Investigation of silica nanoparticles by Auger electron spectroscopy (AES)

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High-priority industrial nanomaterials like SiO$_2$, TiO$_2$, and Ag are being characterized on a systematic basis within the framework of the EU FP7 research project NanoValid. Silica nanoparticles from an industrial source have been analyzed by Auger electron spectroscopy. Point, line, and map spectra were collected. Material specific and methodological aspects causing the special course of Auger line scan signals will be discussed. Copyright © 2014 John Wiley & Sons, Ltd.

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Introduction

By now, a huge range of nanomaterials can be found in consumer and technological products. Recent progress in nanotechnology development has been made in the fields of antimicrobial agents and biosensors. The manifold industrial applications lead to a higher release of nanoscaled chemicals to the environment and therefore rising human exposure. On the other hand, there is a lack of standard toxicological and physicochemical characterization methods for evaluating and managing the risk of engineered nanoparticles.

High-priority industrial nanomaterials like SiO$_2$, TiO$_2$, and Ag are being characterized on a systematic basis within the framework of the EU FP7 research project NanoValid where those issues are being addressed. One of the project tasks aims for establishing reference methods for physicochemical characterization and measurement. In this context, the identification of potential candidates with potential to be developed to a certified reference material is closely connected too. In this work, silica industrially manufactured by sol–gel synthesis has been investigated.

Investigating small surface structures typically scanning electron microscopy (SEM) or analytical electron microscopy (SEM/EDX) is applied. However, analyzing nanoparticles, the support material will be excited too caused by the electron beam penetrating down to the micrometer range. In lieu thereof, Auger electron spectroscopy (AES) with an information depth of only a few nanometers can be applied by analyzing the chemical composition of nanoparticle surfaces. Nanoparticles were analyzed by Auger spectra, line scans, and mappings. However, interpreting line scans material specific and methodological aspects have to be taken into account, which has been done earlier by Ito et al., too. Different effects causing a special course of line scan signals will be discussed.

Experimental

Silica was synthesized by sol–gel technique with an anionic surfactant and Tetraethylorthosilicate (TEOS) as starting materials. The sample powder was dispersed in ultra pure water by sonication. One microlitre was deposited on a conventional TEM carbon coated copper grid. In a first step, several particles have been imaged and preselected by SEM. SEM images are applied to guide subsequent AES measurements. A PHI 700 Auger Scanning Probe (ULVAC-Phi Inc.) equipped with a cylindrical mirror analyzer was used. AES of nanoparticles has to be carried out by applying a very small electron beam diameter getting a good lateral resolution of line scans and mappings. Therefore, Auger electrons were excited by a primary electron beam of 20 keV @ 1 nA or 10 nA and 25 keV @ 1 nA, respectively. The beam size was estimated to be 9 and 15 nm, respectively. The primary electron beam hit the surface in perpendicular direction avoiding effects of non symmetric intensity enhancements as described in Reference too. The relative energy resolution $\Delta E/E$ was 0.5%. Measuring Auger spectra of low noise by point analysis, a compromise had to be made between higher acquisition time (low beam current) and possible particle damage caused by the exciting electron beam.

Results

In the secondary electron image in Fig. 1, two particles identified each by a marker are presented; of which, AES survey spectra in Figs 2a and 2b are displayed. Analyzing dielectric materials like silica charging effects can appear that influences Auger electrons and consequently Auger spectra (remarkable shift to higher energies). Darker interiors and the brighter perimeters of the particles seen in Fig. 1 are hints for charging. However, looking on the spectra in Figs 2a and 2b, only small peak energy shifts appear (C KLL: 275 to 274.5 eV, O KLL: 510 to 515 eV, Si LVV: 96 to 95 eV, and Si KLL: 1621 to 1619 eV). The energy of the silicon peaks shifts towards lower energies but that of the oxygen peak towards higher energies with respect to values well known for SiO$_2$. Caps the report with a title that is different from the above.
Therefore, it can be concluded that negative charge flows off via the carbon film (refer also to Ito et al.\cite{5}).

Both particle surfaces consist of SiO$_2$ (silica). Furthermore, carbon, nitrogen, fluorine, and iron were detected, the latter three only at trace levels. Additionally, a small copper peak on particle 1 appeared in the spectrum.

Looking on the AES mappings in Figs 3a and 3b, oxygen and silicon signals originating from the silica particles appear. The AES mapping of carbon in Fig. 3c shows that the silica particles are covered by carbon contamination, and the higher carbon intensities measured in the surroundings of each particle originate from carbon contamination and the carbon film underneath. Oxygen seems to be almost uniformly distributed on the particle areas. However, for those two particles analyzed by point analyses (Fig. 1), some depletion in O KLL intensity becomes visible. Regarding the traces of iron, fluorine, and nitrogen observed in the spectra (Fig. 2), it can be assumed that these elements exist uniformly distributed in a contamination layer on top or in the bulk of the silica particles and do not originate from other particular matter adjacent to the silica particles. The

**Figure 1.** Secondary electron image providing an overview on silica particles distributed across a TEM grid showing two selected points used for chemical analysis by AES.

