Chemical Physics Letters 521 (2012) 91-97

Contents lists available at SciVerse ScienceDirect

# **Chemical Physics Letters**

journal homepage: www.elsevier.com/locate/cplett



# Effect of interparticle interactions on size determination of zirconia and silica based systems – A comparison of SAXS, DLS, BET, XRD and TEM

Silvia Pabisch<sup>a,b</sup>, Bernhard Feichtenschlager<sup>b</sup>, Guido Kickelbick<sup>c</sup>, Herwig Peterlik<sup>a,\*</sup>

<sup>a</sup> University of Vienna, Faculty of Physics, 1090 Vienna, Austria

<sup>b</sup> Vienna University of Technology, Institute of Materials Chemistry, 1060 Vienna, Austria

<sup>c</sup> Saarland University, Inorganic Solid State Chemistry, 66125 Saarbrücken, Germany

#### ARTICLE INFO

Article history: Received 28 September 2011 In final form 18 November 2011 Available online 25 November 2011

#### ABSTRACT

The aim of this work is a systematic comparison of size characterisation methods for two completely different model systems of oxide nanoparticles, i.e. amorphous spherical silica and anisotropic facet-shaped crystalline zirconia. Size and/or size distribution were determined in a wide range from 5 to 70 nm using small-angle X-ray scattering (SAXS), dynamic light scattering (DLS), nitrogen sorption (BET), X-ray diffraction (XRD) and transmission electron microscopy (TEM). A nearly perfect coincidence was observed only for SAXS and TEM for both types of particles. For zirconia nanoparticles considerable differences between different measurement methods were observed.

© 2011 Elsevier B.V. All rights reserved.

#### 1. Introduction

Nanoparticles are widely used in research and industry to tailor and improve materials properties, ranging from ceramics to polymers or biomedicine [1,2]. An increasingly important research field is the incorporation of nanoparticles into an organic matrix to create inorganic–organic nanocomposites as a promising class of novel materials [3,4]. Mechanical and physical properties of the resulting materials depend on the composition, shape, size and size distribution of the incorporated particles. Therefore, a precise determination of size and size distribution is a major challenge with regard to reproducibility and structure–property relations.

Among the methods used for the determination of the size and size distribution of nanoparticles, only a few are applicable in various chemical environments, i.e. small-angle X-ray scattering (SAXS) and dynamic light scattering (DLS). One particular advantage of SAXS is that it can be used to analyse dispersions as well as powders or solids, whereas DLS is limited only to dilute solutions. Comparing SAXS with an image-guided method like transmission electron microscopy (TEM), SAXS benefits from a higher statistical quality in the size distribution determination within one measurement. Additionally, no high vacuum is required, which limits the samples many times to solid state samples [5]. On the other hand, TEM has its specific benefits as it delivers direct images and local information on size and shape of nanoparticles. Therefore, these two techniques are complementary and combining both methods can lead to superior information with regard to shape

\* Corresponding author. *E-mail address:* herwig.peterlik@univie.ac.at (H. Peterlik). and size of nanoparticles in dispersions or powders [6]. An example for such combined studies is the kinetics of silica nanoparticle formation in various suspensions [7,8]. Other types of particles investigated by SAXS, DLS and TEM were surface functionalized gold nanoparticles [9] and shell crosslinked nanoparticles [10]. These works further support the view that comprehensive information on particle size and shape require the use of more than one characterisation technique.

A less common technique to obtain a particle size distribution is the analysis with nitrogen sorption. The evaluation according to BET theory (Brunauer-Emmet-Teller) [11] allows to obtain information on the size of non-agglomerated and dense particles [12,13]. In many of the cited studies a good agreement between the different measurement techniques was found in particular for silica nanoparticles. Different to the high number of publications investigating silica, much less information is available for other oxides such as ZrO<sub>2</sub> nanoparticles. For this type of particles, DLS showed the stability of the aqueous suspension for several days and supplementary measurements by TEM and SAXS were performed to prove the structural composition of the ZrO<sub>2</sub> nanopowder [14]. The increase in size in dependence on the increasing calcination temperature was investigated for chemically coprecipitated zirconia powders with TEM, XRD, BET and SAXS [15]. As in most of the previous studies only one type of material was investigated, the idea of this Letter is to systematically compare a large number of characterisation methods (SAXS, DLS, BET, XRD and TEM) in detail for two structurally completely different systems, one being amorphous spherical SiO<sub>2</sub> and the other crystalline irregularly shaped ZrO<sub>2</sub>. The particles were synthesized under varying processing conditions to cover a wide size range from 5 to 70 nm.

