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Scanning Probe Microscopy in US Department of Energy Nanoscale Science Research Centers: Status, Perspectives, and Opportunities

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1. Introduction

For the last two decades, the concepts of nanoscience and nanotechnology have been integral to much of the scientific progress. The early visionaries of nanoscience such as Richard Feynman famously predicted that "there is plenty of room at the bottom," and offered a challenge for how this space can be explored and used. Almost 30 years after that quote was first expressed, the interest in nanoscience was rekindled by a 1986 book by Eric Drexler titled "The Engines of Creation",[1] bringing forward the concept of nanoscale control of the structure of matter, self-reproducing machines, and enormous impact on all areas of human knowledge and technology from large-scale manufacturing to medicine they will offer. While many concepts envisioned by Drexler still wait for experimental implementation, the inspiration it bestowed onto generations of scientists entering the field is undeniable. Many areas that emerged since then–from molecular electronics[2,3] to plasmonics[4–6] to nanomagnetism[7]–have become the inseparable part of modern research. The National Nanotechnology Initiative established by a consortium of US government agencies and multiple scientific leaders (most notably Michael Roco) has provided an integrated roadmap for nanoscience and nanotechnology development in the US and worldwide.

However, perhaps equally important, albeit less noticed at that moment, were the factors that made nanotechnology and nanoscience revolution possible in the nineties. As pointed out by Freeman Dyson,[8,9] one of the eminent physicists of twentieth century, "*Science originated from the fusion of two old traditions, the tradition of philosophical thinking that began in ancient Greece and the tradition of skilled crafts that began even earlier and flourished in medieval Europe. Philosophy supplied the concepts for science, and skilled crafts provided the tools.*"[10] While Feynman laid down the philosophical basis of nanoscience, it was the invention of the scientific tools such as electron microscopies,[11,12] and spectacular demonstration of scanning probe microscopies (SPM) including scanning tunneling[13,14] and atomic force microscopy[15] in the mid 1980s that opened the doors to the nanoworld.[16] Returning to the original statement by Feynman, it is the capability to see and manipulate the space at the bottom that makes it truly useful.

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2. Electron Microscopy and SPM

Following the seminal works by Lord Raleigh on resolution in wave optics, it was realized that the much smaller wavelength of high-energy electrons can potentially enable imaging with atomic and subatomic resolution. The early work by E. Ruska in 1931 demonstrated the feasibility of electron microscopy imaging using parallel beam, laying the foundation for the field. In his Nobel lecture he actually notes that learning of the deBroglie criterion (after building his first microscope) he calculated a resolution of 2 Å.[11] Von Ardenne invented scanning transmission electron microscopy (STEM) in 1938,[17,18] but development was stymied by noise inevitable for cold field emission gun.[19] Since the disruption of World War II, electron microscopy has enjoyed multiple decades of almost uninterrupted growth, with notable milestones including development of high resolution STEM and electron energy loss spectroscopy (EELS) in 1966 by Albert Crewe,[20] achieving the first images of individual atoms with an electron microscope,[21] and subsequent introduction of aberration correction that is now the mainstay of the field.[22] Many of these developments are described in several recent books and reviews.[12,23] Currently, STEM/EELS experiences a period of active growth, with recent breakthroughs in spatial and energy resolution allowing direct mapping of order parameter fields,[24–27] single-atom electron spectroscopy of atoms inside crystals[28] and in monolayer graphene,[29,30] and even the direct identification of light atoms in monolayer materials from their image intensity,[31] providing an ultimate imaging and analysis tool for nanoscience.

The operation of (S)TEM equipment by definition requires a high or ultra high vacuum (UHV) environment. Environmental cells to operate in liquids, gas, or active electrochemical environments require significant developmental effort, and are actively pursued in the context of biological and energy–related electrochemical imaging. Similarly, high spatial resolution and low drift required for the spectroscopic imaging require low-noise environments with acoustic, vibrational, and electromagnetic shielding, necessitating construction of low-noise facilities. Finally, the advanced aberration corrected modes are impossible without complex control software that allows practical implementation of high-order corrections. Taken together, these factors have required long-term concentrated and focused developmental effort. The factors that ultimately made electron microscopy a success is a trifecta of (a) significant scientific interest and capability to produce readily interpretable results by an operator, (b) sustained developmental effort by commercial companies and research institutions worldwide to develop new generations of hardware and software and (c) long-term

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governmental support that allowed establishment of (S)TEM research centers including low-noise environment buildings, fleets of multiple machines and sample preparation equipment that allowed seamless operation by cadre of trained personnel, and concurrently developing schools of theoretical thought. This large scale investments in Germany, Japan, US and now many countries worldwide made (S)TEM the power it is now.