**Figure 2.** Selected point AES spectra taken from silica particles 1 (a) and 2 (b) shown in Fig. 1. \([\text{C KLL (275 eV), N KLL (389 eV), F KLL (659 eV), Fe L3M2,3 M2,3 (600 eV), Fe L3M2,3 M4,5 (654 eV), Fe L3M4,5 M4,5 (705 eV), Cu LMM (922 eV), Si LVV (96 eV), and Si KLL (1621 eV)}.\]
The copper signal in the spectrum in Fig. 2a is most probably caused by the copper grid.

In Figs 4a and 4b, line scans across another silica particle already shown in Fig. 1 (upper right corner) are presented. The Si KLL and O KLL intensities increase, reach a plateau, and decrease when the primary electron beam moves across the particle, whereas the C KLL signal changes in a reciprocal manner. Moreover, the signals of silicon and oxygen show a transition effect, that is, a slight increase when the transition region ‘projected particle edge’ – ‘carbon foil on TEM grid’ is crossed.

In Figs 5a, 5b, 6a, and 6b, line scans across other silica particles are presented. The silicon and oxygen line scans show principally
similar shapes. However, transition phenomena do not occur for the silicon and oxygen line scans shown in Fig. 5b but occur again in Fig. 6b. Considering the carbon line scans, quite different results are obtained. Whereas the carbon line scans shown in Figs 5b and 4b qualitatively coincide rather well, the carbon line scan in Fig. 6b shows strong signal oscillations when crossing the particle.

Line scans across a nanoscaled silica particle of about 25 nm diameter and a big silica particle of about 500 nm diameter are presented in Figs 7a, 7b, 8a, and 8b, respectively. The shapes of the oxygen and silicon line scans in Fig. 7b are similar to those shown in Figs 4b and 6b but are showing higher noise levels. The carbon line scan shows only a small dip at the left transition region ‘projected particle edge’ – ‘carbon foil on TEM grid support’. Results obtained with the big 500 nm particle, which shows a complex irregular morphology in the SEM picture, are displayed in Fig. 8a. Multiple transition effects are observed for the line scans for all three elements investigated.

**Discussion**

As mentioned earlier, the two particles analyzed by point measurements show dark spots in the center. The silicon peaks in selected point AES spectra shown in Figs 2a and 2b show a slight shift to lower peak energies. The Si KLL peaks resemble an oxide (Si$^{+4}$) like shape, but the peak shapes of the Si LVV signals tend to be typical for an elemental one (Si$^0$). Therefore, it can be concluded that these spots are caused by the exiting primary beam via electron beam stimulated bond breaking and oxygen desorption. Such beam damage has been discussed in the work of Tanuma et al.\[6\] for thin silicon oxide layers on a Si wafer, too. The information depth of the Si LVV peak is about 0.5 nm, and the one of the Si KLL peak is about 2 nm. Electron beam stimulated desorption of oxygen occurred in the top most atomic layers causing the elemental like peak shape of the Si LVV signal whereas the Si$^{+4}$ like KLL signal originates from less damaged deeper layers of the silica particle.

The valleys of the carbon signal at the particle rims in Figs 6b and 8b are caused by the particle that shields the carbon Auger electrons of the carbon film. The enhancement of the carbon signal at the projected particle rims cannot be attributed to higher carbon concentrations there but to well known edge and topographical effects.\[3–5\] This holds true also for the intensity enhancements of silicon and oxygen Auger emission at the projected particle rims in Figs 4b, 6b, 7b, and 8b. Auger electrons are not only excited within the spot area of the electron beam.
but also in regions next to it caused by electron scattering and/or backscattering. This results in several distortion effects in AES line scans like the intensity enhancement at rims observed in our lines cans. However, there are obviously cases where no transition effects are observed, for example, for line scans of all three elements in Fig. 5b or the carbon line scan shown in Fig. 4b. The latter observation could have different reasons:

(1) A ring of carbonaceous contamination material existing around the deposited particle levels out edge effects. Nanoparticles were deposited by drop casting onto the carbon film of the TEM grid support from water dispersion. Therefore, inevitably hydrocarbons were deposited, too.

(2) The particles are partially embedded in the carbon foil of the TEM grid (Fig. 5b).

Physical reasons for the artifacts are scatter processes of primary, secondary, and Auger electrons. These artifacts can strengthen, compensate, or weaken each other. Some methodological work has to be performed to explain these effects in detail, which are important for data interpretation of AES measurements of nanoparticles.

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References