G Model
ELSPEC-46449; No. of Pages 15
ARTICLE IN PRESS
Journal of Electron Spectroscopy and Related Phenomena xxx (2015) xxx–xxx
Contents lists available at ScienceDirect
Journal of Electron Spectroscopy and Related Phenomena
journal homepage: www.elsevier.com/locate/elspec

# Soft X-ray spectromicroscopy and ptychography

Adam P. Hitchcock*
*Dept of Chemistry and Chemical Biology, McMaster University, Hamilton, ON, L8S 4M1, Canada*

ARTICLE INFO

*Article history:*
Received 12 February 2015
Received in revised form 13 May 2015
Accepted 18 May 2015
Available online xxx

*Keywords:*
Soft X-ray absorption
STXM
SPEM
XPEEM
TXM
Ptychography

ABSTRACT

Instrumentation and current capabilities of soft X-ray (50–2000 eV) spectromicroscopy are outlined with examples from recently published and some new work. Four common techniques are treated—transmission X-ray microscopy (TXM), scanning transmission X-ray microscopy (STXM), X-ray photoemission electron microscopy (XPEEM) and scanning photoemission microscopy (SPEM). I also present a fifth, emerging technique, that of soft X-ray spectro-ptychography which has significantly improved spatial resolution and provides new contrast mechanisms. Perspectives for near future (5–10 years) evolution of soft X-ray spectromicroscopy are outlined based on current trends and instrumentation under development.



## 1. Introduction

Spectromicroscopy refers to methods in which imaging and spectroscopic analysis are used in a balanced way. There are many types of spectromicroscopy since almost all possible forms of imaging and spectroscopy can be combined with sufficient ingenuity. This article restricts its scope to those methods in which tunable energy soft X-rays ($50 < h\nu < 3000$ eV, typically from a synchrotron light source) are used for spectrally sensitive imaging, based on systematic changes of the incident photon energy and/or polarization properties of the soft X-rays, and/or the properties of primary or secondary particles (X-rays, electrons, visible photons, ions, etc) produced by photoionization. There are four common types of soft X-ray spectromicroscopy: scanning transmission X-ray microscopy (STXM), scanning photoelectron microscopy (SPEM), full field transmission X-ray microscopy (TXM) and X-ray photoemission electron microscopy (XPEEM). Fig. 1 presents schematics of these techniques. In addition, this article describes recently developed soft X-ray ptychography, a STXM-based form of coherent diffraction imaging (CDI) which is making dramatic improvements in spatial resolution and spectral sensitivity. All five methods have the potential to perform spectromicroscopy based on near edge X-ray absorption fine structure (NEXAFS) contrast. SPEM, and XPEEM, with addition of an electron dispersive analyzer, can also perform spectromicroscopy based on photoelectron spectroscopy contrast. SPEM and STXM systems can and have been equipped with silicon drift detectors to allow X-ray fluorescence spectroscopy and XRF-yield NEXAFS detection.

There are closely related spectromicroscopy techniques using tunable hard X-rays but the spectral sensitivity typically is restricted to elemental characterization. NEXAFS in the soft X-ray spectral region has incredible sensitivity to the detailed electronic structure needed to do full speciation – identification of individual chemical species – which is central to the interests of the readers of the Journal of Electron Spectroscopy and Related Phenomena. The soft X-ray region also includes the water window (200–520 eV) which facilitates studies of samples in aqueous environments. Furthermore the spectral resolution and the routinely available spatial resolution (as well as the record spatial resolution) is better in the soft X-ray than in the hard X-ray region.

