Cite this: Nanoscale, 2011, 3, 3385

www.rsc.org/nanoscale

High resolution mapping of surface reduction in ceria nanoparticles

Stuart Turner, ** Sorin Lazar, ** Bert Freitag, ** Ricardo Egoavil, ** Johan Verbeeck, ** Stijn Put, ** Yvan Strauven** and Gustaaf Van Tendeloo**

Received 19th May 2011, Accepted 2nd June 2011 DOI: 10.1039/c1nr10510h

Downloaded by University of Pennsylvania Libraries on 12 April 2012 Published on 30 June 2011 on http://pubs.rsc.org | doi:10.1039/C1NR10510H

Surface reduction of ceria nano octahedra with predominant {111} and {100} type surfaces is studied using a combination of aberration-corrected Transmission Electron Microscopy (TEM) and spatially resolved electron energy-loss spectroscopy (EELS) at high energy resolution and atomic spatial resolution. The valency of cerium ions at the surface of the nanoparticles is mapped using the fine structure of the Ce $M_{4,5}$ edge as a fingerprint. The valency of the surface cerium ions is found to change from 4+ to 3+ owing to oxygen deficiency (vacancies) close to the surface. The thickness of this Ce³⁺ shell is measured using atomic-resolution Scanning Transmission Electron Microscopy (STEM)-EELS mapping over a {111} surface (the predominant facet for this ceria morphology), {111} type surface island steps and {100} terminating planes. For the {111} facets and for {111} surface islands, the reduction shell is found to extend over a single fully reduced surface plane and 1–2 underlying mixed valency planes. For the {100} facets the reduction shell extends over a larger area of 5–6 oxygen vacancy-rich planes. This finding provides a plausible explanation for the higher catalytic activity of the {100} surface facets in ceria.

Introduction

Ceria nanoparticles are of great interest for several branches of materials science. Ceria can be used as a new generation threeway catalyst to remove NO_x , CO, and other unreacted hydrocarbons from exhaust fumes.¹⁻³ Mixing ceria particles with diesel is known to dramatically reduce soot in diesel exhausts.⁴ Ceria can also be used in microelectronics and in solid-state fuel cells because of its high ionic conductivity.^{5,6} Its UV-blocking characteristics also make it of interest to the cosmetics industry for use in sun-care products.⁷ The main use of ceria particles however is the chemical-mechanical polishing of silicate glasses, a process which is now used to finish LCD displays.⁸

Almost all these uses of nano ceria depend upon the ease with which the ceria particles are reduced and oxidized. This easy oxidation and reduction (surface catalytic activity) in CeO_{2-x} is known to have several key origins linked to switching between Ce^{4+} and Ce^{3+} oxidation states and the possibility to absorb and release oxygen by inducing oxygen vacancies close to the surface. However, the extent of the reduced shell in cerium oxide nanoparticles has never been directly imaged and has only been measured indirectly from an averaged sample.⁹

^cDepartment of Materials Science and Engineering, McMaster University, L8S 4L7 Hamilton, Canada

^dUmicore Group R&D, Kasteelstraat 7, B-2250 Olen, Belgium

Previously it has been shown using EELS that particles of intermediate sizes (50 to 250 nm) possessed a Ce³⁺ surface shell of several nanometers thick, facilitating easy reduction and oxidation at the surface.¹⁰ Torbrügge *et al.* imaged extensive subsurface oxygen vacancies up to two atomic planes below the (111) ceria surface using atomic resolution dynamic force microscopy.¹¹ Zhang *et al.*¹² showed that small ceria nanoparticles (<20 nm) undergo a significant lattice expansion, and they linked this expansion to the increased presence of oxygen vacancies at the ceria surface. Density functional theory calculations also have shown that surface truncation corners, kinks and steps at material surfaces are highly reactive sites, where reduced Ce³⁺ ions are expected to be present.^{13,14}

In this work, the surface of commercial CeO_{2-x} nanoparticles is studied in detail using a combination of aberration-corrected TEM to study structure, morphology, truncation and surface steps of the particles, and spatially resolved EELS at high energy resolution and atomic spatial resolution to determine the presence and thickness of the reduced Ce^{3+} shell. The oxidation state of cerium is identified by comparing the measured cerium $M_{4,5}$ edge fine structure to known Ce^{3+} and Ce^{4+} references at a high energy resolution.

