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New In-Situ and Operando Facilities for Catalysis Science at NSLS-II: The Deployment of Real-Time, Chemical, and Structure-Sensitive X-ray Probes

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The start of operations at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory heralded a new beginning for photon-science-based research capabilities in catalysis. This new facility builds on many years of pioneering work that was conducted at the NSLS synergistically by many scientists from academia, government labs, and industry. Over several decades, numerous discoveries in catalysis were driven through the emergence of an arsenal of tools at the NSLS that exploited the power of emerging X-ray methods encompassing scattering, spectroscopy, and imaging. In-situ and operando methodologies that coupled reactor environments directly with advanced analytical techniques paved a rapid path towards realizing an improved fundamental understanding at the frontiers of chemical science challenges of the day.

The NSLS-II constitutes a powerful new source that replaces the NSLS; it will deliver unprecedented opportunities to unravel catalytic phenomena through the emergence of new tools for observing working reactions under real time, with high sensitivity to active chemical and structural state of catalysts. The storage ring at NSLS-II and several early beamlines are currently operational; of these, several key beamlines are purpose built for probing catalytic reactions, including CSX-2 (Coherent Soft X-ray: 23-ID-2), ISS (Inner Shell Spectroscopy: 8-ID), XPD (X-ray Powder Diffraction: 28-ID), SRX (Sub-micron Resolution X-ray spectroscopy: 5-ID), and ESM (Electron Spectro-Microscopy: 21-ID). In this short report, we introduce these new facilities and discuss their scientific capabilities for understanding chemical transformations essential for catalysis science.

NSLS-II: A powerful new source

NSLS-II is a state-of-the-art, third-generation synchrotron facility capable of emitting highly focused photons in the energy range of 0.1 eV to >300 keV [1]. The storage ring operates at 3.0 GeV with an electron beam current of 500 mA, 0.5 nm-rad horizontal emittance, and 8 pm-rad vertical emittance, resulting in an exceptionally large flux density that should exceed 10^{15} ph/s/0.1%BW across the entire spectral range [1]. NSLS-II is currently the most advanced synchrotron facility in the US that operates at energies ranging from soft to hard X-ray regions. This gives users sensitivity to chemical shifts in materials and access to surface-sensitive techniques (soft X-rays), but also allows bulk measurements which often resolve long-range ordering and overall chemical composition determination (hard X-rays). NSLS-II also rivals synchrotron facilities around the world with performance comparable to or greater than other sources worldwide. NSLS-II currently has 28 "cutting-edge" beamlines (16 operational, 12 under development), coupled with varied sample environments and support technologies. NSLS-II will eventually accommodate 60 beamlines upon completion.

A number of beamlines are specialized for catalysis applications due to their small focused beam, high flux, optimum resolution, and ability to change polarization, which facilitates in-situ and operando studies. CSX-2 (Coherent Soft X-ray, 23-ID-2) has endstations capable of highly surface-sensitive chemical state characterization (XPS/NEXAFS) of model and powdered catalysts under ambient pressure or flowing gas. ISS (Inner Shell Spectroscopy, 8-ID) and XPD (X-ray Powder Diffraction, 28-ID-2) can elucidate the bulk atomic structure (XPD, ISS) and chemical state (ISS) of powdered catalysts under high pressures and flowing gases. ESM (Electron Spectro-Microscopy, 21-ID) and SRX (Sub-micron Resolution X-ray Spectroscopy, 5-ID) allow the simultaneous in-situ imaging and chemical state characterization of model and powdered catalysts under ambient pressure reaction conditions. Combined, these beamlines are capable of forming a complete "picture" for a multitude of catalytic materials and processes.

CSX-2 (Coherent Soft X-ray: 23-ID-2)

The 23-ID-2 (CSX-2) beamline is an elliptically polarized undulator beamline providing X-rays with energy between 250 and 2000 eV with resolving power of up to 10^4 E/ΔE. This beamline is suitable for soft X-ray spectroscopy measurements, particularly focused on the core levels

