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Development of X-ray Detection System Combined with Photomultiplier and Phosphor for Soft X-ray Absorption Spectroscopy of Dilute Solutions

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Soft X-ray absorption spectroscopy (XAS) is a powerful method to study local structures of liquid. We have developed a liquid flow cell for XAS in transmission mode, and studied the local structures of several aqueous solutions [1]. In normal aqueous solutions, soft X-ray absorption is optimized to several ten % by adjusting the thickness of liquid layers. In dilute solutions, on the other hand, thick liquid samples should be prepared for XAS of the solute because soft X-ray absorption of the solute is low. However, the absorption of solvent is also increased due to the thick liquid samples. It is necessary to detect low flux (10⁵ photons/s) of transmitted soft X-rays at the incident X-rays of 10⁹ photons/s. Because the detection limit of photodiode is 10⁷ photons/s, XAS of 100 mM solution is only measured by the photodiode detector. In this study, we have developed an X-ray detecting system combined with photomultiplier and phosphor for XAS of solute in dilute solutions.

The experiments were performed by using a chamber-type XAS measurement system at BL3U [2]. As shown in Fig. 1, the system consists of two chambers in an ultrahigh vacuum condition and in atmospheric helium condition. These chambers are separated by a 100 nm-thick Si_3N_4 membranes with the window size of 200 × 200 µm². The vacuum chamber is connected to the beam line. In the helium chamber, a liquid flow cell and a soft X-ray detector are installed. In the liquid cell, the liquid layer is sandwiched between two 100 nm-thick Si_3N_4 membranes, and liquid thickness is controllable from 20 nm to several µm. For XAS of liquid samples, transmitted soft X-rays irradiate to phosphor P43 dipped on the inlet of an optical fiber, soft X-rays are converted to visible lights [3], and visible lights are detected by a photomultiplier connected to the outlet of the optical fiber. We have confirmed that soft X-rays with 10³ photons/s are detected in this system.



Fig. 1. A chamber-type XAS measurement system for liquid samples. Soft X-ray transmission by the liquid sample is detected by the system combined with photomultiplier and phosphor dipped on the inlet of the optical fiber.

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In Situ Soft X-ray Absorption Spectroscopy Applied to Solid-Liquid Heterogeneous Cyanopyrazine Hydration on Titanium Oxide Catalyst

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In situ observation of catalytic reaction by spectroscopic approaches is important to obtain some clue to improvements of catalyst activity, selectivity, durability and so on. However, in situ observation of liquid substrate conversion process in solid-liquid heterogeneous catalytic reaction is difficult because the bulk liquids (substrate and/or solvent) hinder the objective spectral change [1]. This type of spectroscopy has been often carried out by using ATR-IR and NMR, but these methods still have problems of the sensitivity and the overlap of the objective absorption peaks.

We have developed a transmission-type liquid cell, which is able to control easily the liquid thin layer, for the soft X-ray XAS [2] and demonstrated that this spectroscopic method is effective to clarify the local structure of various liquid solutions [3]. Thus, in the present study, we have applied this method to the in situ observation of solid-liquid heterogeneous PzCN hydration on TiO₂ catalyst (PzCN+H₂O \rightarrow PzCONH₂). Suspension of catalyst was prepared by mixing of PzCN (3 ml, 0.78 M), EtOH (5 ml), H₂O (35 ml) and TiO₂ (0.15 g). The suspension of thin layer (< 1 µm thickness) was sandwiched between two 100 nm-thick Si₃N₄ membranes for C K-edge XAS (SiC membranes for N K-edge XAS). Then, the measurement was carried out under reaction temperature (323.2 –344.5 K).