Experimental section

Ceria nanoparticles

The ceria particles are nanograin[®], gas-phase produced nano CeO_{2-x} from Umicore NV/SA, Belgium. The material was prepared for TEM by dispersing the powder in ethanol and

^aEMAT, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium. E-mail: stuart.turner@ua.ac.be

^bFEI Company, Europe NanoPort, Achtseweg Noord 5, 5651 GG Eindhoven, The Netherlands

dropping the dispersion onto a holey carbon grid. CeO_2 and CeF_3 references were purchased from Sigma Aldrich.

(Scanning) transmission electron microscopy and electron energy-loss spectroscopy

50 nm

High Resolution High Angle Annular Dark Field (HR-HAADF)-STEM and STEM-EELS experiments were carried out at EMAT on a FEI Titan 80–300 "cubed" microscope fitted with an aberration-corrector for the imaging lens and another for the probe forming lens as well as a monochromator, operated at 120 kV to acquire the data in Fig. 4, Fig. 6 & Fig. 7 and 300 kV for Fig. 1b, Fig. 3 & Fig. 5. Spectroscopy experiments were

{111}

(1 - 11)

{100}

{111}

{111}

[011]

5 nm Fig. 1 TEM and HAADF-STEM images of the studied ceria nanoparticles: (a) The size of the particles averages approximately 30 nm. The crystal structure is the same cubic fluorite structure as bulk CeO₂, as evidenced by the ED ring pattern. Inset: Truncated octahedron model with predominant {111} and {100} type faces. (b) A typical high resolution STEM image of a ceria particle in [011] zone axis. The particle has a truncated octahedral morphology. Inset: model oriented along the [011] zone axis.

(100)

(11-1)

performed on a GIF-QUANTUM spectrometer with the monochromator excited to provide 250 meV energy resolution. The STEM convergence semi-angle used was ~18.5 mrad, providing a probe size of ~15 Å at 120 kV and ~10 Å at 300 kV. The collection semi-angle β was ~80 mrad at 120 kV and ~50 mrad at 300 kV. Proper beam intensity (approx. 60 pA), pixel sampling (0.5 Å/pixel) and dwell time (0.05 s/pixel) were chosen to maximize the EELS signal while ensuring minimal ionization damage. For HAADF-STEM imaging at 300 kV (Fig. 1), an inner collection semi-angle β of 50 mrad was used.

To model the spectra in the EELSMODEL¹⁵ software package, a power-law background AE^{-r} was combined with two cerium $M_{4,5}$ edge reference spectra (for Ce³⁺ and Ce⁴⁺). The intensities of the two reference components as well as the power law background were fitted to the acquired spectra, and the signal intensities were plotted to generate the Ce³⁺ and Ce⁴⁺ maps. The model was fitted using a Levenberg-Marquardt method for Poisson statistics.

Aberration (Cs) corrected high resolution transmission electron microscopy (Fig. 2) was performed on a FEI Titan 80–300 microscope operated at 300 kV (FEI Europe NanoPort - Eindhoven, The Netherlands). Electron diffraction (ED) and bright field TEM (Fig. 1a) experiments were performed in a JEOL 4000EX microscope, operated at 400 kV.

Multiplet calculations

Multiplet calculations of Ce 3d core-level spectra were performed using a version of Robert Cowan's code, as implemented by F. De Groot.¹⁶ The energy-loss near edge structure (ELNES) spectra of Ce³⁺ in CeF₃ were simulated with the 4f¹ ground state. Owing to the strong Ce 4f-O 2p hybridization in CeO₂, charge transfer effects were included to simulate the ELNES spectra of Ce⁴⁺. The initial and final states were described as mixtures of 4f⁰ + 4f¹L and 3d⁹4f¹ + 3d⁹4f²L configurations, where L stands



Fig. 2 Ceria surface structure: (a) A typical ceria nanoparticle in [011] zone axis orientation, the predominant surfaces are $\{111\}$ type, the truncation forms $\{100\}$ type facets. (b) Kinks and $\{100\}$ type truncations are widespread. Minimal $\{110\}$ type truncations are present. (c) A $\{100\}$ type truncation at a twin boundary between particles. An $\{111\}$ surface island is also visible. (d) A surface island on the $\{111\}$ plane of the nanoparticle.