This article is not intended to cover all of this large and rapidly expanding field, but rather to outline the four main types of instrumentation, illustrate their performance with state-of-the-art instruments, and provide a perspective on expected near future developments. Reviews covering all four types of soft X-ray spectromicroscopy include those by Hitchcock in 2012 [1], Ade and Hitchcock in 2008 [2]. Bauer [3] recently authored a book on low energy surface microscopy which gives comprehensive coverage of XPEEM and some treatment of SPEM. Günther et al. [4] published a comprehensive review of photoelectron microscopy (SPEM, XPEEM) applied to surface and materials science. Howells et al. [5] reviewed all types of zone plate based microscopy (STXM, TXM, SPEM) with emphasis on the fundamental physics and X-ray optics. Kaulich et al. [6] recently gave an overview of

* Tel.: +1 905 525 9140 24749; fax: +1 905 521 2773.
*E-mail address:* aph@mcmaster.ca

http://dx.doi.org/10.1016/j.elspec.2015.05.013
0368-2048/

Please cite this article in press as: A.P. Hitchcock, Soft X-ray spectromicroscopy and ptychography, J. Electron Spectrosc. Relat. Phenom. (2015), http://dx.doi.org/10.1016/j.elspec.2015.05.013

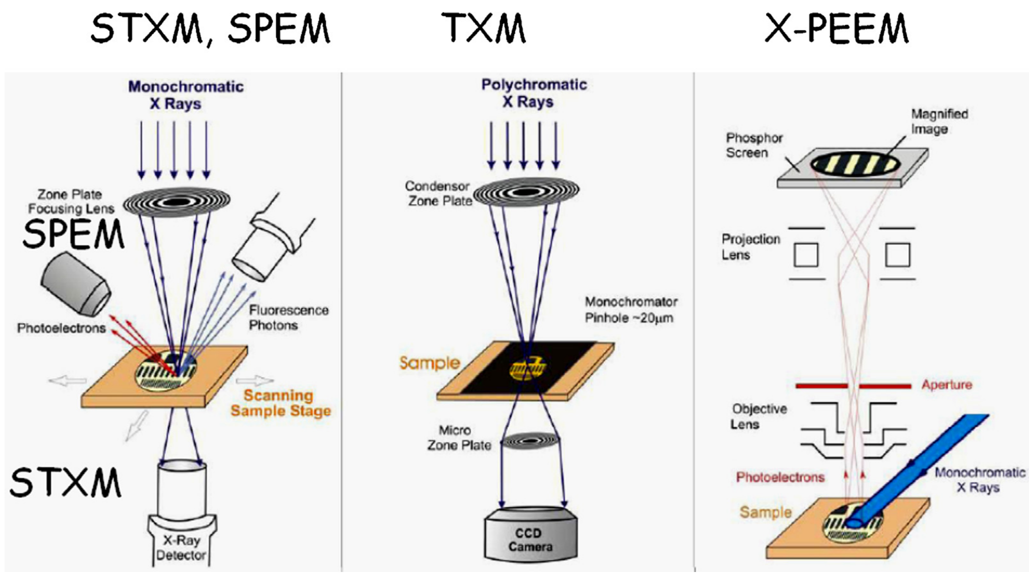


**Fig. 1.** Overview of the four common types of soft X-ray spectromicroscopy: scanning transmission X-ray microscopy (STXM), scanning transmission X-ray microscopy (SPEM), full field transmission (TXM) and full field X-ray photoemission electron microscopy (X-PEEM).

instrumentation and applications for X-ray-in/X-ray-out microscopies (STXM with both transmission and fluorescence detection, as well as ptychography). Falcone et al. [7] presented a review intended for non-experts that surveys the whole field of X-ray microscopy, including laboratory and free-electron-laser methods. Older but still authoritative reviews of the field include the book by David Attwood [8] and the review of biological applications by Kirz et al. [9]. A colorful and informative review of the history of the development of soft X-ray microscopy was recently published by Kirz and Jacobsen [10]. The last time a comprehensive treatment of soft X-ray microscopy was presented in this journal was the Special Issue on Soft X-ray Microscopy, Volume 84 (1997). There is an article in this volume by Carpenter et al. [11] which provides a review and perspective on the complementary methods of soft X-ray resonant and non-resonant scattering. A review article focusing on 3D chemical imaging by soft X-ray spectro-tomography has recently been published by Schmid et al. [12]. I also note recent reviews of hard X-ray spectromicroscopy [13] and tomography [14].