Figure 1a shows the C K-edge XAS spectra of PzCN and PzCONH₂ at 298K, and hydration of cyanopyrazine at 335 K. Three absorption peaks (285.4, 286.0 and 286.6 eV) are observed in PzCN (red line) and one absorption peak (285.3 eV) is observed in PzCONH₂ (blue line). All these peaks are assigned to the C1s $\rightarrow \pi^*$ excitation. In the spectra of PzCN hydration (green lines), the intensity ratio of the absorption peaks varies with the reaction time, corresponding to the production of pyrazinamide. Figure 1b shows a logarithmic plot for the normalized XAS intensity of PzCN, which is obtained from the fitting analysis of Figure 1a (green lines) by using the standard spectra of PzCN and PzCONH₂. This plot shows linear relationship to the reaction time, indicating that the observed catalytic reaction is the first-order reaction for the concentration of PzCN and the slope of the line is a reaction rate constant. The same results are obtained from C K-edge XAS at other temperatures and N K-edge XAS. Furthermore, the obtained rate constants show linear relationship in the Arrhenius plot (E_a=80 kJ/mol).



Fig. 1. (a) C K-edge XAS spectra for the PzCN (0.78 M) solution (red line), PzCONH₂ (0.20 M) solution (blue line) at 298 K and catalytic hydration of PzCN on TiO₂ (green lines) at 335 K. (b) A logarithmic plot of the normalized XAS intensity of PzCN obtained from the fitting analysis of green lines in (a).

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Local Structures of Liquid Benzene at Different Temperatures Studied by C K-edge Soft X-ray Absorption Spectroscopy

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Benzene molecule is a liquid phase at room temperatures by interaction between benzene molecules. Recently, we measured C K-edge X-ray absorption spectroscopy (XAS) of benzene cluster formed by supersonic gas expansion method, and investigated molecular interactions from the energy shifts of C 1s \rightarrow π^* peak of benzene cluster from benzene gas [1]. We also investigated the energy shifts of C K-edge XAS of solid benzene, which is grown on Ru(0001) crystal surface under vacuum condition [2]. However, molecular interaction in liquid benzene has not been investigated yet. In this study, we have measured C K-edge XAS of liquid benzene at different temperatures, and studied the temperature effects of molecular interactions.

Figure 1 shows C K-edge XAS of benzene gas and liquid benzene at different temperatures. The C 1s \rightarrow π^* peak shows adiabatic (0, 0) transition and vibrational fine structures at higher photon energy. Figure 2 shows the energy shifts of (0, 0) transition peaks of liquid benzene from benzene gas as a function of temperature. The π^* peak shows lower photon energy shifts by increasing temperatures. The energy shift of liquid benzene at 25.3 °C is 29.4 meV. This shift is smaller than those of solid benzene and benzene cluster, which is 55 meV [1] and 70 meV [2], respectively.

The energy shifts of π^* peaks are caused by balances between the red-shift effects by induced polarization of the C 1s core holes with surrounding molecules and the blue-shift effects by exchange interaction between the unoccupied π^* orbital with surrounding molecules [4]. Because the exchange interaction is effective in a short range, the peak is shifted to lower photon energy when the molecular distance becomes longer. That is why benzene molecules are apart from each other at higher temperatures. We investigated radial distribution functions between benzene molecules at different temperatures by molecular dynamics simulations, and confirmed the molecular distance becomes longer at higher temperatures. We also discussed interactions between benzene molecules by C-H out-of-plane and C-H stretching vibration mode in infrared spectroscopy. In the future, we will discuss the molecular interaction in liquid benzene by correlating C K-edge XAS results with infrared spectroscopy and molecular dynamics simulations.





Fig. 2. Energy shifts of C 1s $\rightarrow \pi^*$ (0, 0) transition peaks of liquid benzene from benzene gas as a function of temperature.

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Two-Dimensional π -Orbital Delocalization in Superstructure Monolayer of Coronene Physisorbed on Au(111)

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Recently, polyclinic aromatic hydrocarbons (PAHs) have been reattracted attention as a molecular unit of graphene, i.e., nanographene. It is known that PAHs of coronene and perylene form a (4×4) superstructure monolayer on Au(111) and Ag(111) [1]. In the present work, by using angle-resolved photoemission spectroscopy (ARPES), we studied the in-plane electronic structure of the coronene(4×4)/Au(111). The cleanliness of the Au(111) surface was confirmed by the low-energy electron diffraction (LEED) and the Shockley state in ARPES, as obtained from the repeated cycles of the Ar⁺ sputtering ($I \sim 2 \mu A$) and the subsequent annealing at 700 K. The total energy resolution in ARPES was 12 meV.

