ECASIA SPECIAL ISSUE PAPER

Revised: 4 April 2018

Shell thickness determination for PTFE-PS core-shell nanoparticles using scanning transmission X-ray microscopy (STXM)

A. Müller¹ I. S. Swaraj² I. K. Sparnacci³ I. W.E.S. Unger¹

¹ Bundesanstalt für Materialforschung und prüfung (BAM), Berlin, Germany

²Synchroton SOLEIL, Saint-Aubin, France

³Università del Piemonte Orientale, Alessandria, Italy

Correspondence

Anja Müller, Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany. Email: anja-hermanns@live.de

Funding information

European Association of National Metrology Institutes (EURAMET); European Metrology Programme for Innovation and Research (EMPIR) A scanning transmission X-ray microscopy (STXM)-based methodology is introduced for determining the dimensions (shell thickness, core and total diameter) of core-shell nanoparticles, which exhibit a strong X-ray absorption contrast and a well-defined interface between core and shell material. A low radiation dosage during data acquisition and, therefore, less X-ray beam-induced damage of the sample is achieved by recording STXM images only at 2 predetermined energies of maximum absorption contrast, instead of recording a stack of images across the whole absorption edge. A model core-shell nanoparticle, polytetrafluoroethylene (PTFE) cores with polystyrene (PS) shell, is used for demonstration. Near-edge X-ray absorption fine structure spectroscopy confirms the significant difference in X-ray absorption behavior between PTFE and PS. Additionally, because of the insolubility of styrene in PTFE a well-defined interface between particle core and shell is expected. To validate the STXM results, both the naked PTFE cores as well as the complete core-shell nanoparticles are examined by scanning electron microscopy (SEM). The introduced STXMbased methodology yields particle dimensions in agreement with the SEM results and provides additional information such as the position of the particle core, which cannot be extracted from a SEM micrograph.

KEYWORDS

core-shell nanoparticles, polymers, PS, PTFE, SEM, STXM

1 | INTRODUCTION

Nanoparticle fabrication has been developed intensively over the last decades, and today, very sophisticated and well-understood manufacturing methods are available. These methods allow the generation of countless material-morphology combinations exhibiting exciting properties for industrial applications. Consequently, products containing nanoparticles already encounter us in most areas of our daily life including cosmetics, clothing, detergents, paints, batteries, or displays.¹ In most cases, the particles show a core-shell morphology either voluntarily or involuntarily.² The properties of the particles' shell determine the interaction with their surroundings. Thus, reliable control over these properties means reliable control over the particles' performance as well as their risk for our health and the

environment. Beside the chemical composition, the thickness of the shell is a parameter of utmost importance. In this paper, we present a novel methodology for determining the shell thickness of core-shell nanoparticles based on scanning transmission X-ray microscopy (STXM).

Among various tools available for nanoparticle characterization, electron microscopy (EM) and X-ray photoelectron spectroscopy (XPS) are widely used. Even though EM provides adequate solutions to many problems, its direct application for shell thickness determination is limited. As soon as the density and atomic number difference between core and shell material is insufficient, the low contrast leads to indistinguishability of the 2 materials in the micrographs.³ A chemical contrast between core and shell material can be achieved by combining an electron microscope with an electron energy loss

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spectrometer (EM-EELS). Even though EM-EELS provides superior spatial resolution as compared with STXM, radiation damage per unit of analytical information is typically higher in EM-EELS. Additionally, EM depends on vacuum conditions, while STXM investigations can be performed at ambient pressure or in primary vacuum conditions.^{4,5} The advantages of STXM over EM for certain systems will be further discussed and demonstrated by means of the presented results. In principle, XPS is capable of average nanoparticle shell thickness determination for ensembles. However, activities here are still at an early stage.⁶ Particle dimensions from independent techniques are urgently required not only for validation but also, because all models developed so far for quantitative evaluation of XPS data targeting the estimation of nanoparticle shell thicknesses need either core radius or total diameter as an input parameter.⁷⁻⁹ Moreover, XPS experiments can be complicated for nonconductive samples where noncompensated positive charges left after photoionization leads to artifacts in the spectra that falsify the results.

