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Determining shell thicknesses in stabilised CdSe@ZnS core-shell nanoparticles by quantitative XPS analysis using an Infinitesimal Columns model

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ABSTRACT

A novel Infinitesimal Columns (IC) simulation model is introduced in this study for the quantitative analysis of core-shell nanoparticles (CSNP) by means of XPS, which combines the advantages of existing approaches. The IC model is applied to stabilised Lumidot™ CdSe/ZnS 610 CSNP for an extensive investigation of their internal structure, i.e. calculation of the two shell thicknesses (ZnS and stabiliser) and exploration of deviations from the idealised CSNP composition. The observed discrepancies between different model calculations can be attributed to the presence of excess stabiliser as well as synthesis residues, demonstrating the necessity of sophisticated purification methods. An excellent agreement is found in the comparison of the IC model with established models from the existing literature, the Shard model and the software SESSA.

1. Introduction

The increasing importance of engineered nanoparticles (ENP) in advanced industrial applications as well as research purposes in material science and medicine requires accurate control and characterisation of their physical and chemical properties. Particle size and surface chemistry are crucial for interactions with other materials and between individual particles. Accordingly, the physical and chemical properties of core-shell nanoparticles (CSNP) mainly depend on the thickness and composition of the shell in addition to the core size and material. The thorough analysis of ENP and CSNP is essential for manufacturing processes, environmental and medical risk assessment as well as behaviour and interactions in biological systems.

Particle sizes and size distributions are typically measured using electron microscopy (TEM, SEM, T-SEM), X-ray scattering (SAXS) and a number of optical methods (DLS, etc.), whereas the characterisation of the shell, especially determining shell thicknesses and chemistry, requires a quantitative spectroscopic technique with chemical sensitivity. X-ray photoelectron spectroscopy (XPS) is a valuable and commonly used tool that provides quantitative data for chemical analyses with an information depth comparable to typical nanoparticle sizes and shell thicknesses. Previous studies have employed XPS and specifically designed mathematical models to calculate layer thicknesses in planar samples [1–6]. Such approaches can be extended to account for the non-planar geometry of spherical CSNP in order to calculate shell thicknesses by the comparison of simulated and experimental XPS signal intensities [7–10]. In this study, a new simulation model is introduced that is based on a similar but more generally applicable approach as presented in Zorn et al. [8] and Sarma et al. [10]. The aim is to combine the flexibility of the model underlying the software SESSA v2.0 [7] and the simplicity and ease of use of the model presented by Shard [9].

CdSe@ZnS core-shell quantum dots (QD) represent an excellent example class of CSNP for the development and comparison of quantitative evaluation methods for the calculation of shell thicknesses. The CdSe core particles exhibit a narrow and tunable photoluminescence directly dependent on the particle size [11]. The addition of ZnS with its larger band gap improves the photoexciton quantum confinement and reduces surface defects and surface gap states in the cores and thus drastically increases

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the photoluminescence quantum yield [12,13] and provides passivation against photooxidation [14]. This opens up a wide range of applications utilising the QD as photoluminescent probes in molecular diagnostics, imaging for cancer diagnostics and biomedical assays [15–17] as well as laser media [18], optoelectronic [19] and thermoelectric [20] devices, photovoltaics [21], photodetectors [22] and several other semiconductor applications [23]. Accordingly, much research interest is focused on developing and improving synthesis methods in order to meet the requirements of such innovative technologies [12,13,24,25]. Particularly organic coatings are utilised for size control during synthesis [13,24,25], in medical applications to control specificity and biocompatibility [26,27] as well as for chemical stabilisation in electronic applications [28,29].

CdSe@ZnS and similar CSNP have previously been investigated using simulation models that were optimised for the specific situation [8,10]. However, a widely applicable procedure for the determination of shell thicknesses is desirable, also covering material combinations of very dissimilar properties, such as inorganic-core-organic-shell particles. Extensive research is being performed to investigate the comparability of such experiments between different research laboratories and experimental approaches [30]. The simulation models employed and compared in this study have been designed in order to be applicable to a widest possible range of scientific objectives in the characterisation of CSNP.

In this study, a detailed characterisation of the chemistry of organically stabilised CdSe@ZnS CSNP is presented based on XPS experiments and extensive simulations. Existing quantitative approaches are compared and a novel Infinitesimal Columns (IC) model is introduced for a very detailed insight into the internal composition of the investigated CSNP.