Figure 1(a) and 1(b) show a LEED image at 15 K and the corresponding surface Brillouin zone (SBZ) of the coronene monolayer on Au(111), respectively. The LEED image shows the (4×4) single-domain superstructure with respect to the Au(111) hexagonal surface lattice. The ARPES spectra were measured by considering the coronene overlayer's SBZ. The energy-vs-momentum $E(\mathbf{k})$ relation map of the coronene(4×4)/Au(111) along the Γ '-K' and Γ '-M' ($\mathbf{k}_{\Gamma K}$ and $\mathbf{k}_{\Gamma M}$) directions, obtained from ARPES, is shown in Fig. 1(c) and 1(d), respectively. A highest occupied molecular orbital (HOMO, π) derived peak of coronene is observed at the binding energy (E_b) of 1.6 eV. The ARPES spectrum at the K' point ($\mathbf{k}_{\Gamma K} = 1.44$ Å⁻¹) shows a sharp HOMO line shape with the high- E_b satellite due to the hole-vibration coupling, which is the indication of the weak physisorption at the coronene(4×4)/Au(111) interface. Although no intermolecular π - π overlap exist in the coronene monolayer, the HOMO (π) peak shows a quite weak but non-negligible in-plane dispersion of 30 meV at Γ '-K' and of 15 meV at Γ '-M'. The in-plane band dispersion of molecular electronic states has been observed for strongly chemisorbed interfaces with larger dispersion of > 200 meV due to the strong interfacial orbital hybridization [2,3]. Considering the weak interfacial interaction between coronene and Au(111), the observed in-plane π -band dispersion is ascribed to the genuine intermolecular interaction of aromatic hydrocarbons.

On the other hand, the free-electron-like dispersive band is weakly appeared below the Fermi level E_F ($E_b = 0 \sim 0.4 \text{ eV}$), which may originate from the Shockley- type interface state induced by the surface potential. The E_b position of the parabolic dispersion is almost the same to the original Shockley surface state of the clean Au(111) surface. Therefore, the interfacial interaction between coronene and Au(111) is again considered to be quite weak due to the physisorption.



Fig. 1. (a) The LEED image of the coronene(4×4)/Au(111) at 15 K, wherein the red dot is the substrate diffraction spot. The molecular structure of coronene is also shown. (b) The surface Brillouin zone (SBZ) of the Au(111) (black) and the coronene(4×4)/Au(111) (blue). The red line indicates the scanned region in ARPES. (c,d) The $E(\mathbf{k})$ map of the coronene(4×4)/Au(111) at 15 K, obtained from ARPES at $\mathbf{k}_{\rm FK} = 0.76 \sim 1.53$ Å⁻¹ and $\mathbf{k}_{\rm FM} = 1.06 \sim 1.78$ Å⁻¹. The ARPES spectra at $\mathbf{k}_{\rm FK} = 1.08$ Å⁻¹ ($\overline{\Gamma}$) and 1.44 Å⁻¹ (\overline{K}) and $\mathbf{k}_{\rm FM} = 1.25$ Å⁻¹ ($\overline{\Gamma}$) and 1.56 Å⁻¹ (\overline{M}) are also shown.

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Surface-dependent Hydration of Nanodiamonds in Colloidal Dispersions

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The organization of water molecules close to solid surfaces or around proteins differs significantly from pure water [1]. Reorganization of solvent molecules is likely to occur around colloidal nanoparticles and its understanding is of outermost importance to better estimate their reactivity and interaction with biological moieties in aqueous environment. Nanodiamonds (NDs) are of particular interest for the investigation of interfacial water since the existence of an ordered water shell ranging from 2 to 4 water layers was recently suggested. In 2014, we have observed that X-ray Absorption Spectroscopy (XAS) in pure transmission was particularly efficient to probe water interfacial water around NDs [2].