(b)

for a hole in the valence band. To fit the experimental Ce $M_{4,5}$ ELNES spectra for both Ce³⁺ and Ce⁴⁺, the 4f Slater-Condon parameters were reduced to 79% and the 3d spin–orbit parameters to 98% of their Hartree–Fock values.

The charge transfer parameters for Ce⁴⁺ were the following; an energy difference of 2 eV between the 4f⁰ and 4f¹ configurations of the ground state and 1 eV between the 4f¹ and 4f² configurations of the excited state and a mixing strength of 0.30 and 0.85 for the ground and excited states, respectively. The ligand-hole width was 2 eV. Crystal field effects were not included since they are typically negligible for 4f systems.¹⁷ Lifetime broadening was taken into account by using Lorentzians with FWHM of 0.40 eV and 0.65 eV for the M₅ and M₄ edges respectively in the Ce³⁺ and Ce⁴⁺ spectra. Gaussian broadening due to instrumental effects was set at 0.25 eV.

Results

Structure, surface structure and morphology

A typical bright field TEM image of the ceria nanoparticles is shown in Fig. 1a. The particles, which are sharply faceted, have an average diameter of approximately 30 nm. The corresponding electron diffraction ring pattern evidences that the crystal structure is the same cubic fluorite structure as bulk CeO₂ (lattice parameter a = 5.41 Å, space group $Fm\bar{3}m$). No traces of other phases are detected. In Fig. 1b a high resolution HAADF-STEM image of a ceria particle is displayed along the [011] zone axis. The terminating facets of the crystal are {111} and {100} type, {110} type facets and lower-index facets are not present in any significant amount.

This presence of mainly {111} and {100} type surface facets is typical for a truncated octahedral morphology, which is often encountered in nanoparticles with cubic crystal structures.^{18,19} A morphology model is displayed as an inset in Fig. 1a. For clarity, in Fig. 1b the model is shown projected along the [011] zone axis, *i.e.* the same orientation as the HAADF-STEM image in Fig. 1b.

Interesting aspects of the surface of the ceria nanoparticles are highlighted in the high resolution images in Fig. 2. In Fig. 2a, a ceria particle is imaged along the [011] zone axis orientation (as evidenced by the inset FFT pattern). In Fig. 2b, an enlarged area of 2a is displayed. Surface steps and kinks are present, and at the interface with the ceria particle to the right, the atoms form a {100} type surface. This same {100} type arrangement is visible at the interface between the same two particles in Fig. 2c. Several surface islands are visibly present along the {111} surfaces of the particle in Fig. 2c and Fig. 2d.

Surface reduction shell

The ELNES of rare-earth metals is known to be a fingerprint for their valency.²⁰ In order to be able to map the cerium valency in the ceria nanoparticles EELS spectra containing the cerium $M_{4,5}$ edge were acquired at high energy resolution making use of a monochromator in the microscope.²¹ The spectra were subsequently compared to simulated $M_{4,5}$ edge spectra from multiplet calculations (Ce³⁺ from CeF₃ and Ce⁴⁺ from CeO₂) as well as high resolution EELS spectra acquired from bulk CeO₂ and CeF₃ references.