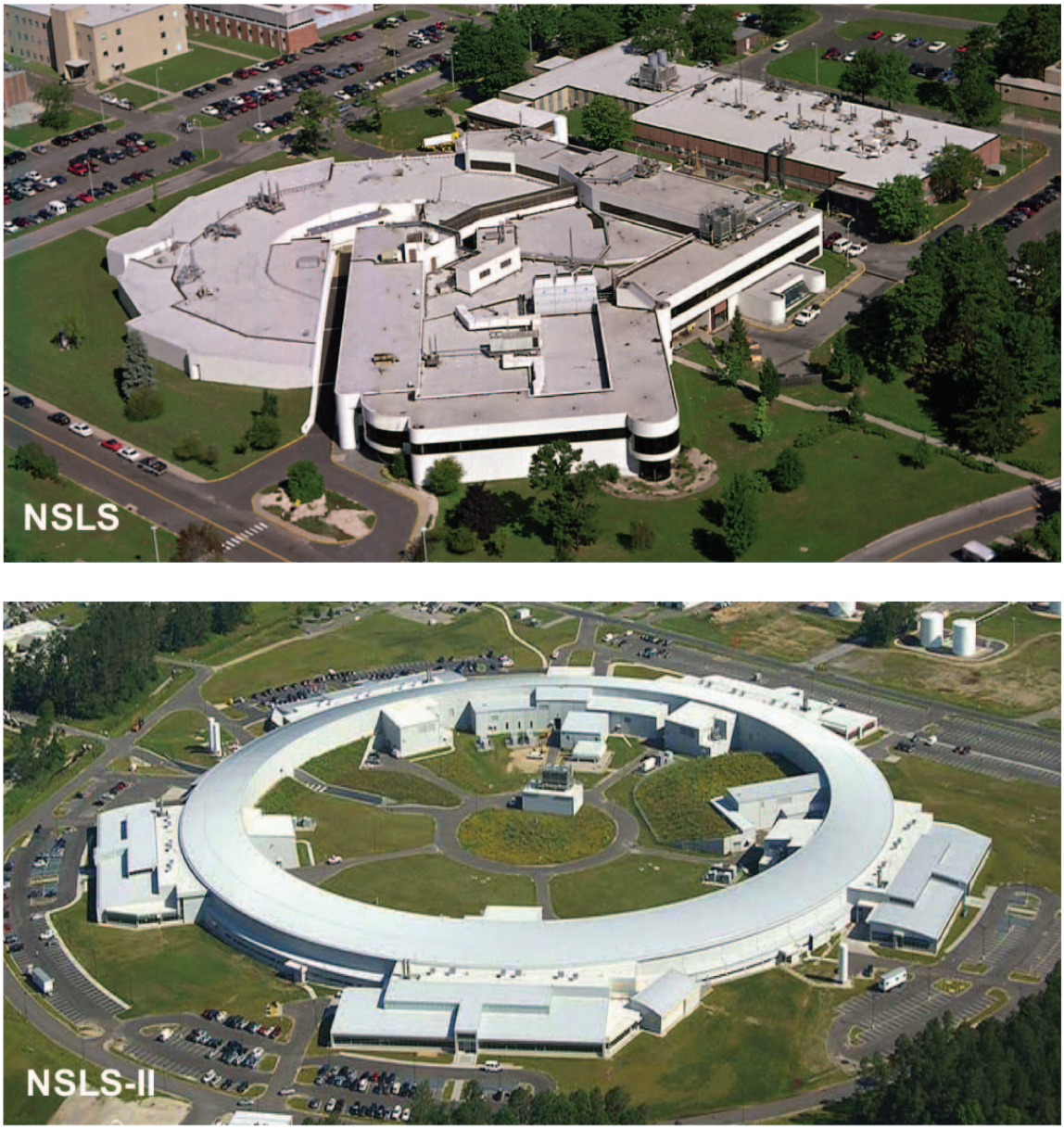

Figure 1: NSLS-I (top) and NSLS-II (bottom) facilities at Brookhaven National Laboratory. The NSLS-II is 5 times the size and 10,000 times brighter than the NSLS.

of light elements such as C, N, O, which are the most common elements present in reactants and products, as well as transition metals, which are commonly found, active components of catalysts. Bright X-ray photons with flux of up to 10^{13} photons/s allow the investigation of catalytic systems under realistic conditions, such as in atmospheric pressures of gases or in liquid environments.

Two endstations are available at the beamline, one for ambient pressure photoelectron spectroscopy (AP-PES) and the other for in-situ and operando X-ray absorption spectroscopy (IO-XAS). The AP-PES endstation, operated in partnership with the Center for Functional Nanomaterials (CFN), is equipped with a SPECS Phoibos 150 NAP analyzer. The sample temperature can be varied from room temperature to a maximum of 900°C in ultra-high vacuum (UHV). XPS is one of the most commonly used surface techniques in catalysis due to its inherent surface sensitivity, elemental specificity, and sensitivity to the chemical environment of the probed atom. Due to the short mean free path of electrons, XPS measurements normally require UHV conditions. However, in a typical AP-XPS set-up, such as in our endstation,