During this beam time at UVSOR-III, aqueous dispersions of NDs with different surface chemistries prepared from the same initial ND produced by detonation synthesis (diameter ~5nm) by Adamas Nanotechnologies were compared. Carboxylated (NDs-COOH), hydroxylated (NDs-OH) and hydrogenated (NDs-H) were characterized. For comparison, NDs produced by High Pressure High Temperature (NDs-HPHT), with a diameter of 16nm, were also characterized. By comparing these XA spectra at oxygen K edge to pure water spectra (Fig. 1), the organization of water molecules in hydration layers of NDs could be investigated.

After normalization to the absorption intensity before and after the oxygen edge, strong intensity variations of the signal were observed, which can be interpreted by surface-dependent variation of the water arrangement around NDs. NDs-OH are positively-charged, like NDs-H and NDs-sp2, but its XA spectrum does not differ from negatively-charged NDs-COOH. This result demonstrates that the water structure is not dependent on the Zeta potential of NDs as previously thought. The strong intensity of the main edge intensity at 538 eV for NDs-H dispersion, although its concentration is half of the other samples, demonstrate that the water organization is extremely different on hydrogenated surface. An enhancement of this feature was previously observed on surface-graphitized NDs (NDs-sp2), also having hydrogenated surface groups.

During this beam time, we could extend the preliminary results obtained in 2014 to NDs with well-defined surface chemistries. This work demonstrates that hydrogenated surface functional groups are the source of particular water arrangement on NDs. These results will be submitted for publication in the coming months, along with complementary infrared and Raman spectroscopies results.



Fig. 1. XAS of oxygen K-edge from water and aqueous dispersion of detonation NDs with different surface chemistries. Concentration is 1 wt % except for NDs-H (0.5 wt %). Surface-graphitized NDs (NDs-sp2) spectrum is extracted from reference 2.

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Mapping Oxygen Activation on Different Surface Facet of Palladium Nanocrystals for Organic Catalysis

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The O_2 activation process where inert ground triplet O_2 is excited to produce highly reactive singlet O_2 involves a key step in many organic oxidation and cancer treatment. However, it puzzles scientist what factor induces the change of electron spin state of O_2 molecules, although it has demonstrated that the presence of noble metal nanoparticles can promote the generation of singlet O_2 . In previous works, Q. Zhang et al., first demonstrated that surface facet of metal nanocrystals is a key parameter for tuning the activities of generating singlet oxygen. The experiments and simulations elucidated that a spontaneous spin-flip process may occur during the molecular absorption when appropriate surface facets are selected. On a selected surface facet, the charge state of the Pd surface is a critical parameter to activate O_2 to generate a species that behaves like singlet O_2 both chemically and physically.[1] Based on this finding, we prepared a metal-semiconductor hybrid system in which the nanocrystals of Pd{100} facets are supported on TiO₂ surface. Through illumination of appropriate light, the electrons are anticipated be transferred from TiO₂ to metallic Pd catalysts and thus enhance the oxygen activation.

To confirm the charge transfer at the heterojunction between TiO_2 and Pd heterojunction, chemical maps of oxygen distributions within microaggregates of SiN/TiO₂-Pd were studied by scanning transmission X-ray microscopy (STXM). The TiO₂-Pd hybrid structures were obtained according to following procedures. The Pd nanocubes with 20 mg TiO₂-P25 were synthesized according to a previously described protocol.[2] In a typical synthesis, 8.0 mL of an aqueous solution containing poly(vinyl pyrrolidone) (PVP, MW = 55 000, Sigma– Aldrich, 856568-100g; 105 mg), l-ascorbic acid (AA, Sigma–Aldrich, A0278-25g; 60 mg), and KBr (300 mg) was heated in a 50 mL three- necked flask for 10 min at 80 °C with magnetic stirring. Subsequently, 3.0 mL of an aqueous solution of potassium palladium(II) chloride ([K2PdCl4], Aladdin, 1098844-1g ; 63 mg) was added with a pipette, and the reaction mixture was stirred at 80 °C for 3 h. The powders were collected by centrifugation and washed with deionized water to remove excess PVP. The final product was dissolved into the deionized water and then dipped onto the SiN substrate.

