

# FUNCTIONAL MATERIALS DEVELOPMENT USING ACCELERATOR-BASED LIGHT SOURCES: CURRENT CAPABILITIES AND FUTURE PROSPECTS\*

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## Abstract

The development of accelerator-based light sources has allowed access to photons of very high brightness and wide tunability. These properties of synchrotron radiation (SR) mean that it can be used to resolve questions that can be answered in no other way, enabling unique contributions to the development of functional materials. Increasingly, these benefits have become essential to material evaluation in manufacturing – ranging from intelligent catalysts for automotive emissions control [1] to next generation photovoltaics [2]. Bright, tunable X-rays have been a boon to nanotechnology [3] in particular, with its requirement for atom-by-atom understanding – and this benefit is enhanced by the microfabrication capabilities of X-ray lithography in LIGA-based techniques. The result is unique potential for nanoscale device manufacture. The application of bright tunable X-rays to the development of nanostructures for a range of industrial applications is illustrated, and the prospects for exploitation of the ultra-high brightness and femtosecond time structure of FEL radiation are discussed.

## INTRODUCTION

The recent DoE report ‘Accelerators for America’s Future’ [4] recognizes the importance of the research conducted at accelerator-based light sources to US industry. However, there are currently very few applications of SR for industrial scale processing; understandably the lack of direct control over the processing route and possible high unit cost are seen as likely disadvantages. However, in the field of materials development – which increasingly relies on developing a detailed understanding of nanoscale objects – the high brightness, coherence and tunability of 3<sup>rd</sup> and 4<sup>th</sup> generation light sources opens up some ‘niche’ applications in nanoscale device manufacture. Some examples of the way in which these three properties of SR are benefiting nanotechnology are reviewed here.

## DEVELOPING NEW CATALYSTS

Catalyst manufacturers are increasingly seeking to replace noxious processes by more environmentally-acceptable ones – which often requires using smaller amounts of catalyst at lower temperatures. It is therefore natural that the accurate characterization of nanoparticles, especially under synthesis [3] or reaction conditions has become important, and industrial catalyst developers are

increasingly recognizing the unique advantages of SR in this application. An important example is the contribution of SR to the development of intelligent vehicle exhaust ‘three-way’ catalysts, producing catalysts that are self-regenerating under the redox conditions encountered in a vehicle exhaust. SR X-rays have been used at a number of sources to tackle this problem.

## Extended X-ray Absorption Fine Structure

Much of this work has used EXAFS techniques, that give the local coordination environment around an absorbing atom, and require a tunable photon source such as a synchrotron; notable examples are the work of the Daihatsu Motor Co Ltd at SPring-8 [1,5], and Toyota at the ESRF [6].

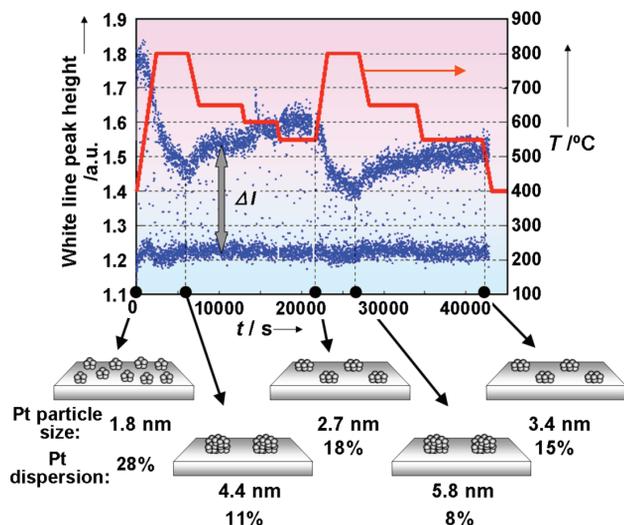


Figure 1: Temporal dependence of the white line peak height of the Pt L<sub>III</sub> edge XANES (obtained at ESRF) for a fresh 2 wt% Pt/CeZrY mixed oxide catalyst under oxidizing and reducing atmospheres at 400–800°C and the schematic representation of the sintering/redispersion behaviour. 4 or 20% O<sub>2</sub>/He gas and 3% H<sub>2</sub>/He gas were alternately introduced into the cell every 60 seconds throughout the measurement [6]. Reproduced with permission.