It is interesting to compare this progress to that of scanning probe microscopy. Many ideas underpinning modern AFM were embodied in the 1927 patent by Schmaltz,[32] who assembled a sample profiler that scanned a sample underneath a cantilever-based force sensor, and sharp probing tip interacting with sample surface. The concept of current-based topographic feedback was introduced almost 50 years later in Topografiner developed by Young group at NIST.[33,34] Finally, the explosive growth of STM was initiated by the demonstrated atomic resolution on Si surface by Binnig, Gerber, and Rohrer,[13,14] who then rapidly introduced AFM in 1986.[15,16] The early 1990s saw the simultaneous commercialization of STM and AFM. Concurrently, the development of microfabricated etched cantilevers by Quate[35] has enabled reproducible and often quantitative AFM measurements (as compared to early practice of cutting AFM cantilevers from foil, with associated highly irreproducible results and low throughputs). While the number of SPM platforms worldwide is by now very significant (>30 000), most of these has been introduced in less than the last two decades.

Similar to (S)TEM, high resolution STM and AFM require imaging in UHV environment to avoid surface contamination and sufficiently low noise environment to achieve stability required in z-direction to maintain tunneling gap and laterally to achieve the atomic resolution and minimize drift. However, the near-field nature of imaging (looking *at* the surface, as opposed to *through* the thin section) necessitates long and time consuming in situ sample preparation. Similarly, tip conditioning requires significant effort and tip stability (e.g., pick-up of surface ad-atoms) can be a significant factor limiting imaging. This results in much longer time requirements for high-resolution imaging. Combined with relative youth of the field, this resulted in much smaller commercial effort, with only few companies offering specialized UHV SPM equipment. Also similar to (S)TEM, high resolution AFM and STM imaging necessitates low noise environments, with a number of dedicated facilities for UHV SPM established worldwide (including, for example, Argonne National Laboratory and National Institute of Standards and Technology in US and MPI Stuttgart in Germany) for high-end UHV instrumentation. Notably, the last several years have seen multiple demonstrations of atomic resolution imaging at liquid-solid interfaces with standard low-cost platforms[36–43] once the low noise conditions and appropriate probes became available.

As with electron microscopy, rapid development of SPM techniques can be expected in the environment that combines the facilities for large scale instrumentation operation and development (platforms, probes, and control/data analysis electronics and software), strong interdisciplinary research and technical teams, and allows for interactions with materials preparation and theoretical efforts. Many of such teams are established in Europe (particularly Germany and Switzerland) and Japan. In US, the Nanoscale Science Research Centers have emerged as multidisciplinary centers for nanoscale research, with significant effort dedicated to development of nanoscale imaging tools. This special issue showcases the recent progress in SPM across the NSRC system, highlights the progress achieved in several SPM directions, and formulates several future directions for future SPM development currently pursued by NSRC teams.

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3. US Department of Energy Nanoscale Science Research Centers

The Nanoscale Science Research Centers (NSRC)[44] have been established by the US Department of Energy (US DOE) as premier user centers for the interdisciplinary research at the nanoscale, including new science, new tools, and new computing capabilities. The 5 NSRCs are the Center for Nanophase Materials Sciences (CNMS)[45] at Oak Ridge National Laboratory, the Molecular Foundry (MF)[46] at Lawrence Berkeley National Laboratory (LBNL), The Center for Integrated Nanotechnologies (CINT)[47] administered by Los Alamos National Laboratory (LANL) and Sandia National Laboratories, The Center for Functional Nanomaterials (CFN)[48] at Brookhaven National Laboratory, and the Center for Nanoscale Materials (CNM)[49] at Argonne National Laboratory.

The operational model of the NSRCs generally combines two elements, namely the support of an external user program and an in house research program and instrument development. This model allows both attraction and retention of skilled scientific staff, development of new commercially unavailable

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instrumental platforms and operation of unique commercial equipment, and dissemination of this expertise and capabilities to a broad scientific community. The details of the user program are available on the websites of the corresponding nanocenters.[45–49] Below, we provide the general overviews of the SPM-related research programs at each NSRC, complementing the focused contributions combined in this special issue.

