment, we measured the fluorescence window temperature at its center by a thermocouple directly attached to the window. Note that the Kapton window was kept at 373 K because of the small power input, by a dotted line as shown in Fig. 3(a), despite the sample temperature at 703 K. However, the problem was the life of the heater; a very large power supply can readily damage the small heater. Therefore, we installed a safety circuit to prevent the current from being exceeded more than the desired one (5 A). We then slowly increased the power to extend the life for a few days, which was sufficient for one experimental run. Figure 3(c) shows the XAFS spectra at room temperature, 613 K and 703 K in dry air flow. We could find little structure change of the Pt local structure at different temperatures.

B. XAFS measurements in and out of the cell

Figure 4 shows the XAFS spectra of Pt- SnO_2 thin film measured in and out of the cell at room temperature. Both

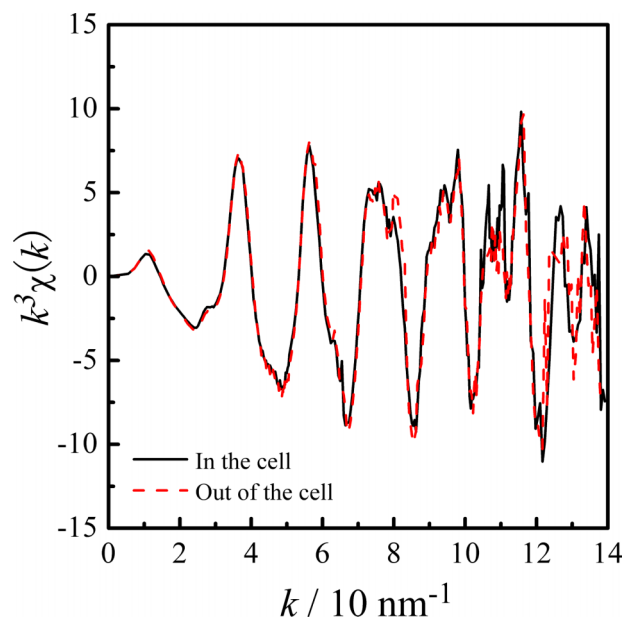


FIG. 4. Comparison of EXAFS oscillation of a Pt- SnO_2 thin film in the cell (solid line) and out of the cell (broken line) at room temperature.

spectra were very similar up to $k = 14 \text{ \AA}^{-1}$. This implies that the data can be accurately analyzed under *in situ* conditions using this cell. Figure 5 shows X-ray absorption near-edge structure (XANES) spectra measured at the temperature increasing process to 703 K under a flow of dry air and 1% H_2 -containing air (flow rates = 200 ml/min). The sensor resistivity was measured in this XAFS measurement cell. Figure 5(b) showed the resistivity at each temperature where XANES spectra were measured as shown Fig. 5(a). There is no difference in sensor resistance when the X-ray beam was on or off. The most reduced state in Pt gave the lowest resistivity. Figure 6 showed XAFS spectra to 703 K under a flow of dry air and 1% H_2 -containing air. We observed small changes in the XANES region in Fig. 6(a). The edge peak (called as white line) decreased when the sample was exposed to the H_2 -containing air at a high temperature (703 K). The white line peak was assigned to the $2p_{3/2} \rightarrow 5d$ transition.⁵³ The decrease in the white line peak indicated an increase in the d-electron density of Pt, which was probably because of the loss of the first nearest-neighbor oxygen atoms and/or the formation of Pt nanoparticles. Identifying the change in the original EXAFS oscillation ($k^3\chi(k)$) was difficult, as shown in Fig. 6(b) so that we calculated its difference before and after contact with the H_2 -containing air, as shown in Fig. 6(c). The difference EXAFS ($k^3\Delta\chi(k)$) showed the oscillation clearly. We performed a Fourier transform, as shown in Fig. 7, where one peak appeared at 0.18 nm, corresponding well with Pt–O. This does not necessarily mean that there was an increase in the Pt–O coordination because Fig. 7 shows only the absolute part of the Fourier transform, which does not contain phase information. Figure 8 shows the imaginary and real parts of the Fourier transform of $k^3\Delta\chi(k)$ together with the absolute part for the Pt– SnO_2 in dry air at 703 K. Compared with the imaginary parts, the phase of the Pt– SnO_2 peak in Fourier transform of $k^3\Delta\chi(k)$ was π rad different from the Pt– SnO_2 before the H_2 -containing air flow, indicating a decrease in the main oscillation arising from Pt–O. We did not find any notable peak above a noise level in the range of 0.2 – 0.3 nm, which showed little Pt–Pt formation. Thus, we concluded that Pt metal nanoparticles were not produced with H_2 -containing air at high temperature, but a partial reduction of Pt ions occurred with the loss of the oxygen maintaining the location at the lattice position of SnO_2 .