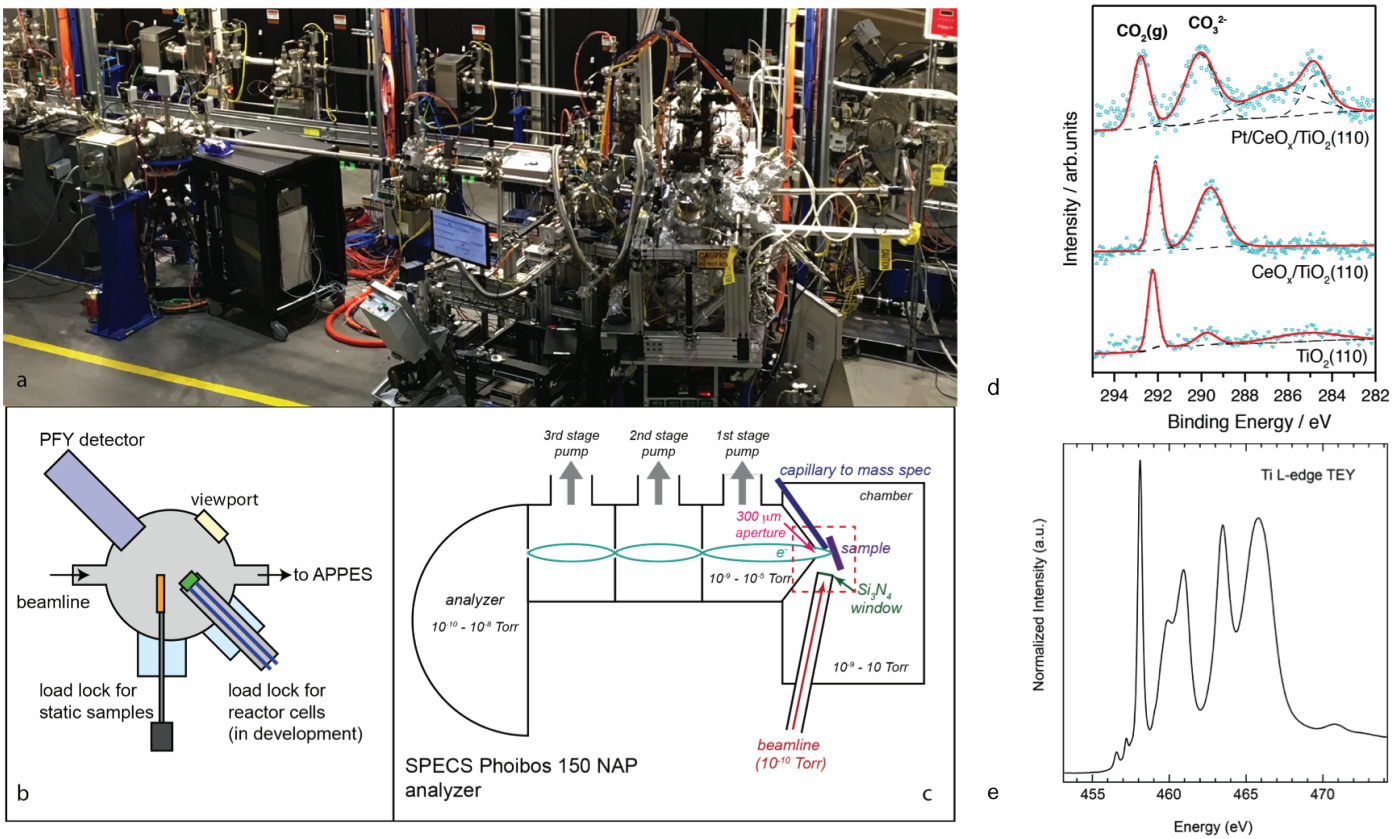

Figure 2: (a) Picture of the 23-ID-2 beamline including the two endstations. (b) Schematic of the IO-XAS endstation. (c) Schematic of the AP-PES endstation. (d) C 1s XPS spectrum from the AP-PES endstation under 100 mTorr CO_2 [2]. (e) Ti L Edge TEY spectrum from the IO-XAS endstation.

a differentially pumped analyzer and a 300 μm diameter aperture allow the analyzer to remain under vacuum while the main chamber can be backfilled to a maximum of 10 Torr. The endstation is separated from the UHV environment of the beamline by a 100-nm-thick Si_xN_y membrane, which is transparent to X-ray photons. This set-up allows the in-situ investigation of surface reactions in heterogeneous catalytic systems under elevated pressures where the reactants and catalyst dynamically interact under thermodynamic conditions that cannot be observed in UHV. AP-XPS yields information such as the chemical and oxidation state of the catalyst and adsorbed chemical species, as well as the identification of reaction intermediates under reaction conditions, which leads to the elucidation of reaction mechanisms [2]. The APS-PES endstation is currently available for general user proposals.

The IO-XAS endstation, available through a partnership with the BNL Chemistry Department, is equipped with a Vortex EM silicon drift detector for partial fluorescence yield (FY) measurements, a drain current measurement for total electron yield (TEY) measurements, and will be equipped with a partial electron yield (PEY) detector in the near future. Reactor cells capable of operating under flowing gas and liquid environments are currently under development. XAS provides complementary information to XPS, such as oxidation states and electronic structure of the material, by probing unoccupied molecular orbitals. Photon-in photon-out techniques allows a versatile sample environment, including ex situ solid samples as well as using in-situ cells. Therefore, XAS provides a bridge to the materials gap, in addition to the pressure gap, by allowing the measurements of much more complex samples, such as industrial powder catalysts, under atmospheric pressures of gases and in liquid environments.

ISS (Inner Shell Spectroscopy: 8-ID)

Inner shell spectroscopy (ISS) is the first hard X-ray (4–36 keV) spectroscopy beamline at NSLS-II dedicated to in-situ and operando research. X-ray absorption spectroscopy (XAS) is one of the most popular and powerful synchrotron-based techniques for catalysis research. XAS comprises X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS), which deliver element-specific information on chemical state and atomic coordination environment, respectively. With an exceptionally powerful damping wiggler as its source, the beamline delivers 5×10^{13} ph/s in the monochromatic beam (projected up 10^{14} ph/s when NSLS-II reaches full current). ISS uses a cryogenically cooled double crystal monochromator designed to manage the heat load of the DW insertion device. The

