Final Report

THREE-DIMENSIONAL IMAGING OF NANOSCALE MATERIALS BY UISNG COHERENT X-RAYS

Date: April 12, 2011

Abstract

X-ray crystallography is currently the primary methodology used to determine the 3D structure of materials and macromolecules. However, many nanostructures, disordered materials, biomaterials, hybrid materials and biological specimens are noncrystalline and, hence, their structures are not accessible by X-ray crystallography. Probing these structures therefore requires the employment of different approaches. A very promising technique currently under rapid development is X-ray diffraction microscopy (or lensless imaging), in which the coherent X-ray diffraction pattern of a noncrystalline specimen is measured and then directly phased to obtain a high-resolution image. Through the DOE support over the past three years, we have applied X-ray diffraction microscopy to quantitative imaging of GaN quantum dot particles, and revealed the internal GaN-Ga_2O_3 core shell structure in three dimensions. By exploiting the abrupt change in the scattering cross-section near electronic resonances, we carried out the first experimental demonstration of resonant X-ray diffraction microscopy for element specific imaging. We performed nondestructive and quantitative imaging of buried Bi structures inside a Si crystal by directly phasing coherent X-ray diffraction patterns acquired below and above the Bi M5 edge. We have also applied X-ray diffraction microscopy to nondestructive imaging of mineral crystals inside biological composite materials - intramuscular fish bone - at the nanometer scale resolution. We identified mineral crystals in collagen fibrils at different stages of mineralization and proposed a dynamic mechanism to account for the nucleation and growth of mineral crystals in the collagen matrix. In addition, we have also discovered a novel 3D imaging modality, denoted ankylography, which allows for complete 3D structure determination without the necessity of sample titling or scanning. We showed that when the diffraction pattern of a finite object is sampled at a sufficiently fine scale on the Ewald sphere, the 3D structure of the object is determined by the 2D spherical pattern. We confirmed the theoretical analysis by performing 3D numerical reconstructions of a sodium silicate glass structure at 2 Å resolution from a 2D spherical diffraction pattern alone. As X-ray free electron lasers are under rapid development worldwide, ankylography may open up a new horizon to obtain the 3D structure of a non-crystalline specimen from a single pulse and allow time-resolved 3D structure determination of disordered materials.

Accomplishments

- The missing data problem, *i.e.* the intensities at the center of diffraction patterns cannot be experimentally measured, was a major limitation for wider applications of coherent diffraction microscopy. We have shown that, when the missing data are confined within the centro-speckle, the missing data problem can be reliably solved. With an improved instrument, we recorded 27 oversampled diffraction patterns at various orientations from a GaN quantum dot nanoparticle and performed quantitative image reconstruction from the diffraction intensities alone. This work in principle clears the way for single-shot imaging experiments using x-ray free electron lasers.

- We developed equally sloped tomography for the reconstruction of a 3D object from a number of 2D projections. In a combination of pseudo-polar fast Fourier transform and the oversampling method with an iterative algorithm, equally-sloped tomography makes superior 3D reconstruction to conventional tomography which has an intrinsic drawback due to the use of equally angled 2D projections.

- In combination of direct phase retrieval of coherent X-ray diffraction patterns with equally sloped tomography, we for the first time carried out quantitative 3D imaging of a heat-treated GaN particle with each voxel corresponding to $17 \times 17 \times 17$ nm^3. We observed the platelet structure of GaN and the formation of small islands on the surface of the platelets, and successfully captured the internal GaN-Ga_2O_3 core shell structure in three dimensions. This work opens the door for non-destructive and quantitative imaging of 3D morphology and 3D internal structure of a wide range of materials at the nanometer scale resolution that are amorphous or possess only short-range atomic organization.

- We have shown that, when the linear oversampling ratio ≥ 2, exactly oversampled diffraction patterns can be directly obtained from measured data through deconvolution. By using computer simulations and experimental data, we have demonstrated that exactly oversampled diffraction patterns distinctively improve the quality of phase retrieval. Furthermore, phase retrieval based on the exact sampling scheme is independent of the oversampling ratio, which can significantly reduce the radiation dosage to the samples. We believe that the present work will contribute to high-quality image reconstruction of materials science samples and biological structures using X-ray diffraction microscopy.

- We developed a novel guided hybrid input-output algorithm (GHIO) for phase retrieval from oversampled diffraction intensities. GHIO is based on the evolution theory to efficiently search for a “global” minimum in a complex non-linear system. Compared with HIO, GHIO is more precise and reliable in phase retrieval from diffraction intensities alone.

- We applied x-ray diffraction microscopy to nondestructive imaging of mineral crystals inside biological composite materials - intramuscular fish bone - at the nanometer scale resolution. We identified mineral crystals in collagen fibrils at different stages of mineralization. Based on the experimental results and biomineralization analyses, we suggested a dynamic mechanism to account for the nucleation and growth of mineral crystals in the collagen matrix. The results

obtained from this study not only further our understanding of the complex structure of bone, but also demonstrate that x-ray diffraction microscopy will become a useful tool to study biological materials.

- We demonstrated resonant x-ray diffraction microscopy for element specific imaging of buried structures with a pixel resolution of ~ 15 nm by exploiting the abrupt change in the scattering cross-section near electronic resonances. We performed nondestructive and quantitative imaging of buried Bi structures inside a Si crystal by directly phasing coherent x-ray diffraction patterns acquired below and above the Bi M5 edge.

- We conducted the recording and reconstruction of X-ray diffraction patterns from single, unstained viruses, for the first time. By separating the diffraction pattern of the virus particles from that of their surroundings, we performed quantitative and high-contrast imaging of a single virion. The structure of the viral capsid inside a virion was visualized. This experiment is directly transferable to the use of X-ray free electron lasers, and represents an experimental milestone towards the X-ray imaging of single macromolecules.

- We report performed quantitative 3D imaging of a whole, unstained cell at a resolution of 50–60 nm by X-ray diffraction microscopy. We identified the 3D morphology and structure of cellular organelles including cell wall, vacuole, endoplasmic reticulum, mitochondria, granules, nucleus and nucleolus inside a yeast spore cell. Furthermore, we observed a 3D structure protruding from the reconstructed yeast spore, suggesting the spore germination process. Using cryogenic technologies, a 3D resolution of 5-10 nm should be achievable by X-ray diffraction microscopy. This work hence paves a way for quantitative 3D imaging of a wide range of biological specimens at nanometer-scale resolutions that are too thick for electron microscopy.

- We developed a 3D imaging modality, termed ankylography (derived from the Greek words ankylos meaning ‘curved’ and graphein meaning ‘writing’), which under certain circumstances enables complete 3D structure determination from a single exposure using a monochromatic incident beam. We demonstrated that when the diffraction pattern of a finite object is sampled at a sufficiently fine scale on the Ewald sphere, the 3D structure of the object is in principle determined by the 2D spherical pattern. We confirmed the theoretical analysis by performing 3D numerical reconstructions of a sodium silicate glass structure at 2 Å resolution, and a single poliovirus at 2–3 nm resolution, from 2D spherical diffraction patterns alone. Using diffraction data from a soft X-ray laser, we also provided a preliminary demonstration that ankylography is experimentally feasible by obtaining a 3D image of a test object from a single 2D diffraction pattern. With further development, this approach of obtaining complete 3D structure information from a single view could find broad applications in the physical and life sciences.

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