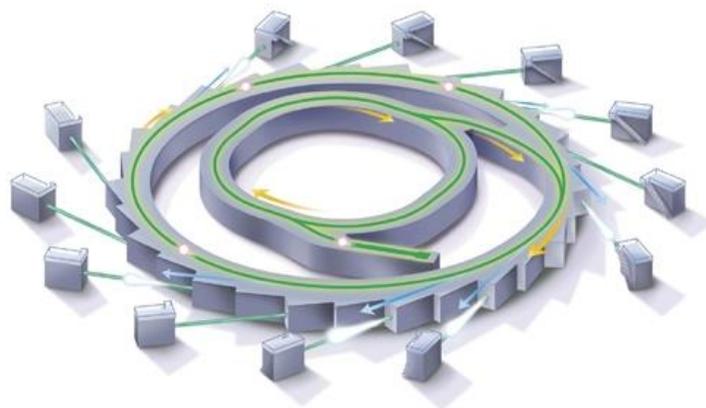


Grand Challenge Science on Diffraction-Limited Storage Rings



A consensus report on future opportunities from scientists at

ALS, LBNL

APS, ANL

NSLS-II, BNL

SSRL, SLAC

together with a broad community of scientists

at laboratories and universities

BESAC Subcommittee on Future Light Sources: July 10-12, 2013

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Introduction

Evolutionary increases in storage ring source brightness over the past several decades have supported a robust array of x-ray capabilities that have had a major impact on many disciplines – physics, chemistry, biology, material science, and others. A large worldwide capacity has been developed and is applied to diverse cutting edge research problems. In recent years an additional, *revolutionary increase in storage ring brightness by a factor of up to 1000* has been proposed and is now being planned or pursued at facilities around the world. This increase will be accomplished by deploying storage ring lattice designs with electron beam emittance comparable to the diffraction limit of the x-rays that are produced. That is, the x-ray beams will be nearly diffraction limited, with smooth wavefronts that can be focused to the smallest possible spot.

A diffraction-limited storage ring (DLSR) is a synchrotron radiation facility optimized for examination of the nano- and meso-scale structure of materials, enabling the highest possible spatial resolution coupled to broad temporal sensitivity and x-ray contrast mechanisms – lattice structure and strain, atomic and chemical species, magnetic structure. The brightness of diffraction-limited x-ray beams will dramatically expand the spatiotemporal dynamic range of x-ray techniques and enhance our ability of address key emerging and future research problems in many disciplines. Groundbreaking applications to heterogeneous materials and functional devices will become possible on a DLSR, as elaborated further below.

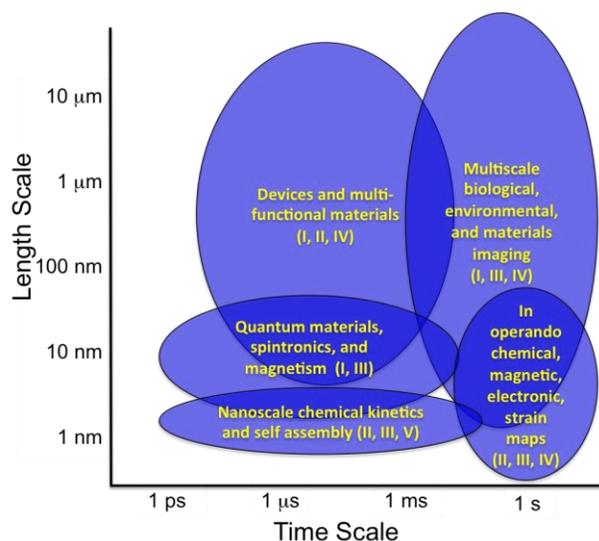


Fig. 1: Spatiotemporal Scales of BES Grand Challenge Science

- I: control electronic processes
- II: perfect materials by design
- III: control emergent material properties
- IV: mastering energy and information
- V: matter far from equilibrium

The impact of this dynamic range on BES Grand Challenge science is illuminated in Fig. 1, and this document presents a compelling case for developing DLSRs in the US. We first briefly describe enhancements to x-ray imaging, scattering, and spectroscopy techniques these new sources will enable and the breakthrough science they will enable. We list the strengths that storage ring technology has developed over several decades, and then provide more detailed descriptions of research highlights that DLSRs will enable. We close with a brief description of the technical features of DLSRs that produce high brightness, diffraction-limited x-ray beams.

Emerging Capabilities using Diffraction Limited X-ray Beams

DLSRs will provide nominally the same total flux as existing sources, but nonetheless will revolutionize most x-ray techniques - absorption, fluorescence, scattering/diffraction, photoemission, etc. - for studying heterogeneous materials and functional devices. The reason for this is the high degree of transverse coherence of the x-ray of beams from DLSRs. Coherence means that all photons are 'useful' in demanding experiments that require focusing the beam into a small spot or projecting a material's complexity into a far-field speckle-diffraction pattern. Most examples presented in the following pages grow from existing capabilities, but doing them now is heroic due to the need to spatially filter a partially coherent beam. The coherent flux or, equivalently, the spatiotemporal dynamic range of an experiment using a DLSR will be as much as 1000 x higher than for existing storage ring sources. This increased coherent flux can be used to enhance spatial or temporal resolution, to access exotic contrast mechanisms, to turn 2D projections into 3D tomographic images, or simply to increase the data rate so complete experiments can be accomplished in a reasonable time. Examples of high profile research problems that will be vastly improved with a DLSR include:

Wavelength resolution x-ray microscopy of functional devices: Many grand challenge problems will be addressed with techniques that provide *in operando* 3D maps of chemical and structural heterogeneity with nanometer resolution. A good example is provided by the poorly understood solid-electrolyte interphase (SEI), a phase-heterogeneous, few-nanometer-thick metastable region that develops at electrochemical interfaces. The SEI determines how well a battery functions and how likely it is to fail. Tools that probe i) the chemical inventory of the SEI, ii) interphase transport of the intercalating species and iii) the structure of granular electrode materials commonly used in batteries to assess the impact of repeated intercalation-de-intercalation cycles, are crucial to developing batteries with high storage capacity and lifetime.

