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Using secondary electron electron beam induced current for characterization of nanoparticle morphologies

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Background incl. aims

Electron tomography (ET) is an indispensable tool for determining the three-dimensional (3D) structure of nanomaterials in (scanning) transmission electron microscopy ((S)TEM). ET enables 3D characterization of a variety of nanomaterials across different fields, including life sciences, chemistry, solid-state physics, and materials science down to atomic resolution. However, the acquisition of a conventional tilt series for ET is a time-consuming process and thus cannot capture fast transformations of materials in realistic conditions. Moreover, only a limited number of nanoparticles (NPs) can be investigated, hampering a general understanding of the average properties of the ensemble. Therefore, alternative characterization techniques that allow for high-resolution characterization of the surface structure without the need to acquire a full tilt series in ET are required which would enable a more time-efficient investigation with better statistical value. Here we propose surface-sensitive secondary electron (SE) imaging in STEM employed using a modification of electron beam-induced current (EBIC) setup as an alternative surpassing electron tomography.

Methods

SEEBIC and ET experiments were performed using an aberration-corrected Thermo Fisher Themis Z TEM operated at an acceleration voltage in a range of 60-200 kV. A custom-made transimpedance amplifier with a total gain of 2 GV/A and bandwidth of 8 kHz, electrically connected to the sample via a DENSsolutions Wildfire holder, was used to convert the SEEBIC signal into a voltage signal digitized by the Attollight OUDS II scan engine. No image filtering was applied during post-processing. ET data were acquired over a tilt range of ±72° with tilt increments of 3°. Reconstructions of the tilt series were performed using the SIRT algorithm implemented in ASTRA Toolbox 1.90 for MATLAB 2022b. Scanning electron microscopy (SEM) images were obtained using Thermo Fisher Helios Nanolab 650 with nominal spatial resolution down to 0.8 nm operated at an acceleration voltage of 5 kV.

Results

We have shown that both general morphology and side faceting of the NPs can be directly observed from SEEBIC images which is less obvious from conventional STEM micrographs. SEEBIC imaging enables a gain of up to 2 orders of magnitude in data collection efficiency in comparison to conventional ET while providing necessary topographical information. The superior spatial resolution compared to SEM was demonstrated. It was shown that even though SEEBIC requires to use of high primary electron beam currents, the optimization of experimental parameters allows for the reduction of the accumulated electron dose rendering SEEBIC equally or even more dose-efficient than ET. Finally, we describe the contrast artefacts arising in SEEBIC images and discuss their origin.

Next, it was shown that direct access to surface morphology obtainable on the order of minutes opens up the possibility of using SEEBIC for high-throughput analysis of the helical morphology of chiral Au nanorods (NRs). The workflow to automatically quantify the helical morphology based on SEEBIC images and a dedicated image quantification procedure was developed and used to calculate the helicity function of the NP ensembles. We have shown that this approach overcomes the limitation of poor statistics obtained by ET, which is limited to analyzing only a few particles per sample batch. Helicity function analysis revealed a significant polydispersity at the level of surface features. We found that the average helicity values, calculated for hundreds of NRs per sample batch were in good agreement with the optical properties of the sample, confirming that helicity measurements enable linking the nanoscale morphology with the chiroptical handedness.

Conclusion

We have demonstrated that SEEBIC can be considered an attractive approach for the characterization of NP morphologies with shorter acquisition and processing times in comparison to ET and superior resolution in comparison to SEM. It was shown that the helical morphology of chiral Au NRs, with significant polydispersity at the level of surface features can be efficiently quantified using high-throughput SEEBIC measurements.

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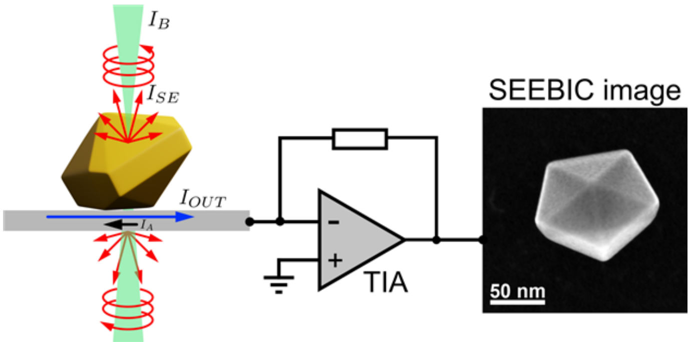
Graphic:



Keywords:

STEM, electron tomography, SE imaging

Reference:

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