Scanning transmission X-ray microscopy (STXM) is a powerful technique with a 35-nm spatial resolution and a material contrast depending on the difference in X-ray absorption behavior of the investigated materials. In 2001, Koprinarov et al¹⁰ investigated microspheres consisting of a polydivinylbenzene-55 (DVB55) core (3.2 µm) and a poly(DVB55-co-ethylene glycol dimethyl acrylate) shell (0.4-0.9 μm) using STXM by taking advantage of the absorption contrast between core and shell material. In 2011, Burke et al¹¹ visualized nanoparticles with STXM composed of poly(9,9-dioctyl-fluorene-2,7-diyl-co-bis-N, N'-(4-butylphenyl)-bis-N, N'-phenyl-1,4-phenylenedi-amine) and poly(9,9-dioctylfluorene-2,7-diyl-co-benzothiadiazole) (52 nm diameter) and, furthermore, presented a methodology for probing their morphology on a sub-10-nm length scale based on chemical compositional mapping by singular value decomposition (SVD) of a stack of images. Using a similar strategy, in 2015, Belcher and coworkers investigated core-shell particles comprising phenyl-C61-butyric acid methyl ester with poly(3-hexylthiophene) as well as core-shell particles comprising poly[4,8-bis(2-ethylhexyloxy)benzo(1,2-b:4,5-b')dithiophe ne-alt-5, 6-bis(octyloxy)-4,7-di(thiophen-2-yl)(2,1,3-benzothiadiazole)-5,5'-diyl] with phenyl-C61-butyric acid methyl ester (23.8- and 23.5nm diameter). Here, simple geometric considerations were applied to determine the core, interface, and shell regions.¹²

In the publications mentioned above, STXM is applied to identify an unknown morphology of certain nanoparticles. As opposed to that, the nanoparticles investigated in this paper are known to exhibit a core-shell morphology and their dimensions (shell thickness, core, and total diameter) are carefully precharacterized by scanning electron microscopy (SEM). This allows a reliable validation of the dimensions obtained by the presented STXM-based methodology. Furthermore, this methodology is not based on SVD targeting a lower radiation dosage during data acquisition and, thus, less X-ray-induced damage and chemical modification of the sample. This is achieved by recording STXM images at only 2 predetermined energies of maximum absorption contrast, instead of a stack of images across the whole absorption edge. Fitting of experimental linear and radial profiles of the particles yields the optimum combination of core diameter, shell thickness, and total diameter. A polymeric model core-shell nanoparticle consisting of polytetrafluoroethylene (PTFE) cores with a polystyrene (PS) shell was selected to demonstrate the strengths of the methodology and its advantages over EM.

2 | EXPERIMENTAL

The PTFE cores (Hyflon MFA 100 LS latex) suspended in water with a concentration of 337 mg/mL were kindly provided by Solvay Specialty Polymers. These consist of a perfluoroalkoxy polymer derived from the polymerization of tetrafluoroethylene and a perfluoromethylvinyl ether comonomer. X-ray photoelectron spectroscopy analysis of the particles revealed that such comonomers make up below 3% of the total number of polymer units.

The PTFE-PS core-shell nanoparticles suspended in water with a concentration of 88.6 mg/mL were synthesized by emulsifier-free batch seeded emulsion polimerization using 2.36 g of PTFE seeds and 63.42 g of styrene.^{13,14} The obtained suspension was purified from the unreacted monomer by repeated dialysis using a membrane with molecular weight cut off of 12.4 kDa.

Scanning electron microscopy (SEM) was performed by using an SEM Zeiss Supra 40 equipped with a high-resolution cathode (Schottky field emitter). InLens micrographs were recorded by using a secondary electron detector and transmission electron micrographs by using a dedicated transmission sample holder as described in detail elsewhere.¹⁵ Scanning electron microscopy samples were prepared by diluting the initial suspensions with ultrapure water, 10 000 times in the case of the PTFE cores and 5 times in the case of the PTFE-PS core-shell nanoparticles, and applying a drop of 3 µL onto a 6- to 10-nm-thick carbon film on a 3.05-mm diameter and 10- to 12-µmthick copper transmission electron microscopy grid of 200 lines/inch purchased from PLANO GmbH (Wetzlar, Germany). Analysis of the electron micrographs for the determination of particle size and particle size distribution was performed by using ImageJ.¹⁶ A detailed description of the analysis procedure can be found in the supporting information.

Scanning transmission x-ray microscopy (STXM) was carried out at the STXM instrument (Research Instruments GmbH) of the HERMES beamline at the synchrotron radiation source SOLEIL (Saint-Aubin, France). A Fresnel zone plate with outer ring width of 30 nm was used with an order sorting aperture of 50 µm. The experimental chamber was pumped down to 10^{-3} mbar during data acquisition. The images were obtained in transmission mode by using a photomultiplier tube as a detector. Beamline energy calibration was performed by aligning the C1s $\rightarrow \pi^*$ feature of a test PS thin film. The STXM core-shell nanoparticle sample was prepared by diluting the initial PTFE-PS nanoparticle suspension 500 times with ultrapure water and applying a drop of $3\,\mu\text{L}$ onto a 1×1 mm broad and 100-nm-thick silicon nitride window in a 5 × 5 mm broad and 500-nm-thick silicon frame manufactured by Norcada Inc (Edmonton, Canada). The sample was air-dried prior to measurements. A total of 13 different particles were imaged across 10 different randomly choosen locations on the sample. The image size was restricted to $0.7 \times 0.7 \,\mu\text{m}^2$ with a step size of 5 nm.