In a first experiment, the cerium $M_{4,5}$ edge spectrum was acquired from nanoparticles of approximately 4, 30 and 60 nm diameter at high energy resolution (~250 meV FWHM). The three spectra are displayed in Fig. 3c, together with the simulated and experimental Ce³⁺ and Ce⁴⁺ references. The ELNES for the largest nanoparticle is nearly identical to the ELNES of Ce⁴⁺, *i.e.* the value for "bulk" CeO₂. However, the smaller nanoparticles show clear signatures typical of Ce³⁺. In fact, the spectrum obtained from the 4 nm particle shows only a minimal Ce⁴⁺ contribution (visible from the features at 889 eV and 907 eV) and is otherwise highly similar to the Ce³⁺ fine structure. Since the smallest nanoparticles show almost solely Ce³⁺ signatures, and the larger particles show more Ce⁴⁺ as their size evolves to "bulk" sizes, it is likely that the reduction of cerium in the smallest nanoparticles is indeed a surface effect.

In Fig. 4, a whole 40 nm nanoparticle is scanned to visualize the reduction shell and to gain insight into its homogeneity. In order to do so, a 60*47 pixel spectrum image (SI – indicated by the white rectangle) was acquired from the particle using spatially resolved EELS – incorporating only the (fine structure of the) cerium $M_{4,5}$ edge in each individual spectrum. In each pixel, the Ce $M_{4,5}$ edge is assumed to be a linear combination of the Ce³⁺ and Ce⁴⁺ signals. To be able to map the individual signals, the spectra were fitted to the Ce³⁺ and Ce⁴⁺ reference spectra using the EELSMODEL software package;^{15,22} the



Fig. 3 *EELS spectroscopy of individual nanoparticles*: (a) & (b) Simulated and experimental Ce⁴⁺ (from bulk CeO₂) and Ce³⁺ (from CeF₃) M_{4,5} edge fine structures. (c) Ce M_{4,5} edge ELNES signatures from a 4 nm (red), 30 nm (black) and 60 nm (green) nanoparticle. Even though all nanoparticles retain the CeO₂ crystal structure, nearly all cerium ions in the smallest 4 nm particle are Ce³⁺.



Fig. 4 Low magnification surface reduction mapping: (a) HAADF-STEM survey image showing the scanned particles and the 60^{*47} pixel SI scan region. (b) Ce⁴⁺map (c) Ce³⁺map (d) Color map with Ce³⁺(Red) and Ce⁴⁺ (Green). Notice that smaller particles on the right are almost fully reduced.

resulting maps for Ce⁴⁺ and Ce³⁺ are displayed in Fig. 4b and 4c respectively.

A color map overlaying the Ce³⁺ and Ce⁴⁺ maps is shown in Fig. 4d. It is immediately apparent that the surface reduction shell is present over the whole particle surface. At its thinnest, the Ce³⁺ shell appears to extend over approximately 2 nm. Where the particle is thin along the direction of the beam (lower HAADF signal) – the shell appears to extend over a larger area. Smaller particles (~ 5 nm) on the right hand side appear to be predominantly in a reduced state. However, particle orientation and thickness play a major role for a quantitative evaluation of the particle reduction shell. As the scanned particle is not in zone axis orientation the surface planes of the particle are not scanned edge-on, possibly leading to misinterpretation. In order to be able to quantify the shell thickness and understand the influence of the surface type on the reduction shell, similar scans were performed on particles in zone axis orientation using smaller scan steps.

In Fig. 5, a (100) truncated surface is scanned using the same technique as for Fig.4. A 3*36 pixel SI was acquired from vacuum into the nanoparticle, oriented along the [011] zone axis orientation. The summed Ce $M_{4,5}$ ELNES signatures from the 8 regions (A–H) indicated in Fig. 5a are displayed in Fig. 5b. From the fine structure signatures it is clear that at the (100) surface all Ce ions are in a reduced state. Position A – which corresponds to the summed spectra from the 3rd, 4th and 5th atomic planes from the surface – still consists of 98% Ce³⁺ signal. As the thickness of the particle increases the "bulk" Ce⁴⁺ signal increases linearly, in good agreement with a thin surface layer of Ce³⁺ on the top and bottom {111} type surface.