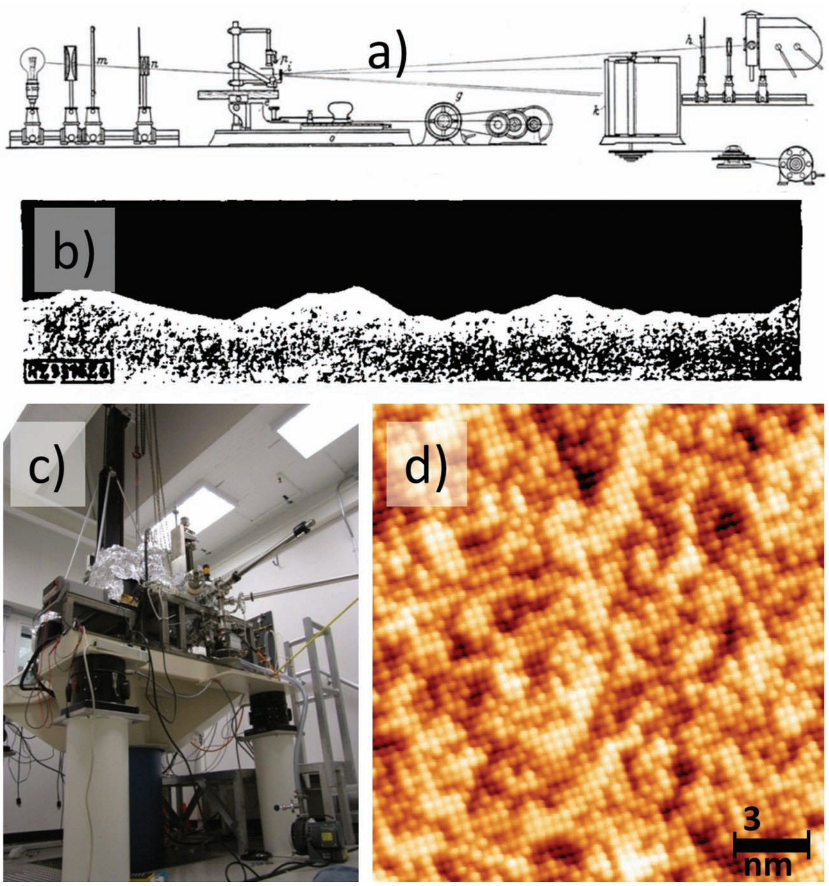

Figure 1. Evolution of SPM from optical lever profilometer of 1929 to modern STM platforms. a) Schematic diagram of the optical detection scheme used to measure the motion of a stylus probe over a surface. This instrument recorded surface topography using photographic film, an example of which is shown in (b). Reproduced with permission.[32] Copyright 1929, VDI-Z. c) The STM platform for low-temperature high magnetic field operation (300 mK, 9 T) built at the Center for Nanophase Materials Sciences and d) and example of atomic-resolution image of FeSeTe superconductor surface illustrating the segregation of chalcogen atoms (courtesy of M. Pan, CNMS).

3.1. Center for Nanophase Materials Sciences

The Scanning Probe Microscopy (SPM) effort at the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) is based on three synergistic components, including (a) development of high-resolution SPM platforms for UHV, ambient, and controlled environment imaging, (b) novel multidimensional data acquisition and image analysis methods based on physical and multivariate statistic models, and (c) in situ surface preparation and imaging under ultra-high vacuum and electrochemically relevant conditions. The first direction is represented by the design and construction of a high-field low-temperature STM (9 T and 300 mK, **Figure 1**c,d), a variable temperature STM, as well as instruments for microwave microscopy[54] and combined STM-STEM imaging. This is complemented by an array of commercial/custom built SPM tools including electron microscope with spin-polarization analysis (SEMPA), four-probe STM as described in contribution by A.P. Li et al., and variable-temperature AFM-STM. This suite of instruments allows comprehensive imaging, spectroscopy, and functional analysis of adsorbed molecular systems, in situ and ex situ grown oxide materials, and layered oxides, graphene, and superconductors.

Development of novel imaging techniques[55] has been pursued in the context of local studies of ferroelectric phenomena[56] and electrochemical reaction on the nanoscale.[57] The band excitation method[58] based on parallel excitation and detection of multiple frequencies has been developed to comprehensively study dissipative processes in magnetic, mechanical, and electromechanical systems, and to enable resonance-enhanced imaging in electromechanical and voltage modulated SPM. Combination with controlled-trajectory SPM scanning allows additional flexibility in image space.[59] Band excitation was further developed to support a broad range of time- and voltage spectroscopies, as featured in the contribution by R. Vasudevan in this volume. These approaches are presently being developed for electrochemical manipulation of matter on molecular levels and for probing the coupling between physical and electrochemical phenomena on the nanometer and atomic scales. This direction is complemented by development of insulated and shielded SPM probes for liquid electrochemical imaging.[60,61]

The quest for high, ultimately atomic, resolution imaging of surfaces by SPM is impossible without appropriate sample preparation. For layered materials such as some oxides and superconductors this can be achieved by simple cleaving. However, most oxide surfaces cannot be prepared (with atomic perfection) by classical surface science techniques such as sputtering and annealing. Hence, significant effort at the CNMS is aimed at the development of in situ growth techniques such as pulsed laser deposition (PLD) and interfacing it with the available fleet of SPM platforms. In this issue, this effort is represented in the contribution by Z. Gai et al. Similar challenges arise in the context of imaging of electrochemical materials for energy conversion and storage. In this case, the usual assumption of kinetic stability in SPM is no longer applicable, and specialized environments (glove box, flow cells, liquid cells) maintaining constant electrochemical potential of the mobile components are required.[62] This effort is complemented by