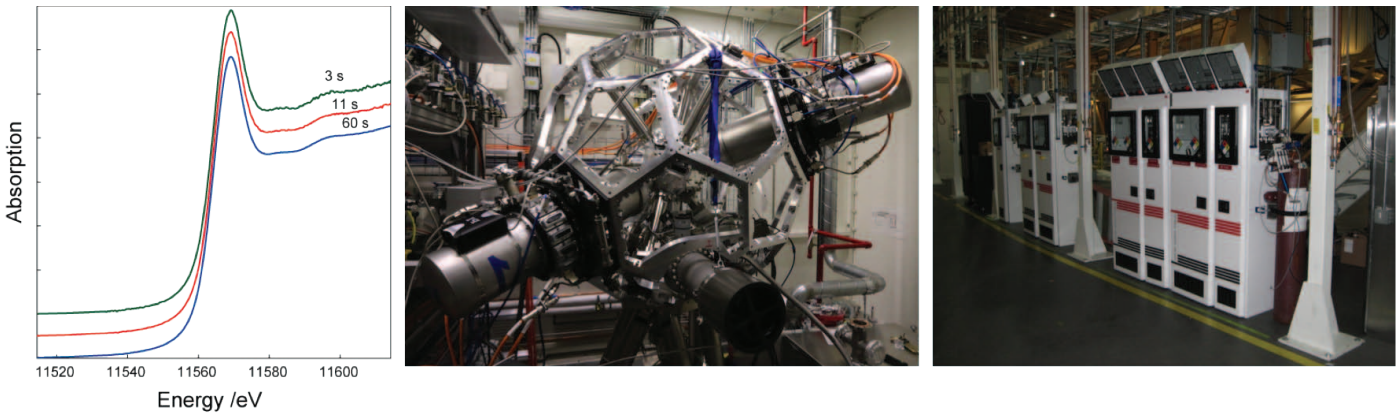

Figure 3: XANES spectra of a PtOx fuel cell catalyst (left panel) recorded with different times per full EXAFS scan; ISS endstation featuring two von Hamos crystal spectrometers (center); and the gas handling system at the ISS fully integrated with the beamline (right panel).

monochromator is driven by a direct drive servo motor, which allows it to perform XAFS scans in continuous (slew scan) mode. With the active element concentrations relevant for catalysis, high-quality XAS spectra can be recorded in several seconds. The speed, combined with the operando infrastructure fully integrated with the controls system, makes the beamline uniquely suited for catalytic experiments.

The beamline features two endstations. The first, dedicated to high-resolution X-ray spectroscopy, is being commissioned, with the main focus on high-energy resolution fluorescence detection (HERFD), X-ray emission spectroscopy (XES), and resonant inelastic X-ray scattering (RIXS). Two von Hamos spectrometers have been installed, and two backscattering analyzers are in development. Crystal spectrometers, as well as 15 silicon drift detectors, are integrated in the vacuum chamber surrounding the liquid nitrogen cryostat. A sample exchange robot allows loading of 10 samples and transfer under inert conditions. When the sample is loaded in position, it is connected to three gas delivery lines and eight electrical contacts, allowing for in-situ (electro)catalytic experiments. This endstation is expected to be fully available for users in Fall 2017. The second endstation, dedicated to high-throughput experiments, features a large stroke positioning stage which permits automated measurements for large (>100) sample groups. It is equipped with ion chambers for transmission experiments, as well as PIPS and SDD detectors for fluorescence measurements.

Operando capabilities at ISS are greatly enhanced by the gas handling system, which is an integral part of the beamline. Catalytically relevant gases are available or can be requested; liquid materials could be delivered as vapors with four evaporators. Two independent channels allow fast (<1 s) switching between gas mixtures, enabling kinetic experiments and modulation spectroscopy. The gas handling system is being commissioned and will be available in the first half of 2017.

XPD (X-ray Powder Diffraction: 28-ID)

The XPD (X-ray Powder Diffraction) beamline consists of two independent branch lines and three end-stations. One end-station (28-ID-C) hosts a three-circle diffractometer that is designed to accommodate a 1D strip detector and a high-resolution detector assembly. The 28-ID-C end-station is also equipped with two Perkin-Elmer large-area detectors and a robotic sample changer to support in-situ, operando, and high-throughput measurements. This allows the atomic structure elucidation of materials under catalytically relevant gasses at atmospheric pressures with fast acquisition times. The downstream end-station (28-ID-D) is designed to support more elaborate/complex or long lead-time set-ups, such as large pressure cells, non-routine reaction chambers, combined spectrometry, and user-custom devices. The 28-ID-B end station is dedicated for pair distribution function (PDF) and is currently under construction. The PDF end-station is due to take first light in early 2018 and will provide complementary small-angle X-ray scattering (SAXS) data along with high-quality PDF data. A variety of sample environments, including a gas flow-cell, a (5–300) K liquid He cryostat, a (80–500) K liquid nitrogen cryostream, and a (300 ~ 2000) K quadruple furnace are available at the XPD beamline. In the near future, a number of gases will also be available for the XPD users. The high-resolution powder diffraction configuration is under commissioning and will be used for structure solving and microstructure analysis on a range of polycrystalline materials. The PDF technique utilizes both Bragg and diffuse scattering signals and emerges as a powerful tool to study the short-range order in complex materials. Therefore, the XPD beamline provides a great platform to study structurally challenging materials on a broad length scale in a variety of sample environments.