To quantify the thickness of the reduction shell on the {111} facets down to the atomic level a typical (111) particle surface was investigated, with the scanned particle being oriented along the [011] zone axis. In this orientation the (111) facet can be scanned edge-on; thickness effects like those encountered scanning over the (100) truncation in Fig. 5 are minimal, making the



Fig. 5 (100) surface truncation scan profile: (a) HAADF-STEM survey image showing the (100) surface truncation and the 3*36 pixel SI scan region. (b) Averaged Ce $M_{4,5}$ spectra from regions A–H (3*3 pixels) indicated on the survey image together with reference spectra for Ce³⁺ and Ce⁴⁺. The fitted weight of Ce³⁺ is given for each spectrum.

thickness of the reduction layer easy to interpret. Fig. 6a shows a high resolution HAADF-STEM image of the scanned (111) surface, with the scan region indicated by the white rectangle. Once again, the $M_{4,5}$ ELNES structures were fitted to the 3+ and 4+ reference spectra, yielding the maps for Ce⁴⁺ and Ce³⁺ in Fig. 6b and 6c respectively.

Interestingly, the atomic resolution information in the survey image is carried through to the valency maps, confirming the extreme resolution of this technique. It is obvious from the Ce^{4+} map that the top 2–3 surface planes contain a lower amount of Ce^{4+} . The top layer appears to contain no cerium in the 4+ state, while the second and third atomic layers are mixed 3+/4+ layers. This is also apparent from the 3+ map; the top layer is fully reduced, whilst the second and third layers are mixed-valency layers. The color map in Fig. 6d clearly evidences this.



Fig. 6 Atomic resolution (111) surface spectrum imaging: (a) HAADF-STEM survey image showing the (111) surface and the 24*59 pixel SI scan region. (b) Ce^{4+} map (c) Ce^{3+} map (d) Color map with Ce^{3+} (Red) and Ce^{4+} (Green).

A second example of this atomic resolution valency mapping is given in Fig. 7. Here, a (111) surface with a surface step and island is studied. Again, valency maps are generated using the EELSMODEL fitting procedure. The results confirm those in Fig. 6; the top atomic layer is almost fully reduced, whilst the underlying 1–2 atomic layers are intermixed. It is therefore also clear why these surface kinks have been identified as catalytically active sites; species can be trapped at the step, and are then surrounded by an oxygen-vacancy-rich environment.

Discussion

Ceria-based materials, especially nanopowders, are important for their surface redox capabilities and their general catalytic activity. Their surface redox capability possibly incorporates switching between Ce^{4+} and Ce^{3+} oxidation states through an ability to absorb and release oxygen by generating oxygen vacancies in the ceria lattice. The gas-phase method used to synthesize the particles used for this work leads to nanoparticles with a well-defined, truncated octahedral shape – as evidenced by the images in Fig. 1. The surfaces are rich in islands and steps (see Fig. 2) – ideal for high catalytic activity.

Surface reduction in ceria abrasives and larger particles has already been demonstrated qualitatively using STEM-EELS,¹⁰ but a comprehensive study of layer thickness was never carried out. In nanoparticles the same effect has been studied using XPS/ XANES,⁹ where a surface content of 22% Ce³⁺ was measured in 10 nm size ceria nanoparticles.

To be able to map the surface reduction shell the fine structure of the cerium $M_{4,5}$ -edge was acquired using the spectrum imaging technique. The drastically improved energy resolution that can be obtained using a monochromator in the (S)TEM, provides spectra that are nearly identical to XANES spectra for Ce³⁺ and Ce⁴⁺ from literature,¹⁷ whilst allowing experiments to be carried out at high spatial resolution.^{21,23}

For all EELS experiments, the dwell times and beam current were adjusted to avoid beam damage to the particles. Even though ceria is known to be resistant to high electron beam currents,²⁴ the high resolution EELS data presented in Fig. 6 and 7 was acquired at a lowered acceleration voltage of 120kV, as atomic resolution spectroscopy of oxides at 300kV has been shown to be more prone to beam damage.²⁵ No change in HAADF-STEM intensity after acquisition was observed, suggesting the influence of the electron beam was minimal.



