Secondary Electron Spectroscopy for Beam-Sensitive Materials - Examples, Challenges and Outlook

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What may we gain from the energy dimension of the secondary electron signal? Despite the prevalence of secondary electron (SE) imaging as a basis to microanalysis and many other materials characterisation approaches, the SE signal is rarely analysed for its information content beyond topography. Specifically, SE energies are often overlooked. In the light of new results, we seek to answer the following questions: Where lies the potential of performing SE spectroscopy in scanning electron microscopes (SEMs)? And what are the current limitations of spatially resolved SE spectroscopy?

SE energy distributions were studied very early in the development of SEMs, but the methods were slow to develop due to concerns about the influence of contamination on the spectra and any resulting analysis [1]. Nonetheless investigations showed that SE spectra can be characteristic of metals [2] and even responsive to structural order in carbon materials [3,4] and can be exploited to increase SE image resolution [5]. The use of highly stable low energy primary beams (typically 1keV) allows the investigation of insulating and beam-sensitive materials, which cannot tolerate commonplace microanalysis techniques requiring high electron beam energies and doses. We will be presenting a range of applications of secondary electron spectroscopy and secondary hyperspectral imaging (SEHI), an example of which is shown in **Fig. 1.** It is known that the mechanical properties of spider silk fibres change with the speed they were force-reeled, and we have observed an associated change in the surface structure with regular SE images (**Fig. 1 a-c**). It is clear that this change in surface properties with reeling speed is also reflected in the SE spectra (**Fig. 1 d**), as the dominant peaks move to higher energy with higher reeling speed. Spider silk is a structurally complex biopolymer, so future work will lie in determining which fibre surface properties the SE spectra respond to.

The response of the SE spectrum to material properties such as order and crystallinity is not accommodated in classical models of SE emission and has only very recently begun to be explored by modelling [6]. Hence, there is further room for improvement in modelling to enable a fundamental understanding of links between SE spectral features and materials properties. Likewise, instrumentation used in this work has potential for improvement: The use of parallel analysers rather than energy-scanning analysers would drastically increase the acquisition efficiency and minimise the beam exposure required to obtain a full spectral dataset. To date, the unavailability of reference detection efficiencies and acceptance diagrams for many SE detection systems hampers widespread uptake of SE spectroscopy, and the comparison of theoretical and experimental literature data.

Nevertheless, the results obtained so far showcase the immense potential of spatially resolved SE spectroscopy and SEHI in the analysis of beam-sensitive materials and provide the impetus to overcome the remaining challenges.

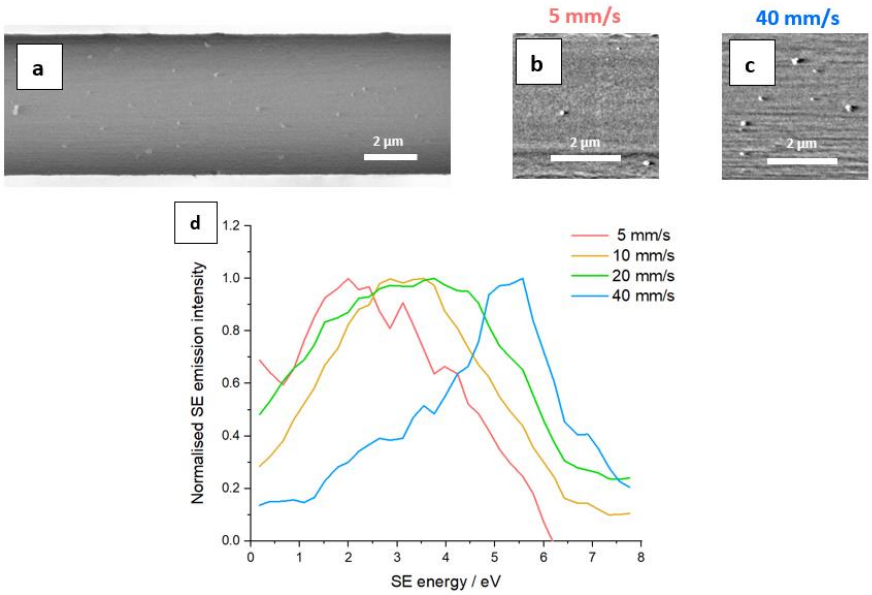

Fig. 1: a) Regular SE overview of a *Nephila edulis* spider silk dragline fibre with a primary beam energy (E_0) of 700 V **b)** Bandpass filtered (3 to 40 px or 32 to 432 nm) SE image detail of fibre at E_0 = 700 V reeled at 5 mm/s and **c)** 40 mm/s **d)** SE spectra with reeling speed at a E_0 = 500 V, averages of 3 acquisitions.

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References:

1. D.H. Bruining: *5 - Variation of Secondary Emission Yield Caused by The External Adsorption of Ions and Atoms*, in: *Physics and Applications of Secondary Electron Emission*, 2nd ed. (Pergamon Press, London, England, 1962), pp. 69 - 77, doi:10.1016/B978-0-08-009014-6.50008-9.
2. D.C. Joy, M.S. Prasad and H.M. Meyer: *Experimental secondary electron spectra under SEM conditions*. J. Microsc. **215**, 77 - 85 (2004).
3. R.F. Willis, B. Fitton and D.K. Skinner: *Study of carbon"fiber surfaces using Auger and secondary electron emission spectroscopy*. J. Appl. Phys. **43**, 4412 - 4419 (1972).
4. Q. Wan, K.J. Abrams, R.C. Masters, A. Talari, I.U. Rehman, F. Claeyssens, C. Holland and C. Rodenburg: *Mapping Nanostructural Variations in Silk by Secondary Electron Hyperspectral Imaging*. Adv. Mater. **29**, 1703510 (2017), doi:10.1002/adma.201703510.
5. R.C. Masters, A.J. Pearson, T.S. Glen, F.-C. Sasam, L. Li, M. Dapor, A.M. Donald, D.G. Lidzey and C. Rodenburg: *Sub-nanometre resolution imaging of polymer-fullerene photovoltaic blends using energy-filtered scanning electron microscopy*. Nat. Commun. **6**, (2015).
6. M. Dapor, R.C. Masters, I. Ross, D.G. Lidzey, A. Pearson, I. Abril, R. Garcia-Molina, J. Sharp, M. UnÄovský, T. Vystavel, F. Mika and C. Rodenburg: *"Secondary electron spectra of semi-crystalline polymers - A novel polymer characterisation tool?"* J. Electron Spectros. Relat. Phenomena **222**, 95 - 105 (2018), doi:10.1016/j.elspec.2017.08.001.