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Reference:

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Ultramicroscopy - ISSN 0304-3991 - 164(2016), p. 11-16

Full text (Publishers DOI): <http://dx.doi.org/doi:10.1016/j.ultramic.2016.03.002>

An alternative approach for ζ -factor measurement using pure element nanoparticles

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The authors declare no competing financial interest

ABSTRACT

It is very challenging to measure the chemical composition of hetero nanostructures in a reliable and quantitative manner. Here, we propose a novel and straightforward approach that can be used to quantify energy dispersive X-ray spectra acquired in a transmission electron microscope. Our method is based on a combination of electron tomography and the so-called ζ -factor technique. We will demonstrate the reliability of our approach as well as its applicability by investigating Au-Ag and Au-Pt hetero nanostructures. Given its simplicity, we expect that the method could become a new standard in the field of chemical characterization using electron microscopy.

KEYWORDS: Electron tomography, bimetallic nanoparticles, EDXS quantification

1. Introduction

New developments in the field of nanotechnology drive the need for advanced quantitative characterization techniques that can be applied to complex nanostructures. Many of these nanostructures are composed of different compounds. For example, it is known that bimetallic nanostructures show enhanced stability and catalytic selectivity in comparison to their parent materials.[1] Understanding the connection between physical properties and the local structure or composition of nanomaterials is therefore of crucial importance.

Although transmission electron microscopy (TEM) is an ideal tool to investigate nanostructures,[2] it is surprisingly difficult to obtain reliable quantitative chemical information at the nanometer level. In the past, investigations using Energy Dispersive X-ray Spectroscopy (EDXS) in a TEM were especially hampered by the low efficiency of the EDXS detector systems. As a result of the development of novel detectors yielding improved performance in combination with brighter electron sources in state-of-the-art TEM instruments, a significant level of X-ray counts can nowadays be collected within realistic acquisition times, also when investigating relatively small nanostructures (>10nm).[3-6] A remaining problem however, is the lack of a reliable quantification method for EDXS spectroscopy in the TEM.[7, 8]

Quantification of EDXS data acquired using TEM is mostly carried out using so-called “k-factors” that form the basis of the Cliff-Lorimer method.[9] Over the past 40 years, this approach has been used extensively, especially during the characterization of thin films and even optimized in combination of tilt schemes.[10] As explained in [11] the Cliff-Lorimer technique is an accurate method when using experimentally estimated k-factors from calibration samples where the composition is accurately known. Unfortunately, such estimation is not always possible due to the lack of suitable standards. Even when standards

are available, the calibration is difficult and time consuming. Therefore, experimental EDXS results are typically quantified using k-factors that are calculated using a priori principles and implemented in commercial software. Although this approach is straightforward and user friendly, inaccuracies of 15%-20% might occur.[12] In parallel, various alternatives have been proposed, including the so-called “ ζ -factor” method.[11] This methodology has been shown to be a powerful approach that is able to overcome some of the main limitations of the Cliff-Lorimer method. In contrast to k-factors, the experimental determination of ζ -factors is possible from a pure element standard and should only be determined once for each element. However, when determining ζ -factors from pure element standards, the thickness of the sample should be precisely measured. In the past, this requirement has limited the applicability of the ζ -factor method to thin films.

In this study, we use electron tomography to overcome this limitation. In this manner, the volume (and thickness) of nanoparticles can be determined. As a consequence, systematic errors resulting from wrong estimations of sample thickness can be overcome. The proposed methodology, coupled with state-of-the-art instrumentation, enables us to expand the use of the ζ -factor method to the study of a variety of nanomaterials. In this manner, reliable and quantitative chemical information can be acquired at the nanometer level.

2. Materials and Methods

Experiments were performed using a FEI Titan probe corrected TEM, operated at 120 kV in Scanning Transmission Electron Microscopy (STEM) mode and equipped with a Super-X detector. A reliable measurement of the beam current is of crucial importance in the ζ -factor method. Therefore we used the pico-ammeter connected to the phosphor screen present in FEI instruments equipped with a Super-X detector. The screen current is typically calibrated by the manufacturer using a Faraday cup and a verification of the linearity of the current

measuring device can be conducted by varying the beam current and acquiring an EDXS map of the same nanoparticle. Plotting the current against the total number of counts over background for the element composing the nanoparticle should result in a linear fit obeying eq. 2 (data for our system is presented in the supporting information). The intercept on the y axis is considered as an estimate of the error on the measured current. Although such experiment cannot determine if the actual current is off by a constant factor, the proportionality factor will cancel out when determining concentrations using the same microscope and voltage.