Ptychography is a revolutionary new variant of coherent diffractive imaging that offers precisely these capabilities. It is a hybrid of scanned and full-field techniques: overlapping spots on a sample are illuminated with a coherent x-ray beam, and a complete image is produced on a computer using phase retrieval algorithms. Ptychography using a DLSR will provide nm-resolution chemical and structural images of the SEI and nano-grains of the battery electrodes. Similarly, the technique will enable nm resolution of particles of green cement as they hydrate (Fig. 2), of nanoparticles embedded in smart windows, and many classes of heterogeneous materials.

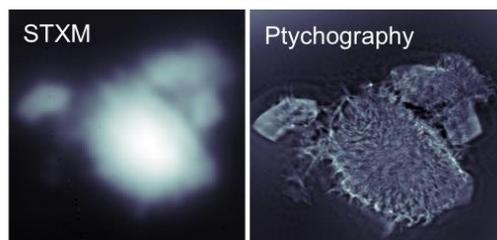


Fig. 2: X-ray micrograph and ptychographic reconstruction of hydrating cement

Nanosecond kinetics on nanometer length scale: Heterogeneous materials often exhibit complex and poorly understood kinetics. More fundamentally, the fluctuation-dissipation theorem is often violated in these systems so that driven dynamics are not simply related to fluctuations near equilibrium. Important problems for study are reaction-diffusion processes in i) a metal-organic framework compound that has been functionalized to achieve high catalytic selectivity, ii) a nanostructured solid designed to be a chemical sensor, iii) a soil particle immersed in a contaminated ground water plume, or iv) a nanoporous separator membrane deployed in a battery or a fuel cell. These are difficult yet very important problems, but we lack the tools to make kinetic measurements on the relevant nanometer/nanosecond scale.

DLSR's will endow x-ray photon correlation spectroscopy (XPCS) with enough temporal dynamic range to have a revolutionary impact on these problems and many more. In an XPCS experiment a coherent x-ray beam illuminates a heterogeneous sample to produce a speckle-diffraction pattern (Fig. 3).[1] Incoherent (i.e., thermally-driven) structural, chemical, or magnetic fluctuations in the sample produce intensity fluctuations in the speckle pattern, and these can be measured to probe the underlying dynamics statistically. XPCS has been developed by spatially filtering the x-ray beams at existing facilities, but low signal seriously limits the spatiotemporal scales that can be probed. An important feature of XPCS is that the available time resolution scales as the square of the scattered signal, which is proportional to source brightness. A 100-fold increase in brightness will provide a 10^4 increase in dynamic range. DLSRs will reach nanosecond time and nanometer space resolution with diverse samples and environments.

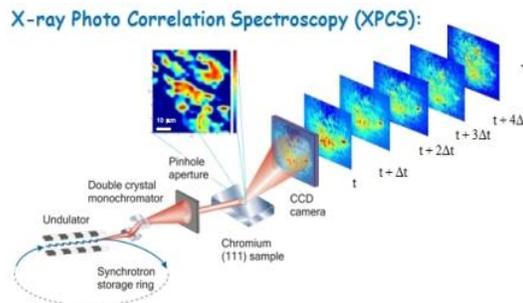


Fig. 3: Schematic of an XPCS experiment

A more challenging goal will be to do XPCS measurements on a time scale less than the pulse width. This will require that we resolve and time-bin photons in a single speckle from a single storage ring pulse. This would open for study the 1-300 ps scale that approaches the crossover between kinetic and dynamical regimes and also connects to the ~ 1 meV resolution of planned resonant inelastic x-ray scattering (RIXS) measurement, which is closely related to XPCS.

Connecting structure to function with x-ray spectromicroscopy: A robust suite of x-ray spectroscopic tools has been developed and applied to every conceivable class of materials. As interest in heterogeneous materials and functioning mesoscale devices has grown, interest in applying these spectroscopies with a focused beam has grown.

Groundbreaking x-ray spectromicroscopy with nanometer-sized beams includes understanding the role of spontaneous heterogeneity in diverse correlated oxide materials with nano-angle resolved photoelectron spectroscopy (nanoAPPES) and nanoRIXS and probing feedback, control, and self-repair mechanisms in artificial photosynthetic systems with high energy ambient pressure x-ray photoelectron spectroscopy (XPS).

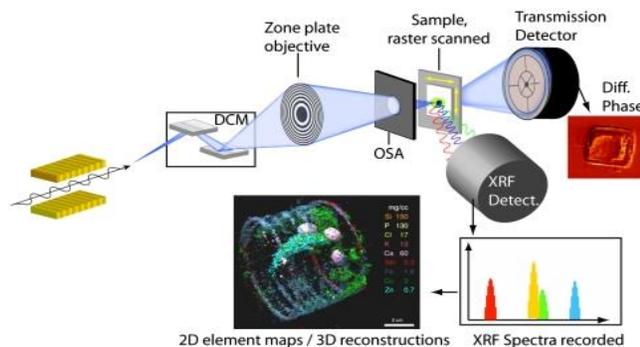


Fig. 4: Schematic and results from an x-ray fluorescence tomography measurement of functional mesostructures de Jonge, et. al., PNAS 107, 15676 (2010).