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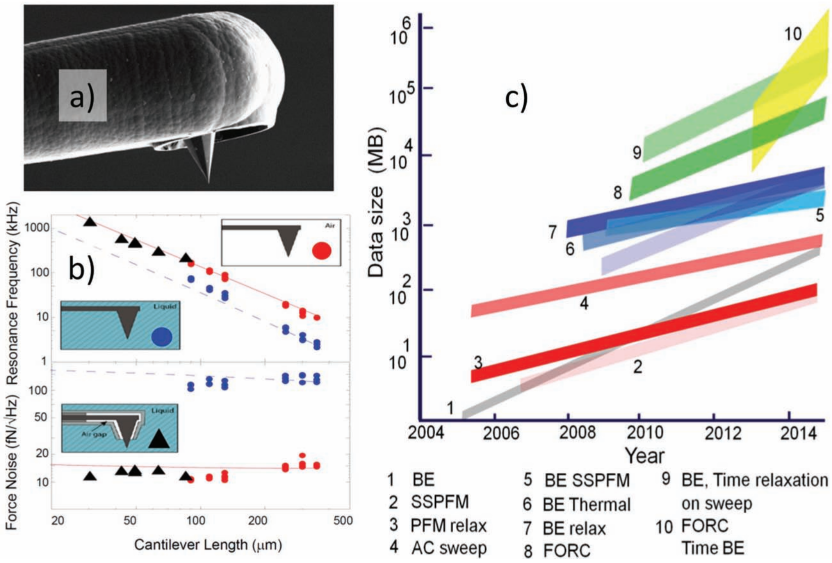

Figure 2. a) Development of advanced probes at the Molecular Foundry. Shown is an SEM image of an encased cantilever. The released probe apex protrudes from the encasement to interact with the sample in solution while the encasement traps a bubble of air keeping the cantilever dry with low damping. b) Graphs of cantilever resonance frequency and force noise for various cantilevers. Regular cantilevers in air (red dots) have high resonance frequency and low force noise for high sensitivity. The same cantilevers in water (blue dots) have lower resonance frequency and much higher noise. Encased cantilevers in solution (black triangles) have high resonance frequency and low force noise as if in air (image and data courtesy of Paul Ashby, Molecular Foundry). c) Development of advanced multidimensional SPM mode for probing bias-induced phase transitions and electrochemical reactions at the Center for Nanophase Materials Sciences. Show is the growth in data volume in a single measurements since the initiation of the program, representing evolution from 3- and 4D imaging modes to 5D[50–53] and planned 6D dynamic regimes. BE is band excitation (parallel frequency detection substituting sinusoidal excitation in single frequency SPM), SSPFM is switching spectroscopy PFM, FORC is first order reversal curve measurements.

development of multivariate methods for analysis of physics and electrochemistry of surfaces from atomically resolved images (following recent developments in the field of high-resolution electron microscopy[24,25,27]) and multidimensional spectroscopic data sets.

3.2. Center for Integrated Nanotechnologies

The SPM effort at the Center for Integrated Nanotechnologies (CINT) is in investigating dynamic properties of soft, biological and composite nanomaterials, particularly membrane-inspired organizations. The rationale and ultimate goal of this effort is to mimic and improve upon 2D organization and function in biological systems for materials applications towards development of 1) responsive membrane-based materials and 2) long-range 2-dimensional functional materials capable of performing complex, multi-step operations. A significant effort is focused on the synthesis of amphiphilic peptides and cofactors as well as surface functionalization and patterning strategies to generate environmentally responsive materials. Characterization of such materials relies heavily upon the utilization of in situ AFM. Utilizing a closed fluid cell enables the ability to add components and/or alter the environment while continually monitoring dynamic organization on the nanoscale via AFM. Combination of in situ AFM with other techniques such as various fluorescence microscopy techniques allows nanoscopic details of 2-dimensional organization and response to be determined. Examples of platforms of interest include lipid bilayer assemblies, amphiphilic block-co-polymer membrane assemblies and grafted heteropolymer assemblies. By introducing cofactors capable of performing functions such as chemical redox reactions and light-induced energy and electron transfer, and creating localized regimes within a 2D and ultimately 3D array of specified reactions, the ability to mimic complex long-range, multi-step biological functions becomes possible. Further, generating responsive materials capable of adjusting to environmental conditions likewise becomes possible.