A Fischione 2020 Single Tilt Tomography holder was used to acquire tilt series for tomography. Alignment of the tomographic series was performed with Matlab routines based on cross-correlation and manually with IMOD.[13] The SIRT algorithm implemented in the ASTRA Toolbox [14-16] was used for all the reconstructions. Amira software has been used for the 3D volume renderings. Synthesis details about the Au, Ag and Pt nanoparticles used can be found in the Supporting Information.

3. Results and discussion

The Cliff-Lorimer method is a ratio technique that was developed to overcome problems related to an absolute quantification of EDXS data acquired by TEM. The technique is still the most commonly used approach to obtain the concentrations of the elements in a TEM sample. Characteristic X-rays intensities I_A and I_B of elements A and B respectively are measured and the ratio of their concentrations C_A and C_B is determined using a predefined factor k_{AB} :

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \quad (1)$$

As discussed above, the main disadvantage of this method is the determination of the k -factors, which can be measured from standards of accurately known composition. These standards are not available for every system and the composition may always change as an effect of thinning or manipulation of the standard in order to perform the measurement.

The ζ -factor method adds to the benefits of a ratio technique such as the Cliff-Lorimer technique, the possibility of determining the sensitivity factors from pure elements standards and a straightforward method for correcting absorption effects.

The ζ -factor is defined by the following equation from [11]:

$$\rho t = \zeta_A \frac{I_A}{C_A D_e} \quad (2)$$

where ρ is the density, t the thickness, I_A the X-ray intensity (net counts), C_A the concentration and D_e the total electron dose, which is defined as:

$$D_e = N_e I_p \tau \quad (3)$$

with N_e the number of electrons per Coulomb, I_p the probe current and τ the total measure time. The beam current can be measured through the use of an in-situ faraday cup, EELS drift tube or a calibrated viewing screen.[11] The ζ -factor method was originally developed for thin films, for which the thickness is expected to be uniform across the sample. However, it is not straightforward to accurately measure the thickness using conventional (2D) TEM. It can be done by using Electron Energy Loss Spectroscopy (EELS),[17, 18] but this requires a calibration of the inelastic mean free path. This calibration is time demanding and requires a needle shaped sample with the same phase of the thin film for which the thickness has to be measured. This might result difficult for some samples, and furthermore, there is an

increasing demand to obtain quantitative results for nanomaterials different from thin films as well.

In this paper, we expand the use of the ζ -factor method to the investigation of nanoparticles by using electron tomography. The use of nanoparticles hereby offers many advantages: they are usually cheaper than a pure element thin film standards and they are often already available in most labs or can be relatively easily synthesized. In order to determine ζ -factors using nanoparticles instead of thin films we propose an equivalent definition of the ζ -factor replacing the sample thickness by the probed sample volume, which can be measured by electron tomography. We assume that the probed volume is the scanned area multiplied by the thickness t . That means that the total (live) time τ can be written as $\tau = \tau_d * A$, where A is the scanned area in m^2 , and τ_d is therefore the spectral acquisition time per pixel area. In this manner, we obtain the expression below, in which C is omitted since we assume a pure element standard during the determination of the ζ -factor:

$$\rho V = \zeta_A \frac{I_A}{N_e I_p \tau_d} \quad (4)$$

Once the ζ -factors are obtained, the concentration of the elements is given by the following expression:

$$C_j = \frac{\zeta_j I_j}{\sum_i \zeta_i I_i} \quad (5)$$

with

$$\sum_i C_i = 1 \quad (6)$$

For a system of two elements we obtain:

$$\frac{C_A}{C_B} = \frac{\zeta_A I_A}{\zeta_B I_B} \quad (7)$$

This expression is equivalent to eq. 1, where $k_{AB} = \frac{\zeta_A}{\zeta_B}$. It should be mentioned that absorption is so far neglected in these expressions. As explained in the work by Watanabe et al.,[11] this approximation is expected to be valid for the samples investigated in this paper.

3.1 Determination of ζ -factors from pure element nanoparticles

In order to determine the ζ -factors, the volumes of 8 particles consisting of Au, Ag and Pt respectively were determined by electron tomography. Figure 1 shows a rendering of the obtained reconstructions. Tilt series for each particle were acquired from -75° to 75° with a tilt increment of 3° . The resulting volume measurements are presented in Tables S1-S3. For each particle, an EDXS map was collected with an acquisition time of 3 minutes and using a current of approximately 250 pA. A tilt angle of 17° was chosen to minimize shadowing effects and increase the collected signal. For all particles, diffraction patterns and High-Resolution STEM images were acquired, confirming the crystallinity and FCC structure. We ensured that this tilt angle corresponded to an off-axis condition for the particles analyzed, in order to avoid unwanted channeling effects. Since the structures of the particles were confirmed to be the same of the relative bulk materials, bulk densities were used in the calculation of the ζ -factor: $\rho_{\text{Au}} = 19,320 \text{ kg/m}^3$, $\rho_{\text{Ag}} = 9,320 \text{ kg/m}^3$ and $\rho_{\text{Pt}} = 21,450 \text{ kg/m}^3$.

