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Influence of Sterilization on the Surface of Nanoparticles Studied with XPS / HAXPES in Comparison to SEM / EDS

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Nanosafety is becoming increasingly important as nanomaterials are widely used in industrial processes and consumer products. Nevertheless, there is still a lack of knowledge about the effects of nanomaterials on human health and on the environment. Therefore, to minimize the risk of exposure and nanohazard and to maximize nanosafety, there is a need for an easy way to find out whether nanoparticles are safe or not, without having to perform time-consuming experiments every time.
This is the aim of the project NanoSolveIT [1,5], in which the behavior of nanoparticles shall be derived from a database with standardized properties of nanomaterials. This nanomaterial fingerprint database leads in the end to the possibility of safe- and sustainable-by-design nanomaterial.

The key-element for these grouping and reading across approaches is the collection of standardized information about nanomaterials [2,3] in combination with modelling and simulations. In the REACH (registration, evaluation, authorization and restriction of chemicals) nanoforms [4] six physico-chemical properties of nanomaterials are considered as essential: particle size, particle shape, chemical composition, surface chemistry, crystallinity, and specific surface area. Here, the first four of them are discussed.

The measurement of the shape and size could be performed using scanning electron microscopy (SEM). For the chemical composition and the surface chemistry energy dispersive X-ray spectroscopy (EDS) and as a complementary method (hard) X-ray photoelectron spectroscopy (HAXPES/XPS) can be used, for an analysis of the surface of the whole nanoparticles. Whereas XPS provides information about the near surface region within the outermost 10 nm, HAXPES with a higher excitation energy allows insight into the outermost 30 nm. In contrast, EDS is bulk (µm)-sensitive. With this approach, a non-destructive analysis is possible to be applied to distinguish between the different regions of the nanoparticles.
For these experiments, a combined XPS/HAXPES spectrometer (*Quantes* from ULVAC-PHI) was used. This spectrometer gives us the possibility to measure XPS at 1486.6 eV (monochromatic Al Kα source) and HAXPES at 5414.9 eV (monochromatic Cr Kα source) on a sample at the same position. For the complete analysis, XPS and HAXPES data are related with those from SEM images and EDS. A *Supra 40* (Zeiss) SEM equipped with a *Quantax 400* (Bruker) SDD EDS spectrometer for elemental analysis was used here.

All these methods have been used to examine nanoparticles (PrometheanParticles, UK) of different composition which were treated differently by means of sterilization. Such sterilization step is usual, before studying the toxicity. On the other hand, the sterilization step is mostly not considered in establishing the structure-activity relationship of the nanomaterial.

As an example, $Co_{0.75}Fe_{2.25}O_4$ nanoparticles are shown here (see Fig. 1). The inhomogeneous sample is composed of ultrafine agglomerated nanoparticles with a size in the range of a few nanometers and larger nanoparticles with sizes of about 100-200 nm. The larger nanoparticles are mostly cube-shaped and show well-defined, straight edges. After sterilization, the SEM images already show that the shape of the particles

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deviates significantly from the ideal cube shape. The corners are rounder, and the particles are more irregularly shaped. Moreover, the particles are smaller overall. Therefore, a clear effect of the sterilization on the particle size and shape is observed.
The quantification with EDS was carried out at 15 kV acceleration voltage and shows clear differences to the quantification of the surface with XPS / HAXPES (see Fig. 2). The influence on the oxygen content can be expected, but even for Co and Fe clear changes can be observed for the various methods. These results reveal a restructuring of the nanoparticles during the sterilization. Thereby, the nanoparticles after both sterilization steps differ rather insignificantly between each other.

These results demonstrate the influence of sterilization on all investigated properties of the nanoparticles: size, shape, composition, and surface chemistry. Therefore, the restructuring of the nanoparticles due to the sterilization must be considered in the physico-chemical description of the particles for establishing reliable quantitative structure-activity relationships of the respective nanomaterial.