Near edge x-ray absorption fine structure (NEXAFS) spectra were obtained at the same instrument as the STXM images. The NEXAFS samples were prepared by diluting the initial suspensions of PTFE cores and PTFE-PS core-shell nanoparticles 4 times and applying a drop of 0.5 μ L onto the same kind of silicon nitride window that was used for the STXM measurements. The samples were air-dried prior to measurements. In the case of the PTFE cores, a region free of large aggregates was chosen and defocused line scans were performed. In the case of the PTFE-PS particles, the spectra were carefully extracted from the edge of more than 1 individual core-shell particle and compared with literature data of PS thin films. The raw signal (I_o) was obtained through a bare silicon nitride window to normalize the measured transmitted signal through the samples.

3 | RESULTS AND DISCUSSION

The investigated nanoparticles consist of PTFE cores, which were coated with PS via seeded emulsion polymerization. To determine dimensions and shape of the particles, SEM was applied, both before and after the growth of the PS shell. Drop-casting the 2 suspensions onto the substrates resulted in some regions containing mostly large particle aggregates and other regions exhibiting a very homogeneous and dense single layer particle distribution. Sample micrographs of the latter are shown in Figure 1. The dimensions gained from a quantitative analysis of the SEM micrographs are summarized in Table 1. Stated core and total diameter from SEM are Feret's diameters (shape descriptor defined by ImageJ).¹⁶

A differentiation between core and shell material was not possible in the SEM micrographs of the core-shell particles, neither in the InLens nor in the transmission mode. The difference in density between PTFE (2.2 g/cm^3) and PS (1.05 g/cm^3) is too small to generate a sufficient



TABLE 1 Dimensions of polytetrafluoroethylene-polystyrene coreshell nanoparticles from STXM and SEM investigations

	Core Diameter	σ_{core}	Shell Thickness	σ_{shell}	Total Diameter	σ_{total}
STXM	42.8	4 (10)	51.8	5 (10)	146.4	11 (8)
SEM	48.0	12 (25)	43.5	8 (18)	135.0	4 (3)

All values are in units of nanometers, apart from the numbers in parentheses, which are relative standard deviations in percent. The scanning transmission X-ray microscopy (STXM) results are based on the analysis of 13 core-shell nanoparticles. The scanning electron microscopy (SEM) results are based on the analysis of 494 naked cores and 452 core-shell nanoparticles.

image contrast.¹⁷ Consequently, for this particle system, a shell thickness from SEM can only be estimated indirectly by subtracting the core from the total diameter. Furthermore, the micrographs revealed a higher polydispersity for the PTFE cores (48 \pm 12 nm) than for the core-shell nanoparticles $(135 \pm 4 \text{ nm})$ indicated by the higher standard deviation for the diameter of the core than for the total diameter. Additionally, the circularity (shape descriptor defined by ImageJ) of the particles increases with the shell growth from 0.80 ± 0.10 to 0.88 ± 0.03 .¹⁶ A detailed description of the SEM analysis as well as the histograms representing the particle size distributions can be found in the supporting information. Because of the insolubility of the styrene monomer in PTFE, it is reasonable to expect a core-shell morphology after the seeded emulsion polymerization with a relatively sharp and distinct interface between core and shell material.¹⁸ However, because of the lacking material contrast, the particles' core-shell morphology cannot directly be confirmed by SEM. It is neither possible to determine



FIGURE 1 Scanning electron microscopy images of naked polytetrafluoroethylene cores (upper row) and of polytetrafluoroethylene-polystyrene coreshell nanoparticles (lower row) recorded in transmission mode (left) and in InLens mode (right). All scale bars equal 100 nm



FIGURE 2 Near-edge X-ray absorption fine structure spectra of the C K-edge of the polytetrafluoroethylene cores and polytetrafluoroethylene-polystyrene core-shell nanoparticles. The vertical lines indicate the energies 285.0 and 292.5 eV, which were used for recording scanning transmission X-ray microscopy images

the position of the PTFE core inside the particles nor whether there is a PTFE core at all.