ESM (Electron Spectro-Microscopy: 21-ID)

The Electron Spectro-Microscopy (ESM) beamline, constructed as part of the NSLS-II Experimental Tools (NEXT) project, aims at providing the scientific community with state-of-the-art instruments to perform soft X-ray photoemission spectro-microscopy measurements [3]. The beamline houses two endstations: a micro-spot angle-resolved photoemission spectroscopy (μ-ARPES) endstation and the X-ray pho-

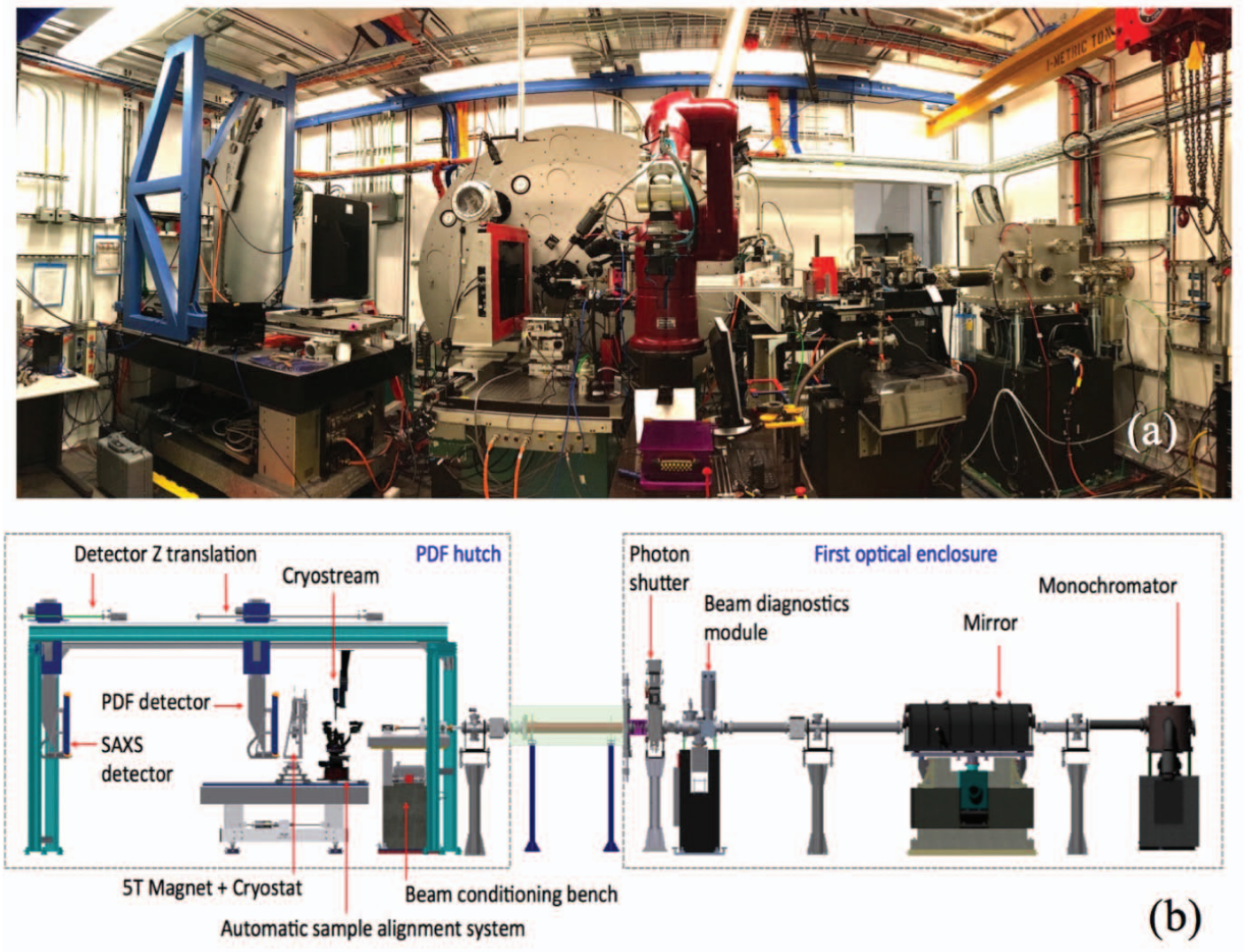

Figure 4: (a) A picture of the 28-ID-C end-station that has been supporting general user operation since the summer of 2015. (b) Schematic diagram of the proposed PDF beamline.

toemission electron microscopy (XPEEM) endstation. The XPEEM endstation is provided via a Partner User Agreement between NSLS-II and BNL's Center for Functional Nanomaterials (CFN).

The source for the ESM beamline (21-ID) is one of the two in-line elliptically polarized undulators (EPUs): EPU57 or EPU105 [4]. The undulator parameters are optimized to provide continuous coverage in the energy range 15–1500 eV. The ESM plane grating monochromator is equipped with four gratings covering the entire energy range. After the monochromator, the beam can be intercepted by either of the two M3 mirrors. M3-A deflects the beam outboard toward the ARPES endstation, while M3-P deflects the beam inboard toward the XPEEM endstation. Optically, the two branches adopt different refocusing schemes. In the ARPES branch, a pair of elliptical cylinders is arranged in the KB configuration to focus the beam down to 1 μm, while the beam is focused into the 40 μm × 40 μm spot in the XPEEM endstation using a single ellipsoidal mirror.