3.3. Molecular Foundry

At the Molecular Foundry, SPMs are playing a central role in understanding and designing novel materials systems, providing insight into nanoscale properties as well as functionalities that emerge from mesoscale interactions of localized states. The Foundry SPM efforts are focused on two interrelated themes: (1) the development of multimodal and multidimensional SPM;[63] and (2) in situ SPM, particularly at solid-liquid interfaces.[64,65] Critical to both directions is a strong effort in designing and fabricating new types of functional engineered scan probes (FESPs) and related imaging systems, which demonstrate dramatically increased SPM performance and functionality.[66]

The goal behind multimodal and multidimensional imaging is to explore the basic principles underlying functionality by correlating chemical information (e.g., molecular composition, reaction rates) with physical properties (e.g., electronic structure, optoelectronic properties) and morphological structure. A specific area of emphasis at the Foundry has been in combining the chemical information and ultrafast temporal resolution (fs) inherent in optical studies with the capabilities of modern scanning probe techniques. This has required the longstanding 'nanospectroscopy imaging' problem, a problem defined by the difficulty of optically probing *local* material properties in a widely-applicable fashion, to be tackled. Recently, simple and general solutions to this problem have been demonstrated, as highlighted in the "Life Beyond Diffraction: Opening New Routes to Materials Characterization with Next-Generation Optical Near-Field Approaches" contribution of this volume. These new capabilities are currently being applied to the systematic development of efficient energy conversion materials, where energy conversion and transport need to be understood at the length scales relevant to these processes.

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Investigating the technologically- and biologically-relevant phenomena occurring at solid-liquid interfaces has motivated extensive in situ SPM efforts. For example, understanding how complex biological processes are related to protein assembly and organization is a relatively untapped frontier in biology and source of inspiration for materials science. SPM provides the resolution to directly observe these complex and dynamic processes. Moreover, the recent advent of high-speed imaging has expanded the range of problems that can be addressed even to the extent of enabling direct observation of conformational fluctuations by individual proteins. As discussed in the contribution "In situ AFM as a tool for investigating interactions and assembly dynamics in biomolecular and biomineral systems," the intrinsic link between the system dynamics and energetics allows building a picture of the complex energy landscapes that underlie protein assembly and tissue mineralization. Ultimately, the MF team aims to elucidate these processes by pushing the limits of temporal and spatial resolution in fluids while adding chemical specificity.

3.4. Center for Nanoscale Materials

The SPM effort at the Center for Nanoscale Materials (CNM) at Argonne National Laboratory (ANL) is focused on (a) the use of UHV STM and AFM to explore the structural and electronic properties of cutting edge materials and nanoscale molecular systems and (b) the development of new techniques and instruments to expand the understanding of these systems to include magnetic, chemical, and optical properties that can be correlated with structure down to the atomic scale. Several commercial Omicron instruments, including a UHV VT-AFM/STM, a four-probe STM/SEM, and a 4 K UHV STM/AFM with a 6 T magnetic field serve as the backbone of these characterization efforts, while several UHV microscopes developed in-house are dedicated to correlating the UHV STM and STS capabilities to optical and X-ray spectroscopies. All of these systems are coupled to UHV preparation chambers, where a variety of substrate surfaces can be fabricated and controlled down to the atomic scale through careful surface preparation and/or material and molecular deposition.

These UHV STM and STS instruments have been brought to bear on a number of physics and chemical problems. These include the morphology and electronic behavior of self-assembled molecular heterojunctions[67] and correlation between size and Néel temperature in magnetic nanostructures addressed using spin-polarized STM.[68] Graphene, as discussed in contribution by Guisinger in this issue, has been studied to explore its CVD growth dynamics,[69] structure,[70] electronic behavior, and chemical functionalization.[71,72] As discussed in contribution by Wu and Guest in this issue, several UHV VT-AFM modalities in UHV—such as piezoresponse force microscopy (PFM), electric force microscopy (EFM), conductive atomic force microscopy (cAFM), and Kelvin probe force microscopy (KPFM)—have been used to reveal the intriguing role of electric polarization in multiferroics on modulating charge transport through the domains[73] and in emergent charged domain walls.[74]

One of the most promising areas of materials research is complex oxides and complex oxide heterostructures, which exhibit a wide variety of functionalities due to the strong coupling of the electron to the lattice, orbital and spin degrees of freedom. The key challenge has been the direct characterization of oxide interfaces at the nanoscale in order to understand their physical properties. To address this challenge, CNM team has developed a novel characterization technique that applies cross-sectional scanning tunneling microscopy (STM) to directly probe fractured oxide interfaces at the atomic scale[75] as discussed in contribution by Guisinger in this issue. This cross-sectional method has become an optimized technique and a key characterization tool that is a core part of the CNM and drawing external users from around the country. Currently, the team is developing a program in collaboration with oxide MBE scientists to apply this technique to the systematic characterization of oxide junctions that are fabricated using the CNM's molecular beam epitaxy (MBE) system. This core research will help to map band alignment and the physical properties of these oxide interfaces. Understanding the detailed electronic structure (local electronic density of states (LDOS), charge transfer, band bending, etc.) at oxide interfaces is of key interest to both fundamental and applied science. Ultimately, these efforts will help guide the design and engineering of oxide interfaces for the development of novel oxide technologies.