It should be noted that during the measurement of the ζ -factors, all experiments (different particles and different elements) were performed using the same experimental conditions, such that the effects of shadowing remain the same. However, once the ζ -factors are determined, they can be used to quantify maps at any tilt angle, since shadowing will affect the signal from different elements in the same manner. Therefore, the ratio between the intensities will still be proportional to the ratios between the ζ -factors. An exception has to be made for soft X-rays with energy less than 3 keV, for which absorption effects can lead to quantification errors.[19] In general, it should be verified that the specimen thickness is less

than a certain critical value for which absorption is below 5%, this is known as the *thin film approximation*. If not, absorption effects should be taken into account.[6, 11]

Following the acquisition, the raw datacubes were treated in Matlab in which a two window method [20] was used to fit the background radiation. The net counts for the L lines of Au, Ag and Pt were obtained by integrating over the signal characteristic peaks, after the background subtraction. The net counts measured for each particle are listed in Table S1-S3 along with the measured beam current.

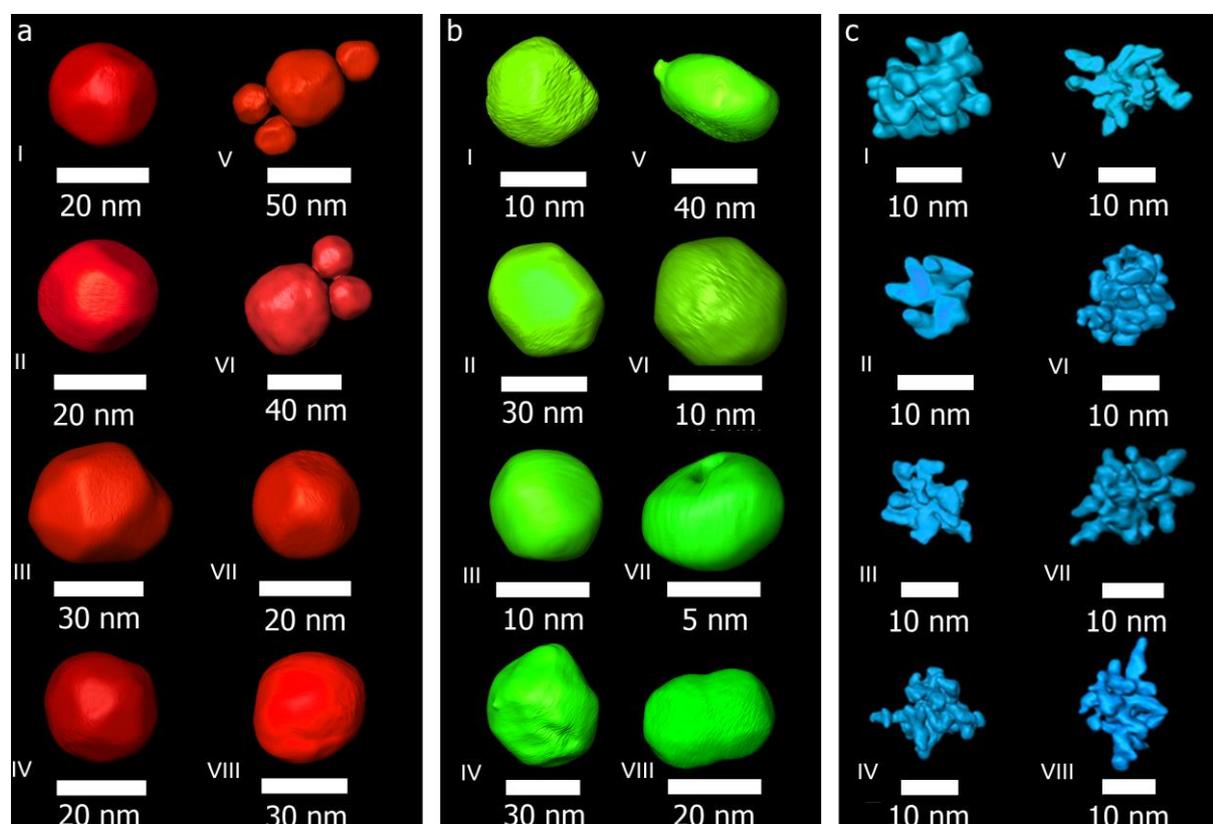


Figure 1: Renderings of the Au (a), Ag (b) and Pt (c) particles used for the determination of the ζ -factors.

