SPECTRAL MIXTURE ANALYSIS OF LOCALIZED SURFACE PLASMON RESONANCES FROM ELECTRON ENERGY-LOSS SPECTROSCOPY SPECTRUM IMAGES

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Monochromated electron energy-loss spectroscopy (EELS) imaging has recently been used to map localized surface plasmon resonances (LSPRs) in supported Au and Ag particles and three-dimensional imaging of LSPRs has been demonstrated by combining multivariate analysis, compressed sensing and electron tomography [1]. The application of algorithms based on spectral unmixing (SU) to low-loss EELs is promising for surface plasmon resonance mapping of complex structures, for which the direct calculation of LSPRs cannot be achieved. The robustness of SU-based algorithms for extracting spectral components from large datasets without introducing prior knowledge also opens the way to direct reconstruction of three-dimensional information about the LSPRs of complex structures.

Figure 1a shows EEL spectra recorded from a AuAg nanobox at the positions indicated in Fig. 1b. The spectra show a variation in plasmon resonance energy at ~2.3 eV and a broader peak at ~3.5eV. Here, we aim to separate different plasmon resonances that have complex spectral signatures, i.e., to obtain more information than simply the shift in maximum peak position that is typically extracted using standard fitting routines. We apply the following decomposition techniques: independent component analysis (ICA) [2] (Figs. 2 c, d), vertex component analysis [3-4] (VCA) (Figs. 2 a, b) and Bayesian linear unmixing (BLU) [5] (Fig. 3) to a low-loss EELS dataset acquired from a AuAg nanobox. The spectral signatures obtained from VCA decomposition (Fig. 2 a) are in better agreement with the spectra extracted from the raw dataset (Fig. 1 a) than are the spectral signatures obtained from ICA. However, VCA requires the assumption of the presence of pure pixels in the analyzed image, which limits its ability to recover spectral plasmonic signature from EELS datasets (as a pixel is unlikely to contain the spectral signature of a *single* plasmonic mode). Therefore, a more complicated SU-based algorithm, BLU, was used. Figure 3 shows the initial decomposition and the result after 5 iterations, obtained using the implementation proposed by Dobigeon *et al*. [5]. An improvement in the spectral signatures and the associated maps is visible (see, for example, background component 1). By combining improved VCA decomposition with the BLU algorithm, we expect to recover truly unmixed spectral signatures of plasmon modes in such nanoparticles from low-loss EELS data.

[1] Nicoletti, O. *et al.* Nature **502,** 80 (2013). [2] De la Peña, F. *et al.* Ultramicroscopy **111,** 169 (2011). [3] Duchamp, M. *et al. Appl. Phys. Lett.* **102,** 133902 (2013). [4] Nascimento, J. M. P. & Bioucas Dias, J. M. IEEE Trans. Geosci. Remote Sens. **43,** 898 (2005). [5] Dobigeon, N *et al.* IEEE Trans. Signal Processing 57, 4355 (2009).

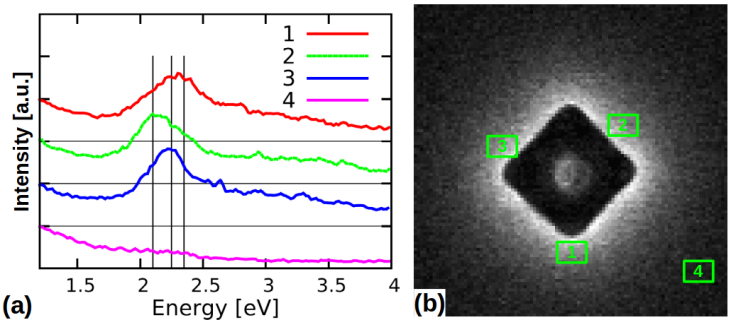

Figure 1: (a) Averaged EELS spectra extracted from the positions indicated (b). (b) Energy loss of image of a AuAg nanoboxe integrated over the 2.0-2.5eV range..

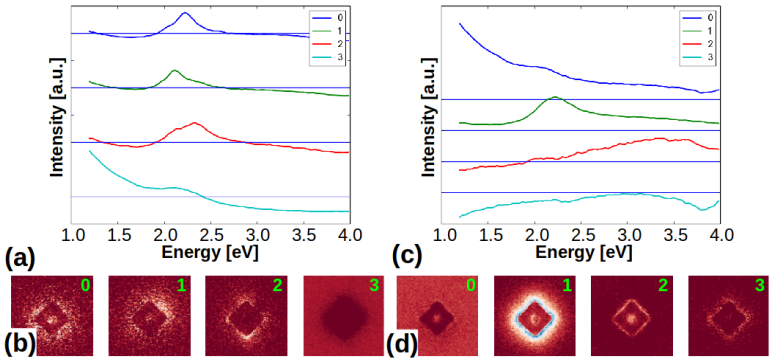

Figure 2: Spectral components extracted by (a) VCA and (c) ICA from the AuAg nanoboxe shown in fig. 1. The corresponding maps are depicted in (b, d).

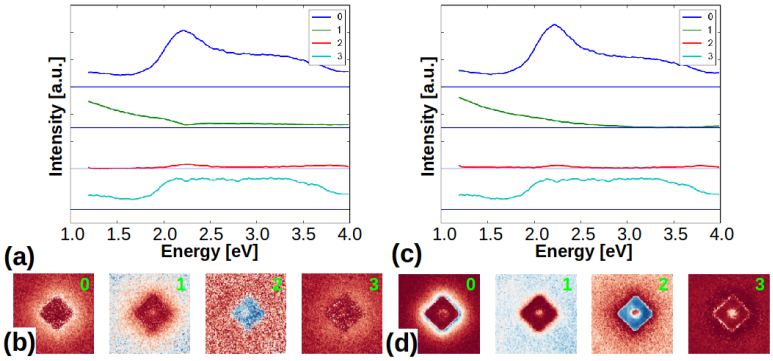

Figure 3: (a, c) Spectral components extracted by BLU after 0 and 5 iterations of the BLU decomposition from the AuAg nanoboxe shown in fig. 1. The corresponding maps are depicted in (b, d).

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