3.5. Center for Functional Nanomaterials

One of the frontiers of modern microscopy lies in the development of in situ/operando methods that allow interrogating the properties of functional materials and their response to external stimuli with suitable spatial and temporal resolution in relevant environments. In heterogeneous catalysis, for instance, this entails the imaging of operating catalysts at sub-nm to μm spatial resolution and fs to ms time resolution, during exposure to gases at high pressure and temperature. The Interface Science & Catalysis group at the Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory (BNL) focuses on in situ/operando surface microscopy and spectroscopy applied to the investigation of chemical processes underlying energy conversion (e.g., catalysis, photocatalysis[76]), energy storage (e.g., hydrogen storage,[77] greenhouse gas capture), and the synthesis of advanced materials (e.g., 2D materials such as graphene and boron nitride). This scientific focus is reflected in the associated suite of user facilities. The CFN is one of the major centers worldwide for cathode lens microscopy, operating a field-emission low-energy electron microscope (LEEM), as well as an energy-filtered spectroscopic LEEM instrument at beamline U5UA of the National Synchrotron Light Source (NSLS).[78] With the transition to the next generation synchrotron source at BNL, NSLS II, the latter will be upgraded to a state-of-the-art aberration-corrected LEEM with extensive spectroscopy capabilities stationed at a soft X-ray beamline.[79] Real-time microscopy in LEEM, complemented by several associated spectroscopy modes (diffraction, photoelectron spectroscopy, band structure mapping, work function measurements and mapping, etc.) is especially powerful for studying the growth, processing and properties of novel thin film materials, as illustrated by the contributions by Sutter (on graphene and other 2D materials) and by Sadowski

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(on pentacene), and in investigating the chemical reactivity of nanoscale heterogeneous surfaces.[80,81]

A second group of advanced instruments at the CFN provides unique tools for studying chemical processes at surfaces in operando, i.e., in complex environments and during the application of external stimuli. These include catalytic chemistry in a reactor-scanning tunneling microscope (R-STM), allowing atomic-resolution imaging of samples in a catalytic flow reactor and simultaneous gas analysis at high pressures (up to 5 bar) and temperatures. This instrument is the only one of its kind operated in any user facility worldwide. Complementary chemically specific spectroscopy is performed in an ambient pressure X-ray photoelectron spectroscopy (AP-XPS) system at NSLS beamline X1A1. For UHV studies, a STM with various sample preparation and electron/ion spectroscopy techniques is available. Photocatalysis and surface photochemistry are investigated at the single molecule level in a cryogenic ($T = 5$ K) STM with excitation by femtosecond laser pulses that can be coupled directly into the STM tunneling gap. The laser excitation is used to develop methods for realizing ultrafast time resolution in STM,[82] and for experiments on light-stimulated chemical reactions.[83] (c) For electrical transport measurements on individual nanostructures,[84] a UHV four-point Nanoprobe is available. Integrated with a high-resolution field emission scanning electron microscope, in situ Auger electron spectroscopy and Auger mapping,[85,86] and a custom designed "Nanostencil" stage for in situ nanolithography by shadow-mask evaporation,[87,88] the system is exceptionally well equipped for combined electrical and chemical analysis of nanomaterials.

The advanced cathode lens microscopy and in situ/operando scanning probe systems are complemented by a suite of instruments operating in air or in controlled ambients (gases or liquids), including an AFM/Raman/optical combination microscope, an ambient/electrochemical AFM, and a scanning confocal optical microscope with electrical probes for photocurrent microscopy at high magnetic fields.[89] To provide in-house research and user science with unique capabilities, instrument and technique development aims to customize these advanced instruments, explore advanced experimental methods and enable complex modes of operation. An example is the development of a powerful, highly configurable software/hardware combination for SPM instrument control and data analysis (GXSM).[90] This system and the associated open-source SPM software, available free of charge on the internet, have found broad distribution and is used by more than 30 SPM groups worldwide.

3.6. Future Perspective

Despite the relative youth, NSRCs have emerged as a hotbed of SPM development and application, both in terms of platform, probe, and technique developments, and applications for electrochemical, physical, materials science, and biological problems, taking advantage of the interdisciplinary collaborative nature of user centers. This includes both in-house technique development, acquisition and operation of latest commercial instruments, and joint (inter-NSRC, NSRC-academia, and NSRC-industry) development of new imaging modalities and their further incorporation into the user program for the good of the broader community. The future will undoubtedly see development along many lines, both science and instrument related. This will likely involve:

Multimodal and Multidimensional SPM: The near-universal limitation of classical SPMs is that they provide information only on one aspect of materials properties, or provide signal containing (inseparable) contributions from multiple sources. However, in many cases comprehensive understanding of materials functionality is possible only if multimodal information is available, with local chemical composition being most obvious one (**Figure 3**). Some of the possible development vectors include combined functional SPM-near field optical techniques,[63] optically- and thermally assisted SPMs,[82] simultaneous current and force detection. Similarly, need to understand phenomena on multiple time scales will likely lead to development of multidimensional spectroscopic imaging techniques[50,53] and associated data analysis methods. An important aspect of this topic is the high-speed imaging and manipulation based on ultrafast SPM platforms and optically-enabled approaches.

