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Towards standardising electron spectroscopy measurement of nanoparticle coatings

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A thorough understanding of nanoparticle surfaces is essential to many potential applications. In particular, measurement of coatings or overlayers on nanoparticles is of great importance, due to the ubiquity of core-shell or coated nanoparticle systems. Due to their surface-sensitivity, electron spectroscopies are ideally suited to the characterisation of nanostructures. While several methods and analyses for characterisation of such nanoparticles using electron spectroscopies have been reported, there is a growing need for these to be addressed by standardization bodies. Here we present the development of an ISO technical report on the topic of measurement of nanoparticle coatings using electron spectroscopies, and relevant considerations.

Nanoparticles are increasingly synthesised, developed and studied in a broad variety of fields. These include applications in biology such as drug delivery, therapeutics and biosensors; in optoelectronics such as photovoltaics or LEDs; and in heterogeneous catalysis. The defining aspect of nanoparticles and their behaviour is their size. As the size of a nanoparticle decreases, their surface-area-to-volume ratio increases, which in turn significantly affects the properties and behaviour of the material as the behaviour of the interface becomes more important relative to that of the bulk. Understanding the nature of the surfaces of nanoparticles is therefore key to understanding their properties and interactions with their environment. Surface analysis techniques such as electron spectroscopies (XPS, AES, etc.) are therefore ideally suited to the analysis of nanoparticulate samples, due to their information depth being on the order of a few nanometres.

In the vast majority of cases, nanoparticles are not formed of a single uniform material. Whether by design, by exposure to contaminants, or by processes such as oxidation, they form some kind of 'core-shell' or coated structure, in which the outer layer of material is distinct from the centre. Understanding such coatings is vital to the development of many nanoparticle systems towards real-world applications as well as for purposes of risk assessment. Measurement of overlayers using electron spectroscopy has long been applied for planar systems, but this becomes more complex for samples with nanoscale topography. In recent years, several methods have been developed to aid in the interpretation of electron spectroscopy data from core-shell nanoparticles, however for efficient development of nanoparticle-based commercial products there is a strong need for these to be discussed in a standardisation context.

Here we present the development of an International Standards Organisation (ISO) technical report on the use of electron spectroscopy for the measurement of the thickness and nature of nanoparticle coatings, developed under ISO Technical Committee 201 – Surface Chemical Analysis. Within this report, a range of example methods for nanoparticle shell thickness calculation based on electron spectroscopy data are presented, their applications discussed, and their applicability and validity compared

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to one another. This report will also discuss some specifics of measurement and interpretation of nanoparticle data from XPS AES, NAP-XPS, and Synchrotron XPS. Methods for thickness calculation are predominantly discussed as they relate to lab-based XPS analysis, although many of the methods described may be applied similarly for most electron spectroscopy techniques. Three main types of analysis method are detailed; descriptive formulae such as the T_{NP} method[1]; numerical-modelling based methods, typically using the straight-line approximation for detected electrons (see figure 1), for which an example script is provided; and more complex simulation software such as SESSA[2]. This type of analysis is most often applied with the assumption of an idealised nanoparticle model – one in which the core and shell are both uniform, homogeneous, and concentric; the effects of sample deviation from this ideal model are discussed with respect to their effect on the observed peak intensities.

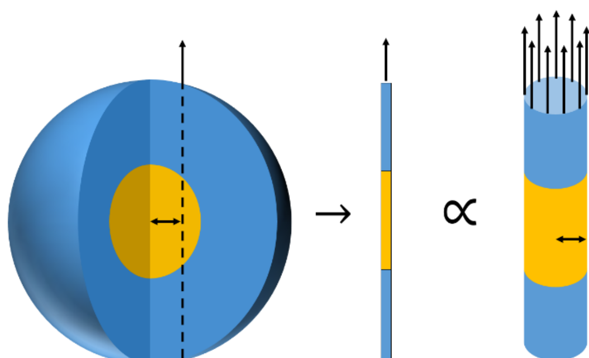

Fig. 1 - A schematic illustration of how XPS measurements of a nanoparticle may be broken down for numerical modelling as a sum of the intensities from individual hollow cylinders of material. These cylinders thus have equivalent intensity ratios to a single column of material thus simplifying calculations.

5. References

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