Fig. 7 Atomic resolution (111) surface step spectrum imaging: (a) HAADF-STEM survey image showing the (111) surface step and the 30*53 pixel SI scan region. (b) Ce^{4+} map (c) Ce^{3+} map (d) Color map with Ce^{3+} (Red) and Ce^{4+} (Green).

From the results in Fig. 3 and 4 it is clear that the thickness of the reduction shell is dependent upon several parameters. The size of the nanoparticle plays a major role; the smallest particles in the maps in Fig. 4 appear to be almost completely in the reduced state, whilst larger particles show only a thin surface shell. This is in good agreement with size dependant measurements in the literature.¹² However, the crystallographic type of ceria surface is also important.²⁶ Material morphology is of pivotal importance in interpreting the maps in projection, as is always the case for TEM and STEM. EELS data must therefore be obtained under a known crystallographic orientation in order to make a correct interpretation of the influence of the different surface types.

In Fig. 5, the [011] zone axis orientation of the particle allows the (100) surface truncation to be scanned edge-on. The spectra show that at the (100) surface the first 5–6 atomic layers are all in a reduced state, intermixing gradually sets in after 5–6 atomic planes. Further into the interior of the nanoparticle it becomes difficult to separate the thickness effect of the truncated octahedral particle (*i.e.* the reduction layer on the top and bottom {111} surfaces) from the effects of Ce³⁺ working its way into the bulk over the (100).

The situation is easier for the {111} surfaces and surface islands scanned in Fig. 6 and Fig. 7. The thickness variation over the scans is minimal so that (unlike the case in Fig. 5) the influence of the top and bottom surfaces remains approximately constant. By scanning the particle in sub-Å steps, atomic resolution valency maps could be generated; these showed that the reduction shell on the close-packed {111} surfaces extended over only 2–3 atomic planes. The fact that the reduction shell on the {111} type surfaces stretches over a smaller area is in good agreement with the observed lower catalytic activity of the {111} surfaces compared to {100} surfaces.^{26,27}

This type of atomic resolution valency mapping in 2D is very new. It has been used recently to distinguish between Mn columns with different valency in a Mn_3O_4 test sample,²⁸ but has never been used to examine such surface effects in nanoparticles. It promises to be a widely applicable, with a plethora of surface or core-shell effects being of great importance in many 0D nanoparticle, 1D nanorod or 2D layered systems.

Conclusions

The surface of CeO_{2-x} nanoparticles is studied in detail using a combination of aberration-corrected TEM and spatially resolved EELS at high energy resolution and atomic spatial resolution. The CeO_{2-x} nanoparticles are truncated octahedra with predominantly {111} and {100} type surface facets. The presence of surface islands is only detected only on {111} surfaces.

Using a monochromatic electron probe, the valency of cerium in the nanoparticles is mapped using the fine structure of the cerium $M_{4,5}$ edge as a fingerprint. The surface cerium ions are found to change from Ce^{4+} to Ce^{3+} owing to oxygen deficiency near to the surface of all nanoparticles. The surface reduction of cerium is mapped in large and small nanoparticles: in particles below ~ 5 nm in diameter cerium is found to be predominantly in the reduced Ce^{3+} state. The thickness of the Ce³⁺ shell has been measured using STEM-EELS mapping over a {100} and a {111} surface as well as at a surface island step. The reduction shell was found to extend over a fully reduced surface layer and 1–2 underlying mixed-valency atomic layers for the {111} surfaces and islands, but over a larger area of ~ 6 atomic planes of oxygen vacancy-rich layers for the {100} surfaces. This type of 2D atomic resolution valency mapping promises to be widely applicable to nanoparticles and other 1D and 2D systems, where surface or core-shell effects are of crucial importance.

Acknowledgements

This work was supported by funding from the European Research Council under the Seventh Framework Program (FP7), ERC grant $N^{\circ}246791 - COUNTATOMS$. S.T. gratefully acknowledges the financial support from the Fund for Scientific Research Flanders (FWO).