Vehicle exhaust catalysts consist of finely-divided precious metals (such as Pt) on an oxide support. They need to be capable of both the reduction of NO<sub>x</sub> and the oxidation of CO in the exhaust, operate at temperatures up to 1000°C, and in an exhaust gas that switches rapidly between oxidizing and reducing compositions. With time, the metal nanoparticles aggregate and sinter, leading to a reduction in active surface area and hence in catalytic

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activity. EXAFS has played a unique role in *in situ* dynamic observation of the sintering and redispersion phenomena of the precious metal, allowing the design of intelligent catalysts that renew themselves under the exhaust conditions. An example is shown in Figure 1, where the Pt/CeZrY mixed oxide catalyst is monitored by time-resolved fluorescence yield EXAFS in an *in situ* cell held under exhaust conditions [6].

In this collaborative work with Toyota, the change in the intensity of the Pt  $L_{III}$  edge white line between oxidized and reduced Pt is used, and it is found that this difference varies with Pt particle size. This allows the variation in Pt particle size with exhaust gas temperature to be determined (Figure 1). This led to the discovery of an unexpected oxidative redispersion of the Pt nanoparticles during redox cycling (over around 60 seconds). This understanding can be incorporated into ‘on board’ control aimed at curtailing the effects of metal sintering during operation.

EXAFS (at SPring-8) was also used in the design of an ‘intelligent’ (self-regenerating) catalyst system by Daihatsu, which shows in-built structural reversibility of the noble metal component [1,5]. In this case, a perovskite oxide is used as the support. The action of the self-generating catalyst is based on the repeated movement of the precious metals in and out of the perovskite lattice, between a solid solution and metallic nanoparticles during the natural changes in the redox conditions. The possibility of forming very large particles is intrinsically reduced as the grain growth of the precious metals is suppressed. This technology has been successfully commercialized, and was installed in more than 4 million vehicles by 2008 [5].

### X-ray microtomography

The high intensity and transverse coherence of third generation SR X-rays (typically in the 100  $\mu\text{m}$  range) have allowed for spectacular developments in X-ray microtomography, including phase contrast imaging. These now allow ‘3D’ imaging with spatial resolution rapidly heading towards 100 nm combined with quantitative analysis, and acquisition times as low as a few seconds. The industrial applications are many, including cosmetics, foams, reservoir rocks and composite materials and catalysts. A striking example is recent work at the ESRF which has enabled the catalytic activity of Raney-type nickel catalysts to be improved [7].

Raney or ‘spongy’ nickel is one of the oldest and most important industrial catalysts, used in hydrogenation reactions and for hydrogen fuel cell electrodes. The morphology is porous, traditionally prepared by taking a ‘cast-and-crush’ manufactured Ni-Al alloy, and leaching out the Al with concentrated NaOH, leaving a pyrophoric, highly reactive catalyst. The emphasis of current research is to develop cheaper and more efficient nickel catalysts. In collaborative work between the ESRF, the ILL Neutron Source and the European Space Agency, SR X-ray microtomography has been used to identify the microstructures of the different alloys within catalysts

prepared by a new process of gas atomization [7] (Figure 2). From this work it has been possible to correlate the microstructure with catalytic performance, and hence to design a catalyst with an activity twice that of a conventionally-prepared material.

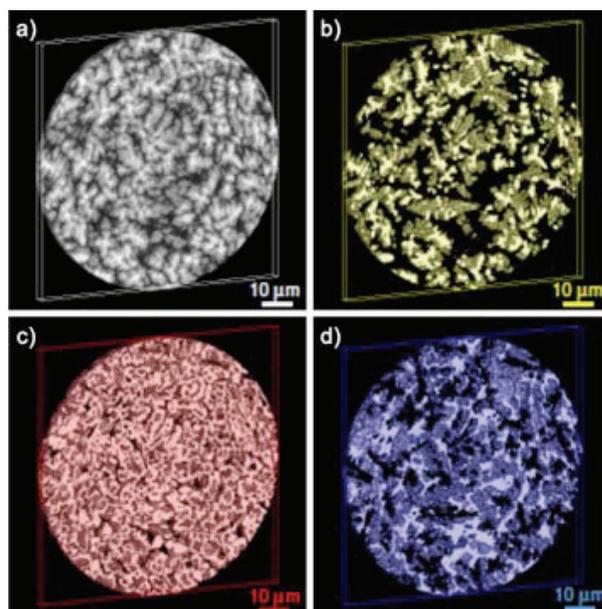


Figure 2. X-ray microtomography images (obtained at ESRF) of 1.2  $\mu\text{m}$  thick cylindrical cross sections of atomised alloy grains (before leaching) showing (a) the inner microstructure of a Ni -77.5 at % Al droplet, (b-d) 3D distribution of  $\text{Ni}_2\text{Al}_3$ ,  $\text{NiAl}_3$  and eutectic phases respectively [7]. Figure courtesy of G Reinhart, ESA.