Figure 1 displays the STXM images of (a) SiN/TiO₂-Pd (cubes {100} facets) and (b) SiN/TiO₂-Pd (octahedrons {111} facets), which are optical density (OD) maps obtained at 530.9 eV, the major characteristic absorption peaks of TiO₂. The bright region represents elemental distributions of O in TiO₂. The resonance at 530.9 eV for both surface facet is assigned to $1\sigma u \rightarrow 1\pi g^*$ transition for TiO₂ contacted with Pd surface. The preliminary results indicate that the chemical mapping of oxygen activation on different surface facet of Pd nanocrystals will shed light on designing high efficient noble metal nanocatalysts for organic oxidation and cancer treatments.



Fig. 1. The OD images of (a) SiN/TiO_2 -Pd (cubes {100} facets) and (b) SiN/TiO_2 -Pd (octahedrons {111} facets) obtained at 530.9 eV.

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Effect of Fe₂O₃ coating on ZnO nanorod probed by scanning transmission x-ray microscopy

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A novel Fe_2O_3/ZnO core-shell nanorods for photoelectrochemical (PEC) water splitting is developed recently.^[1] The PEC performances, such as photocurrent response and incident photons to electrons (IPCE), vary with the thickness of Fe_2O_3 coating layer. However, the mechanism of the improved PEC activity remains unclear. In this work, pristine and Fe_2O_3 coated-ZnO core-shell nanorods have been investigated by using x-ray spectroscopic coupled with microscopic approaches (i.e., x-ray absorption near-edge structure (XANES) and scanning transmission X-ray microscopy (STXM)).

Figures 1(a)-(d) present the O *K*-edge STXM images and its stack mappings of selected single nanorod of Fe_2O_3/ZnO and pristine ZnO. The stack mappings display blue, yellow, red and green areas, corresponding to the different regions that are associated with different thickness and chemical properties of the nanorods. Figures 1 (e)-(h) show the XANES spectra, which correspond to Figs. 1 (a)-(d). The different colored spectra reflect the various region of the nanorods. The O *K*-edge probes the electron transitions from O 1s core level to the O 2p-Zn 3d/4sp hybridized states. The area under the spectrum reflect the amount of density of unoccupied O 2p-derived states. Thus, based on the spectroscopic results, the electronic structures of the layer region and the core area differ in both samples. Besides, strong anisotropic effects are observed for both samples based on polarized-XANES. Notably, the density of states in the surface of the coated- and pristine nanorods are different and the results suggest that the oxygen-related deficiency is formed in the core-shell nanorods which



can affect the photocatalytic activity.

The enhanced PEC performance of Fe_2O_3 coated ZnO compared with pristine ZnO is likely to be owing to the presence of interface that causes varied electron density of states in the core-shell structured nanorods.

Fig. 1 Upper panel: Polarized O *K*-edge scanning transmission X-ray microscopy image and its corresponding stack mappings of selected single Fe_2O_3 coated- ((a)and (b)) and pristine ZnO nanorods ((c) and (d)). Lower panel: Polarized O *K*-edge STXM-XANES spectra of Fe_2O_3 coated- ((e) and (g)) and pristine ZnO nanorods ((f) and (h)). The color corresponds to the different region of the nanorods.

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Influence of the oxygen vacancy at Ta/TaO_x interface on resistive switching memories