<sup>0009-2614/\$ -</sup> see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.cplett.2011.11.049

# 2. Experimental section

#### 2.1. Materials

The solvents (HPLC grade) and chemicals were purchased from Sigma–Aldrich and ABCR. Water was deionized before use. Methanol was purified using a PureSolv (Innovative Technology Inc.) solvent purification system. All chemicals were used without further purification.

# 2.2. Synthesis of silica nanoparticles

Small silica nanoparticles were prepared applying a literature known procedure [16]. Hundred millilitres methanol were mixed with 29 mmol water and 0.1 mL of 16 M aqueous ammonia solution. Afterwards 47.45 mmol tetraethyl orthosilicate were added dropwise under stirring in a 250 mL round bottom flask. The reaction mixture was then stirred at room temperature for 3 days. The solvent was evaporated and the remaining product was washed three times with *n*-hexane to destabilize the colloid within the washing step, separated by centrifugation at 4615g and dried over  $P_2O_5$  at 5 mbar resulting in 2.17 g white powder (each batch being in a diameter range between 5 and 10 nm according to SAXS). Larger silica nanoparticles were prepared by mixing 50 mL ethanol with 11 mmol water and 3.0 mL of 16 M aqueous ammonia solution in a 250 mL round bottom flask [16,17]. A solution of 50 mL ethanol mixed with 18.05 mmol tetraethyl orthosilicate was then added slowly under stirring. The reaction mixture was stirred at room temperature for 16 h. Then the solvent was evaporated and the remaining product was washed three times with *n*-hexane to destabilize the colloid, separated by centrifugation at 4615g and dried over  $P_2O_5$  at 5 mbar resulting in 0.86 g white powder (each batch being in a diameter range between 40 and 60 nm according to SAXS).

# 2.3. Synthesis of zirconia nanocrystallites

Small zirconia nanocrystallites were prepared applying a literature known procedure [18]. Thirteen millilitres of a 4 M solution of ZrOCl<sub>2</sub> were thermally decomposed in water in an autoclave with a 20 mL-Teflon-inlay at 200 °C. The reaction was carried out for 3 days and the particles were isolated by precipitation with acetone and centrifugation at 4615g, washed with a mixture of water and ethanol (1:5) three times and dried over  $P_2O_5$  at 5 mbar to yield 3.50 g of a white powder (each batch in a diameter range between 5 and 10 nm according to SAXS). Powder-XRD: 100% crystalline ZrO<sub>2</sub>, Baddeleyite phase (monoclinic). Larger zirconia nanocrystallites were prepared by a procedure described in literature [19] under hydrothermal conditions. A mixture of 19 mmol H<sub>2</sub>O, 7.3 mmol acetic acid and 2.25 mmol Zr acetate solution (16 wt.% in acetic acid) was heated in an autoclave with 20 mL-Teflon-inlay for 16.5 h at 170 °C. The resulting stable particle-dispersion was then destabilized by removing two thirds of the volume by evaporation and adding 10 mL acetone. The product was separated and washed three times with a mixture of acetone:water = 10:1 (centrifugation at 6150g), then dried over P<sub>2</sub>O<sub>5</sub> at 5 mbar to give 0.71 g of a white powder (each batch in a diameter range between 20 and 30 nm according to SAXS). Powder-XRD: 100% crystalline ZrO<sub>2</sub>, Baddeleyite phase (monoclinic).