Catalysts were imaged after initial grain formation, producing a mixture of Ni-Al alloys (Figure 2), and again after leaching the Al. Quantitative microtomography showed that during preparation, a dendritic network of  $\text{Ni}_2\text{Al}_3$  was formed, which is the first phase to solidify from the melt, being later covered by  $\text{NiAl}_3$ . The interdendritic space is filled with Al-rich material from the eutectic. The  $\text{Ni}_2\text{Al}_3$  phase is most resistant to etching, and was shown to remain in the leached catalyst, leaving a high degree of porosity in the interdendritic space, crucial to high catalytic activity. Screening the catalytic activity of a range of compositions in combination with microtomography allowed the optimal parameters for best activity to be determined, a powerful example of ‘intelligent redesign’ of an important catalyst.

### CHARACTERISING QUANTUM DOTS

A further example of ‘niche’ applications of SR in nanotechnology is non-destructive depth-profiling of quantum-confined semiconductor nanocrystals (quantum dots, or ‘QDs’) which are widely used for their light-emitting properties, and are potentially suitable light absorbers for next generation solar cells. Photovoltaic devices based on QDs may be able to exceed the theoretical maximum efficiency of single junction solar

cells by making use of multiple exciton generation (MEG), where the excess energy of an absorbed photon is used to generate extra electron-hole pairs rather than being wasted as heat [2,8]. QDs typically have a 'core-shell' or more complex structure, containing several different semiconductors with their band gaps engineered to control the carrier wavepackets created by light absorption. Depth-profiling X-ray photoelectron spectroscopy (XPS) using a synchrotron source allows the chemical composition of the QDs to be probed as a function of depth, over sampling depths commensurate with the size of the QDs (typically 3-5 nm) – crucial information for QD manufacturers that is difficult to obtain in any other way. This is achieved by using the tunability of SR to adjust the kinetic energy of the photoelectrons, and hence their mean free pathlengths in the QDs [2,9]. Because small QDs have such a high surface:volume ratio, surface properties (and surface reactivity) may dominate their characteristics, and this is sensitively probed by SR-XPS. Indeed, very rapid aerial oxidation of colloidal QDs (sufficient to produce an oxide layer that consumes 30-50% of the QD in a matter of hours [2,10]) has been demonstrated in this way, as shown in Figure 3.

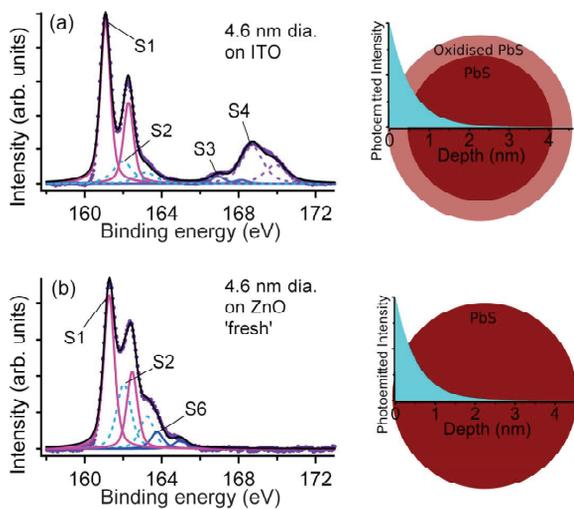


Figure 3: High resolution S 2p SR-XPS (recorded at ELETTRA and SOLEIL) revealing the effect of surface oxidation on 4.6 nm PbS QDs. Components S1 and S2 are due to PbS and neutral S respectively, while S6 is due to the capping ligand. Components S3 and S4 (due to surface sulphite and sulphate respectively) appear within a few hours of aerial exposure (a) and are absent in a sample introduced into the spectrometer within a few minutes (b). The surface layer thickness calculated from XPS is around 0.5 nm, or 30% of the volume of the QD [2]. The righthand schematics indicate the depth distribution of the XPS signal.

Surface oxidation of the QDs acts to reduce the size of the QD core. As the structures are quantum confined, this changes the energies of light absorption and emission, and, crucially, the threshold for MEG. These are crucial parameters for the manufacturers of QDs, leading a

number to engage in collaborative SR experiments in this field.