IV. DISCUSSION

There have been many reports about *in situ* cells for the fluorescence XAFS. Cells are classified into two types. The first type of cell is a tubular type. The fluorescence X-ray is measured through an incident window made of quartz.^{7–10} These materials are stable at high temperatures and are thus allowed to have direct contact with the sample. This cell type can provide large half-cone angles. Its drawback is the scattered X-rays from the quartz tube, which increases the background.

The second type of cell is the one that has the sample and windows separated from each other. Different X-ray incidence and fluorescence windows are used for X-ray scattering to be largely reduced. When a thin polymer window is applied, the window temperature has to be kept low. As such, the

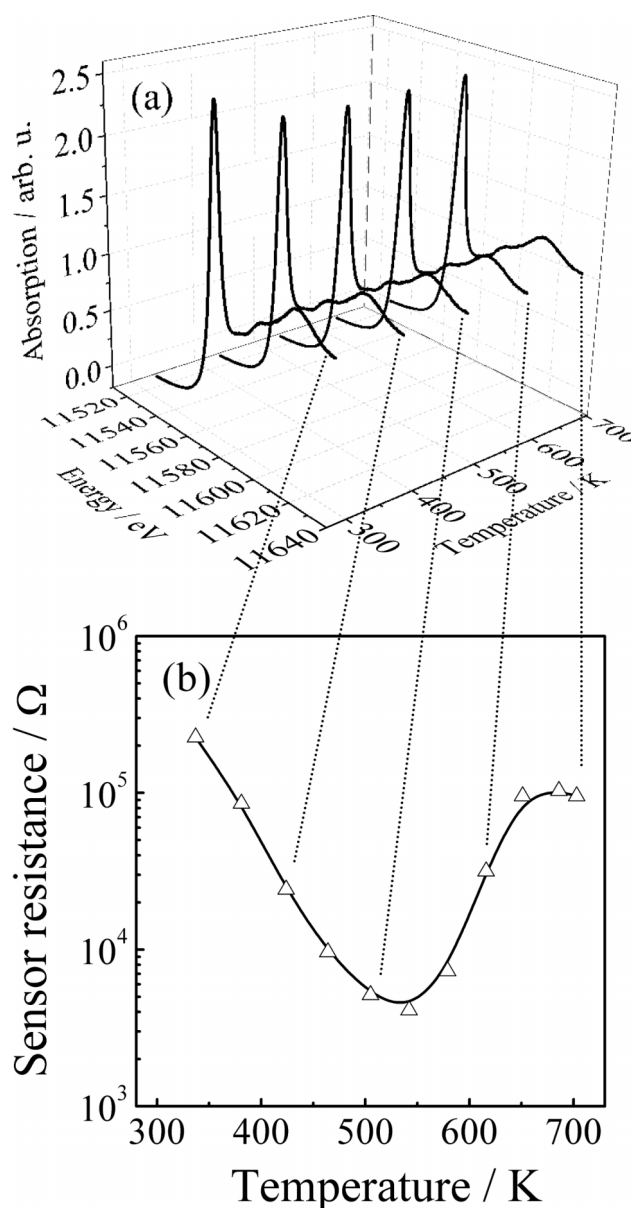


FIG. 5. XANES spectra at the temperature increasing process to 703 K under a flow of dry air and 1% H_2 -containing air (flow rates = 200 ml/min) in (a). Sensor property on model sample under the hydrogen based on the dry air flow in (b).