#### 2.4. Measurement techniques

Powder-XRD-measurements were carried out on a Philips X'Pert Pro instrument at  $CuK_{\alpha}$ -radiation with a Bragg–Brentano-arrangement at an angle speed of 6°/min, with the sample mounted on

Si-single-crystal-wafers and measured under ambient conditions. Crystallite size was calculated using the TOPAS software via refinement using five metric parameters. The average crystallite size *D* was determined from the broadening of the peaks by Scherrer's equation  $D = 0.9\lambda/(\beta \cos \theta)$ , where  $\lambda$  is the wavelength of the X-rays,  $\theta$  the Bragg angle and  $\beta$  the calibrated breadth of a diffraction peak (here the (111) reflection) at half-maximum intensity.

Nitrogen sorption measurements were performed on a Micromeritics ASAP 2020 instrument. The samples were degassed under vacuum at 60 °C for at least 8 h prior to measurement. The surface area was calculated according to Brunauer, Emmett and Teller (BET) [11].

Dynamic light scattering (DLS) measurements were carried out by non-invasive backscattering on an ALV/CGS-3 compact goniometer system with an ALV/LSE-5003 and a multiple tau correlator at a wavelength of 632.8 nm (He–Ne Laser) and a goniometer angle of 90°. The dispersing media were purified before use with a syringefilter (200 nm mesh). The determination of the particle size was carried out by the analysis of the correlation-function via the g2(t) method followed by a linearised number-weighting (n.w.) and mass weighting (m.w.) of the distribution function.

SAXS measurements were performed under vacuum using a rotating anode X-ray generator with a pinhole camera (Nanostar, Bruker AXS) with CuK<sub>α</sub> radiation monochromatized and collimated from crossed Goebel mirrors and detected by a 2D position sensitive detector (Vantec 2000). The sample-to-detector distance was varied from 13 to 108 cm to cover a wide range of the scattering vector *q* from 0.1 to 15 nm<sup>-1</sup>. All SAXS patterns were radially averaged and corrected for background scattering to obtain the scattering intensities in dependence on the scattering vector  $q = 4\pi/\lambda \sin\theta$ , where  $2\theta$  is the scattering angle and  $\lambda = 0.1542$  nm the X-ray wavelength.

TEM images were recorded on a JEOL JEM-100CX and on a FEI TECHNAI G20 transmission electron microscope. The particle powder samples were attached to Formvar copper grids by dispersing them in ethanol using an ultrasound cleaning bath, adding one drop on the copper grid and evaporating the solvent. The images were evaluated automatically by the software ImageJ [20] or manually in the case of a very low contrast. At least 50 particles were measured for each size and type of particle and the equivalent spherical diameter was evaluated.

# 3. Theory

DLS primarily measures time-dependent fluctuations of scattered coherent light, i.e. the decay of the autocorrelation function, which is caused by diffusive motion of the particles. The experimentally measured diffusion coefficients can be converted to a hydrodynamic radius via the Stokes–Einstein equation.

$$D = \frac{k_{\rm B}T}{6\pi\eta R_{\rm h}} \tag{1}$$

where  $k_{\rm B}$  is Boltzmann's constant, *T* the temperature,  $\eta$  the viscosity of the suspension medium and  $R_{\rm h}$  the hydrodynamic radius [21].

In contrast to dynamic light scattering, SAXS probes differences in electron densities. To get information on the size and arrangement of nanoscaled objects from SAXS data, either direct methods (from fitting the purely mathematical Fourier transforms to the intensities) [22,23] or indirect methods (which intend to restore the distribution function in real space from SAXS data) are available [24–26]. In this Letter, we focus on the first ones, where the scattering intensities of weakly ordered structures are described in the monodisperse model by the product of form factor and structure factor,  $I_q = I_0 V_0^2 P(q) S(q)$ , with q being the absolute value of the scattering vector,  $V_0$  the volume of the particle, S(q) the structure factor and P(q) the form factor.  $I_0$  contains experimental parameters such as the scattering contrast, the beam intensity and additional variables due to the setup of the experiment. In the case of polydispersity, the simplest approach is a formal factorization with a mean form factor and to replace the structure factor by a so-called effective one [27].

$$I(q) = I_0 V_0^2 \bar{P}(q, r) S_{\text{eff}}(q)$$
(2)

In the case of a Gaussian size distribution of spherical particles, the form factor is given by

$$\overline{P}(q) \propto \int_{r=0}^{\infty} dr \left(\frac{4\pi}{3}r^3\right)^2 \exp\left(-\frac{1}{2}\frac{(r-R)^2}{b^2}\right) \left(3\frac{\sin(qr) - qr\cos(qr)}{(qr)^3}\right)^2$$
(3)

In the case that the distribution is sufficiently small, the integral can be extended from minus infinity to infinity and its analytical solution is given in Supplementary information.

