



In situ X-ray-based imaging of nano materials

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Functional nanomaterials are heterogeneous and understanding their behavior during synthesis and operation requires high resolution diagnostic imaging tools that can be used *in situ*. Over the past decade, huge progress has been made in the development of X-ray based imaging, including full field and scanning microscopy and their analogs in coherent diffractive imaging. Currently, spatial resolution of about 10 nm and time resolution of sub-seconds are achievable. For catalysis, X-ray imaging allows tracking of particle chemistry under reaction conditions. In energy storage, *in situ* X-ray imaging of electrode particles is providing important insight into degradation processes. Recently, both spatial and temporal resolutions are improving to a few nm and milliseconds and these developments will open up unprecedented opportunities.

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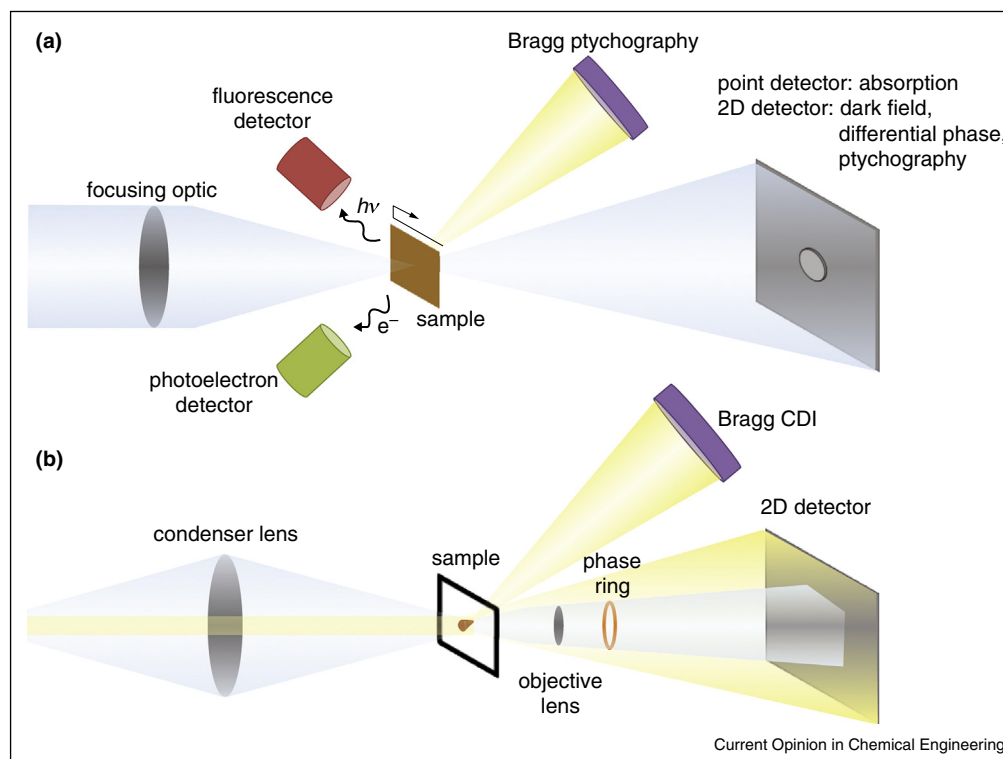
Introduction

Within the past few decades, nanomaterials have been increasingly used in products ranging from sunscreen to antimicrobial treatments to catalysts to rechargeable batteries, and as new nanomaterials continue to be developed, they will find increasing use especially for sustainable energy conversion and storage, such as quantum dots (QDs), batteries and new catalysts. In order to develop better functional nanomaterials, it is essential to understand how they are formed during synthesis and how they operate in realistic environments. To this end, many *in situ* diagnostic approaches are being used, but since nanomaterials are often heterogeneous (energy storage, fuel cells, catalysts on supports) imaging these processes is required — ‘seeing is believing’ to quote the old adage.

Over the past few years, X-ray based imaging or microscopies (XMs) have been developing rapidly and have been increasingly applied to *in situ* imaging of functional nanomaterials. The current spatial and time resolutions are approximately 10 nm and sub-seconds and are steadily improving. Due to the penetration power of X-rays and excellent spatial and temporal resolutions, XMs can visualize materials in realistic synthesis environments and operating conditions for real time investigations far from equilibrium. Although *in situ* transmission electron microscopy (TEM) has far better spatial resolution, TEM requires the use of less realistic environments because of strong interaction between electrons and the material. For example, TEM observations of lithiation of silicon nanowires (a promising anode for Li-ion batteries) required the use of a solid state Li₂O electrolyte rather than the organic liquid electrolyte used in Li-ion batteries [1]. Thus, TEM and XM are complementary [2].