Progress has been made along these lines at existing facilities, but limited coherence leads to limited spatial or detection dynamic range. A good example is provided by Fig. 4, which presents elementally-resolved x-ray fluorescence holography measurements in a freshwater diatom with submicron resolution.[2] A DLSR will bring these efforts to their natural limit since the efficiency of focusing depends directly on source brightness. We can expect studies with higher spatial resolution and higher dilution and a higher throughput, especially for 3D tomographic imaging.

Advantages of Storage Ring X-ray Sources

This document explores the revolutionary impact that DLSRs will have on emerging research problems, but DLSRs benefit from a very robust storage ring technology that has been developed over several decades. After the 1st generation of parasitic operation on high energy physics machines, the second generation machines were optimized for smaller beams and higher brightness and allowed for the first time the inclusion of undulators. 3rd generation machines were optimized for higher brightness again, now with the primary radiation sources being undulators. DLSRs are the next logical extension of this development and continues the trend that each generation is up to 1000x brighter than the previous one. The DOE has made major investments to facilitate these advances, particularly in 3rd generation facilities. Storage rings have many notable strengths that underpin the research directions discussed in this document:

Reliably serve ~50 instruments simultaneously at 100s of MHz rep rate: Storage rings typically operate with well over 95% reliability. Their high capacity will not be replaced any time soon. The photon energy is easily tuned over a broad range, and different beamlines serve experiments from the infrared through the hard x-ray regime.

Shot noise limited intensity variation turn-to-turn: Temporal stability is particularly important for XPCS experiments, where the noise spectrum of the source can severely impact the ability to isolate the desired intensity fluctuations due to sample dynamics.

High positional and energy stability: Positional stability is obviously important to achieve the highest resolution x-ray microscopy, but it is equally important in XPCS experiments, where changing the sample illumination will mimic de-correlation of the speckle patterns and spurious source of dynamics.

Long pulses at high repetition rates: X-ray science is not alone in needing sources with diverse time structures. DLSR's tend to mitigate intrabeam scattering (space charge) by lengthening the electron bunches. This produces an unusually large duty cycle of up to ~10%, which is nicely complementary to ultrafast x-ray pulses, e.g., from a free electron laser. Most of the techniques and experiments discussed here benefit from as near to a CW source as possible since:

- Quasi-CW operation minimizes sample perturbation due to high peak power. This is important in all the techniques discussed here since generally they probe a specific region of the sample serially and need to avoid beam-induced modification.
- Heating due to average focused x-ray power is sample and spot size dependent for all light sources. We have looked in some detail at sample heating and it will be a problem in some cases, particularly in the scanned microprobe techniques. Heating is mitigated somewhat with ptychography and XPCS where, as for any scattering technique, the spot size is much larger than the target resolution.
- Space charge resolution limit in electron spectroscopy is minimized with long pulses. High resolution ARPES on a nominally high pulse energy source, for example, will often require operation at low power and will be used when the desire is to measure ultrafast dynamics. This is another example of the complementarity of pulsed and CW sources.

Flexible detector systems are enabled: These include the capability to do single-photon counting at high count rates with energy discrimination to suppress inelastic backgrounds. This will greatly improve signal to background and significantly reduce the number of photons needed for coherent diffraction techniques.

Science Highlights using Diffraction Limited Storage Rings

Optimizing the structure and function of nanoparticles: A holy grail for nanoscience is to observe the electronic and atomic structure of individual nanoparticles in three dimensions (3D) with nm resolution while they are functioning. This goal is relevant to many existing and emerging technologies: catalysis and catalytic networks, artificial photosynthesis, fuel cells and batteries, and smart windows, to name just a few.

Nanoparticles control heterogeneous catalytic activity, though this relationship is rarely well understood. Nanoparticles with different sizes have different lattice terminations and surface defects that can provide sites with unique catalytic properties. If we knew what particle aspects resulted in these reactive sites, we could synthesize all catalyst particles with extremely high selectivity and activity; this is a common modality in homogeneous catalysis. While much work has been done on supported nanoparticle ensembles using x-ray methods and electron microscopies, *in operando* studies at the single nanoparticle level would be groundbreaking.

Battery electrode materials often employ nanoparticles to speed the charge/discharge processes and to mitigate the detrimental effect of high resistivity materials. The behavior of these particles during battery cycling is complicated and poorly understood. In Li-ion batteries we do not know how the individual particles transform, how Li diffuses into the lattice, and how the SEI influences charge/discharge (Fig. 5). These processes depend on the properties of the individual electrode nanoparticles, but since most experiments probe ensembles of particles or are not conducted *in operando*, we do not understand this relationship in any detail. Coherent diffraction imaging (CDI) techniques enabled by the DLSR will lead to groundbreaking experiments observing the electronic and atomic structure of individual nanoparticles *in operando*. Nanoprobe hard and soft spectroscopies will allow measurement of local electronic and chemical structure at nm spatial resolution to study the above issues.

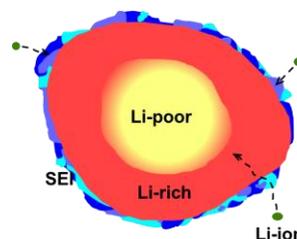


Fig. 5: Schematic of battery electrode particle illustrating pathways for lithiation through the SEI layer (blue) to react and form a Li-rich phase (red).