For hard spheres, the Percus–Yevick approximation [28] delivers a structure factor for weakly aggregated systems, which describes the interference of the scattering of particles with two parameters, a hard-sphere radius  $R_{\rm HS}$  and a mean hard-sphere volume fraction  $\eta$  [29,30].

$$S(q) = \frac{1}{1 + 24\eta G(2qR_{\rm HS})/(2qR_{\rm HS})}$$
(4)

with the function  $G(2qR_{\rm HS})$  being defined by Kinning and Thomas [29]. The hard-sphere radius  $R_{\rm HS}$  gives information on the correlation distance of particles within a cluster or an aggregate and the hard-sphere volume fraction  $\eta$  on the probability to find particles in vicinity to each other.

To describe the effect of a small anisotropy of the particles on the scattering intensity, their interaction can be assumed to be independent of their orientation and is given by their average size [25]. Therefore, the decoupling approximation can be used [31].

$$I(q) \propto I_0 V_0^2 P(q) [1 + \beta(q)(S(q) - 1)]$$
(5)

where  $\beta(q) = \langle F(q) \rangle_0^2 / \langle F^2(q) \rangle_0$  with an orientational averaged form factor  $P(q) = \langle F^2(q) \rangle_0$  [31]. In the case of polydispersity, the equations are similar, but the orientational average has to be replaced by an integral taken over the size [30,31]. For including the effect of larger polydispersity, the local monodisperse approximation is frequently used [30,32]. It is based on the assumption that a particle of a certain size is always surrounded by particles with the same size. Therefore, the model consists of monodisperse sub-systems weighted by the size distribution

$$I(q) \propto I_0 \int dR V_0^2(R) F^2(q, R) S(q, R)$$
(6)

An overview on the different theoretical models is discussed in the literature [30].

Different to Eq. (3), an unified equation for the form factor has been proposed by Beaucage [33–36], consisting of a Guinier like and a limited power law regime.

# 4. Results

Figure 1a shows the scattering intensities from XRD for silica nanoparticles with the strong short range order peak from the distance of the silica tetrahedra, Figure 1b for the zirconia nanoparticles, with broad Bragg reflections typical for nanoparticles. Rietveld refinement revealed a composition of the zirconia nanoparticles of ~100% crystalline monoclinic  $ZrO_2$  (Baddeleyite). The crystallite size was determined to be 4.5 nm for small  $ZrO_2$  and 2.9 nm for large  $ZrO_2$  as evaluated from the Scherrer equation with an estimated standard error of 10%. The surprisingly smaller value for

the large  $ZrO_2$  nanoparticles suggests that they are built up as aggregates from smaller particles, which is supported by the TEM-images (Figure 2).

In these TEM images it is clearly visible that small zirconia particles consist of crystal-facet-shaped nanocrystals (Figure 2a), whereas the large zirconia particles (Figure 2b) are built up of aggregates of smaller units. The crystallinity is also observed in the inserts of Figure 2, the selective area diffraction (SAD-) images. Together with HRTEM images (Figure 3) the conclusion from XRD is further confirmed that small nanoparticles are single crystallites and larger ones are polycrystalline aggregates, visible by the presence of different lattice fringes of every single crystallite in the aggregate (HRTEM images, Figure 3b). Different to the complex shape of zirconia, the silica nanoparticles reveal a poor contrast to the carbon coated copper grid in the TEM micrographs and are therefore not shown.

DLS was used to determine the number-weighted and the massweighted particle size distribution of the nanoparticles dispersed in ethanol (SiO<sub>2</sub>) and water (ZrO<sub>2</sub>). According to these DLS-measurements, the number-weighted size distribution of the nanoparticles is rather uniform as shown in Figure 4 (data and figure for massweighted evaluation are found in Supplementary information). For the samples presented in Figure 4, particle diameters of 7.8 ± 2.3 nm for small and 64 ± 12.8 nm for large silica, furthermore 17.8 ± 3.6 nm for small and 54 ± 10.8 nm for large zirconia were measured with DLS.

