Characterisation of nanomaterials: XPS analysis of Core-Shell Nanoparticles

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Different approaches to quantify shell thicknesses are presented and compared. These comprise: (1) The infinitesimal columns model (IC), (2) Shard’s empirical formula (TNP-model) and (3) SESSA (Simulation of Electron Spectra for Surface Analysis) simulations with and (4) without elastic scattering. Experimental data on a round robin experiment of PMMA@PTFE CSNPs were analysed with the aforementioned approaches and show a good mutual consistency and agree with the nominal shell thickness. However, use of the F1s signal leads to significant deviations. Transmission Electron Microscopy measurements revealed that the core-shell structure is non-ideal, i.e. the particles are aspherical and the cores are acentric within the particles. SESSA simulations were employed to estimate the effect of various types of deviations of ideal NPs on the outcome of shell thickness determination. The usefulness and importance of different kind of electron beam techniques for CSNP analysis and in particular shell thickness determination is discussed.

1 Introduction

Determining shell thicknesses and chemistry of Core-Shell Nanoparticles (CSNPs) presently constitutes one of the most important challenges related to characterisation of nanoparticles[1, 2, 3]. While for particle number concentration various routine analysis techniques as well as methods providing reference measurements have been or are in the process of being developed, one of the most promising candidates for shell thickness determination is x-ray photoelectron spectroscopy (XPS). In the present work, analysis XPS peak intensities for shell-thickness measurement is put to a test, highlighting the advantages and pitfalls of the method. Three different approaches to quantify shell thicknesses from XPS peak intensities are compared: (1) The infinitesimal columns model (IC,[4]), (2) Shard’s empirical formula (TNP-model, [3]); and (3) SESSA (Simulation of Electron Spectra for Surface Analysis, [5, 6]) simulations with and (4) without elastic scattering. CSNP XPS intensities simulated with SESSA for different combinations of core/shell-material combinations for a wide range of core and shell thicknesses have been evaluated with the TNP-model and the retrieved thicknesses are in good agreement with the nominal thickness, even when elastic scattering is turned on during the simulation, except for pathological cases [6]. For organic shell materials these simulations fully confirm the validity of the (much simpler) TNP-method, which also coincides with the IC model. Within the EMPIR project Innopart (http://empir.npl.co.uk/innopart/) a round robin interlaboratory experiment was conducted on PMMA@PTFE CSNPs involving three research institutions (NPL, BAM and TUVienna). XPS intensities were analysed with the aforementioned approaches and show a good consistency in that evaluations of the shell thicknesses among the institutions agree within 10% (and are in good agreement with the nominal shell thickness).
2 Results

The calibration curve for the shell thickness of PMMA@PTFE CSNPs, established with SESSA, is shown in Fig. 1. It shows the shell to core XPS intensity ratio as a function of shell thickness on the basis of the C-core signal (blue and green curves) as well as on the basis of the F-core signal (red and orange). The solid, dashed and dotted lines indicate the retrieved shell thicknesses on the basis of the XPS measurements performed at the TU Vienna, NPL and BAM, respectively. Calibration curves on the basis of the IC and TNP-model (not shown) are indistinguishably similar to the SESSA results. The results for the C-core signal are seen to agree to within $\pm 10\%$. This consistency is promising since it suggests that the error due to sample preparation can be controlled by following a strict protocol. Use of the F1s signal leads to significantly different values of the retrieved shell thickness. Independent measurements using Transmission Electron Microscopy were also performed, which revealed that the core-shell structure is non-ideal, i.e. the particles are aspherical and the cores are acentric within the particles. The electron microscopy measurements clearly showed that the NPs are polydisperse in size, non-uniform, nonconcentric and asymmetric while the core and shell composition may be inhomogeneous.

SESSA simulations were employed to estimate the effect of various types of deviations of ideal NPs on the outcome of shell thickness determination. These non-ideal morphologies included single (ideal) nanoparticles, a nanoparticle powder, acentric cores, non-complete shells (pores) and combinations of the above. It was found that deviations of ideal morphology can lead to changes in the peak intensity ratios by up to a factor of two and are more pronounced when the F-1s peak intensity is used for the core signal.

The possibility to use the XPS background for nanoparticle characterisation has also been investigated. It was found that it is helpful in this case to consider the background extending over a wide energy range. In this case it turns out to be no longer admissible to employ the quasi-elastic approximation (QEA) to simulate the background, i.e. the change of the interaction cross section with the energy of the electrons which have participated in multiple inelastic scattering needs to be accounted for. This is generally only possible by means of a full slowing down Monte Carlo simulation, which is impractical for routine use. An effective approach has been studied in which the quasi-elastic spectrum is multiplied a-posteriori with the energy dependence of the inelastic mean free path (IMFP). This so-called QEA’-approximation [7] agrees with a full slowing down Monte Carlo simulation to within 10%, both for single nanoparticles as well as for powders consisting of CSNPs, making it an effective tool for simulating NP intensities for analysis of XPS-data.

![Fig. 1 Calibration curves for shell thickness on the basis of XPS shell-core ratios (C-core signal: green and blue; F-core signal: orange and red) calculated using SESSA.](image)

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