Hydrogen production through water splitting using transition metal oxide photocatalysis, specifically Fe_2O_3 in Fig 6, is a promising approach for chemical storage of solar energy, but is complicated by these materials' non-optimal electronic properties.[3] High water-splitting photocurrents are obtained with mesoporous Fe_2O_3 photoanodes prepared by a solution-based colloidal method [4]. This work further indicates that independent control over the nanoparticle distortion, doping, and size will be necessary to achieve high efficiency with hematite [5].



Fig. 6: Schematic of photo-electrochemical splitting of water in an Fe_2O_3 nanocatalyst

A DLSR will provide the necessary coherent power for spectroscopic imaging at the nm scale for all of these pioneering applications on nanoparticle structure. Understanding the 3D structure through ptychographic imaging and the local chemistry and charge transfer through nano-x-ray absorption spectroscopy and nano-x-ray emission spectroscopy will allow dramatic steps toward understanding of this important class of materials.

Controlling mesoscale function with lattice strain: The design and perfection of revolutionary new materials requires deep understanding of both materials synthesis and structure-property

relationships. Synchrotron x-ray techniques have been used to directly probe long-lived growth intermediates using *in situ*, real time techniques. However, steady-state processes that are crucial for crystal growth and self-assembly often remain unknown. DLSR sources, particularly in the hard x-ray regime, will allow unprecedented studies of materials synthesis at the relevant length and time scales using XPCS, CDI, and x-ray nanoprobe diffraction and spectroscopy.

Of particular interest in the creation of new materials are the complex interactions that occur on the mesoscale. For example, CDI shows great promise in imaging nanoscale regions and visualizing their interaction via strain fields, a key step to allow designed modification of material properties based on strain.[6] Perhaps the most sophisticated design and synthesis example today is the top-down construction of high performance integrated circuits. In a state-of-the-art device, a stressor layer is used to improve the conductivity of the conducting channel. Designing these devices requires predictive models of stress and strain on the nanoscale. Recently, coherent diffraction imaging was used to test these models in prototype device structures by measuring a projection of a static displacement field.[7]

These capabilities can be fully developed and utilized with the high performance of a DLSR to image, on the nanoscale, both the morphological and lattice responses induced by changing environments, thereby obtaining insight into processes ranging from defect dynamics to phase evolution and growth. Enabling this breakthrough in characterization will be the approaches that use the relatively broad spectrum of a DLSR undulator fundamental to measure coherent scattering from volumes of reciprocal space.

The development of revolutionary materials by strain engineering will require the controlling the interaction between different materials and material properties. For example, coupling ionic conductivity, catalytic activity, and ferroelectricity in a complex mesoscale structure might allow external control of the balance between binding of reactants and desorption of the resultant products. Fig. 7 shows a hypothetical composite material that uses an active ferroelectric layer to modulate the chemical attractiveness of a thin film for the reactants. It may be possible to create an extreme performance catalyst in such a material by first attracting the reactants, allowing the reaction to occur on the surface, and then flipping the ferroelectric polarization to drive off the products.

The development and optimization of such materials requires a detailed local knowledge of the time-dependent chemical state and structure. Measurement of local chemical properties using nanoscale spectroscopy and measurements of the structural dynamics using XPCS and time-dependent CXDI while the material is switching in an active chemical environment will greatly accelerate the development of new classes of functional materials. The system can be controlled the microsecond on the nanosecond time scale, and the high coherent flux and the very high repetition rate of a DLSR will be crucial to following these time-dependent processes. In addition, the high stability of a DLSR will allow a combination of ptychography to define the x-ray beam shape and phase, followed by time dependent keyhole CDI imaging[8] to create movies of atomic processes, providing a unique view into the nanoscale world of these materials.

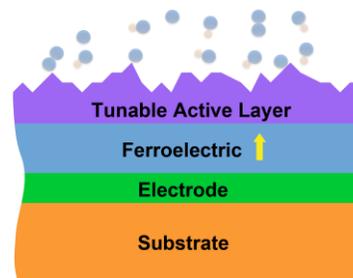


Fig. 7: A conceptual active material that uses a ferroelectric polarity inversion to modulate the performance of an active tunable layer to create a high performance catalyst.

Chemical transport and structure in self assembled functional materials: Many useful properties exist in or result from the partially ordered nature of complex materials. Examples include nano-porous and nano-crystalline materials, organic photovoltaics, and functionalized nanocomposites [9,10]. Understanding these complex materials requires that we probe physical and chemical structure-property relationships and dynamics in self assembled nanostructures which have partial order (e.g., fuel cell membranes, battery polymer electrolytes/electrodes, organic electronics, photocatalytic electrodes...) often over a very broad range of length and time scale.

For example, due to its unusually high ionic conductivity, Nafion is the workhorse polymer membrane in fuel cells and is becoming important in solar fuel devices as well. Existing x-ray scattering probes do not give enough information on structure and pore chemistry to tell us why a disordered network has such high ionic conductivity.

Nafion is but one example of a class of nanoporous materials that will be critical in energy storage and conversion. Functional nanocomposites, composed of organic and inorganic building blocks, can combine the properties from the parent constituents and generate entirely new properties.(Fig. 8) The past century of organic and organometallic chemistry has produced an enormous array of building blocks for self-assembly. Moreover, recent developments in nanoparticle synthesis provide a plethora of inorganic building blocks as well, building the foundation to construct hybrid nanocomposites with a virtually unlimited range of possibilities.