For comparison to nitrogen sorption, two batches for each oxide were measured. With the assumptions of a spherical shape and a complete coverage of the surface with nitrogen molecules, one may derive the particle size distribution. The value for the specific surface area was  $710.6 \pm 7.1 \text{ m}^2/\text{g}$  for small and  $76.2 \pm 0.8 \text{ m}^2/\text{g}$  for large SiO<sub>2</sub> nanoparticles. As a consequence of the lower specific surface of the large SiO<sub>2</sub> nanoparticles, this results in a smaller size of only 34 nm compared with the size of 53.4 nm from SAXS evaluation. Differently, the specific surface for large ZrO<sub>2</sub> nanoparticles is higher than for small ones, i.e.  $171.1 \pm 1.7 \text{ m}^2/\text{g}$  in comparison to  $140.3 \pm 1.4 \text{ m}^2/\text{g}$ . This would indicate a smaller size. However, taking into account the results from TEM and SAXS, this can also be attributed to polycrystalline aggregates, which build up the large ZrO<sub>2</sub> nanoparticles.

For each of the batches of nanoparticles prepared, SAXS patterns were collected and fitted by different models with the software Mathematica<sup>™</sup>. The form factor was obtained either by spheres with a Gaussian size distribution and an effective structure factor, Eqs. (3) and (4), or the Beaucage model with a lognormal distribution (Eqs. (S1) and (S2) shown in Supplementary information). Using the decoupling (Eq. (5)) or the local monodisperse approximation (Eq. (6)) led to fit parameters, which did not differ considerably from the ones of the simple model with an effective structure factor (shown for selected examples of silica as well as zirconia nanoparticles in Supplementary information). For the Gaussian model, the number length-weighted, the numberweighted as well as the mass-weighted diameter mean,  $d_{1,0}$ ,  $d_{3,0}$ and  $d_{4,3}$ , were calculated [37]. For comparison of the methods, in the following diagrams the number-weighted mean  $d_{3,0}$  was chosen and is denoted as d<sub>SAXS</sub>. Numerical values are also listed in Supplementary information: There are certainly some general trends the relation  $d_{4,3} > d_{3,0} > d_{1,0}$  holds due to the different weight of the distribution and the Beaucage model gives slightly larger values than the Gaussian sphere model - however, the deviation between different evaluation methods is within about 30% at maximum.

For large zirconia particles, two levels of hierarchy are visible as two characteristic humps in the scattering intensities and were therefore fitted with a system with two different radii, i.e. a bimodal size distribution. To our interpretation, the second maximum



Figure 1. XRD of (a) silica, (black: 4.3 nm and grey: 53.4 nm) and (b) zirconia samples: 4.0 nm (black) and 33.8 nm (grey) nanocrystallites, diameter from SAXS evaluation.



Figure 2. Representative TEM micrographs of (a) small ZrO<sub>2</sub> nanoparticles of a size of 3.8 nm, (b) large ZrO<sub>2</sub> nanoparticles (15.2 nm) and (c) large SiO<sub>2</sub> nanoparticles (53.5 nm), diameter from SAXS evaluation. Selective area electron diffraction images are displayed in (a) and (b) to confirm the crystallinity.

at large *q*-values arises from small crystallites building up a porous aggregate, as just mosaic crystals with grain boundaries would not have sufficient electron density contrast to give a second maximum. A typical short range order distance of 2.7 nm is observed

in SAXS, which is similar to the size of 2.9 nm as obtained from XRD.

The stronger tendency to agglomerate is visible from the more pronounced scattering intensity maximum in particular for small

a b <u>10 nm</u>

Figure 3. Representative HRTEM micrographs of (a) small ZrO<sub>2</sub> nanoparticles of a size of 3.8 nm and (b) large ZrO<sub>2</sub> nanoparticles (15.2 nm), diameter from SAXS evaluation.