## FABRICATING NEW STORAGE MEDIA

The recent DoE report 'Accelerators for America's Future' [4] comments that 'Electron synchrotrons...are not suitable for the industrial processing of materials'. Taken as a reflection on unit cost and the lack of control over the production process, this is still in general the case. However, extreme UV lithography (EUV), or X-ray lithography (XIL) as part of a LIGA-based approach is widely used to produce research devices at a large number of SR sources. These include a number of laboratories focusing on technological applications such as CAMD [11] and KIT Karlsruhe (using ANKA) [12], and also many larger facilities such as the ESRF, ELETTRA, the SLS and SRC. Again, techniques are emerging where the use of synchrotron radiation offers unique advantages to industry. One such newly emerging nanolithography method is extreme ultraviolet interference lithography (EUV-IL) (or X-ray interference lithography, XIL), which combines the advantages of parallel fabrication with high resolution, and may realistically become the method of choice (over, for example, electron beam lithography, EBL) for the production of master copies of nanodevices for subsequent production. The technique is exemplified at the SLS [13], where sub 10 nm features were achieved in October 2011 - the current record in photon-based lithography, and normally the province of 'bottom-up' techniques [14]. Here, fully coherent undulator radiation is used in two- and multi-beam interference schemes to generate line and hole-dot patterns respectively in an electron beam resist such as hydrogen silsesquioxane (HSQ). This may be subsequently elaborated by LIGA processing. Highly accurate patterns can be created in a step-and-repeat way, allowing several mm<sup>2</sup> to be exposed in each step, considerably faster than EBL.

In collaborative work, Hitachi Global Storage Technologies have demonstrated the potential of EUV-IL in the creation of bit-patterned media (BPM) for magnetic data storage [15], as shown in Figure 4. The Figure shows a BPM – an array of nanoscale magnetic islands – where each bit of information can be stored in an individual island (the size of which defines the magnetic anisotropy energy). This is produced by EUV-IL exposure of a 30 nm thick HSQ resist, which is developed to produce an array of SiO<sub>x</sub> pillars. Co/Pd is then deposited by dc magnetron sputtering, giving 50 nm period magnetic islands that are decoupled from the magnetic material in the trenches between the pillars, and are created over an area of 20x20 μm<sup>2</sup> with a very narrow size distribution [15]. Smaller dot periods (of around 25 nm) have already been achieved [13]. This corresponds to a data storage density of 1 Tbit/in<sup>2</sup>, which is a key milestone in the data storage roadmap, and is beyond the range of optical interference lithography. X-ray systems show much smaller proximity effects (where sections of the resist adjacent to the required pattern are exposed due to secondary electron blurring) than EBL, allowing very

sharp and deep features to be achieved over large areas, with high throughput. These advantages make EUV-IL increasingly competitive for the production of masters (for subsequent nanoimprinting and production of daughter copies for large scale stamping) and in specialized applications (for example in satellite technology).

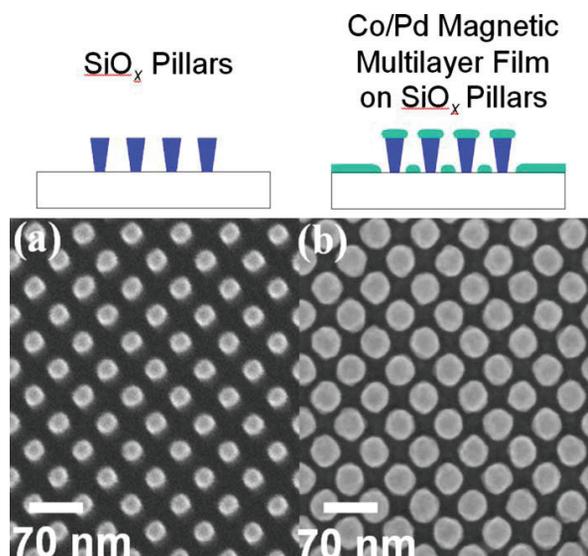


Figure 4: Schematic diagram of the fabrication of nanoscale magnetic island arrays with EUV-IL and corresponding SEM images of SiO<sub>x</sub> pillars with periods of 50 nm (a) before and (b) after Co/Pd multilayer film deposition [15]. Reproduced with permission.

### PROSPECTS FOR FELS

The enormous brightness and coherence of 4<sup>th</sup> generation light sources means that we can only partially imagine what we might discover using these sources of ultra-short pulse light. These properties have led scientists around the world to consider the possibility that it might be possible to use them to control the direction of a chemical reaction, perhaps even to synthesise molecules (such as drugs) that are currently difficult or expensive to make. Even before the advent of hard and soft X-ray FELs, workers at the Thomas Jefferson National Accelerator Facility, Virginia, have shown that their infrared (IR) FEL source is an ideal tool for synthesising high purity carbon nanorods – in economically viable kilogramme quantities – material that is difficult to make in a highly pure state by other routes [16]. The nanorods have been used by NASA in fibre-reinforced material for aerospace applications.