The properties of nanocomposite materials depend not only on those of individual building blocks but also on their spatial organization at different length scale. Block copolymers, which microphase separate into various nanostructures, have shown their potential for organizing inorganic nanoparticles in bulk/thin films. Block copolymer-based supramolecules provide additional versatile routes to control spatial arrangement of the nanoparticles over multiple length scales.

A high-resolution structural probe with chemical sensitivity, enabled with spectro-ptychography and the high coherent power of a DLSR, coupled to the nm/ns sensitivity of XPCS to chemical kinetics, will unveil the link between connectivity and self-assembly with reactivity and function. This should allow us to design the functionality of the channels of hierarchical soft materials using synthetic polymers, peptides and proteins, small organic molecules and nanoparticles as building blocks, leading to broad new classes of materials.

A DLSR will revolutionize the process of designing and assembling new, hierarchical functional materials.

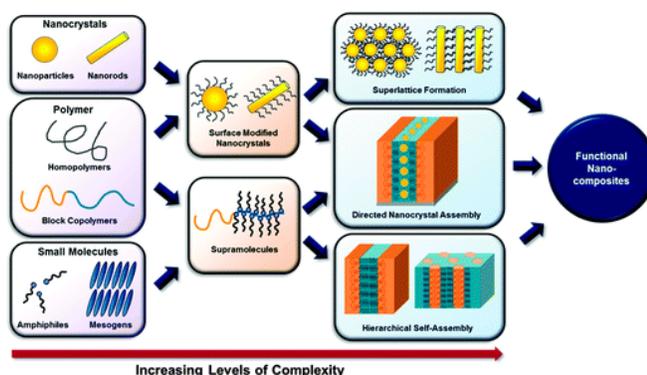


Fig. 8: Schematic of the self-assembly process of a functional nanocomposite.

Controlling emergent properties in correlated oxides: Strongly correlated electron systems are fascinating materials that exhibit a number of remarkable properties, including giant response to external stimuli and high-temperature superconductivity. They are promising materials for the next generation sensors, for energy storage technologies such as solid oxide fuel cells, and for revolutionary energy storage, transmission and generation.

Unfortunately, these materials have largely resisted understanding and control. The nature of the strong correlations means that the relevant electrons are neither completely localized nor delocalized – the electron mean free path is 15 nm in cuprates, for example. Further, it has recently been shown that these materials are electronically inhomogeneous on just these length scales. Spatially resolved STM measurements of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ have shown large variations in the superconducting gap on length scales of a few nm [11] (Fig. 9). In CMR manganites, metallic and insulating behavior is seen on length scales from a few nm to several microns [12]. A large barrier in our understanding, and ultimately to achieving control of these remarkable properties has been that our most powerful spectroscopic probes average over these inhomogeneities. In doing so, such techniques obtain completely the wrong picture of the essential physics of these materials – the average answer is precisely the wrong answer.

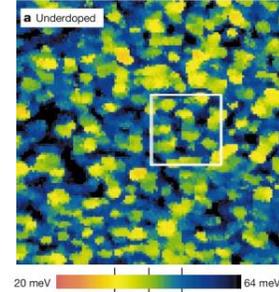


Fig. 9: Local variation of superconducting gap in copper-oxide superconductor

What is required is to combine the advanced x-ray characterization tools, such as XAS, ARPES and RIXS, with nanoscale spatial resolution, to probe these materials at length scales relevant to the underlying physics. Herein lies the groundbreaking promise of a DLSR - to enable nanospectroscopies which image electronic textures that can be brought to bear on this problem. Cu L-edge RIXS at 940 eV with spot sizes of 10 nm would be achievable with zone plate optics. This would allow potentially, “smoking gun” experiments in which the excitation spectra were measured as a function of position and temperature. Changes in the phonon or magnon spectra, for example, could then be correlated with regions of large or small superconducting gap and their connection to superconductivity identified (or ruled out). Present day RIXS experiments are able to only measure the average response and find no change across the entire phase diagram.

Spatially resolved ARPES measurements would revolutionize the study of these materials as well. Initial steps have already been taken in this direction with studies reported with 100 nm resolution [13]. DLSRs would allow this to be improved to its ultimate limit of ~10nm. This will require the long pulses of DLSRs to minimize space-charge effects from the high photon density.

Another groundbreaking experiment would be to image the charge, spin and orbital domains in these materials using soft x-ray resonant CDI and XPCS. To date, sources have lacked sufficient brightness to make this practical and experiments have achieved limited success [14]. A DLSR would have sufficient coherent flux to image these textures with wavelength-limited resolution. This would allow the first ever 3D images of the bulk correlations and would be a huge advance in the field. XPCS experiments could probe the dynamics of these domains down to time scales of ~1 ns to search for non-trivial correlations. Fundamental questions including the microscopic relationship between stripe order and superconductivity, the nature of the nematic phase in cuprates, and the pinning dynamics of domain walls would be addressed.

Mesoscale functional networks of nanoscale catalytic centers: Future chemical syntheses will be performed in catalytic networks, self-contained mesoscale structures in which nanoscale catalytic centers are compartmentalized and controlled by feedback to produce products with high efficiency and selectivity. This dream connects ideas from previous sections - single nanoparticle analysis, materials by design, and self-assembly – and systematizes them with a systems engineering approach. The concept of a catalytic network provides an excellent framework that illuminates the revolutionary capabilities of a DLSR.