**Figure 4.** Typical number-weighted particle diameter distributions from DLS for the respective nanoparticle powder dispersed in ethanol (SiO<sub>2</sub>, diameter from SAXS evaluation 4.4 and 53.4 nm) or water (ZrO<sub>2</sub>, SAXS: 4.0 and 33.8 nm).

silica (Figure 5a). This higher intensity leads to a higher numerical value for the volume fraction  $\eta$  in the hard-sphere model, Eq. (4). The higher the hard sphere volume fraction, the higher is the probability to find in the vicinity of a particle another neighbouring one.

The results for the diameter and the distribution width (standard deviation) of the different nanoparticles obtained from the respective measurement technique are presented in Figure 6 (TEM, filled squares, DLS, circles, BET, triangles, XRD, diamonds, only for zirconia), in dependence on the particle diameter  $d_{3,0}$  obtained from SAXS. For BET and XRD, only the size but not the distribution width is given, but for both methods a measurement error of at least 10% is estimated. A complete list of the numerical data is found in Supplementary information.

# 5. Discussion

Each of the techniques has its specific advantages: TEM delivers direct images, from which information on size and shape of nanoparticles is obtained, SAXS is able to measure powders, solids and also particles in solution, DLS is a fast and cheap method to measure a high number of samples, and XRD and BET give the size of nanoparticles as a by-product from the main aim of the method, e.g. the determination of phases within a sample or the specific surface.



**Figure 5.** Experimental SAXS profiles I(q) (symbols) and fitting curves (solid lines) of small and large (a) silica and (b) zirconia using the analytic approach with spheres and a Gaussian size distribution and an effective structure factor (Eq. (2)). The profiles are shifted vertically for better visibility.

For silica nanoparticles, all presented experimental methods give a nearly perfect agreement (Figure 6a), with the exception of BET for large silica nanoparticles. A possible explanation could



Figure 6. Particle diameter and distribution width (standard deviation) from DLS (circles), TEM (filled squares), as well as particle diameter from BET (triangles) and XRD (diamonds, only for zirconia) in dependence on the particle diameter obtained from SAXS, *d*<sub>SAXS</sub>: (a) silica and (b) zirconia nanoparticles.

be microporosity, as micropores were sometimes found in large Stöber silica particles [38]. DLS gives slightly larger values, but within the error bars, which is probably due to the hydrodynamic shell. None of the typical difficulties reported in the literature for TEM might have had an effect, such as aggregation by capillary forces between the particles during drying [39], or a collapse of highly hydrous and open-structured silica particles due to the dehydration and relaxation processes under high vacuum [7]. Whereas in TEM one has to take care about magnification, imaging type and analysis method, which can affect the resulting size distribution, especially in case of small nanoparticles [40], the difficulty in SAXS is that the method relies on mathematical modelling of scattering intensities, where the choice of the respective analytical or numerical approach is not always unique. The upper size limit of SAXS in the laboratory is about 50 nm, and larger objects require USAXS at a synchrotron radiation source. Nevertheless, SAXS agreed well with the other methods, as the typical oscillations in the scattering intensities from the narrow size distribution of silica nanoparticles allowed a precise measurement up to the 50 nm regime.

Differently, zirconia nanoparticles (Figure 6b) exhibited a considerable discrepancy. Whereas SAXS and TEM are close to each other, the size of zirconia nanoparticles from DLS exceeds SAXS and TEM by a factor of two to three. The significantly larger value from DLS might be attributed to the larger hydrodynamic shell, which probably is dependent not only on the composition (the larger coordination sphere of zirconia), but also on the shape and roughness of the particle. A complex shape of particles [41] as well as their interaction [42] could influence the numerical evaluation from DLS. Also even a small amount of 1–2 vol.% of larger particles can significantly change the DLS derived particle size distribution, whereas SAXS measurements are less susceptible to the presence of larger aggregates [7].

Furthermore, a higher tendency to agglomerate was observed for silica in comparison to zirconia nanoparticles. A possible cause is that the surface energy and surface charge of silica nanoparticles is relatively high and agglomeration leads to a reduction of surface and gain in enthalpy. The enthalpy is one of the crucial parameters controlling the dispersion of nanoparticles in polymers [43]. As the aqueous dispersions of zirconia particles have a pH of 4 (large) and 2.9 (small), it is also proven that the zeta potential of the dispersion of zirconia particles is electrostatically stable until pH of 7 (see Supplementary information). This electrostatic stabilization is responsible for the good dispersion quality of zirconia nanoparticles in water used in this work.