Whereas the densities of PTFE and PS are very much alike, their X-ray absorption behavior differs significantly. This becomes clear when comparing the NEXAFS spectra of the C K-edge in Figure 2. The transition of electrons from C1s orbitals to the empty σ^* antibinding molecular orbitals of C-F bonds is responsible for a sharp

resonance at 292.5 eV in the spectrum of PTFE.¹⁹ In contrast to that, the most dominant resonance in the PS spectrum can be found at 285.0 eV and is caused by the transition of electrons from the C1s orbitals to the empty π^* antibinding molecular orbitals of C=C bonds in the phenyl rings.²⁰ In STXM, such a difference in absorption behavior leads to an image contrast enabling a direct differentiation between particle core and shell. Consequently, STXM images of the core-shell particles were recorded at 292.5 and 285.0 eV. Since a lower particle density at the surface was desired to enable single particle characterization, the core-shell nanoparticle suspension was further diluted before drop-casting it onto the substrate for the STXM measurements. The software aXis2000²¹ was used for processing the images. The I_0 signal (incident photon flux) obtained at a particle-free region was used to convert the absorption images into optical density images. Drift correction and noise filtering (fast Fourier transform filter) were performed before the images at 292.5 eV were subtracted from the image at 285.0 eV. This subtraction was necessary to further enhance the contrast between core and shell region. The enhancement of contrast is further clarified by Figure S13 in the supporting information.

Figure 3A shows an image resulting from such a subtraction that contains 2 core-shell particles. Both particles consist of a dark area of low optical density representing the core surrounded by a bright area of high optical density representing the shell. Thus, in opposition to the SEM micrographs, STXM enables a direct differentiation between core and shell because of the image contrast. The existence



FIGURE 3 Scanning transmission X-ray microscopy image resulting from the subtraction of an image recorded at 292.5 eV from an image recorded at 285.0 eV (A). The scale bar equals 200 nm. The position of a radial profile is indicated in A, by a yellow circle. The result of this profile is shown in B, together with a fit indicated by the red curve. The position of a linear profile is indicated in (A) by a red line. The result of this profile is shown in D, together with fits on both sides of the particle center indicated by red curves. The black dots in C, show shell thicknesses and core diameters resulting from all linear profiles indicated in (A). Shell thickness and core diameter resulting from the radial profile are also shown in the diagram by the red dot. The error bars of the linear profiles are the standard deviations of core diameter and shell thickness. The error bars of the radial profile reflect an error of 5% that originates from fitting

of the core can be verified, and its position with respect to the shell can be identified. In this case, the core seems to be not fully central and the shell thickness not fully homogeneous, respectively. As a consequence, the center of the core does not equal the center of the complete core-shell particle. To extract the particle dimensions from the STXM images, a mixture of linear and radial profiles was analyzed. Linear profiles were applied whenever the close proximity to neighboring particles or a high background due to carbon contaminations made the application of a radial profile impossible. The center of the core was considered for positioning of linear and radial profiles as opposed to the center of the particle. The experimental profiles of the particles were fitted with theoretical profiles (Figure 3B,D). Theoretical profiles were obtained by convoluting the calculated zone plate intensity profile with a calculated core-shell thickness profile. The best core radius and shell thickness were obtained by systematically varying these 2 parameters during a least squares fitting procedure. More detailed information about the generation of experimental and theoretical radial profiles can be found in the supporting information.

Table 1 lists the dimensions of shell, core, and total core-shell particle derived from STXM. It also contains the dimensions from SEM for comparison. Corresponding histograms can be found in the supporting information. Because of the elaborate analysis procedure, the STXM results are based on 30 times less particles then the SEM results. The investigation of a higher number of particles would lead to an improvement of the standard deviations; however, the tendencies indicated by Table 1 are reasonable. The values for the total diameter from STXM and SEM are in best agreement (9% difference), while the core diameter from STXM is 12% smaller and the shell thickness 19% larger than from SEM. The reason for these differences is the nonspherical shape of the nanoparticle cores.

During the ImageJ analysis of the SEM micrographs, the largest possible diameter within a nonspherical particle is counted, which leads to an overestimation of the average nanoparticle core diameter. Additionally, the overall diameter distribution becomes broader, which causes a higher standard deviation compared with STXM. In contrast, the analysis of particles in STXM images with a radial profile (compare Figure 3A,B) underestimates the average core diameter. Furthermore, the core diameters of different particles are tendentially equalized and the standard deviation is, therefore, smaller. The analysis of particles in STXM images with a linear profile (compare Figure 3A,D) yields a realistic representation of the corresponding cross section of the particle. However, calculating the average of many linear profiles has the same underestimation effect as the radial profile analysis.