For each particle, the ζ -factor is determined from equation 4 using the volume V measured by electron tomography and the intensity I measured by EDXS for the same particle. As

expected, a linear behavior is observed as demonstrated in Figure 2. The final values of the ζ -factors for Au, Ag and Pt for our experimental conditions are calculated through a weighted mean as described in [11] and found to be $\zeta_{\text{Au}} = 751 \pm 52 \text{ kg/m}^2$, $\zeta_{\text{Ag}} = 300 \pm 35 \text{ kg/m}^2$ and $\zeta_{\text{Pt}} = 724 \pm 50 \text{ kg/m}^2$. The methodology is explained in more detail in the Supporting Information. The values that we obtained for the ζ -factors cannot be compared directly with values reported in literature since the outcome of our approach depends on experimental parameters such as e.g. the holder, grid and tilt angle chosen. Nevertheless, ratios of the ζ -factors should be similar for different experimental settings.

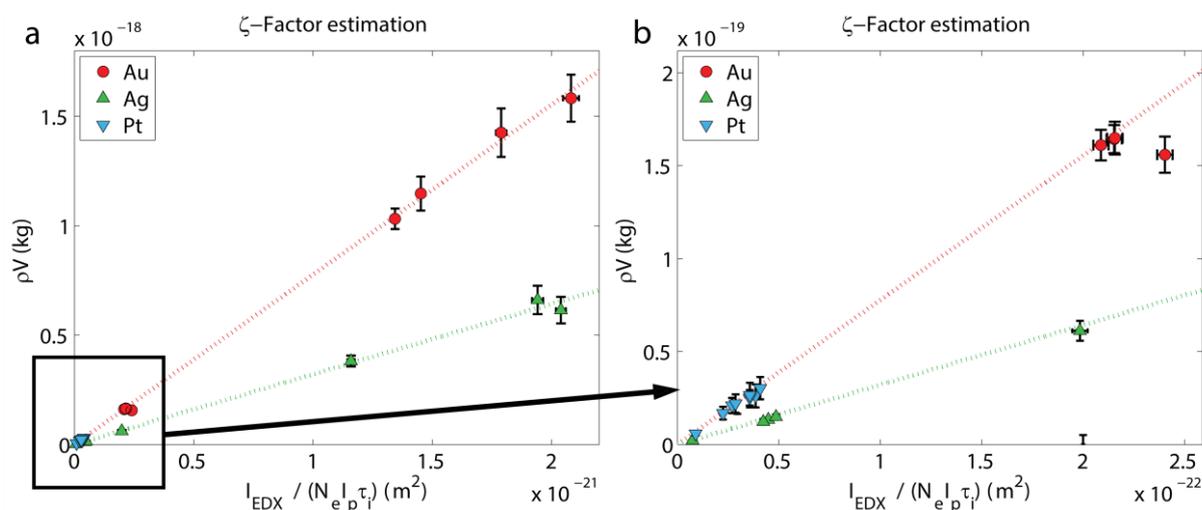


Figure 2: a) The linear relation is clearly shown by the plots. b) shows a magnification of the area close to the origin, where multiple data points are condensed due to the similar volumes of the particles. Error bars smaller than the markers are omitted.

3.2 Quantification of overall chemical compositions in hetero nanoparticles

To test the validity of the proposed methodology, the composition of a Au@Ag core-shell nanoparticle was quantified (Figure 3a). In a previous study, these particles were found to yield sharp interfaces without any alloying [21]. The outcome of the EDXS quantification based on our methodology will be compared to the volumes of the Au core and the Ag shell

obtained from an independent 3D HAADF-STEM reconstruction (Figure 3b), which we here consider as the ground truth. Quantification of the 3D HAADF-STEM reconstruction is relatively straightforward, based on the different intensities observed for Au and Ag. In this manner, the volumes were measured to be $247,450 \pm 37,118 \text{ nm}^3$ and $49,470 \pm 4,452 \text{ nm}^3$ for Ag and Au respectively. This corresponds to approximately 1.86 fg (femtograms) of Ag and 0.95 fg of Au and the weight concentrations estimated in this manner are found to be $C_{\text{Au-STEM}} = 0.65 \pm 0.05$ and $C_{\text{Ag-STEM}} = 0.35 \pm 0.05$.

