Element-Specific X-Ray Phase Tomography of 3D Structures at the Nanoscale

Claire Donnelly,1,2 Manuel Guizar-Sicairos,2,‡ Valerio Scagnoli,1,2 Mirko Holler,2 Thomas Huthwelker,2 Andreas Menzel,2 Ismo Vartiainen,2 Elisabeth Müller,2 Eugenie Kirk,1,2 Sebastian Gliga,1,2 Jörg Raabe,2 and Laura J. Heyderman1,2

1Laboratory for Mesoscopic Systems, Department of Materials, ETH Zurich, 8093 Zurich, Switzerland
2Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

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Recent advances in fabrication techniques to create mesoscopic 3D structures have led to significant developments in a variety of fields including biology, photonics, and magnetism. Further progress in these areas benefits from their full quantitative and structural characterization. We present resonant ptychographic tomography,combining quantitative hard x-ray phase imaging and resonant elastic scattering to achieve ab initio element-specific 3D characterization of a cobalt-coated artificial buckyball polymer scaffold at the nanoscale. By performing ptychographic x-ray tomography at and far from the Co K edge, we are able to locate and quantify the Co layer in our sample to a 3D spatial resolution of 25 nm. With a quantitative determination of the electron density we can determine that the Co layer is oxidized, which is confirmed with microfluorescence experiments.

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With recent advances in technology opening up the possibilities of true three-dimensional (3D) nano- and microfabrication [1], new opportunities for applications have emerged within a large number of fields [1,2]. Extending metamaterials into the third dimension allows increased control over photonic properties, such as the introduction of structural chirality resulting in broadband circular polarizing effects [3]. With a quasi-3D system, the first complete photonic band gap at near-IR frequencies was achieved [4], making the 3D regime an obvious route for further advances in photonics. Three-dimensional structures are of great interest in magnetism enabling, for example, high-density data storage architectures [5] and the control of magnetic properties [6]. Furthermore, 3D advanced materials have been employed in many other fields, with the potential for the manipulation of mechanical properties [7] and for medical applications [2] such as drug delivery with fabricated 3D magnetic microbots [8]. The quantitative characterization of these designed materials, as well as other complex materials including catalysts or composites [9], is essential to further improve their performance.

Here we present the full structural and elemental characterization of a polymer-metal artificial buckyball at 25 nm spatial resolution by resonant x-ray ptychographic tomography. While ptychography measurements across absorption edges have been demonstrated in 2D [10–12], to our knowledge this is both the first demonstration of 3D resonant ptychography and the first time that phase contrast off and on resonance has been combined to determine the atomic density of a specific element. In contrast to nonresonant phase tomography, which relies on having different electron densities for different phases [13], resonant ptychographic tomography is element specific, allowing not only for an element to be located but also for further information on its chemical state to be determined, so providing a unique tool for the characterization of 3D materials at the nanoscale.

X-ray ptychography is a scanning variant of coherent diffractive imaging [14,15] and provides access to the full complex transmission function, $T$, of a specimen with both phase, $\phi$, and amplitude, $A$, contrast:

$$T(x,y) = Ae^{i\phi} = \exp\left(-\frac{2\pi}{\lambda}\int[\beta(r) + j\delta(r)]dz\right)$$

(1)

where $r = (x, y, z)$ is the 3D set of Cartesian coordinates with $z$ the direction of x-ray propagation and $n = 1 - \delta - j\beta$ the complex refractive index. For x-ray ptychography, the sample is illuminated with a coherent beam, and far-field diffraction patterns are recorded for many overlapping areas. The resulting data redundancy allows for the reconstruction of both the illumination and the specimen [15–17]. This ability to quantitatively measure the phase, which provides superior contrast compared to absorption at hard x-ray energies, allows high-contrast imaging of large-scale $\mu$m-sized structures. The spatial resolution is limited by the scattering angle of the measurable diffraction pattern and the accuracy and stability of the positioning of the sample [18], currently reaching 5 nm in 2D [19] and 16 nm in 3D [20]. Here we demonstrate that combining phase tomography with the probing of element-specific resonances enables the determination of both the atomic and electron density, providing information on both the location and electronic state of atoms of a specific element with high spatial resolution.

An artificial buckyball polymer scaffold was fabricated by two-photon absorption lithography using a Nanoscribe 3D direct laser write system with the negative-tone Nanoscribe IP-Dip resist. To ensure a clear 360° view of...
the sample for tomographic imaging, the buckyball was fabricated on top of a high aspect ratio silicon pillar of height 36 \( \mu \)m and diameter 10 \( \mu \)m, which was produced using a combination of electron beam lithography and reactive-ion etching performed with the Bosch process [21]. The buckyball was 6 \( \mu \)m in diameter with a width of the connecting bars of around 240 nm and was coated with 30 nm of Co capped with 6 nm of gold using an ultrahigh vacuum sputtering system. As a final step, the 3D nanostructure was transferred and attached to the sample mount using a focused ion beam and micromanipulator. Scanning electron micrographs of the sample on the tomography pin are given in Fig. 1.