The results from BET coincide with the results from SAXS, TEM and DLS only for small silica nanoparticles and deviate for large ones, whereas for zirconia a considerable difference was found for small as well as large nanoparticles. This is attributed in the latter case mainly to effects of a rough and porous surface, which is obviously the case for the large zirconia particles. Furthermore, small nanoparticles lead to a high surface area and any mixture of particles of different size is dominated by the specific surface area of the small particles [15]. The existence of more than one type of porosities in large nanoparticles cannot be excluded, as the isotherm type can be classified to be between type II and IV using the IUPAC classification of nitrogen sorption isotherms [44] and the hysteresis is not of uniform shape (H1-H2 mixed with H3). Differently, in small nanoparticles only mesopores are present, as they exhibit type IV behaviour with H1 hysteresis (typical isotherms of nitrogen sorption are found in Supplementary information). This might be the reason for the good agreement of the size from BET to the other methods for small as well as the huge difference for large nanoparticles.

XRD could only be applied to zirconia nanoparticles due to the crystallinity of the latter. It coincides only for small zirconia, which is attributed to the observation that large zirconia nanoparticles are built up of smaller crystalline units. It is therefore natural that the measured diameter from XRD reflects the size of the small crystallites and not the one of the nanoparticle aggregate.

# 6. Conclusion

Two oxide nanoparticle systems, amorphous SiO<sub>2</sub> and crystalline ZrO<sub>2</sub>, were studied by DLS, SAXS, TEM, BET and XRD (only for crystalline ZrO<sub>2</sub>). SAXS and TEM are in nearly perfect agreement for both materials in the whole measured range covering a nanoparticle diameter from 5 to 70 nm. BET shows large deviations in case of the large silica nanoparticles and is not applicable to zirconia due to the irregular shape and the high surface roughness of the latter. DLS leads to a slightly higher value for the size within the error bars for silica and considerably higher values for zirconia nanoparticles compared to TEM and SAXS. This is attributed to the influence of the hydrodynamic shell, and is more pronounced for facet-shaped zirconia than for spherical silica. XRD can only be used for crystalline materials and gave a reasonable size only for small zirconia, but clearly not for large zirconia nanoparticles, which were polycrystalline aggregates. In conclusion, one should be careful with the interpretation of numerical values of the size of nanoparticles from different methods, as not only the type of material, but also its shape and porosity might have a considerable influence. An approach using not only one single measurement method is favourable to obtain general information on size, size distribution and shape of nanoparticles.

# Acknowledgements

The Austrian Science Fund (FWF), Project No. 20693, is gratefully acknowledged for the financial support of this work. The authors thank Berthold Stöger and Robert Haberkorn for XRD measurements and the University Service Center for Transmission Electron Microscopy, Vienna University of Technology for their help in recording the TEM-images.

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2011.11.049.

#### References

- [1] H. Presting, U. König, Mater. Sci. Eng. C 23 (2003) 737.
- [2] R.Y. Kannan, H.J. Salacinski, P.E. Butler, A.M. Seifalian, Acc. Chem. Res. 38 (2005) 879.
- [3] G. Kickelbick, Prog. Polym. Sci. 28 (2003) 83.
- [4] C. Sanchez, B. Julián, P. Belleville, M. Popall, J. Mater. Chem. 15 (2005) 3559.
- [5] V. Goertz, N. Dingenouts, H. Nirschl, Part. Part. Syst. Charact. 26 (2009) 17.