distance between the window and the sample must be long and/or window size is small enough for effective cooling of the window both of which sacrifice a large fluorescence yield. Koziej *et al.* have reported a XAFS cell for a gas-phase reaction of Pt in Pt– SnO_2 , where the sample is heated by a built-in small heater.^{13–15} Gurlo *et al.* have reported also another XAFS cell for research of mechanism of sensor with a small integrated heater.^{16,17} Although the samples can be heated effectively keeping the large cone angle for the fluorescence XAFS using these cells, the measurements were limited to those systems with samples that could have a built-in or an integrated heater. In this paper, we used a small sample and a small separate heater. Consequently, the window is not heated up, even with its large window size (116 mm ϕ) at a close distance (approximately 35 mm). As a result, we have had a

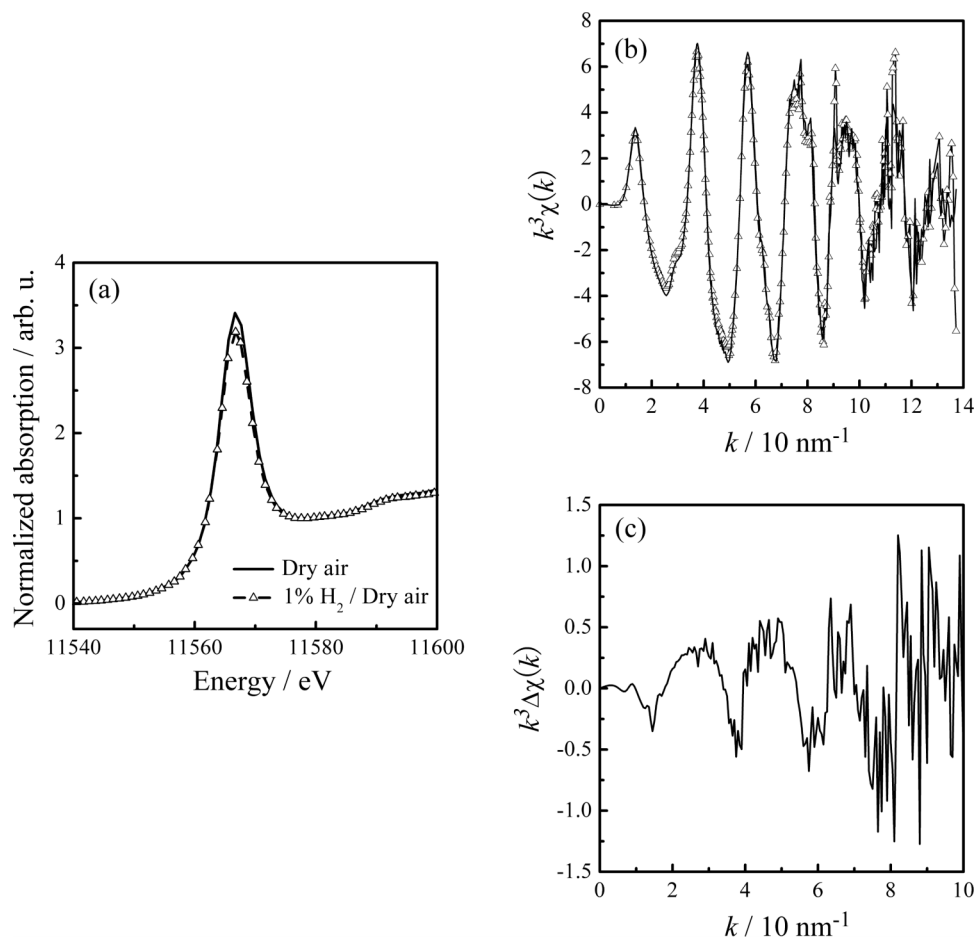


FIG. 6. Pt L₃-edge XANES (a) and EXAFS (b) spectra to 703 K under a flow of dry air (solid line) and 1% H₂-containing air (triangle with broken line). (a) XANES spectra, (b) k^3 -weighted EXAFS oscillations, and (c) their difference spectrum $k^3\Delta\chi(k)$.