The vision of the previous paragraph is embodied in the context of artificial photosynthesis. Cell function involves active feedback between the various compartmentalized components, and repair mechanisms to keep metabolism going for extended periods. These natural structures for solar energy conversion are paradigms for the design of hierarchical systems that capture solar photons to drive energy-conserving catalytic chemistry. However, photosynthesis is not designed for optimized solar energy conversion, and a critical research mission addresses the need to produce artificial photosynthetic systems capable of efficient, sustainable solar fuels production. The central scientific challenge lies in the discovery of artificial photosynthetic systems that efficiently couple light-harvesting and photo-excited states to multiple proton-coupled electron transfer reactions at transition metal catalysts, and to accomplish this using economic processing, self-assemble/repair, with sustainable atomic compositions.

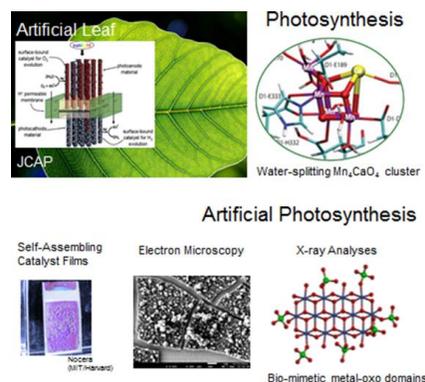


Fig. 10: Schematic of the JCAP artificial photosynthesis cell

Scientific challenges for artificial photosynthesis include the discovery of solar fuels catalysts and light-harvesting materials, and in creating functionally integrated multi-component architectures. JCAP's tandem, nano-structured artificial leaf architecture illustrated in Figure 10 is a leading candidate for artificial photosynthesis design. Critical research is needed on *in situ* structure characterization of the catalysts and light-harvesting materials to resolve the structures and fundamental physical-chemical reaction mechanisms that underpin artificial photosynthesis. This information is essential for further artificial leaf design, synthesis, and development.

X-ray analyses provide the primary means to achieve structural discovery at the atomic scale. For example, figure 1 illustrates an example of an amorphous metal-oxide water-splitting catalyst film that is representative of an emerging class of solar fuels catalysts that are electrolytically deposited from simple inorganic solution state precursors, and mimic the assembly, repair, and catalysis of natural photosynthesis.[15,16] A combination of synchrotron X-ray spectroscopy[17] and scattering[18] analyses have revealed that the amorphous oxides are composed of molecular-dimensioned, auxiliary ligand-capped metal-oxo domains, that mimic the Mn_4CaO_4 cluster catalyst in photosynthesis.

Progress in artificial leaf devices requires *in operando* characterization of light-harvesting and catalytic layers, that is both spatially and time-resolved. The DLSR capability to deliver intense, collimated, nanoscale focused soft and hard X-ray beams offers unprecedented opportunities to achieve dynamically-resolved structure profiling of light-harvesting and catalytic active layers under functional conditions. These new capabilities include nanoRIXS/XAS, nanoAPXPS, ptychography, and XPCS to map chemical and atomic structure and kinetics.

Measuring and controlling mesoscale intermittency: A variety of mesoscale systems exhibit thermal- or field-driven intermittent behaviors that are a manifestation of dynamical heterogeneity in a macroscopically homogeneous material. For example, Fig. 11 shows luminescence intermittency in a single quantum dot, which can show self-similarity over several decades.[19] Intermittent events represent an important kind of nonequilibrium behavior on a short length scale that can limit the utility of a mesoscale device or mesostructured material to store, process, or transmit information, to sense the environment, to harvest and convert energy, and a host of other applications. An important goal is to probe, understand, and control mesoscale intermittency so as to exercise some control over emergent material properties.

The primary difficulty in studying intermittent events is that they are spontaneous: they are not a response to a temporally well-defined stimulus. A speckle pattern is related to the precise microscopic configuration illuminated. For this reason, transversely coherent x-ray beams have been successfully applied to study nanoscale intermittency and dynamical heterogeneity in a variety of contexts, primarily using XPCS and related techniques based on higher order correlation functions. Unfortunately the limited coherent flux available at existing x-ray facilities means these measurements have had very restricted dynamic range. This is a serious limitation given that power law behaviors are common in these systems, meaning that all time scales are important, from the intrinsic switching time for an intermittent event out to seconds or even hours.

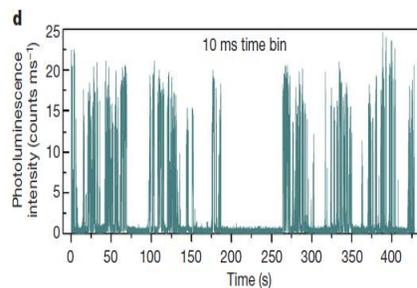


Fig. 11: Luminescent intermittency in ZnSe quantum dots.[19]

The high coherent power from a DLSR will provide revolutionary advances in our ability to probe mesoscale intermittency. For systems with stationary correlations can be probed with XPCS at the nanosecond/nanometer time scale, which will approach the domain at which intermittent switching occurs. More importantly, spin-echo quasielastic neutron scattering can be applied down to energy losses $\sim 1 \mu\text{eV}$, corresponding to $\sim 1 \text{ ns}$, and XPCS experiments on a DLSR will be able to connect to this spatiotemporal regime. Many heterogeneous systems exhibit complex and unexplored nanometer/nanoscale dynamics: small molecule, polymer, and colloidal systems approaching the glass transition, ferroelectric and magnetic domains near transition temperatures, charge- and orbital-ordered domains in correlated electron systems, etc.