The high intensity and coherence of the sources also lead to powerful opportunities in imaging. In the hard X-ray regime, the objective is single molecule diffraction – in particular to be able to determine the structure of a single biomolecule (e.g. a large macromolecule or virus) in a molecular jet, without the constraint of having to produce a single crystal sample. This is combined with

unique opportunities for dynamic experiments – enabling us to understand how molecules or devices function on timescales of tens of fs. This is the fundamental timescale on which molecules vibrate and on which bonds are made or broken, so time-resolved single molecule diffraction could allow reaction pathways to be elucidated for the first time.

In the last few years, particularly since the advent of LCLS, progress towards this objective has been spectacular. The high fluence of the pulses from the X-ray FELs results in the molecule or cluster under study being destroyed by undergoing a ‘Coulomb explosion’ and turning into a plasma on timescales of tens of fs. The experiment is thus intrinsically a ‘one-shot’ experiment, and data must be gathered from an individual molecule before it is destroyed, requiring fast detection and data readout. In the absence of the crystalline order of the lattice giving systematic absences, the data are ‘oversampled’ and it is possible to use techniques developed from electron diffraction to retrieve the phase information necessary to allow image reconstruction from the coherent pattern [17]. By combining around 15,000 FEL shots from the LCLS, Henry Chapman and co-workers were able to reconstruct the structure of the photosystem I protein at resolutions as small as 8.5 Å, from a jet of hydrated protein nanocrystals [18]. These experiments were carried out only two months after the LCLS opened for research. In a companion experiment, Janos Hajdu and co-workers obtained single shot diffraction patterns of single Mimivirus particles at a resolution of 32 nm [19].

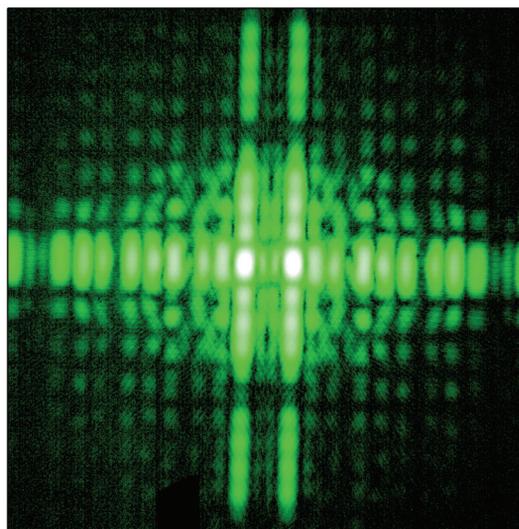


Figure 5. The hologram recorded when two 23.5 nm FLASH pulses (separated by 50 fs) illuminate overlapping regions of the object (a microstructure representing the Brandenburg Gate) [20]. Credit: Stefan Eisebitt/HZB.

In order to make time-resolved measurements of dynamic processes, sequential images must be obtained on timescales of tens of fs or less. At the FLASH soft X-ray FEL, two sequential diffraction images have been

obtained at a separation of 50 fs – an achievement recorded in the 2012 Guinness Book of World Records as the world's fastest movie [20] (Figure 5). This was achieved by splitting the X-ray beam using an autocorrelator and introducing a 50 fs time delay between the two pulses. The two images were recorded as superimposed holograms on one detector in a single exposure (single shot holography), from which two images of the object (a NiFe foil containing several microstructures) were subsequently reconstructed.

The long-term goal of these experiments is to track the movements of molecules and nanostructures in real time. While the initial focus has been on the structure of biomolecules, it is clear that there is substantial scope for the imaging of nanostructures in operation – whether catalysts, photovoltaics or magnetic storage media [21], adding dynamic information to the largely static information provided by 3<sup>rd</sup> generation SR.

## CONCLUSIONS

Accelerator-based light sources are well-matched to highly specialized ‘one-off’ applications (for example in military or satellite applications) where performance rather than unit cost is the driving force. However, the high brightness, coherence and tunability of 3<sup>rd</sup> generation SR has opened up a wider range of ‘niche’ industrial applications in the development of nanoscale functional materials, illustrated here by the development of better catalysts, photovoltaics and magnetic storage materials. FELs offer the prospect of completing the picture by adding dynamic information that can elucidate chemical reaction pathways in catalysts, charge transport in photovoltaics or spin manipulation in magnetic storage materials. The industrial potential of FELs is not yet realized; but already applications have been demonstrated – for example in the synthesis of materials that cannot be easily produced by other routes.

## ACKNOWLEDGEMENTS

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