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In this work, we have studied the electronic structure and the location of oxygen vacancy in the interface of the Ta/TaO_x/Pt thin film and identify the type of conducting path by scanning transmission x-ray microscopy (STXM). The amorphous TaO_x thin film of thickness of \sim 150 nm was deposited by electron beam evaporation on Pt/SiO₂/Si substrates. Active electrodes of Ta were thermally evaporated respectively on the TaO_x thin film with an equivalent thickness of ~150 nm. As shown in Fig. 1, the STXM stack mapping displays the cross-sectional views of the Ta/TaO_x/Pt thin film. Obviously, due to a uniform diffusion occurs in the vicinity of the Ta/TaO₂ interface, the image of the Ta/TaO_x/Pt thin film revealed that the interfacial TaO_x was \sim 180 nm in thickness. The experiments were performed at the 4U beamline. Fig. 2 presents the corresponding O K-edge x-ray absorption near-edge structure (XANES) spectra of the $Ta/TaO_x/Pt$ thin film. The O K-edge STXM-XANES spectra were recorded at three selected regions, cyan, red and yellow, in the Ta/TaO_x/Pt thin film, respectively. According to the dipole-transition selection rule, the features at ~530-545 eV are attributed to the electron excitations from O 1s-derived states to 2p-derived states, which are approximately proportional to the density of the unoccupied O 2p-derived states.¹ The intensities of the O K-edge STXM-XANES spectra of the red region are significantly higher than that of the cyan region, which reflects the increase in the number of unoccupied O 2p-derived states. In other words, the STXM-XANES results demonstrate that the population of defects at the O sites in the Ta/TaO_x interface and confirming the enhanced density of states of O 2*p*-derived states, as the population of defects and dangling bonds at/above E_{CBM} or E_F in the Ta/TaO_x interface. The STXM-XANES results intensely support the phenomena that the occurrence of O 2p vacancy at Ta/TaO_x interface affects the resistive switching effect of the Ta/TaO_x/Pt thin film.



Fig. 1. The STXM stack mapping of the cross-sectional views of the $Ta/TaO_x/Pt$ thin film.



Fig. 2. The corresponding O K-edge STXM-XANES spectra were recorded at three selected regions, *cyan*, *red* and *yellow*, in the Ta/TaO_x/Pt thin film, respectively.

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Resolving the electronic structure of TiO₂ core-shell nanostructures using scanning transmission X-ray microscope

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In this work, a three-dimensional (3D) hierarchical TiO_2 is successfully constructed using scanning transmission x-ray microscopy (STXM). The core portion of the sample contains rutile TiO_2 nanowire (NW) while the rutile nanoparticles (RNP) and anatase TiO_2 are sequentially located on the shell region. The TiO_2 NW array provides a fast electron transport pathway due to its quasi-single-crystalline structure and the 3D configuration with NPs in the shell portion provides a large surface area for more efficient photo-charge separation without significantly sacrificing the electron collection efficiency¹ which attracted our interest to probe this nano-scale interface phenomenon.

Fig. 1 shows the (a) scanning electron microscope (SEM) and (b) STXM images of focused ion beam (FIB) milled ANP/RNP/NW sample (above the red dashed line) on fluorine doped tin oxide (FTO) substrate (below the red dashed line). The STXM image was recorded at 460 eV. Fig. 2 (a) shows the magnified STXM image in middle of sample of fig. 1 (b), where Ti $L_{2,3}$ -edge x-ray absorption near edge spectra (XANES) had been measured and analyzed by principle component analysis (PCA) method. Fig. 2 (b) was generated by PCA method analyzed in the same area shown in fig. 2 (a) and indicates similar spectra with the same color which defines the spatial distribution of background (blue), Pt (yellow), carbon film (purple) and surface (red), semi-surface (green), shell (brown), semi-core (orange), core (cyan) regions of ANP/RNP/NW.

Fig. 2 (c) depicts the Ti $L_{2,3}$ -edge XANES of different regions of ANP/RNP/NW. Line shapes of eg-states in L_3 -edge around 458 eV show the anatase phase TiO₂ in the surface (red) and semi-surface (green) regions², the rutile phase TiO₂ in core (cyan) region and mixed spectra of anatase and rutile phases in shell (brown) and semi-core (orange) regions. These results reveal that even the size of ANP is smaller than the spatial resolution of STXM³, the spatial distribution of different phases of TiO₂ core-shell structures can still be successfully resolved under STXM after FIB milling.



Fig. 1 (a) SEM image of ANP/RNP/NW on FTO. (b) STXM image of ANP/RNP/NW on FTO measured at 460 eV.

Fig. 2 (a) Magnified STXM image of ANP/RNP/NW. (b) Spatial distribution of background (blue), Pt (yellow), carbon film (purple) and surface (red), semi-surface (green), shell (brown), semi-core (orange), core (cyan) regions of ANP/RNP/NW. (c) Corresponding Ti $L_{2,3}$ -edge XANES of different regions of ANP/RNP/NW.

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