References

- 1 J. Kaspar, P. Fornasiero and M. Graziani, *Catal. Today*, 1999, **50**, 285–298.
- 2 E. Aneggi, M. Boaro, C. de Leitenburg, G. Dolcetti and A. Trovarelli, J. Alloys Compd., 2006, 408, 1096–1102.
- 3 A. Trovarelli, C. de Leitenburg, M. Boaro and G. Dolcetti, *Catal. Today*, 1999, **50**, 353–367.
- 4 A. Aneggi, C. de Leitenburg, G. Dolcetti and A. Trovarelli, *Catal. Today*, 2006, **114**, 40–47.
- 5 M. Mogensen, N. M. Sammes and G. A. Tompsett, *Solid State Ionics*, 2000, **129**, 63–94.
- 6 B. C. H. Steele and A. Heinzel, Nature, 2001, 414, 345-352.
- 7 L. X. Yin, Y. Q. Wang, G. S. Pang, Y. Koltypin and A. Gedanken, J. Colloid Interface Sci., 2002, 246, 78–84.
- 8 T. Katoh, H. G. Kang, U. Paik and J. G. Park, Jpn. J. Appl. Phys., Part 1, 2003, 42, 1150-1153.

- 9 F. Zhang, P. Wang, J. Koberstein, S. Khalid and S. W. Chan, Surf. Sci., 2004, 563, 74–82.
- 10 S. R. Gilliss, J. Bentley and C. B. Carter, Appl. Surf. Sci., 2005, 241, 61–67.
- 11 S. Torbrugge, M. Reichling, A. Ishiyama, S. Morita and O. Custance, *Phys. Rev. Lett.*, 2007, 99.
- 12 F. Zhang, S. W. Chan, J. E. Spanier, E. Apak, Q. Jin, R. D. Robinson and I. P. Herman, *Appl. Phys. Lett.*, 2002, **80**, 127–129.
- 13 M. M. Branda, C. Loschen, K. M. Neyman and F. Illas, J. Phys. Chem. C, 2008, 112, 17643–17651.
- 14 C. Loschen, A. Migani, S. T. Bromley, F. Illas and K. M. Neyman, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5730–5738.
- 15 This program can be downloaded from www.eelsmodel.ua.ac.be.
- 16 F. De Groot and A. Kotani, Core level spectroscopy of solids. Advances in Condensed Matter Science., CRC Press, Boca Raton FL, 2008.
- 17 S. O. Kucheyev, B. J. Clapsaddle, Y. M. Wang, T. van Buuren and A. V. Hamza, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, 76.
- 18 Characterization of nanophase materials, ed. Z. L. Wang, Wiley-VCH Verlag Gmbh, Weinheim, 2000.
- 19 Z. L. Wang and X. D. Feng, J. Phys. Chem. B, 2003, 107, 13563– 13566.
- 20 R. F. Egerton. *Electron energy-loss spectroscopy in the TEM*. Plenum Press, New York and London, 1996.
- 21 S. Lazar, G. A. Botton and H. W. Zandbergen, *Ultramicroscopy*, 2006, **106**, 1091–1103.
- 22 J. Verbeeck and S. Van Aert, Ultramicroscopy, 2004, 101, 207–224.
- 23 R. Erni, S. Lazar and N. D. Browning, *Ultramicroscopy*, 2008, 108, 270–276.
- 24 J. Bentley, S. R. Bentley, C. B. Carter, J. F. Al-Sharab, F. Cosandey, I. M. Anderson and P. J. Kotula, *EMAG-NANO 2005: Imaging, Analysis and Fabrication on the Nanoscale*, 2006, 26, 69–72.
- 25 G. A. Botton, S. Lazar and C. Dwyer, *Ultramicroscopy*, 2010, 110, 926–934.
- 26 K. Kaneko, K. Inoke, B. Freitag, A. B. Hundria, P. A. Midgley, T. W. Hansen, J. Zhang, S. Ohara and T. Aschiri, *Nano Lett.*, 2007, 7, 421–425.
- 27 T. X. T. Sayle, S. C. Parker and C. R. A. Catlow, Surf. Sci., 1994, 316, 329–336.
- 28 H. Tan, S. Turner, E. Yücelen, J. Verbeeck and G. Van Tendeloo, Submitted for publication.