For ptychographic tomography [22], 2D projections are measured at a number of sample orientations with respect to the incident x-ray beam. Here, these were performed at a photon energy of 6.20 keV and then at 7.71 keV, where the latter energy corresponds to the \( K \) absorption edge (the 1\( s\)-4\( p \) transition) of cobalt. The experiments were performed at the cSAXS beam line at the Swiss Light Source, Paul Scherrer Institute, Switzerland, using an interferometrically controlled high-resolution 3D scanning setup [20,23], which allows for nanometer precision positioning combined with full sample rotation over 360°. The illumination on the sample was defined by a combination of a 40 \( \mu \)m central stop, a 30 \( \mu \)m order-sorting aperture, and gold Fresnel zone plates with 1.2 \( \mu \)m gold thickness, 60 nm outermost zone width, and 170 \( \mu \)m and 120 \( \mu \)m diameters for photon energies of 6.20 keV and 7.71 keV, respectively, giving similar focal distances that accommodate for the mechanical constraints of the setup.

Ptychography scans with a field of view of 10 \( \mu \)m \( \times \) 10 \( \mu \)m were performed on a circular grid with a spacing of 0.5 \( \mu \)m between the circular shells and 5 points in the center shell. A diffraction pattern was measured at each of 323 scanning points with a 0.2 second exposure time using a Pilatus detector [24,25] at a distance of 7.38 m from the sample. Including sample and detector positioning [20], each projection took approximately 3 min, with each tomogram composed of 160 projections equally distributed over 180°, administering an estimated total dose of 116 MGy and 19 MGy to the cobalt and resist, respectively. Ptychographic reconstructions were performed with the data from 400 \( \times \) 400 pixels of the detector, resulting in pixel sizes of 21.48 nm and 17.27 nm for the 6.20 keV and 7.71 keV reconstructions, respectively. For the reconstruction we applied 400 iterations of the difference map [15], followed by 200 iterations of a nonlinear optimization routine for maximum likelihood estimation [26].

The reconstructed amplitude and phase of one of the 2D projections taken at an energy of 6.20 keV can be seen in Figs. 2(a) and 2(b), respectively. The cobalt layer around the buckyball bars lying parallel to the x-ray beam has relatively high contrast in the amplitude projection as indicated by the arrows in Fig. 2(a). It is only possible, however, to see the full structure in the reconstruction of the phase, which has a much higher signal to noise ratio, as seen in Fig. 2(b). Here the bars perpendicular to the x-ray beam can now be seen clearly.

To quantify the atomic density of a specific element, we first need to consider the complex refractive index, \( n \), which, for the case of small-angle scattering resulting from the interaction of x rays with the electrons of the sample, can be expressed in terms of the atomic scattering factor \( f_0 = f_1 + jf_2 \) [27]:

\[
n = 1 - \delta - j\beta = 1 - \frac{\pi}{2\alpha} n^2 \sum_k \frac{n_k^2 f^2_k + f_k^2}{f_k^2}
\]

FIG. 1. Scanning electron micrographs of the Co-coated artificial buckyball mounted on the tomography pin.

FIG. 2 (color online). Reconstructed (a) amplitude and (b) phase of the 2D complex-valued transmission function at an x-ray photon energy of 6.20 keV. The high-contrast cobalt layers on the bars parallel to the x-ray beam in the amplitude projection are indicated with arrows. The integrated atomic density of Co, \( \int n_{Co} dz \), calculated from (c) the absorption and (d) the phase, respectively. (e) The real part of the Co scattering factor, \( f_1 \), encompassing the Co \( K \) edge, with the change in \( f_1 \) between the two energies, \( \Delta f_1 \), indicated.
The atomic density of a specific element can then be obtained from
\[
n_{at}^k = \frac{1}{\Delta f_1^k} \frac{2\pi}{r_e} \left( \frac{\delta_{off}^k}{\lambda_{off}^k} - \frac{\delta_{on}^k}{\lambda_{on}^k} \right) \tag{3}
\]
with \( off \) and \( on \) denoting off resonance and on resonance, respectively, and where \( \Delta f_1^k \) can be calculated from absorption data from bulk reference samples by making use of the Kramers-Kronig relation [27].