large half cone angle¹ of 56° by minimizing the sample heater size ($25 \times 35 \text{ mm}^2$). This cell also has no water-cooling system because the Kapton window temperature was kept at less than 373 K due to the high thermal conductivity of Al, even at a

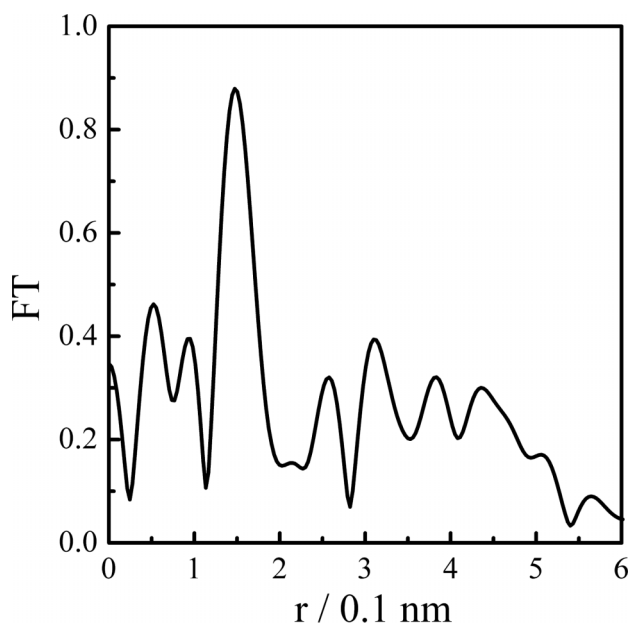


FIG. 7. Fourier transform of the difference spectrum $k^3\Delta\chi(k)$.

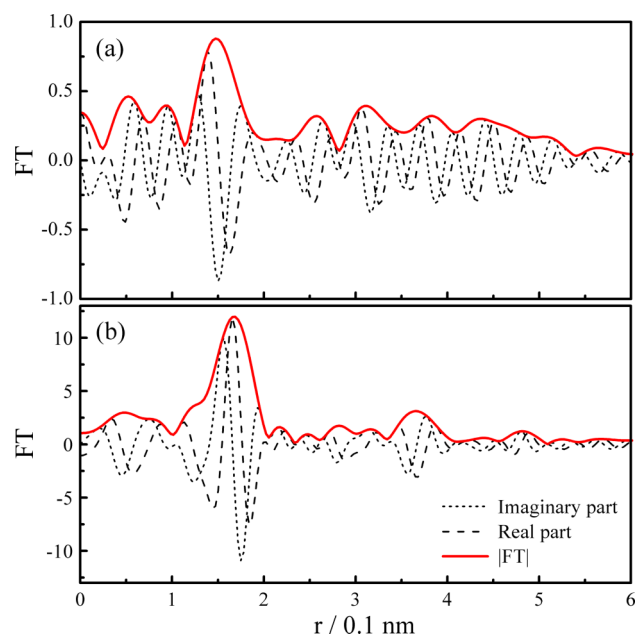


FIG. 8. The Fourier transforms. (a) The difference spectrum $k^3\Delta\chi(k)$. (b) Dry air at 703 K. Dotted, broken, and solid red lines indicated imaginary, real, and absolute parts, respectively.

sample temperature of 703 K. The system can be applied to reaction analysis of solid oxide, bimetallic catalyst for fuel cells,^{19–22} and *in situ* analysis of W oxide photo/electrochromic materials.^{54,55} These powder samples are loaded into a small container made of BN or graphite and fixed to the heater. The cell is thus universally applicable to many systems in the measurements of fluorescence XAFS under the reaction conditions.

V. CONCLUSIONS

We have developed a new type of *in situ* fluorescence XAFS cell, which has a large solid angle, a half-cone angle of 56°, and no water-cooling system. The sample is locally heated using a small heater, which prevents the unwanted heating of system components other than the sample. We obtain a good S/N ratio of *in situ* fluorescence XAFS signal under the reaction conditions, which allows data analysis by difference spectra to elucidate minute changes in XAFS oscillations during reactions.

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