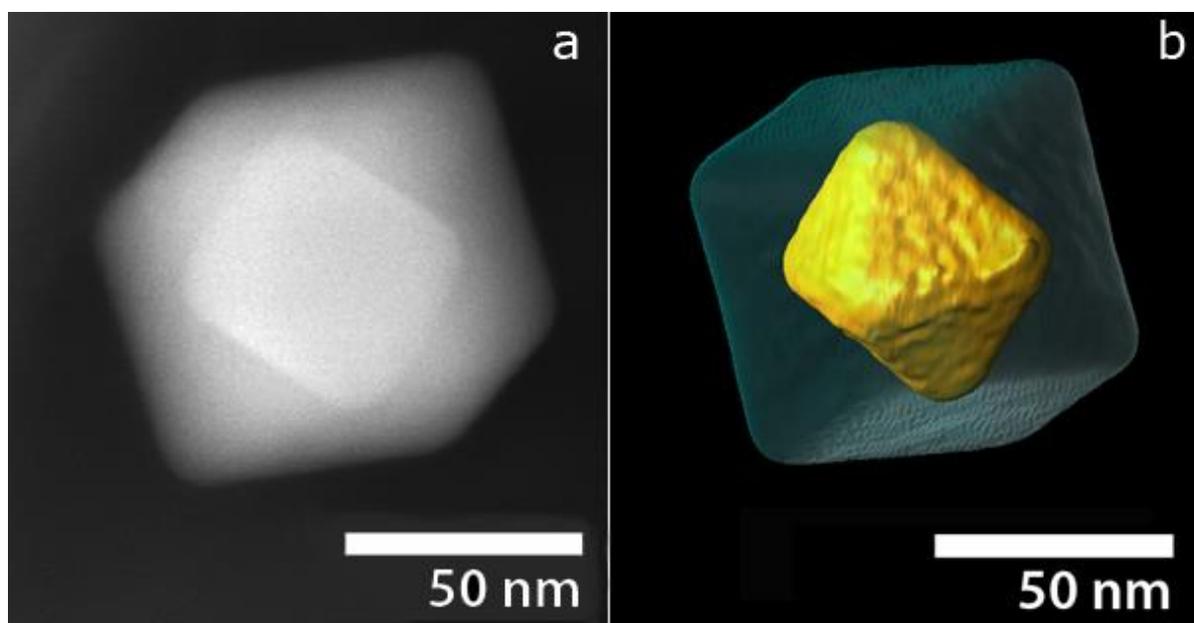


Figure 3: (a) HAADF STEM projection. (b) HAADF STEM tomography reconstruction rendering after segmentation of the core (Au) and shell (Ag).

In order to evaluate the reliability of the approach based on the ζ -factors, these values were compared to the quantified 2D EDXS data. An EDXS map was collected from the same particle for 120 s with a current of 258 pA at 120 kV and a tilt angle of -60° . The concentrations were determined using the measured ζ -factors and were found to be: $C_{\text{Au}} = 0.64 \pm 0.04$ and $C_{\text{Ag}} = 0.36 \pm 0.04$. These values are clearly in good agreement with the

quantification based on HAADF-STEM electron tomography. The same data was also quantified using the Cliff-Lorimer method, implemented in the available software (Bruker Esprit). The values obtained were $C_{\text{Ag}} = 0.73 \pm 0.22$ and $C_{\text{Au}} = 0.27 \pm 0.08$. From this comparison, we conclude that quantification using the modified ζ -factor approach is reliable and that the method can be used to investigate nanostructures for which it is difficult or even impossible to use HAADF-STEM tomography to determine the chemical concentrations of the elements present.

It should be mentioned, that the discrepancy with the quantification performed using Bruker Esprit is due to the calculated k-factor obtained by the software. Using a different theoretical model would lead to a different result.

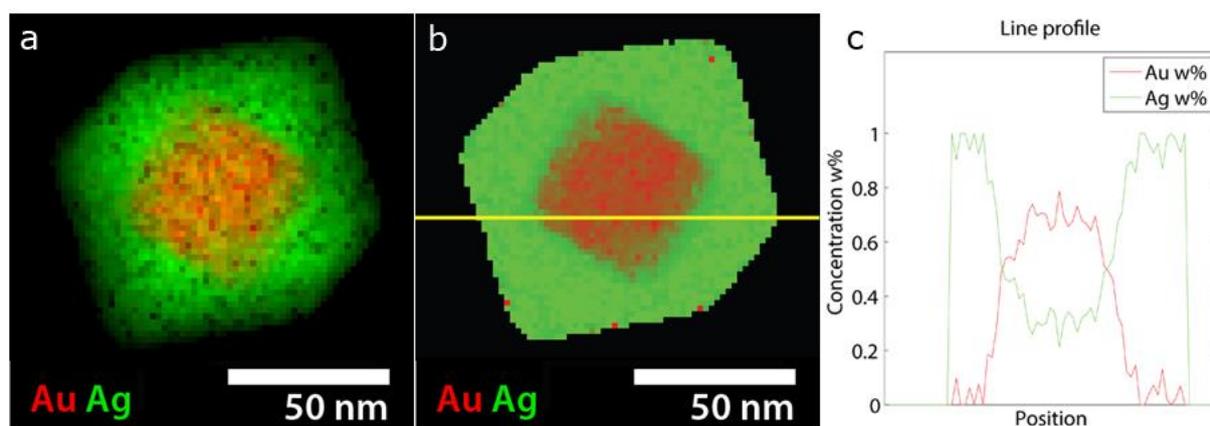


Figure 4: (a) EDXS map of the particle of Figure 4. (b) Quantified EDXS map. (c) Line profile through the quantified map (yellow line in (b)) showing the concentrations of Au and Ag in the projection direction.