Laser-Assisted SPM: Correlating the optical and photophysical behavior of nanoscale organic or inorganic systems with their atomic-scale structure and local environment remains a persistent challenge with potential far-reaching impact. The interaction of light and the separation or recombination of charge in nanostructured materials and molecular systems depends

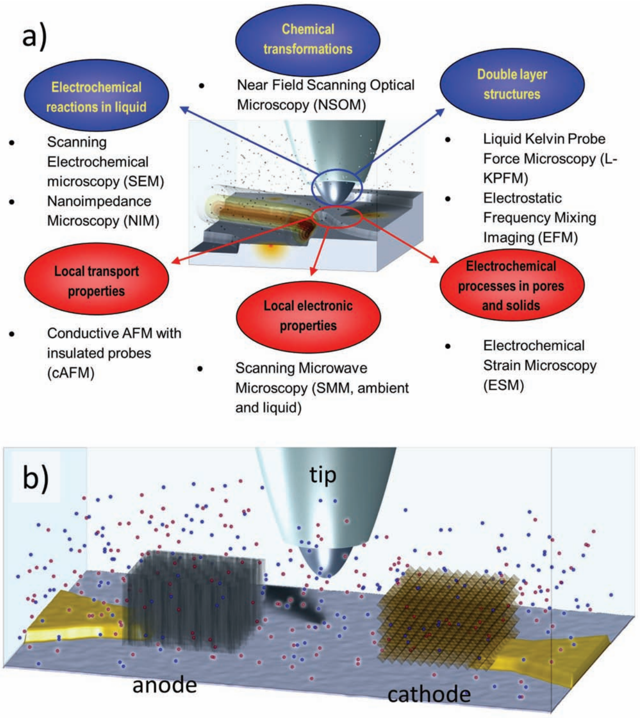

Figure 3. a) Applications of scanning probe microscopy for synergistic probing of phenomena on liquid-solid interfaces in energy storage materials. The functionality of these systems can be deciphered only if the integrated approach combining multiple SPM techniques addressing different aspects of interfacial, solution, and solid processes are available. b) Once available, these methods can be used to explore phenomena in functional electrochemical devices (figures courtesy of S. Jesse, ORNL)

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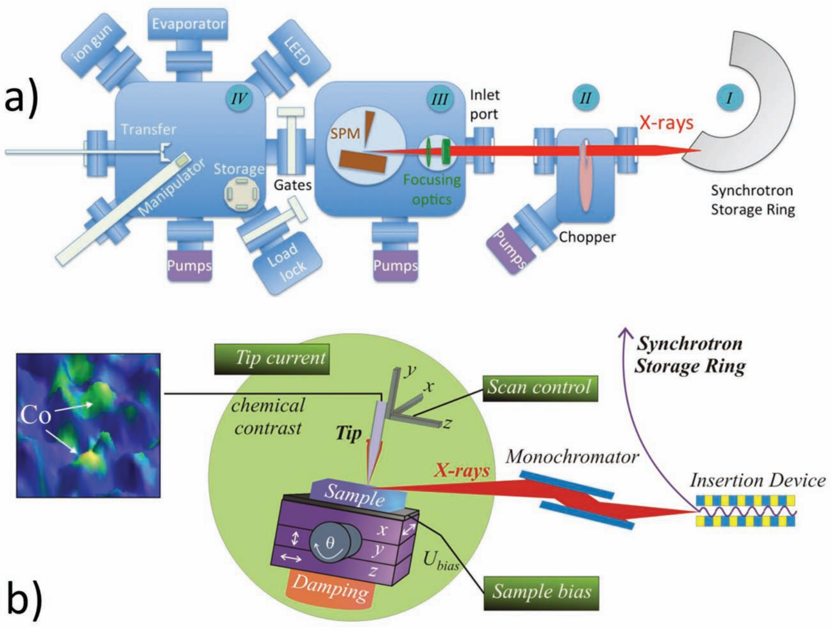

Figure 4. a) Schematic representation of the SXSTM system under development at the CNM. The microscope is operated at the Advanced Photon Source, Argonne National Laboratory. Monochromatic X-rays that pass through a beam chopper illuminate the sample surface while the tip is rastering over the surface. A preparation chamber allows in situ sample preparation and characterization. b) An insertion device serves as photon source. The photon energy can be selected by a monochromator. Rotational (θ) and translational (x, y, z) degrees of freedom are available at both the sample and the tip. A damping stage provides vibration isolation of the microscope. The tip current offers direct chemical contrast as a function of photon energy. Figure courtesy of V. Rose, ANL.