Interesting systems that are not statistically stationary, e.g., Ostwald ripening and martensitic transitions, have also been studied with coherent x-ray scattering, though with poorer time resolution since correlation functions cannot be averaged over time so two-time correlation functions must be used. Again, the high coherent power from a DLSR will improve the ability to study such systems markedly.

Finally, resonant XPCS is based on the same second order perturbation theory as RIXS and the results of these two are related by a temporal Fourier transformation. The $\sim 1 \text{ meV}$ target resolution for RIXS corresponds to $\sim 1 \text{ ps}$ time resolution for XPCS. As noted in the introduction, a challenging XPCS experiment will measure and bin pairs of photons in a single speckle from a single storage ring pulse. This will move the study of intermittency into the very interesting time scale where chemical kinetics crosses over into chemical dynamics, and very many groundbreaking experiments on physical, chemical, and biological system will be possible.

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The fundamental limit on the radiation emittance ε_r , depends only on the x-ray wavelength λ and is, in the simplest case, related to the rms photon beam size σ_r and divergence σ_r' via the equation $\varepsilon_r = \sigma_r \sigma_r' = \lambda / 4\pi$. For a photon energy of 1 (10) keV, the value is 80 (8) pm-rad, well below the horizontal electron beam emittance of present-day storage ring light sources. A diffraction-limited light source (DLSR) for wavelength λ is one for which the electron beam emittance is smaller than or equal to ε_r .

Two related concepts are the spectral brightness $B(\lambda)$ and the coherent fraction $f_c(\lambda)$. The brightness is proportional to the spectral flux (photons per second per unit bandwidth) divided by the product of the total photon beam emittances $E_x(\lambda)$ and $E_y(\lambda)$. The total photon beam emittances are computed by convolving the single-electron photon distribution with the electron distribution. For a given electron beam emittance, the total emittance is minimized when the beta function of the electron beam matches that of the single-electron radiation distribution for an undulator of length L , which requires $\beta = L/2\pi$. It is also minimized, of course, by achieving diffraction-limited emittance, in which case $E_x \rightarrow \varepsilon_r$. The coherent fraction is a related concept and is given by $f_c = \varepsilon_r^2 / E_x E_y$.

While existing storage ring light sources routinely reach diffraction limited emittances in the vertical plane through careful correction of coupling errors, until fairly recently it was thought that there was no practical way to approach the diffraction limit in the horizontal plane. However, experience with 3rd generation sources and recent advances in accelerator technology make it clear that dramatic improvements in storage ring brightness and coherence are possible. These improvements will result in reduction of the horizontal emittance to values that are, at present, typically associated with the vertical emittance (compare Fig. 12). The forerunners of these future diffraction-limited storage rings are being built now.

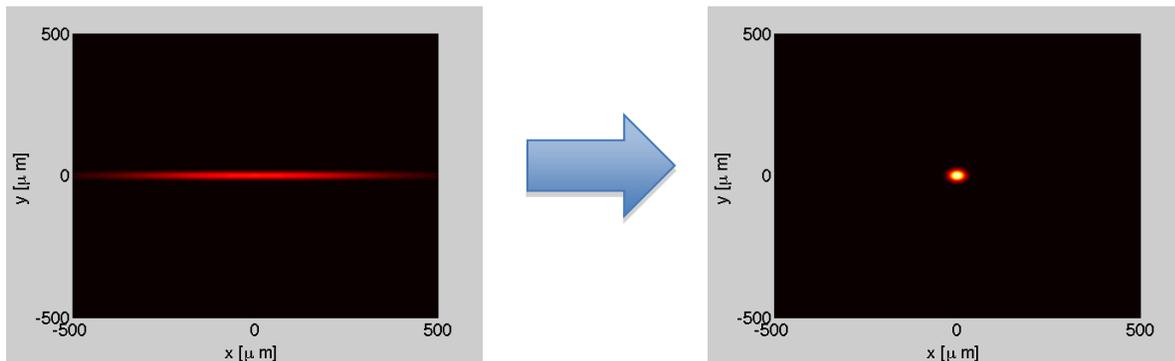


Figure 12: Illustration of typical current beam dimensions in 3rd generation light sources (left) and the big reduction possible in horizontal emittance at DLSRs (right).

The natural emittance ε_0 in a light source ring is governed by $\varepsilon_0 = C_\gamma E^2 / (N_s N_d)^3$, where C_γ is a constant, E is the beam energy, N_s is the number of straight sections, and N_d is the number of dipoles per cell. Most light sources have what is known as a double-bend ($N_d=2$) or triple-bend ($N_d=3$) achromat. Until recently, it was not widely appreciated that multi-bend achromats ($N_d > 3$, MBA) could practically take advantage of the very large $1/N_d^3$ reduction in the emittance, due to the high complexity of the lattice and nonlinearities due to strong focusing required. Note that, for fixed energy and cell design, the emittance scales as $1/C^3$, where C is the circumference.

Hence, to approach the diffraction limit for very hard x-rays, one needs a fairly large circumference. On the other hand, reaching the diffraction limit for softer X-rays can be achieved with lower beam energy and smaller circumference.

As proposed by Einfeld *et al.* in 1995, a seven-bend achromat ($N_d=7$) can provide near diffraction-limited performance in a rather small package (compare Fig. 13). The groundbreaking 3 GeV MAX-IV facility, now under construction in Sweden, is the first instance of this idea, but others are soon to follow, such as the 3 GeV, $N_d=5$ SIRIUS project in Brazil, which recently began construction. There are also plans for 5-6 GeV rings, either as new facilities or upgrades, in France, Japan, and China.

