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Analytical transmission electron microscopy at organic interfaces

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ABSTRACT

Organic materials are ubiquitous in all aspects of our daily lives. Increasingly there is a need to understand interactions between different organic phases, or between organic and inorganic materials (hybrid interfaces), in order to gain fundamental knowledge about the origin of their structural and functional properties. In order to understand the complex structure–property–processing relationships in (and between) these materials, we need tools that combine high chemical sensitivity with high spatial resolution to allow detailed interfacial characterisation. Analytical transmission electron microscopy (TEM) is a powerful and versatile technique that can fulfil both criteria. However, the application of analytical TEM to organic systems presents some unique challenges, such as low contrast between phases, and electron beam sensitivity. In this review recent analytical TEM approaches to the nanoscale characterisation of two systems will be discussed: the hybrid collagen/mineral interface in bone, and the all-organic donor/acceptor interface in OPV devices.

1. Introduction

Recent instrumental advances in the transmission electron microscope (TEM) include aberration correctors for improved electron optics, as well as monochromators [1] which reduce the energy spread of the electron beam. These allow the formation of smaller (sub-angstrom) electron probes, and the resolution of finer (>100 meV) energy features in electron energy-loss spectra (EELS), respectively. It is now possible to acquire chemical signals from atomic columns [2,3] or even single atoms [4,5] in certain favourable, mainly *inorganic*, samples. These recent analytical benefits have been slow to translate to organic systems. In fact, it could be argued that the use of brighter, smaller electron probes actually makes electron-beam induced damage more common in sensitive materials and therefore makes the analysis of organic materials even more challenging!

The aim of this review is to explore the possibilities and limitations of current analytical electron microscopy in the characterisation of organic interfaces, and to discuss the different methodological approaches that are necessary to overcome challenges such as poor materials contrast, or the significant damage to organic samples, which has to date severely limited the chemical information obtained. We consider two examples taken from the fields of biology and physics; the organic–mineral interface in bone, and the interface between organic donor and acceptor molecules in OPV devices. Both systems consist of domains with hierarchical structures, which require structural and chemical characterisation on a range of length-scales in order to gain an understanding of the material architecture, function and properties. We begin by providing an overview of the variety of analytical techniques available in the TEM. The following two sections deal with each system separately, and consist of a brief background to the characterisation question and a discussion of recent analytical TEM studies. For more comprehensive material-oriented reviews, the reader is referred elsewhere [6,7]. Finally, we summarise the commonalities and differences between characterisation approaches in these two systems, and discuss the challenges and directions for future organic interface studies.

2. Analytical TEM

Inelastic scattering of incident fast electrons occurs as a result of interactions with atomic electrons in the sample. These interactions include the excitation of collective oscillations such as plasmons or phonons, as well as the promotion of an atomic electron from an occupied to an unoccupied electronic state. The energy lost by the fast electron (corresponding to the energy gained by the sample) can be measured directly using a post-specimen

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spectrometer in a process known as electron energy-loss spectroscopy (EELS). Energy-losses up to ~50 eV correspond to collective excitations and transitions from valence or semi-core levels, while higher energy-loss events arise from transitions from core electronic levels. The information available in these regions is detailed in Table 1. Meanwhile, secondary processes may also occur in which the excited state relaxes by emission of an X-ray photon. The photon energy, which is characteristic of the element probed, is measured using energy-dispersive X-ray (EDX) analysis. The intensity of both EELS and EDX signals are proportional to the number of atoms of a particular element that is present in the sample, and therefore both can provide *quantitative* elemental information. Additionally, the fine structure present in EEL edges can be used to identify different local bonding environments and chemical states of the atom. Structure within the first ~50 eV of the edge onset is known as energy-loss near-edge structure (ELNES). ELNES is analogous to X-ray absorption near-edge structure (XANES), also known as near-edge X-ray absorption fine structure (NEXAFS), which is measured using X-ray absorption rather than fast electron scattering [8]. Currently the highest spatial resolution offered by soft X-ray microscopy is 10 nm [9], limited by the ability to fabricate the zone plates which focus the probe. While electron microscopes are capable of forming sub-angstrom probes, the spatial resolution of EELS measurements in organic samples is reduced by (a) the delocalisation of inelastic scattering (which can be ~5 nm for low energy-loss transitions [10]) and (b) electron-beam damage which varies with parameters such as beam current, accelerating voltage, specimen temperature and the ratio of the collected signal versus the number of electrons incident on the sample [11]. Compared to the electron microscope, XANES provides a combination of high energy resolution and low sample damage which has been shown to be extremely powerful for the study of functional groups in organic systems e.g. proteins and polymers [12,13].

An electron energy-loss spectrum (EELS) displays the intensity of scattered electrons as a function of energy-loss (Fig. 1a). EEL spectra can be acquired at each position as a scanning transmission electron microscopy (STEM) probe is rastered over the specimen. In this way a three-dimensional data-cube (two spatial dimensions and one spectral dimension) is built up, which is known as an EELS spectrum image (EELS SI, Fig. 1b). Alternatively, energy-filtered TEM images can be formed using only electrons which have lost certain energies. These electrons are selected using an energy slit, often between 1 and 10 eV in width. For quantitative analysis at core-loss edges, a "three-window method" is used. Two "pre-edge" images are collected in order to fit the background signal, and one "post-edge" image measures the intensity above the ionization edge (Fig. 1c). A larger series of EFTEM images may also be acquired forming a similar 3D data-cube known as an EFTEM SI, or electron spectroscopic image (ESI) (Fig. 1d). EFTEM SI provides a convenient method to map large sample areas with high spatial resolution. However, the total dose received by the sample increases with the acquisition of each EFTEM image. Therefore, if high spectral resolution is required (for improved background modelling, peak fitting or resolution of spectral features), it is often more appropriate to use the alternative data acquisition sequence provided by STEM-EELS spectrum imaging.

3. Mineralised tissues

In the field of medicine, an increased understanding of the structure of mineralised tissues is hoped to facilitate the development of therapies to treat an increasing number of bone-related pathologies in our ageing society. Additionally, these tissues are of interest to the materials scientist as their sophisticated compositions and hierarchical architecture result in a highly improved material benefiting from the elasticity of collagen and the strength of mineral – the building blocks of these materials.

While the structure of mineralised biological tissues are well known at the macro- and micrometre scales, current studies have been aimed at increasing our understanding of the *nanoscale* structure and chemistry of these complex systems [14,15]. Analytical TEM has already played a large role in the current understanding of bone at the nanometre scale and further TEM studies will play an important role in answering remaining questions about: (a) the mechanisms of bone mineralisation (in particular the evolution

Table 1
Detailing the range of information which may be obtained using low loss and core loss EELS, as well as corresponding photon spectroscopy techniques.

Alternative techniques	Energy-loss (eV)		Excitations	Information available	Examples from this review
IR spectroscopy Raman spectroscopy Optical spectroscopy UV spectrostopy	0.01 0.1 1 10	Low loss EELS	• Collective excitations (plasmons and phonons) • Single-electron transitions from valence or semi-core levels	• Band gap • Electron density • Relative sample thickness • Dielectric function	• Different plasmon peak position, providing contrast between OPV materials • π - π* transition in PCBM
Soft X-ray absorption spectroscopy	100	Core loss EELS	• Single electron transitions from core levels	• Elemental composition	• Identify mineral and organic phases in bone by mapping Ca and C
Energy dispersive X-ray (EDX) spectroscopy	1000			• Valence state • Local bonding environment	• Distinguishing between carbonate and collagen at the carbon K edge

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