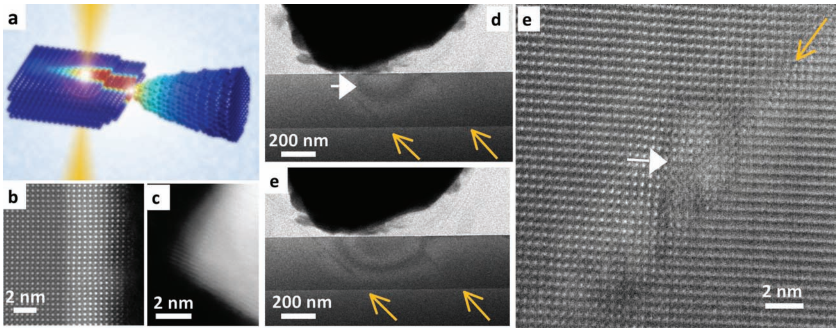

Figure 5. a) Artistic vision of the (S)TEM-SPM combination. Here, the STEM allows both atomic and mesoscopic functionality of the probe (atoms, chemical state, plasmons) to be visualized, and enables mapping of probe induced phenomena on atomic and mesoscopic levels. The SPM allows concentration of electric, mechanical, or pressure field in the selected region of the sample, and detection of associated mesoscopic responses (force, current, electromechanical strain). b,c) HAADF STEM images of b) cross-section of a $BiFeO_3$ (BFO) thin film and c) tungsten STM tip. d,e) BF STEM images recorded during tip-induced ferroelectric polarization switching in a thicker BFO film; domain walls are indicated by yellow arrows, and nucleating domain is indicated by a white arrow. e) HRTEM image of a domain wall in BFO (yellow arrow) pinned by a dislocation core (white arrow). Panels (a,d,e) reprinted with permission.[92] Copyright 2011, American Institute of Physics. Panels (b,f,e) courtesy of A. Borisevich, H.-J. Chang, ORNL.

sensitively on the morphology of interfaces. While electronic and magnetic properties of materials can be accessed at the atomic scale though scanning tunneling spectroscopy (STS) and spin-polarized STS respectively, optical interrogation at these length scales remains extremely challenging due to the optical diffraction limit and challenges associated with tip-sample heating. Combining STM and laser excitation also provides a possible path to realize ultrafast measurements of electronic dynamics at the relevant length scales.[63,66,82] Additionally, sharp plasmonically-active STM and AFM tips can be used as optical antennas to focus the optical field, providing a localized probe region for sub-diffraction-limited optical spectroscopy such as tip enhanced raman spectroscopy (TERS).

Combined SPM-Mass Spectrometry: The combination of the SPM with mass-spectrometry will allow extremely high resolution chemical probing of multicomponent organic materials and exploring effects of local thermal and electrochemical processes. The development of recent mass-spectrometric systems allow achieving this goal even in ambient environments,[91] even though development of a low-pressure cell will allow to significantly increase detection limits and spatial resolution.

Combined SPT-STEM and SPM-Focussed X-Ray: Combination of SPM with a focused synchrotron X-ray microdiffraction and microfluorescence can be a powerful tool to provide the needed phase composition, crystal orientation, and micron-scale chemical and strain change (**Figure 4**). The X-ray fluorescence mapping can be used to locate and identify local composition, while combined energy-wire scans will be used to measure spatially-resolved d-spacings. Note that strain sensitivity, Δd/d, is 10^{-4}, while electrochemical strains can be as large as 10^{-2}–10^{-1}, offering enormouspotential for this method. The second modality offered by this combination is synergy of the high spatial resolution of scanning tunneling microscopy with the chemical and magnetic contrast provided by synchrotron X-rays. This technique combines the high spatial resolution of STM with the electronic, chemical, and magnetic sensitivity of synchrotron X-rays. While the tip is rastering across the surface, absorption of photons by the sample can excite electrons to unoccupied levels close to the Fermi energy. The conducting tip that is tunneling over a sample surface can locally measure these excited electrons.[93–96] Additionally, magnetic contrast can be obtained due to the dependence of photoabsorption by a magnetic material on the helicity of the X-rays.[93]

Similarly, the combination of SPM with (scanning) transmission electron microscopy (STEM) offers an obvious advantage for gaining atomic level understanding of

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dynamic processes (**Figure 5**).[92,97–99] While in these studies the primary effort is the STEM component, the SPM studies can: (a) for in situ SPM-STEM studies provide vital information on optimization the experiment ex-vacuo and hence greatly improving the throughput, and (b) for device characterization provide (unavailable from STEM) information on local relaxation times, field structures, and other functional parameters.

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