Using this method, we can determine the location of the cobalt in 2D by extracting its atomic density integrated along the x-ray direction \( J n_{Co}^k dz \). Thus far, element-specific imaging involving resonant energies has primarily employed the absorption information of a sample to characterize various material properties. Here we demonstrate the effectiveness of the phase in resonant experiments. A single projection provides the real or imaginary part of \( J [\sum_k n_{at}^k (f_1^k + jf_2^k)] dz \), calculated from the reconstructed phase or amplitude, respectively. By taking the difference between projections taken at two different energies, either for the phase or for the amplitude, with one energy tuned to the resonant element, Co, and dividing through by \( \Delta f_1^{Co} \) or \( \Delta f_2^{Co} \), we can obtain \( J n_{Co}^k dz \) calculated from the phase or amplitude, respectively. To obtain \( \Delta f_1^{Co} \), the real part of the atomic scattering factor \( f_1^{Co} \), shown in Fig. 2(e) with \( \Delta f_1^{Co} \) indicated, was calculated using Eq. (2).

In determining the spatial resolution, the Fourier shell correlation [31] gives a pessimistic estimate of 55 nm as the sample is mostly empty. Instead we obtain a more realistic value of 25 nm given by the full width at half maximum of the line profile taken across the thinnest cobalt layer in Fig 3(c), as shown in Fig. 3(d).

In addition to the Co distribution within the sample, knowledge of both the cobalt atomic density and electron density of the sample components gives added insight into the electronic state of the Co. Figure 4(a) shows a bivariate histogram of the electron density, \( \sum_k n_{at}^k f_1^k \) off resonance at 6.20 keV, and the cobalt atomic density, which reveals the relationship between the two densities for individual pixels.

\[ \text{FIG. 3 (color online). Tomographic axial slice of } \sum_k n_{at}^k f_1^k \text{ in } \AA^{-3} \text{ (a) off resonance at } 6.20 \text{ keV and (b) on resonance at } 7.71 \text{ keV. (c) Tomographic axial slice of the atomic density of Co, } n_{at}^{Co} \text{ within the sample. A line profile taken along the red line is shown in (d) with a FWHM of } 25 \text{ nm. Insets in (a)–(c) show a magnified portion of the slice. Scale bars represent } 1 \mu m. \]
cross-linked polymer. To reduce partial volume effects, we calculate the electron density of the Co from Co-containing voxels surrounded only by Co. The mean value of the electron density within these areas was found to be $(1.39 \pm 0.11)/\text{Å}^3$, indicated in Fig. 4(a), with a maximum of $(1.64 \pm 0.17)/\text{Å}^3$, much more similar to the electron density of $\text{Co}_3\text{O}_4$, $1.66/\text{Å}^3$, than that of metallic Co, $2.44/\text{Å}^3$, giving an indication of the sample being oxidized.

For the Co, a higher mean value than expected for the atomic density of $(0.119 \pm 0.020)/\text{Å}^3$ was measured. This systematic error in $n_{\text{at}}^\text{Co}$ could be due to radiation damage to the polymer scaffold introducing structural disorder as well as diluting or further oxidizing the Co over time. As the off-resonance measurements were performed after the on-resonance measurements, the lowering of the electron density with time would result in a higher calculated value of the atomic density, consistent with our experimental results. The presence of radiation damage is supported by measurements of the electron density of the polymer phase, $n_{\text{poly}}^e$, at the two energies, where a ratio of 0.92 of $n_{\text{poly}}^e(7.71 \text{ keV})/n_{\text{poly}}^e(6.20 \text{ keV})$ is found, indicating that there is indeed a modification of the polymer in the x-ray beam.

The oxidation state of the Co was confirmed with microfluorescence spectroscopy experiments performed at the PHOENIX beam line, Swiss Light Source, Paul Scherrer Institute, Switzerland. A focused beam of 4–5 μm in size was used to measure the fluorescence spectrum across the K edge of Co at several points across the sample, both on the buckyball and, as a reference, on the Co-coated Si pillar. Comparing spectra taken for Co on the buckyball and on the Si pillar, shown in Fig. 4(c), a blue shift of the edge and a broadening of the white line are observed, indicating the presence of oxidation and disorder in the Co film on the buckyball, respectively, in agreement with our resonant ptychographic tomography results.

To conclude, in this Letter we have presented full structural and elemental 3D characterization at the nanoscale, achieved by performing resonant ptychographic tomography and exploiting resonant anomalous elastic scattering. We determined the location of Co atoms in a 6 μm artificial buckyball to within a spatial resolution of 25 nm, and quantitative data revealed that the Co layer on our test sample was predominantly oxidized. Resonant ptychographic tomography enables element-specific characterization, which can be extended to many elements within a sample by taking additional measurements at their corresponding absorption edges. This combination of tomography with resonant scattering opens the door to the full determination of 3D electronic and magnetic functionality of materials, spatially resolved at the nanoscale.

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†manuel.guizar-sicairos@psi.ch

1laura.heyderman@psi.ch