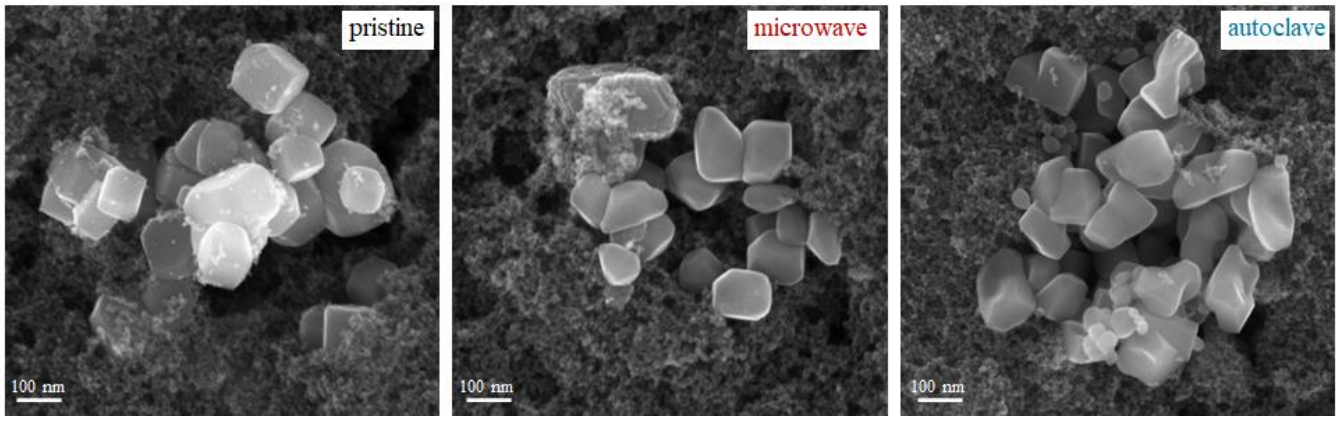

Figure 1. SEM images recorded with a secondary electron InLens detector at 10 kV beam voltage that show shape differences of differently treated $Co_{0.75}Fe_{2.25}O_4$ nanoparticles (pristine and sterilized either by microwave or by autoclave). The samples have been prepared as drop cast on silicon wafers.

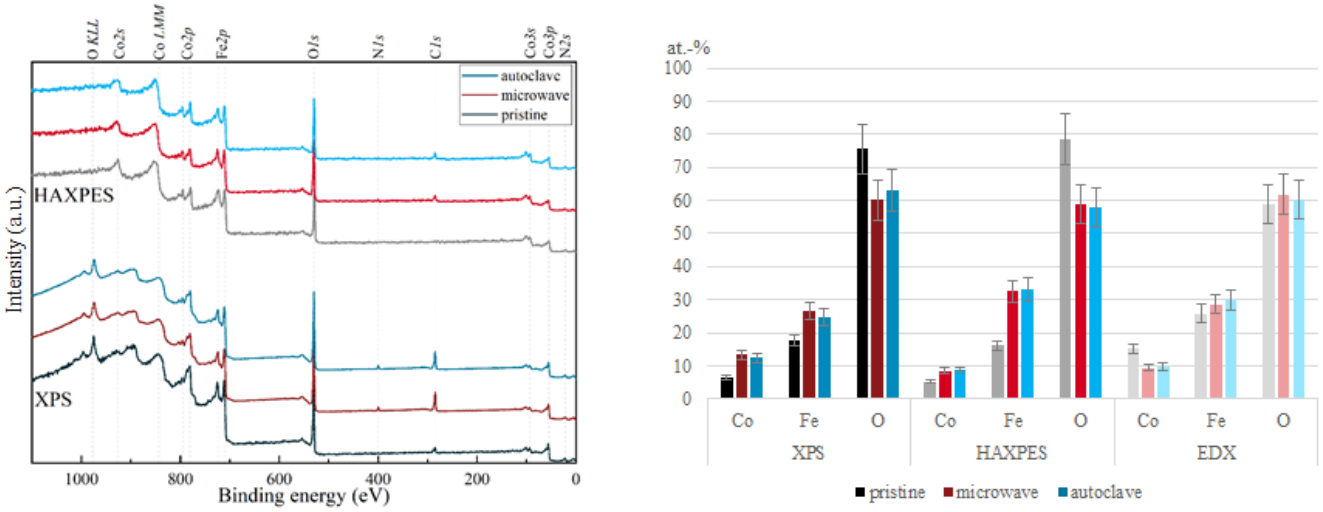

Figure 2. XPS survey spectra of $Co_{0.75}Fe_{2.25}O_4$ nanoparticles, which were obtained with 100 µm spot sizes at 25 W and 15 kV with an Al Kα source (XPS) and at 50 W and 20 kV with a Cr Kα source (HAXPES). The

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quantification results obtained with XPS, HAXPES and EDS for Co, Fe and O are shown on the right side. The stochiometric values are Co 10.7 at.-%, Fe 32.1 at.-%, and O 57.1 at.-%.

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[4] https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32018R1881 (accessed on February 15th, 2022)
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