2. Experimental

The CdSe@ZnS CSNP investigated in this study were manufactured by *Nanoco Technologies Group plc* and purchased from *Sigma-Aldrich Co. LLC* under the product name *Lumidot*™ *CdSe/ZnS 610, core-shell type quantum dots*, denoting the photoluminescence maximum at a wavelength of 610 nm. A mixture of hexadecylamine (HDA) and trioctylphosphine (TOPO) was used to stabilise the particles. The diameter of the CSNP particles is specified as 5.2 nm, the diameter of the CSNP including the organic stabiliser is specified as 7.7 nm, i.e. a stabiliser shell thickness of 1.25 nm. The particles were provided as a 5 mg/mL dispersion in toluene and prepared for the XPS experiments by spin-coating onto a clean Au-coated silicon substrate (10 μl on approx. $12 \times 12\ mm^2$). The sample preparation was performed following the approach by Kersting et al. [31], but the substrate was changed from Si to Au in order to avoid an overlap of the Si signals from the substrate with the S and Se signals from the particles in the XPS experiments. The size of the CdSe@ZnS CSNP (excluding the stabiliser shell) was confirmed by transmission electron microscopy (TEM).

The XPS measurements were carried out using an *AXIS Ultra DLD* electron spectrometer manufactured by *Kratos Analytical Ltd., UK*. XPS spectra were recorded using monochromated Al Kα excitation at pass energy of 80 eV for survey spectra and 20 eV for the core level spectra. The electron emission angle was 0° and the source-to-analyser angle was 60°. The binding energy scale of the instrument was calibrated following a *Kratos Analytical* procedure based on ISO 15472 [32] binding energy data. All spectra were taken by setting the instrument to the hybrid lens mode and the slot mode providing approximately a $300 \times 700\ \mu m^2$ analysis area. The charge neutraliser was used and the binding energy scale was corrected for charging [33], using an electron binding energy of 285.0 eV [34] for the aliphatic hydrocarbon component of the C 1s line.

3. Simulations

Usually, XPS software for quantitative elemental analysis uses relative sensitivity factors. These have been established assuming a planar surface and in-depth homogeneity. CSNP do not fulfil this condition as they exhibit a highly curved surface and a heterogeneous in-depth composition within the probed volume in XPS experiments. Therefore, an accurate model is needed to link the origin of photoelectrons within the particles to their relative contributions to the overall signal intensities. For this, the differences in the attenuation of photoelectrons depending on their trajectory through the different materials have to be accounted for. In this study, two established approaches [7,9,35] will be compared with a novel concept that combines the advantages of both concepts.

SESSA [7] simulates individual photoelectron trajectories and calculates the resulting intensities statistically over a large number of trajectories using a very detailed but complex model. The simulations are performed iteratively and shell thicknesses are calculated by finding the best match between experimental and simulated data. The Shard model [9] is initially based on iterative calculations as well, but a generalising fit was performed to a large set of model calculations in order to produce a single formula for forward calculation of shell thicknesses from experimental intensity ratios. While this eliminates the necessity of iterative calculations, the model published in [9] is limited to the idealised core-shell model. Both models have been compared using two theoretical examples [35] and have shown very good agreement.

The Infinitesimal Columns model introduced in this study is based on a simpler iterative calculation model than SESSA [7], but retains the ability for e.g. simulating multi-shell particles in comparison with the Shard model [9].

3.1. Infinitesimal Columns (IC) model

The attenuation of photoelectrons is commonly assumed to follow an exponential dependence. A signal I_0 originating from a depth x within an attenuating layer results in a signal intensity I of

$$I = I_0 \cdot e^{-x/\lambda}, \tag{1}$$

where λ is the inelastic mean free path (IMFP) which depends on the kinetic energy of the photoelectrons as well as the attenuating material. For the calculations presented here, the IMFPs were calculated according to [36] for inorganic and [37] for organic materials.

For a uniform overlayer of thickness d on a planar and infinitely thick substrate, the ratio between the respective photoelectron signal intensities can be calculated according to reference [1]:

$$\frac{I_O/S_O}{I_S/S_S} = \frac{1 - e^{-d/\lambda_{Oo}}}{e^{-d/\lambda_{Os}}}, \tag{2}$$

for which the photoelectron emission angle is assumed to be normal to the sample surface. $S_{O,S}$ are the respective relative sensitivity factors for the two signals and $\lambda_{Oo,Os}$ are the IMFPs within the overlayer for photoelectrons originating from overlayer and substrate, respectively.

A similar approach can be used to calculate core-shell signal intensity ratios of core-shell nanoparticles for which the particle geometry is approximated as spherical. The particle is divided into Infinitesimal Columns which are later treated as individual planar layer stack. As schematically shown in Fig. 1, each column consists of a core "layer" of thickness $2L_C$ and two shell "layers" of thickness L_S, each, above and below the core. For each column, L_C and