A Vision on Functional Polymer Systems

3D Visualization of Nanostructures by STEM Tomography

Advances in detector sensitivity and electron illumination flexibility allow for application of Scanning Transmission Electron Microscopy (STEM) in atypical conditions. Recently we have demonstrated that in optimized imaging conditions modern STEM detectors are able to provide contrast between purely carbon-based organic materials without the need of additional heavy element staining, and we have introduced virtually parallel illumination STEM imaging of micrometer thick carbon-based specimens with nanometer resolution.

Applying High Sensitive ADF Detectors
Scanning Transmission Electron Microscopy (STEM) is a powerful technique to investigate the organization of materials down to the atomic scale. In general, STEM can be used in incoherent imaging condition to provide images that are easy to interpret due to the lack of phase contrast, the high signal-to-noise ratio, and the linearity of the signal intensity [1]. STEM accounts for mainly elastic scattering events consecutive to the interaction of the primary beam with the target material. The total scattering elastic cross section varies roughly as $Z^{3/2}$, therefore local variation of elemental composition will generate relatively strong contrast in the STEM image, so-called Z-contrast [2]. As a consequence, STEM is rarely applied for the investigation of complex organic materials like polymers, their blends or composites with carbon allotropic nanofillers (carbon black, graphene, nanotubes), or the vital class of biomaterials.

Some time ago, we have demonstrate that STEM imaging of various polymer systems - all purely carbon-based and unstained - by applying high sensitive annular dark field (ADF) detectors capable of single-electron counting may result in excellent contrast and allows for detailed morphology analysis with nanometer resolution [3, 4]. The detector collects with high efficiency elastically scattered electrons at large angle which results in a dark-field image where bright contrast corresponds to the presence of scattering centers. With the average $Z$ nearly constant for these systems, the signal intensity will vary linearly with the mass-thickness - typically up to $pt \sim 10^{-5}$ g/cm$^2$ [5] - and contrast can be optimized by accurate tuning of convergence angle, camera length and detector parameters.

**ADF-STEM Imaging of Polymer Systems**

Figure 1 presents two examples of ADF-STEM imaging of polymer systems.
The left image shows details of the composition of a rubber blend filled with nanosized carbon black (CB) particles as it is utilized for car tires [6]. The imaging conditions were adjusted such to create optimum contrast between the three components. For this system the CB has the highest density which results in strongest scattering and high signal collection by the detector at the location of CB (bright particles). At the same time both rubber phases can be identified as dark island-like areas surrounded by a grayish continuous matrix. Creating similar contrast between the rubber components for conventional TEM (CTEM) investigation the specimen needs to be stained; however, the interaction of the staining agent with the CB results in uncontrolled staining and a more or less homogeneous blackish appearance of the whole specimen.

Comparing with CTEM

The right ADF-STEM image shows the organization of a so-called bulk heterojunction blend as it is used as photoactive layer in polymer solar cells [7]. In such functional system PCBM, a modified C60 molecule, acts as electron acceptor and needs to be dispersed in the electron donor polymer matrix to create maximum interface for exciton dissociation but at the same time constitutes a path to the electrode collecting the electrons; therefore morphology control is of outmost importance for high performance devices. Because of its higher density PCBM is the stronger scatterer and appears bright in the dark field image surrounded by the dark polymer. Applying ADF-STEM allows for artefact less imaging at higher resolution when comparing with CTEM, where defocus is required to create contrast but at the same time limits the achievable reliable resolution. For the present system high resolution ADF-STEM imaging has made visible for the first time additional interconnections between the PCBM domains. Such morphology information has helped better understanding functional properties of the system [4].

Applying CTEM and ADF-STEM Tomography

In another comprehensive study we have compared the volume morphology of a well-defined CB/polymer system by applying CTEM and ADF-STEM tomography [8]. In both cases we have obtained good contrast between the CB particles and the polymer matrix. Figure 2 demonstrates the influence of the imaging conditions on CB contrast and on the diameter of a gold bead. For CTEM imaging, contrast between CB and the polymer matrix is increased by slight defocus; however, such imaging conditions result in increasing the apparent diameter of the gold bead and
other features, too. On the other hand, for incoherent ADF-STEM imaging good contrast is achieved between CB and the polymer matrix and the original sizes of features are maintained. Reconstruction of the volume morphology after tilt series acquisition and alignment, and subsequent careful quantification of the CB phase volume in the polymer matrix has resulted in significant different CB volume percentage for the two acquisition modes. In case of CTEM tomography the average measured CB volume concentration is much larger than the known concentration of the sample, which is caused by the distortion of particle sizes and makes the obtained data set unreliable. On the other hand, volume concentration data obtained by ADF-STEM tomography are close to the known CB loading, which in conclusion makes data set acquired by ADF-STEM imaging very suitable for further quantification.

However, the investigated volume still is very small and compared with e.g. x-ray scattering experiments of cubic millimeter volumes, the statistical relevance of the probed volume might be questionable. To overcome this limitation of conventional (S)TEM tomography we have developed the imaging methodology of low-convergence angle STEM tomography [9, 10]. Standard STEM imaging is performed with relative large convergence angle to provide smallest probe size for highest resolution. On the other hand, modern electron optics allow flexibility of the convergence angles easily tuned below 1 mrad down to an almost parallel electron beam. As a consequence, the probe size is relatively large and not suitable for atomic resolution imaging but a large depth of field can be achieved which allows for nanometer scale resolution throughout micrometer thick specimens.

The inset of Figure 3 illustrates the geometrical differences of the probe geometries for nano- (conventional convergence angle, light green) and microprobe setup (low-convergence angle, dark green). The two STEM images show the same specimen area of an about 1 micrometer thick polymer sample coated on top and bottom surface with 5 nm gold beads. For both cases the electron beam converges in the middle of the specimen. However, only for the low-convergence angle (right) the gold beads appear sharp on both surfaces, which proves a resolution throughout the whole thickness of the specimen better than 5 nm.

Figure 4 shows two examples of specimens investigated with low-convergence angle ADF-STEM tomography. For the rubber blend (left) connectivity of domains on the micrometer scale is important information that cannot be obtained by conventional methods. Also percolation of nanoparticles in the bulk case, as shown for CB forming macroscopic conductive networks in the polymer matrix (right), can be analyzed in a quantitative and reliable way.
Conclusions

In summary, potential applications for ADF-STEM are investigations for various polymer systems such as block copolymers, polymer blends or polymers composites filled with low electron scattering nanoparticles (e.g. CB as discussed in this article), or biomaterials. Moreover, low convergence angle ADF-STEM allows for volume analysis and imaging of specimens several micrometers thick with local resolution in all three dimensions potentially down to a few nanometers, which provides statistically relevant datasets of the practically bulk specimens and likely allows for imaging of whole cells.

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References

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