As already mentioned the shell thickness in SEM was calculated indirectly by subtracting an average core from an average total diameter. Consequently, the overestimation of the core leads to an underestimation of the shell thickness. Vice versa, the underestimation of the core in STXM leads to an overestimation of the shell thickness. The reason for the higher standard deviation of the average shell thickness in SEM than in STXM is the same as for the standard deviation of the average core diameters.

Finally, the small deviation of the total diameter between STXM and SEM can be explained by the high degree of sphericity of the complete core-shell nanoparticle as opposed to the cores. Thus, the effects of overestimation and underestimation described above cancel each other in both the case of SEM and STXM analysis. The standard deviation of the total core-shell particle diameter from STXM is higher than from SEM. That is because the total diameter from STXM is derived from core diameter and shell thickness, whereas it is a directly measured quantity in the SEM experiment.

In the end it should be mentioned that variations of core diameter and shell thickness within a single particle are lost in the SEM analysis of the core-shell nanoparticles. Only the variations among different particles are reflected by the standard deviation. The same is true for a full radial profile applied to a nanoparticle in a STXM image. However, application and analysis of single linear profiles of that same nanoparticle in a STXM image make it possible to determine shell thickness and core diameter variations even within a single particle. The diagram in Figure 3C shows shell thicknesses and core diameters of 6 linear profiles through the same core-shell nanoparticle. The position of these profiles is indicated in Figure 3A by red and white lines. The distribution of dots in the diagram indicates that the shell thickness within this particle varies between 55 and 67 nm, while the core diameters vary between 25 and 53 nm. A broader standard deviation for the core diameter than of the shell thickness reflects the nonsphericity of the nanoparticle cores. The variation of the total diameter underlines the observation that the core is not in the center of the particle. The possibility to extract such information about the internal structure of single particles is a clear advantage of the STXM analysis compared with SEM.

4 | CONCLUSION

For the first time, a STXM-based methodology for determining the dimensions (shell thickness, core and total diameter) of core-shell nanoparticles has been validated by applying it to a model system, which is known to exhibit a core-shell morphology and which dimensions have been carefully precharacterized by SEM. The methodology is not based on SVD leading to a reduction of the radiation dosage during data acquisition and, therefore, less beam-induced damage of the sample.

For a PTFE-PS core-shell model nanoparticle system, dimensions that are in acceptable agreement with results from SEM were obtained. The total diameter from STXM and SEM are in best agreement (9% difference), while the core diameter from STXM is 12% smaller and the shell thickness 19% larger than from SEM. These differences could be explained by the corresponding analysis mechanisms. No direct differentiation between particle core and shell was possible in the SEM micrographs because of similar material densities. As opposed to that, a strong image contrast between core and shell region was found in the STXM micrographs caused by the characteristic X-ray absorption behavior of PTFE and PS. Here, the existence of the core could be verified and its position identified. Furthermore, the application of linear profiles for nanoparticle analysis in STXM visualizes the variation of shell thickness and core diameter within a single particle. This information is not accessible by SEM analysis at least not for the investigated model core-shell particle and comparable systems. Consequently, for certain material combinations, STXM provides information that cannot be extracted from SEM.

6 WILEY-SURFACE and NTERFACE ANALYSIS

The next step will be the testing of the novel methodology's applicability and accuracy for alternative systems such as nanoparticles with inorganic core and organic shell. Further effort will also be focused on automatization of the STXM data analysis to improve statistics to report average values.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to Mrs. Sigrid Benemann for recording the SEM micrographs. Furthermore, the authors thank the synchrotron radiation source SOLEIL for the allocation of beamtime at the HERMES beamline. This project has received funding from the European Metrology Programme for Innovation and Research (EMPIR) as part of the InNanoPart 14IND12 project. The EMPIR program is co-financed by the European Union's Horizon 2020 research and innovation program and the EMPIR Participating States.

ORCID

- A. Müller D http://orcid.org/0000-0003-2085-3687
- S. Swaraj b http://orcid.org/0000-0001-7351-2320
- K. Sparnacci http://orcid.org/0000-0003-2102-9649

W.E.S. Unger b http://orcid.org/0000-0002-7670-4042

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Müller A, Swaraj S, Sparnacci K, Unger WES. Shell thickness determination for PTFE-PS coreshell nanoparticles using scanning transmission X-ray microscopy (STXM). *Surf Interface Anal.* 2018;1–6. <u>https://doi.org/</u> 10.1002/sia.6464