The XPEEM endstation is served by an Elmitec aberration-corrected low-energy electron microscope (AC-LEEM) equipped with an imaging energy analyzer for the spectroscopic characterization of the surfaces. By combining XPEEM with LEEM, structural sensitivity and diffraction techniques are added to spectroscopy, enabling a powerful multi-technique approach to the study of nanostructured surfaces in-situ under extreme conditions, such as elevated temperature and gas pressure, thus enabling powerful studies of surface chemistry, growth and self-assembly, electronic properties, etc. [5, 6]. This system enables direct imaging of the topographic, chemical, and magnetic properties of the surfaces, as well as the electronic band structure with spatial resolution of ~3 nm.

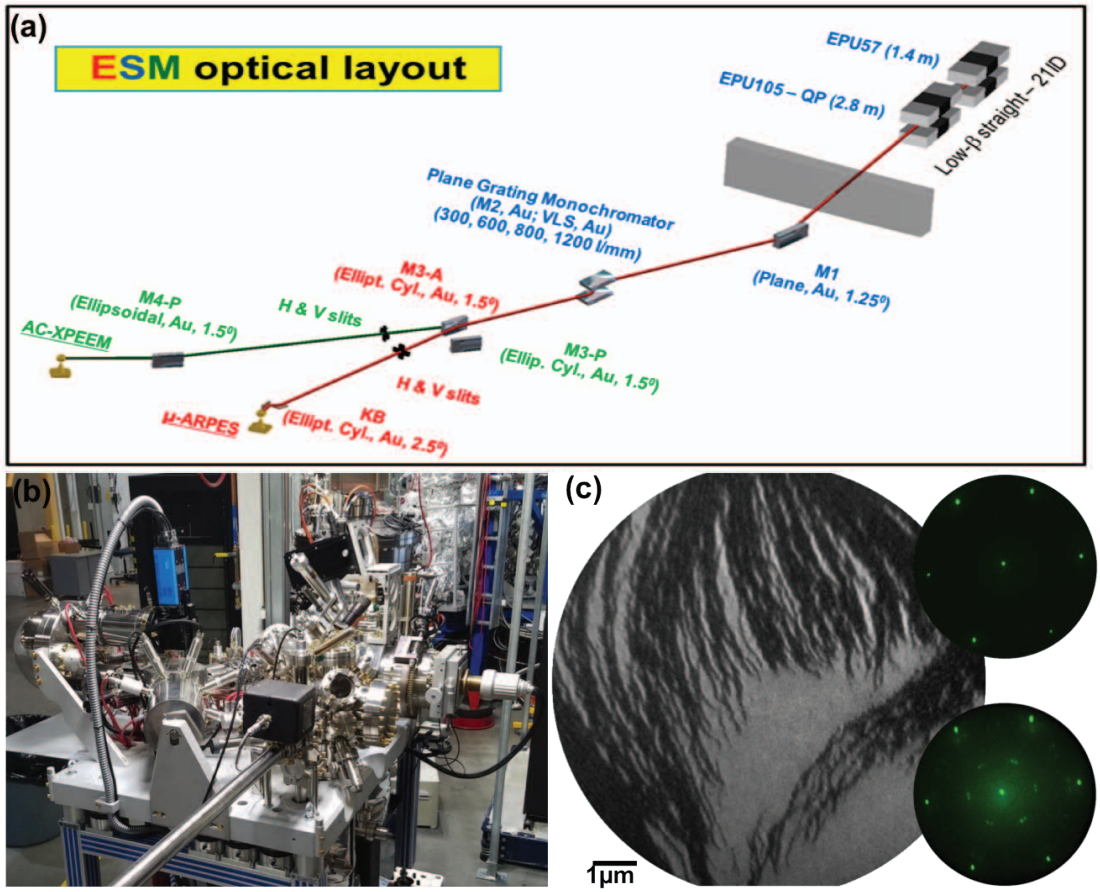

Figure 5: (a) Schematic of the optical layout of the ESM beamline at the NSLS-II. (b) A photo of the XPEEM endstation at the ESM beamline. (c) A LEEM image recorded during the CO reduction of Cu_2O/Cu(111) at 575 K; insets show LEED pattern evidencing the hexagonal packing of metallic Cu after reduction (top), and a LEED pattern from the initial Cu_2O film (bottom), respectively [6].

The combined XPEEM/LEEM system has great potential to monitor dynamic surface processes; for example, in catalytically relevant chemical reactions on surfaces. Whereas currently the time resolution of PEEM using core-level photoelectrons is limited to a few seconds per frame, LEEM can image at video rates. LEEM is therefore crucial in directly following dynamic phenomena, such as adatom diffusion and propagation of chemical waves. Moreover, the high brilliance of NSLS-II, combined with much improved transmission in the state-of-the art aberration-corrected XPEEM/LEEM systems, allows reducing the acquisition time in the XPEEM to hundreds, or possibly tens, of milliseconds, allowing for the observation of both space and time characteristics of reaction wavefronts. These faster acquisition times will also allow minimizing radiation damage and sample charging, opening the way to the investigation of several oxide systems that are now "off-limits" to standard XPEEM/LEEM systems.

The XPEEM/LEEM endstation at the NSLS-II ESM beamline will be open to a general user program in May 2017. It will fill a critical need in the user community for highest-resolution in-situ microscopy and spectroscopy in complex environments, responding to grand challenges in catalysis, carbon capture, and materials genome.