This article is organized as follows. Section 2 gives an overview of soft X-ray spectromicroscopy instrumentation using the highest performing instruments of each of the four classes as examples. This is followed by a set of recent scientific examples using each of the 4 types, chosen to illustrate state-of-the-art capabilities. Section 4 focuses on the emerging technique of soft X-ray ptychography (note hard X-ray ptychography is relatively well developed and is extensively covered in a recent review [13]). Section 4 describes the ptychography method and presents some recently published results on lithium battery materials and new results on biological magnetism. The final section provides my perspective on near future directions, focusing on new capabilities that are now, or will soon be, possible due to improvements to instrumentation. Emerging applications of soft X-ray spectromicroscopy are also noted.

## 2. Current instrumentation and facilities

Table 1 is a list of the soft X-ray spectromicroscopy facilities around the world. It lists both existing operational systems and also those under construction or commissioning. Fig. 2a is a temporal display of the evolution of the numbers of each of the 4 types of instruments at synchrotron facilities, as well as their productivity (Fig. 2b). The annual numbers of publications from each type of microscopy is derived from a bibliography of soft X-ray spectromicroscopy that I maintain, which is available as a supplemental material to this article. Periodic updates are available at http://unicorn.chemistry.mcmaster.ca/xrm-biblio/xrm_bib.html. While I have done the best I could to bring this document up to date with

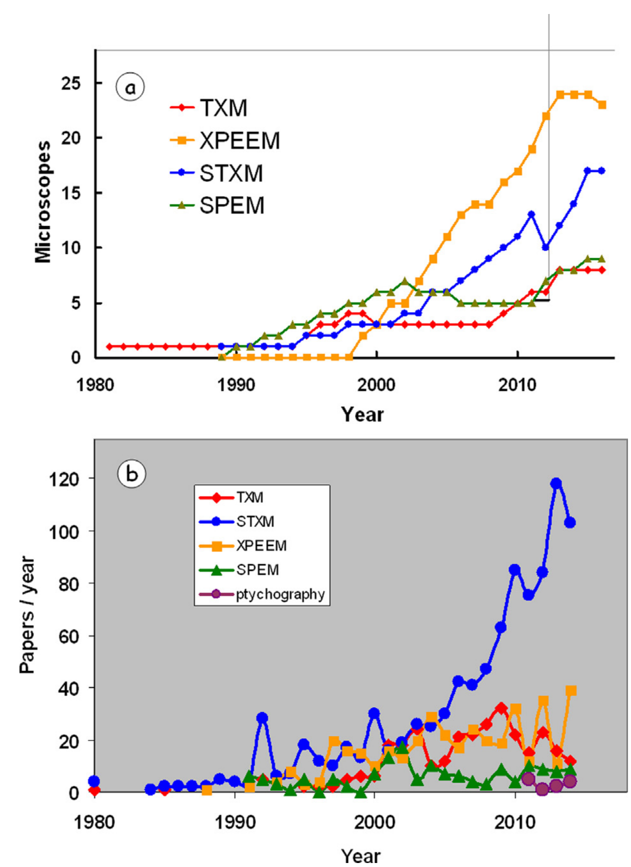


**Fig. 2.** Overview of (a) the growth internationally in numbers of soft X-ray microscopes, and (b) scientific output of the 4 types of soft X-ray microscopes. Publications based on soft X-ray ptychography are just starting to appear but this technique is expected to develop rapidly.

Please cite this article in press as: A.P. Hitchcock, Soft X-ray spectromicroscopy and ptychography, J. Electron Spectrosc. Relat. Phenom. (2015), http://dx.doi.org/10.1016/j.elspec.2015.05.013