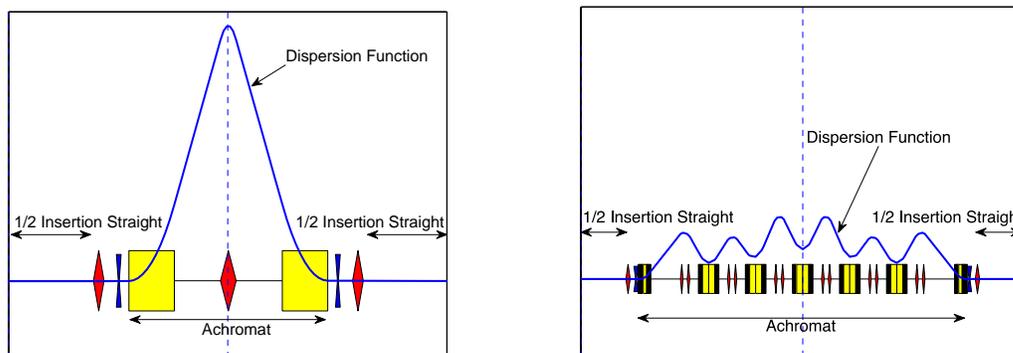


Figure 13: (Left) Simplified double bend achromat lattice similar to the ones typically used in today's 3rd generation light sources. (Right) Seven bend achromat lattice as used in Max-IV. Similar Lattices are envisioned for future DLSR projects.

Among the other technological developments responsible for the widespread interest in such sources are the following: the widespread success of top-up operation in compensating for short beam lifetime; new magnet and vacuum technology (MAX-Lab) that allows low-cost, tightly-packed MBA lattices; advances in simulation fidelity and optimization techniques; understanding of how to provide round beams, including acceptance of on-axis injection; precision correction of linear and non-linear optics in real machines; and achievement of ultra-precise alignment (NSLS-II).

Based on these concepts, most of the accelerator facilities in the US have developed concepts for green-field or upgrade sources that provide diffraction-limited performance over a significant wavelength regime. Figure 14 shows the results of calculations of brightness and coherent fraction envelopes for each of these designs. (Advances in undulator technology are also assumed.) Also shown is the performance envelope for existing US facilities, another envelope for funded US projects, along with a similar envelope for overseas projects and planned facilities. Here we see that significant jumps in brightness are possible, along with the promise of reaching the diffraction limit up to about 10 keV and the resulting high level of transverse coherence extending even beyond 10 keV. In general terms, the performance is 2-3 orders of magnitude better than present-day machines.

Predicted performance is subject to on-going optimization, partly as a result of continued design competition among US and foreign labs. Modest departures from expected scaling (e.g. with

circumference) result from different design choices, such as beta function matching, emittance ratio, and desired nonlinear performance.

These rings will complement FELs, offering a number of attractive features such as high transverse coherence; a high average brightness with low peak brightness and a high repetition rate; high stability, large capacity, and low cost per experiment as in present-day rings.

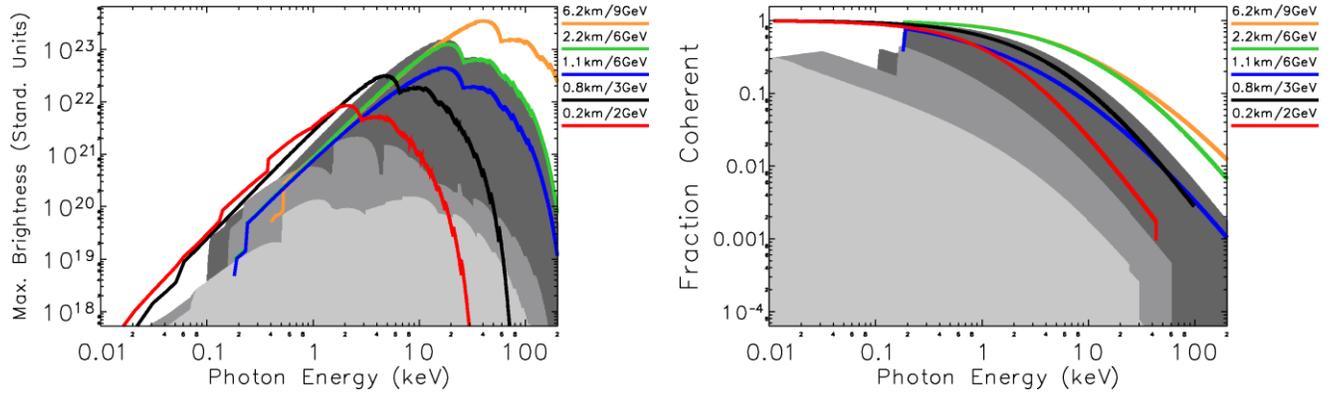


Figure 14: Brightness and coherent fraction performance of present US facilities (light grey), US rings under construction and upgrade project (medium grey), and foreign projects and plans (dark grey). The envisioned performance of US diffraction-limited storage ring designs is shown as colored graphs. Red: ALS-2, 0.2km/2.0GeV, 52pm, Black: NSLS-3, 0.8km/3.0GeV, 30pm, Blue: APS-2, 1.1km/6.0GeV, 80pm, Green: PEP-X, 2.2km/6.0GeV, 5pm, Orange: TAU, 6.2 km/9.0 GeV, 3 pm

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