3.3 Quantification of elemental maps in hetero nanoparticles

During the chemical analysis of nanoparticles by EDXS, the final goal is often to determine the distribution of the different elements over the particle. Such investigations are mostly

based on EDXS maps. These so-called “elemental” maps are obtained by analyzing the collected datacube pixel-by-pixel, fitting the background with a two window method and measuring the net counts for each element in the specified energy interval.[20] An example is provided in Figure 4a. After elemental maps are obtained, *quantified* maps can be calculated by applying eq. 5 in each pixel of the elemental map. The result, shown in Figure 4b, is a concentration map for each element with values ranging from 0 to 1. In this case, the HAADF-STEM image was used as a mask to define the boundaries of the particle and improve the visualization by suppressing any signal outside the particle. A line profile (indicated by the yellow line Figure 4b) is presented in Figure 4c to enable a more straightforward interpretation of the quantified data.

3.4. Application to Au-Pt heterostructures

Once the validity of our approach has been determined, we can apply the method to nanostructures for which HAADF-STEM fails to determine the chemical composition. For example, since Au and Pt have an atomic number Z equal to 79 and 78 respectively, no contrast difference is expected when using HAADF-STEM to investigate Au-Pt heterostructures. However, these structures are of great interest due to their catalytic activity [22-25]. We here investigated a Au-Pt hetero-nanostructure, shown in Figure 5a, that consists of spherical Au particles, grown on a platinum nanodendritic seed, yielding a core-satellite structure [25]. In order to quantify the chemical composition and the distribution of the different elements, we applied the ζ -factor method using the values for Au and Pt. In this manner, the overall concentration was measured to be $C_{\text{Au}} = 0.77 \pm 0.02$ and $C_{\text{Pt}} = 0.23 \pm 0.02$. Background subtraction and a peak deconvolution, implemented in Matlab, were applied to the EDXS data to separate the Au and Pt contributions to the signal, since the L peaks for Au and Pt overlap partially. A map representing the resulting Au and Pt counts is

shown in Figure 5b. Figure 5c, shows a quantified map from the same data, based on equation 5, which confirms the core-satellite structure with the Pt seed located at the center and pure Au particles surrounding it. The line profile in Figure 5d, shows the actual values of the wt% concentration of Pt and Au along the yellow line, and we can conclude that the Au particles around are pure Au particles and no alloying with Pt is observed.

