PA12

SPECTRAL UNMIXING OF LOCALIZED SURFACE PLASMON RESONANCES FROM AN ELECTRON ENERGY-LOSS SPECTROSCOPY DATASET

Martial Duchamp[§], Aziz Genç[†], Jordi Arbiol[†,‡], and Rafal E Dunin-Borkowski[§]

[§]Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, 52425 Jülich, Germany
[†]Institut de Ciència de Materials de Barcelona, CSIC, Campus de la UAB, 08193 Bellaterra, Catalonia, Spain
[‡]Institucio Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona, Catalonia, Spain

Abstract

Monochromated electron energy-loss spectroscopy (EELS) imaging combined with scanning transmission electron microscopy (STEM) has been used to map localized surface plasmon resonances (LSPRs) in supported Au and Ag particles. Recently, 3D imaging of LSPRs has been demonstrated by combining non-negative matrix factorization (NMF), compressed sensing and electron tomography. Such statistical analysis methods, based on decomposition of a dataset into a product of two matrices (factors and loading matrices that contain the spectral signature and the weighting of the factor components, respectively), are closely related to principal component analysis (PCA) and blind source separation (BSS). NMF-based algorithms introduce constraints on the resulting matrices to be positive. Spectral unmixing (SU) decomposition apply both positive and sum-to-one constraints. Vertex component analysis (VCA), a geometric algorithm used to perform SU, relies on the "pure pixel" hypothesis, often not satisfied for EELS datasets. A more complicated SU-based algorithm, bayesian linear unmixing (BLU) does not need this pure pixel requirement.

Here, we apply the following decomposition techniques: BSS, NMF using independent component analysis and SU using VCA and BLU, to a low-loss EELS dataset acquired from AuAg nanoboxes. We demonstrate the superiority of SU-based decomposition in terms of its ability to recover a loading matrix. The application of SU-based algorithms to low-loss EEL spectra opens the way to the decomposition of more complex structures, for which the direct calculation of LSPRs cannot be achieved. Moreover, the robustness of SU-based algorithms for extracting spectral components from large datasets without introducing prior knowledge opens the way to the direct reconstruction of 3D information about the LSPRs of complex structures.

The authors acknowledge Javier Patarroyo and Victor Puntes for providing the samples and financial support from the European Union under the Seventh Framework Programme under a contract for an Integrated Infrastructure Initiative, reference 312483 – ESTEEM2.