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Combined three-dimensional structure and chemistry imaging with nanoscale resolution

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Abstract

While there is great interest in characterizing and modifying materials at the nanoscale, progress has been slow because few techniques allow for critical observations at this length scale. This work presents a data fusion technique that combines synchrotron-based X-ray nano computed tomography and nano X-ray fluorescence to non-destructively investigate complex nanoscale materials and provide combined three-dimensional (3-D) renderings of microstructure and chemistry. The technique has been named nano tomography-assisted chemical correlation (nTACCo) and is demonstrated on fly ash particles with nanoscale chemical inhomogeneities. Our findings show that nTACCo is capable of providing the concentration and location of seven different nano-inclusions within a particle. This work also provides direct observations of reactivity and chemical distribution of fly ash. This ability to combine 3-D structure and chemistry at the nanoscale will provide unprecedented tools for nanoscience in material science, biology, chemistry and medical science.

Keywords: nTACCo; X-ray computed tomography; X-ray fluorescence; Data fusion; Fly ash

1. Introduction

1.1. Background

Progress in a number of research fields has been halted because direct investigation of three-dimensional (3-D) nanostructure and chemistry are very difficult to achieve [1,2]. A number of fields could benefit from this ability, including corrosion [3–5], battery design [6–9], green cements [10–12], porous materials [13,14], cancer research [15], and interactions between tissue and prosthetics [16,17]. In each of these fields there are critical mechanisms involving changes in the structure and chemistry at the nanoscale that are unknown.

A powerful method to study these applications is X-ray radiation produced at bright light sources [18]. X-rays offer high penetration power and great chemical sensitivity. Unique synchrotron-based techniques including nano X-ray diffraction, fluorescence and tomography have been developed at the hard X-ray nanoprobe beamline, which is operated in partnership between the Advanced Photon Source (APS) and the Center for Nanoscale Materials (CNM) at Argonne National Laboratory. These techniques in their current capability are able to image length

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scales of ~15 nm, and even smaller scales will be possible in the future [19–22].

A new analytical technique is presented that combines nano computed tomography (nCT) and nano X-ray fluorescence (nXRF) to quickly and efficiently produce 3-D maps of the microstructure and distribution of chemical constituents within fly ash particles. This methodology has been named nano tomography-assisted chemical correlation (nTACCo). This technique has been demonstrated with fly ash, a complex material of paramount importance for the production of the next generation of green cements [10,23,24]. Trace deposits of metals such as arsenic, cesium, lead, selenium, cadmium and zirconium have been found within these materials and have made them controversial as the metals pose a threat to the environment if not handled correctly [10,12,24–26]. This paper presents for the first time a 3-D combined chemical and microstructure map at the nanometer length scale that was obtained non-destructively and is the latest evolution of fusing imaging and microanalysis measurements [27,28].

1.2. Nano computed tomography

X-ray CT is commonly used in the medical sciences to non-destructively image the internal structure of organisms. This technique combines a series of X-ray radiographs at small angles of rotation to produce a 3-D tomograph [29–31]. Typically the technique is used to investigate volumes larger than a cubic micron. This is common for laboratory or synchrotron micro-CT (mCT). With mCT, useful contrast can be found between materials with different mass absorption coefficients and density. These differences can be used to determine the spatial distribution of material constituents by looking at the different X-ray intensities transmitted [28,32].

However, when CT is used at the nanoscale the number of atoms interacting with the beam is much smaller. This means that the difference in the X-ray absorption of the constituent matter is also much smaller [33]. Because of this it is challenging to use these techniques to detect the difference between two materials unless there is a great difference between their mass absorption coefficients or electron density. Nevertheless, 3-D structural investigations have recently become possible at the nanoscale. For example, the first 3-D view of the pore structure of an aluminosilicate geopolymer gel has been reported, which has the potential to improve the strength and reduce the permeability of concretes based on this class of binders [26]. Others have had to use dyes, nano contrast agents or atomic layer deposition in order to image their samples [33,34]. Although structural information is obtained, a detailed knowledge about the distribution of different unique constituents cannot be extracted unless assisted chemical analysis techniques have been applied, which could involve sample modification, or the knowledge of the constituents' composition has been well established for those manufactured materials [28].

1.3. Nano X-ray fluorescence

nXRF can provide elemental maps with detection below the parts per million (ppm) level. In this technique a primary X-ray beam illuminates a sample and an energy-dispersive detector is used to measure the fluorescence X-rays leaving the sample. Each chemical element will emit fluorescence radiation at characteristic energies. By rastering the primary X-ray beam over the sample it is possible to create 2-D maps of materials.

Notwithstanding its undisputable success, the technique is hindered by two major factors: (i) the X-ray beam will penetrate into the material and cause X-ray fluorescence along its path, making it challenging to directly render depth-dependent information; and (ii) X-ray fluorescence is self-absorbed in the sample before it can reach the detector, which, depending on the severity, complicates adequate quantification of the signal. Both effects make it difficult to determine the distribution of the elements through the depth of the sample. Other work has translated the focus of the X-ray beam at different points of a sample to learn more about the spatial distribution of elements within a specimen [20,35,36]. However, this approach is very time consuming and limited to the depth-of-view of the focusing optics. X-ray fluorescence tomography has recently become available [37–39]. However, this technique is limited to lower-resolution X-ray fluorescence microscopy, since it requires high-efficiency X-ray optics. The high-resolution focusing optics used in nanoprobes exhibit inherently low efficiency. Consequently, dwell times are relatively high, which prohibits the acquisition of many 2-D maps of the sample. For example, an X-ray fluorescence tomography scan with a voxel resolution of 30 nm would require about 1800 maps taken at angles between 0° and 180°. In conclusion, the lack of 3-D information from nXRF is a current limitation of the method.

1.4. Fly ash

Currently, there is a need to better understand the composition and microstructure of fly ash [10,28]. Fly ash is a waste product from the combustion of coal during power generation. These materials are typically landfilled if other applications are not found. The particles are generally spherical with diameters ranging from <1 μm to >1 mm [5,10,40,41]. Fly ash is commonly used as a low-cost construction binder for stabilization of soil, a partial replacement of Portland cement in a concrete mixture, and the predominate binder in a geopolymer concrete [10,24]. By using this material within other binders it is thought that these metals are bound within the hydration products and not available for leaching. However, this is not well understood. If a better understanding of the location and concentration of these metals could be found, then this might better guide the usage of these materials.

Previous research on fly ash has primarily focused on the measurement of its bulk properties [42–45]. Only a