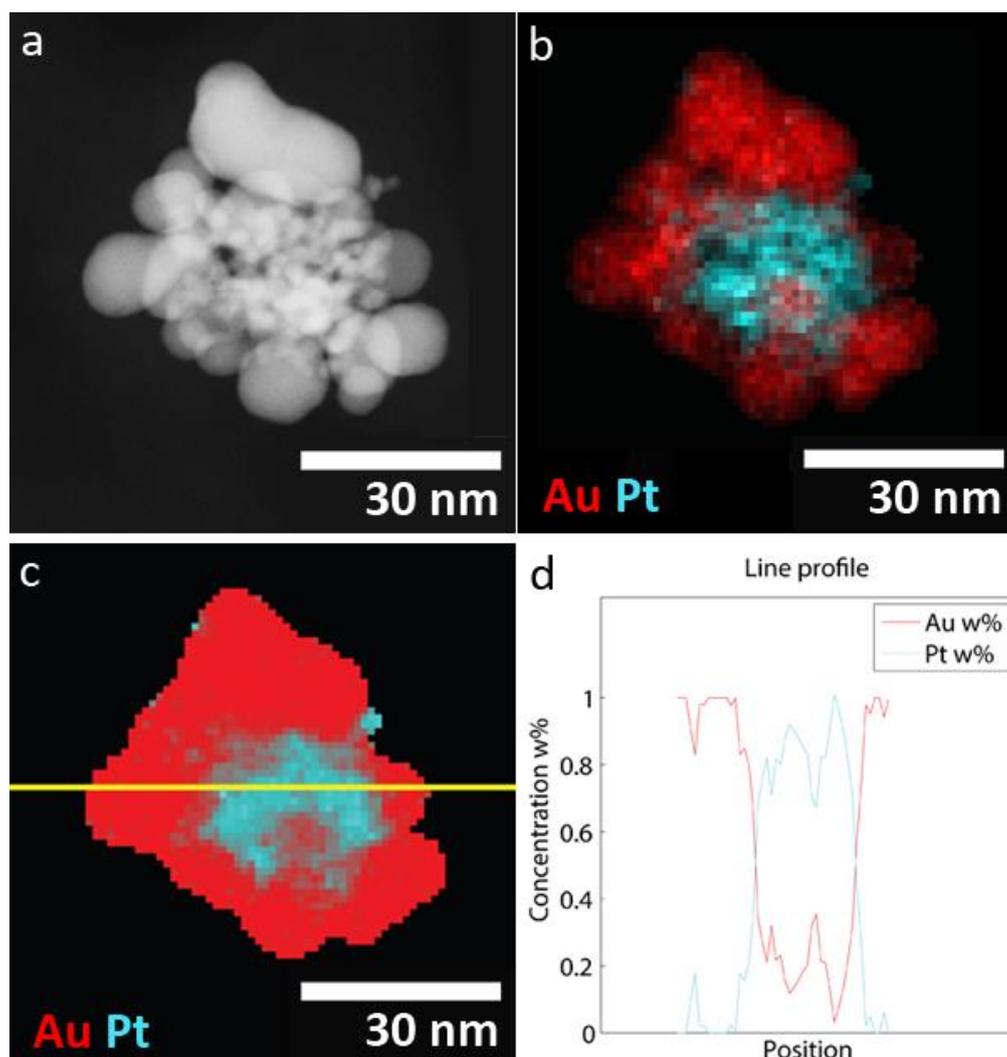


Figure 5: (a) HAADF STEM image. (b) EDXS elemental map. (c) Quantified EDXS map. (d) Line profile through the quantified map (yellow line in (c)) showing the concentrations of Au and Pt in the projection direction.

4. Conclusions

In this paper we presented an alternative approach for the experimental determination of ζ -factors and subsequently quantified chemical compositions in nanoparticles. The methodology is based on the determination of ζ -factors from pure element nanoparticles, using a combination of electron tomography and EDXS. In this manner, the thickness/volume of the sample can be measured in a reliable manner and systematic errors resulting from wrong estimations of sample thickness can be avoided. We demonstrated the accuracy of our quantification procedure by comparing our results to the outcome of a 3D HAADF-STEM reconstruction. It must be noted that the method we propose here is not restricted to bimetallic nanoparticles and can be applied in a straightforward manner to a broad range of hetero nanostructures. Furthermore, the limitation to obtain elemental distributions by HAADF-STEM tomography for samples containing similar atomic number Z elements can be overcome by extending the presented method to 3D EDXS.

Acknowledgements

The authors acknowledge financial support from the European Research Council (ERC Starting Grant # 335078-COLOURATOMS) and the European Union under the FP7 (Integrated Infrastructure Initiative N. 312483 - ESTEEM2).

The authors would also like to thank Luis M. Liz-Marzán, Ana Sánchez-Iglesias, Stefanos Mourdikoudis and Cristina Fernández-López for sample provision and useful discussions.