This review covers a brief overview of XM based *in situ* imaging of nanomaterials with a focus on catalysis and energy storage and how nanomaterials evolve during operation. There are two major modalities of XM, scanning and full field, which are conceptually illustrated in **Figure 1**. In scanning mode, images are acquired pixel-by-pixel using a finely focused (10–100 nm) X-ray beam; fluorescent (providing elemental sensitivity) or transmitted (morphology) X-rays are collected, frequently simultaneously, to form an image. Auger electrons can also be collected for mapping surface-sensitive elemental distributions. If a 2D segmented detector is used, dark field images or differential phase contrast images can be measured. In full field, a large, typically incoherent, X-ray beam is focused onto the sample, defining the field of view, and the scattered and transmitted X-rays are collected by the objective lens that forms a real-space, absorption contrast image on an area detector in a single shot. A phase ring can be used to measure Zernike phase contrast. The full field mode allows rapid image acquisition which is ideal for tomography. In both modalities, chemical mapping is obtained using X-ray absorption spectroscopy (XAS), where the incident X-ray energy is scanned across an absorption edge to measure chemical signatures. Both modes have advantages and disadvantages as discussed in Refs. [2,3]. Additionally, the two modes have coherent diffractive imaging (CDI) analogs (**Figure 1** yellow), where the use of coherent illumination and oversampling of the data allow the use of iterative algorithms to reconstruct the complex-valued image at a resolution finer than limited by the imaging optics [4]. The remainder of this perspective discusses XMs as applied to catalyst nanomaterials, energy storage

Figure 1



Schematics of different X-ray microscopy geometries. In a scanning technique **(a)**, the beam is focused to a very small spot size and the sample is scanned through the X-ray beam. Transmitted X-rays, fluorescence X-rays, or Auger electrons (or several of these) are collected to form an image and allow for elemental or chemical mapping. If a coherent beam is used, then scattered intensity patterns can be collected either in transmission or near a Bragg diffraction peak and reconstructed into an image with a resolution below the beam size. In the full field technique **(b)**, a beam is focused onto the sample and the scattered and transmitted X-rays are collected with an objective lens onto an area detector forming the image. If a coherent beam (yellow) is used without any focusing optics, the scattered intensity pattern can be collected either in transmission or near a Bragg peak for higher resolution imaging.

electrodes, porous fuel cell electrodes, and nanomaterials synthesis electrodeposition. We finish with some thoughts on future directions.

Catalysts

In order to characterize nanoparticle catalysts *in situ*, they should be observed within their porous support and under reactive conditions. Standard imaging techniques, such as visible light and electron microscopies, struggle to resolve nanometer structures on support particles which are tens to hundreds of microns in diameter, especially at high temperature and pressure. However, with its relatively large penetration depth and high resolution, *in situ* X-ray microscopy is uniquely poised to tackle this challenging problem.

With soft X-rays (defined here as X-rays having energies below ~ 2 keV), the chemical and morphological changes in individual supported catalytic nanoparticles should be able to be tracked, although current microscope resolutions are limiting. Due to their relatively large scattering

cross-section, soft X-rays are ideal for mapping chemistries of thin samples such as nanoparticle catalysts. On the other hand, the limited working distance between the optics and the sample (hundreds of microns to a few millimeters), makes *in situ* sample environments more difficult to design. A proof of technique demonstration of *in situ* scanning transmission X-ray microscopy (STXM) (Figure 1a), allowing temperatures up to 350°C and various gas environments at 1 bar, mapped the Fe L-edge chemistries of supported iron oxide particles during reduction and the Fisher–Tropsch synthesis [5]. The resolution of the chemical maps was limited to ~ 40 nm. The oxygen and carbon chemistries were also measured in specific locations, but not spatially mapped.

Hard X-rays (above ~ 2 keV) can penetrate thicker samples making them ideal for studying catalysts in their intact support. Working distances are also longer (tens of millimeters or longer) allowing more complex sample environments, such as high pressure. *In situ* hard X-ray transmission X-ray microscopy (TXM) (Figure 1b) was

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