SRX (Sub-micron Resolution X-ray Spectroscopy, 5-ID)

The Sub-micron Resolution X-ray Spectroscopy (SRX, 5-ID) Beamline is designed to deliver advanced scanning spectroscopic microscopy capabilities [7–9]. SRX enables micro-beam X-ray fluorescence microscopy (μ-XRF) for elemental mapping and micro-beam X-ray absorption near-edge structure (μ-XANES) spectroscopy for chemical specification. Two separate sets of Kirkpatrick-Baez (KB) mirrors provide high spatial resolution. Firstly, the high-flux KBs provide a submicron beam with high (~10^{12}–10^{13} ph/s) photon flux. This set-up is operational and accepts user proposals. Secondly, the high-resolution KBs will provide a sub-100 nm beam with a moderate (~10^{11} ph/s) photon flux. This system is currently in its commissioning phase. Besides conventional 2D XRF imaging and point XANES, multi-dimensional spectroscopic imaging such as XRF tomography and XANES stack im-

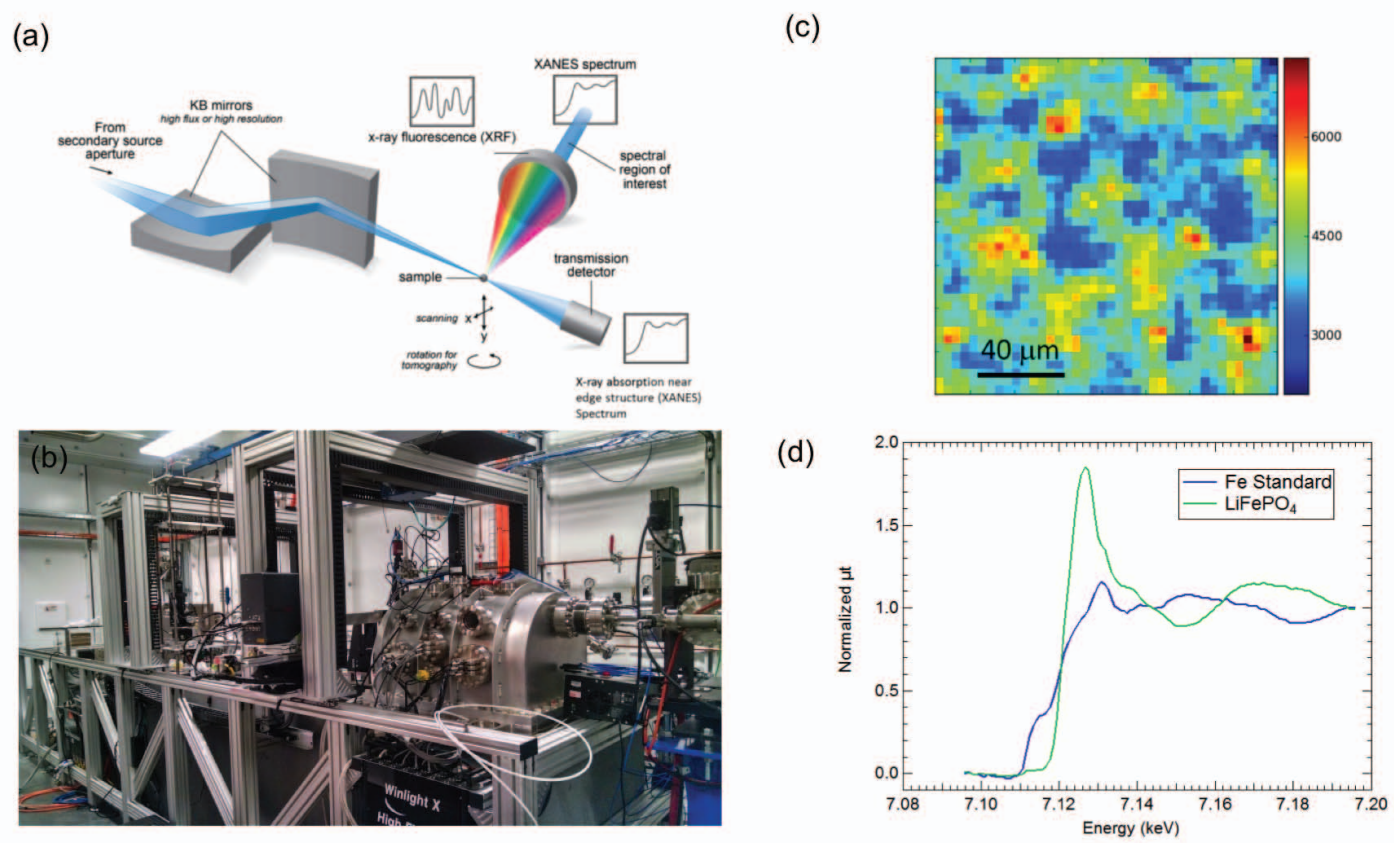

Figure 6: (a) Schematic of the SRX (5-ID, NSLS-II) beamline showing XRF imaging and XANES spectroscopy capabilities with sub-micron resolution [10]. (b) An image of the end-station of SRX with the gantries providing flexibility of detector positioning between two set-ups: the high-flux and high-resolution modes. (c) An XRF map of a nanoporous material for catalysis application studied at SRX, showing the Ni concentration. (d) XANES spectra collected at SRX show $LiFePO_4$ and an Fe standard, resolving chemical species/oxidation states.*

aging are also under development, along with the capability for micro-Extended X-ray Absorption Fine-Structure (µ-EXAFS) spectroscopy.