- [6] J. Moonen, C. Pathmamanoharan, A. Vrij, J. Colloid Interface Sci. 131 (1989) 349.
- [7] D.J. Tobler, S. Shaw, L.G. Benning, Geochim. Cosmochim. Acta 73 (2009) 5377.
- [8] D.L. Green, J.S. Lin, Y.-F. Lam, M.Z.-C. Hu, D.W. Schaefer, M.T. Harris, J. Colloid Interface Sci. 266 (2003) 346.
- [9] S. Connolly, S.N. Rao, D. Fitzmaurice, J. Phys. Chem. B 104 (2000) 4765.
- [10] Y. Li, I. Akiba, S. Harrisson, K.L. Wooley, Adv. Funct. Mater. 18 (2008) 551.
- [11] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.
- [12] G. Beaucage, H.K. Kammler, S.E. Pratsinis, J. Appl. Cryst. 37 (2004) 523.
- [13] H.K. Kammler, G. Beaucage, R. Mueller, S.E. Pratsinis, Langmuir 20 (2004) 1915.
- [14] A. Rizzuti, C. Leonelli, A. Corradi, E. Caponetti, D. Chilura Martino, G. Nasillo, M.L. Saladino, J. Dispersion Sci. Technol. 30 (2009) 1511.
- [15] J.L. Shi, C.W. Lu, C.L. Kuo, Z.X. Lin, T.S. Yen, Ceram. Int. 18 (1992) 155.
- [16] W. Stöber, A. Fink, E. Bohn, J. Colloid Interface Sci. 26 (1968) 62.
- [17] A.M. Lipski, C.J. Pino, F.R. Haselton, I.W. Chen, V.P. Shastri, Biomaterials 29 (2008) 3836.
- [18] Y. Murase, E. Kato, J. Am. Ceram. Soc. 84 (2001) 2705.
- [19] D. Carriere, M. Moreau, P. Barboux, J.-P. Boilot, O. Spalla, Langmuir 20 (2004) 3449.
- [20] M.D. Abramoff, P.J. Magelhaes, S.J. Ram, Biophot. Int. 11 (2004) 36.
- [21] U. Kätzel, M. Vorbau, M. Stintz, T. Gottschalk-Gaudig, H. Barthel, Part. Part. Syst. Charact. 25 (2008) 19.
- [22] A. Guinier, G. Fournet, Small-angle Scattering of X-rays, Chapman & Hall Ltd., 1955.
- [23] H. Peterlik, P. Fratzl, Monatsh. Chem. 137 (2006) 529.
- [24] D. Svergun, J. Appl. Cryst. 26 (1993) 258.
- [25] J. Brunner-Popela, O. Glatter, J. Appl. Cryst. 30 (1997) 431.
- [26] B. Weyerich, Appl. Cryst. 32 (1999) 197.
- [27] J. Brunner-Popela, R. Mittelbach, R. Strey, K.-V. Schubert, E.W. Kaler, O. Glatter, J. Chem. Phys 110 (1999) 10626.
- [28] J.K. Percus, G. Yevick, J. Phys. Rev. 110 (1958) 1.
- [29] D.J. Kinning, E.L. Thomas, Macromolecules 17 (1984) 1712.
- [30] J.S. Pedersen, Adv. Colloid Interface Sci. 70 (1997) 171.
- [31] M. Kotlarchyk, S.H. Chen, J. Chem. Phys. 79 (1983) 2461.
- [32] J.S. Pedersen, J. Appl. Cryst. 27 (1994) 595.
- [33] G. Beaucage, J. Appl. Crystallogr. 28 (1995) 717.
- [34] G. Beaucage, J. Appl. Crystallogr. 29 (1996) 134.
- [35] G. Beaucage, D.W. Schaefer, J. Non-Cryst. Solids 172 (1994) 797.
- [36] S. Trabelsi et al., Macromolecules 38 (2005) 6068.
- [37] A. Rawle, Surf. Coat. Int. 86 (2003) 58.
- [38] M. Szekeres, J. Tóth, I. Dékány, Langmuir 18 (2002) 2678.
- [39] J.K. Bailey, M.L. Mecartney, Colloids Surf. 63 (1992) 151.
- [40] W.D. Pyrz, D.J. Buttrey, Langmuir 24 (2008) 11350.
- [41] V.M. Gun'ko, V.I. Zarko, R. Leboda, E. Chibowski, Adv. Colloid Interface Sci. 19 (2001) 1.
- [42] A. Aerts et al., Chem. Mater. 19 (2007) 3448.
- [43] M.E. Mackay et al., Science 311 (2006) 1740.
- [44] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603.