References

- [1] D. Wang, Y. Li, Bimetallic nanocrystals: liquid-phase synthesis and catalytic applications, *Advanced Materials*, 23 (2011) 1044-1060.
- [2] G. Van Tendeloo, S. Bals, S. Van Aert, J. Verbeeck, D. Van Dyck, Advanced electron microscopy for advanced materials, *Advanced Materials*, 24 (2012) 5655-5675.
- [3] B. Goris, L. Polavarapu, S. Bals, G. Van Tendeloo, L.M. Liz-Marzán, Monitoring galvanic replacement through three-dimensional morphological and chemical mapping, *Nano letters*, 14 (2014) 3220-3226.
- [4] T.J. Slater, A. Macedo, S.L. Schroeder, M.G. Burke, P. O'Brien, P.H. Camargo, S.J. Haigh, Correlating catalytic activity of Ag–Au nanoparticles with 3D compositional variations, *Nano letters*, 14 (2014) 1921-1926.
- [5] A. Genc, L. Kovarik, M. Gu, H. Cheng, P. Plachinda, L. Pullan, B. Freitag, C. Wang, XEDS STEM tomography for 3D chemical characterization of nanoscale particles, *Ultramicroscopy*, 131 (2013) 24-32.
- [6] P. Burdet, Z. Saghi, A.N. Filippin, A. Borrás, P.A. Midgley, A novel 3D absorption correction method for quantitative EDX-STEM tomography, *Ultramicroscopy*, (2015).
- [7] P. Schlossmacher, D. Klenov, B. Freitag, H. Von Harrach, Enhanced detection sensitivity with a new windowless XEDS system for AEM based on silicon drift detector technology, *Microscopy today*, 18 (2010) 14-20.
- [8] S. Kawai, I. Onishi, T. Ishikawa, K. Yagi, T. Iwama, K. Miyatake, Y. Iwasawa, M. Matsushita, T. Kaneyama, Y. Kondo, A Double Silicon Drift Type Detector System for EDS with Ultrahigh Efficiency and Throughput for TEM, *Microscopy and Microanalysis*, 20 (2014) 1150-1151.
- [9] G. Cliff, G. Lorimer, The quantitative analysis of thin specimens, *Journal of Microscopy*, 103 (1975) 203-207.
- [10] Z. Horita, T. Sano, M. Nemoto, A new form of the extrapolation method for absorption correction in quantitative X-ray microanalysis with the analytical electron microscope, *Ultramicroscopy*, 35 (1991) 27-36.
- [11] M. Watanabe, D. Williams, The quantitative analysis of thin specimens: a review of progress from the Cliff-Lorimer to the new ζ -factor methods, *Journal of microscopy*, 221 (2006) 89-109.
- [12] D. Newbury, D. Williams, J. Goldstein, C. Fiori, Observation on the calculation of k AB factors for analytical electron microscopy. *Analytical Electron Microscopy— 1984*, in, San Francisco Press, San Francisco, CA, 1984.
- [13] J.R. Kremer, D.N. Mastrorade, J.R. McIntosh, Computer visualization of three-dimensional image data using IMOD, *Journal of structural biology*, 116 (1996) 71-76.
- [14] W.J. Palenstijn, K.J. Batenburg, J. Sijbers, Performance improvements for iterative electron tomography reconstruction using graphics processing units (GPUs), *Journal of structural biology*, 176 (2011) 250-253.
- [15] W.J. Palenstijn, K.J. Batenburg, J. Sijbers, The ASTRA tomography toolbox, in: 13th International Conference on Computational and Mathematical Methods in Science and Engineering. CMMSE, 2013.
- [16] W. van Aarle, W.J. Palenstijn, J. De Beenhouwer, T. Altantzis, S. Bals, K.J. Batenburg, J. Sijbers, The ASTRA Toolbox: A platform for advanced algorithm development in electron tomography, *Ultramicroscopy*, 157 (2015) 35-47.
- [17] T. Malis, S. Cheng, R. Egerton, EELS log-ratio technique for specimen-thickness measurement in the TEM, *Journal of electron microscopy technique*, 8 (1988) 193-200.

- [18] G. Kothleitner, W. Grogger, M. Dienstleder, F. Hofer, Linking TEM Analytical Spectroscopies for an Assumptionless Compositional Analysis, *Microscopy and Microanalysis*, 20 (2014) 678-686.
- [19] B.L. Henke, E.M. Gullikson, J.C. Davis, X-ray interactions: photoabsorption, scattering, transmission, and reflection at $E= 50\text{-}30,000$ eV, $Z= 1\text{-}92$, *Atomic data and nuclear data tables*, 54 (1993) 181-342.
- [20] D.B. Williams, C.B. Carter, *The transmission electron microscope*, Springer, 1996.
- [21] S. Bals, B. Goris, L.M. Liz-Marzán, G. Van Tendeloo, Three-Dimensional Characterization of Noble-Metal Nanoparticles and their Assemblies by Electron Tomography, *Angewandte Chemie International Edition*, 53 (2014) 10600-10610.
- [22] S. Zhou, K. McIlwrath, G. Jackson, B. Eichhorn, Enhanced CO tolerance for hydrogen activation in Au-Pt dendritic heteroaggregate nanostructures, *Journal of the American Chemical Society*, 128 (2006) 1780-1781.
- [23] J. Zeng, J. Yang, J.Y. Lee, W. Zhou, Preparation of carbon-supported core-shell Au-Pt nanoparticles for methanol oxidation reaction: the promotional effect of the Au core, *The Journal of Physical Chemistry B*, 110 (2006) 24606-24611.
- [24] J. Sachtler, G. Somorjai, Influence of ensemble size on CO chemisorption and catalytic n-hexane conversion by Au-Pt (111) bimetallic single-crystal surfaces, *Journal of Catalysis*, 81 (1983) 77-94.
- [25] S. Mourdikoudis, M. Chirea, D. Zanaga, T. Altantzis, M. Mitrakas, S. Bals, L.M. Liz-Marzán, J. Pérez-Juste, I. Pastoriza-Santos, Governing the morphology of Pt–Au heteronanocrystals with improved electrocatalytic performance, *Nanoscale*, 7 (2015) 8739-8747.