SRX suits the studies of heterogeneous systems under operando conditions for several reasons: (1) the scanning probe is designed to investigate the elemental and chemical heterogeneity by analyzing the local composition; (2) the sample can be mounted under ambient conditions, in air, within a relatively large area on the mm to cm range, which is ideal for setting up operando sample environments; and (3) the achromatic nature of KB mirrors allows for a very quick and easy change of energy over a wide range (4.4–25 keV) of operation enabling absorption spectroscopy experiments for a variety of scientifically interesting elements. Figure 6(a) shows the schematic of the SRX end-station, where µ-XRF and µ-XANES experiments can be conducted [10]. A realistic view of the end-station is shown in Figure 6(b). As an example of scanning µ-XRF imaging, a nanoporous material for potential catalyst applications [11, 12] is shown in Figure 6(c). The µ-XANES spectra can then be collected at any position to determine the local chemical speciation. Two such spectra from iron-containing lithium ion battery electrode samples are shown here; further examples can be found in previous works from SRX [9, 13].

Galvanizing a community of catalysis users

Creating and supporting catalysis user community at synchrotrons has proven to be an efficient way to help advance catalysis and electrocatalysis science, enhance catalysis research from a broad range of users (from experienced to beginners), develop new beamline capabilities and better utilize existing ones [14]. One successful example is the Synchrotron Catalysis Consortium (SCC) consisting of catalysis researchers from academic, national, and industrial laboratories. This consortium has enabled, since its inception in 2005, advancement of our understanding of catalytic materials and phenomena through the utilization of the state-of-the-art synchrotron techniques and training several generations of synchrotron users in applying them under in-situ and operando conditions (Figure 7). The productivity of the facility beamlines that were co-supported by the SCC and used by the catalysis community, as measured by the percentage of beamtime utilization and publication output by catalysis researchers, has increased by more than three times after the establishment of the consortium. In 2017, SCC PIs submitted a PU proposal to the suite of spectroscopy beamlines (ISS, TES, and QAS) of NSLS-II. Under this proposal, the PUs will provide a wide range of expertise and resources in surface science, catalysis,

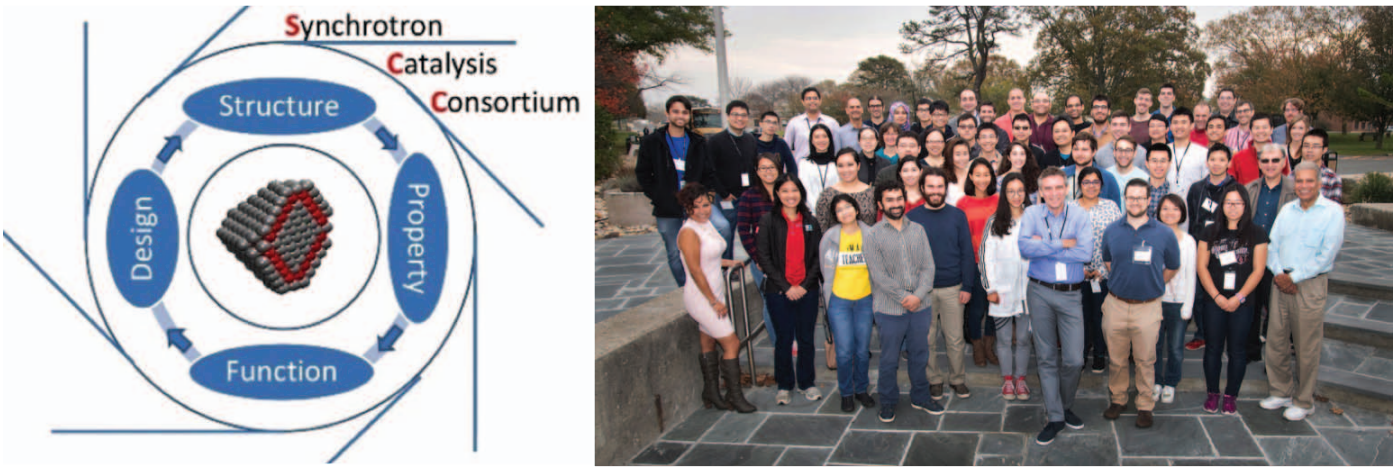

Figure 7: Members of the Synchrotron Catalysis Consortium (SCC) develop dedicated facilities and advanced synchrotron methods for solving problems in catalysis science (left). The picture on the right was taken at the 2016 XAFS short course at BNL, organized by SCC.

electrocatalysis, beamline science, and instrumentation to existing and new general users.

Conclusions

The Catalysis Science program at BNL is intimately connected to the photon science capabilities at the NSLS-II. NSLS-II is a valuable resource for both experienced and new catalysis science users, who are encouraged to seek access to the various facilites described here. In-situ and operando investigations through scattering, spectroscopy and imaging, enhanced with a powerful new X-ray source, will be the cornerstone of studies that are focused on revealing new insights into catalytic phenomena. These new facilities will be the enabler for discoveries that will strive to answer challenging questions in catalysis and meet technological demands in the consumer/industrial world.

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